

**STUDY OF THERMODYNAMICAL PROPERTIES OF
SALICYLATES IN AQUEOUS SALT SOLUTIONS:
VOLUMETRIC-ACOUSTICAL APPROACH.**

Thesis Submitted for the Award of the Degree of

DOCTOR OF PHILOSOPHY

in

Physics

By

Mashahid Hussain Choudhary

Registration Number: 12213539

Supervised By

Dr. Nabaparna Chakraborty (27727)

Department of Physics (Assistant Professor)

Lovely Professional University

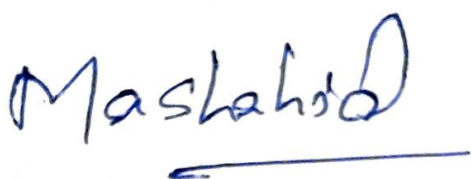


LOVELY PROFESSIONAL UNIVERSITY, PUNJAB

2026

DECLARATION

I hereby declared that the presented work in the thesis entitled “**Study of Thermodynamical Properties of salicylates in aqueous salt Solutions: Volumetric-Acoustical approach.**” in fulfilment of degree of Doctor of Philosophy (Ph.D.) is outcome of research work carried out by me under the supervision of Dr. Nabaparna Chakraborty, working as Assistant Professor, in the Department of Physics of Lovely Professional University, Punjab, India. In keeping with general practice of reporting scientific observations, due acknowledgements have been made whenever work described here has been based on findings of another investigator. This work has not been submitted in part or full to any other University or Institute for the award of any degree.



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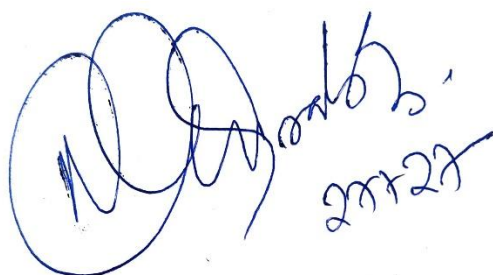
Name of the scholar: Mashahid Hussain Choudhary

Registration No.: 12213539

Department/school: Physics/ School of Chemical Engineering and Physical Sciences Lovely Professional University, Phagwara, Punjab.

CERTIFICATE

This is to certify that the work reported in the Ph.D. thesis entitled “**Study of Thermodynamical Properties of salicylates in aqueous salt Solutions: Volumetric-Acoustical approach**” submitted in fulfilment of the requirement for the award of degree of **Doctor of Philosophy (Ph.D.)** in the Department of Physics, is a research work carried out by Mashahid Hussain Choudhary , 12213539, is Bonafide record of his original work carried out under my supervision and that no part of thesis has been submitted for any other degree, diploma or equivalent course.



(Signature of Supervisor)

Name of supervisor: Dr. Nabaparna Chakraborty

Designation: Assistant Professor

Department/school: Physics,/ School of Chemical Engineering and Physical

Sciences University: Lovely Professional University, Phagwara, Punjab

ABSTRACT

The objective of this work is to elucidate temperature-dependent physicochemical interactions, hydration phenomena, and the structure-making or structure-breaking tendencies in binary and ternary aqueous electrolyte systems using magnesium, choline and sodium salicylate + water mixtures as solvent media with salicylate concentrations ranging from 0.010 to 0.090 mol·kg⁻¹ and inorganic salts as solutes at molalities of 0.10–0.50 mol·kg⁻¹. Density and ultrasonic velocity measurements were carried out using an Anton Paar DSA 5000 M at 0.1 MPa over the temperature range 288.15–318.15 K. From these data, parameters such as apparent and partial molar volumes (V_ϕ , V_ϕ^0), apparent and partial molar isentropic compressibilities ($K_{\phi,s}$ and $K_{\phi,s}^0$), transfer volumes (ΔV_ϕ^0 , $\Delta K_{\phi,s}^0$), the limiting apparent molar expansibilities (E_ϕ^0) along with their first-order derivatives ($\frac{\partial E_\phi^0}{\partial T}$), pair and triplet interaction coefficients (V_{AB} , V_{ABB} , K_{AB} and K_{ABB}), isobaric thermal expansion coefficients, apparent specific volume were evaluated.

The research comprises nine systematic studies grouped into three sections. In the first section, magnesium salicylate systems were analysed using the co-sphere overlap model and McMillan–Mayer theory to explain solvation geometry and intermolecular interactions. The results indicated strong solute–solvent association, cooperative hydration and predominantly structure-making behaviour. Ion-specific effects significantly influenced compressibility and expansibility, while temperature variations governed the stability and reorganization of solution structure, highlighting pharmaceutical relevance.

The second section focuses on Choline salicylate systems. Volumetric and acoustic results demonstrated reduced compressibility, enhanced molecular association and stable solvent structuring. Passynski's equation was employed to evaluate hydration numbers, while Hepler's relations were used to assess structure-making tendencies. The evaluated association and relaxation parameters confirmed strong ion–dipole interactions and hydrogen-bond mediated solvation, emphasizing the suitability of these systems for environmentally friendly solvent design and formulation studies.

The third section addresses sodium salicylate systems, which exhibited temperature-dependent behaviour. Structure-making tendencies were observed at lower temperatures, whereas higher temperatures promoted partial structure-breaking due to changes in hydration and ion pairing.

Across all nine studies, the combined volumetric and acoustic analyses consistently demonstrated strong solute–solvent interactions governed by ion-specific effects, molecular association, and hydration phenomena. The integration of thermodynamic results provides a unified interpretation of hydration, solvation geometry and structural organization in salicylate-based ternary systems. These findings offer valuable insights into electrolyte behaviour relevant to pharmaceutical formulation, materials science and physicochemical modelling of complex aqueous systems.

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THESIS OUTLINE

This thesis is organized into four chapters, each addressing a specific component of the research work.

Chapter 1: Introduction

This chapter introduces the background and motivation of the present study. The fundamental principles of ultrasonic and volumetric techniques are briefly described. The rationale behind the selection of salicylates and inorganic salts as model systems is clearly explained. The practical relevance of these systems in pharmaceutical formulations and electrolyte solutions is highlighted.

Chapter 2: Review of Literature

This chapter reviews previous volumetric and acoustic studies on electrolyte and organic solute systems. Earlier findings on molecular interactions, solvation behavior, and hydration effects are critically discussed. The research gaps addressed in the present study are clearly identified, establishing the need for the current investigation.

Chapter 3: Methodology

This chapter presents the objectives of the present investigation and describes the experimental materials, solution preparation methods, and measurement procedures adopted for density and ultrasonic velocity studies. The working principles of the ultrasonic and densimetric techniques are briefly outlined. The methodologies employed for the evaluation of derived thermodynamic parameters are also discussed, thereby establishing a systematic experimental framework for the analysis presented in the subsequent chapter.

Chapter 4: Results and Discussion

This chapter presents the experimental results and discusses the variation of volumetric and acoustic parameters with concentration and temperature. The data are interpreted using fundamental thermodynamic concepts and established models such as the co-sphere overlap model, McMillan–Mayer theory, Passynski’s equation, and Hepler’s constant to elucidate solute–solvent interactions, hydration behavior, and structure-making or structure-breaking tendencies of the studied systems.

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LIST OF ABBREVIATIONS

c	Speed of sound
ρ	Density of samples
K	Kelvin (Temperature in absolute)
V_{ϕ}	Apparent molar volume
m_A	Molality of the solute
R_a	Relative association
r_s	Relaxation strength
m_b	Molal concentration of co-solute
S_V^*, S_K^*	Experimental Slopes
A_V	Debye–Hückel limiting slope
p	Pressure
T	Temperature
V_{ϕ}^0	Partial molar volume
ΔV_{ϕ}^0	Partial molar volume of transfer
a, b, c	Constants of least square fitting of equation 4.4
E_{ϕ}^0	Partial molar expansibility
$K_{\phi,s}$	Apparent molar isentropic compression
K_S	Isentropic compressibility
$K_{\phi,s}^0$	Partial molar isentropic compression

A_V	Debye–Hückel limiting slope
$\Delta K_{\phi,S}^0$	Partial molar isentropic compression of transfer
V_{AB}	Pair interaction coefficient for volume
K_{AB}	Pair interaction coefficient for isentropic compression
V_{ABB}	Triplet interaction coefficient for volume
K_{ABB}	Triplet interaction coefficient for isentropic compression
ASV	Apparent specific volume
α_P	Isobaric thermal expansion coefficients
n_h	Hydration number
γ	Specific heat ratio
C_p	specific heat at constant pressure
C_v	specific heat at constant volume
NaSl	Sodium salicylate
MgSl	Magnesium Salicylate
ChSl	Choline Salicylate

Chapter 1

INTRODUCTION

Ultrasonics Research and Its Role in Thermodynamical Studies:

1.1.Fundamental of ultrasonics

Ultrasonics deals with the study of mechanical waves with frequencies above the human hearing audible limit (>20 kHz). In physics, these acoustic waves are understood as elastic disturbances propagating through media via local particle oscillations. The velocity and attenuation of ultrasonic waves in fluids depend critically on physical parameters such as density, elastic modulus, viscosity, and molecular-scale interactions [1,2]. The propagation velocity of an ultrasonic wave u in a fluid can be expressed by the Newton-Laplace equation:

$$u = \frac{1}{\sqrt{\beta_s \rho}} \quad (1.1)$$

where ρ is the fluid density and β_s is the isentropic compressibility—an adiabatic property reflecting the fluid's elastic response to pressure variations under constant entropy. The tight coupling between ultrasonic velocity, compressibility, and density makes ultrasonic measurements a sensitive physical probe for detecting changes in fluid structure or molecular interactions [3,4].

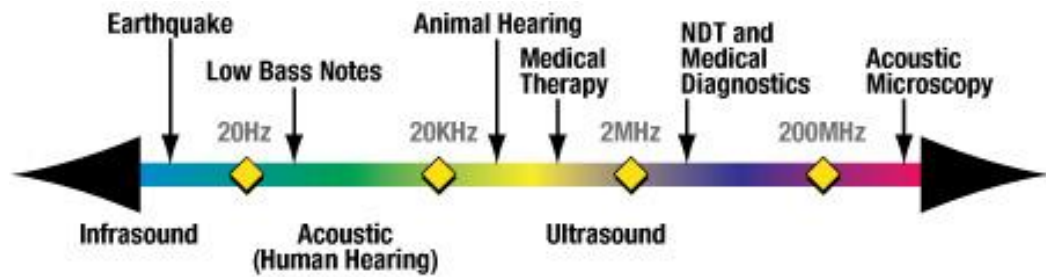


Figure 1.1 Frequency ranges of infrasound, acoustic (human hearing), and ultrasound with their common applications.

1.2.Ultrasonic Techniques in Thermophysical and Molecular Interaction Studies

Ultrasonics has gained prominence in studying thermophysical properties of liquids due to:

- i) **Microscopic Interaction Sensitivity:** Ultrasonic velocity measurements are directly influenced by changes in intermolecular forces, solvent reorganization, and solute-induced structural alterations.
- ii) **Thermodynamic Parameter Extraction:** By combining ultrasonic velocity with density data, various thermos-acoustic parameters and hydration numbers can be derived. These quantities characterize solute–solvent interaction energetics and structural effects [5,6].
- iii) **Non-destructive Probing:** The mechanical nature of the wave propagation allows non-invasive sampling, preserving sample integrity and facilitating repeated measurements [7,8].
- iv) **Broad Applicability:** Ultrasonic measurements engage well with complex mixtures relevant in pharmaceutical, chemical, and material sciences, supporting theoretical model validation and prediction [9-11].

1.3.Traditional Measurement setups for density and ultrasonic Velocity

Before integrated instruments, physicists performed density and ultrasonic velocity measurements using different apparatuses based on distinct physical principles:

i) Density Measurement by Oscillating U-Tube:

The oscillating U-tube densitometer is a classic device where a thin glass U-shaped tube is made to oscillate around its axis with the fluid sample inside. The resonant frequency of oscillation depends on the combined mass (tube plus fluid), which varies with fluid density. Precise frequency measurements yield density values with high accuracy, usually to four or five decimal places in g/cm³ [12,13].

ii) Ultrasonic Velocity Measurements:

- a) **Pulse-Echo Technique:** Involves sending short ultrasonic bursts into the liquid and measuring the time taken for echoes to return from a reflecting surface. Velocity is computed from the travel distance and time delay [14]
- b) **Through-Transmission Technique:** Uses paired transducers; one emits an ultrasonic pulse, and another detects it on the opposite side of the sample. The transit time directly determines the velocity [15].

- c) Digital Signal Processing Methods: Phase-slope and cross-correlation approaches improve velocity measurement precision, especially in attenuating or dispersive media [15,16].

These methods were performed separately, necessitating careful sample handling, temperature control, and calibration to ensure reliable data, leading to increased experimental complexity and possible systematic errors during cross-measurements.

1.4.Modern Integrated Measurement: Anton Paar DSA 5000 M

The Anton Paar Density and Sound Velocity Analyzer (DSA 5000 M) is a sophisticated, modern instrument that integrates the precise measurement of both density and ultrasonic velocity within a single, temperature-controlled system. For density determination, it utilizes the oscillating U-tube principle, where a liquid sample is contained in a U-shape tube that vibrates at a natural frequency sensitive to the mass of the fluid; changes in this frequency allow for highly accurate determination of the sample's density with exceptional precision. Concurrently, the instrument measures ultrasonic velocity using fixed path length transducers positioned within the same measurement cell. Ultrasonic pulses are transmitted through the sample, and the time taken for these pulses to traverse the known distance is measured with nanosecond timing accuracy, allowing for highly precise calculation of the sound velocity through the fluid. This simultaneous measurement under identical thermal and compositional conditions ensures that both parameters reflect the same sample state, greatly reducing measurement uncertainties that can arise from temperature fluctuations, sample evaporation, or degradation in separate analyses [14]. Consequently, this integrated approach enhances the reproducibility and accuracy of thermophysical data, streamlines the experimental process by significantly reducing measurement time, and facilitates automated sequential measurements across varying sample conditions. Moreover, the combination of density and ultrasonic velocity data enables direct computation of important thermodynamic properties such as isentropic compressibility, apparent molar volume, and hydration number, which are critical for comprehensive physicochemical characterization of complex solutions [17-19]. Features like automated sample handling verification, precise temperature control with the Thermobalance™ system, and a user-friendly touchscreen interface further

contribute to the instrument's reliability and ease of use. Altogether, the Anton Paar DSA 5000 M stands as an essential tool that empowers researchers to obtain high-precision volumetric and acoustic data efficiently, making it particularly valuable for the thorough thermodynamical investigation of salicylates in aqueous salt solutions presented in this thesis.

Acoustic and Volumetric characteristics of binary along with ternary solutions are crucial in understanding the physicochemical behaviour of liquid mixtures across various fields. Liquid mixtures, with their distinctive behaviour, are a focus of study for their thermodynamic properties. This research supports process design, molecular dynamics, and simulations. Binary mixtures, known for their simplicity, help unravel intricate phenomena. Experimental measurements of excess properties in these systems are vital for studying intermolecular interactions and validating model [9-11]. Investigating the density and the speed at which sound travels through various liquid mixtures allows us to understand their properties and molecular interactions. Ultrasonic waves help us see the forces and structures within these liquids. This technique is non destructive and useful for exploring interactions in polymers and organic solutions. The insights gained from this research are valuable for many industries, including automotive, pharmaceuticals, textiles, and cosmetics [3]. Molecular acoustics emphasizes on understanding how the properties of materials affect the velocity and propagation of high frequency sound waves [4] Recently, acoustic parameters have gained prominence in scientific research, particularly for their ability to provide insights into interactions at molecular level within fluid system. ultrasonic methods have become indispensable essential for analysing these interactions, whether in polar or nonpolar substances. This approach has provided new perspective on the essential characteristics of these mixtures at the molecular scale [20]. Exploration of drug interactions within biological systems is a captivating area of study for researchers. This interest is fuelled by the progressive integration of insights from biotech genetics and a range of scientific disciplines. The action of a drug triggers a series of thermodynamic shifts, which are tied to molecular interactions. These effects, including hydrophobic, hydrophilic, and ionic forces, are crucial in determining how a pharmaceutical compound is delivered, absorbed, and processed within the body. To shed more light on these interactions, these interactions,

researchers scrutinize the action of drugs across diverse physiological environments. They utilize parameters such as volumetric and acoustic properties as key indicators. This approach offers a comprehensive view of how drug molecules interact with each other and their surrounding environment, providing valuable insights for the field [21]. Our research explores the thermal and physical characteristics of mixtures of ionic liquids. By conducting experimental assessments and utilizing molecular dynamics simulations, our goal is to comprehend the mechanisms of interaction and the alterations in structure caused by these cosolvents, providing valuable knowledge for their wide-ranging uses

Understanding the principles behind this measurement technology bridges theoretical physics with experimental thermodynamics. The interplay between wave propagation, fluid elasticity, and molecular interactions manifests in observable ultrasonic and volumetric phenomena. The Anton Paar DSA 5000 M's capability allows experimental investigation of complex multicomponent systems, such as salicylate-salt aqueous solutions, providing quantitative data indispensable for elucidating microscopic physical mechanisms driving macroscopic thermodynamic behaviour.

1.5. Selection of Salicylates and Salts for the Present Study

The choice of solute systems plays a crucial role in understanding the molecular interactions and thermodynamic behaviour of multicomponent liquid mixtures. In the present work, salicylate-based compounds and inorganic salts were selected due to their pharmaceutical relevance, complex ion–dipole interactions, and ability to form structured aqueous environments. Their distinct physicochemical characteristics make them ideal for investigating solute–solvent and solute–solute interactions using ultrasonic and volumetric techniques.

1.5.1. Choice of salicylates

Salicylates play a key role in treating various types of arthritis. Although the understanding of how they function in the body has improved, there are still some widespread misunderstandings about their effective use in patient care [22]. Grasping how drugs interact with solvents, and how temperature and solutes affect these interactions is the root of understanding how these drugs work in the body. This view

helps us understand how drugs pass biological membranes in aqueous solutions [23]. The following salicylates were studied:

Sodium salicylate ($C_7H_5NaO_3$; NaSl) a derivative of salicylic acid, is a well-established non-steroidal anti-inflammatory drug (NSAID) widely used for its analgesic and antipyretic properties [24]. It is frequently employed as a model compound in physicochemical and pharmaceutical studies due to its amphiphilic nature and ability to form hydrogen bonds and ionic interactions.

Choline salicylate ($C_{12}H_{19}NO_4$; ChSl) is an ionic liquid composed of choline cations and salicylate anions. The choline cation is very hydrophilic with its positive charge and performs vital functions in biological systems. Salicylate has anti-inflammatory and analgesic activities, which render this compound of pharmaceutical interest. Its hydrophilic behaviour in water, such as hydrogen bonding and molecular aggregation, influences its use in formulations and biochemistry. Choline salicylate's significance extends beyond its pharmaceutical activities; it behaves similarly to ionic liquids and has been investigated as a component in green solvents such as deep eutectic solvents (DES) [31-34].

Magnesium salicylate ($C_{14}H_{10}MgO_6$; MgSl) is a divalent salicylate salt that introduces stronger electrostatic interactions and higher charge density compared to monovalent sodium salicylate. The presence of magnesium (Mg^{2+}) ions influences hydration and coordination structures, offering insights into cation-dependent variations in solution properties. It is a non-steroidal anti-inflammatory drug (NSAID) commonly used in pharmaceutical formulations [35-37].

The selection of sodium salicylate, choline salicylate, and magnesium salicylate was based on their distinct cationic characteristics, which enable a systematic investigation of ion-specific effects on thermodynamic properties. Sodium salicylate contains a monovalent inorganic cation (Na^+), choline salicylate contains a bulky organic cation (choline⁺), whereas magnesium salicylate contains a divalent cation (Mg^{2+}) with high charge density. These differences significantly influence hydration behaviour, ion–dipole interactions, and molecular packing in aqueous electrolyte solutions. Therefore,

a comparative investigation of these salicylates provides a comprehensive understanding of the influence of cation identity on density, ultrasonic velocity, apparent and partial molar properties, and related thermodynamic properties as well as solute–solvent interactions in aqueous electrolyte systems.

1.5.2. Choice of salts

Six salts with distinct ionic characteristics were chosen to study the influence of ion size, charge, and hydration behaviour on salicylate–water systems. These include monovalent and divalent electrolytes, allowing systematic evaluation of ion-specific effects on thermodynamic and acoustic parameters. Besides the influence of different anions, the nature of the salicylate cation also plays an important role in determining the thermodynamic behaviour of the studied systems. Differences in ionic charge, ionic radius, charge density, and hydration characteristics affect ion–water and ion–solute interactions, thereby influencing the measured volumetric and acoustic properties. Consequently, replacing sodium, choline, or magnesium with other cations (e.g., calcium or zinc) would be expected to produce different thermodynamic behaviour owing to their different physicochemical characteristics.

Sodium chloride (NaCl) A typical structure-making electrolyte, used as a reference salt due to its simple ion pair and strong hydration tendency.

Sodium sulphate (Na_2SO_4) A strong structure-making salt with a divalent anion, used to study ion–solvent interactions under high electrostatic field effects.

Sodium bicarbonate (NaHCO_3) A weak electrolyte and buffer component that can alter solution pH, thus influencing hydrogen bonding and solvation dynamics.

Sodium nitrate (NaNO_3) Contains a larger, less-hydrated anion compared to chlorine (Cl^-), helping assess the influence of ion size and polarizability on solution compressibility.

Trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) A multivalent organic salt, enabling investigation of hydrogen bonding and ion–association effects due to its multiple carboxylate groups.

Potassium chloride (KCl) Used to study cationic effects by comparing potassium (K^+) and sodium (Na^+) in salicylate–water systems, revealing how cation size and hydration modify solution structure.

1.5.3. Significance of studying these systems

The selected combination of salicylates and salts covers a broad range of molecular sizes, charges, and hydration tendencies. Such a variation allows a structured study of the effect of the components on one another and thus provides a clearer insight into their physicochemical characteristics in multicomponent aqueous mixtures as reflected in density and ultrasonic velocity data.

Chapter Summary

This chapter presents the fundamental principles of ultrasonics and their significance in thermophysical and molecular interaction studies. The working concepts of ultrasonic and densimetric measurement techniques, including traditional and modern integrated methods using the Anton Paar DSA 5000 M, are discussed. The relevance of volumetric and acoustic parameters in understanding molecular interactions in liquid mixtures is highlighted. The rationale for selecting salicylate-based compounds and various inorganic salts as model systems is also explained in view of their pharmaceutical relevance and their ability to elucidate solute–solvent and solute–solute interactions in aqueous solutions.

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CHAPTER 2

REVIEW OF LITERATURE

Rai et al. (1989)¹ investigated ultrasonic propagation in several ternary liquid mixtures, namely (n-pentane + n-hexane + benzene), (n-hexane + cyclohexane + benzene), and (cyclohexane + n-heptane + toluene) at 298.15 K. Ultrasonic velocities were measured experimentally and compared with values predicted from different empirical, semi-empirical, and statistical models. The authors reported reasonable agreement between experimental and theoretical results and employed excess isentropic compressibility to elucidate the nature of intermolecular interactions present in these ternary systems.

Kannappan and Rajendran (1991)² investigated molecular interactions in ternary liquid mixtures using ultrasonic velocity and density data, deriving isothermal compressibility and excess compressibility to analyze interaction strength.

Aminabhavi et al. (1994)³ measured density, refractive index, and viscosity for aqueous DEG and dimethyl ether mixtures with several solvents, and their analysis showed strong intermolecular interactions.

Magazù et al. (1997)⁴ measured density and ultrasonic velocity of aqueous α,α -trehalose solutions using ultrasonic techniques. Their results indicated a clear deviation from ideal mixing behaviour. Analysis of excess compressibility revealed that, at higher concentrations, the solute molecules tend to form intramolecular hydrogen bonds, influencing the overall solution structure.

Eliassi and Modarres (1998)⁵ measured the density of binary mixtures of water with PEG 400, PEGs over a range of temperatures. Their results offered meaningful insight into the interaction patterns and structural behaviour of these polymer–water systems.

Tamura et al. (1998)⁶ determined excess enthalpy, heat capacity, and densities at three temperatures and ultrasonic velocity at 298.15 K on the ethoxyethanol–water mixtures to examine the thermodynamic behaviour. These combined data provided deeper insight into the temperature-dependent structural and interactional characteristics of the mixtures.

Ali et al. (1999)⁷ measured viscosities, densities, and ultrasonic velocities for several pure liquids such as 1-octanol, ethanol, acetonitrile, and 1-hexanol. Based on these measurements, they assessed various thermophysical parameters, revealing the existence of molecular associations within these compounds.

Souto et al. (1999)⁸ measured density and sound velocity in borate glasses doped with different lithium salts. LiCl, Li Br, and Li I anions occupy interstitial sites, while Li F and Li₂ SO₄ directly modify the boron–oxygen network. The results show how each salt alters the glass structure.

Taboada et al. (2001)⁹ The review of the thermodynamic characteristics of the antidepressant drugs in solutions has been accomplished by the study of their solubility, enthalpy, and entropy. The study focused on enhancing drug design and dosing based on the behaviour of three amphiphilic antidepressants, namely amitriptyline, nortriptyline, and desipramine drugs, in the human body.

Baluja and Oza (2001)¹⁰ examined methanol mixtures with anisole–dimethylformamide and anisole–chloroform, using thermodynamic parameters to interpret molecular interactions and structural effects.

Graber et al. (2002)¹¹ measured viscosity, density, and refractive index for water–PEG–sodium nitrate mixtures at different temperatures and used the data to evaluate excess molar volumes and interaction behaviour.

Rodr guez et al. (2002)¹² measured density, refractive index, viscosity and sound velocity, of DL alanine–NaCl solutions and derived apparent molar volumes and compressibilities. They found positive volume transfer, reduced hydration-shell compressibility and increased viscosity at higher NaCl concentrations reflecting strong interactions between amino acid and ions.

Dutour et al. (2002)¹³ Acoustic parameters are measured using density, speed of sound and isentropic compressibility of tri-decyl-benzene and penta-decyl-benzene at variation of temperature. Tait like equation was fitted for the density data to calculate the isentropic compressibility. The results contribute to the thermodynamic characterization of these high-molecular-weight hydrocarbons, significant in the petroleum industry for their presence in heavy oils.

Valen et al. (2002)¹⁴ The ternary system of 1-butanol+1-chlorobutane+tetrahydrofuran was investigated at three different temperatures, for research data on ρ and c . These properties were used to evaluate V_{ϕ}^0 and $K_{\phi,s}^0$ deviations. Thermodynamic characterization concerning the variation of temperature has also been performed and discussed.

Sorenson et al. (2003)¹⁵ investigated V_{ϕ} and heat capacities of aqueous L-proline mixtures with up to equimolar HCl/NaOH additives at 0.35 MPa. Their interpretation, in particular for Na Prol(aq.), employed Young's Rule to include speciation effects in solution.

George and Sastry (2003)¹⁶ were discussed the binary mixtures of 2-butoxyethanol, 2-methoxyethanol, 2-ethoxyethanol, and with several aromatic and cyclic hydrocarbons, including benzene, toluene, xylene isomers, ethylbenzene, and cyclohexane. They provided a comprehensive view of the structural and interactional behaviour in these liquid systems based on density, viscosity, ultrasonic velocity, excess molar properties, and dielectric constants at various temperatures.

Galan et al. (2003)¹⁷ measured density and ultrasound velocity for aqueous tetradecyltrimethylammonium nitrate within the temperature range 15-35°C and estimated molar volume, thermal expansibility, and compressibility in monomeric and micellar forms using these data. They compared their results with related alkyl trimethylammonium bromide system.

Nayakulu et al. (2004)¹⁸ analysed ultrasonic velocity of cresols in ethyl acetate at a constant temperature of 311 K with the help of an ultrasonic pulse echo system. Internal pressure and molar free volume were calculated. Ultrasonic velocity rose linearly with the rise in acidity constant, which means it depends on acidity. Ultrasonic velocity was also influenced by the polarity of the solvent.

Marczak et al. (2005)¹⁹ computed the properties methanol exhibits with various pyridine derivatives at 298.15 K. Like their interactions with water, the hydrogen-bonding capacity of pyridines with methanol was enhanced by the ortho effect. With stronger hydrogen bonds, the changes in compressibility and volume are smaller, and enthalpy of solution is more negative.

Bolotnikov et al. (2005)²⁰ The speed of sound and density of hexane + hexadecane were measured across compositions and temperatures from 293.15 to 373.15 K. Using precise ultrasonic and pycno-metric measurements, the authors derived excess molar volume, and isentropic compressibility using the Redlich–Kister equation.

Sankarappa et al. (2005)²¹ measured density and ultrasonic velocity of different edible oils at a frequency of 3MHz in the temperature range 298-333 K. Nonlinear decreases of velocity with temperature were exhibited by some oils. Density for all the oils decreased with the rise of temperature. From the measured data, various physical parameters have been estimated.

Salabat et al. (2005)²² presented viscosity, density, water activity and refractive index, for aqueous $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ at 25°C. Isopiestic water activity data were used to evaluate Pitzer ion-interaction parameters. From density measurements, V_ϕ was determined, allowing a revised value of the V_ϕ^0 of the citrate ion to be obtained.

Moattar et al. (2005)²³ measured the density and sound velocity of BMIM Br in water, methanol, and ethanol, then calculated apparent molar volume and compressibility and fitted them to a Redlich–Mayer equation. Their results showed stronger ionic liquid–solvent interactions in water than in the alcohols.

Zorębski et al. (2006)²⁴ presents a study on the binary liquid mixtures of 1,3-butanediol and 1-pentanol at various temperatures. The analysis revealed that mixing these compounds causes increased rigidity and volume expansion; this effect is enhanced with rising temperature. This phenomenon tells changes of molecular interactions in the studied system.

Nain et al. (2007)²⁵ investigated mixtures of aniline with different alkanols at various temperatures. interactions among aniline and alkanol molecules were indicated by negative excess molar volumes of such mixtures. The degree of interaction depended upon the positions of hydroxyl and methyl groups in the alkanols studied. This study brings into light the negative excess molar volumes of mixtures of aniline and alkanols, which illustrates specific interactions. Results indicate that hydrogen bonding and other weak interactions are responsible for volume contraction. Increase in temperature increases V_ϕ due to reduced interactions causing volume expansion. Temperature

coefficients of V_ϕ also support this trend since higher the temperature, lower the interaction.

Blodgett et al. (2007)²⁶ investigated V_ϕ properties and heat capacities of several water-based sugar alcohol mixtures. In their study, a vibrating-tube densimeter and a fixed-cell temperature-scanning calorimeter assessed the molecular interactions operating within these systems.

Roy et al. (2007)²⁷ measured viscosities and densities for mixtures of formamide with compounds such as 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane, and dimethyl sulfoxide. Their results provided useful information of intermolecular interactions in these samples.

Sadeghi et al. (2007)²⁸ determined ASV and $K_{\phi,s}$ compressibilities of polyvinylpyrrolidone (PVP) in aqueous sodium citrate solutions by measuring density and sound velocity. Their results indicated a positive ΔV_ϕ^0 of PVP from pure water to sodium citrate solutions. Temperature-dependent trends in apparent specific isentropic compressibility showed that the hydration environment around PVP is less compressible than bulk water at lower temperatures and more compressible at higher temperatures. Besides, the compressibility values increased with increasing sodium citrate concentration, underlining the effect of electrolyte–polymer interactions on solution structure.

Ayranci and Sahin (2008)²⁹ determined ultrasonic velocities and densities of polyethylene glycol (PEG) and ethylene glycol (EG). The parameters calculated and analysed graphically, helped characterize the molecular behaviour of said substances.

Palani and Geetha (2008)³⁰ obtained the ultrasonic velocity, viscosity, and density for aqueous propylene glycol mixed with tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and 1,4-dioxane at different temperatures. The data thus obtained allowed the calculation of excess functions and the interaction parameter d , which are useful in understanding solute and solvent interactions.

Sadeghi et al. (2009)³¹ measured density and ultrasonic velocity for ternary mixtures of water, polypropylene glycol, and various phosphate salts at several temperatures under conditions of constant pressure. Using these measurements, they evaluated a

range of thermodynamic properties including isentropic compressibility, apparent specific volume, and deviations in both compressibility and volume.

Riyazuddeen et al. (2010)³² measured ρ and c of the several amino acids in 2 mol·L⁻¹ NaNO₃ and NaCl solutions. From these data, they calculated the isentropic compressibilities and observed κ_s to decrease with rising amino-acid concentration and temperature. These variations were interpreted to reflect molecular interactions in the mixed electrolyte system.

Patil et al. (2010)³³ measured viscosity, c , and ρ of 1-hexanol and 1-heptanol with nitrobenzene across all compositions and temperatures. They used the data to derive interaction-related parameters through Redlich–Kister analysis.

Raman et al. (2010)³⁴ studied viscosity, c , and ρ for aqueous D-arabinose solutions. Using these measurements, the authors calculated several thermodynamic parameters such as shear relaxation time, classical sound absorption, intermolecular free length, hydration number, and isentropic compressibility in order to characterize the interactions among solute solvent.

Dzida et al. (2010)³⁵ reports on the physicochemical properties of (2-methyl-2-butanol + heptane) studied by an acoustic method. The effect of the branched structure of the alcohol on its association with heptane and on the departure from ideality at various temperatures and pressures was studied. ρ and c were measured, excesses, heat capacities, and molar volume were computed. The results reveal in terms of molecular size, self-association capability, packing effect, and non-specific interactions using the modified ERAS model.

Dubey et al. (2010)³⁶ measured thermophysical properties of diethylene glycol monomethyl ether mixed with various alcohols. They reported excess volume, viscosity deviation, compressibility, and sound-speed deviation, and used semi-empirical relations to interpret the viscosity trend.

Thirumaran et al. (2011)³⁷ took measurements on the amino acids mixed with various molar concentrations in aqueous magnesium acetate solution. The parameters were evaluated. Viscosity A and B coefficients were also determined. Interionic interactions and structure effects were discussed.

Rajagopal *et al.* (2011)³⁸ measured the density, viscosity, and ultrasonic speed of 2M2P mixed with AN, PN, and BN over extended temperatures and compositions. They calculated the excess and deviation parameters using two approaches; these results suggested only weak interactions among components.

Shakya *et al.* (2011)³⁹ determined viscosity, ρ , and c using a single-crystal interferometer, and from these measurements, acoustic parameters such as specific acoustic impedance and solvation number were calculated for a solution containing iron acetylacetonate and liquid sodium hydroxide. The authors have found strong interaction in the aqueous solution at higher concentrations.

Pandey *et al.* (2013)⁴⁰ reported the data of ultrasonic speed and density for the mixtures of formamide and N-methyl formamide with 2-chloroethanol at several temperatures and computed the excess and compressibility parameters. Infrared spectra at 298.15 K supported the acoustic and volumetric results, indicating hydrogen bond-driven association in the mixtures.

Kumar *et al.* (2013)⁴¹ reported the data of density and ultrasonic speed for trisodium and tri-potassium citrate in aqueous N-acetyl glycine at different temperatures. They calculated molar and transfer properties, compressibility parameters, and interaction coefficients using this data; these parameters facilitated the interpretation of ion–ion and ion–solvent interactions of the mixed systems.

Ryshetti *et al.* (2014)⁴² measured densities and sound velocities of betaine hydrochloride in NaCl and KCl aqueous solutions over 293.15–313.15 K and derived the corresponding volumetric and compressibility parameters, including transfer properties and Hepler's constants. The latter were applied to evaluate the temperature and co-solute effects on drug–solvent interactions.

Singh *et al.* (2014)⁴³ reports density and sound speed for an ionic liquid, two carboxylic acids, and their mixtures across different temperatures. From these data, they evaluated excess volumes and compressibility-related parameters using Redlich–Kister correlations, concluding that hydrogen bonding plays a key role in the mixed systems.

Golabiazar et al. (2014)⁴⁴ investigated the volumetric and compressibility properties of the [C₁₂mim] Br in water without salts and in the presence of various electrolytes. This work examined six chloride salts and five sodium-based salts to separate the cation and anion effects on aggregation behaviour. Critical aggregation concentration (CAC) values were measured, and all the electrolytes produced a salting-out effect, decreasing the CAC according to the Hofmeister series.

Kharat et al. (2014)⁴⁵ measured ρ , viscosity, and c of aqueous sodium salicylate solutions at 298.15–313.15 K and used these data to compute various interaction parameters. Hydration free energy was also calculated using DFT. The results reveal to understand the nature and strength of solute–solvent interactions in the system.

Chauhan et al. (2015)⁴⁶ used ρ , c , and viscosity measurements to examine how furosemide interacts with glycine and DL-alanine in water. From these data, they estimated key thermodynamic parameters and found clear evidence of strong solute–co-solute interactions, with both amino acids showing a structure-making effect in the drug solutions.

Kumar et al. (2015)⁴⁷ reported that molar volume and compression of glucose and fructose both varied with temperature and concentration, and interaction parameters pointed toward different stereochemistry and interactions in mixtures.

Dhondge et al. (2015)⁴⁸ report the thermodynamics of some important bioactive compounds in aqueous solutions. The ρ and c were measured and other parameters calculated to analyse the nature of solute-solvent interactions.

Kumar et al. (2016)⁴⁹ measured density and sound speed to calculate apparent and partial molar volumes, compressibility, and expansion coefficients for D (+)-glucose and D(-)-fructose in water and trisodium citrate solutions. Their results showed that interactions increase with trisodium citrate concentration, highlighting ion–hydrophilic and hydrophilic–hydrophilic effects.

Klimaszewski et al. (2016)⁵⁰ Densities and ultrasonic sound velocity in T4EG + water mixtures were measured. The calculated physicochemical parameters included molar volume, compressibility, and their derivatives and ΔV_{ϕ}^0 . These values were interpreted to understand the nature of mixture interactions and structure. This research has

pointed out the internal structure of mixtures, with an emphasis on hydrogen bond interactions. The results are compared with data on other glycol-water mixtures, pointing out the importance of accurate density measurements for detailed insights.

Banipal et al. (2016)⁵¹ investigated the densities, viscosities, and dilution enthalpies of L-serine and L-proline in water and in sodium propionate and calcium propionate aqueous. Based on these measurements, the authors interpreted the interactions among solute and co-solute, hydration behaviour, and even changes in flavour-related properties. Supporting evidence from both calorimetric and NMR data gave ample proof that dehydration processes were predominant, confirming the type of interactions established in these systems.

Krishna et al. (2016)⁵² determined the thermophysical properties of the ionic liquid [BMIM][PF₆] + 2-propoxyethanol (including pure components) at various temperatures under atmospheric pressure. The authors estimated excess properties and partial molar quantities from the experimentally obtained data, by interpreting these properties in terms of intermolecular interactions present in the binary mixtures.

Apelblat et al. (2017)⁵³ measured sound velocities of aqueous Li NO₃, NaNO₃, and KNO₃ solutions at three concentrations and used these data, along with densities, to calculate compressibilities, apparent molar volumes, thermal pressure coefficients, expansion coefficients, heat-capacity derivatives, and hydration numbers. Ultrasonic relaxation times were also evaluated. The trends in these properties were interpreted in terms of structural changes in water induced by the dissolved alkali metal nitrates.

Malladi et al. (2017)⁵⁴ measured ρ and c of procaine hydrochloride in water and in NaCl/KCl solutions to derive thermodynamic parameters. From these data, they obtained thermodynamic parameters. The results were analysed to understand how electrolyte concentration and temperature influence solute–solute and solute–solvent interactions.

Gaba et al. (2017)⁵⁵ Thermodynamic properties of l-threonine and l-valine were studied in [C₅mim] [Cl] solution at three temperatures using volumetric and ultrasonic properties. V_ϕ and $K_{\phi,s}$ were calculated, and parameters such as Hepler's constant

values, hydration numbers, and specific volume were determined. These parameters provide insight into the solution's structure, solvation, and taste behaviour.

Naseem et al. (2017)⁵⁶ Measurements of ρ and c were taken for alcohols and nitroimidazole solutions at varying temperatures. The resulting parameters indicated strong solute-solvent interactions and closely packed antibiotic structures in alcohols. Additionally, strong intermolecular interactions were observed in solutions.

Jengathe et al. (2017)⁵⁷ measured the densities and sound speeds of sodium salicylate in the aqueous solutions of NaCl and myo-inositol at different temperatures. They calculated the molar volume, compressibility, and thermal expansion, indicating that sodium salicylate acts as a structure maker and interacts with ions and hydroxyl groups, while water electrostriction decreases with increased temperature.

Dhondge et al. (2017)⁵⁸ had derived thermodynamic properties by obtained values in thiamine hydrochloride and pyridoxine hydrochloride solution. They resulted weak ion- ion interaction in binary mixture.

Chakraborty et al. (2018)⁵⁹. explored the effect of temperature on the interactions of D-Panthenol with glycols through studies in density and sound speed, calculating molar volume, compressibility, and interaction coefficients, and showing that ion-hydrophilic and hydrophilic-hydrophilic interactions increase with an increase in molar mass of D-panthenol and glycols. In the case of p-cymene mixed with halo-benzenes,

Makavana et al. (2019)⁶⁰ measured density and sound speed of sound of p-cymene mixed with halo-benzenes at several temperatures. They derived the properties of excess molar volumes and isentropic compressibility to analyze molecular interactions and property changes with composition and temperature.

Hnedkovsky et al. (2020)⁶¹ measured densities of up to sixteen aqueous zinc sulphate solutions using a vibrating-tube densimeter, ensuring accurate control of concentration and pH. Additional density measurements were performed at 343.15 and 373.15 K under 0.3 MPa using a high-temperature Pt/Rh densimeter, and the overlapping data at 343.15 K showed excellent consistency. From the density values, V_ϕ were calculated and fitted using an extended Redlich–Rosenfeld–Meyer equation. However, the

standard molar volumes obtained from the fit showed noticeable deviations—up to about $2 \text{ cm}^3 \cdot \text{mol}^{-1}$ —compared with independently determined infinite dilution values.

Sharma et al. (2020)⁶² measured density, sound speed, and viscosity of Metformin hydrochloride in water with urea and thiourea at different temperatures. They calculated molar volumes, compressibility, and expansion parameters, showing how solute–solvent and solute–solute interactions influence structure formation in the solutions.

Chakraborty et al. (2020)⁶³ This study calculates volumetric and acoustical parameters to understand the interaction among xylitol and glycols. Results suggest stronger interaction between tri-ethylene glycol and aqueous xylitol.

Bhanuprakash et al. (2020)⁶⁴ reports on the experimental ρ and c data for benzyl alcohol mixed with acetic acid, propionic acid, and n-butyric acid. Excess thermodynamic properties were negative. Attenuated total reflection Fourier transform infrared spectra were also recorded to evaluate intermolecular H-bonding in the binary solutions.

Han et al. (2020)⁶⁵ This study compared non-thermal processing techniques for milk, focusing on high-pressure homogenization and ultrasound. The study analysed the structural changes and functional characteristics of casein treated with these techniques. Both methods improved foaming and emulsifying properties, and reduced casein allergenicity.

Sharma et al. (2020)⁶⁶ The ρ , viscosity, and c for L-Histidine in an aqueous solution of the ionic liquid $[\text{C}_4\text{mim}][\text{BF}_4]$ were measured at different temperatures. The data was used to determine different properties, such as volumetric, viscometric, and compressibility parameters, as well as the hydration number. Viscosity coefficients were also calculated to understand the interactions among the ionic liquid and the amino acid.

Dubey et al. (2020)⁶⁷ Experimental ρ and c were measured for binary mixtures of di-n-butylamine and di-isopropyl-amine with 2-butanol and 2-pentanol. Various thermodynamic parameters were calculated and analysed, and a polynomial equation was used to correlate all the calculated properties. The effects of temperature, chain

length, and branching were examined, and FT-IR spectroscopy was used to support the results obtained.

Amirchand et al. (2021)⁶⁸ Studied saccharide molecules in aqueous calcium salt solution at two temperatures. Evaluated volumetric properties and interactions affecting taste behaviour. Found hydrophobic interactions to be dominant. ¹H NMR showed presence of hydrophobic-ionic interactions.

Sharma et al. (2021)⁶⁹ ρ , c , and viscosity measurements were taken for mixtures of aqueous streptomycin sulphate with six different electrolytes at various concentrations and temperatures. Derived parameters were calculated and used to investigate interactions and the effect of electrolytes on structure making and breaking properties.

Jamal et al. (2021)⁷⁰ investigated escitalopram oxalate by measuring its ρ and c in water and various alcohols. From these measurements, calculated parameters such as compressibility and partial molar volume and also identified micelle formation using a fitting approach. The results obtained were discussed in terms of how the drug influences the structure of the surrounding medium.

Ankita et al. (2021)⁷¹ determined the values of density, sound speed, and viscosity for sodium salicylate in water and in D-xylose/L-arabinose solutions, demonstrating temperature-dependent solute-solute and solute-solvent interactions dominated by hydrophilic and hydrophobic groups.

Kumar et al. (2021)⁷² focused on a mixture of an imidazolium-based ionic liquid with selected amino acids. From experimentally obtained density and sound velocity, and spectroscopic data, volumetric and acoustic parameters were derived. These findings were used to interpret how the components of the mixture modify the structural arrangement of the solution.

Kaur et al. (2022)⁷³ determined the density and sound speed of chlorhexidine in methanol with propylene and he-xylene glycols at several temperatures, calculated molar volume and compressibility parameters that reflected marked solute-solvent interactions.

Zhen et al. (2022)⁷⁴ highlighted growing environmental concerns associated with persistent plastic waste used in food packaging. To mitigate this issue, the authors

emphasized the necessity for biodegradable polymers with inherent antibacterial properties. Their work reviewed several commonly used protein-based biodegradable materials—such as zein, soy protein isolate, gelatine, and whey protein—and discussed their relevance and applications in modern food packaging. The study also summarized natural antimicrobial agents and explored how these can be incorporated into biodegradable films for improved food preservation.

Momeni et al. (2022)⁷⁵ The authors explored the potential of the ionic liquid [Ch][Lac] as an entrainer for separating azeotropic mixtures. They collected p and c data for binary systems (water + [Ch][Lac]) with different alcohols, as well as ternary systems (water + alcohol + [Ch][Lac]) at various temperatures and pressures. The study unveiled that 2-propanol exhibited the strongest interaction with [Ch][Lac], suggesting its promise for effective separation in combination with [Ch][Lac].

Guzik et al. (2022)⁷⁶ investigated consumer attitudes toward seven different food preservation technologies and examined the factors influencing these perceptions, including the credibility of product labelling. Using microwave treatment as a case study, the research demonstrated how renaming or reframing a preservation process can alter consumer acceptance “dielectric heating,” for example, was viewed more favourably. The findings provide an important perspective for businesses and researchers by clarifying how consumers interpret preservation methods and by offering insights for improving communication and market adoption of emerging food preservation technologies.

Abedi et al. (2022)⁷⁷ Efforts to improve pharmaceuticals have led to new drug discoveries and delivery systems. Thermodynamic investigation provides crucial knowledge of drug-membrane interactions and suitable compounds. This study measures CDP in amino acid solutions to calculate molar volumes and isentropic compression using the Redlich-Meyer equation.

Jamal et al. (2022)⁷⁸ A study was conducted on the characteristics of an aqueous solution of the ionic liquid [BMIM] [PF₆] with L-leucine. Various parameters, including molar volumes and compression, were measured at different temperatures. The results revealing that L-leucine plays a role in solute-solvent interactions.

Shahazidy et al. (2022)⁷⁹ Sugar alcohols are important in the food and pharmaceutical industries as they affect blood glucose levels and are used as artificial sweeteners. A study was conducted on meso-erythritol in water and water-DMSO mixtures to evaluate their solvation behaviour and taste quality. The obtained parameters characterize the hydration properties and solvation behaviour of sugar alcohol in aqueous solutions.

Kumar et al. (2022)⁸⁰ The ρ and c of L-leucine and N-acetyl-L-leucine in aqueous 1-hexyl-3-methylimidazolium bromide were measured. Using these data, they calculated molar volume-related parameters together with interaction coefficients to understand the nature of solvation and molecular interactions in the ternary mixtures.

Limalia et al. (2023)⁸¹ examines the mixtures of oct-1-ene with propan-1-ol or propan-2-ol by measuring density, sound speed, and refractive index. The outcomes distinctly demonstrated non-ideal behaviour, and these results were analysed using Redlich-Kister correlations, elucidating both thermodynamic and optical properties.

Asadzadeh et al. (2023)⁸² measured ρ , c , and viscosities of aqueous solutions of an imidazolium ionic liquid with L-serine and L-threonine. Calculated volumetric and transport parameters indicated strong ion-solvent interactions and changes in water activity and solute-solute interactions dependent on temperature.

Sawale et al. (2023)⁸³ This study investigates sodium salicylate and 4-aminoantipyrine in aqueous solutions of glycine/L-proline, delving into their thermophysical properties and revealing key insights into solute interactions, thus aiding valuable information for drug design and development. The study found increased solute-solvent interactions with higher glycine/L-proline concentration. These interactions suggest ion-ion/hydrophilic and hydrophilic-hydrophilic effects. Rising values with temperatures and co-solute concentration hold implications for pharmacokinetics and protein chemistry.

Sheikh et al. (2023)⁸⁴ The ρ and c of L-Citrulline were measured in aqueous solutions with Urea and Dextrose. The methodology involved experimental measurements to determine crucial parameters. The results helped determine important parameters and understand different interactions in these solutions. The study on L-Citrulline in water

and ternary solutions (with Urea and Dextrose) revealed positive values for thermodynamic properties, indicating interactions with co-solutes. Hepler's constant hinted at a structure breaker tendency in specific systems, and acoustic parameters supported these observations, providing insights into molecular interactions

Lamba et al. (2023)⁸⁵ In this study, molecular interactions were studied under constant pressure. The study focused on aqueous solutions of Disodium EDTA (0.01-0.03) in combination with Propylene and He xylene glycol. c and ρ measurements, as well as FTIR spectroscopy, revealed significant solute-solvent interactions.

Srisanthi et al. (2023)⁸⁶ evaluated the behaviour of benzene with butyl/pentyl parabens in isopropanol using volumetric and acoustic experiments at different temperatures. The properties studied provided insights into the intermolecular interactions among the constituents.

Rathi (2023)⁸⁷ investigated the temperature and concentration affect the acoustic, viscometric and volumetric properties of KIO_3 solutions in 1% KH_2PO_4 , exploring intermolecular interactions. The study provides acoustical parameters and viscosity coefficients for the solution and pure water systems at different temperature.

Zavala et al. (2023)⁸⁸ A method to extract and detect four categories of pharmaceuticals in compost from biological hazardous waste was developed and validated. The eight compounds of interest were extracted using ultrasonic ethyl acetate and methanol. Separation and detection were achieved using UHPLC with MRM. The limits of detection and quantification were lower than literature values. The validation showed good linearity, precision, and low matrix effect. The method is expected to reduce analysis time and cost for complex matrices like compost.

Awasthi et al. (2023)⁸⁹ Density measurements were taken for binary mixtures of 2-ethoxyethanol with 2-pyrrolidinone and N-methyl acetamide at different temperatures and compositions. V_ϕ and V_ϕ^0 were calculated from the data, revealing negative variations indicating specific intermolecular interactions between the molecules. The results provide insight into molecular interactions.

Dhingra et al. (2023)⁹⁰ This study investigates liquid mixtures of 1-butoxy-2-propanol with amines, analysing density, speed of sound, and intermolecular interactions. They

utilized the Redlich–Kister polynomial, Jouban–Acree model, and Prigogine–Flory–Patterson theory to correlate properties with composition. Additionally, the researchers analysed ¹H-NMR spectra at equimolar composition to gain further insights into the mixture's characteristics. The study found strong interactions in 1-butoxy-2-propanol and amine mixtures, with 1B2P + DEA showing the highest strength.

Bankar et al. (2023)⁹¹ reported densities, sound velocities, and viscosities for aqueous NaCl, KCl, Mg Cl₂, and Ca Cl₂ solutions across a wide concentration range and seven temperatures (288.15–318.15 K). From these data, they derived key thermodynamic quantities to interpret ion–solvent interactions. The trends revealed the nature and strength of interactions in these electrolytic systems. Complementary DFT calculations, focusing on HOMO–LUMO characteristics, were performed to support and rationalize the experimental findings.

Kaur et al. (2023)⁹² showed that the addition of glycols to chloroxylenol-methanol mixtures led to a decrease in the density and an increase in the viscosity of the solutions. The authors attributed this to the formation of H- bonds among the glycols and chloroxylenol. They also found that the speed of sound in the solutions increased with the addition of the glycols, which was attributed to the increase in the compressibility of the solutions.

Syal et al. (2024)⁹³ examined how two imidazolium ILs, [EMIm]Cl and [BMIm]Br, on the behaviour of sodium salicylate in water in the range of 283.15–313.15 K. The interactions in these mixtures were interpreted using the data on the density and sound velocity as well as viscosity to evaluate molar volume–related and compressibility parameters. Their results exhibited predominantly hydrophilic and ion–hydrophilic interactions with more intense interactions of sodium salicylate in systems with [BMIm]Br than in the systems containing [EMIm]Cl.

Forghani et al. (2024)⁹⁴ The authors investigated mono-ethanolamine and 1-alcohol binary mixtures under various conditions. They performed ρ and c to understand the properties of these mixtures. The study also included thermodynamic properties such as excess molar volumes and isentropic compressibilities. The results offer insights into the thermodynamic behaviour and molecular interactions within these binary mixtures.

Borović et al. (2024)⁹⁵ The study explored caffeine's behaviour in water with 0.1 mol·kg⁻¹ of [B mim] [Sal]. They measured properties like density and viscosity across temperatures. Findings suggested [B mim] [Sal] increased caffeine solubility and promoted self-aggregation. Molecular simulations revealed stronger interactions at higher temperatures, particularly π - π interactions.

Bhakri et al. (2024)⁹⁶ investigated PEG-lactobionic acid mixtures over a range of temperatures by interpreting density and sound-speed data in terms of molecular interactions. They also conducted a spectroscopic examination of the lactobionic acid-water system, quantifying several key bonding features in this system.

Pathan et al. (2025)⁹⁷ The study measured sound velocity and density of l-isoleucine in Mg (NO₃)₂ and MgSO₄ solutions. They calculated various thermo-acoustic and volumetric parameters and discussed intermolecular interactions. Isothermal compressibility decreased with temperature, indicating strong interactions. Mg (NO₃)₂ showed stronger interactions than MgSO₄.

Shahvarpour et al. (2025)⁹⁸ This study investigated molecular interactions in acetophenone + chloroalkane/chloroalkene mixtures using volumetric, acoustic, and electromagnetic measurements. They measured ρ , c and refractive index, and calculated V_ϕ , $K_{\phi,s}$, and excess refractive index. Results showed mostly negative excess molar volumes and compressibilities, indicating strong specific interactions, except for acetophenone + 1,2-dichloroethane showing positive volume. This work highlights how molecular structure and chlorine atoms influence interactions.

Dorosti et al. (2025)⁹⁹ examined how choline-based ionic liquids influence the thermodynamic behaviour of D (+)-glucose to better understand their potential role in improving sugar-to-bioethanol conversion. They measured density, ultrasonic velocity, viscosity, and electrical conductivity of glucose in aqueous [Ch][Sal], [Ch][For], and [Ch][Ace] over different concentrations and temperatures. From these data, they derived parameters such as V_ϕ , $K_{\phi,s}$, viscosity B-coefficients, and molar conductivity to assess intermolecular interactions. The results showed stronger glucose-ionic-liquid interactions in [Ch][Sal], supported by transfer volumes, Hepler's constants, and DFT-COSMO calculations. Hydration studies indicated decreasing

hydration numbers with temperature due to weakened hydrogen bonding. Overall, the findings identify [Ch][Sal] as the most effective among the tested ionic liquids for enhancing sugar conversion toward bioethanol production.

Ammari et al. (2025)¹⁰⁰ investigated aqueous solutions of choline salicylate ([Ch][Sal]), in the presence of L-glycine to simulate a simple biological environment. They measured density, ultrasonic velocity, viscosity, and electrical conductivity to evaluate thermodynamic and transport behaviour. From these measurements, key parameters—including, V_ϕ , $K_{\phi,s}$, viscosity B-coefficients, ion-association constants, and limiting molar conductivity—were calculated. Transfer properties indicated that hydrophilic–hydrophilic interactions between ChSl and L-glycine increased with L-glycine concentration. Computational COSMO analysis further showed stronger hydration and stability of [Ch][Sal] due to its molecular size and hydrogen-bonding capability. Overall, the study provides meaningful insight into solute–solvent interactions relevant for optimizing pharmaceutical formulations.

2.1 Research Gap and Scope of the Present Investigation

The literature reviewed in this chapter shows that extensive work has been carried out on the volumetric, acoustical and thermodynamic properties of binary and ternary liquid mixtures. Several researchers have investigated different pharmaceutical compounds, electrolyte solutions and ionic liquid systems using density, ultrasonic velocity, viscosity, electrical conductivity and spectroscopic techniques. These studies have provided valuable information regarding molecular interactions, hydration behaviour, ion–solvent interactions and structural changes occurring in solution systems.

Although considerable information is available in the literature, most of the reported investigations are confined to individual systems studied under different experimental conditions. The reported studies mainly deal with a single salicylate, a particular electrolyte or a specific binary or ternary mixture. As a result, the available information is scattered and does not provide a systematic comparison of the behaviour of different salicylates in the presence of a common set of electrolytes. Moreover, the influence of cation chemistry on the physicochemical properties of salicylate-based aqueous systems has not been comparatively discussed under identical experimental conditions.

The studies discussed in the preceding sections indicate that only limited studies have combined volumetric, acoustical and FTIR spectroscopic techniques to obtain a comprehensive understanding of molecular interactions in salicylate-based aqueous systems. Most investigations explain the behaviour of individual systems, whereas comparative studies involving different salicylates together with different electrolytes using the same experimental methodology remain limited. Therefore, a comprehensive comparative investigation is required to understand the effect of different cations and electrolytes on molecular interactions, hydration behaviour and structural characteristics of salicylate solutions.

Keeping these observations in view, the present investigation has been undertaken to systematically study aqueous solutions of sodium salicylate, choline salicylate and magnesium salicylate in the presence of selected inorganic electrolytes over a range of temperatures. Density and ultrasonic velocity measurements have been employed to evaluate various volumetric and thermodynamic parameters, and the experimental observations have been further supported by FTIR spectroscopic analysis. The use of a common experimental methodology for all the investigated systems provides a reliable basis for comparing the influence of different salicylates and electrolytes on molecular interactions and solution structure. The results obtained in the present investigation are expected to contribute to a better understanding of ion-specific effects in salicylate-based aqueous systems and may also provide useful information for pharmaceutical and thermodynamic applications.

Chapter Summary

This chapter reviewed the available literature, critically identified the existing research gaps, and established the scope of the present investigation. The information presented in this chapter provides the scientific foundation for the experimental work discussed in the subsequent chapters.

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CHAPTER 3

OBJECTIVES AND EXPERIMENTAL PROCEDURES

3.1. Research Objectives

This research focuses on the experimental investigation of fundamental physical properties—density and ultrasonic velocity—of liquid mixtures containing salts and salicylates at various concentrations and temperatures. By deriving acoustical and thermodynamic parameters from these measurements, the study aims to gain insight into molecular interactions and the underlying physical behaviour of these systems. This analysis contributes to the broader understanding of fluid thermodynamics and molecular acoustics, which are central topics in physical chemistry and condensed matter physics. The following are the proposed objectives:

1. To find the density of samples and speed of sound in the liquid mixture of salt and salicylates at different concentrations and temperatures.
2. To calculate various acoustical and thermodynamic parameters for different values of temperatures.
3. To analyze the molecular interactions of calculated thermo-acoustic parameters.

3.2. Rationale for the Selection of the Investigated Systems

The selection of the investigated systems was based on the objectives of the present study and the need to systematically compare the effect of different salicylates and inorganic electrolytes on the physicochemical behaviour of aqueous solutions. Sodium salicylate, choline salicylate and magnesium salicylate were selected to examine the influence of different salicylate systems, while sodium chloride, sodium sulphate, sodium nitrate, trisodium citrate, sodium bicarbonate and potassium chloride were chosen because of their different ionic characteristics. The selected combinations provide a common experimental framework for evaluating the effect of electrolyte type and temperature on density, ultrasonic velocity and the derived volumetric and thermodynamic parameters under identical experimental conditions. The detailed scientific basis for the selection of these salicylates and electrolytes has been presented in Chapter 1.

3.3. Research Methodology

3.3.1. Preparation of Samples

In this investigation, Salicylates such as Magnesium salicylate, Choline salicylate, Sodium Salicylate with molar masses 298.53, 241.28 and 160.11 g·mol⁻¹ respectively were used to prepare aqueous solutions. Binary mixtures were prepared by dissolving salicylates in 100 mL of double-distilled, degassed, and triple-distilled water at different concentrations. For ternary mixtures, salts of varying molalities were added as solutes. The chemicals were purified by vacuum drying and stored in desiccators over P₂O₅. The conductivity of the water used was less than 10⁻⁶ S·cm⁻¹. All chemicals were weighed precisely using an analytical balance (Sartorius CPA225D, readability ±0.00001 g). Prepared samples were stored in glass vials sealed with PFE septa lids and parafilm to prevent atmospheric moisture absorption and sample aging. Degassing of solutions was performed prior to measurements to minimize dissolved gases. Visual inspection confirmed absence of turbidity or precipitation in all samples. The solutions were sealed during measurements to minimize atmospheric exposure.



Figure 3.1: Sartorius CPA -225D electronic weighing balance and vials with samples.

As Choline salicylate was obtained as a pharmaceutical-grade aqueous solution with an assay of 50.53% w/v. Here, 50.53% w/v indicates that 50.53 g of choline salicylate are present per 100 mL of the supplied solution. This value refers to the concentration of the solution and should not be confused with the chemical purity. Stock solutions of choline salicylate were prepared using double-distilled water (100.0 g solvent for each). The required pure solute mass was first calculated according to

$$M_{\text{pure}} = m_{\text{target}} \times m_{\text{solvent}} \times M$$

Where m_{target} is the target molality, $m_{solvent}$ is the solvent mass (0.100 kg) and M is the molar mass of choline salicylate ($241.28 \text{ g}\cdot\text{mol}^{-1}$). Since the supplied material was an aqueous solution of choline salicylate with assay 50.53% w/v (i.e. 0.5053 g of solute per mL of solution), the corresponding assay volume required was obtained from

$$V_{assay} = \frac{M_{pure}}{0.5053}$$

For example, for $0.0590 \text{ mol}\cdot\text{kg}^{-1}$, 1.45 g pure solute is required, which corresponds to 2.87 mL of the assay solution. Similarly, the assay volumes required for 0.0688 and $0.0885 \text{ mol}\cdot\text{kg}^{-1}$ were 3.35 mL and 4.29 mL, respectively. These volumes were accurately weighed and added to 100.0 g of water to prepare the stock solutions. Thus, the calculations were made based on the assay concentration reported by the supplier, ensuring correct molalities of the prepared mixtures. Based on supplier specifications for pharmaceutical-grade choline salicylate, the chemical purity of the main substance is typically $\geq 99\%$. Accordingly, the required mass of pure choline salicylate for each molality was calculated from the supplied solution concentration, and the corresponding volume was used in solution preparation. This approach ensured that the reported molalities accurately reflect the true concentration of pure choline salicylate in each solution.

3.3.2. Measurements of experimental densities and ultrasonic velocity

We used the DSA 5000 M (Density and sound velocity analyser) **Figure 3.2** instrument to measure the density and ultrasonic velocity of aqueous salicylate-salt solutions at temperatures between 288.15 K and 318.15 K in this study. The instrument uses the vibrating U-tube principle to find density and ultrasonic propagation techniques to find ultrasonic velocity.



Figure 3.2: Anton Paar DSA 5000M

3.3.3. Measurement of density and ultrasonic velocity

The density and ultrasonic velocity for the binary and ternary mixtures were determined using a DSA 5000 M instrument (Anton Paar) at 0.1 MPa and 3 MHz frequency. The Anton Paar DSA 5000 M applies two physically independent principles for the simultaneous measurement of density and speed of sound. Density is measured using the oscillating U-tube method, where a U-shaped borosilicate tube is electronically excited to vibrate at its characteristic frequency, which depends on the density of the filled sample. In contrast, the speed of sound is determined in a dedicated acoustic cell using a fixed path transmission technique: an ultrasonic pulse is sent through the sample over a precisely defined path, and the travel time is measured between a transmitter and receiver. This allows the instrument to calculate the speed of sound based on the known path length and travel time, as per established physical principles (sing-around and fixed-path methods). By combining these two independent methods, the instrument provides rapid and accurate determination of both properties under identical conditions as shown in **figure 3.3**. Before starting the measurements, the instrument was calibrated with triple-distilled water across the temperature range of 288.15–318.15 K. For verification of calibration, ethanol was used as a secondary standard fluid to ensure the accuracy of the density and sound velocity measurements. The instrument can measure densities ranging from 0 to 3 g/cm³ and sound velocities within the span of 1000 to 2000 m/s. The sensitivities of the instruments for density and ultrasonic velocity were $\pm 0.001 \text{ kg}\cdot\text{m}^{-3}$, and $\pm 0.01 \text{ m}\cdot\text{s}^{-1}$, respectively.

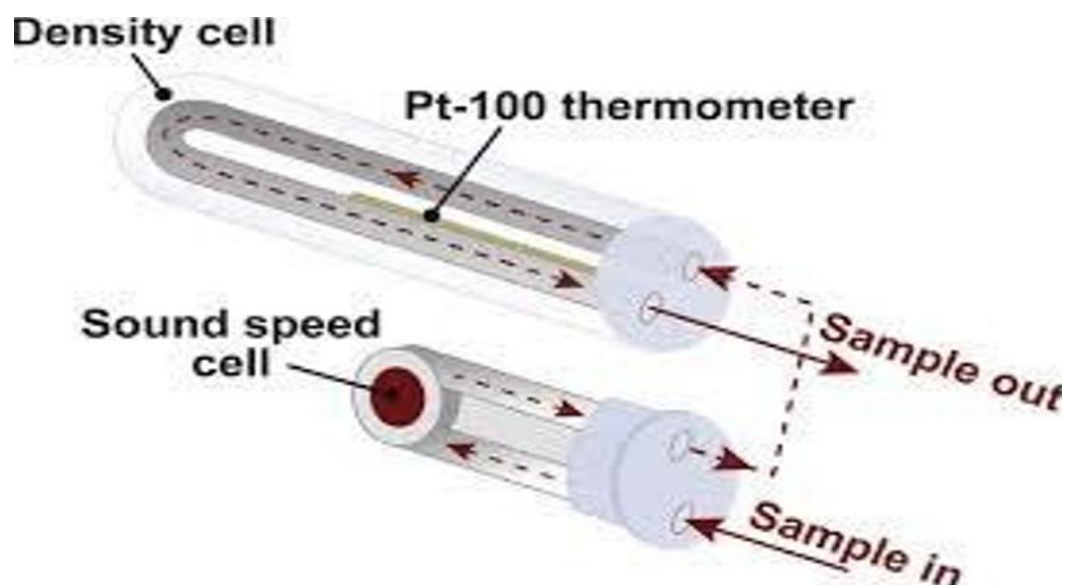


Figure 3.3 Density and ultrasonic Velocity (sound speed) cell of DSA 5000 M

3.4. Fourier Transform Infrared Spectrometer

Attenuated total reflection Fourier Transform Infrared spectroscopy (ATR-FTIR spectroscopy) is a powerful tool for identifying functional groups and understanding the interactions between different components in a mixture. The ATR technique was used to record the spectra of the samples in the wavelength range $400\text{--}4000\text{ cm}^{-1}$ using PerkinElmer FTIR Spectrum One with a resolution of 0.5 cm^{-1} . ATR-FTIR is different from conventional FTIR due to its limited penetration depth, which is estimated between 0.9 and $1\text{ }\mu\text{m}$ at 2000 cm^{-1} and does not exceed $2\text{ }\mu\text{m}$. Unlike conventional transmission FTIR, which analyses the bulk properties of a sample using pressed pellets or discs, ATR-FTIR primarily detects surface interactions. Sample preparation for ATR involved placing a small droplet of the aqueous solution directly onto the cleaned diamond ATR crystal, ensuring good contact by gently pressing with the applicator. Measurements were taken after appropriate background scans, with atmospheric vapor compensation applied to reduce interferences from CO_2 and H_2O . The spectra revealed significant information about molecular-level interactions and structural alterations in the samples. The ATR-FTIR technique was employed to evaluate the molecular interactions and structural characteristics of aqueous salicylate solutions and their mixtures with various salts at different concentrations.

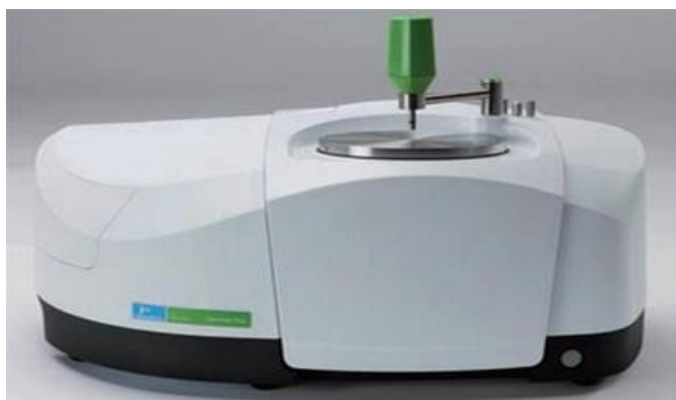
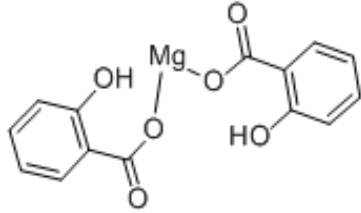
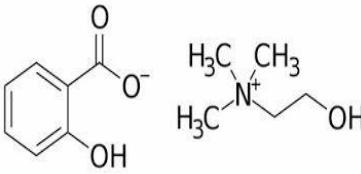
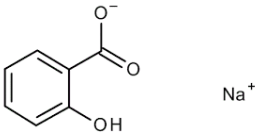


Figure 3.4 PerkinElmer FTIR Spectrometer

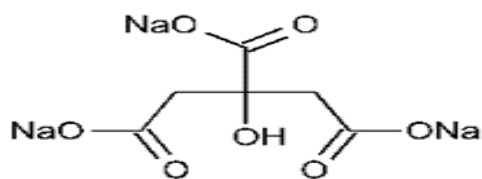
3.5. Chemical Structures

The structure of the chemicals is provided in the table below:

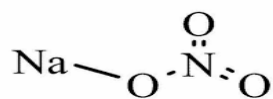
Table 3.1. List of chemical structures

Chemical	Structure
Magnesium salicylate	
Choline salicylate	
Sodium salicylate	
Sodium chloride	Na — Cl

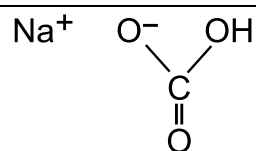
Trisodium Citrate



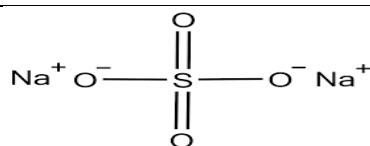
Sodium Nitrate



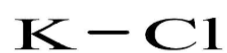
Sodium bicarbonate



Sodium sulphate



Potassium chloride



3.6. Details of Chemicals

Table 3.2. Chemicals name with their specifications

S. No.	Chemical	CAS No.	Suppliers	Formula	Molar mass g·mol ⁻¹	Mass fraction Purity	Purification process
1.	Magnesium salicylate	18917-89-0	New Alliance Fine Chem Private Limited.	C ₁₄ H ₁₀ MgO ₆	298.53	≥0.99	Dried under vacuum, kept in P ₂ O ₅ desiccator
2.	Choline salicylate	2016-36-6	Triveni Interchem Pvt Ltd.	C ₁₂ H ₁₉ NO ₄	241.28	≥0.99	Used as such
3.	Sodium salicylate	54-21-7	Central Drug House Pvt Ltd.	C ₇ H ₅ NaO ₃	160.104	≥0.99	Dried under vacuum, kept in P ₂ O ₅ desiccator
4.	Sodium chloride	7647-14-5	Central Drug House Pvt Ltd.	NaCl	58.44	≥0.99	Dried under vacuum, kept in P ₂ O ₅ desiccator
5.	Trisodium Citrate	68-04-2	Central Drug House Pvt Ltd.	C ₆ H ₅ Na ₃ O ₇	258.07	≥0.99	Dried under vacuum, kept in P ₂ O ₅ desiccator
6.	Sodium Nitrate	7631-99-4	Central Drug House Pvt Ltd.	NaNO ₃	84.99	≥0.99	Dried under vacuum, kept in P ₂ O ₅ desiccator

7.	Sodium bicarbonate	144-55-8	Central Drug House Pvt Ltd.	NaHCO_3	84.007	≥ 0.99	Dried under vacuum, kept in P_2O_5 desiccator
8.	Sodium sulphate	7757-82-6	Central Drug House Pvt Ltd.	Na_2SO_4	142.04	≥ 0.99	Dried under vacuum, kept in P_2O_5 desiccator
9.	Potassium chloride	7447-40-7	Central Drug House Pvt Ltd.	KCl	74.55	≥ 0.99	Dried under vacuum, kept in P_2O_5 desiccator

^aPurity as mentioned by supplier. Choline salicylate was supplied as a 50.53% w/v aqueous solution, as reported in the supplier's Certificate of Analysis. This value refers to the concentration of the solution, not the chemical purity. The estimated chemical purity of choline salicylate is >99%. The required mass of pure choline salicylate for each molality was calculated from the supplied solution accordingly.

3.7. Calculation of various Volumetric, Acoustic and Thermodynamic parameters:

3.7.1. Apparent molar volume (V_ϕ)

The V_ϕ describes the contribution of a solute to the total volume of a solution, accounting for the volume of pure solvent and of the solution per mole of solute. It is calculated from density measurements using the below equation:

$$V_\phi = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m_A \rho \rho_0} \quad (3.1)$$

Where M indicates molar mass of the solute, ρ_0 is the density of the solvent, ρ is the density of the ternary solution and m_A is the molality of the solute ($\text{mol} \cdot \text{kg}^{-1}$) based on one kilogram of the solvent.

3.7.2. Partial molar volume (V_ϕ^0)

The V_ϕ^0 is the change in total solution volume per mole of solute added, under constant temperature, pressure, and composition. Values of (V_ϕ^0) are obtained by extrapolating apparent molar volume data to infinite dilution using the Redlich–Meyer equation:

$$V_\phi = V_\phi^0 + A_V \sqrt{m} + S_V m_A \quad (3.2)$$

where A_V represents the Debye–Huckell limiting slope, and S_V is the experimental slope accounting for solute–solute interactions.

3.7.3. Partial molar volume of transfer

This quantify the change in V_ϕ^0 when the solute is transferred from water to aqueous salicylate. This volume change can be present mathematically as

$$\Delta V_\phi^0 = \Delta V_\phi^0 (\text{in aqueous salicylate solution}) - V_\phi^0 (\text{in water}) \quad (3.3)$$

where V_ϕ^0 is the partial molar volume.

3.7.4. Temperature dependent partial molar volume

The temperature dependence of the partial molar volume at infinite dilution is described by fitting the experimental data to a quadratic equation

$$V_\phi^0 = a + b(T - T_{ref}) + c(T - T_{ref})^2 \quad (3.4)$$

where a , b , and c are empirical coefficients, $T_{ref} = 298.15\text{K}$ and T is the absolute temperature (K). The fit quality was assessed using the relative deviation (Δ), and high R^2 values confirmed the validity of this model

3.7.5. Apparent molar isentropic compression ($K_{\phi,s}$)

The ($K_{\phi,s}$) expresses the compressibility contribution of the solute and is calculated as:

$$K_{\phi,s} = \frac{MK_s}{\rho} - \left\{ \frac{(K_{s,0}\rho - K_{s,0})}{m_a \rho \rho_0} \right\} \quad (3.5)$$

Here, $K_{s,0}$ represents isentropic compressibility of pure solvent and K_s represents solution. K_s is determined using equation below

$$K_s = \frac{1}{c^2 \rho} \quad (3.6)$$

Here, c is ultrasonic velocity.

3.7.6. Partial molar isentropic compression

Change in $K_{\phi,s}$ along with molar concentration is shown in the equation.

$$K_{\phi,s} = K_{\phi,s}^0 + S_K^* \sqrt{m_a} \quad (3.7)$$

Here $K_{\phi,s}^0$ show limiting isentropic compression, S_K^* is an empirical slope parameter that reflects solute–solute interactions at finite concentrations

3.7.7. Partial molar isentropic compression of transfer

At infinite dilution, change in $K_{\phi,s}^0$ in liquid mixture of salts is determined by the given equation.

$$\Delta K_{\phi}^0 = K_{\phi,s}^0 (\text{in aqueous salicylate solution}) - K_{\phi,s}^0 (\text{in water}) \quad (3.8)$$

3.7.8. Pair and triplet interaction coefficients

The below equations were used to compute pair and triple interaction coefficients of volume and compression.

$$\Delta V_{\phi}^0 (H_2O - \text{salicylate}_{(aq.)}) = 2V_{AB}m_B + 3V_{ABB}m_B^2 \quad (3.9)$$

$$\Delta K_{\phi,s}^0 (H_2O - \text{salicylate}_{(aq.)}) = 2K_{AB}m_B + 3K_{ABB}m_B^2 \quad (3.10)$$

Here A mean salicylates and B mean salts and m_B represents the molality of liquid salts solution. V_{AB} represents pair interaction for volume K_{AB} and V_{ABB} represents triplet interaction coefficient for volume K_{ABB} for isentropic compression.

3.7.9 Isobaric thermal expansion coefficient

The α_p , quantifies the fractional change dependence of apparent molar volume on temperature under constant pressure conditions. It was calculated using the relation

$$\alpha_p = \frac{1}{V_\phi^0} \left(\frac{\partial V_\phi^0}{\partial T} \right) \quad (3.11)$$

3.7.10 Apparent specific volume (ASV)

The ASV is a fundamental thermodynamic indicator that signifies the true volume taken by the solute in a solution per unit mass. It reflects information about solute-solvent interactions and molecular organization of the system. An increased ASV usually signifies stronger solute-solvent interactions, which have an effect on numerous physicochemical properties of the solution. The ASV is determined from the following equation:

$$ASV = \left(\frac{V_\phi}{M} \right) \quad (3.12)$$

M is the molar mass of the solute.

3.7.11 Hydration number

The hydration number is calculated to estimate the extent to which solvent molecules, particularly water, associate with each solute particle. This parameter helps assess the strength of solute-solvent interactions in the system. The hydration number (n_h) for the investigated liquid systems was calculated using the following relation:

$$n_h = \frac{n_w}{n_s} \left[1 - \frac{k_s}{k_s^0} \right] \quad (3.13)$$

Here, n_s indicates the number of moles of the solute present, n_w refers to the number of moles of water, k_s is isentropic compression of the ternary solution and k_s^0

corresponds to the isentropic compression of the solvent. Hydration number is critical for understanding molecular interactions in aqueous systems, especially for ions and polar molecules, as it reveals the degree to which water molecules organize around solutes, influencing physical properties and reaction dynamics.

3.7.12 Relaxation strength

Relaxation strength is a measure of the energy dissipation capability of a solution in response to external perturbations, such as pressure or temperature changes. It characterizes the efficiency with which the molecular system can relax or return to equilibrium after being disturbed. In electrolyte solutions, relaxation strength provides insight into the dynamic behaviour and mobility of solvent and solute molecules, as well as the degree of structural organization within the solution. The relaxation strength was calculated by using the formula

$$r_s = 1 - \left(\frac{c}{c_\infty}\right)^2 \quad (3.14)$$

Here c is the ultrasonic velocity and the value of c_∞ is constant, set at $1600 \text{ m}\cdot\text{s}^{-1}$.

3.7.13 Relative association

It is a dimensionless parameter that quantifies the extent of associative interactions among solute and solvent molecules in a solution. It reflects how the addition of a solute, such as a salt, influences the structural organization and interaction strength among the components of the solution. Higher R_a values typically indicate stronger or more extensive solute-solvent associations, often resulting from enhanced hydrogen bonding, ion pairing, or other intermolecular forces. Relative association (R_a) has been calculated via following formula

$$R_a = (\rho/\rho_0)(c_0/c)^{1/3} \quad (3.15)$$

3.7.14 Specific heat ratio

The specific heat ratio, often denoted by γ , is an important thermodynamic parameter calculated using a semi-empirical relation involving experimental data such as temperature T and solution density ρ . This was calculated using the semi-empirical relation

$$\gamma = \frac{17.1}{T^{\frac{4}{9}} \rho^{\frac{1}{3}}} \quad (3.16)$$

Where T is the absolute temperature and ρ is the solution density.

3.8. Spectroscopy study

Fourier Transform Infrared Spectroscopy (FTIR) was performed using the PerkinElmer FTIR Spectrum One instrument equipped with an Attenuated Total Reflection (ATR) accessory. ATR-FTIR is a powerful technique that allows direct analysis of aqueous solutions with minimal sample preparation by measuring the infrared absorption of molecules near the surface of the ATR crystal. Spectra were recorded in the range of 400 to 4000 cm^{-1} with a resolution of 0.5 cm^{-1} . The ATR method provides information about molecular vibrations and functional groups involved in solute-solvent interactions by analyzing characteristic absorption bands. Its shallow penetration depth ($\sim 1 \mu\text{m}$) ensures sensitivity to surface or near-surface molecular interactions, making it well-suited to probing structural changes in salt solutions. A small volume of solution was placed directly on the diamond ATR crystal, ensuring good contact for optimal spectral quality. Background scans and atmospheric compensation were applied to minimize interferences from CO_2 and water vapour. The ATR-FTIR results complement the volumetric and acoustic measurements by providing molecular-level insight into ion hydration, hydrogen bonding, and solvation structure modifications induced by varying salt concentrations.

Chapter summary

This chapter presents the objectives of the present investigation and describes the experimental methodology employed for the preparation of binary and ternary salicylate–salt aqueous solutions. The procedures for density and ultrasonic velocity measurements using the Anton Paar DSA 5000 M instrument are detailed. The chapter also outlines the spectroscopic techniques and the calculation methods adopted for evaluating various volumetric, acoustic, and thermodynamic parameters. These methodologies establish a systematic experimental framework for the analysis and interpretation of molecular interactions discussed in the subsequent chapter.

CHAPTER 4

RESULTS AND DISCUSSION

Section I

Problem 1 Thermophysical and Spectroscopic studies of Magnesium Salicylate–Trisodium Citrate and Sodium Chloride Mixtures.

In this work, the density (ρ) and ultrasonic velocity (c) were obtained for trisodium citrate and sodium chloride mixtures prepared in aqueous magnesium salicylate solutions of concentrations 0.010, 0.020, and 0.030 $\text{mol}\cdot\text{kg}^{-1}$ at 288.15, 298.15, 308.15, and 318.15 K temperatures. These measurements were carried out with a DSA 5000 instrument with a frequency of 3 MHz to analyze solute–solute and solute–solvent interactions. Further FTIR spectroscopy was done to validate and support the molecular interaction interpretations derived from thermophysical measurements.

Density and ultrasonic velocity

Experimental data of density and ultrasonic velocity for sodium chloride/ trisodium citrate have been obtained for binary and ternary mixture at four varying temperatures and three different concentrations (0.01000, 0.02000 and 0.03000 $\text{mol}\cdot\text{kg}^{-1}$) of magnesium salicylate. The obtained values indicate that as temperature increases, the density decreases, whereas the density increases with increasing magnesium salicylate concentration. The decrease in density with increasing temperature can be attributed to the increase in the kinetic energy of the molecules. As the temperature increases, the molecules acquire higher kinetic energy, which weakens the intermolecular attractive forces and increases the average intermolecular separation. Consequently, the solution undergoes thermal expansion, leading to an increase in volume. Since the mass of the solution remains constant while its volume increases, the density decreases. In contrast, the increase in density with increasing magnesium salicylate concentration is due to the increase in the mass of solute per unit volume together with enhanced solute–solvent interactions, which produce a more compact solution structure. On the other hand, ultrasonic velocity increases with increasing magnesium salicylate concentration

due to stronger solute–solvent interactions and the formation of a more compact solution structure, which facilitates faster propagation of sound waves. The increase in ultrasonic velocity with temperature may be attributed to the enhanced mobility of the molecules and the corresponding reduction in the resistance offered to the propagation of sound under the present experimental conditions. **Table 4.1.** indicates the values of densities and speed of sound at 0.1MPa pressure. A comparison plots of density of a binary mixture (Water + Sodium chloride) [1–4] and plots of speed of sound of a binary mixture (Water + sodium chloride) [1–5] presented in **Figure 4.1 (a)** and **Figure 4.1 (b)**, respectively. A comparison plots of density of a binary mixture (Water + trisodium citrate) [5–7] and plots of speed of sound of a binary mixture (Water + trisodium citrate) [5–7] presented in **Figure. 4.1(c)** and **4.1(d)**, respectively. The differences in density and speed of sound that have been noted highlights how temperature and solute-solvent interactions affect the mixes' physical characteristics. Thus, the observed increase in density and ultrasonic velocity with increasing magnesium salicylate concentration can be attributed to enhanced solute–solvent interactions, improved molecular packing, and the resulting reduction in free volume [8].

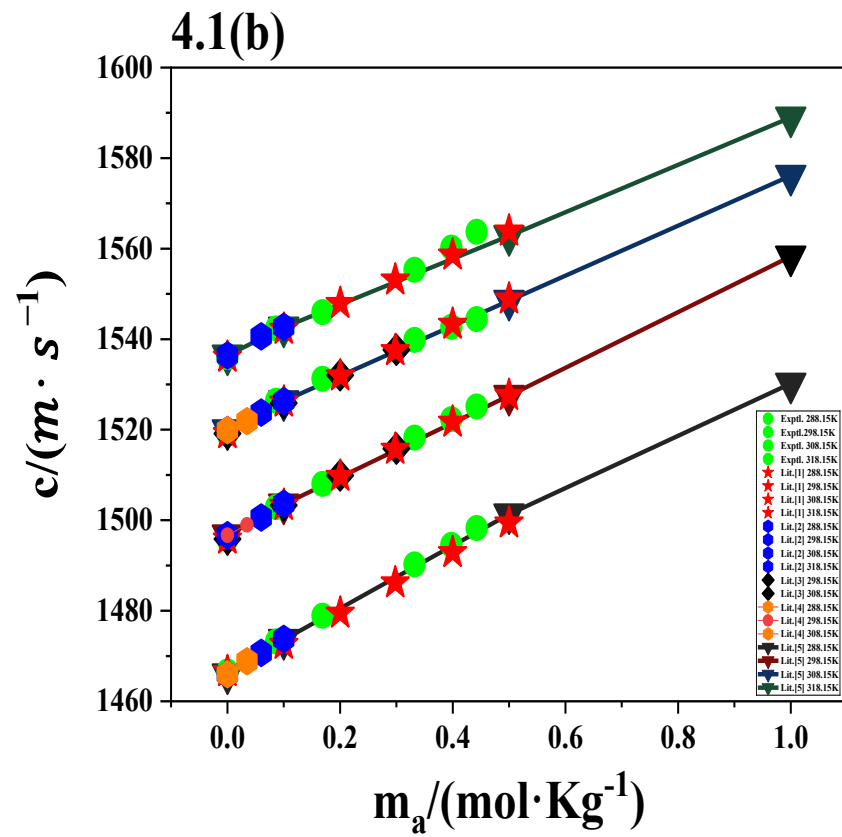
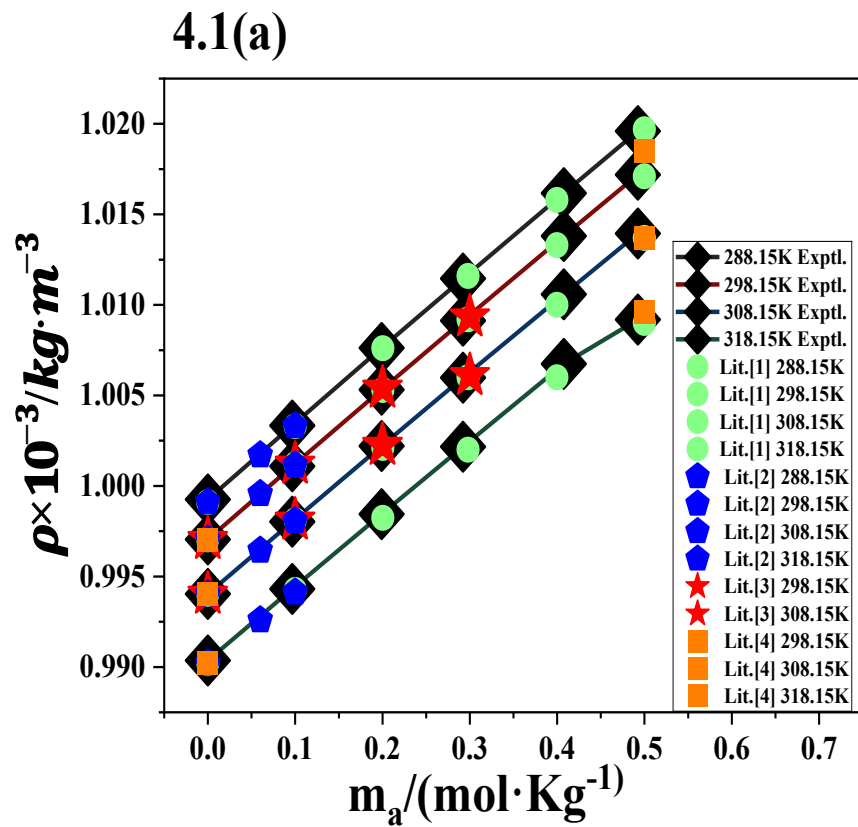
Apparent molar volume

The measured densities were utilized to determine the apparent molar volumes of sodium chloride or trisodium citrate dissolved in aqueous magnesium salicylate solutions. The following equation were used to calculate V_ϕ [1]:

$$V_\phi = (M/\rho) - \{(\rho - \rho_0)/(m_A\rho\rho_0)\} \quad (4.1)$$

In the above equation, ρ_0 is the density of the solvent (aqueous magnesium salicylate solution), whereas ρ is the density of the corresponding ternary solution. The calculated V_ϕ summarized in **Table 4.2** and from table values it is clear that all values are positives and increasing with increase in temperature and concentration. The apparent molar volume means the volume that one mole of a solute in a solution appears to occupy considering the volume of the pure solvent and the volume of the actual solution. Hence, it tries to explain how solutes interact with solvents by showing how adding solutes changes the total volume of the solution. A higher-than-expected apparent molar volume indicates that the presence of the solute tends to expand the

solvent structure; a lower-than-expected value may therefore be due to very strong solute-solvent forces that compress the structure. This concept is especially important for characterizing ion hydration, molecular interactions, and the behaviour of substances in highly diluted solutions [9–11]. Additionally, the trend of apparent molar volume is visually displayed in **Figure. 4.2**. For both sodium chloride and trisodium citrate, the apparent molar volume values observed in this study show good agreement with previously reported binary data in aqueous systems at similar conditions [1][12][13], supporting the accuracy and reliability of the present measurements. This is explained by the solvation phenomena and the solutes' high solute-solvent affinity, which shed light on the molecular interactions in the system [14]. These interactions are governed by various forces present in the solution, including dipole-dipole and dipole-induced dipole interactions resulting from sodium chloride or trisodium citrate and water, as well as both inter- and intramolecular hydrogen bonding, hydrophobic hydration, and the hydrophobic effect [15–17]. The observed trends in density, ultrasonic velocity, and apparent molar volume can be directly linked to the presence and nature of charged moieties in the studied systems. Magnesium salicylate dissociates in aqueous solution to yield Mg^{2+} cations and salicylate[−] anions, while sodium chloride and trisodium citrate provide Na^+ , Cl^- , and citrate^{3−} ions, respectively. The high charge density of Mg^{2+} and citrate^{3−} leads to strong electrostatic (ion–ion) interactions, which promote significant molecular association and structuring within the solution. Additionally, the organic anions salicylate[−] and citrate^{3−}, with their carboxylate and aromatic groups, are capable of forming hydrogen bonds and participating in complexation with cations, further enhancing molecular interactions. Na^+ and Cl^- , as monovalent ions, primarily influence the solvation environment through ion–dipole interactions, modulating the hydration shell structure and the extent of ion pairing. The interplay of these charged moieties results in the observed changes in solution properties, with multivalent ions (Mg^{2+} , citrate^{3−}) generally exerting a stronger effect on molecular association and solution structure than monovalent ions. These molecular-level interactions underpin the macroscopic thermophysical trends reported in this study.



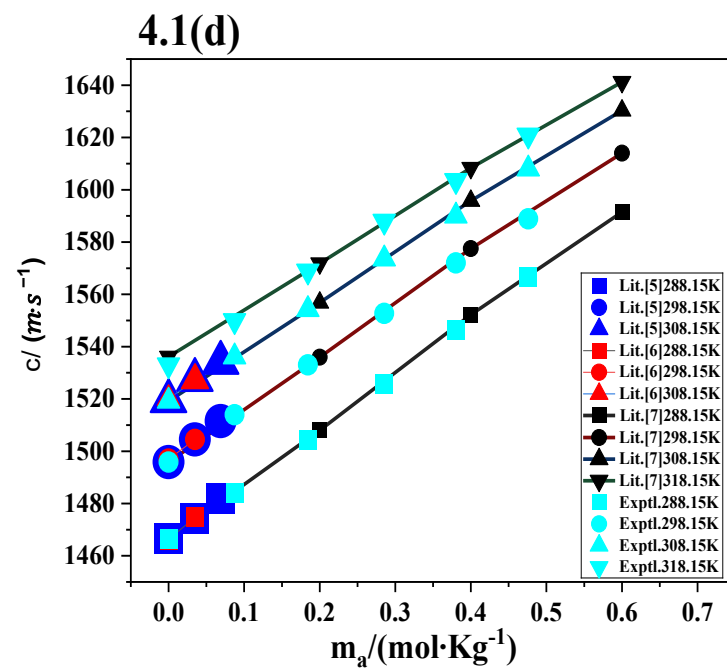
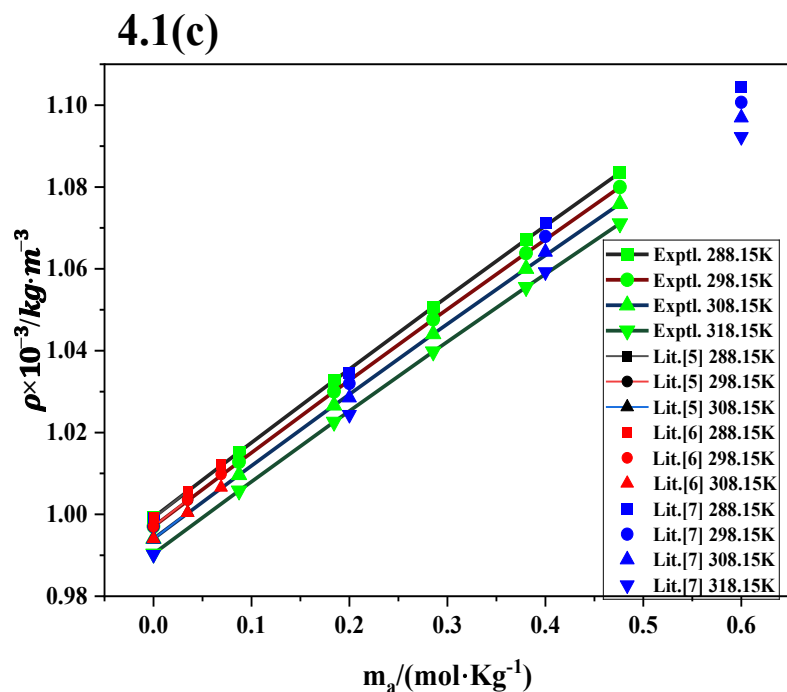


Figure 4.1 Comparison plots of density of a binary mixture (Water + Sodium chloride) [1-4] and plots of ultrasonic velocity of a binary mixture (Water + Sodium chloride) [1-5] presented in Fig. 4.1 (a) and Fig. 4.1 (b), and comparison plots of density of a binary mixture (Water + trisodium citrate) [5-7] and plots of ultrasonic velocity of a binary mixture (Water + trisodium citrate) [5-7] presented in Fig. 4.1 (c) and Fig. 4.1 (d), respectively.

Table 4.1. ρ and c for ternary mixtures of Sodium chloride/ trisodium citrate in magnesium salicylate aqueous solutions.

$^a m_a / (mol \cdot kg^{-1})$	$\rho \times 10^{-3} / (kg \cdot m^{-3})$				$c / (m \cdot s^{-1})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium chloride + 0.00000 Magnesium salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036	1466.59	1495.85	1519.14	1533.02
0.09669	1.00334	1.00109	0.99803	0.99431	1473.21	1502.91	1526.41	1542.35
0.19897	1.00762	1.00532	1.00221	0.99844	1478.91	1508.03	1531.23	1545.96
0.29215	1.01146	1.00913	1.00598	1.00217	1490.23	1518.23	1539.81	1555.31
0.40757	1.01617	1.01380	1.01059	1.00674	1494.53	1522.32	1542.71	1560.21
0.49242	1.01960	1.01719	1.01394	1.00919	1498.25	1525.14	1544.41	1563.73
Sodium chloride + 0.01000 Magnesium salicylate								
0.00000	1.00012	0.99804	0.99501	0.99117	1468.56	1498.18	1521.74	1538.72
0.09601	1.00414	1.00198	0.99887	0.99495	1474.36	1503.78	1526.56	1542.91
0.20788	1.00883	1.00656	1.00336	0.99935	1482.47	1512.78	1532.17	1549.78
0.30592	1.01293	1.01057	1.00730	1.00322	1490.40	1518.01	1539.71	1555.15
0.40093	1.01690	1.01445	1.01111	1.00695	1498.45	1526.49	1545.78	1561.45
0.47819	1.02014	1.01761	1.01420	1.01000	1503.25	1532.16	1549.88	1567.11

Sodium chloride + 0.02000 Magnesium salicylate

0.00000	1.00126	0.99919	0.99601	0.99229	1469.65	1499.19	1521.91	1538.31
0.10258	1.00541	1.00332	1.00010	0.99633	1477.03	1506.00	1528.21	1544.26
0.19784	1.00928	1.00717	1.00390	1.00010	1482.45	1512.45	1533.48	1550.49
0.30710	1.01373	1.01158	1.00827	1.00442	1492.11	1519.90	1541.17	1556.53
0.39450	1.01728	1.01511	1.01177	1.00788	1497.57	1525.48	1545.78	1560.45
0.50152	1.02166	1.01943	1.01604	1.01212	1502.88	1529.44	1550.15	1564.63

Sodium chloride + 0.03000 Magnesium salicylate

0.00000	1.00230	1.00018	0.99711	0.99324	1471.35	1500.62	1523.11	1539.34
0.10501	1.00655	1.00439	1.00127	0.99736	1477.72	1506.55	1528.63	1544.58
0.19386	1.01015	1.00796	1.00480	1.00086	1485.47	1513.91	1534.82	1550.17
0.29807	1.01439	1.01214	1.00894	1.00498	1491.99	1519.92	1541.90	1557.20
0.41208	1.01902	1.01671	1.01346	1.00946	1497.01	1524.79	1546.21	1564.12
0.49266	1.02228	1.01998	1.01670	1.01266	1502.86	1529.52	1550.00	1570.64

trisodium citrate + 0.00000 Magnesium salicylate

0.00000	0.99926	0.99705	0.99404	0.99036	1466.59	1495.85	1519.14	1533.02

0.08744	1.00457	1.00214	0.99898	0.99508	1484.13	1513.93	1536.09	1549.95
0.18432	1.01023	1.00761	1.00429	1.00019	1504.24	1533.04	1554.19	1568.93
0.28217	1.01565	1.01301	1.00958	1.00526	1525.78	1552.69	1573.54	1587.98
0.39429	1.02190	1.01914	1.01545	1.01095	1546.43	1572.03	1589.94	1603.52
0.48416	1.02691	1.02376	1.01995	1.01531	1566.68	1588.88	1607.93	1620.91

trisodium citrate + 0.01000 Magnesium salicylate

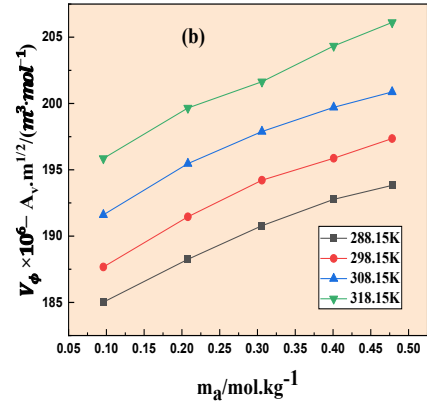
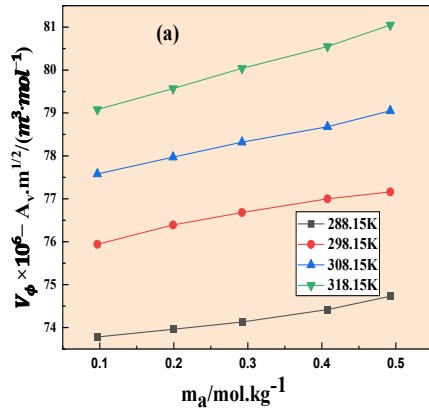
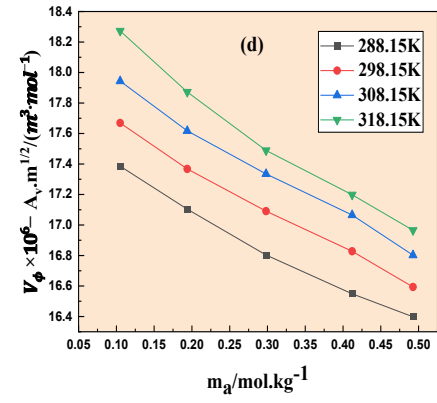
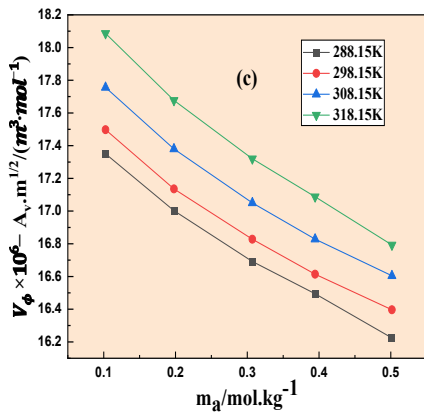
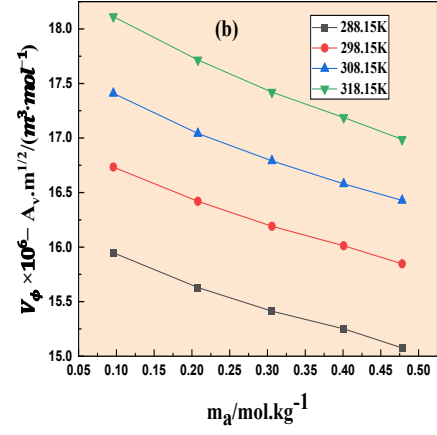
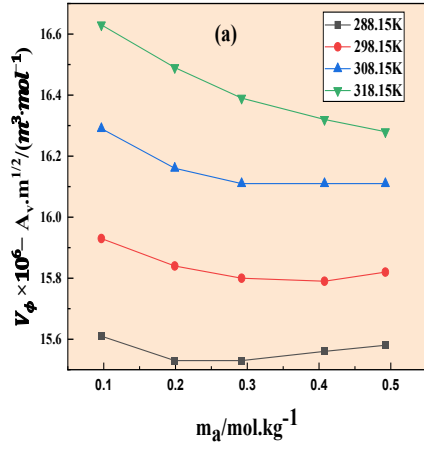
0.00000	1.00012	0.99804	0.99501	0.99117	1468.56	1498.18	1521.74	1538.72
0.09745	1.00664	1.00435	1.00098	0.99681	1488.15	1516.64	1538.37	1554.06
0.20002	1.01311	1.01048	1.00675	1.00222	1507.45	1534.45	1556.57	1569.14
0.29679	1.01855	1.01560	1.01164	1.00692	1522.56	1549.00	1568.94	1583.10
0.38987	1.02333	1.02023	1.01595	1.01065	1541.70	1567.78	1588.47	1599.47
0.49545	1.02870	1.02514	1.02069	1.01475	1561.44	1585.46	1603.23	1615.43

trisodium citrate + 0.02000 Magnesium salicylate

0.00000	1.00126	0.99919	0.99601	0.99229	1469.65	1499.19	1521.91	1538.31
0.10435	1.00857	1.00623	1.00280	0.99855	1492.76	1520.79	1542.63	1558.56
0.19312	1.01401	1.01135	1.00755	1.00310	1508.78	1534.80	1555.47	1569.89

0.29515	1.01969	1.01669	1.01270	1.00788	1525.39	1551.44	1571.23	1585.21
0.39107	1.02475	1.02138	1.01704	1.01170	1545.78	1569.78	1589.45	1604.00
0.49251	1.02956	1.02596	1.02148	1.01551	1563.57	1587.22	1604.73	1617.83
trisodium citrate + 0.03000 Magnesium salicylate								
0.00000	1.00230	1.00018	0.99711	0.99324	1471.35	1500.62	1523.11	1539.34
0.09592	1.00967	1.00731	1.00391	0.99970	1491.90	1519.83	1541.34	1556.56
0.19152	1.01547	1.01279	1.00899	1.00456	1507.78	1534.78	1556.78	1570.45
0.29500	1.02112	1.01809	1.01410	1.00941	1529.69	1554.81	1573.88	1587.15
0.39616	1.02636	1.02294	1.01870	1.01332	1548.78	1572.45	1588.94	1601.79
0.49666	1.03099	1.02735	1.02285	1.01689	1562.87	1586.16	1603.43	1615.19

^a m_a is the molality of Sodium chloride/ trisodium citrate in the aqueous solution of Magnesium salicylate in $\text{mol} \cdot \text{kg}^{-1}$; The uncertainties of molalities of each component, is 0.0762 (for sodium chloride + H_2O), 0.0744 (for 0.01000 magnesium salicylate+ sodium chloride), 0.0762 (for 0.02000 magnesium salicylate+ sodium chloride), 0.0762 (for 0.03000 magnesium salicylate+ sodium chloride), 0.0751 (for trisodium citrate + H_2O), 0.0753 (for 0.01000 magnesium salicylate+ trisodium citrate), 0.0748 (for 0.02000 magnesium salicylate+ trisodium citrate), 0.0761 (for 0.03000 magnesium salicylate+ trisodium citrate), $u(T) = \pm 0.001 \text{ K}$, $u(\rho) = 0.15 \text{ kg} \cdot \text{m}^{-3}$, $u(T) = 0.001 \text{ K}$, $u(s) = 1.0 \text{ m} \cdot \text{s}^{-1}$, $u(p) = 0.01 \text{ MPa}$.



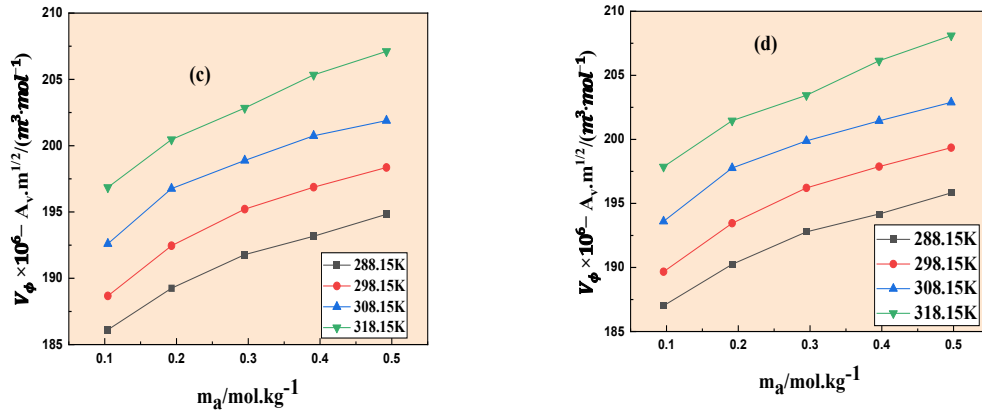


Fig. 4.2. Plots of V_ϕ (I) Sodium chloride and (II) trisodium citrate from H_2O to an aqueous magnesium salicylate solution (a) 0.00000 magnesium salicylate, (b) 0.01000 magnesium salicylate, (c) 0.02000 magnesium salicylate, and (d) 0.03000 magnesium salicylate ($mol \cdot kg^{-1}$).

Partial molar volume

The Redlich-Mayer equation was applied to extrapolate the $\{(V_\phi - A_V\sqrt{m})-m\}$ curve to determine the partial molar volumes of the electrolytes at zero concentration [18]

$$V_\phi = V_\phi^0 + A_V\sqrt{m} + S_V m_A \quad (4.2)$$

Here, m_A is solute's molality, and S_V and A_V , are the two adjustable parameters. The experimental slope and partial molar volume values, together with their error, are given in **Table 4.3** and shown visually in **Fig. 4.3**. The fact that every value V_ϕ^0 is positive suggests that the system contains solvent-solvent interactions. The overlapping of co-spheres between two ionic species can account for the volume increase, according to the co-sphere overlap model [18–20]. On the other hand, interactions involving hydrophobic groups or between ions and hydrophobic regions typically lead to a reduction in volume. In these systems, ion-hydrophilic interactions are generally more influential than hydrophobic-hydrophobic interactions, which accounts for the observed positive values [21]. The understanding of solvent-solvent interactions is further increased by observing how standard partial molar characteristics change with temperature. As the solute's molar mass increases, the computed values of some thermodynamic parameters typically tend to climb as well. The S_V values are also included in **Table 4.3**, which indicates that the values are negative for sodium chloride

and positive for trisodium citrate. This implies that there aren't many solute-solute interactions in these mixtures. The measured values' lack of a discernible pattern suggests that a number of factors affect solute-solute interactions. Interestingly, solute-solvent interactions have a greater impact than solute-solute interactions. The negative slopes for sodium chloride arise from strong ion-solvent interactions and electrostriction, leading to contraction of the hydration shell and a decrease in V_ϕ with rising concentration. In contrast, the positive slopes observed for trisodium citrate result from its bulky, multivalent structure and strong hydration, which promote solute-solute repulsion and structural expansion in solution [22,23].

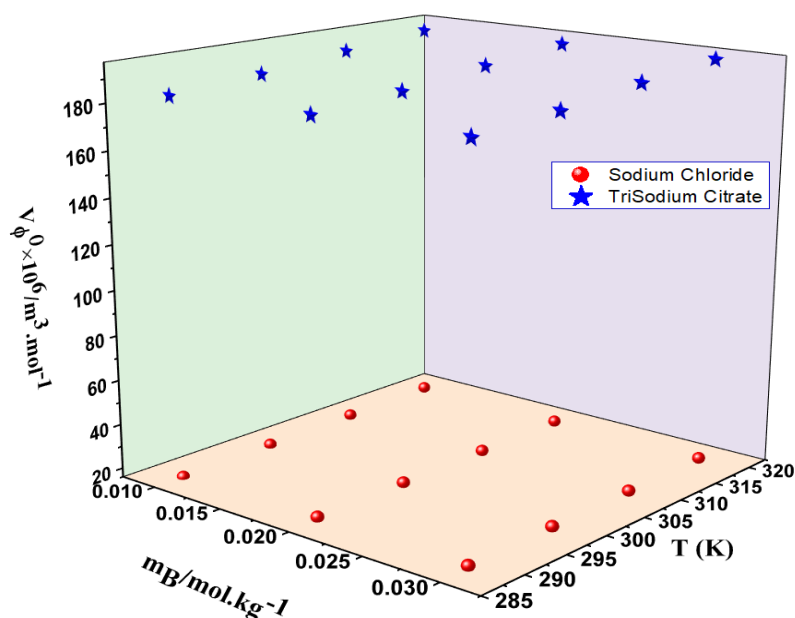


Fig. 4.3 Plots illustrating the changes in, V_ϕ^0 , for Sodium chloride (red) and trisodium citrate (blue) in a magnesium salicylate aqueous solution.

Table 4.2. V_ϕ of NaCl/C₆H₅Na₃O₇ in water and aqueous magnesium salicylate solutions.

$^a m_a /$ (mol · kg ⁻¹)	$V_\phi \times 10^6 / (m^3 \cdot mol^{-1})$				$^a m_a /$ (mol · kg ⁻¹)	$V_\phi \times 10^6 / (m^3 \cdot mol^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K		T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride + 0.00000 Magnesium salicylate					trisodium citrate + 0.00000 Magnesium salicylate				
0.09669	15.61	15.93	16.29	16.63	0.09669	73.78	75.94	77.58	79.08
0.19897	15.53	15.84	16.16	16.49	0.19897	73.96	76.39	77.97	79.57
0.29215	15.53	15.80	16.11	16.39	0.29215	74.13	76.68	78.32	80.04
0.40757	15.56	15.79	16.11	16.32	0.40757	74.42	77.00	78.68	80.55
0.49242	15.58	15.82	16.11	16.28	0.49242	74.73	77.16	79.05	81.05
Sodium chloride + 0.01000 Magnesium salicylate					trisodium citrate + 0.01000 Magnesium salicylate				
0.09601	15.95	16.73	17.41	18.11	0.09601	185.02	187.67	191.60	195.86
0.20788	15.63	16.42	17.04	17.72	0.20788	188.25	191.45	195.47	199.66
0.30592	15.41	16.19	16.79	17.42	0.30592	190.78	194.21	197.89	201.64
0.40093	15.25	16.01	16.58	17.19	0.40093	192.77	195.87	199.71	204.34
0.47819	15.08	15.85	16.43	16.99	0.47819	193.82	197.35	200.87	206.11
Sodium chloride + 0.02000 Magnesium salicylate					trisodium citrate + 0.02000 Magnesium salicylate				

0.10258	17.35	17.50	17.76	18.09	0.10435	186.12	188.67	192.60	196.86
0.19784	17.00	17.14	17.38	17.68	0.19312	189.25	192.45	196.77	200.46
0.30710	16.69	16.83	17.05	17.32	0.29515	191.78	195.21	198.89	202.84
0.39450	16.49	16.61	16.83	17.09	0.39107	193.17	196.87	200.75	205.34
0.50152	16.22	16.40	16.60	16.79	0.49251	194.82	198.35	201.89	207.11
Sodium chloride + 0.03000 Magnesium salicylate					trisodium citrate + 0.03000 Magnesium salicylate				
0.10501	17.39	17.67	17.94	18.27	0.09592	187.02	189.67	193.60	197.86
0.19386	17.10	17.37	17.62	17.87	0.19152	190.25	193.45	197.77	201.46
0.29807	16.80	17.09	17.34	17.49	0.29500	192.78	196.21	199.89	203.44
0.41208	16.55	16.83	17.07	17.20	0.39616	194.17	197.87	201.45	206.14
0.49266	16.40	16.59	16.80	16.97	0.49666	195.82	199.35	202.89	208.10

^a m_a is the molality of Sodium chloride/ trisodium citrate in the aqueous solution Magnesium salicylate; For apparent molar volume, the relative combined standard uncertainties (expressed as percentages and without units) are as follows: **0.3** for sodium chloride + water; **0.6–0.3** for magnesium salicylate + sodium chloride across 0.01000–0.03000 mol·kg⁻¹; **0.7** for trisodium citrate + water; and **1.5** for magnesium salicylate + trisodium citrate at all concentrations.

Table 4.3: Calculated V_ϕ^0 values along with S_V^* of Sodium chloride/ trisodium citrate in magnesium salicylate aqueous solutions.

$^a m_B / (mol \cdot kg^{-1})$	$V_\phi^0 \times 10^6 (m^3 \cdot mol^{-1})$				$S_V^* \times 10^6 (m^3 \cdot kg \cdot mol^{-2})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium Chloride								
0.00000	15.57(±0.04)	15.92(±0.04)	16.28(±0.05)	16.68(±0.04)	-0.03(±0.12)	-0.27(±0.13)	-0.41(±0.16)	-0.87(±0.11)
0.01000	16.13(±0.04)	16.92(±0.03)	17.61(±0.05)	18.35(±0.04)	-2.23(±0.12)	-2.29(±0.11)	-2.55(±0.15)	-2.92(±0.13)
0.02000	17.59(±0.05)	17.72(±0.06)	17.99(±0.07)	18.35(±0.06)	-2.78(±0.14)	-2.74(±0.19)	-2.87(±0.21)	-3.20(±0.19)
0.03000	17.61(±0.05)	17.92(±0.03)	18.21(±0.04)	18.55(±0.07)	-2.55(±0.14)	-2.70(±0.10)	-2.85(±0.12)	-3.30(±0.22)
trisodium Citrate								
0.00000	73.50(±0.07)	75.73(±0.08)	77.24(±0.03)	78.60(±0.04)	2.35(±0.21)	3.05(±0.25)	3.64(±0.09)	4.91(±0.11)
0.01000	183.19(±0.54)	185.85(±0.69)	189.95(±0.73)	193.66(±0.40)	23.31(±1.65)	25.06(±2.10)	24.03(±2.24)	26.39(±1.24)
0.02000	184.58(±0.77)	187.13(±1.03)	191.38(±1.16)	194.85(±0.71)	21.84(±2.37)	24.32(±3.15)	23.03(±3.56)	25.98(±2.17)
0.03000	185.70(±0.75)	188.35(±0.96)	192.61(±1.06)	196.03(±0.56)	21.38(±2.29)	23.61(±2.92)	22.07(±3.24)	24.98(±1.72)

$^a m_B$ is the molality of magnesium salicylate is given per kg of pure water; u is $u(m) = 0.0100 mol \cdot kg^{-1}$.

Partial molar volume of Transfer

The volume change that happens when a solute is moved from pure water to an aqueous solution that contains magnesium salicylate in addition to sodium chloride or trisodium citrate is measured by the ΔV_{ϕ}^0 . The following is a mathematical expression for this volume change [24] [25]:

$$(\Delta_{tr}V_{\phi}^0) = V_{\phi}^0(\text{in aqueous MgSl solution}) - V_{\phi}^0(\text{in water}) \quad (4.3)$$

The partial molar volumes in this expression are denoted by V_{ϕ}^0 . **Table 4.4** summarises the computed ΔV_{ϕ}^0 values and offers important information about the interactions between the solute, water, and magnesium salicylate systems. Greater magnesium salicylate concentrations clearly result in greater values of ΔV_{ϕ}^0 for the sodium chloride and trisodium citrate solute systems. This trend suggests that adding magnesium salicylate to the sodium chloride or trisodium citrate systems causes a notable increase in volume. This behaviour can be attributed to enhanced solute–solvent interactions, particularly ion–dipole interactions between the ions and surrounding water molecules. These interactions promote the formation of well-defined hydration shells around the ions and increase the organization of the surrounding water molecules, thereby modifying the local solvent structure and contributing to the observed increase in the apparent transfer volume. Furthermore, the positive ΔV_{ϕ}^0 values imply the presence of dipole-dipole interactions, hydrogen bonds, and strong ion-ion interactions in the system. In addition to facilitating enhanced solvation, these kinds of interactions also raise the system's overall volume. The co-sphere overlaps model states that the ΔV_{ϕ}^0 values mainly represent solute-solvent interactions as solute -solute interaction is negligible. According to the co-sphere overlap model, overlap of the hydration shells surrounding the solute and solvent species enhances solute–solvent interactions while the contribution of direct solute–solute interactions remains comparatively small at the concentrations investigated. Therefore, the positive transfer volume observed in the present system can be qualitatively interpreted on the basis of hydration-shell overlap and enhanced solute–solvent interactions. [26,27]. It is possible to deduce that the ion-hydrophilic and hydrophilic-hydrophilic interactions have a greater influence on the system under study (magnesium salicylate + water + sodium chloride/ trisodium

citrate) than do the ion-hydrophobic and hydrophobic-hydrophobic interactions. Interactions are increasing from one solute to another shown in **Figure 4.4**.

Table. 4.4. ΔV_{ϕ}^0 of Sodium chloride/ trisodium citrate in aqueous Mg salicylate solutions.

$^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$\Delta V_{\phi}^0 \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium chloride				
0.01000	0.56	1.00	1.33	1.67
0.02000	2.02	1.80	1.71	1.77
0.03000	2.04	2.00	1.93	1.87
trisodium citrate				
0.01000	109.68	110.13	112.72	115.07
0.02000	111.08	111.41	114.14	116.26
0.03000	112.20	112.62	115.37	117.43

standard uncertainties u are $u(m) = 0.0100 \text{ mol} \cdot \text{kg}^{-1}$, $u(p) = 0.01 \text{ MPa}$.

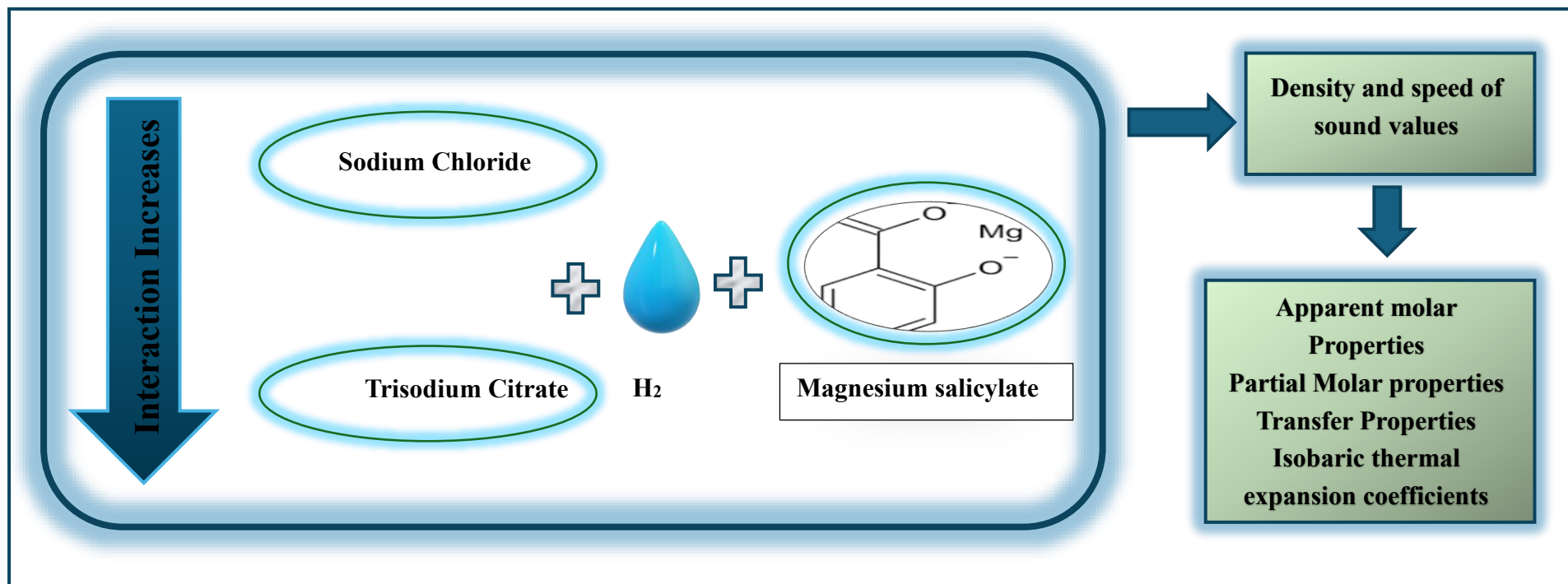


Figure 4.4. Schematic representation of the interactions between Sodium chloride/ trisodium citrate and in magnesium salicylate aqueous solutions.

Temperature dependent partial molar volume

The thermodynamic properties and molecular interactions of the solutions are reflected in the different temperature-dependent behaviours of the partial molar volume (V_ϕ^0) of magnesium salicylate in water and sodium chloride/ trisodium citrate. The empirical parameters a, b, and c for both solutes characterise the temperature dependence of the partial molar volume, as shown in **Table 4.5**. The following polynomial equation is used to assess this relationship [28]:

$$V_\phi^0 = a + b(T - T_{ref}) + c(T - T_{ref})^2 \quad (4.4)$$

where $T_{ref} = 298.15\text{K}$. The differences between the computed and observed V_ϕ^0 values are also displayed in **Table 4.5** and are computed using the below formula:

$$\sigma = (1/n) \sum [\text{abs}((Y_{\text{Exptl.}} - Y_{\text{Calc.}})/Y_{\text{Exptl.}})] \quad (4.5)$$

According to the R^2 values, the polynomial equation fitted to the data in this case, $Y = V_\phi^0$, shows very low deviation values, confirming that it accurately depicts the relationship [27]. Finding the E_ϕ^0 , which are determined using the following formula, is the main objective of analysing the V_ϕ^0 data:

$$E_\phi^0 = (\partial V_\phi^0 / \partial T)_p = b + 2c(T - T_{ref}) \quad (4.6)$$

E_ϕ^0 , the partial molar expansibility at infinite dilution, offers important information about the dynamics of the solute-solvent interaction in the mixture. The following thermodynamic equation can be used to determine whether a solute can create or break structures in solution:

$$(\partial E_\phi^0 / \partial T)_p = (\partial^2 V_\phi^0 / \partial T^2)_p = 2c \quad (4.7)$$

This second derivative is known as Hepler's constant. A positive value of Hepler's constant indicates that the solute behaves as a structure-maker, enhancing the hydrogen-bonded structure of water. Conversely, a negative value suggests structure-breaking behaviour. E_ϕ^0 and $(\partial E_\phi^0 / \partial T)_p$ values are shown in **Table 4.6**. In this study, all calculated E_ϕ^0 values were positive, and most Hepler's constants ($2c$) were also positive, indicating that magnesium salicylate, NaCl, and trisodium citrate enhance the structural organization of water through ion-dipole interactions and hydrogen bonding with surrounding water molecules. This behaviour is attributed to strong ion-dipole

and hydrogen bonding interactions, especially in ternary systems with citrate. The only exception was sodium chloride at $0.01000 \text{ mol}\cdot\text{kg}^{-1}$, where a slightly negative value suggests marginal structure-breaking at very dilute conditions. These results agree with the volumetric and acoustic data, further confirming enhanced solute–solvent interactions in these systems [29,30].

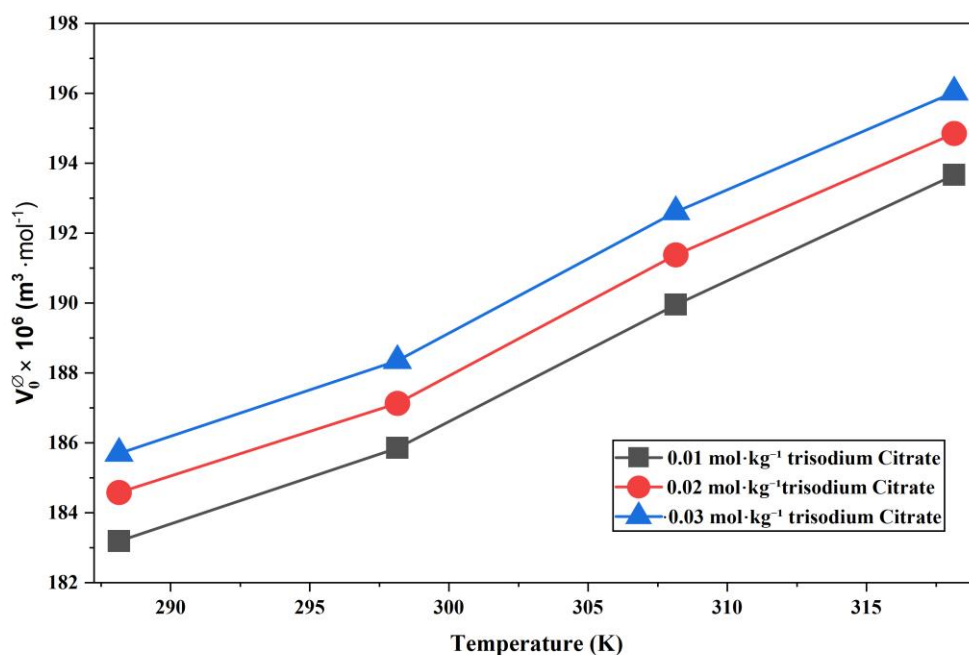


Figure 4.3.1 Variation of the limiting apparent molar volume (V_ϕ^0) with temperature for magnesium salicylate in aqueous trisodium citrate solutions. The solid lines represent the polynomial fit obtained using **Equation (4.4)**.

Figure 4.3.1 shows that the limiting apparent molar volume (V_ϕ^0) increases systematically with temperature for all studied magnesium salicylate concentrations in aqueous trisodium citrate solutions. The smooth variation confirms that the polynomial relationship given by **Equation (4.4)** adequately represents the experimental data and supports the empirical parameters listed in **Table 4.5**.

Apparent molar isentropic compression

The $\kappa_{\phi,s}$ calculated from speed of sound values by using the following equation [31];

$$\kappa_{\phi,s} = (Mk_S/\rho) - \{(k_{S,0}\rho - k_{S,\rho_0})/m_A\rho\rho_0\} \quad (4.8)$$

Where k_S is an isentropic compressibility, that is evaluated by following equation.

$$k_s = 1/c^2\rho \quad (4.9)$$

All computed $\kappa_{\phi,s}$ values are listed in **Table 4.7**. All concentrations and temperatures have consistently negative values of $\kappa_{\phi,s}$, as seen in **Figure 4.5**, which also shows how it varies with molality. The $\kappa_{\phi,s}$ values obtained for sodium chloride and trisodium citrate in this study are in good agreement with literature data reported for their respective binary aqueous systems at comparable temperatures and concentrations [1],[7][5]. This consistency supports the reliability of the present measurements, even in the absence of ternary system data. This trend suggests that, in comparison to bulk water, the water molecules around the ionic groups of sodium chloride/ trisodium citrate are less compressible. A solution's overall compressibility may be decreased by adding a solvent, such as magnesium salicylate, as indicated by the decrease in $\kappa_{\phi,s}$. Strong interactions between the solute and solvent, where magnesium salicylate forms hydration shells with water to provide a highly structured solution that resists compression, are primarily responsible for this impact [32,33]. The ultrasonic velocity in the solution rises with temperature, which further reduces isentropic compressibility and makes $\kappa_{\phi,s}$ negative. Furthermore, these interactions are strengthened by increasing magnesium salicylate concentration, which further reduces compressibility and strengthens the negative trend of $\kappa_{\phi,s}$. This pattern demonstrates how temperature, concentration, and solute-solvent interactions all work together to decrease the solution's compressibility in isentropic conditions [33–35].

Table 4.5: Empirical constants, R^2 , and ARD values for sodium chloride/trisodium citrate in aqueous magnesium salicylate solutions.

$^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$a \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$	$b \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R^2	ARD
Sodium chloride					
0.01000	16.8967(± 0.02)	0.0749(± 0.02)	-0.0001(± 0.01)	0.9999	0.00096
0.02000	17.7237(± 0.04)	0.0197(± 0.01)	0.0006(± 0.03)	0.9999	0.00023
0.03000	17.9092(± 0.01)	0.0301(± 0.01)	0.0001(± 0.01)	0.9999	0.00045
trisodium citrate					
0.01000	186.1254(± 0.30)	0.3291(± 0.02)	0.0026(± 0.01)	0.9999	0.00097
0.02000	187.5029(± 0.40)	0.3276(± 0.03)	0.0023(± 0.02)	0.9999	0.00131
0.03000	188.7153(± 0.40)	0.3331(± 0.03)	0.0019(± 0.02)	0.9999	0.00129

$^a m_B$ is the molality of magnesium salicylate.

Table 4.6. E_{ϕ}^0 and helper constants of Sodium chloride/ trisodium citrate in aqueous magnesium salicylate solutions.

$^a m_B \text{ (mol} \cdot \text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p / \text{(m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	
Sodium chloride					
0.01000	0.0774	0.0749	0.0724	0.0700	-0.0002
0.02000	0.0079	0.0197	0.0316	0.0435	0.0012
0.03000	0.0283	0.0301	0.0319	0.0337	0.0002
Trisodium citrate					
0.01000	0.2767	0.3291	0.3814	0.4338	0.0052
0.02000	0.2814	0.3276	0.3737	0.4199	0.0046
0.03000	0.2943	0.3331	0.3719	0.4107	0.0039

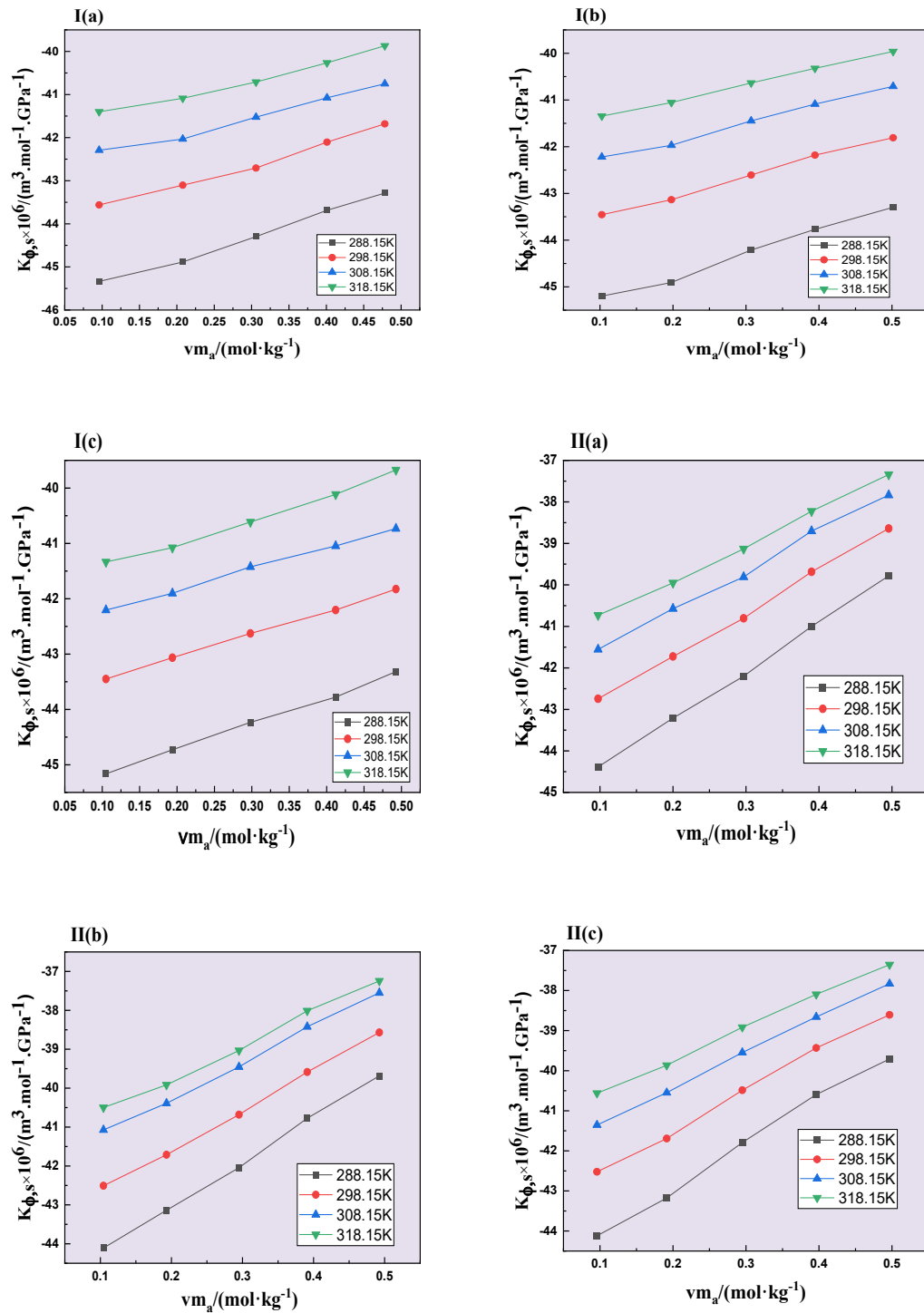


Fig. 4.5. Plots of $\kappa_{\phi,s}$ (I) Sodium chloride and (II) trisodium citrate in aqueous magnesium salicylate solution (a) 0.01000 magnesium salicylate, (b) 0.02000 magnesium salicylate, and (c) 0.03000 magnesium salicylate ($\text{mol} \cdot \text{kg}^{-1}$).

Partial molar isentropic compression

For ternary combinations including sodium chloride/ trisodium citrate and magnesium salicylate, the analysis of partial molar isentropic compression ($\kappa_{\phi,s}^0$) and their associated experimental slopes (S_K^*) offers important information about system interactions at different temperatures and concentrations. To calculate $\kappa_{\phi,s}^0$ and S_K^* , utilise the following formula [2]:

$$K_{\phi,s} = K_{\phi,s}^0 + S_K^*(m_A)^{1/2} \quad (4.10)$$

All $\kappa_{\phi,s}^0$ and S_K^* values are negative, in accordance with the data in **Table 4.8**, and the results are visually displayed in **Figure 4.6**. The consistently negative $\kappa_{\phi,s}^0$ readings show a significant decrease in compressibility as the magnesium salicylate concentration rises. This pattern emphasises how crucial hydrophilic interactions are to the system. The addition of magnesium salicylate appears to significantly change the structural arrangement of water molecules around its charged or polar groups, based on the negative compressibility values. This behaviour suggests strong solute-solvent interactions that improve the stability of the solution as a whole. The existence of negative compressibility values suggests that the way water molecules align themselves around the solute is dramatically altered by the addition of magnesium salicylate. The charged or polar groups in magnesium salicylate draw in water molecules, creating a more rigid and structured hydration shell that limits the compressive strength of the solution. Strong solute-solvent interactions are the immediate cause of this, as water molecules bind to magnesium salicylate to form stable bonds that lower the free volume and lessen the solution's vulnerability to compression from outside pressure [36]. Furthermore, when the solute concentration increases, the negative slopes (S_K^*) indicate further decreases in compressibility. This trend supports the notion that a more rigid solution structure results from stronger solute-solvent interactions caused by rising magnesium salicylate content. Thus, in the presence of magnesium salicylate, the solvent's molecular structure significantly rearranges around the solute, as indicated by the negative values of $\kappa_{\phi,s}^0$ and S_K^* , which highlight the importance of hydrophilic interactions in stabilising the solution and decreasing its compressibility [37,38].

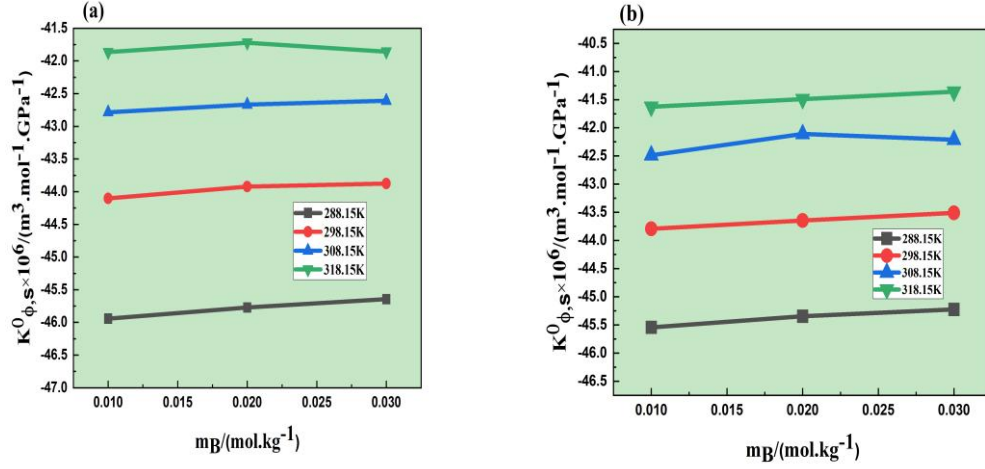


Fig. 4.6. Plots of $K_{\phi,s}^0$ (a) Sodium chloride and (b) trisodium citrate in aqueous solutions of magnesium salicylate.

Partial molar isentropic compression of Transfer

From water to aqueous magnesium salicylate solution $\Delta\kappa_{\phi}^0$ calculated by the following equation.

$$\Delta\kappa_{\phi}^0 = \kappa_{\phi,s}^0 (\text{in aqueous magnesium salicylate solution}) - \kappa_{\phi,s}^0 (\text{in water}) \quad (4.11)$$

With the exception for sodium chloride at 0.01 magnesium salicylate concentrations and temperature 308.15K of 0.02 magnesium salicylate $mol \cdot kg^{-1}$, as indicated in **Table 4.9**, all values of $\Delta\kappa_{\phi}^0$ are positive for sodium chloride/ trisodium citrate. Positive values of $\Delta\kappa_{\phi}^0$ show that the solute can improve the structure of water by functioning as a "structure maker." This indicates that magnesium salicylate improves the stability and bonding of water molecules surrounding the solute. This kind of behaviour is usually seen when interactions between the solute and the solvent result in a system that is more ordered and less compressible. Water creates structured hydration shells around the solute, which lowers compressibility. Structure breakers increase the fluidity and mobility of water molecules by interfering with the H-bonding network of water. The presence of magnesium salicylate at these lower concentrations affects the solvent's structural integrity, increasing the solution's compressibility, as indicated by the negative $\Delta\kappa_{\phi}^0$ values [39,40].

Table 4.7. $\kappa_{\phi,S}$ of NaCl /C₆H₅Na₃O₇ in water and aqueous magnesium salicylate solutions.

$^a m_A /$ (mol · kg ⁻¹)	$\kappa_{\phi,S} \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$^a m_A /$ (mol · kg ⁻¹)	$\kappa_{\phi,S} \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K		T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride + 0.00000 magnesium salicylate					trisodium citrate + 0.00000 magnesium salicylate				
0.09669	-45.41	-43.61	-42.29	-41.41	0.08744	-44.63	-42.89	-41.67	-40.93
0.19897	-45.11	-43.38	-42.08	-41.28	0.18432	-43.46	-41.86	-40.74	-39.99
0.29215	-44.33	-42.70	-41.53	-40.70	0.28217	-42.10	-40.67	-39.61	-38.91
0.40757	-43.91	-42.32	-41.22	-40.30	0.39429	-40.77	-39.47	-38.61	-37.99
0.49242	-43.57	-42.05	-41.01	-40.04	0.48416	-39.55	-38.48	-37.61	-37.04
Sodium chloride + 0.01000 magnesium salicylate					trisodium citrate + 0.01000 magnesium salicylate				
0.09601	-45.34	-43.56	-42.29	-41.40	0.09745	-44.39	-42.74	-41.56	-40.73
0.20788	-44.89	-43.10	-42.03	-41.09	0.20002	-43.21	-41.73	-40.57	-39.95
0.30592	-44.30	-42.71	-41.52	-40.71	0.29679	-42.20	-40.81	-39.81	-39.13
0.40093	-43.69	-42.10	-41.08	-40.27	0.38987	-41.00	-39.69	-38.70	-38.22
0.47819	-43.29	-41.68	-40.75	-39.87	0.49545	-39.78	-38.64	-37.84	-37.34
Sodium chloride + 0.02000 magnesium salicylate					trisodium citrate + 0.02000 magnesium salicylate				
0.10258	-45.20	-43.46	-42.22	-41.34	0.10435	-44.11	-42.51	-41.07	-40.50
0.19784	-44.91	-43.13	-41.97	-41.06	0.19312	-43.14	-41.71	-40.39	-39.92
0.30710	-44.21	-42.61	-41.45	-40.64	0.29515	-42.04	-40.68	-39.45	-39.03

0.39450	-43.77	-42.18	-41.09	-40.32	0.39107	-40.77	-39.59	-38.42	-38.01
0.50152	-43.30	-41.81	-40.71	-39.96	0.49251	-39.69	-38.57	-37.55	-37.25
Sodium chloride + 0.03000 magnesium salicylate					trisodium citrate + 0.03000 magnesium salicylate				
0.10501	-45.16	-43.45	-42.20	-41.34	0.09592	-44.12	-42.52	-41.36	-40.56
0.19386	-44.73	-43.07	-41.90	-41.08	0.19152	-43.18	-41.69	-40.55	-39.87
0.29807	-44.23	-42.63	-41.42	-40.61	0.29500	-41.79	-40.49	-39.55	-38.92
0.41208	-43.78	-42.20	-41.05	-40.11	0.39616	-40.60	-39.43	-38.66	-38.09
0.49266	-43.32	-41.83	-40.73	-39.67	0.49666	-39.71	-38.61	-37.83	-37.35

^a m_A is the molality of Sodium chloride / trisodium citrate in the aqueous solution magnesium salicylate. standard uncertainties u are $u(T) = 0.001K$, $u(p) = 0.01MPa$.

Table 4.8 $\kappa_{\phi,s}^0$ and experimental slope S_K^* of NaCl /C₆H₅Na₃O₇ in water and aqueous magnesium salicylate solutions.

$^a m_B / (mol \cdot kg^{-1})$	$\kappa_{\phi,s}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$S_K^* \times 10^6 (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium chloride								
0.00000	-45.91(±0.14)	-44.05(±0.13)	-42.64(±0.11)	-41.86(±0.12)	4.87(±0.44)	4.18(±0.39)	3.42(±0.33)	3.72(±0.37)
0.01000	-45.94(±0.08)	-44.10(±0.09)	-42.78(±0.10)	-41.86(±0.09)	5.52(±0.26)	4.94(±0.28)	4.20(±0.30)	4.02(±0.27)
0.02000	-45.77(±0.09)	-43.92(±0.05)	-42.67(±0.06)	-41.72(±0.02)	4.97(±0.27)	4.27(±0.17)	3.93(±0.18)	3.52(±0.07)
0.03000	-45.64(±0.04)	-43.88(±0.02)	-42.61(±0.04)	-41.86(±0.07)	4.66(±0.13)	4.13(±0.07)	3.82(±0.11)	4.32(±0.22)
trisodium citrate								
0.00000	-45.77(±0.06)	-43.87(±0.04)	-42.57(±0.07)	-41.77(±0.07)	12.80(±0.18)	11.17(±0.13)	10.21(±0.22)	9.75(±0.23)
0.01000	-45.54(±0.06)	-43.79(±0.04)	-42.49(±0.10)	-41.63(±0.06)	11.58(±0.20)	10.39(±0.22)	9.43(±0.31)	8.62(±0.20)
0.02000	-45.35(±0.08)	-43.64(±0.07)	-42.11(±0.09)	-41.49(±0.12)	11.51(±0.23)	10.28(±0.22)	9.25(±0.26)	8.64(±0.35)
0.03000	-45.22(±0.14)	-43.51(±0.11)	-42.21(±0.04)	-41.36(±0.06)	11.34(±0.43)	10.04(±0.33)	8.89(±0.13)	8.14(±0.18)

$^a m_B$ is the aqueous magnesium salicylate molality. standard uncertainties u are $u(T) = 0.001K$, $u(p) = 0.01MPa$.

Thus, magnesium salicylate exhibits a destabilising effect under certain temperatures and concentrations, where it disrupts the water structure and increases compressibility, while positive $\Delta\kappa_{\phi}^0$ values indicate that magnesium salicylate encourages a more rigid and ordered structure in the solution.

A direct comparison of the density and ultrasonic (compressibility) parameters for magnesium salicylate in water, NaCl, and trisodium citrate solutions reveals clear differences in molecular interactions. Both density and speed of sound increase when NaCl or trisodium citrate are present, with the effect being most pronounced for trisodium citrate. This trend indicates that the addition of salts—especially multivalent citrate³⁻—enhances solute–solvent and solute–solute interactions through stronger electrostatic forces and hydrogen bonding. Correspondingly, compressibility decreases in the order: water > NaCl > trisodium citrate, reflecting increased molecular association and structuring in the ternary systems. These results, as illustrated in **Figures 4.1, 4.2 and 4.3**, demonstrate that solutions containing multivalent ions and complex anions exhibit the strongest interactions, which is consistent with the observed increases in density and ultrasonic velocity and the reduction in compressibility.

Table 4.9. $\Delta\kappa_{\phi,s}^0$ of Sodium chloride/ trisodium citrate in aqueous magnesium salicylate solutions.

^am_B ($mol \cdot kg^{-1}$)	$\Delta\kappa_{\phi,s}^0 \times 10^6 (m^3 \cdot mol^{-1} GPa^{-1})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium chloride				
0.01000	-0.03	-0.05	-0.14	-0.01
0.02000	0.14	0.13	-0.02	0.13
0.03000	0.27	0.18	0.03	0.00
trisodium citrate				
0.01000	0.23	0.08	0.09	0.14
0.02000	0.42	0.23	0.46	0.27
0.03000	0.54	0.37	0.36	0.41

Standard uncertainties u are $u(m) = 0.0100 \text{ mol} \cdot kg^{-1}$, $u(T) = 0.001K$, $u(p) = 0.01MPa$.

Pair and triplet coefficients

In order to clarify a solute's transfer characteristics in aqueous magnesium salicylate solution, Friedman and Krishnan [41] built on McMillian and Mayer's [42] idea. The molecular interactions in the sodium chloride/ trisodium citrate and magnesium salicylate mixes are revealed by the interaction coefficients shown in **Table 4.10**. The interaction coefficients are computed using the following formulas:

$$V_{\phi}^0(H_2O - \text{magnesium salicylate}_{(aq.)}) = 2V_{AB}m_B + 3V_{ABB}m_B^2 \quad (4.12)$$

$$\Delta\kappa_{\phi,s}^0(H_2O - \text{magnesium salicylate}_{(aq.)}) = 2K_{AB}m_B + 3K_{ABB}m_B^2 \quad (4.13)$$

For sodium chloride/ trisodium citrate, all pair (V_{AB}) interaction coefficients of volume are positive and triplet (V_{ABB}) interaction coefficients of volume are negative. For sodium citrate, the pair (K_{AB}) interaction coefficient of compressibility are all positives, whereas as for sodium chloride the pair (K_{AB}) interaction coefficient of compressibility are negative except at temperature 318.15K. Furthermore, for sodium chloride triplet interaction coefficients for compressibility (K_{ABB}) are positive at all temperatures whereas for trisodium citrate it is positive and negative. At temperatures 288.15K and 308.15K triplet interaction coefficients for compressibility (K_{ABB}) are negative for trisodium citrate and at rest two temperature it is positive. These coefficients mainly highlight differing behaviours of sodium chloride/ trisodium citrate when mixed with magnesium salicylate. The temperature dependence of these interactions emphasizes the critical role of thermal effects in determining the thermodynamic properties of these mixtures, which is important for applications in formulation chemistry [43,44].

Thermal expansion coefficient

The α_p quantifies the proportional change in a material's volume per degree of temperature change under constant pressure. Its mathematical definition is[1]:

$$\alpha_p = \frac{1}{V_{\phi}^0} \left(\frac{\partial V_{\phi}^0}{\partial T} \right) \quad (4.14)$$

Table 4.11 lists the values of α_p . In essence, it gauges how sensitive a material is to variations in temperature while maintaining a constant pressure.

Table 4.10. Interaction coefficients (V_{AB} , V_{ABB} , K_{AB} and K_{ABB}) of Sodium chloride/ trisodium citrate in aqueous magnesium salicylate solution.

T/K	$V_{AB} \times 10^6 (m^3 \cdot mol^{-2} \cdot kg)$	$V_{ABB} \times 10^6 (m^3 \cdot mol^{-3} \cdot kg^2)$	$K_{AB} \times 10^6 (m^3 \cdot mol^{-2} \cdot kg \cdot GPa^{-1})$	$K_{ABB} \times 10^6 (m^3 \cdot mol^{-3} \cdot kg^2 \cdot GPa^{-1})$
Sodium chloride				
288.15	51.37	-339.64	-1.60	139.91
298.15	63.01	-650.44	-0.95	94.20
308.15	74.64	-959.72	-7.20	179.00
318.15	88.53	-1310.86	4.25	-87.12
trisodium citrate				
288.15	6059.61	-95208.98	12.86	-83.53
298.15	6080.46	-95529.72	3.97	48.66
308.15	6225.51	-97779.65	12.20	-122.12
318.15	6352.95	-99902.17	7.00	-5.01

As mentioned in [45], the α_p values for sodium chloride/ trisodium citrate in combination with magnesium salicylate are positive, although they change with temperature and concentration. Hepler's constant, $\left(\frac{\partial V_\phi^0}{\partial T}\right)$, aids in categorising a solute's impact on the solution's structure in accordance with Hepler's theory. Positive values of $\left(\frac{\partial V_\phi^0}{\partial T}\right)$, indicate that the solute acts as a structure promoter, helping to create or improve the structure.

Table 4.11. α_p of Sodium chloride/ trisodium citrate in aqueous magnesium salicylate solutions.

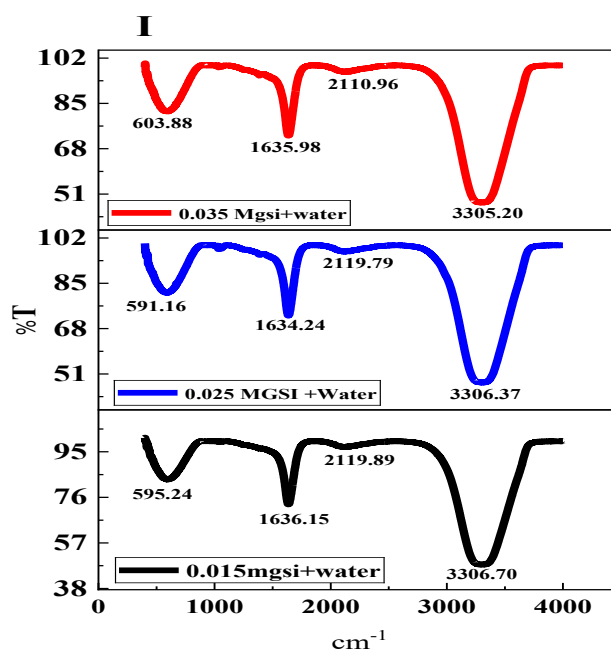
$^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$\alpha_p \times 10^3 / (K^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride				
0.01000	139.22	74.57	54.45	41.83
0.02000	3.89	10.96	18.50	25.99
0.03000	13.86	15.03	16.55	18.04
trisodium citrate				
0.01000	2.52	2.99	3.38	3.77
0.02000	2.53	2.94	3.27	3.61
0.03000	2.62	2.96	3.22	3.50

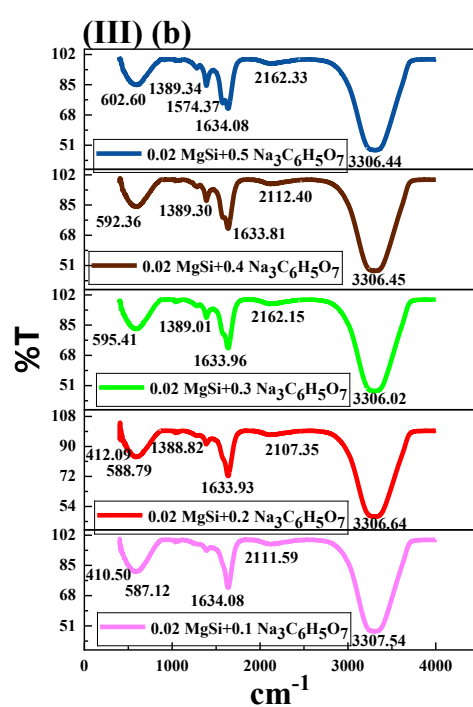
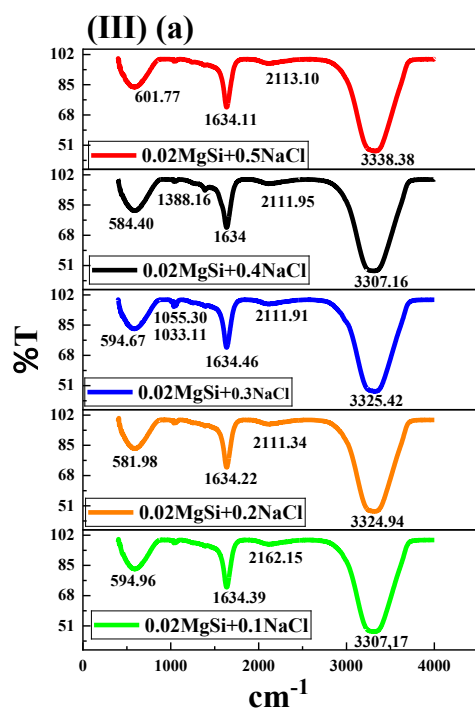
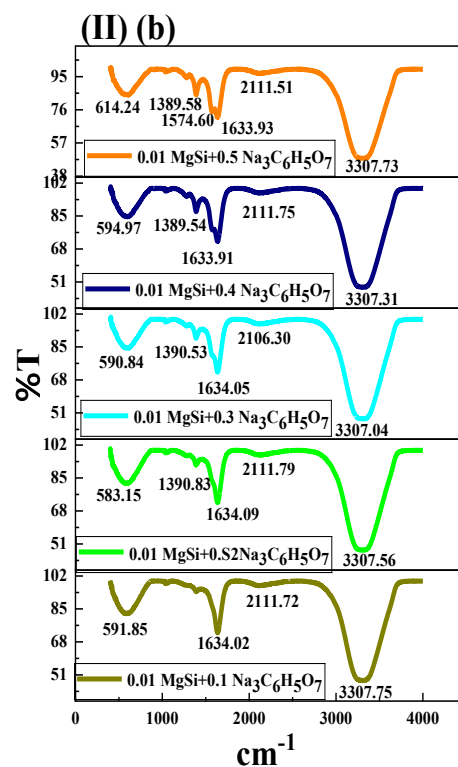
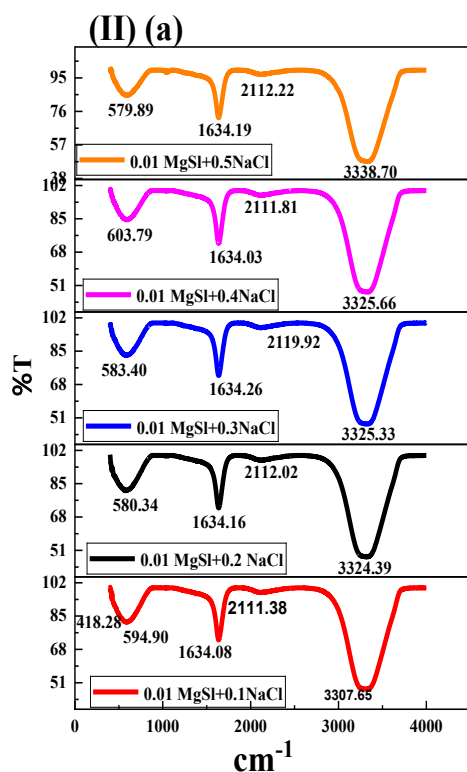
$^a m_B$ is the molality of magnesium salicylate.

ATR-FTIR studies

The ATR (Attenuated Total Reflectance) method was employed in the FTIR spectroscopic study covering the wavelength range of 400–4000 cm^{-1} . The technique is useful in determining the intensity of molecular interactions and identifying hydrogen bonding in the mixture. **Fig. 4.7** presents the FTIR spectra for the different concentrations of magnesium salicylate with different combinations. FTIR spectroscopy effectively identifies molecular interaction characteristics and often reveals details not easily captured by NMR spectroscopy [46,47]. Magnesium salicylate has an infrared spectrum that provides information on its molecular structure and interactions. This enables the detection of minute changes in bond properties that NMR may overlook because of its poorer sensitivity. This study found that the sort of contacts

present can be inferred from variations in the strength of spectral bands associated with hydrogen bonding. In particular, an increase in spectral band strength indicates intermolecular interactions, whereas a decrease in intensity indicates intramolecular bonding. In the present study, FTIR spectra exhibit visible shifts in the O–H stretching region. Specifically, the prominent absorption band near 3285 cm^{-1} in the binary system shifts toward 3302 cm^{-1} in ternary systems, indicating enhanced intermolecular hydrogen bonding due to the presence of NaCl or trisodium citrate. These blue shifts correspond to stronger hydrogen-bonded networks and reduced hydrogen bond lengths. Additional bands at 1638 cm^{-1} (assigned to --OH bending or asymmetric COO^- stretching) and in the $580\text{--}592\text{ cm}^{-1}$ region show increased intensity and minor shifts, confirming ion–dipole interactions between $\text{Mg}^{2+}/\text{Na}^+$ and polar functional groups. These spectral features strongly support the volumetric and acoustic findings, particularly the structure-making behaviour indicated by positive V_ϕ^0 and negative $\kappa_{\phi,s}^0$ values. The overlay spectra (**Fig. 4.7**) further confirm systematic shifts across all systems, validating stronger solute–solvent interactions in the ternary mixtures.





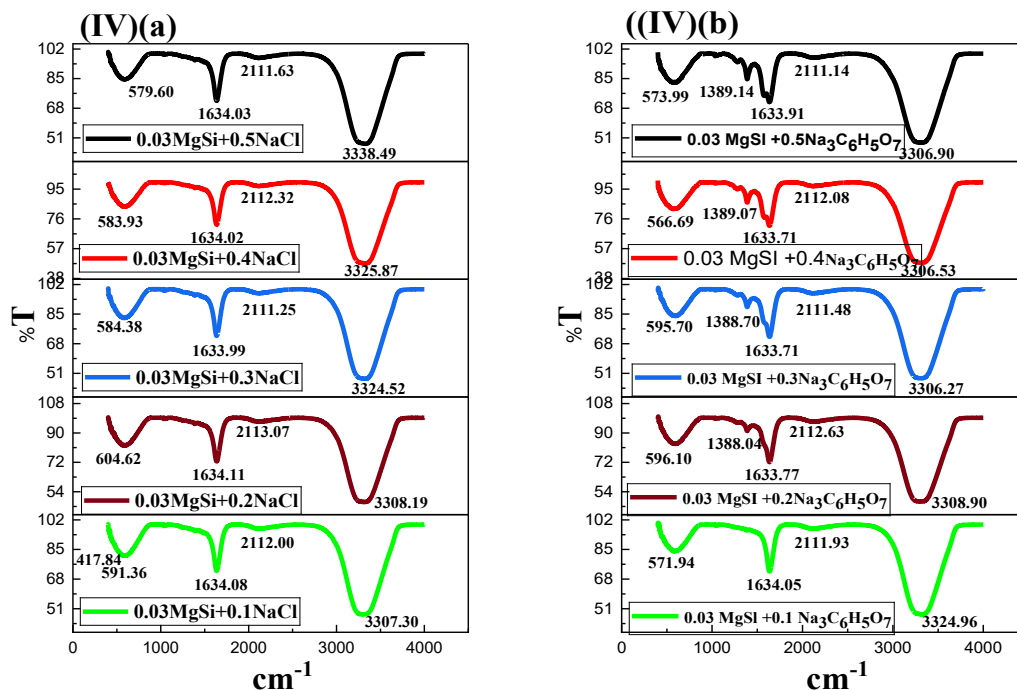


Figure 4.7. FTIR spectra for NaCl/C₆H₅Na₃O₇ having molality (0.1-0.5) $\text{mol} \cdot \text{kg}^{-1}$ in (0.01000, 0.02000, and 0.03000) $\text{mol} \cdot \text{kg}^{-1}$ magnesium salicylate solutions (I) magnesium salicylate + H₂O (black: 0.01000 magnesium salicylate, Blue: 0.02000 magnesium salicylate, red: 0.03000 magnesium salicylate) (II) (a) NaCl in 0.1-0.5 $\text{mol} \cdot \text{kg}^{-1}$ (b) C₆H₅Na₃O₇ in 0.1-0.5 $\text{mol} \cdot \text{kg}^{-1}$ in 0.01000 magnesium salicylate solution. (III)NaCl in 0.1-0.5 $\text{mol} \cdot \text{kg}^{-1}$ (b) C₆H₅Na₃O₇ in 0.1-0.5 $\text{mol} \cdot \text{kg}^{-1}$ in 0.02000 magnesium salicylate solution. (IV)in 0.1-0.5 $\text{mol} \cdot \text{kg}^{-1}$ (b) C₆H₅Na₃O₇ in 0.1-0.5 $\text{mol} \cdot \text{kg}^{-1}$ in 0.03000 magnesium salicylate solution.

Problem 2

Problem 2: Thermodynamic Investigation of Magnesium Salicylate Solutions with Sodium Salts by Volumetric and Acoustic Approach

In this section, we reported ρ and c for magnesium salicylate in “(0.010, 0.030, 0.050) $\text{mol} \cdot \text{kg}^{-1}$ aqueous solutions of sodium salts (sodium bicarbonate/sodium nitrate) at temperatures $T = (288.15, 298.15, 308.15, 318.15) \text{ K}$ ” to study solute–solvent interactions and to evaluate volumetric and acoustic parameters using a DSA 5000 M at 3 MHz frequency.

Density (ρ) and Apparent Molar Volume (V_ϕ)

The values of density were experimentally determined in magnesium salicylate solutions with concentrations of (0.000, 0.010, 0.030, and 0.050) $\text{mol} \cdot \text{kg}^{-1}$ at $T = 288.15\text{--}318.15\text{ K}$ in ternary mixtures. The results indicate that density increases as the molality of $\text{NaHCO}_3/\text{NaNO}_3$ rises in the aqueous magnesium salicylate solution. This increase primarily results from the greater mass of the solution. Additionally, the rise in density suggests stronger solute-solvent interactions [48–50]. The experimentally obtained density values for sodium bicarbonate + H_2O and sodium nitrate + H_2O at different temperatures align well with existing literature. A comparison of these values with previously reported data for sodium nitrate + H_2O [51,52] and sodium bicarbonate + H_2O [53] is presented in **Fig. 4.8(a) and 4.8(b)** respectively. Furthermore, the density measurements were used to determine the V_ϕ by using **equation 4.1**. In **Table 4.12** values of densities and V_ϕ are provided. The calculated V_ϕ values were positive and increased with temperature and molality of the sodium salts. In addition, since the systems are electrolytes, the values of $(V_\phi - A_V\sqrt{m})$ have been plotted against molality and are presented in **Figure 4.9** Which shows the trend of V_ϕ , graphically. The observed increase in V_ϕ with rising solute concentration and temperature reflects the overall volumetric changes in the solution. This increase primarily results from enhanced solute–solvent interactions (ion–ion interactions) at higher concentrations, which modify the hydration structures around ions and influence the packing of molecules in the solution. As these ion–ion interactions intensify, the structure of the solvent is perturbed, contributing to the expansion in solution volume captured by V_ϕ . Thus, the apparent molar volume provides valuable insight into the volumetric

behaviour and molecular interactions within the ternary magnesium salicylate–sodium bicarbonate/sodium nitrate–water system[54–57].

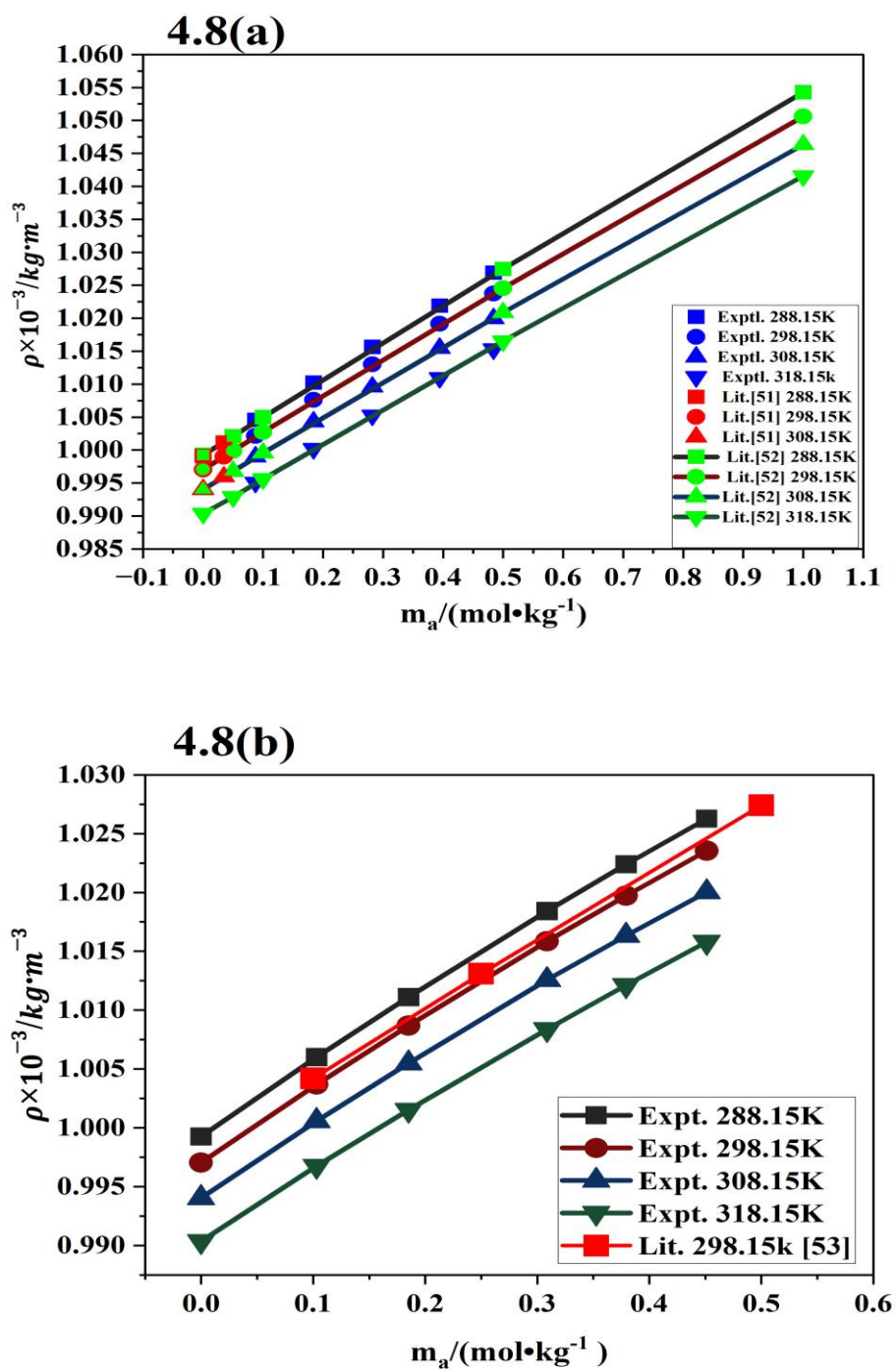


Figure 4.8. Agreement between experimental and literature densities of binary systems **4.8(a)** sodium Nitrate + water [51,52], **4.8(b)** sodium Bicarbonate +water [53].

Table 4.12 ρ and V_ϕ data for ternary Mixtures of Magnesium Salicylate, Sodium Bicarbonate and Sodium Nitrate at Various Concentrations and Temperatures (0.1 MPa).

$^a m_a / (mol \cdot kg^{-1})$	$\rho \times 10^{-3} / (kg \cdot m^{-3})$				$V_\phi \times 10^6 / (m^3 \cdot mol^{-1})$			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
0.000 Magnesium Salicylate + sodium Bicarbonate								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.10313	1.00591	1.00396	1.00078	0.99681	17.82	18.94	19.59	20.71
0.18524	1.01083	1.00859	1.00549	1.00144	19.04	20.04	20.82	22.21
0.30886	1.01817	1.01594	1.01257	1.00829	20.59	21.57	22.22	23.65
0.37932	1.02213	1.01973	1.01623	1.01197	21.41	22.42	23.19	24.40
0.45128	1.02627	1.02356	1.02003	1.01580	22.35	23.26	24.18	25.17
0.010 Magnesium Salicylate + sodium Bicarbonate								
0.00000	1.00012	0.99804	0.99501	0.99117				
0.09812	1.00654	1.00422	1.00105	0.99705	17.91	20.27	21.52	22.89
0.19832	1.01274	1.01024	1.00699	1.00290	19.37	21.30	22.23	23.25
0.31057	1.01938	1.01670	1.01330	1.00915	20.63	22.38	23.36	24.12
0.40525	1.02460	1.02193	1.01838	1.01413	21.96	23.21	24.28	25.06

0.48462	1.02896	1.02618	1.02248	1.01826	22.63	23.86	25.02	25.57

0.030 Magnesium Salicylate + sodium Bicarbonate

0.00000	1.00230	1.00018	0.99711	0.99324				

0.10720	1.00895	1.00666	1.00346	0.99943	21.34	22.80	23.85	25.13

0.20935	1.01501	1.01266	1.00927	1.00517	22.32	23.26	24.59	25.46

0.32264	1.02149	1.01900	1.01549	1.01127	23.18	24.15	25.30	26.17

0.40433	1.02592	1.02341	1.01991	1.01559	24.00	24.77	25.63	26.52

0.49791	1.03088	1.02841	1.02496	1.02043	24.74	25.25	25.79	26.89

0.050 Magnesium Salicylate + sodium Bicarbonate

0.00000	1.00433	1.00216	0.99905	0.99454				

0.10005	1.01036	1.00812	1.00493	1.00032	23.21	23.76	24.41	25.21

0.19593	1.01598	1.01368	1.01040	1.00572	23.66	24.19	24.83	25.48

0.28745	1.02120	1.01884	1.01549	1.01079	24.15	24.62	25.26	25.71

0.39562	1.02720	1.02478	1.02133	1.01661	24.67	25.12	25.76	26.08

0.50111	1.03282	1.03033	1.02693	1.02212	25.32	25.76	26.13	26.47

0.000 Magnesium Salicylate + sodium Nitrate

0.00000	0.99926	0.99705	0.99404	0.99036				
0.08744	1.00457	1.00214	0.99898	0.99508	23.61	26.00	27.58	29.98
0.18432	1.01023	1.00761	1.00429	1.00019	24.44	26.52	28.04	30.18
0.28217	1.01565	1.01301	1.00958	1.00526	25.55	26.91	28.22	30.33
0.39429	1.02190	1.01914	1.01545	1.01095	25.87	27.09	28.62	30.52
0.48416	1.02691	1.02376	1.01995	1.01531	25.93	27.67	29.12	30.91

0.010 Magnesium Salicylate + sodium Nitrate

0.00000	1.00012	0.99804	0.99501	0.99117				
0.09854	1.00595	1.00370	1.00053	0.99644	25.16	26.78	28.07	30.41
0.19983	1.01174	1.00924	1.00591	1.00180	25.80	27.76	29.07	30.29
0.29791	1.01723	1.01451	1.01104	1.00683	26.16	28.15	29.44	30.52
0.39821	1.02279	1.01984	1.01622	1.01190	26.38	28.36	29.67	30.69
0.47369	1.02681	1.02394	1.02008	1.01546	26.73	28.21	29.77	31.23

0.030 Magnesium Salicylate + sodium Nitrate

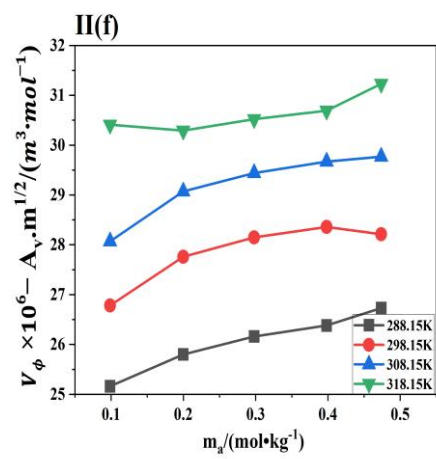
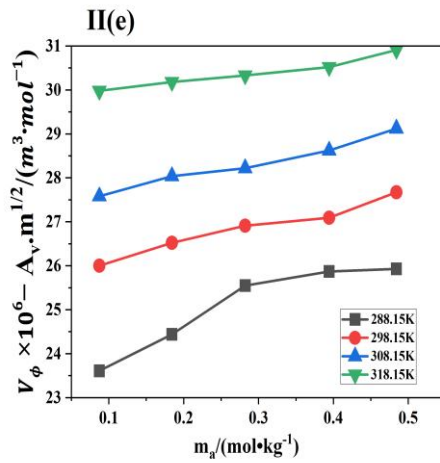
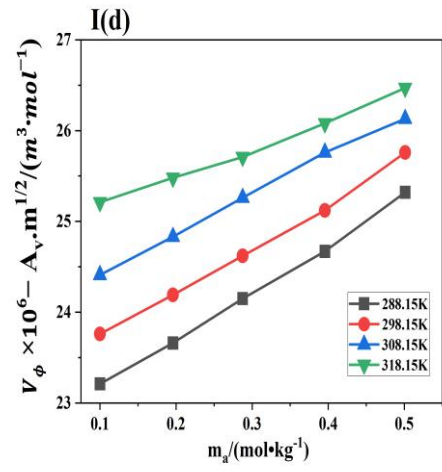
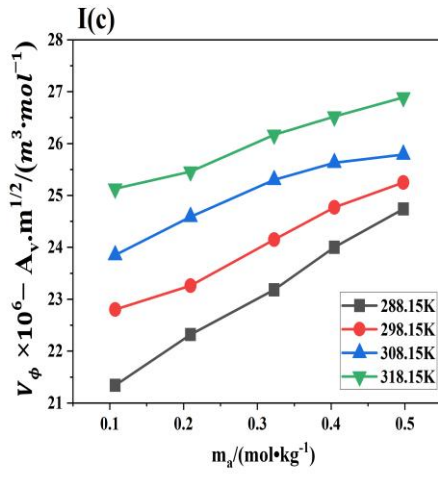
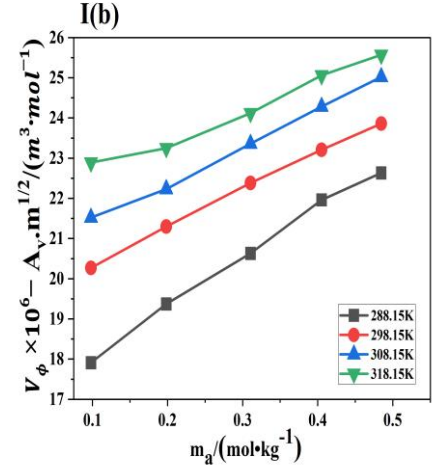
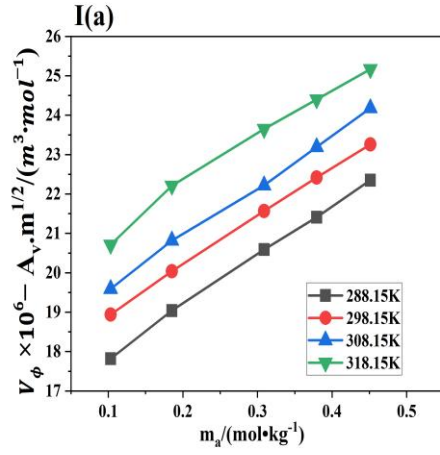
0.00000	1.00230	1.00018	0.99711	0.99324				
0.09759	1.00805	1.00573	1.00253	0.99845	25.43	27.34	28.60	30.56

0.19433	1.01357	1.01104	1.00771	1.00351	26.03	27.96	29.14	30.70
0.29186	1.01899	1.01632	1.01284	1.00853	26.50	28.21	29.44	30.78
0.39859	1.02480	1.02190	1.01830	1.01392	26.91	28.67	29.81	30.90
0.47945	1.02920	1.02603	1.02234	1.01777	27.02	28.99	30.09	31.37

0.050 Magnesium Salicylate + sodium Nitrate

0.00000	1.00433	1.00216	0.99905	0.99454				
0.10754	1.01045	1.00814	1.00491	1.00026	27.45	28.61	29.59	30.77
0.20945	1.01612	1.01368	1.01086	1.00555	27.73	28.84	29.74	30.96
0.30007	1.02103	1.01850	1.01566	1.01014	28.06	29.08	29.91	31.18
0.38329	1.02546	1.02284	1.02055	1.01426	28.31	29.30	30.11	31.42
0.46923	1.02992	1.02723	1.02560	1.01840	28.65	29.55	30.38	31.73

Standard uncertainties u are $u_r(m) = 0.01$, $u(\rho) = 0.5 \text{ kg} \cdot \text{m}^{-3}$, $u(p) = 0.01 \text{ MPa}$, and $u(T) = 0.01 \text{ K}$.



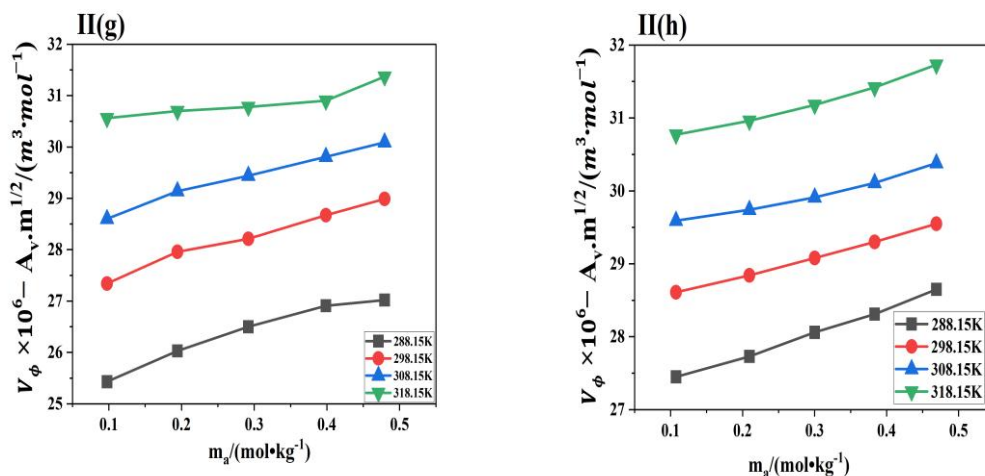


Figure 4.9: V_ϕ plots for sodium bicarbonate (I) and sodium nitrate (II) in water and aqueous magnesium salicylate solutions. Plots correspond to Mg-salicylate concentrations of (a, e) 0.000, (b, f) 0.010, (c, g) 0.030, and (d, h) 0.050 mol·kg⁻¹.

Partial molar volume

V_ϕ^0 were computed by extrapolating the V_ϕ versus molality data to equation 4.2. The Debye–Hückel limiting slope (A_V) values for sodium nitrate and sodium bicarbonate, both classified as 1:1 electrolytes, at the investigated temperatures were obtained from previously reported literature data [58,59], and S_V is an experimentally derived slope that accounts for deviations at higher concentrations. As both NaNO₃ and NaHCO₃ are 1:1 electrolyte, the same A_V values were applied. These slopes, derived for water, were used without further correction since the Mg-salicylate background concentrations were low, and their influence on the dielectric properties of the solvent was negligible within experimental uncertainty [60,61]. The least squares approach was employed to fit the parameters for both solutes, enabling the determination of V_ϕ^0 at infinite dilution [60,61]. The V_ϕ^0 positive values across all concentrations and temperatures (**Table 4.13**, **Figure 4.10**) indicate strong solute-solvent associations, consistent with the co-sphere overlap model. The V_ϕ^0 values for both sodium bicarbonate and sodium nitrate exhibit an increasing trend with rising temperature, reflecting the combined effects of thermal expansion and reduced solvent structuring around isolated ions. Sodium nitrate displays consistently higher V_ϕ^0 values compared to sodium bicarbonate, indicating a larger intrinsic volumetric contribution per mole in the magnesium salicylate aqueous

medium. The positive values of the interaction parameter S_V observed at all investigated temperatures indicate predominant ion–ion repulsive interactions that intensify with increasing concentration. The positive sign of S_V reflects hydrophilic interactions, implying strong repulsive forces between hydrated ions that disrupt hydration shells, leading to expansion of the hydration spheres and a corresponding increase in V_ϕ . The gradual decrease in the magnitude of S_V with increasing temperature suggests that thermal agitation mitigates these ion–ion repulsions, allowing for more efficient ion packing in the solution [62–64].

Partial molar volume of transfer (ΔV_ϕ^0)

Using **equation 4.3**, ΔV_ϕ^0 of salts by H₂O into mixtures of magnesium salicylate in aqueous solutions are determined. **Table 4.14** shows the positive values of ΔV_ϕ^0 for both sodium bicarbonate and sodium nitrate, indicating an increase in solute V_ϕ^0 upon transfer from water to aqueous magnesium salicylate. Such positive transfer volumes have often been associated with structure-making effects in mixed solvents, where solutes enhance the local hydrogen-bond network or solvent ordering, leading to expansion of the solvation shell volume. The trend of an increasing ΔV_ϕ^0 with solute concentration reinforces the idea that ion–hydrophilic interactions dominate, as solute–solvent associations promote greater structuring and increased partial molar volume. Literature also points out that these hydrophilic interactions typically outweigh hydrophobic contributions in such aqueous salt systems, consistent with our observations [65–69]. The positive partial molar transfer volumes (ΔV_ϕ^0) observed for sodium bicarbonate and sodium nitrate agree with reported trends for other drug-related electrolytes such as sodium salicylate and magnesium sulphate. The findings suggest that ion–hydrophilic interactions dominate in mixed electrolyte systems, and magnesium salicylate acts as a structure-making cosolute, promoting greater hydration and solvent ordering similar to other pharmaceutical electrolytes. **Figure 4.11** is Schematic representation of the interactions between NaHCO₃ and NaNO₃ and in Magnesium salicylate aqueous solutions.

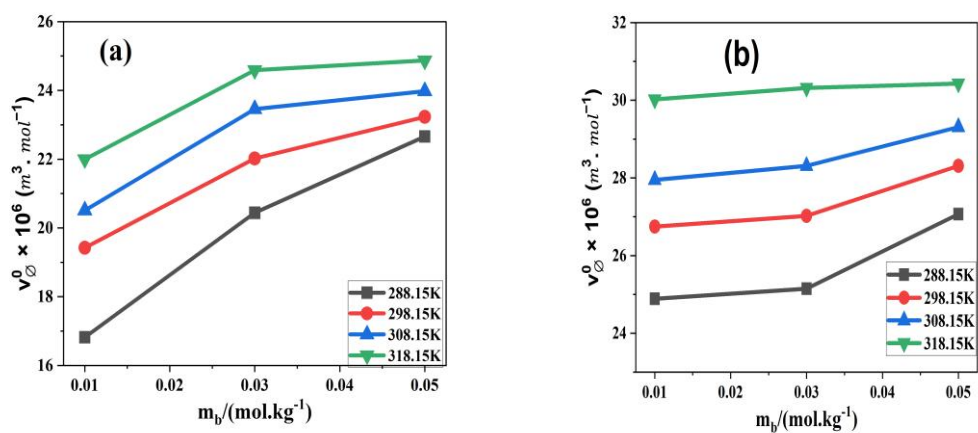


Fig. 4.10. V_{ϕ}^0 , of (a) NaHCO_3 and (b) NaNO_3 in magnesium salicylate solutions across studied temperatures.

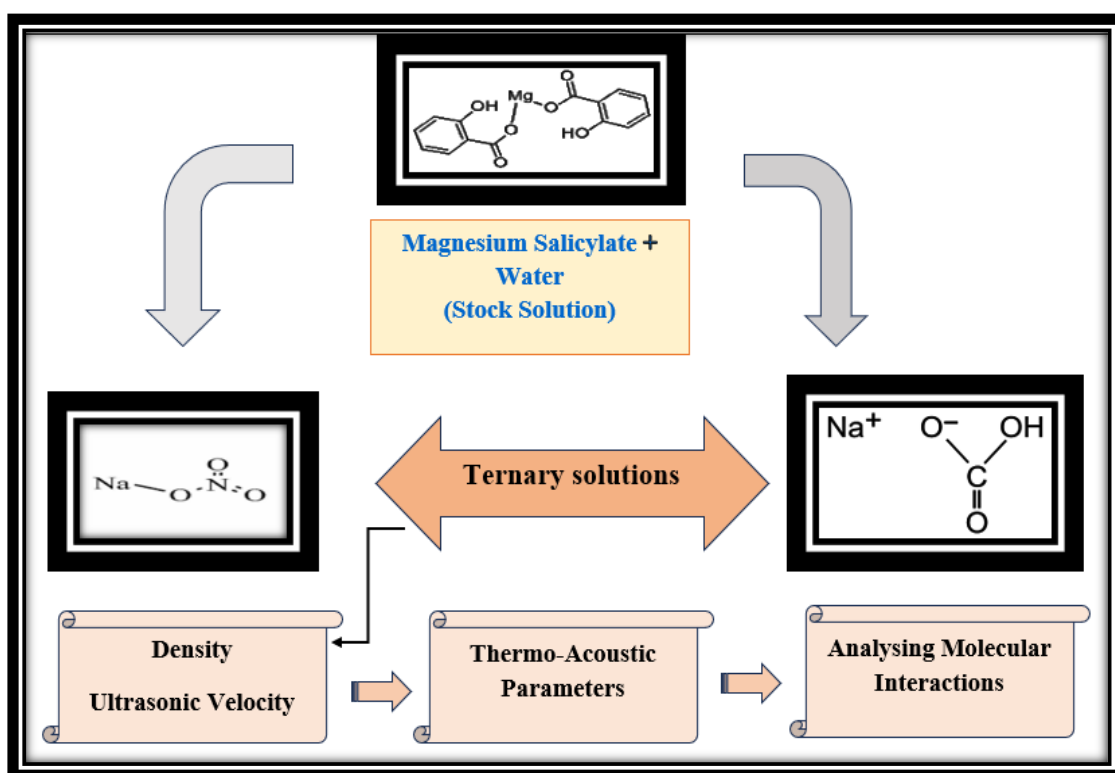


Figure 4.11 Schematic representation of the interactions between NaHCO_3 and NaNO_3 and in Magnesium salicylate aqueous solutions

Table 4.13 V_ϕ^0 , and S_V , parameters of salts in the Mg-salicylate systems at studied temperatures.

$^a m_b (\text{mol} \cdot \text{kg}^{-1})$	$V_\phi^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$				$S_V \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-2})$			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
Sodium Bicarbonate								
0.000	16.57(±0.08)	17.71 (±0.05)	18.31 (±0.10)	19.65 (±0.24)	12.86 (±0.27)	12.39 (±0.16)	12.94 (±0.32)	12.52 (±0.77)
0.010	16.82(±0.16)	19.42 (±0.07)	20.51 (±0.09)	22.00 (±0.19)	12.29 (±0.51)	9.30 (±0.23)	9.25 (±0.29)	7.28 (±0.59)
0.030	20.44(±0.06)	22.02 (±0.11)	23.46 (±0.22)	24.59 (±0.08)	8.68 (±0.35)	6.56 (±0.29)	5.09 (±0.65)	4.69 (±0.26)
0.050	22.66(±0.04)	23.23 (±0.05)	23.98 (±0.04)	24.87 (±0.04)	5.22 (±0.14)	4.92 (±0.17)	4.37 (±0.12)	3.12 (±0.14)
Sodium Nitrate								
0.000	23.35(±0.39)	25.72 (±0.13)	27.27 (±0.10)	29.76 (±0.08)	6.05 (±0.22)	3.88 (±0.41)	3.64 (±0.32)	2.19 (±0.27)
0.010	24.89(±0.13)	26.75 (±0.38)	27.95 (±0.31)	30.02 (±0.23)	3.93 (±0.41)	3.75 (±0.42)	4.26 (±0.96)	2.09 (±0.73)
0.030	25.15(±0.15)	27.02 (±0.09)	28.31 (±0.07)	30.32 (±0.15)	4.21 (±0.48)	4.15(±0.29)	3.77 (±0.24)	1.84 (±0.46)
0.050	27.07(±0.03)	28.31 (±0.02)	29.31 (±0.06)	30.43 (±0.06)	3.30 (±0.10)	2.59 (±0.07)	2.16 (±0.19)	2.64 (±0.20)

Standard uncertainties u is $u(T) = 0.001\text{K}$, $u(p) = 0.01\text{MPa}$, $u(V_\phi^0) = 0.01 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ and $u(S_V) = 0.73 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-2})$.

Table 4.14 ΔV_ϕ^0 of NaHCO_3 and NaNO_3 in magnesium salicylate solution at studied temperatures with 0.1 MPa.

$^a m_b (\text{mol} \cdot \text{kg}^{-1})$	$\Delta V_\phi^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Bicarbonate				
0.010	0.25	1.71	2.20	2.35
0.030	3.87	4.32	5.15	4.94
0.050	6.09	5.52	5.67	5.21
Sodium Nitrate				
0.010	1.54	1.03	0.68	0.26
0.030	1.80	1.30	1.04	0.57
0.050	3.72	2.59	2.03	0.68

$U_r(m) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$, and $u(\Delta V_\phi^0) = 1.28 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$.

Temperature-Dependent Partial Molar Volume

The experimental limiting apparent molar volume (V_ϕ^0) values listed in Tables **4.13** and **4.14** were fitted using the polynomial relationship given by Equation (4.4). The obtained polynomial parameters are presented in Table **4.15**, confirming that **equation (4.4)** adequately represents the temperature dependence of V_ϕ^0 for the studied systems[70]. Here $T_{ref} = 298.15\text{K}$. The a, b, c describing the temperature dependence of V_ϕ^0 for both solutes, are listed in **Table 4.15**. The fit quality was assessed by evaluating the relative deviation (σ) among experimental and calculated V_ϕ^0 values, as expressed in **equation 4.5**. The very low deviations and high R^2 values confirm the reliability of the polynomial model. Taking $Y = V_\phi^0$, the polynomial regression yielded very small deviations, and the R^2 values indicate that the model effectively describes the relationship[71]. The primary objective of evaluating the V_ϕ^0 data is to evaluate the expansibilities, calculated using **equation 4.6** [70,72]. At infinite dilution, E_ϕ^0 provides valuable insights into the interaction dynamics between solute and solvent molecules. The ability of a solute to induce structural organization or disintegration within a solution medium can be assessed through a corresponding thermodynamic expression given in **equation 4.7**. The calculated E_ϕ^0 values for

magnesium salicylate with both sodium bicarbonate and sodium nitrate are summarized in **Table 4.16**. The values of E_{ϕ}^0 and $(\partial E_{\phi}^0/\partial T)_p$ provide critical insight into solute–solvent interactions. Positive or slightly negative values of $(\partial E_{\phi}^0/\partial T)_p$ reflect structure-making (order-promoting) effects, whereas strongly negative values imply structure-breaking tendencies. As shown in **Table 4.16**, the calculated E_{ϕ}^0 and $(\partial E_{\phi}^0/\partial T)_p$ values for magnesium salicylate in the presence of both sodium bicarbonate and sodium nitrate indicate predominantly structure-making behaviour, evidencing strong solute–solvent interactions that tend to enhance solvent organization with increasing temperature [73,74].

Table 4.15 Empirical parameters determined for salts in aqueous magnesium salicylate solutions.

$^a m_b/$ (mol·k g ⁻¹)	$a \times 10^6/(\text{m}^3 \cdot \text{mol}^{-1})$	$b \times$ $10^6/(\text{m}^3 \cdot \text{m}$ $\text{ol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6/$ ($\text{m}^3 \cdot \text{mol}^{-1}$ $\cdot \text{K}^{-2}$)	R^2	ARD
Sodium Bicarbonate					
0.010	19.76357	0.20441	-0.00127	0.98607	0.04320
0.030	20.98861	0.24178	-0.00421	0.976166	0.05368
0.050	22.38216	0.23406	-0.00517	0.981789	0.05319
Sodium Nitrate					
0.010	26.48576	0.07382	0.00066	0.95332	0.03342
0.030	27.81155	0.05678	0.00078	0.97887	0.03732
0.050	30.05204	0.02713	-0.00037	0.98981	0.04509

Ultrasonic Velocity and Apparent molar isentropic compression

The ultrasonic velocity (c) in the solutions was experimentally recorded. A graphical comparison of the sound speed values for the binary system - sodium Nitrate + water with literature [52,75] at different concentrations and temperatures is presented in **Figure 4.12** further illustrating the observed trends and highlighting the consistency of the experimental data with established literature values. The increase in ultrasonic velocity with concentration is mainly attributed to enhanced solute–solvent interactions, reflecting stronger molecular association and reduced intermolecular free

length in the solution. However, alternative explanations such as ion-pair formation or aggregation phenomena could also contribute to these trends by affecting solution compressibility and molecular arrangement. Using these values, the k_s (isentropic compressibility) of each solution was computed according to the Newton–Laplace relation equation 4.8. To further investigate solute–solvent interactions, the $\kappa_{\phi,s}^0$ was determined using equation 4.9. The measured values of the sound speed and the calculated $\kappa_{\phi,s}^0$ for magnesium salicylate with sodium bicarbonate and sodium nitrate are presented in Table 4.17 (Figure 4.13). The results reveal a clear trend: the speed of sound increases with both increasing solute concentration and temperature, which is indicative of enhanced solute–solvent interactions and a more structured solution environment [76]. Conversely, the $\kappa_{\phi,s}^0$ values become more negative with decreasing concentration, reflecting the formation of a tightly bound hydration shell around the solute ions and a decrease in the compressibility of the solution. The trends observed in this study confirm that magnesium salicylate, in the presence of sodium bicarbonate or sodium nitrate, significantly influences the acoustic and compressibility properties of the solution, underscoring the importance of solute–solvent interactions in determining the physicochemical behaviour of such systems [76–79].

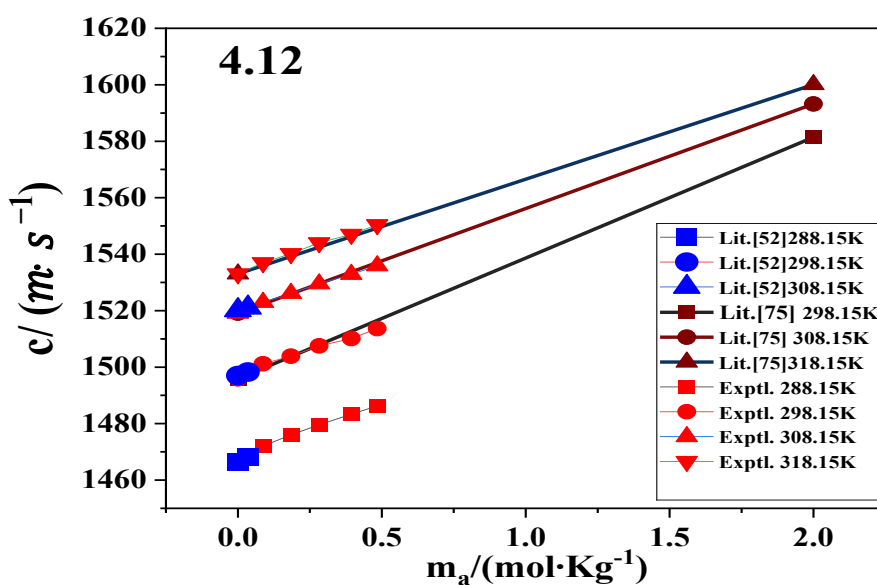
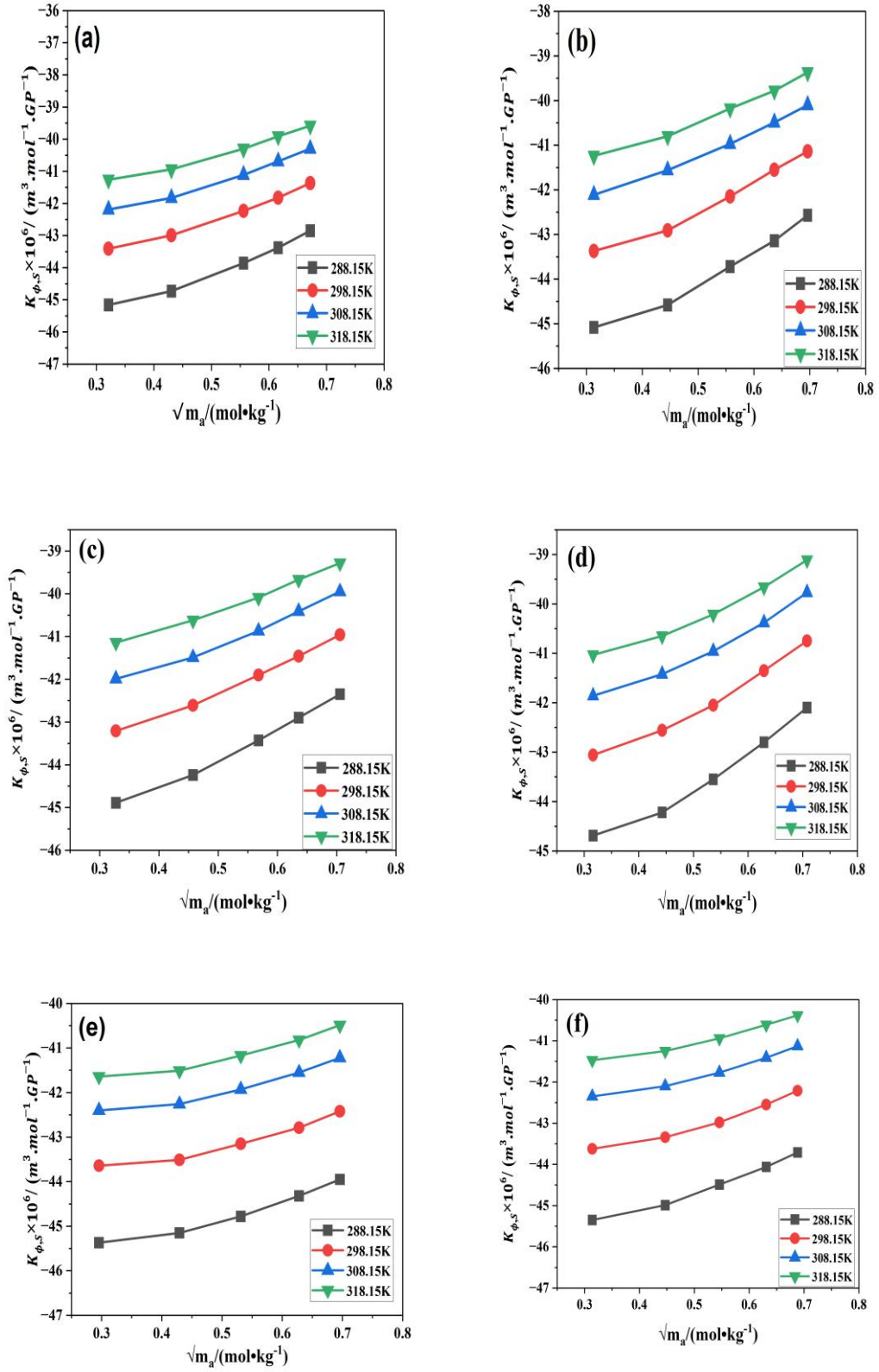


Figure 4.12. Comparison graph of sodium Nitrate +water with literature at different temperature.

Table 4.16 E_{ϕ}^0 for the magnesium salicylate in aqueous solutions with sodium bicarbonate and Sodium Nitrate.

$^a m_b / (mol \cdot kg^{-1})$	$E_{\phi}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot K^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p / (m^3 \cdot mol^{-1} \cdot K^{-2})$
	288.15 K	298.15 K	308.15 K	318.15K	
Sodium Bicarbonate					
0.010	0.22972	0.20441	0.17909	0.15378	-0.00253
0.030	0.32592	0.24178	0.15764	0.07351	-0.00841
0.050	0.33755	0.23406	0.13058	0.02709	-0.01035
Sodium Nitrate					
0.010	0.06066	0.07382	0.08698	0.10014	0.00132
0.030	0.04109	0.05678	0.07247	0.08816	0.00157
0.050	0.03451	0.02713	0.01975	0.01237	-0.00074



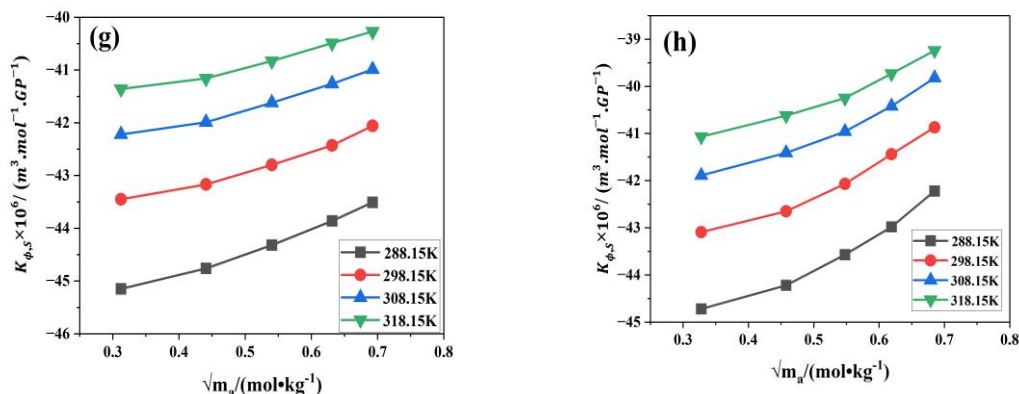


Figure 4.13 $K_{\phi,s}$ versus m_a (molality) plots for: (a)–(d)) sodium Bicarbonate and (e)–(h) sodium nitrate in H_2O and in aqueous magnesium salicylate at 0.01, 0.03, and 0.05 $mol \cdot kg^{-1}$.

Partial molar and transfer Isentropic Compressibility

In this study, $K_{\phi,s}^0$ was determined for sodium bicarbonate and sodium nitrate in aqueous magnesium salicylate solutions by extrapolating the $K_{\phi,s}$ versus $\sqrt{m}$ (m is molality) to infinite dilution, according to the Redlich–Mayer relation (**equation 4.10**). Here S_K^* is an empirical slope parameter that reflects solute–solute interactions at finite concentrations. The values presented in **table 4.18** (**figure 4.14**) of $K_{\phi,s}^0$, thus reflects the limiting compressibility of the solute in the solvent, under conditions where solute–solute interactions are minimal and solute–solvent interactions are the primary contributors. These values provide insight into the structural effects of magnesium salicylate on ion hydration and compressibility behaviour in the ternary system [80–83]. To further elucidate the effect of magnesium salicylate on the hydration and compressibility properties of the solutes, ΔK_{ϕ}^0 was computed using **equation 4.11**. The data in **Table 4.19** show that ΔK_{ϕ}^0 increases with magnesium salicylate concentration and temperature. Because these values are evaluated at infinite dilution, the observed variations reflect changes in solute–solvent interactions rather than solute–solute associations. The positive values suggest a weakening of the structured hydration layer around the ions in the presence of magnesium salicylate, leading to increased compressibility of the solvation shell.

Table 4.17: Values of ultrasonic velocity, c , and $K_{\phi,S}$ for salts in magnesium salicylate solutions at studied temperatures.

$m_a/(\text{mol.kg}^{-1})$	$c/ (m. s^{-1})$				$K_{\phi,S} \times 10^6 / (m^3 . mol^{-1} . GP^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
0.000 Magnesium Salicylate + sodium Bicarbonate								
0.00000	1466.59	1495.85	1519.14	1536.02				
0.10313	1475.78	1505.00	1526.73	1544.01	-45.16	-43.41	-42.19	-41.26
0.18524	1482.42	1512.09	1532.92	1549.76	-44.73	-42.99	-41.83	-40.94
0.30886	1493.35	1521.81	1542.69	1558.44	-43.86	-42.23	-41.11	-40.30
0.37932	1499.02	1526.91	1548.31	1563.69	-43.38	-41.82	-40.69	-39.91
0.45128	1505.67	1532.57	1553.10	1567.49	-42.85	-41.37	-40.30	-39.58
0.010 Magnesium Salicylate + sodium Bicarbonate								
0.00000	1468.56	1498.18	1521.74	1538.72				
0.09812	1476.94	1505.95	1528.34	1544.39	-45.08	-43.37	-42.11	-41.24
0.19832	1484.42	1513.39	1537.82	1552.29	-44.58	-42.91	-41.56	-40.80
0.31057	1495.52	1523.45	1545.50	1560.71	-43.72	-42.15	-40.97	-40.18
0.40525	1502.29	1531.13	1551.31	1565.42	-43.14	-41.55	-40.49	-39.78

0.48462	1509.34	1535.79	1556.15	1570.58	-42.57	-41.14	-40.10	-39.37

0.030 Magnesium Salicylate + sodium Bicarbonate

0.00000	1471.35	1500.62	1523.11	1539.34				

0.10720	1480.59	1509.15	1531.02	1546.79	-44.89	-43.21	-41.99	-41.14

0.20935	1490.29	1518.71	1539.19	1555.81	-44.24	-42.61	-41.49	-40.62

0.32264	1500.69	1528.12	1547.51	1562.55	-43.43	-41.90	-40.87	-40.09

0.40433	1507.12	1533.21	1553.29	1568.12	-42.90	-41.46	-40.41	-39.67

0.49791	1513.49	1539.23	1558.75	1572.50	-42.35	-40.96	-39.95	-39.28

0.050 Magnesium Salicylate + sodium Bicarbonate

0.00000	1474.93	1503.76	1526.04	1541.91				

0.10005	1483.79	1511.77	1533.20	1548.53	-44.69	-43.06	-41.86	-41.03

0.19593	1491.29	1520.12	1540.93	1555.59	-44.22	-42.56	-41.42	-40.65

0.28745	1499.99	1526.60	1546.92	1561.32	-43.55	-42.05	-40.96	-40.21

0.39562	1509.39	1535.78	1554.39	1568.43	-42.80	-41.35	-40.38	-39.66

0.50111	1518.08	1543.24	1562.30	1575.65	-42.10	-40.75	-39.77	-39.11

0.000 Magnesium Salicylate + sodium Nitrate

0.00000	1466.59	1495.85	1519.14	1533.02				
0.08743	1472.01	1501.16	1522.95	1536.96	-45.37	-43.64	-42.40	-41.64
0.18432	1476.04	1503.89	1526.15	1540.19	-45.15	-43.51	-42.26	-41.51
0.28217	1479.58	1507.55	1529.53	1544.03	-44.78	-43.15	-41.93	-41.17
0.39429	1483.32	1510.14	1532.89	1547.04	-44.32	-42.79	-41.55	-40.82
0.48416	1486.29	1513.63	1535.93	1550.46	-43.95	-42.42	-41.22	-40.49

0.010 Magnesium Salicylate + sodium Nitrate

0.00000	1468.56	1498.18	1521.74	1538.72				
0.09854	1472.97	1502.11	1524.47	1540.67	-45.35	-43.62	-42.35	-41.47
0.19983	1478.43	1506.65	1528.79	1544.76	-44.99	-43.34	-42.10	-41.25
0.29791	1483.92	1510.32	1532.23	1547.98	-44.49	-42.98	-41.77	-40.94
0.39821	1487.83	1514.59	1535.69	1550.99	-44.06	-42.55	-41.41	-40.61
0.47369	1491.04	1517.82	1538.20	1552.92	-43.71	-42.21	-41.13	-40.38

0.030 Magnesium Salicylate + sodium Nitrate

0.00000	1471.35	1500.62	1523.11	1539.34				
0.09759	1476.36	1504.98	1526.92	1542.73	-45.15	-43.45	-42.22	-41.36

0.19433	1482.39	1509.79	1530.98	1546.57	-44.76	-43.17	-41.99	-41.16
0.29186	1487.14	1513.65	1535.33	1550.23	-44.32	-42.80	-41.62	-40.83
0.39859	1491.29	1516.78	1538.43	1553.32	-43.86	-42.43	-41.26	-40.49
0.47945	1494.47	1520.77	1540.75	1555.09	-43.51	-42.06	-40.99	-40.27

0.050 Magnesium Salicylate + sodium Nitrate

0.00000	1474.93	1503.76	1526.04	1541.91				
0.10754	1479.879	1508.07	1530.2	1545.53	-44.96	-43.30	-42.06	-41.23
0.20945	1485.43	1512.78	1533.98	1549.51	-44.58	-42.99	-41.80	-40.99
0.30007	1490.99	1516.96	1537.92	1553.32	-44.10	-42.61	-41.44	-40.66
0.38329	1496.48	1521.54	1541.12	1556.77	-43.61	-42.21	-41.10	-40.35
0.46923	1501.08	1525.24	1544.3	1559.65	-43.18	-41.84	-40.75	-40.06

Standard uncertainties u is $u_r(m) = 0.01$, $u(T) = 0.01$ K, $u(p) = 0.01$ MPa, and $u(c) = 2.79$ m·s⁻¹.

This trend aligns with the co-sphere overlap model, where overlapping hydration spheres between solute and co-solute disrupt the tightly ordered water structure. At higher concentrations of magnesium salicylate, this disruption becomes more pronounced, contributing to an increase in ΔK_{ϕ}^0 . These findings reinforce the idea that magnesium salicylate acts as a structure-modifying co-solute, affecting the dynamic compressibility and hydration environment of the solute ions [84,85].

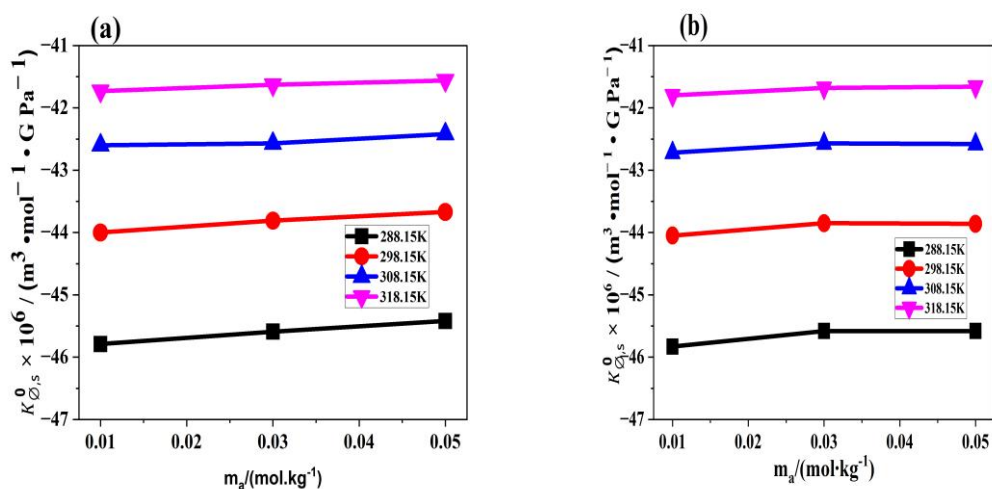


Figure 4.14 $K_{\phi,s}^0$ plotted against molality for (a) Sodium bicarbonate and (b) sodium nitrate in aqueous magnesium salicylate solutions at different temperatures.

Pair and triplet interaction coefficients

Friedman and Krishnan advanced the hypothesis proposed by McMillan and Mayer offering a framework to understand the transfer properties of solutes in aqueous magnesium salicylate solutions. **Table 4.20** displays the interaction coefficients. The **equations 4.12** and **4.13** were used to compute interaction coefficients of volume and compressibility. The coefficients for salts in aqueous magnesium salicylate solutions, reveal significant trends that illuminate the molecular interactions governing these multi-component systems. These coefficients, derived using the extended McMillan-Mayer approach, quantitatively separate the contributions from direct solute–solute (pair) and cooperative (triplet) interactions, enabling a nuanced interpretation of the volumetric and compressibility data.

Table 4.18 The coefficient $K_{\phi,S}^0$ and, S_K^* values of Salts in the aqueous magnesium salicylate.

$^a m_b (mol \cdot kg^{-1})$	$K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$S_K^* \times 10^6 / (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$			
$^l)$	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Bicarbonate								
0.000	-45.91(±0.06)	-44.05 (±0.03)	-42.80 (±0.04)	-41.80 (±0.04)	6.71 (±0.20)	5.89 (±0.10)	5.52 (±0.15)	4.92 (±0.14)
0.010	-45.79 (±0.07)	-44.00 (±0.06)	-42.60 (±0.03)	-41.73 (±0.09)	6.59 (±0.23)	5.94 (±0.20)	5.21 (±0.05)	4.86 (±0.09)
0.030	-45.59 (±0.06)	-43.81 (±0.03)	-42.57 (±0.02)	-41.63 (±0.03)	6.58 (±0.09)	5.79 (±0.11)	5.28 (±0.07)	4.79 (±0.08)
0.050	-45.42 (±0.06)	-43.67 (±0.04)	-42.42 (±0.04)	-41.56 (±0.04)	6.59 (±0.20)	5.81 (±0.12)	5.22 (±0.13)	4.83 (±0.14)
Sodium Nitrate								
0.000	-45.76 (±0.06)	-44.00 (±0.08)	-42.75 (±0.07)	-41.98 (±0.07)	3.66 (±0.19)	3.15 (±0.09)	3.06 (±0.23)	2.97 (±0.23)
0.010	-45.83 (±0.04)	-44.05 (±0.06)	-42.72 (±0.04)	-41.80 (±0.03)	4.44 (±0.12)	3.78 (±0.19)	3.29 (±0.14)	2.95 (±0.11)
0.030	-45.58 (±0.01)	-43.85 (±0.04)	-42.57 (±0.04)	-41.68 (±0.03)	4.31 (±0.04)	3.64 (±0.12)	3.27 (±0.09)	2.95 (±0.12)
0.050	-45.56 (±0.13)	-43.79 (±0.11)	-42.50 (±0.07)	-41.63 (±0.09)	5.02 (±0.40)	4.10 (±0.36)	3.66 (±0.24)	3.32 (±0.09)

standard uncertainties u is $u(K_{\phi,S}^0) = 0.32 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$, $u(T) = 0.001K$, $u(p) = 0.01MPa$, $u(S_K^*) = 0.3 \times 10^6 (kgm^3mol^{-2}GPa^{-1})$.

Table 4.19 Variation of $\Delta K_{\phi,S}^0$ for ternary systems of NaHCO_3 and NaNO_3 in aqueous magnesium salicylate systems at studied temperatures and concentrations at 0.1 MPa

$^a m_b (\text{mol}\cdot\text{kg}^{-1})$	$\Delta K_{\phi,S}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Bicarbonate				
0.010	0.12	0.05	0.20	0.07
0.030	0.32	0.23	0.23	0.17
0.050	0.49	0.37	0.38	0.24
Sodium Nitrate				
0.010	-0.06	-0.05	0.03	0.18
0.030	0.18	0.16	0.18	0.29
0.050	0.19	0.20	0.24	0.34

For magnesium salicylate + H_2O + sodium bicarbonate, the positive V_{AB} values across all studied temperatures indicate net expansion in partial molar volume upon the addition of sodium bicarbonate, suggesting that the solute–solute pair interactions tend to disrupt the water structure and weaken ion–solvent association. The magnitude of V_{ABB} varies considerably with temperature, showing large positive values at 288.15 K and a transition to strongly negative values at higher temperatures. This change implies a shift from cooperative volume-expanding interactions at low temperatures to compact, volume-contracting arrangements at elevated temperatures, likely due to enhanced ion–ion association and decreased hydration. The positive K_{AB} values suggest that sodium bicarbonate pair interactions increase the adiabatic compressibility of the system, consistent with a reduction in structural rigidity of the hydration shells. Conversely, the negative K_{ABB} values (except at 298.15 K) reflect triplet interactions that produce a more rigid and compact structure, counteracting the compressibility increase from pair interactions. For magnesium salicylate + water + sodium nitrate, V_{AB} decreases markedly with temperature, indicating that sodium nitrate pair

interactions favour compact packing and strong electrostatic association at higher temperatures. The V_{ABB} values are consistently negative (except at low temperature), signifying cooperative interactions that enhance structural compactness and reduce free volume. The K_{AB} trend is positive and increases sharply at 318.15 K, implying that elevated temperatures disrupt hydration layers around the ions, leading to a more compressible medium. The negative K_{ABB} values at higher temperatures support the interpretation that cooperative triplet interactions impose structural constraints, decreasing compressibility[72,86–89]. The observed temperature-dependent sign changes in V_{AB} , K_{AB} , V_{ABB} , K_{ABB} reflect significant changes in solute–solute and solute–solvent interactions with temperature. Such behaviour is consistent with known structural rearrangements and variations in hydration in mixed electrolyte systems. Although the terms “structure-making” and “structure-breaking” are commonly used to describe solute-induced changes in water structure, alternative factors such as speciation, ion pairing, and precipitation were also considered. The measured, and ultrasonic velocity values exhibited smooth, consistent trends with concentration and temperature. These observations indicate that the variations arise primarily from solute–solvent interactions rather than from ion pairing or speciation effects, supporting the validity of the “structure-making” interpretation.

Table 4.20 V_{AB} , K_{AB} , V_{ABB} , K_{ABB} of salts in aqueous Mg-salicylate solutions at different temperatures.

T/K	$V_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg)$	$V_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2)$	$K_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg GPa^{-1})$	$K_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2 GPa^{-1})$
Sodium Bicarbonate				
288.15	45.9465	221.1380	6.1763	-17.5384
298.15	94.5489	-521.8340	3.4668	4.1823
308.15	125.4634	-912.4948	6.4564	-37.9966
318.15	127.4459	-1004.0784	3.5952	-16.0304
Sodium Nitrate				
288.15	42.8765	-97.0580	1.7836	3.3574
298.15	30.0661	-69.2437	1.8673	-4.3827
308.15	21.4317	-22.4913	3.6531	-25.3488
318.15	13.6210	-91.2519	8.4022	-71.3647

Isobaric thermal expansion coefficient (α_p)

The calculation was performed using the **equation 4.14**. The values of α_p for sodium bicarbonate and sodium nitrate in aqueous magnesium salicylate mixes are reported in **Table 4.21**. For sodium bicarbonate, α_p increases with increasing concentration but decreases as temperature rises. This suggests that higher bicarbonate concentration leads to greater thermal expansivity, while increasing temperature reduces this effect, likely due to weakening hydration structures. In contrast, for sodium nitrate, α_p decreases with concentration but increases with temperature, reflecting differing ion-solvent interactions and hydration dynamics compared to bicarbonate. The decrease with concentration may indicate more compact ion hydration or clustering, while the increase with temperature corresponds to enhanced thermal motion and volume expansion. These opposing trends highlight the distinct influences of the two salts on the thermal volumetric behaviour of aqueous magnesium salicylate solutions [90,91].

Table 4.21 Isobaric thermal expansion coefficients of NaNO_3 and NaHCO_3 within aqueous Mg-salicylate media at various temperatures (0.1 MPa).

$m_b / (\text{mol} \cdot \text{kg}^{-1})$	$\alpha_p \times 10^3 / (K^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Sodium Bicarbonate				
0.010	13.66	10.52	8.73	6.99
0.030	15.95	10.98	6.72	2.99
0.050	14.90	10.08	5.44	1.09
Sodium Nitrate				
0.010	2.44	2.76	3.11	3.34
0.030	1.63	2.10	2.56	2.91
0.050	1.27	0.96	0.67	0.41

standard uncertainty $u(\alpha_p) = 0.032 \times 10^{-3} / (K^{-1})$, $u(T) = 0.001K$, $u(p) = 0.01\text{MPa}$.

Relative Association (R_a)

It reflects how the addition of a solute, such as a salt, influences the structural organization and interaction strength among the components of the solution. Higher R_a values typically indicate stronger or more extensive solute-solvent associations, often

resulting from enhanced hydrogen bonding, ion pairing, or other intermolecular forces. R_a has been calculated via following formula [92].

$$R_a = (\rho/\rho_0)(u_0/u)^{1/3} \quad (4.15)$$

The values of relative association (R_a) for aqueous magnesium salicylate solutions containing varying molality's of sodium bicarbonate and sodium nitrate are presented in **Table 4.22**. The data reveal that R_a increases with increasing salt molality at all studied temperatures for both salts. The R_a parameter reflects the degree of ion–solvent and ion–ion association in the system; values greater than unity indicate enhanced molecular association due to stronger solute–solvent interactions and possible aggregation effects. In aqueous electrolyte systems, such increases in R_a with concentration are often attributed to cooperative structuring of solvent molecules around solute ions [93,94].

Relaxation Strength (r_s)

This was evaluated by using the expression

$$r_s = 1 - \left(\frac{u}{u_\infty}\right)^2 \quad (4.16)$$

Here u refers ultrasonic velocity and u_∞ values is constant, i.e. $1600 \text{ m}\cdot\text{s}^{-1}$ [95]. The values of r_s are presented in **Table 4.22**. The relaxation strength data show a decreasing trend with rising molality of both sodium bicarbonate and sodium nitrate. This suggests that at higher ionic strengths, the solution becomes more structurally compact or less responsive to ultrasonic perturbation. In addition, r_s decreases with increasing temperature at constant molality, consistent with the thermal breakdown of hydration structures and weaker solute–solvent coupling. These trends are consistent with previous ultrasonic studies on electrolyte solutions, where relaxation strength diminishes when molecular organization is reduced by either thermal motion or high ionic strength [96–99].

Table 4.22 Variation of relative association (R_a) and relaxation strength (r_s) with molality for salts in magnesium salicylate solutions across the studied temperature range.

$m_a/(\text{mol}\cdot\text{kg}^{-1})$	Relaxation Strength (r_s)				Relative Association (R_a)			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
0.000 Magnesium Salicylate + sodium Bicarbonate								
0.00000	0.15981	0.12595	0.09852	0.07838	1.00000	1.00000	1.00000	1.00000
0.10313	0.14925	0.11522	0.08949	0.06876	1.00456	1.00489	1.00511	1.00477
0.18524	0.14157	0.10687	0.08209	0.06181	1.00796	1.00794	1.00848	1.00819
0.30886	0.12887	0.09535	0.07035	0.05128	1.01280	1.01312	1.01343	1.01320
0.37932	0.12224	0.08928	0.06357	0.04487	1.01546	1.01576	1.01586	1.01576
0.45128	0.11444	0.08251	0.05777	0.04022	1.01807	1.01832	1.01861	1.01878
0.010 Magnesium Salicylate + sodium Bicarbonate								
0.00000	0.15755	0.12323	0.09543	0.07513	1.00000	1.00000	1.00000	1.00000
0.09812	0.14791	0.11411	0.08757	0.06830	1.00451	1.00445	1.00462	1.00470
0.19832	0.13926	0.10533	0.07621	0.05875	1.00900	1.00882	1.00850	1.00888

0.31057	0.12634	0.09340	0.06696	0.04851	1.01310	1.01303	1.01313	1.01334
0.40525	0.11841	0.08423	0.05994	0.04276	1.01675	1.01654	1.01694	1.01731
0.48462	0.11011	0.07865	0.05406	0.03644	1.01949	1.01974	1.01998	1.02034

0.030 Magnesium Salicylate + sodium Bicarbonate

0.00000	0.15435	0.12037	0.09380	0.07439	1.00000	1.00000	1.00000	1.00000
0.10720	0.14369	0.11034	0.08437	0.06541	1.00454	1.00458	1.00463	1.00462
0.20935	0.13244	0.09903	0.07457	0.05447	1.00837	1.00844	1.00866	1.00843
0.32264	0.12028	0.08783	0.06454	0.04626	1.01246	1.01267	1.01305	1.01309
0.40433	0.11273	0.08174	0.05754	0.03945	1.01540	1.01592	1.01619	1.01620
0.49791	0.10521	0.07452	0.05090	0.03408	1.01888	1.01955	1.02004	1.02010

0.050 Magnesium Salicylate + sodium Bicarbonate

0.00000	0.15023	0.11668	0.09031	0.07129	1.00000	1.00000	1.00000	1.00000
0.10005	0.13999	0.10725	0.08176	0.06330	1.00400	1.00417	1.00432	1.00438
0.19593	0.13127	0.09736	0.07247	0.05474	1.00789	1.00785	1.00810	1.00827
0.28745	0.12111	0.08965	0.06525	0.04777	1.01110	1.01155	1.01186	1.01210
0.39562	0.11006	0.07866	0.05620	0.03907	1.01493	1.01542	1.01605	1.01639

0.50111	0.09978	0.06969	0.04657	0.03021	1.01853	1.01927	1.01989	1.02034

0.000 Magnesium Salicylate + sodium Nitrate

0.00000	0.15981	0.12595	0.09852	0.08197	1.00000	1.00000	1.00000	1.00000

0.08743	0.15359	0.11973	0.09399	0.07725	1.00408	1.00392	1.00413	1.00456

0.18432	0.14895	0.11653	0.09018	0.07337	1.00882	1.00879	1.00876	1.00901

0.28217	0.14486	0.11222	0.08615	0.06874	1.01342	1.01337	1.01333	1.01329

0.39429	0.14053	0.10917	0.08213	0.06510	1.01880	1.01892	1.01847	1.01836

0.48416	0.13709	0.10505	0.07848	0.06097	1.02311	1.02275	1.02231	1.02200

0.010 Magnesium Salicylate + sodium Nitrate

0.00000	0.15755	0.12323	0.09543	0.07513	0.00000	1.00000	1.00000	1.00000

0.09854	0.15248	0.11862	0.09218	0.07279	0.09854	1.00482	1.00479	1.00494

0.19983	0.14619	0.11328	0.08703	0.06786	0.19983	1.00936	1.00932	1.00940

0.29791	0.13984	0.10896	0.08292	0.06397	0.29791	1.01359	1.01377	1.01379

0.39821	0.13530	0.10391	0.07877	0.06032	0.39821	1.01823	1.01814	1.01821

0.47369	0.13156	0.10009	0.07576	0.05798	0.47369	1.02150	1.02151	1.02152

0.030 Magnesium Salicylate + sodium Nitrate

0.00000	0.15435	0.12037	0.09380	0.07439	0.00000	1.00000	1.00000	1.00000
0.09759	0.14858	0.11525	0.08926	0.07031	0.09759	1.00460	1.00458	1.00460
0.19433	0.14161	0.10958	0.08441	0.06567	0.19433	1.00872	1.00881	1.00890
0.29186	0.13610	0.10502	0.07920	0.06124	0.29186	1.01304	1.01321	1.01307
0.39859	0.13127	0.10132	0.07548	0.05750	0.39859	1.01787	1.01808	1.01785
0.47945	0.12756	0.09659	0.07269	0.05535	0.47945	1.02151	1.02130	1.02138

0.050 Magnesium Salicylate + sodium Nitrate

0.00000	0.15023	0.11668	0.09031	0.07129	0.00000	1.00000	1.00000	1.00000
0.10754	0.13999	0.10725	0.08176	0.06330	0.10754	1.00409	1.00419	1.00430
0.20945	0.13111	0.09895	0.07241	0.05362	0.20945	1.00799	1.00815	1.00854
0.30007	0.12111	0.08965	0.06525	0.04777	0.30007	1.01093	1.01121	1.01204
0.38329	0.11231	0.07895	0.05653	0.03866	0.38329	1.01363	1.01354	1.01534
0.46923	0.09978	0.06969	0.04657	0.03021	0.46923	1.01566	1.01620	1.01857

standard uncertainties u is $U_r(m) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$, $u(T) = 0.001 K$, $u(R_a) = 0.0013$ and $u(p) = 0.01$.

Specific Heat Ratio (γ)

This was calculated using the semi-empirical relation[100]:

$$\gamma = \frac{17.1}{T^{\frac{4}{9}}, \rho^{\frac{1}{3}}} \quad (4.17)$$

The calculated γ values in **table 4.23** for sodium nitrate and sodium bicarbonate in water and aqueous magnesium salicylate solutions show a systematic decrease with rising temperature at all studied concentrations. This trend can be attributed to the fact that, in liquids, the C_p increases more rapidly with temperature than the C_v , resulting in a lower $\gamma = C_p/C_v$. Additionally, increasing thermal agitation at higher temperatures weakens intermolecular cohesive forces, which reduces the efficiency of adiabatic sound propagation and further lowers γ . Small decreases in γ with rising solute concentration suggest that solute–solvent interactions, such as ion–dipole forces and modifications to the hydrogen-bond network of water, influence the compressibility and heat capacity of the mixture. Magnesium salicylate, due to its ionic and aromatic nature, can either enhance or disrupt solvent structuring depending on concentration, thereby affecting the thermodynamic response functions used in γ determination[100,101].

Hydration Number

The n_h for the studied liquid systems is determined using an equation as follows [102,103].

$$n_h = \frac{n_w}{n_s} \left[1 - \frac{k_s}{k_s^0} \right] \quad (4.18)$$

The n_h for sodium nitrate and sodium bicarbonate in aqueous magnesium salicylate indicate a downward trend with an increasing in temperature, which is placed in **Table 4.24**.

Table 4.23 Specific heat ratio values for NaHCO₃ and NaNO₃ in water and aqueous magnesium salicylate solutions.

$^a m_A /$ (mol·kg ⁻¹)	Specific Heat ratio (Y)				$^a m_A /$ (mol · kg ⁻¹)	Specific Heat ratio (Y)			
	288.15	298.15	308.15	318.15		288.15	298.15	308.15	318.15
0.000 Magnesium Salicylate + sodium Bicarbonate					0.000 Magnesium Salicylate + sodium Nitrate				
0.00000	1.38019	1.36043	1.34198	1.32470	0.00000	1.38019	1.36043	1.34198	1.32470
0.10313	1.37714	1.35730	1.33896	1.32184	0.08744	1.37776	1.35812	1.33976	1.32260
0.18524	1.37491	1.35522	1.33686	1.31980	0.18432	1.37518	1.35566	1.33740	1.32035
0.30886	1.37159	1.35194	1.33374	1.31680	0.28217	1.37273	1.35324	1.33506	1.31812
0.37932	1.36982	1.35026	1.33214	1.31520	0.39429	1.36992	1.35053	1.33248	1.31564
0.45128	1.36798	1.34858	1.33048	1.31355	0.48416	1.36769	1.34849	1.33052	1.31376
0.010 Magnesium Salicylate + sodium Bicarbonate					0.010 Magnesium Salicylate + sodium Nitrate				
0.00000	1.37980	1.35998	1.34154	1.32434	0.00000	1.37980	1.35998	1.34154	1.32434
0.09812	1.37686	1.35718	1.33884	1.32173	0.09854	1.37713	1.35742	1.33907	1.32200
0.19832	1.37404	1.35448	1.33620	1.31915	0.19983	1.37450	1.35493	1.33668	1.31964
0.31057	1.37105	1.35161	1.33342	1.31643	0.29791	1.37201	1.35258	1.33441	1.31744
0.40525	1.36872	1.34929	1.33120	1.31427	0.39821	1.36953	1.35021	1.33214	1.31523
0.48462	1.36678	1.34743	1.32942	1.31249	0.47369	1.36773	1.34841	1.33046	1.31370
0.030 Magnesium Salicylate + sodium Bicarbonate					0.030 Magnesium Salicylate + sodium Nitrate				
0.00000	1.37880	1.35901	1.34060	1.32342	0.00000	1.37880	1.35901	1.34060	1.32342
0.10720	1.37576	1.35608	1.33776	1.32068	0.09759	1.37617	1.35650	1.33818	1.32111

0.20935	1.37302	1.35340	1.33519	1.31816	0.19433	1.37367	1.35412	1.33588	1.31889
0.32264	1.37011	1.35059	1.33246	1.31551	0.29186	1.37123	1.35177	1.33362	1.31670
0.40433	1.36813	1.34864	1.33054	1.31364	0.39859	1.36863	1.34931	1.33123	1.31436
0.49791	1.36593	1.34646	1.32834	1.31156	0.47945	1.36668	1.34749	1.32948	1.31270
0.050 Magnesium Salicylate + sodium Bicarbonate					0.050 Magnesium Salicylate + sodium Nitrate				
0.00000	1.37786	1.35811	1.33973	1.32284	0.00000	1.37786	1.35811	1.33973	1.32284
0.10005	1.37512	1.35543	1.33711	1.32029	0.10754	1.37508	1.35542	1.33712	1.32031
0.19593	1.37258	1.35295	1.33469	1.31792	0.20945	1.37252	1.35295	1.33449	1.31800
0.28745	1.37024	1.35066	1.33246	1.31572	0.30007	1.37031	1.35081	1.33238	1.31600
0.39562	1.36756	1.34804	1.32991	1.31320	0.38329	1.36834	1.34890	1.33025	1.31421
0.50111	1.36508	1.34562	1.32750	1.31083	0.46923	1.36636	1.34697	1.32807	1.31243

standard uncertainties u is $U_r(m)=0.01 \text{ mol}\cdot\text{kg}^{-1}$, $u(T)=0.001\text{K}$, $u(Y)=0.006$.

Table 4.24 n_h of NaHCO₃ and NaNO₃ in H₂O and aqueous solutions of magnesium salicylate.

$m_a/(\text{mol.kg}^{-1})$	n_h				$m_a/(\text{mol.kg}^{-1})$	n_h			
	288.15	298.15	308.15	318.15		288.15	298.15	308.15	318.15
0.010 Magnesium Salicylate + sodium Bicarbonate					0.010 Magnesium Salicylate + sodium Nitrate				
0.10313	10.20529	9.71841	8.51874	8.59100	0.08744	8.00390	7.69116	6.30115	6.25157
0.18524	9.73086	9.31098	8.31575	8.15570	0.18432	7.07822	6.33926	5.81057	5.73450
0.30886	9.61072	8.88197	8.23931	7.86141	0.28217	6.56367	6.09818	5.65534	5.67465
0.37932	9.40533	8.60398	8.14739	7.77558	0.39429	6.21203	5.65048	5.43412	5.36017
0.45128	9.38156	8.45315	7.93815	7.48834	0.48416	6.02987	5.60374	5.34652	5.32354
0.010 Magnesium Salicylate + sodium Bicarbonate					0.010 Magnesium Salicylate + sodium Nitrate				
0.09812	9.97810	8.84176	7.87931	7.11807	0.09854	6.61846	6.10747	5.11473	4.40233
0.19832	9.37033	8.50291	8.66758	7.71992	0.19983	6.84889	6.16634	5.54325	5.09592
0.31057	9.65074	8.63787	8.18771	7.72641	0.29791	6.91311	5.96491	5.46175	5.09080
0.40525	9.21657	8.49075	7.82130	7.27962	0.39821	6.60266	5.92510	5.38216	5.01136
0.48462	9.15314	8.14027	7.58822	7.18069	0.47369	6.46757	5.90588	5.31749	4.88902
0.030 Magnesium Salicylate + sodium Bicarbonate					0.030 Magnesium Salicylate + sodium Nitrate				

0.10720	9.36536	8.71435	8.58659	7.78033	0.09759	7.08436	6.41937	5.89841	5.45853
0.20935	9.47825	9.03541	8.64620	8.26917	0.19433	7.37312	6.49678	5.90849	5.56470
0.32264	9.32132	8.77946	8.40646	7.68187	0.29186	7.07259	6.23424	5.92744	5.51007
0.40433	9.01916	8.35858	8.24027	7.54214	0.39859	6.68099	5.85408	5.60504	5.28967
0.49791	8.62901	8.04536	7.93877	7.15524	0.47945	6.49284	5.89317	5.43260	5.07124

0.050 Magnesium Salicylate + sodium Bicarbonate

0.050 Magnesium Salicylate + sodium Nitrate

0.10005	9.42575	8.69293	8.00221	7.91848	0.10754	9.24421	8.49406	7.80054	7.33681
0.19593	8.93126	8.79332	8.17899	8.06281	0.20945	8.84482	8.17567	8.15753	7.80170
0.28745	9.04806	8.39991	7.84413	7.80483	0.30007	9.06130	8.38042	7.91201	7.36307
0.39562	8.89025	8.35862	7.65514	7.65415	0.38329	9.05015	8.74793	8.13519	7.64315
0.50111	8.67626	8.08364	7.58757	7.56212	0.46923	9.41123	8.72434	8.35642	7.67262

Problem 3

Thermodynamic and Spectroscopic studies of aqueous magnesium salicylate in Potassium chloride and Sodium sulphate

In this problem we measured densities and ultrasonic velocity of KCl and Na₂SO₄ in aqueous magnesium salicylate at 0.000, 0.015, 0.025, and 0.035 $\text{mol} \cdot \text{kg}^{-1}$ concentrations. Additionally, FTIR spectroscopic analysis was performed for both binary and ternary systems to validate and support the molecular interaction interpretations derived from thermophysical measurements.

Density and Ultrasonic Velocity

The ρ and c values were experimentally determined in magnesium salicylate solutions with concentrations of (0.000, 0.015, 0.025, and 0.035) $\text{mol} \cdot \text{kg}^{-1}$ at $T = 288.15\text{--}318.15\text{K}$ in ternary mixtures. The data that were taken through experimentation of density and ultrasonic velocity are presented in **Table 4.25**. The results indicate that density and ultrasonic velocity increase as the molality of sodium sulphate/potassium chloride rises in the aqueous magnesium salicylate solution. This increase primarily results from the greater mass of the solution. Additionally, the rise in density and speed of sound suggests stronger solute-solvent interactions [48–50]. A comparison of these values with previously reported data [76] [79] [104] for (potassium chloride + water) is present in **Figures 4.15(a), (b)** and [105] [106] [107] for (sodium sulphate + water) is presented in **Fig. 4.16(a), (b)** respectively which shows experimentally obtained density and speed of sound values for potassium chloride + H₂O and sodium sulphate + H₂O at different temperatures align well with existing literatures.

Apparent molar volume (V_ϕ)

The ρ measurements were used to determine the V_ϕ by using equation 4.1 where M indicates molar mass of the salts, ρ_0 is the density of the solvent (aqueous magnesium salicylate), and ρ is the density of the ternary solution. The obtained V_ϕ values (**Table 4.26**) are positive and show an increasing trend with both temperature and salt molality. The variation of $(V_\phi - A_V\sqrt{m})$ with molality (**Figure 4.17**) exhibits a linear relationship, confirming the consistency of the experimental data.

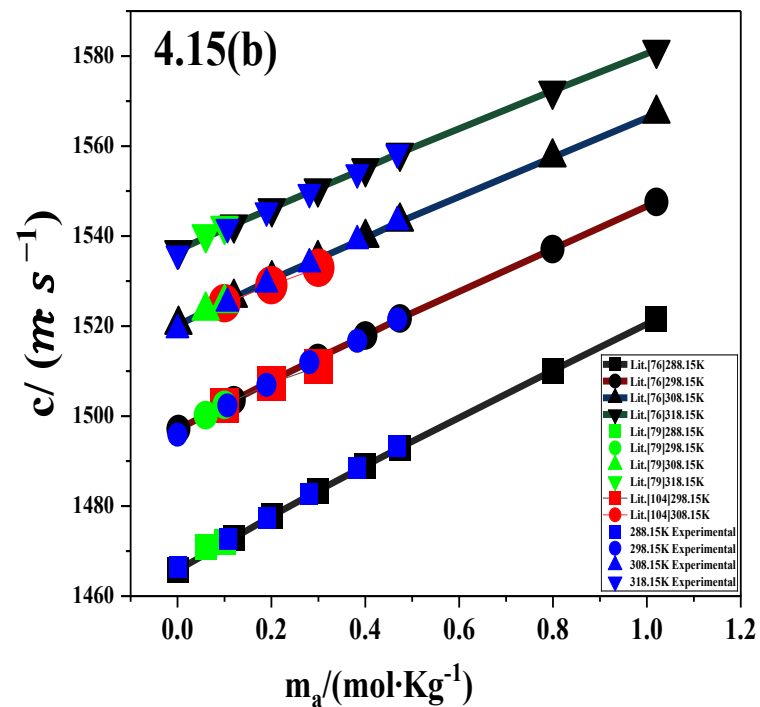
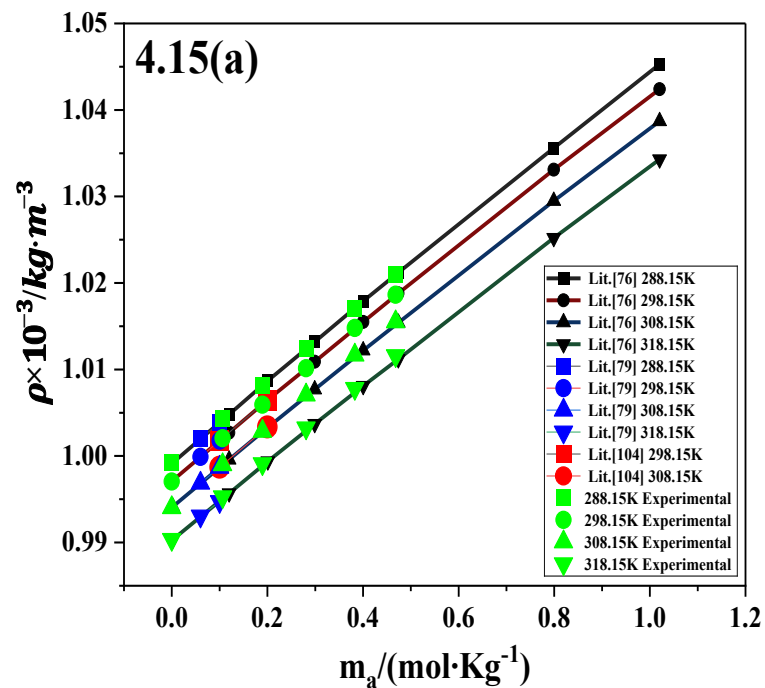


Figure 4.15: Comparison plots of density of Water + Potassium chloride and plots of ultrasonic velocity of Water + Potassium chloride presented in Fig. 4.15 (a) and Fig. 4.15 (b), respectively.

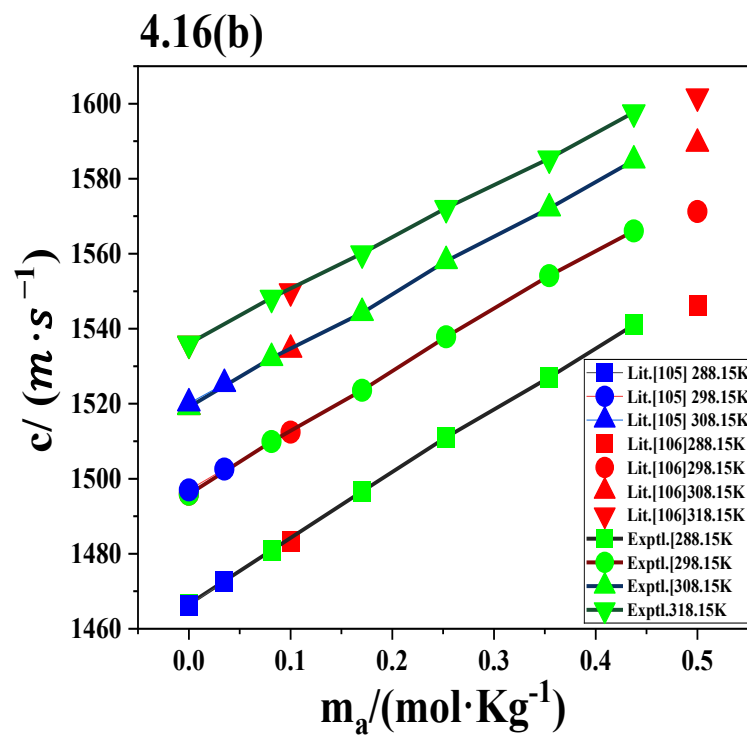
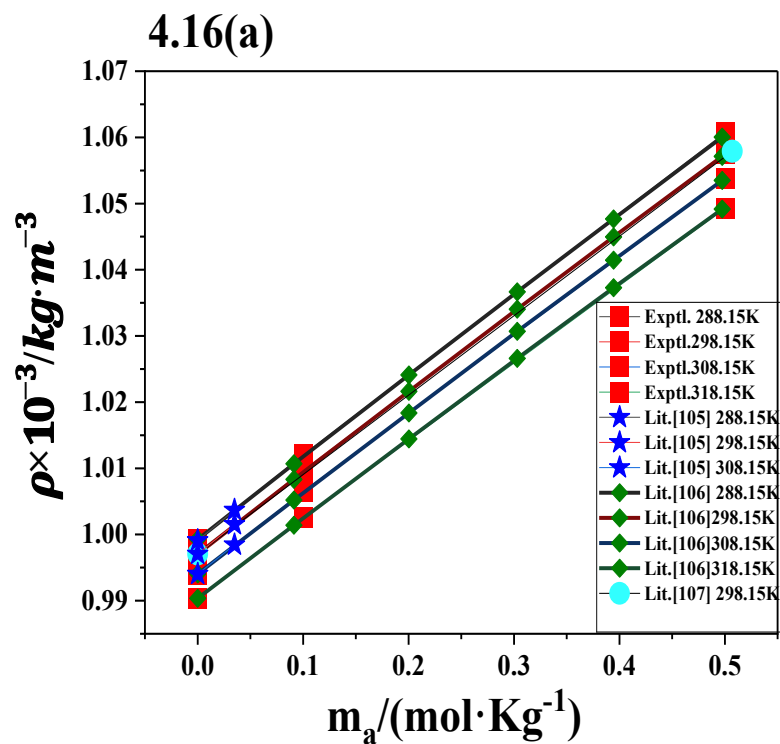


Figure 4.16 Comparison of density of a Water + Sodium sulphate and plots of ultrasonic velocity of a binary mixture (Water + Sodium sulphate) presented in Fig. 4.16 (a) and Fig. 4.16 (b) respectively.

Table 4.25: Experimental data of densities, ρ and ultrasonic velocity (c), data for magnesium salicylate with potassium chloride or sodium sulphate.

$^a m_A / (mol \cdot kg^{-1})$	$\rho \times 10^{-3} / (kg \cdot m^{-3})$				$u / (m \cdot s^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Potassium chloride + 0.00 $mol \cdot kg^{-1}$ Magnesium salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036	1466.59	1495.85	1519.14	1536.02
0.10621	1.00429	1.00205	0.99900	0.99528	1472.79	1502.36	1525.07	1541.95
0.18956	1.00820	1.00593	1.00285	0.99910	1477.49	1506.92	1529.29	1545.63
0.28101	1.01243	1.01014	1.00705	1.00325	1482.79	1511.96	1533.79	1549.73
0.38281	1.01710	1.01479	1.01167	1.00781	1488.45	1516.72	1538.93	1554.11
0.46818	1.02097	1.01864	1.01551	1.01159	1493.37	1521.51	1543.17	1558.56
Potassium chloride + 0.015 $mol \cdot kg^{-1}$ Magnesium salicylate								
0.00000	1.00075	0.99866	0.99551	0.99176	1469.06	1498.43	1521.86	1538.88
0.10183	1.005504	1.003356	1.000127	0.996324	1474.66	1503.78	1526.2	1542.43
0.20492	1.010218	1.008013	1.004719	1.000872	1479.98	1508.49	1530.19	1546.96
0.28066	1.013614	1.011384	1.008033	1.004164	1484.96	1513.22	1534.94	1550.72
0.37300	1.017696	1.01542	1.012023	1.008124	1490.92	1517.49	1539.32	1555.28

0.47551	1.022159	1.019854	1.016416	1.012457	1495.71	1523.05	1544.04	1559.27
Potassium chloride + 0.025 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate								
0.00000	1.00179	0.99967	0.99658	0.99278	1470.65	1500.05	1522.59	1539.08
0.08970	1.005892	1.003689	1.000578	0.996739	1475.65	1503.75	1526.19	1542.18
0.18879	1.010338	1.008065	1.004915	1.001038	1481.59	1508.5	1531.98	1546.6
0.27928	1.014332	1.011985	1.008772	1.004865	1487.38	1513.69	1536.79	1549.89
0.36800	1.018188	1.015786	1.012508	1.008531	1492.29	1518.69	1541.29	1554.43
0.47757	1.022843	1.020344	1.017073	1.012959	1497.56	1524.63	1545.37	1560.36
Potassium chloride + 0.035 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate								
0.00000	1.00284	1.00069	0.99760	0.99378	1472.08	1501.28	1523.72	1539.90
0.10009	1.007374	1.005171	1.002028	0.998173	1477.08	1505.28	1525.72	1542.9
0.19173	1.011448	1.009201	1.006008	1.002128	1482.79	1509.89	1530.99	1546.67
0.30271	1.016259	1.013952	1.010723	1.006794	1489.29	1515.59	1535.89	1551.59
0.38645	1.01979	1.017484	1.014226	1.010241	1494.59	1520.89	1540.89	1557.78
0.48488	1.02385	1.021521	1.018219	1.014162	1499.15	1526.03	1546.7	1561.64
Sodium sulphate+ 0.00 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate								

0	0.99926	0.99705	0.99404	0.99036	1466.59	1495.85	1519.14	1536.02
0.09136	1.01068	1.00834	1.00521	1.00141	1480.92	1509.9	1532.18	1548.23
0.20034	1.0241	1.02162	1.01837	1.01445	1496.62	1523.6	1544.23	1560.09
0.30305	1.03667	1.03405	1.03069	1.02662	1511.04	1537.84	1558.04	1572.17
0.39442	1.04769	1.04496	1.04146	1.03729	1527.02	1554.15	1572.09	1585.37
0.49751	1.06004	1.05713	1.05349	1.04918	1541.01	1566.07	1584.88	1597.67

Sodium sulphate + 0.015 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate

0.00000	1.00075	0.99866	0.99551	0.99176	1469.06	1498.43	1521.86	1538.88
0.09997	1.01325	1.011007	1.00771	1.003818	1486.4	1514.31	1535.54	1551.07
0.20691	1.026434	1.024051	1.020601	1.016538	1502.28	1529.29	1549.39	1564.89
0.29601	1.037315	1.034824	1.031188	1.027018	1516.77	1542.26	1561.39	1576.56
0.38319	1.047792	1.04521	1.041498	1.03713	1529.89	1555.29	1573.94	1587.77
0.50046	1.061806	1.059094	1.055084	1.050598	1549.4	1571.42	1589.27	1602.44

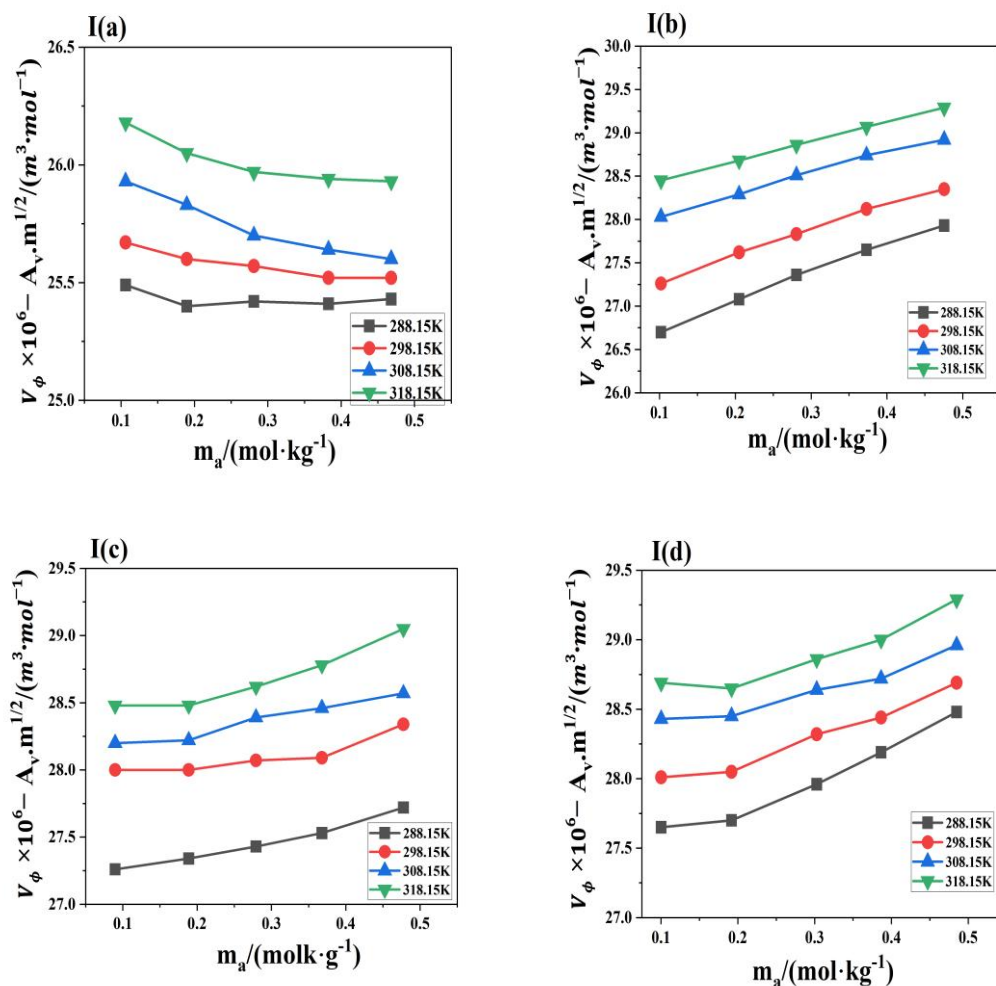
Sodium sulphate + 0.025 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate

0.00000	1.00179	0.99967	0.99658	0.99278	1470.65	1500.05	1522.59	1539.08
0.09920	1.014298	1.012017	1.008783	1.004838	1486.85	1515.18	1536.79	1552.38

0.19134	1.027495	1.025057	1.021674	1.017584	1501.29	1528.89	1548.89	1564.58
0.30942	1.038259	1.035812	1.032237	1.027986	1520.44	1546.55	1566.16	1580.03
0.38808	1.04878	1.046194	1.042517	1.038056	1532.29	1557.39	1576.67	1590.21
0.49405	1.062519	1.059964	1.056059	1.051521	1547.39	1571.71	1589.82	1602.26
Sodium sulphate + 0.035 mol · kg ⁻¹ Magnesium salicylate								
0.00000	1.00284	1.00069	0.99760	0.99378	1472.08	1501.28	1523.72	1539.90
0.09754	1.015333	1.01304	1.009793	1.005828	1488	1516.13	1538.56	1554.02
0.19305	1.028507	1.026082	1.022693	1.018563	1502.19	1530.58	1552.21	1566.39
0.30113	1.039289	1.03677	1.033245	1.028986	1520.26	1546.25	1566.78	1580.56
0.38539	1.049723	1.047115	1.043518	1.039048	1533.34	1558.95	1577.81	1591.59
0.48787	1.063605	1.060872	1.057081	1.052491	1547.61	1571.75	1590.75	1603.11

For ternary mixes, aqueous magnesium salicylate (0.015, 0.025, and 0.035 mol·kg⁻¹) solutions were used as solvents, and the added salts molality (m_a) was computed using 1 kg of the respective magnesium salicylate solution. The standard uncertainties are $u(\rho) = 0.00133 \text{ g}\cdot\text{cm}^{-3}$, $u(c) = 2.32 \text{ m}\cdot\text{s}^{-1}$, $u(p)=0.01 \text{ MPa}$ and $u(T) = 0.01 \text{ K}$.

The increase in V_ϕ with solute concentration is primarily governed by solute–solute (ion–ion) interactions, which intensify as ions approach each other at higher molality. These stronger ion–ion interactions disturb the hydration shells that surround individual ions in dilute solutions. The resulting disruption leads to a less compact water structure and expansion of the solution volume. Consequently, solute–solvent interactions weaken, while the overall volumetric contribution from solute–solute interactions become dominant. The observed rise in V_ϕ thus reflects the systematic increase in ion–ion interactions and the associated loosening of the hydration network in the magnesium salicylate + sodium sulphate/potassium chloride + water systems [54–57,108].



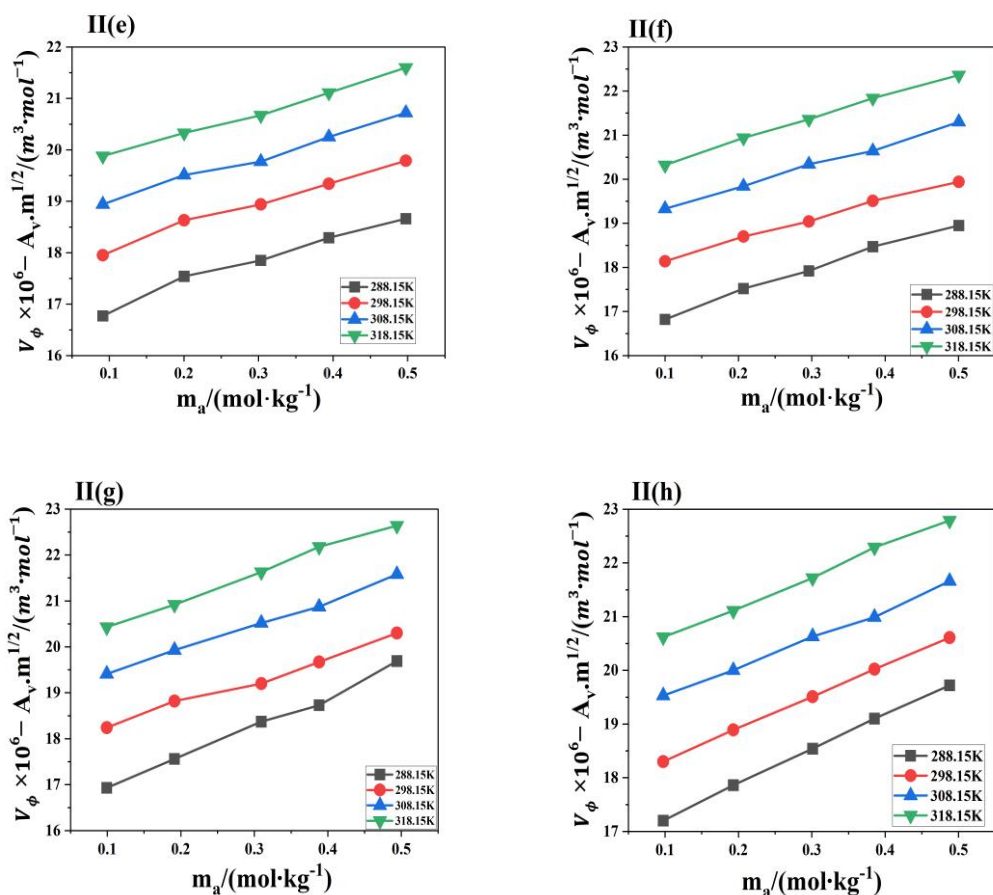


Figure 4.17. Plots of V_ϕ (I) Potassium chloride and (II) Sodium sulphate from water to an aqueous magnesium salicylate solution (a)(e) 0.00000 magnesium salicylate, (b)(f) 0.015 magnesium salicylate, (c) (g) 0.025 magnesium salicylate, and (d) (e) 0.035 magnesium salicylate ($\text{mol} \cdot \text{kg}^{-1}$).

Partial molar volume (V_ϕ^0)

Partial molar volumes at infinite dilution (V_ϕ^0) were obtained by extrapolating the experimental V_ϕ versus molality data to zero concentration using the Redlich–Meyer equation 4.2. The Debye–Hückel limiting slope (A_v) values for sodium sulphate (2:1 electrolyte) and potassium chloride (1:1 electrolyte) at the investigated temperatures were obtained from literature sources [58,59,108]. The parameter S_v , derived experimentally, accounts for deviations from ideal behaviour at higher concentrations and represents specific ion–ion interactions [60,61]. The derived V_ϕ^0 values (Table 4.27 graphically plotted in figure 4.18) reflect the strength of solute–solvent interactions, since at infinite dilution the solute particles are well separated and do not interact

significantly with each other. The magnitude of V_ϕ^0 increases with temperature for both sodium sulphate and potassium chloride systems, indicating a reduction in ion–solvent electrostriction and partial dehydration of ions at elevated temperatures. This behaviour suggests that the structural ordering of water around the ions weakens with heating, leading to an expansion of the solvent structure and an increase in V_ϕ^0 . The S_V parameter provides insight into solute–solute (ion–ion) interactions at finite concentrations. Positive S_V values observed in these systems imply structure-making behaviour and dominance of ion–ion attractions, whereas negative or near-zero values would suggest structure-breaking tendencies. The positive sign and magnitude of S_V thus confirm that, as the salt concentration increases, ion–ion associations become significant and contribute to the volumetric expansion of the ternary system [62–64].

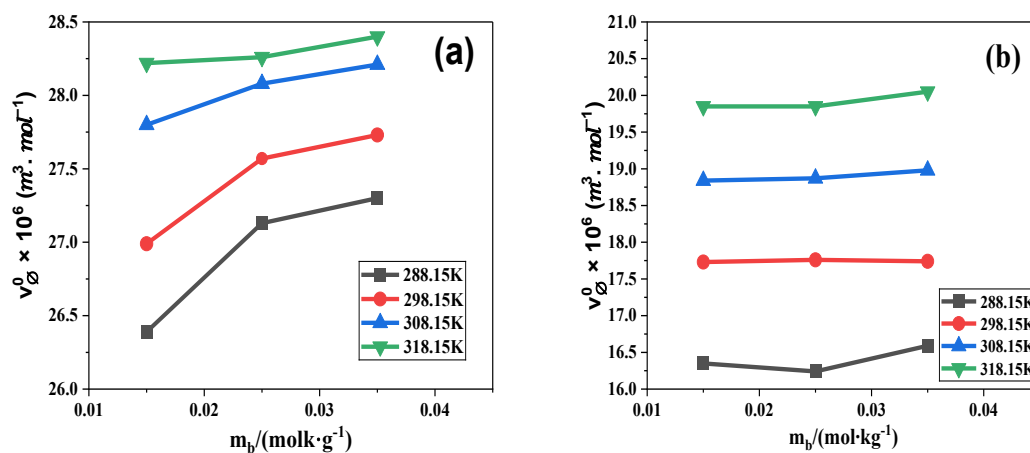


Figure 4.18 V_ϕ^0 , for Potassium chloride (a) and sodium sulphate (b) within a magnesium salicylate aqueous solution at various temperatures.

Table 4.26: V_ϕ and $K_{\phi,S}$ for magnesium salicylate with potassium chloride/sodium sulphate solutions.

$^a m_A / (mol \cdot kg^{-1})$	$V_\phi \times 10^6 / (m^3 \cdot mol^{-1})$				$\kappa_{\phi,S} \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Potassium chloride + 0.00 $mol \cdot kg^{-1}$ Magnesium salicylate								
0.10621	25.49	25.67	25.93	26.18	-45.43	-43.66	-42.37	-41.44
0.18956	25.40	25.60	25.83	26.05	-45.16	-43.41	-42.15	-41.26
0.28101	25.42	25.57	25.70	25.97	-44.72	-43.02	-41.80	-40.95
0.38281	25.41	25.52	25.64	25.94	-44.22	-42.59	-41.37	-40.57
0.46818	25.43	25.52	25.60	25.93	-43.79	-42.19	-41.01	-40.21
Potassium chloride + 0.015 $mol \cdot kg^{-1}$ Magnesium salicylate								
0.10183	26.70	27.26	28.03	28.45	-45.31	-43.58	-42.31	-41.42
0.20492	27.08	27.62	28.29	28.68	-45.00	-43.32	-42.10	-41.20
0.28066	27.36	27.83	28.51	28.86	-44.61	-42.96	-41.76	-40.92
0.37300	27.65	28.12	28.74	29.07	-44.11	-42.59	-41.40	-40.55
0.47551	27.93	28.35	28.92	29.29	-43.67	-42.12	-40.99	-40.20
Potassium chloride + 0.025 $mol \cdot kg^{-1}$ Magnesium salicylate								
0.08970	27.26	28.00	28.20	28.48	-45.22	-43.55	-42.28	-41.40
0.18879	27.34	28.00	28.22	28.48	-44.93	-43.34	-42.02	-41.23
0.27928	27.43	28.07	28.39	28.62	-44.48	-42.95	-41.67	-40.98

0.36800	27.53	28.09	28.46	28.78	-44.06	-42.55	-41.31	-40.62
0.47757	27.72	28.34	28.57	29.05	-43.58	-42.06	-40.94	-40.16
Potassium chloride + 0.035 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate								
0.10009	27.65	28.01	28.43	28.69	-45.17	-43.44	-42.29	-41.35
0.19173	27.70	28.05	28.45	28.65	-44.86	-43.26	-42.08	-41.23
0.30271	27.96	28.32	28.64	28.86	-44.34	-42.81	-41.69	-40.85
0.38645	28.19	28.44	28.72	29.00	-43.90	-42.40	-41.31	-40.42
0.48488	28.48	28.69	28.96	29.29	-43.49	-41.97	-40.86	-40.09
Sodium sulphate+ 0.00 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate								
0.09136	16.77	17.95	18.94	19.88	-44.57	-42.88	-41.64	-40.79
0.20034	17.54	18.63	19.51	20.33	-43.33	-41.82	-40.71	-39.90
0.30305	17.85	18.94	19.77	20.67	-42.06	-40.62	-39.59	-38.89
0.39442	18.29	19.34	20.25	21.11	-40.79	-39.39	-38.51	-37.88
0.49751	18.66	19.79	20.72	21.60	-39.60	-38.37	-37.48	-36.89
Sodium sulphate+ 0.015 $\text{mol} \cdot \text{kg}^{-1}$ Magnesium salicylate								
0.09997	16.82	18.14	19.33	20.32	-44.13	-42.59	-41.42	-40.60
0.20691	17.52	18.70	19.84	20.94	-42.91	-41.48	-40.41	-39.63
0.29601	17.92	19.04	20.34	21.36	-41.72	-40.43	-39.46	-38.71

0.38319	18.47	19.51	20.64	21.84	-40.63	-39.39	-38.47	-37.82
0.50046	18.95	19.94	21.30	22.36	-39.11	-38.10	-37.27	-36.68
Sodium sulphate+ 0.025 mol · kg ⁻¹ Magnesium salicylate								
0.09920	16.93	18.24	19.41	20.43	-44.21	-42.58	-41.39	-40.57
0.19134	17.56	18.82	19.93	20.92	-43.02	-41.49	-40.43	-39.63
0.30942	18.37	19.20	20.52	21.63	-41.59	-40.21	-39.22	-38.55
0.38808	18.73	19.67	20.87	22.18	-40.56	-39.28	-38.34	-37.71
0.49405	19.69	20.30	21.58	22.64	-39.28	-38.09	-37.25	-36.69
Sodium sulphate+ 0.035 mol · kg ⁻¹ Magnesium salicylate								
0.09754	17.20	18.30	19.53	20.62	-44.14	-42.52	-41.29	-40.47
0.19305	17.86	18.89	20.00	21.11	-42.97	-41.40	-40.26	-39.54
0.30113	18.54	19.51	20.63	21.72	-41.60	-40.22	-39.19	-38.52
0.38539	19.10	20.02	20.99	22.29	-40.51	-39.21	-38.29	-37.65
0.48787	19.72	20.61	21.66	22.79	-39.27	-38.09	-37.21	-36.65

The standard uncertainties are $u(V_\phi) = 0.32 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, $u(K_{\phi,S}) = 0.16 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1}$, $u(p) = 0.01 \text{ MPa}$, and $u(T) = 0.01 \text{ K}$.

Table 4.27: V_ϕ^0 values along with experimental slope (S_V^*) for magnesium salicylate with potassium chloride/sodium sulphate.

$^a m_B / (mol \cdot kg^{-1})$	$V_\phi^0 \times 10^6 (m^3 \cdot mol^{-1})$				$S_V^* \times 10^6 (m^3 \cdot kg \cdot mol^{-2})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Potassium chloride								
0.000	25.47(± 0.03)	25.69(± 0.02)	26.00(± 0.03)	26.21(± 0.04)	-0.13(± 0.12)	-0.41(± 0.07)	-0.93(± 0.11)	-0.67(± 0.15)
0.015	26.39(± 0.03)	26.99(± 0.03)	27.80(± 0.03)	28.22(± 0.01)	3.31(± 0.12)	2.93(± 0.12)	2.43(± 0.12)	2.28(± 0.02)
0.025	27.13(± 0.03)	27.57(± 0.08)	28.08(± 0.03)	28.26(± 0.09)	1.16(± 0.10)	0.82(± 0.25)	1.03(± 0.12)	1.52(± 0.29)
0.035	27.30(± 0.01)	27.73(± 0.08)	28.21(± 0.07)	28.40(± 0.12)	2.38(± 0.33)	1.93(± 0.26)	1.47(± 0.24)	1.71(± 0.38)
Sodium sulphate								
0.000	16.48(± 0.12)	17.63(± 0.09)	18.57(± 0.07)	19.48(± 0.05)	4.52(± 0.37)	4.38(± 0.27)	4.26(± 0.23)	4.18(± 0.15)
0.015	16.35(± 0.08)	17.73(± 0.05)	18.84(± 0.05)	19.85(± 0.04)	5.34(± 0.25)	4.51(± 0.17)	4.86(± 0.17)	5.10(± 0.14)
0.025	16.24(± 0.10)	17.76(± 0.09)	18.87(± 0.06)	19.85(± 0.06)	6.79(± 0.33)	5.02(± 0.30)	5.36(± 0.19)	5.76(± 0.20)
0.035	16.59(± 0.02)	17.74(± 0.01)	18.98(± 0.05)	20.05(± 0.04)	6.46(± 0.07)	5.89(± 0.04)	5.39(± 0.16)	5.67(± 0.14)

The standard uncertainties are $u(V_\phi^0) = \pm 0.01 \times 10^{-6} m^3 \cdot mol^{-1}$, $u(S_V^*) = 1.47 \times 10^{-6} m^3 \cdot kg \cdot mol^{-2}$, $u(T) = 0.01K$.

Partial molar volume of transfer

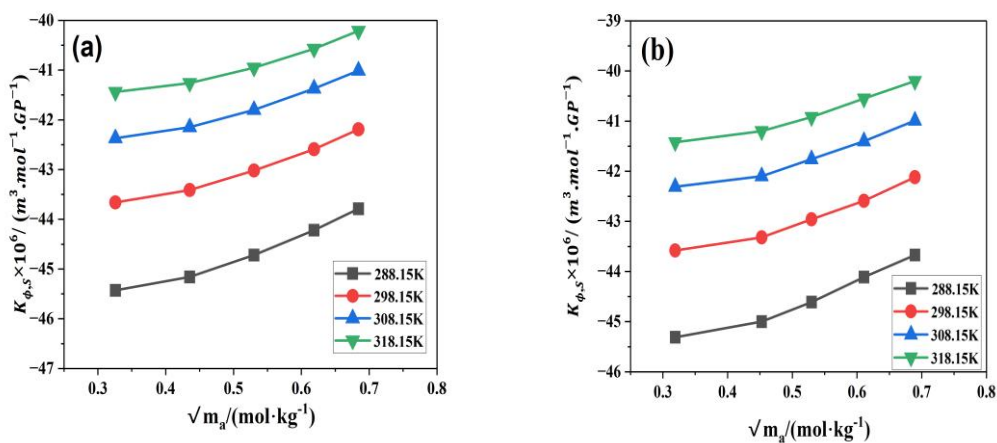
Equation 4.3 was used for ΔV_{ϕ}^0 . The calculated ΔV_{ϕ}^0 values (Table 4.28) are positive for potassium chloride and increase with temperature, indicating weakening ion–solvent interactions and partial dehydration of ions due to reduced electrostriction in the mixed solvent. In contrast, sodium sulphate exhibits slightly negative ΔV_{ϕ}^0 values at lower temperatures that become positive at higher temperatures, suggesting a transition from strong ion–solvent to dominant ion–ion interactions with heating. A slight non-monotonic concentration dependence is observed at 288.15 K and 298.15 K. However, the magnitude of these variations is smaller than the estimated standard uncertainty of the calculated transfer partial molar volume values and therefore does not represent a statistically significant deviation from the overall trend. These results confirm that the transfer of electrolytes from water to aqueous magnesium salicylate reduces the structural ordering of water and enhances ion–ion associations in the ternary system. The findings suggest that ion–hydrophilic interactions dominate in mixed electrolyte systems, and magnesium salicylate acts as a structure-making co- solute, promoting greater hydration and solvent ordering similar to other pharmaceutical electrolytes [65–69,109].

Table 4.28: Calculated values of ΔV_{ϕ}^0 for magnesium salicylate with potassium chloride/sodium sulphate at 0.1 MPa.

$^a m_b / (mol \cdot kg^{-1})$	$\Delta V_{\phi}^0 \times 10^6 (m^3 \cdot mol^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Potassium chloride				
0.015	0.93	1.30	1.80	2.01
0.025	1.66	2.18	2.08	2.05
0.035	1.83	2.04	2.20	2.19
Sodium Sulphate				
0.015	-0.13	0.10	0.27	0.37
0.025	-0.23	0.13	0.30	0.38
0.035	0.12	0.11	0.41	0.57

Apparent molar isentropic compressibility (K_S)

The k_s of each solution was determined from the experimentally measured ultrasonic velocity and density values using 4.9. To gain further insight into solute–solvent and solute–solute interactions, the $K_{(\phi,s)}$ was calculated using equation 4.8. The computed $K_{(\phi,s)}$ values (Table 4.26 graphically plotted in figure 4.19) are negative for both potassium chloride and sodium sulphate systems but become progressively less negative with increasing concentration and temperature. This trend indicates a decrease in the compressibility of the medium, suggesting the formation of a more compact and ordered structure due to enhanced ion–solvent and ion–ion interactions [76]. The reduction in compressibility reflects the structure-making tendency of both salts in the aqueous magnesium salicylate medium. The gradual increase in $K_{(\phi,s)}$ with temperature further confirms the weakening of electrostrictive effects and rearrangement of hydration shells around ions, resulting in a denser and less compressible ternary system [76–79].



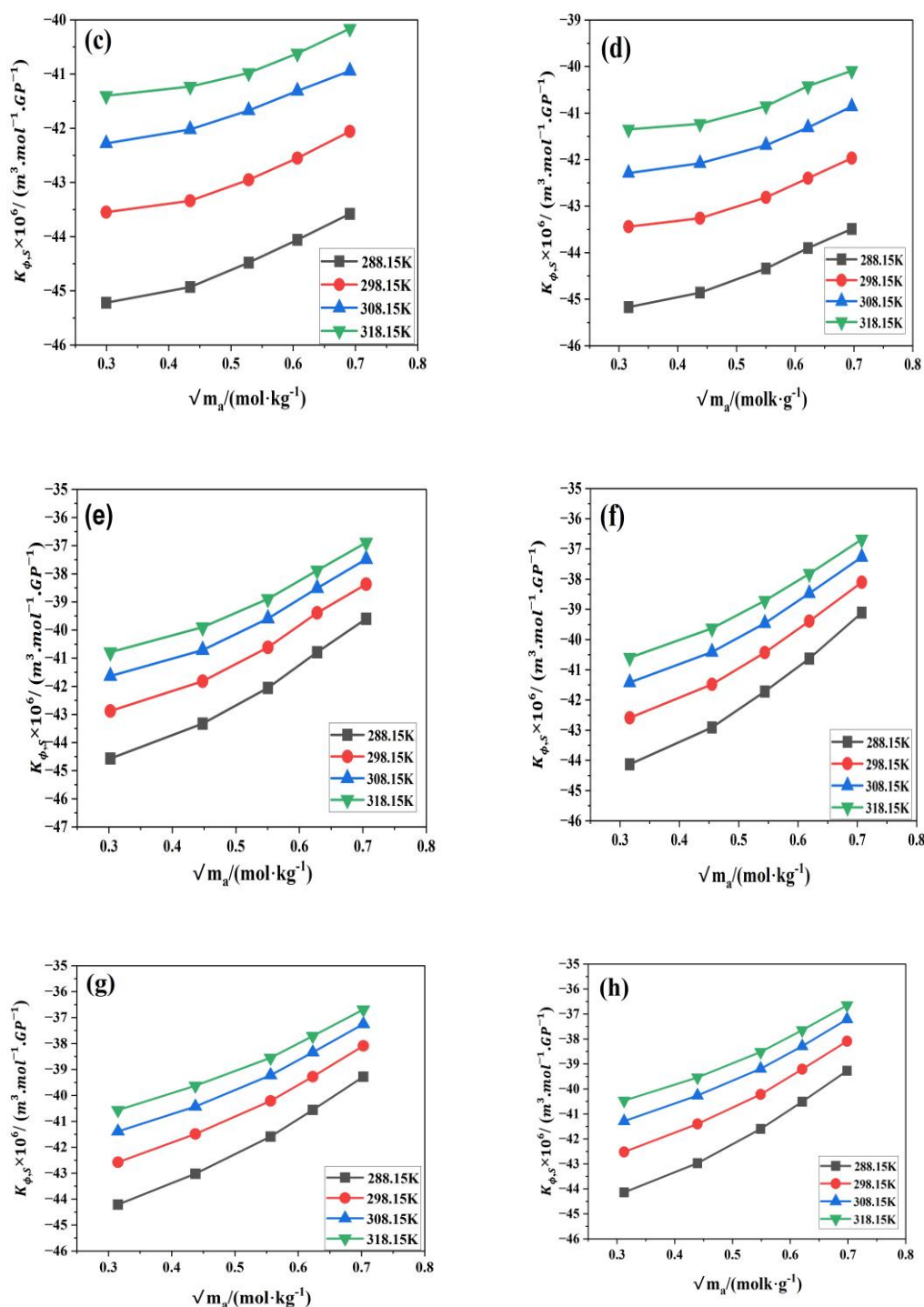


Figure 4.19 Plots of $K_{(\phi,s)}$ (a) Potassium chloride + water, (e) Sodium sulphate + water, (b), (c), (d), (f), (g), (h) Potassium chloride and sodium sulphate in aqueous magnesium salicylate solution at 0.015, 0.025, 0.035 magnesium salicylate ($mol \cdot kg^{-1}$) respectively.

Partial molar and transfer isentropic compressibility

The $K_{(\phi,s)}^0$ was obtained by extrapolating the $K_{(\phi,s)}$ versus $\sqrt{m_A}$ to infinite dilution using the 4.10. Here S_K^* is an empirical slope parameter that reflects solute–solute interactions at finite concentrations. The extrapolated $K_{(\phi,s)}^0$ values (Table 4.29, graphically plotted in figure 4.20) are negative for both potassium chloride and sodium sulphate systems and become progressively less negative with increasing temperature, indicating a decrease in compressibility of the medium. This behaviour suggests stronger ion–solvent and ion–ion interactions at higher temperatures, leading to a more compact and less compressible solvation structure. The positive empirical slope parameter (S_K^*) decreases with temperature for both salts, implying that the magnitude of solute–solute interactions diminish upon heating[80–83]. To further elucidate the effect of magnesium salicylate on the hydration and compressibility properties of the solutes, ΔK_{ϕ}^0 was computed by equation 4.11. The $\Delta K_{(\phi,s)}^0$ values (Table 4.30) are generally small and positive at lower temperatures for both salts, indicating slightly higher compressibility of the solvation shells in the presence of magnesium salicylate due to partial disruption of the hydration network. With increasing temperature, $\Delta K_{(\phi,s)}^0$ decreases and, for potassium chloride, becomes slightly negative at higher concentrations, reflecting increased structural compactness and reduced compressibility. Sodium sulphate maintains positive $\Delta K_{(\phi,s)}^0$ values across all temperatures, consistent with stronger hydration of the divalent sulphate ion. Overall, the less negative $K_{(\phi,s)}^0$ values and the small positive $\Delta K_{(\phi,s)}^0$ values confirm that magnesium salicylate acts as a structure-modifying cosolute, influencing the hydration and compressibility behaviour of the ternary systems through subtle ion–solvent and ion–ion interaction effects [84,85].

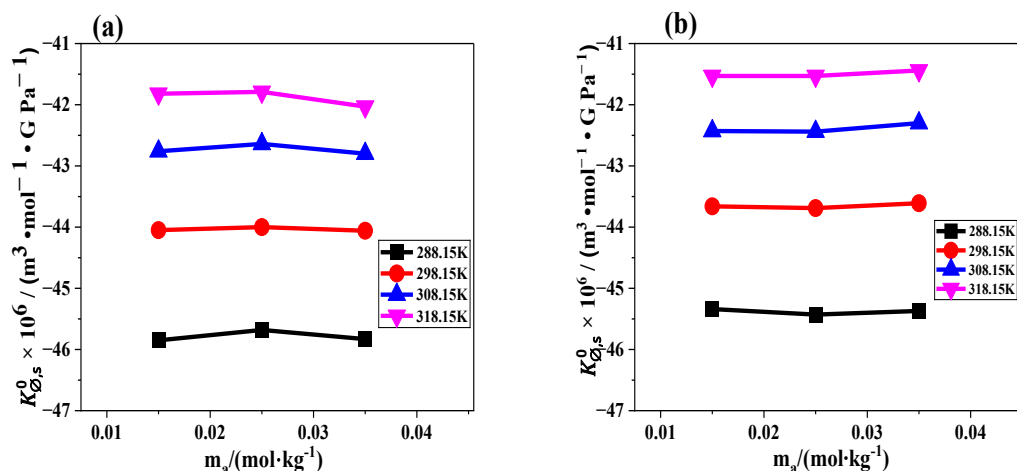


Figure 4.20 Plots of $K_{\phi,s}^0$ (a) Potassium chloride and (b) Sodium sulphate in aqueous solutions of magnesium salicylate.

Temperature dependent partial molar volume

The experimental V_{ϕ}^0 data were fitted to equation 4.4 where $T_{ref} = 298.15\text{K}$. The a, b, c, describing the temperature dependence of V_{ϕ}^0 for both solutes, are listed in **Table 4.31**. The fit quality was assessed by evaluating the relative deviation (σ) among experimental and calculated V_{ϕ}^0 values, with very low deviations and high R^2 values confirming the reliability of the polynomial model equation 4.5. Taking $Y = V_{\phi}^0$, the polynomial regression yielded very small deviations, with R^2 values indicating that the model effectively describes the relationship[71]. The objective of evaluating the V_{ϕ}^0 data is to evaluate the expansibilities, which are determined by the equation (4.6) [70,72]. At infinite dilution, the E_{ϕ}^0 provides valuable insights into the interaction dynamics among solute and solvent molecules. The ability of a solute to induce structural organization or disintegration within a solution medium can be assessed through a corresponding thermodynamic expression given in equation 4.7. The calculated E_{ϕ}^0 values for magnesium salicylate with both potassium chloride and sodium sulphate are summarized in **Table 4.32**. The values of E_{ϕ}^0 and $(\partial E_{\phi}^0 / \partial T)_p$ provide critical insight into solute–solvent interactions. Positive or slightly negative values of $(\partial E_{\phi}^0 / \partial T)_p$ reflect structure-making (order-promoting) effects, whereas strongly negative values imply structure-breaking tendencies. As in **Table 4.32**, the

calculated E_{ϕ}^0 and $(\partial E_{\phi}^0 / \partial T)_P$ values for magnesium salicylate in the presence of both potassium chloride and sodium sulphate indicate predominantly structure-making behaviour, evidencing strong solute–solvent interactions that tend to enhance solvent organization with increasing temperature [73,74].

Table 4.29: Values for $K_{\phi,S}^0$ and, S_K^* of potassium chloride and sodium sulphate in the aqueous magnesium salicylate.

^a m_b (mol·kg ⁻¹)	$K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$S_K^* \times 10^6 / (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Potassium chloride								
0.000	-45.98(±0.05)	-44.15(±0.05)	-42.83(±0.05)	-41.87(±0.06)	4.61(±0.18)	4.11(±0.16)	3.82(±0.18)	3.45(±0.20)
0.015	-45.85(±0.07)	-44.05(±0.07)	-42.76(±0.08)	-41.82(±0.06)	4.56(±0.24)	3.97(±0.24)	3.64(±0.26)	3.36(±0.20)
0.025	-45.68(±0.60)	-44.00(±0.09)	-42.64(±0.04)	-41.79(±0.09)	4.36(±0.19)	3.96(±0.29)	3.54(±0.14)	3.24(±0.31)
0.035	-45.83(±0.08)	-44.06(±0.09)	-42.80(±0.09)	-42.03(±0.08)	3.79(±0.26)	3.27(±0.29)	3.17(±0.27)	3.09(±0.26)
Sodium Sulphate								
0.000	-45.76(±08)	-44.00(±0.11)	-42.70(±0.10)	-41.76(±0.09)	12.39(±0.24)	11.37(±0.35)	10.46(±0.31)	9.73(±0.27)
0.015	-45.34(±0.13)	-43.66(±0.09)	-42.43(±10)	-41.53(±0.09)	12.23(±0.40)	10.99(±0.29)	10.17(±0.32)	9.58(±0.27)
0.025	-45.43(±0.02)	-43.69(±0.02)	-42.44(±0.02)	-41.53(±0.03)	12.47(±0.08)	11.33(±0.08)	10.51(±0.06)	9.80(±0.10)
0.035	-45.37(±0.02)	-43.61(±0.03)	-42.30(±0.02)	-41.44(±0.02)	12.53(±0.07)	11.34(±0.09)	10.42(±0.07)	9.80(±0.06)

standard uncertainties u is $u(K_{\phi,S}^0) = 0.31 \times 10^{-6} m^3 \cdot mol^{-1} \cdot GPa^{-1}$, $u(S_K^*) = 0.50 \times 10^{-6} kg^{-1} \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1}$, $u(T) = 0.01$ K, and $u(p) = 0.01$ MPa.

Table 4.30: Values for $K_{\phi,S}^0$ and, S_K^* of potassium chloride and sodium sulphate in the aqueous magnesium salicylate at varying temperatures and 0.1 MPa.

^a m_b (mol·kg ⁻¹)	$\Delta K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Potassium chloride				
0.015	0.13	0.09	0.07	0.05
0.025	0.31	0.15	0.19	0.08
0.035	0.15	0.09	0.03	-0.16
Sodium Sulphate				
0.015	0.42	0.33	0.26	0.23
0.025	0.33	0.31	0.25	0.23
0.035	0.39	0.38	0.39	0.32

standard uncertainties are $u(\Delta K_{\phi,S}^0) = 0.08 \times 10^{-6} m^3 \cdot mol^{-1} \cdot GPa^{-1}$, $u(T) = 0.01K$, $u(p) = 0.01MPa$.

Pair and triplet interaction coefficient

Friedman and Krishnan extended the McMillan–Mayer theory offering a framework to understand the transfer properties of solutes in aqueous magnesium salicylate solutions. The equations **4.12** and **4.13** were used to compute pair and triple interaction coefficients of volume and compressibility. The interaction coefficients (**Table 4.33**) provide quantitative insight into solute–solute and cooperative interactions in these ternary systems. For potassium chloride, positive V_{AB} values that increase with temperature indicate predominant solute–solute (ion–ion) attractions, leading to volumetric expansion due to partial disruption of hydration shells. The negative V_{ABB} values, which become more pronounced at higher temperatures, suggest that cooperative triplet interactions promote a more compact structure as ion–ion association strengthens. Positive K_{AB} values indicate increased compressibility associated with weakened hydration, whereas negative K_{ABB} values imply that cooperative interactions limit structural flexibility and reduce compressibility. In contrast, sodium sulphate exhibits small negative or slightly positive V_{AB} values that increase with temperature, implying weak but progressively strengthening ion–ion

interactions. The positive V_{ABB} values at lower temperatures convert to negative values at higher temperatures, indicating a temperature-dependent transition from structure-expanding to compact cooperative behaviour. The relatively large positive K_{AB} values at 288.15 K suggest enhanced compressibility due to disruption of hydration layers, while negative K_{ABB} values reflect the development of a rigid, less compressible structure at elevated temperatures. Overall, the temperature-dependent sign and magnitude variations of V_{AB} , V_{ABB} , K_{AB} , and K_{ABB} confirm that both salts exhibit a balance between ion–ion attraction and hydration effects. These findings demonstrate that magnesium salicylate acts as a structure-making co-solute, modulating the volumetric and compressibility properties of the mixed electrolyte systems [72,86–89].

Isobaric thermal expansion coefficients

The α_p quantifies the fractional temperature dependence of V_ϕ^0 at constant pressure. It was obtained using the equation 4.14. The calculated α_p values (Table 4.34) show positive values at lower temperatures that gradually decrease and become negative at higher temperatures. This behaviour indicates that the apparent molar volume initially expands with temperature but later contracts as ion–ion interactions strengthen, and the structured hydration shells weaken. The larger magnitude of α_p for potassium chloride compared to sodium sulphate suggests a greater sensitivity of the system to temperature, consistent with weaker hydration of monovalent chloride ions relative to divalent sulphate ions. These results confirm that increasing temperature weakens ion–solvent electrostriction and promotes compact molecular association in the mixed electrolyte systems [90,91].

Table 4.31: Calculated values for empirical parameters for magnesium salicylate with potassium chloride/sodium sulphate at 0.1 MPa.

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$"a \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})"$	$b \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R^2	ARD
potassium chloride					
0.015	26.45050	0.08129	-0.00190	0.99412	0.01217
0.025	27.08266	0.10599	-0.00360	0.97071	0.01549
0.035	27.59637	0.11062	-0.00418	0.934371	0.01499
Sodium Sulphate					
0.015	17.72487	0.00653	-0.00029	0.99960	0.06312
0.025	18.79496	0.01669	-0.00041	0.94491	0.05765
0.035	19.76438	0.02155	-0.00044	0.91272	0.07524

$^a m_b$ - molality of aqueous magnesium salicylate is given per kg of pure water.

Table 4.32 Calculated E_{ϕ}^0 values for magnesium salicylate with sodium sulphate/potassium chloride 0.1 MPa.

$^a m_b \text{ (mol} \cdot \text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	288.15K	298.15K	308.15K	318.15K	
potassium chloride					
0.015	0.17792	0.10599	0.03406	-0.03787	0.012173
0.025	0.19421	0.11062	0.02704	-0.05654	0.015487
0.035	0.20641	0.11288	0.01935	-0.07418	0.014993
Sodium Sulphate					
0.015	0.01236	0.00653	0.00071	-0.00511	-0.00058
0.025	0.02479	0.01669	0.00859	0.00049	-0.00081
0.035	0.03031	0.02155	0.01278	0.00402	-0.00088

standard uncertainties u is $u(E_{\phi}^0) = 0.00500 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $u(\frac{\partial E_{\phi}^0}{\partial T}) = 0.00055 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$, $u(T) = 0.01 \text{ K}$.

Table 4.33: V_{AB} , K_{AB} and V_{ABB} , K_{ABB} for Potassium chloride and Sodium sulphate in aqueous magnesium salicylate solutions.

T/K	$V_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg)$	$V_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2)$	$K_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg GPa^{-1})$	$K_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2 GPa^{-1})$
Potassium chloride				
288.15	40.33	-386.43	9.57	-132.58
298.15	63.01	-937.82	5.36	-75.88
308.15	76.12	-1293.07	6.96	-118.43
318.15	83.81	-1533.04	7.01	-170.57
Sodium Sulphate				
288.15	-12.90	402.52	16.36	-215.15
298.15	4.697	-88.65	12.69	-142.73
308.15	9.668	-114.11	8.514	-60.57
318.15	12.08	-123.69	7.878	-66.91

T/K is temperature, Uncertainties u , $u(T) = 0.01K$, $u(p) = 0.01MPa$

Table 4.34: Values of thermal expansion for potassium chloride and sodium sulphate dissolved in aqueous magnesium salicylate.

$m_b/(\text{mol} \cdot \text{kg}^{-1})$	$\alpha_P \times 10^3 / (K^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Potassium Chloride				
0.015	6.74	3.93	1.22	-1.34
0.025	7.16	3.97	0.96	-2.00
0.035	7.56	4.07	0.69	-2.61
Sodium sulphate				
0.03	0.76	0.37	0.04	-0.26
0.06	1.53	0.94	0.46	0.02
0.09	1.83	1.21	0.67	0.20

Hydration number

The n_h values for the studied liquid systems were computed using equation 4.18 proposed by Passynski [102,103]. The hydration number (n_h) values were found to decrease with increasing temperature for all studied systems (Table 4.35). This behaviour is attributed to the weakening of ion–dipole interactions and the consequent reduction in electrostriction of H₂O molecules surrounding the solute ions. At lower temperatures, strong hydrogen bonding and solvent structuring lead to the formation of stable hydration shells; however, as temperature rises, enhanced molecular motion disrupts these ordered structures, releasing water molecules into the bulk phase. The decrease in n_h thus reflects partial de-solvation and a reduction in the size of the hydration sphere. Moreover, the replacement of solute–solvent interactions by solute–solute associations at elevated temperatures further contributes to the decline in hydration number, consistent with earlier observations in aqueous and mixed electrolyte systems.

Specific heat ratio

This was calculated using the semi-empirical relation given in equation 4.17. The computed γ values (Table 4.36) for potassium chloride and sodium sulphate in aqueous

magnesium salicylate show a systematic decrease with increasing temperature across all studied concentrations. This decreasing trend reflects the weakening of cohesive forces and loss of rigidity in the solution as the temperature rises. The reduction in γ with temperature also signifies enhanced molecular mobility and disruption of the hydration network, consistent with the observed thermal and volumetric behaviour of the ternary systems.

FTIR study

FTIR is a reliable technique for identifying functional groups and detecting changes in their vibrational frequencies, which indicate specific solute–solvent interactions mixture [110]. The samples were scanned in the range of 400–4000 cm^{-1} . The FTIR spectra of magnesium salicylate in H_2O at three concentrations (Figure 4.21(a)) show the characteristic vibrational bands of salicylate, particularly the O–H stretching region near 3306–3308 cm^{-1} , the C=O/C–O stretching around 1634 cm^{-1} , and the aromatic skeletal/C–H vibrations near 590–600 cm^{-1} . Across the studied concentrations, these peaks exhibit only minor shifts, indicating that increasing the amount of magnesium salicylate primarily alters the intensity rather than the position of the functional group bands. This behaviour suggests that no new bonds are formed in solution and that the solute remains molecularly dispersed, with interactions dominated by hydrogen bonding between salicylate groups and surrounding water molecules. In the ternary mixtures (Figures 4.21(b) and 4.21(c)), where 0.035 $\text{mol}\cdot\text{kg}^{-1}$ magnesium salicylate is combined with KCl and Na_2SO_4 at varying molalities, noticeable yet small shifts are observed in the O–H stretching band (3306–3339 cm^{-1}) and in the C–O/C=O region (1634–1635 cm^{-1}). These shifts become slightly more pronounced at higher salt concentrations. The presence of K^+ , Na^+ , and SO_4^{2-} perturbs the hydration environment around salicylate by competing for water molecules, thereby weakening the extent of hydrogen bonding between water and salicylate ions. The variations in peak intensities and slight band displacements reflect modifications in the solute–solvent and ion–solvent interactions rather than the formation of any new chemical species.

Table 4.35 Values for Hydration number of potassium chloride and sodium sulphate in water and aqueous magnesium salicylate solutions.

$m_a/(\text{mol.kg}^{-1})$	n_h				$m_a/(\text{mol.kg}^{-1})$	n_h			
	288.15	298.15	308.15	318.15		288.15	298.15	308.15	318.15
0.00 Magnesium Salicylate + potassium chloride					0.00 Magnesium Salicylate + sodium sulphate				
0.10621	6.99	6.76	6.64	6.58	0.09136	18.45	17.95	16.95	16.16
0.18956	6.87	6.84	6.42	6.17	0.20034	17.48	16.44	15.35	14.87
0.28101	6.81	6.70	6.26	5.98	0.30305	16.86	16.08	15.24	14.51
0.38281	6.70	6.43	6.17	5.81	0.39442	16.93	16.35	15.32	14.61
0.46818	6.65	6.40	6.10	5.83	0.49751	16.32	15.58	14.86	14.24
0.015 Magnesium Salicylate + potassium chloride					0.015 Magnesium Salicylate + sodium sulphate				
0.10183	6.70	6.41	5.60	5.00	0.09997	19.59	18.24	16.47	15.27
0.20492	7.77	6.09	5.40	5.27	0.20691	18.17	17.12	15.82	15.18
0.28066	7.60	6.29	5.78	5.42	0.29601	17.83	16.71	15.55	15.00
0.37300	7.43	6.12	5.73	5.49	0.38319	17.30	16.40	15.42	14.75
0.47551	7.02	6.10	5.67	5.36	0.50046	16.95	15.83	14.96	14.37
0.025 Magnesium Salicylate + potassium chloride					0.025 Magnesium Salicylate + sodium sulphate				
0.08970	6.70	5.51	5.38	4.94	0.08970	18.89	17.83	16.95	16.16
0.18879	6.78	5.71	6.01	5.26	0.18879	18.70	17.77	16.67	16.24
0.27928	6.85	5.95	6.02	5.12	0.27928	17.47	16.53	15.71	15.02

0.36800	6.71	6.02	5.96	5.28	0.36800	17.19	16.25	15.53	14.91
0.47757	6.45	6.00	5.68	5.41	0.47757	16.68	15.85	15.12	14.49
0.035 Magnesium Salicylate + potassium chloride					0.035 Magnesium Salicylate + sodium sulphate				
0.10009	6.23	5.41	3.90	4.59	0.10009	18.98	17.91	17.68	17.00
0.19173	6.60	5.71	5.15	4.92	0.19173	18.32	17.76	17.27	16.42
0.30271	6.58	5.81	5.24	5.09	0.30271	17.57	16.63	16.02	15.36
0.38645	6.62	6.00	5.49	5.57	0.38645	17.22	16.40	15.63	15.09
0.48488	6.37	5.95	5.63	5.41	0.48488	16.73	15.88	15.27	14.66

standard uncertainties are $u(n_h) = 0.41$, $u(T) = 0.01$ K, and $u(p) = 0.01$ MPa.

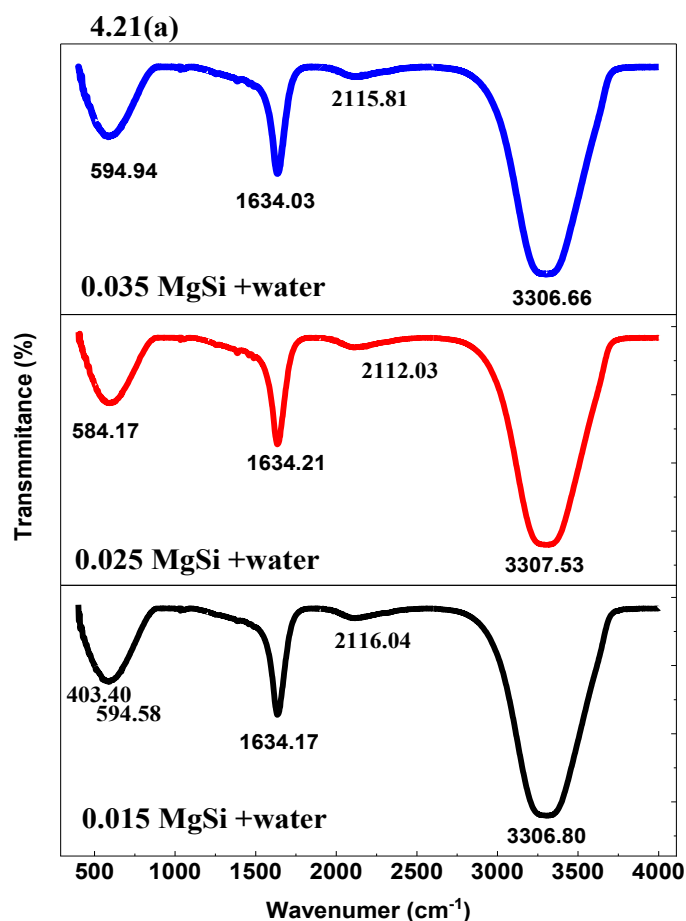
Table 4.36 Values of specific heat ratio for potassium chloride and sodium sulphate in water and aqueous magnesium salicylate solutions.

$^a m_A /$ (mol·kg ⁻¹)	Specific Heat ratio (Y)				$^a m_A /$ (mol · kg ⁻¹)	Specific Heat ratio (Y)			
	288.15	298.15	308.15	318.15		288.15	298.15	308.15	318.15
0.000 Magnesium Salicylate + potassium chloride					0.000 Magnesium Salicylate + sodium sulphate				
0.00000	1.38019	1.36043	1.34198	1.32470	0.00000	1.3802	1.3604	1.3420	1.3247
0.10621	1.37788	1.35816	1.33975	1.32251	0.10313	1.3750	1.3553	1.3370	1.3198
0.18956	1.37610	1.35641	1.33804	1.32083	0.18524	1.3689	1.3494	1.3312	1.3141
0.28101	1.37418	1.35452	1.33617	1.31900	0.30886	1.3634	1.3440	1.3259	1.3089
0.38281	1.37207	1.35245	1.33414	1.31701	0.37932	1.3586	1.3393	1.3213	1.3044
0.46818	1.37034	1.35075	1.33245	1.31537	0.45128	1.3533	1.3341	1.3162	1.2995
0.015 Magnesium Salicylate + potassium chloride					0.015 Magnesium Salicylate + sodium sulphate				
0.00000	1.37951	1.35970	1.34131	1.32408	0.00000	1.3795	1.3597	1.3413	1.3241
0.10183	1.37733	1.35757	1.33925	1.32205	0.09812	1.3738	1.3541	1.3359	1.3188
0.20492	1.37518	1.35548	1.33721	1.32005	0.19832	1.3679	1.3484	1.3302	1.3132
0.28066	1.37365	1.35397	1.33574	1.31860	0.31057	1.3631	1.3437	1.3257	1.3087
0.37300	1.37181	1.35217	1.33398	1.31687	0.40525	1.3585	1.3392	1.3213	1.3045
0.47551	1.36981	1.35021	1.33206	1.31499	0.48462	1.3525	1.3333	1.3156	1.2989
0.025 Magnesium Salicylate + potassium chloride					0.025 Magnesium Salicylate + sodium sulphate				
0.00000	1.37903	1.35924	1.34083	1.32362	0.00000	1.3790	1.3592	1.3408	1.3236
0.08970	1.37715	1.35742	1.33905	1.32187	0.10720	1.3733	1.3537	1.3354	1.3183

0.18879	1.37513	1.35545	1.33712	1.31997	0.20935	1.3674	1.3479	1.3298	1.3128
0.27928	1.37332	1.35370	1.33541	1.31830	0.32264	1.3627	1.3432	1.3252	1.3083
0.36800	1.37159	1.35201	1.33377	1.31670	0.40433	1.3581	1.3388	1.3208	1.3041
0.47757	1.36950	1.34999	1.33177	1.31477	0.49791	1.3522	1.3330	1.3152	1.2985
0.035 Magnesium Salicylate + potassium chloride					0.035 Magnesium Salicylate + sodium sulphate				
0.00000	1.37855	1.35878	1.34038	1.32318	0.00000	1.3785	1.3588	1.3404	1.3232
0.10009	1.37648	1.35675	1.33840	1.32123	0.10005	1.3729	1.3532	1.3350	1.3179
0.19173	1.37463	1.35494	1.33663	1.31949	0.19593	1.3670	1.3475	1.3293	1.3124
0.30271	1.37245	1.35282	1.33455	1.31745	0.28745	1.3622	1.3428	1.3248	1.3079
0.38645	1.37087	1.35126	1.33301	1.31595	0.39562	1.3577	1.3384	1.3204	1.3037
0.48488	1.36905	1.34948	1.33127	1.31425	0.50111	1.3518	1.3326	1.3148	1.2981

standard uncertainties are $u(T) = 0.01$ K and $u(\gamma) = 0.00600$.

Overall, the FTIR spectra confirm that both KCl and Na_2SO_4 induce electrolyte-mediated changes in the hydrogen-bonding network, causing subtle structural rearrangements in the hydration shell of magnesium salicylate. The absence of any new peaks throughout all systems confirms that the mixtures are physically, not chemically, interacting. These FTIR trends are fully consistent with the interaction patterns inferred from density and ultrasonic measurements, validating that the observed physicochemical changes arise from ion-induced perturbation of intermolecular hydrogen bonding in the aqueous environment.



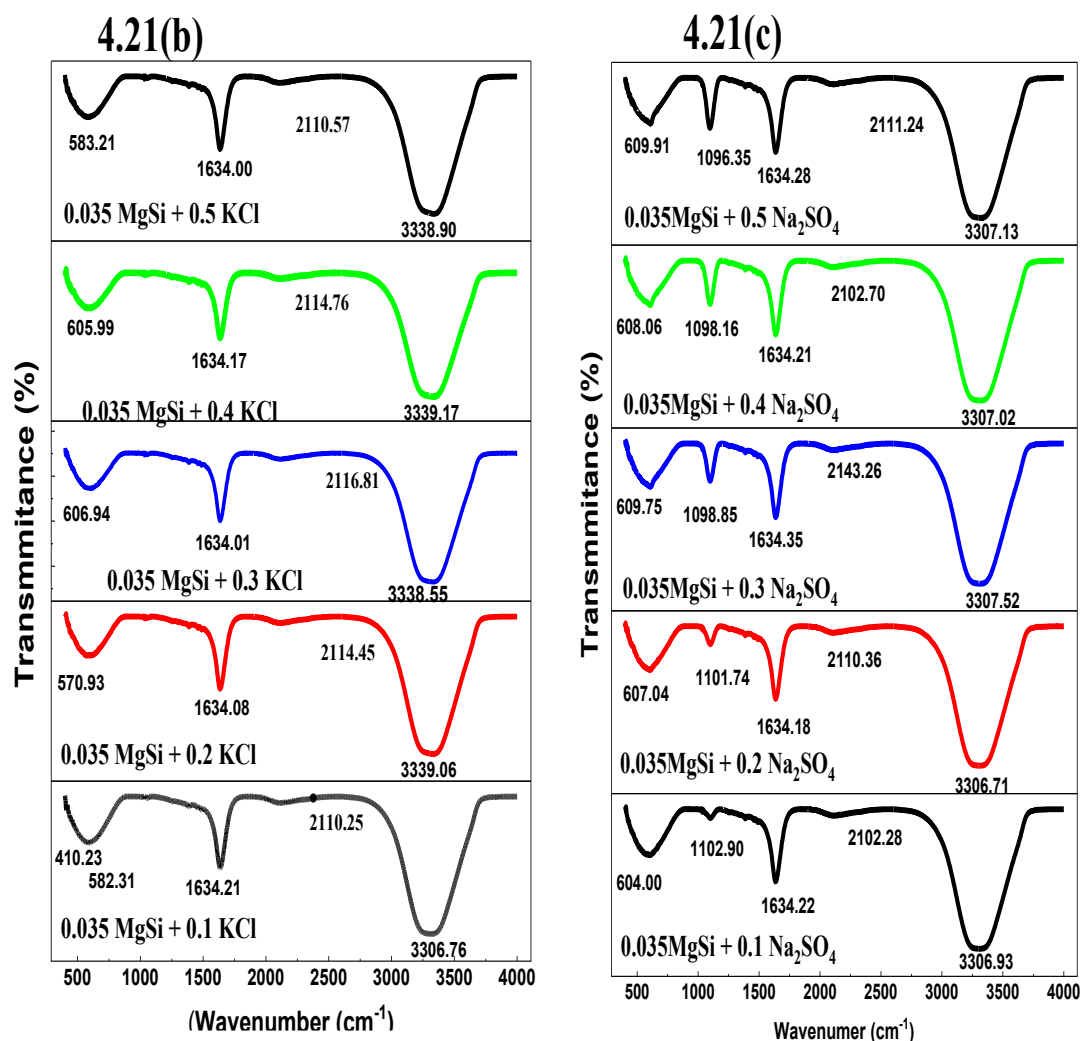


Figure 4.21 FTIR spectra for binary mixture (water + Magnesium salicylate) at three different concentrations in **4.21(a)** and **4.21(b)**, **(c)** are spectra of ternary mixtures of 0.035 concentration of magnesium salicylate in potassium chloride and sodium sulphate at 0.1-0.5 molalities respectively.

Section II

Problem 4 Thermodynamic, Acoustic and Spectroscopic Investigation of Choline Salicylate Ternary Mixtures with Sodium Salts over temperature range 288.15–318.15 K

In this problem, densities and ultrasonic velocity for the $C_6H_5Na_3O_7/NaNO_3$ in aqueous Choline Salicylate were measured. Also conducted FTIR analysis of binary and ternary mixtures of choline salicylate with salts to further reveal bonding characteristics. **Figure 4.22** is schematic representation of the interactions between $C_6H_5Na_3O_7/NaNO_3$ and in Choline salicylate aqueous solutions

Density and Apparent molar volume

The density values were experimentally determined in choline salicylate solutions with 0.00, 0.03, 0.06, and 0.09 mol · kg⁻¹ concentrations at T= 288.15-318.15K in ternary mixtures. The results indicate that density increases as the molality of $C_6H_5Na_3O_7/NaNO_3$ rises in the aqueous choline salicylate solution. This increase primarily results from the greater mass of the solution. Additionally, the rise in density suggests stronger solute-solvent interactions [48–50]. The experimentally obtained density values for trisodium citrate + H₂O and sodium nitrate + H₂O at different temperatures align well with existing literature. A comparison of these values with previously reported data for trisodium citrate + H₂O [5–7] and sodium nitrate + H₂O [51,52] is presented in **Fig.4.1 (c) and 4.8(a)** respectively. Also, we plotted comparison graph of density and sound velocity of choline salicylate + water with literature [111,112]. As shown in **Figure 4.23**, our experimental values for density **fig 4.23 (a)** and velocity **fig 4.23 (b)** of choline salicylate + water align closely with the literature data, and the overall trends with respect to concentration and temperature are in excellent agreement. The observed deviations are within the combined experimental uncertainties reported in both studies, supporting the reliability and reproducibility of our measurements. Furthermore, the density measurements were used to compute the apparent molar volume (V_ϕ) by using equation 4.1. Where M indicates molar mass of the salts, ρ_0 = densities of solvent (water + choline salicylate), and ρ is the densities of the solutions. In **Table 4.37** values of densities and V_ϕ are provided. All values are

positives and V_ϕ values are increasing with rise in temperature, concentrations and with molality's of sodium nitrate and trisodium citrate. Furthermore, being electrolytes ($V_\phi - A_V\sqrt{m}$) values are plotted and are depicted in **Figure 4.24** Which shows the trend of V_ϕ , graphically. The occurrence of solute-solvent interactions is supported by V_ϕ positive values, , which reflect a consistent linear behaviour with increasing temperature and sodium nitrate and trisodium citrate's molality. This can be attributed to the solvation phenomenon and the strong affinity of the solutes for the solvent, providing molecular interactions within the system [54,55]. The primary interactions in these ternary aqueous systems are H-bonding and ion–dipole interactions. This is evidenced by the broadening and shift of the O–H stretching band in the FTIR spectra, which reflect changes in the hydrogen bond network upon addition of choline salicylate and salts[113].The presence of sodium nitrate and trisodium citrate introduces strong ion–dipole forces between the dissolved ions and the polar water molecules, further influencing the solution structure. These observations are consistent with literature reports [113–117] that highlight the dominance of hydrogen bonding and ion–dipole interactions in aqueous salt solutions, as well as the ability of FTIR to probe such molecular interactions. The present investigation, therefore, highlights the various interactions present in the ternary mixtures under study, further emphasizing the complexity of these mixtures, and it also distinguishes solvent-solvent and solute-solute interactions more effectively through partial molar volume values at infinite dilution, which provide qualitative insights into the fundamental molecular interactions within system [56,57,118,119].

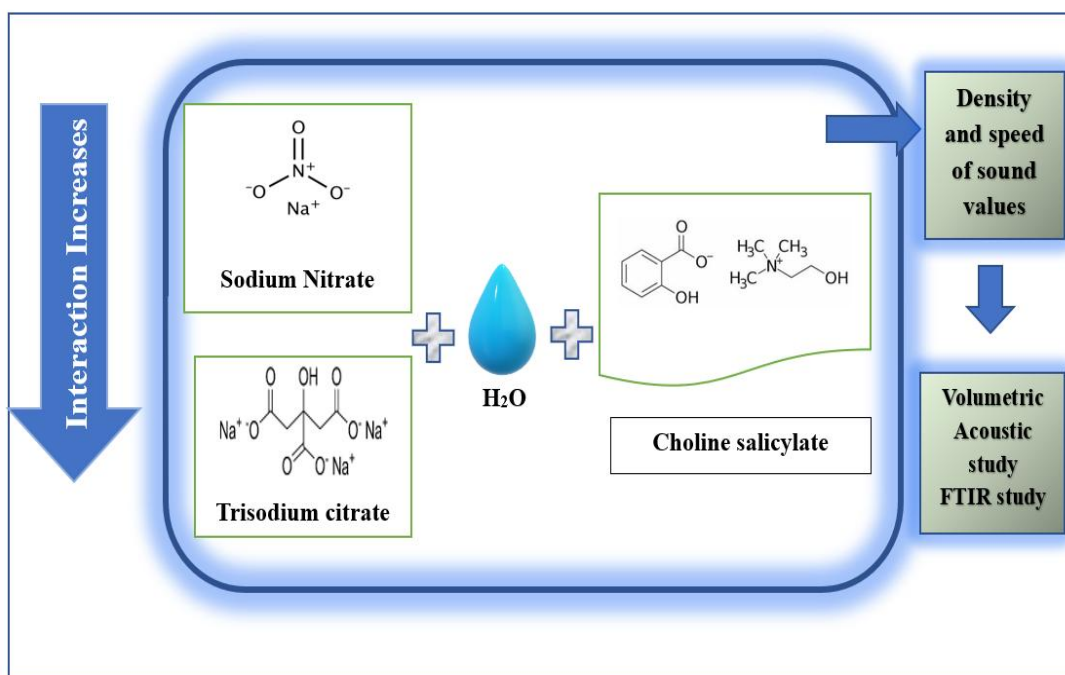


Figure 4.22: Trisodium citrate/sodium nitrate in aqueous choline salicylate interactions.

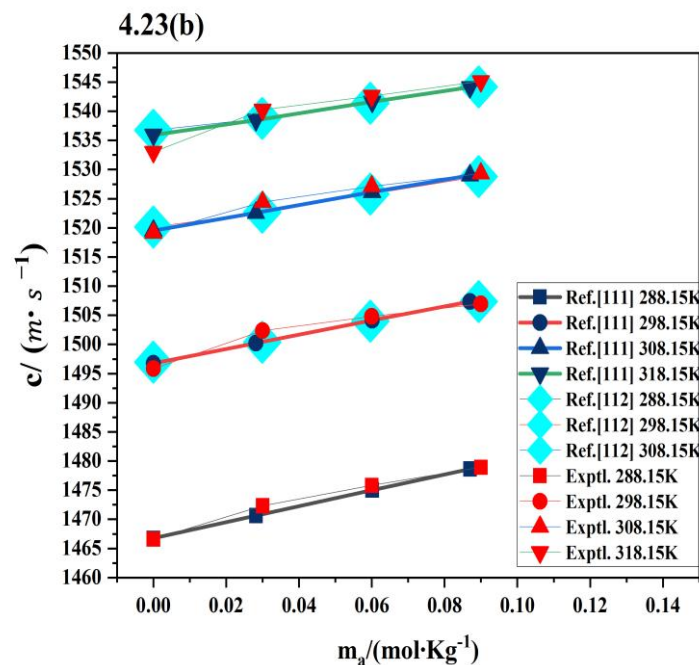
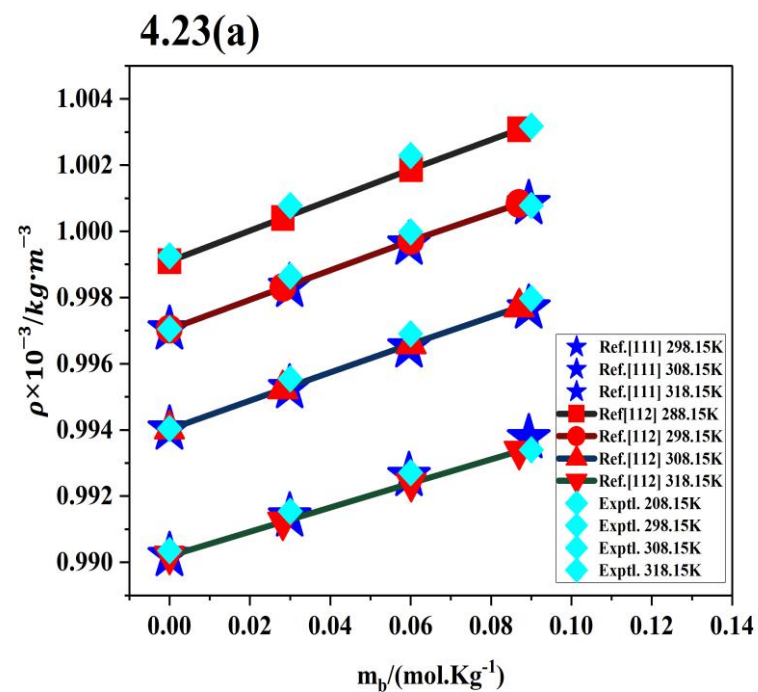


Figure 4.23. A comparison of density 4.23(a) and ultrasonic velocity 4.23(b) for experimental data with literature of choline salicylate + water.

Table 4.37: Measured densities, ρ and V_ϕ , data for ternary mixture of choline salicylate with sodium nitrate/trisodium citrate.

$^a m_A / (kg^{-1})$	$\rho \times 10^{-3} / (kg \cdot m^{-3})$				$V_\phi \times 10^6 / (m^3 \cdot mol^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Nitrate + 0.00 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.08744	1.00457	1.00214	0.99898	0.99508	23.61	25.94	27.52	29.91
0.18432	1.01023	1.00761	1.00429	1.00019	24.44	26.49	28.01	30.15
0.28217	1.01565	1.01301	1.00958	1.00526	25.55	26.86	28.17	30.27
0.39429	1.02190	1.01914	1.01545	1.01095	25.87	27.08	28.62	30.52
0.48416	1.02691	1.02376	1.01995	1.01531	25.93	27.66	29.11	30.90
Sodium Nitrate + 0.03 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1.00078	0.99865	0.99554	0.99154				
0.10205	1.00688	1.00404	1.00133	0.99874	24.72	26.13	27.80	30.10
0.20083	1.01259	1.00960	1.00675	1.00396	25.24	26.62	28.06	30.19
0.30085	1.01822	1.01512	1.01209	1.00915	25.72	26.92	28.40	30.28
0.40169	1.02375	1.02053	1.01741	1.01420	26.18	27.34	28.60	30.60
0.49193	1.02871	1.02539	1.02209	1.01874	26.33	27.42	28.77	30.66
Sodium Nitrate + 0.06 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1.00229	0.99998	0.9969	0.99271				

0.09643	1.00702	1.00484	1.00206	0.99959	27.67	28.31	28.95	29.51
0.19994	1.01276	1.01050	1.00764	1.00511	27.94	28.54	29.13	29.64
0.31793	1.01910	1.01678	1.01384	1.01126	28.38	28.92	29.42	29.84
0.39181	1.02298	1.02062	1.01764	1.01505	28.65	29.14	29.63	29.96
0.48364	1.02774	1.02531	1.02230	1.01968	28.91	29.42	29.84	30.11
Sodium Nitrate + 0.09 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate								
0.00000	1.00318	1.00078	0.99797	0.9934				
0.10652	1.00839	1.00663	1.00384	1.00109	27.85	28.36	29.03	29.61
0.19729	1.01341	1.01035	1.00746	1.00590	28.06	28.60	29.31	29.84
0.30981	1.01946	1.01633	1.01332	1.01170	28.45	28.96	29.74	30.19
0.39501	1.02394	1.02074	1.01765	1.01597	28.75	29.25	30.04	30.51
0.49257	1.02896	1.02570	1.02243	1.02070	29.09	29.56	30.51	30.94
Trisodium citrate + 0.00 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.08734	1.01524	1.01282	1.00964	1.00580	73.78	75.94	77.58	79.08
0.18432	1.03272	1.03001	1.02665	1.02261	73.96	76.39	77.97	79.57
0.28550	1.05066	1.04764	1.04407	1.03979	74.13	76.68	78.32	80.04
0.38023	1.06713	1.06382	1.06005	1.05551	74.42	77.00	78.68	80.55
0.47605	1.08350	1.07998	1.07590	1.07109	74.73	77.16	79.05	81.05
Trisodium citrate + 0.03 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate								

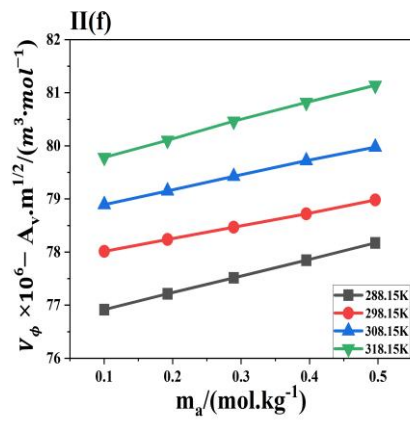
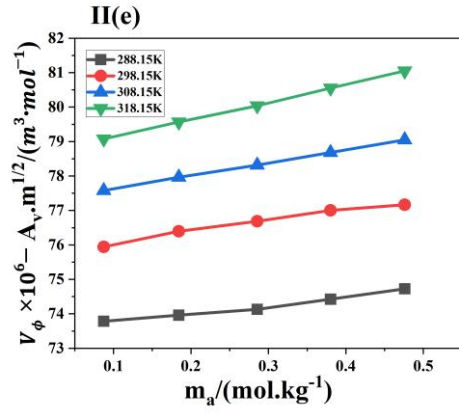
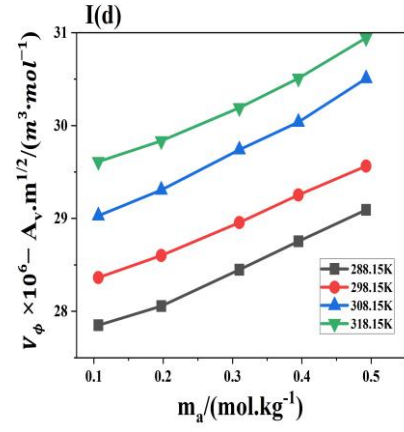
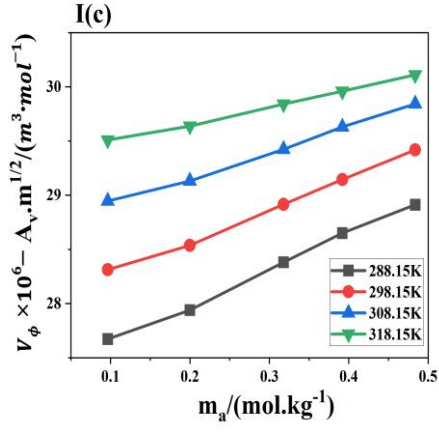
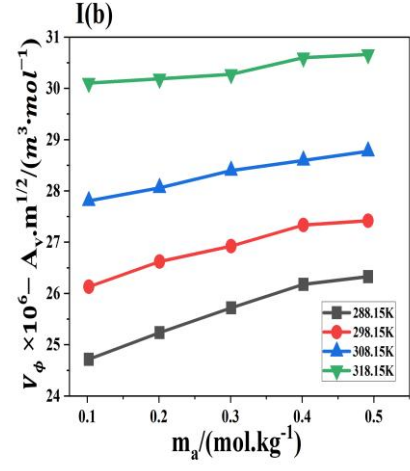
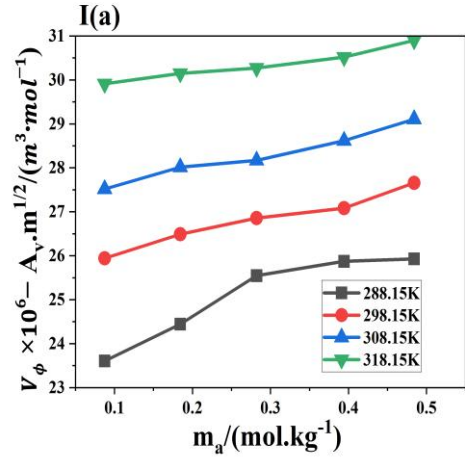
0.00000	1.00078	0.99865	0.99554	0.99154				
0.10020	1.01881	1.01600	1.01335	1.01090	76.91	78.01	78.89	79.78
0.19263	1.03514	1.03221	1.02945	1.02688	77.21	78.24	79.15	80.10
0.28933	1.05191	1.04887	1.04599	1.04328	77.51	78.47	79.42	80.46
0.39530	1.06994	1.06680	1.06377	1.06090	77.85	78.72	79.72	80.82
0.49600	1.08673	1.08351	1.08035	1.07731	78.17	78.98	79.98	81.14

Trisodium citrate + 0.06 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate

0.00000	1.00229	0.99998	0.9969	0.99271				
0.09724	1.01902	1.01679	1.01396	1.01145	77.25	78.30	79.16	80.03
0.19724	1.03666	1.03430	1.03137	1.02876	77.52	78.54	79.36	80.22
0.29255	1.05317	1.05070	1.04767	1.04492	77.75	78.76	79.59	80.52
0.40389	1.07209	1.06950	1.06634	1.06343	78.05	79.02	79.86	80.87
0.48379	1.08542	1.08276	1.07949	1.07641	78.29	79.21	80.07	81.22

Trisodium citrate + 0.09 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate

0.00000	1.00318	1.00078	0.99797	0.9934				
0.10043	1.02034	1.01857	1.01576	1.01298	77.97	78.53	79.22	80.11
0.19511	1.03698	1.03515	1.03225	1.02936	78.19	78.71	79.43	80.30
0.29212	1.05374	1.05184	1.04883	1.04581	78.42	78.95	79.68	80.61
0.39598	1.07136	1.06937	1.06627	1.06307	78.65	79.19	79.92	80.99
0.49757	1.08826	1.08619	1.08302	1.07961	78.88	79.46	80.12	81.33



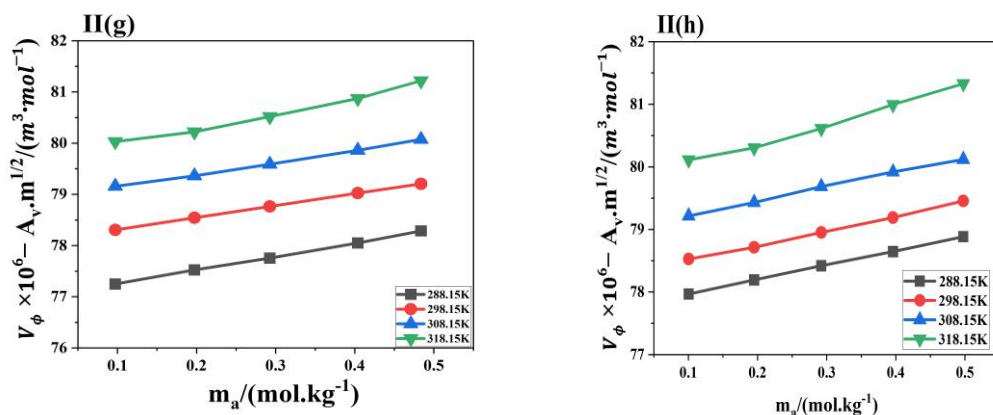


Fig. 4.24 Plots representing the, V_ϕ , against the molality (m_a) of Sodium nitrate/trisodium citrate in aqueous Choline Salicylate; [I(a) sodium Nitrate +water, I(b) $0.03 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate+ sodium nitrate, I(c) $0.06 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate+ sodium nitrate I(d) $0.09 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate+ sodium nitrate,], II(e) trisodium Citrate +water, II (f) $0.03 \text{ mol}\cdot\text{kg}^{-1}$ Choline salicylate+ trisodium citrate, II(g) $0.06 \text{ mol}\cdot\text{kg}^{-1}$ Choline salicylate+ trisodium citrate II(h) $0.09 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate+ trisodium citrate,] at multiple temperature.

Partial molar volume at infinite dilution and transfer volumes

V_ϕ^0 were computed by extrapolating the V_ϕ versus molality data to infinite dilution using eq. 4.2. A_v denotes Debye–Hückel limiting slope (temperature-dependent-The values of the Debye–Huckell limiting slope (A_v) for sodium nitrate (1:1 electrolyte) and trisodium citrate (1:3 electrolyte) at the studied temperatures were taken from the literature values[120][58][59], and S_v is an experimentally derived slope that accounts for deviations at higher concentrations. The least squares approach was employed to fit the parameters for both solutes, enabling the determination of V_ϕ^0 at infinite dilution [60,61]. The positive values of V_ϕ^0 across all concentrations and temperatures (**Table 4.38, Figure 4.25**) indicate strong solute-solvent associations, consistent with the co-sphere overlap model. According to this model, overlapping of co-spheres between ionic species leads to volume increases, while ion-hydrophobic and hydrophobic-hydrophobic interactions can cause decreases. In our system, ion-hydrophilic interactions generally prevail, resulting in the observed positive values [121][122–124]. Partial molar volumes of transfer (ΔV_ϕ^0) quantify the change in V_ϕ^0 when the

solute is transferred from water to aqueous choline salicylate. This volume change can be expressed mathematically using relation 4.3. Table 4.39 shows that ΔV_{ϕ}^0 increases with choline salicylate concentration, suggesting enhanced structure-making effects and increased ion-hydrophilic interactions [125–127].

Results indicate that ion-hydrophilic and hydrophilic-hydrophilic interactions exert a stronger influence compared to ion-hydrophobic and hydrophobic-hydrophobic interactions [117,128,129].

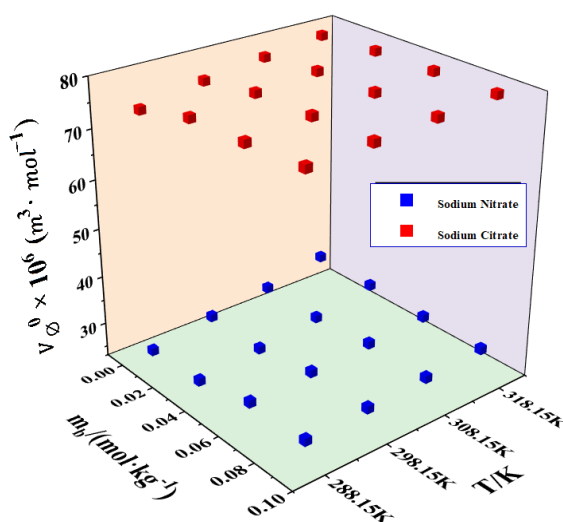


Figure 4.25 Partial molar volumes, V_{ϕ}^0 , of sodium nitrate (blue) and trisodium citrate (red) in aqueous choline salicylate solutions.

Table 4.38: Calculated V_ϕ^0 values along with experimental slope (S_V^*) for choline salicylate with sodium nitrate/trisodium citrate.

$^a m_B / (mol \cdot kg^{-1})$	$V_\phi^0 \times 10^6 (m^3 \cdot mol^{-1})$				$S_V^* \times 10^6 (m^3 \cdot kg \cdot mol^{-2})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium Nitrate								
0.00	23.74(±0.42)	26.16(±0.14)	27.75(±0.10)	30.27(±0.07)	7.74(±0.44)	5.74(±0.46)	5.67(±0.32)	4.40(±0.22)
0.03	24.36(±0.12)	25.88(±0.11)	27.57(±0.05)	29.90(±0.07)	4.26(±0.07)	3.37(±0.36)	2.53(±0.15)	1.56(±0.24)
0.06	27.33(±0.03)	28.00(±0.03)	28.69(±0.02)	29.34(±0.01)	3.30(±0.11)	2.91(±0.10)	2.37(±0.09)	1.58(±0.04)
0.09	27.46(±0.04)	28.00(±0.02)	28.58(±0.05)	29.19(±0.07)	3.28(±0.13)	3.15(±0.07)	3.80(±0.16)	3.44(±0.21)
Trisodium Citrate								
0.00	73.52(±0.06)	75.75(±0.08)	77.25(±0.01)	78.62(±0.02)	2.41(±0.21)	3.13(±0.28)	3.76(±0.04)	5.07(±0.06)
0.03	76.60(±0.00)	77.77(±0.00)	78.62(±0.01)	79.45(±0.01)	3.16(±0.01)	2.44(±0.02)	2.75(±0.03)	3.44(±0.05)
0.06	76.99(±0.01)	78.08(±0.00)	78.91(±0.02)	79.66(±0.07)	2.65(±0.04)	2.33(±0.00)	2.38(±0.06)	3.08(±0.22)
0.09	77.74(±0.00)	78.27(±0.01)	78.99(±0.02)	79.74(±0.05)	2.30(±0.01)	2.34(±0.05)	2.30(±0.06)	3.14(±0.16)

$u(m) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$, $u(V_\phi^0) = \pm 0.01 \times 10^{-6} (m^3 \cdot \text{mol}^{-1})$, $u(S_V^*) = 1.47 \times 10^{-6} (m^3 \cdot \text{kg} \cdot \text{mol}^{-2})$, $u(T) = \pm 0.001 K$, $u(\rho) = 0.5 \text{ kg} \cdot \text{m}^{-3}$

$^3 u(p) = 0.01 \text{ MPa}$.

Table 4.39: Calculated ΔV_{ϕ}^0 values for choline salicylate with $C_6H_5Na_3O_7/NaNO_3$.

$m_B/(mol \cdot kg^{-1})$	$\Delta V_{\phi}^0 \times 10^6 (m^3 \cdot mol^{-1})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium Nitrate				
0.03	0.62	-0.28	-0.18	-0.37
0.06	3.59	1.84	0.94	-0.93
0.09	3.72	1.85	0.84	-1.08
Sodium Citrate				
0.03	3.08	2.01	1.37	0.82
0.06	3.47	2.33	1.65	1.04
0.09	4.22	2.52	1.74	1.11

. standard uncertainties u is $u(m_b) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$ u $(\Delta V_{\phi}^0) = 0.09 \times 10^{-6} / (m^3 \cdot \text{mol}^{-1})$, $u(T) = \pm 0.001\text{K}$, $u(p) = 0.01\text{MPa}$.

Temperature-Dependent Partial Molar Volume

As described in **Table 4.40**, the a, b, and c for both solutes describe how the V_{ϕ}^0 varies with temperature. This relationship is evaluated using the following polynomial equation 4.4. Here $T_{ref} = 298.15\text{K}$. **Table 4.40** also illustrates the deviations between the computed and observed V_{ϕ}^0 values, which are assessed using the equation 4.5, with, $Y = V_{\phi}^0$, the polynomial equation fitted to the data demonstrates very low deviation values, as indicated by the R^2 values, confirming that it accurately represents the relationship [71]. The primary objective of evaluating the V_{ϕ}^0 data is to derive the E_{ϕ}^0 , which are determined using the following eq. 4.6. The E_{ϕ}^0 , provides critical insights into the solute-solvent dynamics within the mixture. The solute's capacity to form or disrupt structures in solution can be evaluated using the following thermodynamic equation 4.7. The $(\partial E_{\phi}^0 / \partial T)_p$ reveals whether the solute's exhibit structure-forming or structure-breaking tendencies. Positive or less negative values suggest a structure-forming tendency, while more negative values indicate structure-breaking behaviour. In **Table 4.41**, E_{ϕ}^0 and $(\partial E_{\phi}^0 / \partial T)_p$ values are presented that highlight that $C_6H_5Na_3O_7/NaNO_3$ in the aqueous choline salicylate solution predominantly exhibit structure-making capabilities [130,131].

Table 4.40: Calculated values for empirical parameters for choline salicylate with sodium nitrate/trisodium citrate.

$m_B/(\text{mol} \cdot \text{kg}^{-1})$	$a \times 10^6(\text{m}^3 \cdot \text{mol}^{-1})$	$b \times 10^6(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R^2	ARD
Sodium Nitrate					
0.03	25.80809	0.16276	0.00202	0.999	0.00172
0.06	28.00745	0.06781	-0.00005	0.999	0.00000
0.09	28.00471	0.05635	0.00013	0.999	0.00004
Sodium Citrate					
0.03	77.72351	0.102476	-0.00085	0.999	0.00035
0.06	78.05046	0.096787	-0.00083	0.999	0.00000
0.09	78.29684	0.061684	0.00054	0.999	0.00019

^a m_B is the molality of aqueous choline salicylate is given per kg of pure water.

Table 4.41: Calculated partial molar expansibilities, (E_{ϕ}^0) values for choline salicylate with $C_6H_5Na_3O_7/NaNO_3$.

$^a m_B$ ($mol \cdot kg^{-1}$)	$E_{\phi}^0 \times 10^6 (m^3 \cdot mol^{-1} \cdot K^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p / (m^3 \cdot mol^{-1} \cdot K^{-2})$
	288.15 K	298.15 K	308.15 K	318.15 K	
Sodium Nitrate					
0.03	0.12222	0.16277	0.20332	0.24387	0.00406
0.06	0.06873	0.06781	0.06689	0.06597	-0.00009
0.09	0.05362	0.05635	0.05908	0.06180	0.00027
Sodium Citrate					
0.03	0.11946	0.10248	0.08549	0.06851	-0.00170
0.06	0.11338	0.09679	0.08019	0.06360	-0.00166
0.09	0.05088	0.06168	0.07249	0.08329	0.00108

standard uncertainties u is $u(E_{\phi}^0) = 0.005 \times 10^{-6} / (m^3 \cdot mol^{-1} \cdot K^{-1})$, $u(\frac{\partial E_{\phi}^0}{\partial T}) = 0.00055 / (m^3 \cdot mol^{-1} \cdot K^{-2})$, $u(T) = \pm 0.001 K$, $u(p) = 0.01 MPa$.

Ultrasonic velocity and apparent molar isentropic compression

The ultrasonic velocity values are experimentally obtained for sodium nitrate/trisodium citrate in (0.00, 0.03, 0.06, and 0.09) $mol \cdot kg^{-1}$ of choline salicylate solutions at $T/K = (288.15-318.15)$. All values of sound velocity rise with concentration of $C_6H_5Na_3O_7/NaNO_3$ in the aqueous choline salicylate solution. A comparison plot of sound velocity for experimental data of a binary mixture with published data for $NaNO_3 + H_2O$ [52,75] and for $C_6H_5Na_3O_7 + water$ [5–7] shown in **Fig. 4.12** for sodium nitrate and **4.1(d)** for trisodium citrate +water). The values of $K_{\phi,s}$ computed from speed of sound values by using the equation 4.8. where k_s is an isentropic compressibility, that is evaluated by applying the Newton-Laplace equation 4.9. All obtained values of $K_{\phi,s}$ together with experimental data of sound velocity given in **Table 4.42**, shows that the $K_{\phi,s}$ values are consistently negative across various temperatures and concentrations, as illustrated in **Figure. 4.26**, showing its variation with molality. This negative trend indicates that H_2O molecules enveloping

the ionic groups of sodium nitrate/ trisodium citrate are less compressible relative to bulk water. The decrease in apparent molar isentropic compressibility ($K_{\phi,S}$) suggests that introducing solvent like aqueous choline salicylate into a solution reduces its overall compressibility. This effect is mainly ascribed to robust solute -solvent interactions, where choline salicylate forms hydration shells with water, leading to a more structured solution that resists compression [132–134] . As temperature increases, the sound velocity in the solution rises, leading to a further decrease in isentropic compressibility, thus making $K_{\phi,S}$ more negative. Additionally, increasing the concentration of choline salicylate enhances these interactions, further lowering compressibility and reinforcing the negative trend of $K_{\phi,S}$. This pattern highlights how the interplay between solute-solvent interactions, temperature, and concentration collectively reduces the compressibility of the solution under isentropic conditions [134,135].

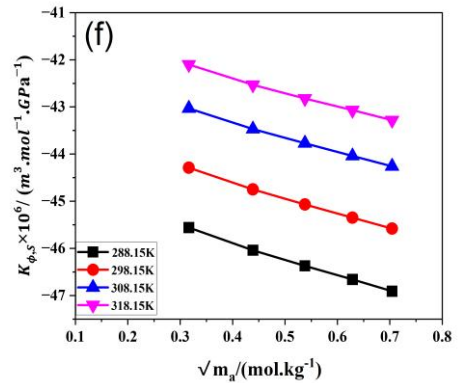
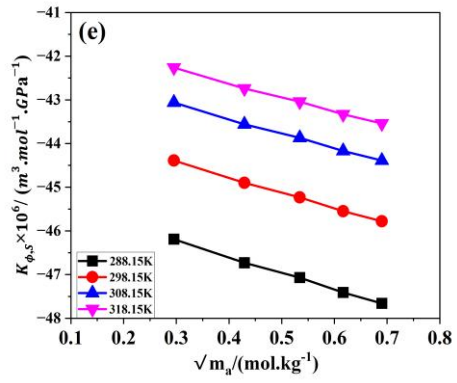
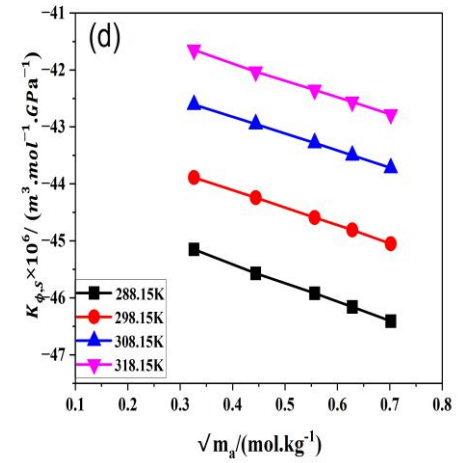
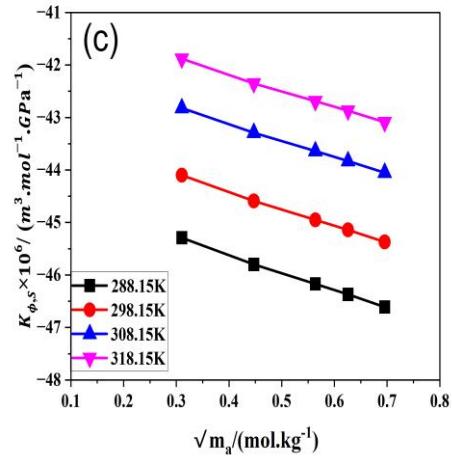
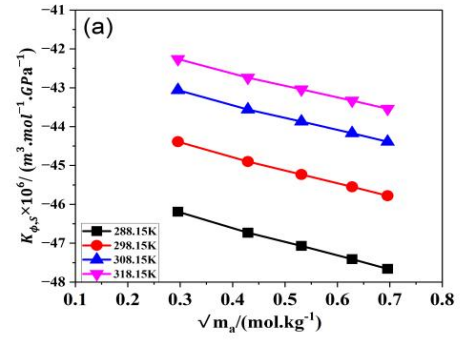
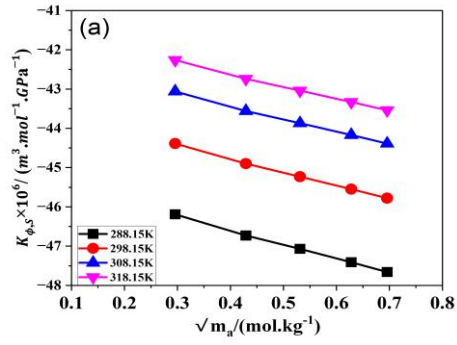
Table 4.42: Ultrasonic velocity (c) values and $K_{\phi,S}$ values for choline salicylate with sodium nitrate/trisodium citrate.

$^a m_A / (mol \cdot kg^{-1})$	$c / (m \cdot s^{-1})$				$\kappa_{\phi,S} \times 10^6 / (m^3 \cdot mol^{-1} \cdot Gpa^{-1})$			
	T 288.15K	= T 298.15K	= T 308.15K	= T 318.15K	= T 288.15K	= T 298.15K	= T 308.15K	= T 318.15K
Sodium Nitrate + 0.00 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1466.59	1495.85	1519.14	1533.02				
0.08744	1472.01	1501.16	1522.95	1536.96	-46.19	-44.39	-43.06	-42.26
0.18432	1476.04	1503.89	1526.15	1540.19	-46.73	-44.90	-43.56	-42.74
0.28217	1479.58	1507.55	1529.53	1544.03	-47.07	-45.23	-43.87	-43.04
0.39429	1483.32	1510.14	1532.89	1547.04	-47.41	-45.55	-44.17	-43.33
0.48416	1486.29	1513.63	1535.93	1550.46	-47.66	-45.78	-44.39	-43.54
Sodium Nitrate + 0.03 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1472.32	1502.35	1524.43	1540.24				
0.10205	1480.58	1503.35	1524.96	1540.71	-45.56	-44.29	-43.03	-42.10
0.20083	1482.52	1506.81	1528.06	1543.95	-46.04	-44.75	-43.47	-42.53
0.30085	1484.52	1510.04	1531.18	1547.60	-46.37	-45.07	-43.77	-42.82
0.40169	1486.92	1513.32	1534.79	1550.89	-46.66	-45.35	-44.04	-43.07
0.49193	1488.93	1516.49	1538.03	1553.58	-46.91	-45.58	-44.26	-43.28
Sodium Nitrate + 0.06 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1475.81	1504.83	1527.14	1542.62				
0.09643	1484.04	1505.16	1526.57	1543.73	-45.29	-44.10	-42.82	-41.88

0.19994	1486.19	1508.92	1529.92	1546.71	-45.80	-44.59	-43.29	-42.35
0.31793	1488.64	1512.84	1533.18	1549.93	-46.17	-44.95	-43.64	-42.69
0.39181	1490.09	1515.32	1536.14	1551.95	-46.37	-45.14	-43.83	-42.87
0.48364	1492.30	1518.64	1539.21	1554.57	-46.61	-45.37	-44.05	-43.09
Sodium Nitrate + 0.09 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1478.92	1506.93	1529.32	1545.14				
0.10652	1487.65	1509.09	1530.93	1548.55	-45.15	-43.89	-42.61	-41.65
0.19729	1489.12	1511.83	1533.02	1550.62	-45.57	-44.24	-42.95	-42.03
0.30981	1490.81	1515.19	1535.84	1552.69	-45.92	-44.59	-43.28	-42.35
0.39501	1492.32	1518.12	1538.02	1554.72	-46.16	-44.81	-43.50	-42.56
0.49257	1494.36	1521.40	1540.88	1556.92	-46.41	-45.05	-43.72	-42.78
Trisodium Citrate + 0.00 $mol \cdot kg^{-1}$ choline Salicylate								
0.00000	1466.59	1495.85	1519.14	1533.02				
0.08734	1484.13	1513.93	1536.09	1549.95	-46.73	-44.91	-43.54	-42.74
0.18432	1504.24	1533.04	1554.19	1568.93	-47.82	-45.95	-44.54	-43.73
0.28550	1525.78	1552.69	1573.54	1587.98	-48.75	-46.83	-45.38	-44.55
0.38023	1546.43	1572.03	1589.94	1603.52	-49.55	-47.59	-46.12	-45.26
0.47605	1566.68	1588.88	1607.93	1620.91	-50.34	-48.34	-46.83	-45.95
Trisodium Citrate + 0.03 $mol \cdot kg^{-1}$ choline Salicylate								
0.00000	1472.32	1502.35	1524.43	1540.24				
0.10020	1496.57	1518.97	1540.02	1554.60	-46.13	-44.83	-43.56	-42.62

0.19263	1514.29	1536.92	1557.39	1573.38	-47.09	-45.77	-44.46	-43.51
0.28933	1532.94	1556.64	1575.38	1590.70	-47.94	-46.59	-45.26	-44.28
0.39530	1553.92	1576.97	1593.91	1608.60	-48.80	-47.42	-46.07	-45.07
0.49600	1574.75	1594.11	1612.27	1626.35	-49.59	-48.19	-46.81	-45.79
Trisodium Citrate + 0.06 $\text{mol} \cdot \text{kg}^{-1}$ choline Salicylate								
0.00000	1475.81	1504.83	1527.14	1542.62				
0.09724	1499.26	1520.38	1542.22	1556.65	-45.86	-44.65	-43.35	-42.41
0.19724	1518.31	1540.49	1559.86	1575.90	-46.90	-45.66	-44.33	-43.36
0.29255	1536.87	1559.65	1576.97	1593.08	-47.73	-46.46	-45.11	-44.12
0.40389	1558.39	1580.29	1597.06	1611.49	-48.63	-47.33	-45.95	-44.94
0.48379	1573.80	1594.07	1613.05	1626.12	-49.25	-47.94	-46.54	-45.51
Trisodium Citrate + 0.09 $\text{mol} \cdot \text{kg}^{-1}$ choline Salicylate								
0.00000	1478.92	1506.93	1529.32	1545.14				
0.10043	1502.73	1522.50	1543.65	1559.80	-45.68	-44.41	-43.11	-42.14
0.19511	1520.49	1541.18	1560.70	1577.51	-46.65	-45.35	-44.03	-43.03
0.29212	1539.92	1560.92	1578.91	1595.06	-47.48	-46.16	-44.81	-43.79
0.39598	1558.80	1581.06	1596.72	1612.42	-48.32	-46.97	-45.60	-44.55
0.49757	1580.37	1598.98	1617.56	1630.63	-49.10	-47.73	-46.34	-45.27

standard uncertainties u is $u(c) = 2.69 \text{ m} \cdot \text{s}^{-1}$, $u(T) = \pm 0.001 \text{ K}$, $u(p) = 0.01 \text{ MPa}$.



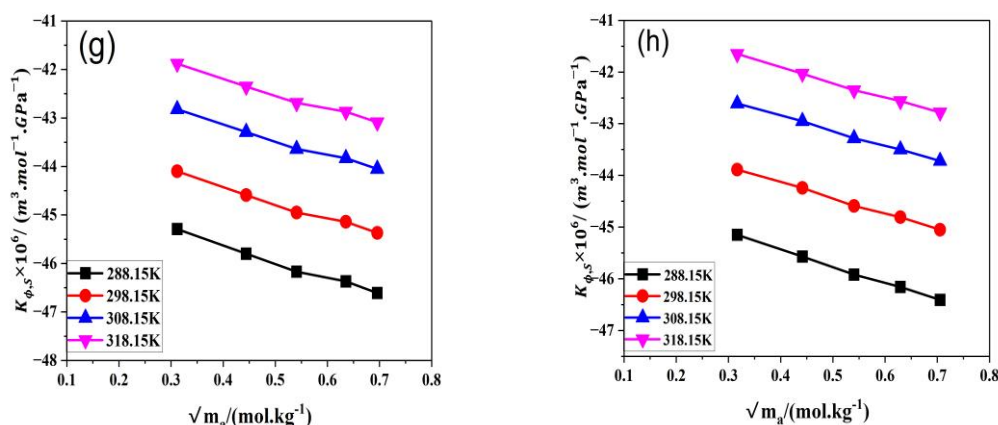


Figure 4.26. Apparent molar isentropic compressions, $K_{\phi,s}$, plotted against molality for Sodium nitrate/trisodium citrate in aqueous Choline Salicylate; [(a) sodium Nitrate +water, (b) $0.03 \text{ mol} \cdot \text{kg}^{-1}$ choline salicylate+ sodium nitrate, (c) $0.06 \text{ mol} \cdot \text{kg}^{-1}$ choline salicylate+ sodium nitrate (d) $0.09 \text{ mol} \cdot \text{kg}^{-1}$ choline salicylate+ sodium nitrate,], e) trisodium Citrate +water, (f) $0.03 \text{ mol} \cdot \text{kg}^{-1}$ Choline salicylate+ trisodium citrate, (g) $0.06 \text{ mol} \cdot \text{kg}^{-1}$ Choline salicylate+ trisodium citrate (h) $0.09 \text{ mol} \cdot \text{kg}^{-1}$ choline salicylate+ trisodium citrate,] at multiple temperature.

Partial molar isentropic compressibility ($K_{\phi,s}^0$) and Transfer Isentropic Compressibilities(ΔK_{ϕ}^0)

These properties provide deeper insight into the structural effects and the strength of intermolecular interactions in the studied systems. Partial molar isentropic compressibility ($K_{\phi,s}^0$) values were computed by extrapolating the $K_{\phi,s}$ versus molality ($\sqrt{m}$) data to infinite dilution using equation 4.10. The least squares method was employed to fit these parameters, enabling the determination of $K_{\phi,s}^0$ at infinite dilution for both solutes. The sign and magnitude of $K_{\phi,s}^0$ (see Table 4.43, Figure 4.27) reflect the degree of structure-making or structure-breaking in the system. Generally, negative $K_{\phi,s}^0$ values indicate structure-making (enhanced rigidity of the solvent structure), while positive values suggest structure-breaking [80–83]. The ΔK_{ϕ}^0 quantifies the change in $K_{\phi,s}^0$ when the solute is transferred from pure water to aqueous choline salicylate and is computed using equation 4.11. The ΔK_{ϕ}^0 values are presented in Table 4.44. An increase in ΔK_{ϕ}^0 with rising choline salicylate concentration suggests

enhanced structure-making effects and stronger ion-hydrophilic interactions within the ternary system. These trends are consistent with the co-sphere overlap model, where solute-induced changes in the hydration shell and solvent structure are reflected in the compressibility data [136–138].

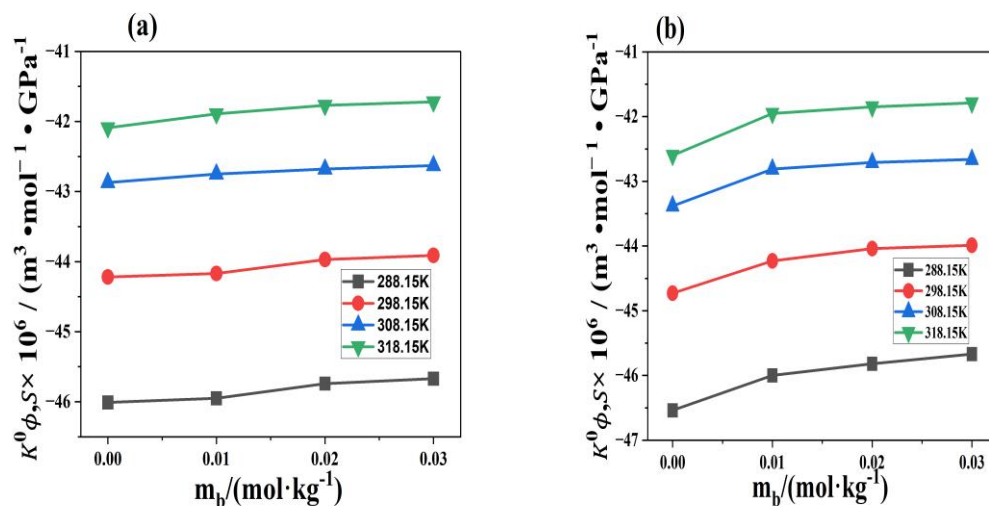


Fig. 4.27 $K^0_{\phi,S}$ plots (a) Sodium Nitrate and (b) Trisodium citrate in aqueous choline salicylate solutions at different temperatures.

Table 4.43: Values for $K_{\phi,S}^0$ and, S_K^* of Sodium nitrate and trisodium citrate in the aqueous choline salicylate.

^a	m_b	$K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$S_K^* \times 10^6 / (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$			
(mol·kg ⁻¹)		T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Nitrate									
0.00		-45.98(±0.09)	-44.20(±0.09)	-42.88(±0.09)	-42.09(±0.09)	-3.61(±0.30)	-3.41(±0.30)	-3.25(±0.29)	-3.12(±0.28)
0.03		-45.29(±0.07)	-44.03(±0.07)	-42.78(±0.07)	-41.87(±0.07)	-3.40(±0.24)	-3.26(±0.23)	-3.11(±0.22)	-2.97(±0.22)
0.06		-45.05(±0.08)	-43.87(±0.08)	-42.59(±0.04)	-41.67(±0.08)	-3.35(±0.25)	-3.24(±0.25)	-3.13(±0.24)	-3.06(±0.23)
0.09		-44.88(±0.07)	-43.62(±0.05)	-42.35(±0.05)	-41.41(±0.06)	-3.21(±0.22)	-2.99(±0.15)	-2.86(±0.15)	-2.89(±0.21)
trisodium Citrate									
0.00		0.00(±0.09)	-46.04(±0.08)	-44.26(±0.08)	-42.91(±0.08)	-8.17(±0.28)	-7.74(±0.27)	-7.43(±0.26)	-7.22(±0.26)
0.03		0.03(±0.09)	-45.36(±0.09)	-44.08(±0.08)	-42.83(±0.08)	-8.68(±0.28)	-8.41(±0.27)	-8.14(±0.27)	-7.93(±0.27)
0.06		0.06(±0.09)	-45.11(±0.08)	-43.92(±0.08)	-42.65(±0.08)	-8.68(±0.27)	-8.42(±0.27)	-8.15(±0.26)	-7.94(±0.26)
0.09		0.09(±0.10)	-44.91(±0.10)	-43.67(±0.10)	-42.39(±0.10)	-8.55(±0.34)	-8.30(±0.32)	-8.04(±0.32)	-7.82(±0.32)

Table 4.44: $\Delta K_{\phi,S}^0$ values of sodium nitrate and trisodium citrate in aqueous choline salicylate.

^a m_b (mol·kg ⁻¹)	$\Delta K_{\phi,S}^0 \times 10^6 / (m^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate				
0.01	0.69	0.16	0.10	0.22
0.02	0.93	0.33	0.28	0.42
0.03	1.10	0.57	0.52	0.68
Trisodium Citrate				
0.01	0.68	0.18	0.08	0.22
0.02	0.93	0.33	0.26	0.41
0.03	1.13	0.59	0.51	0.70

Pair and triplet interaction coefficients

Friedman and Krishnan expanded upon McMillan and Mayer's hypothesis to elucidate a solute's transfer properties in aqueous choline salicylate solution. The interaction coefficients presented in **Table 4.45**. The equations **4.12,4.13** were used to compute pair and triple interaction coefficients of volume and compression. The V_{AB} and K_{AB} for sodium nitrate and trisodium citrate are all positives except for sodium nitrate at 318.15K it becomes negative. The triplet interaction coefficients of volume (V_{ABB}) for sodium nitrate are negative at 288.15 K, while they turn positive at other temperatures. In contrast, for trisodium citrate, all V_{ABB} values are negative.

Additionally, triplet interaction coefficients for compressibility K_{ABB} are positive for sodium nitrate and trisodium citrate at temperatures 298.15, 308.15 and 318.15 K and negative at 288.15 K. These coefficients primarily reflect different behaviours of sodium nitrate and trisodium citrate when combined with choline salicylate. The positive data highlights the strength of solute-solvent interactions and suggest favourable volumetric and compressibility characteristics of sodium nitrate and trisodium citrate in solutions of choline salicylate at various temperatures. The temperature dependence of these interactions underlines the essential role of thermal effects in controlling the thermodynamic properties of these mixtures, which

is significant for formulation chemistry applications. In the calculation of triplet interaction coefficients, only alternating cation–anion–cation (or anion–cation–anion) arrangements are considered. This is because, in dilute electrolyte solutions, such alternating configurations are both statistically most probable and energetically favored, as predicted by the co-sphere overlap model and McMillan–Mayer theory. Triplet interactions involving like charges (e.g., cation–cation–anion or anion–anion–cation) are highly disfavoured due to electrostatic repulsion, making their contribution to the overall interaction energy negligible. This approach is consistent with established theoretical treatments of ionic solutions, which focus on the dominant alternating ionic arrangements ([111][112][139]).

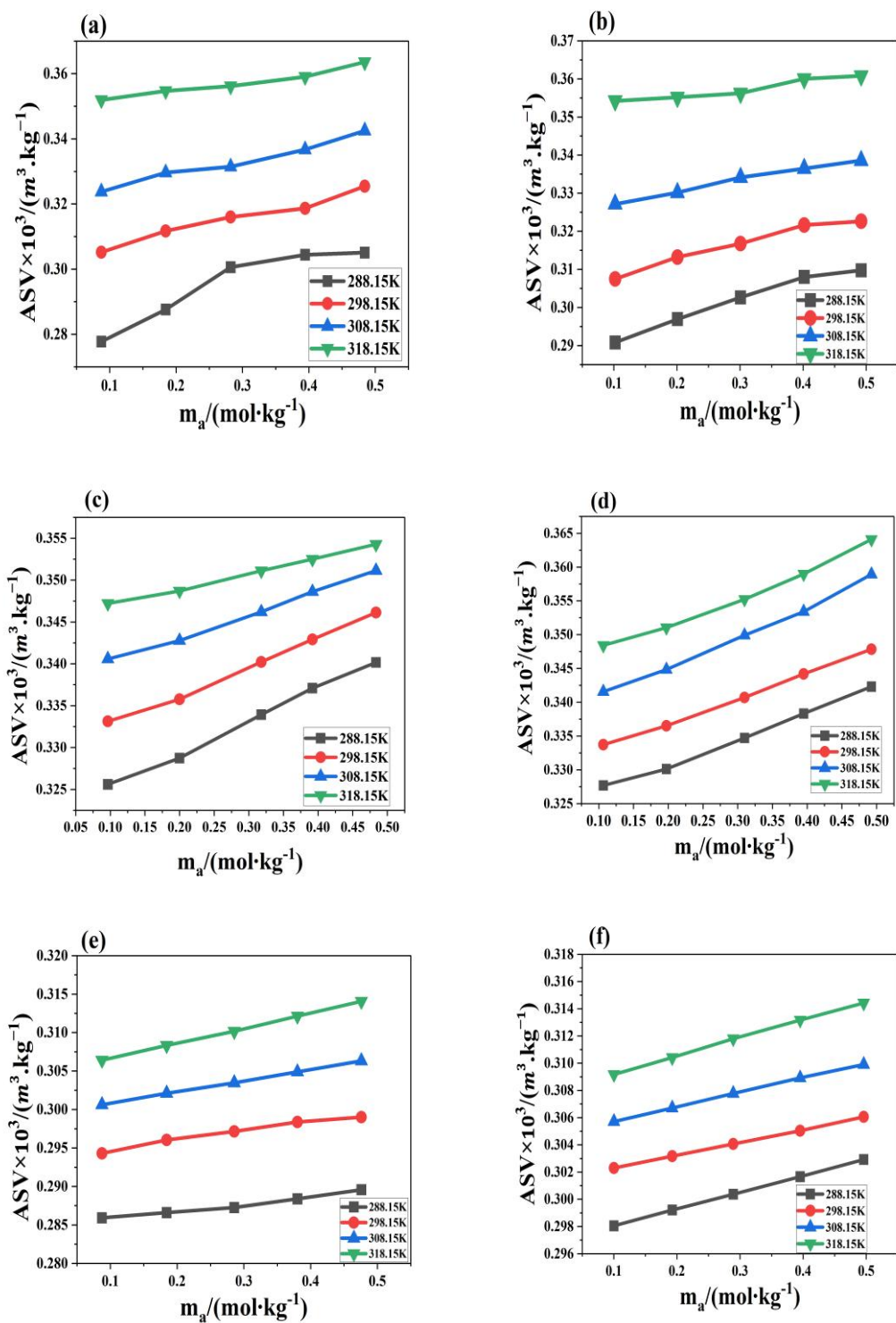
ASV (Apparent specific volume)

The ASV is a fundamental thermodynamic indicator that signifies the true volume taken by a solute in a solution per unit mass. It reflects information about solute-solvent interactions and molecular organization of the system. An increased ASV usually signifies stronger solute-solvent interactions, which have an effect on numerous physicochemical properties of the solution. The ASV is determined from the following equation:

$$ASV = \left(\frac{V_{\phi}}{M} \right) \quad (4.19)$$

The ASV values are presented in **table 4.46**(figure 4,28). For comprehending how molecules behave in mixtures, ASV is a crucial parameter. Moreover, it could be related to the quality of taste in solutions, particularly of importance in food and beverages. It has been found that only molecules with ASV values between 0.1 and 0.95 m³·kg⁻¹ are detectable by human taste receptors. The ASV values were then compared to standard taste ranges, which classify taste as: salt (<0.33×10⁻³m³kg⁻¹), sour (0.33-0.52 ×10⁻³m³kg⁻¹), sweet (0.52-0.71×10⁻³m³kg⁻¹), bitter (0.71-0.93×10⁻³m³kg⁻¹) [140–142]. **Table 4.46** provides ASV values and the values for trisodium citrate and sodium nitrate in aqueous solutions of choline salicylate are predominantly in the range of the salt <0.33×10⁻³m³kg⁻¹ at all concentrations and temperatures. This indicates that the addition of choline salicylate will not bring about any significant change in the natural taste properties of these salts. These findings agree

with the available literature [143–145] in which taste quality of solutes was unaffected in various aqueous and mixed solvents.



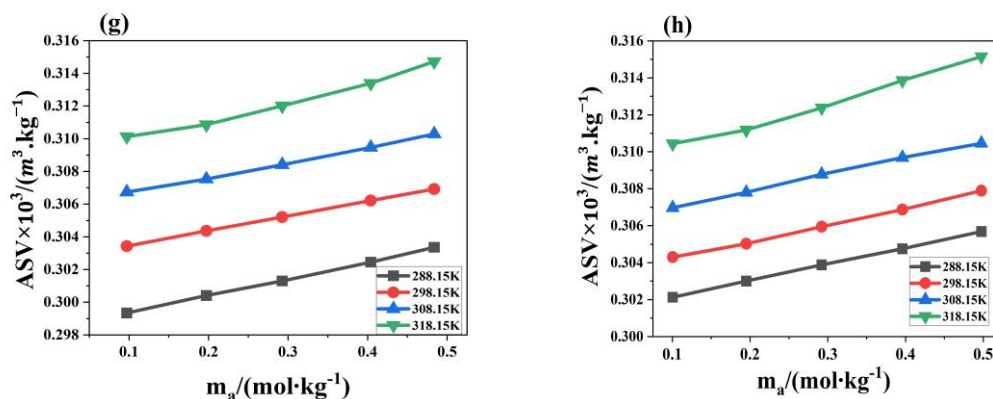


Figure 4.28: ASV plots for $\text{NaNO}_3/\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ in aqueous Choline Salicylate; [(a) NaNO_3 + water, (b) $0.03 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate + NaNO_3 , (c) $0.06 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate + NaNO_3 (d) $0.09 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate + NaNO_3 ,], e) $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ + water, (f) $0.03 \text{ mol}\cdot\text{kg}^{-1}$ Choline salicylate + $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$, (g) $0.06 \text{ mol}\cdot\text{kg}^{-1}$ Choline salicylate + $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ (h) $0.09 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate + $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$,].

Isobaric thermal expansion coefficient (α_p)

The equation 4.14 used to calculate α_p . Table 4.47 shows, α_p values. The positive α_p values demonstrates that there exists a strong interaction between $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7/\text{NaNO}_3$ and aqueous choline salicylate solutions [143] [146] [147]. The data reveal that for sodium nitrate, α_p increases with increasing temperature, indicating larger volume expansion at high temperatures. Conversely, trisodium citrate follows a declining trend due to increased solute-solvent interactions with restricted molecular movement and limited expansion. The differing behaviour of the two solutes can be correlated with their ionic character, hydration, and the degree of intermolecular interaction with choline salicylate. Sodium nitrate, with comparatively weaker ion-dipole interactions, has larger thermal expansion, while sodium citrate, with its more ordered hydrogen-bonded network, has smaller expansion. Such differences in thermal expansion behaviour emphasize the influence of solute properties on the solution's physicochemical properties. The rising α_p values for sodium nitrate imply that its solutions are more sensitive to temperature, while the falling values for trisodium citrate imply structural stiffness as a result of enhanced molecular interactions. [148,149].

Table 4.45: V_{AB} , K_{AB} and V_{ABB} , K_{ABB} coefficients of (NaNO_3 and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) salts present in aqueous solutions of choline salicylate.

T/K	$V_{AB} \times 10^6 / (m^3 \cdot \text{mol}^{-2} \cdot \text{kg})$	$V_{ABB} \times 10^6 / (m^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2)$	$K_{AB} \times 10^6 / (m^3 \cdot \text{mol}^{-2} \cdot \text{kgGPa}^{-1})$	$K_{ABB} \times 10^6 / (m^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2 \text{GPa}^{-1})$
Sodium Nitrate				
288.15	74.79	-184.30	38.06	-444.90
298.15	15.21	434.30	6.57	64.82
308.15	8.52	169.74	3.28	122.17
318.15	-25.45	153.20	10.10	27.17
Trisodium Citrate				
288.15	160.81	-2070.74	37.40	-421.16
298.15	111.93	-1584.54	6.94	61.66
308.15	78.04	-1107.92	1.82	150.58
318.15	47.16	-644.13	9.16	51.85

^a m_B is the molality of choline salicylate is given per kg of pure water.

Table 4.46 ASV for sodium nitrate and trisodium citrate in water and aqueous solutions of choline salicylate.

$^a m_A / (\text{mol} \cdot \text{kg}^{-1})$	$ASV \times 10^3 / (\text{m}^3 \cdot \text{kg}^{-1})$				$^a m_A / (\text{mol} \cdot \text{kg}^{-1})$	$ASV \times 10^3 / (\text{m}^3 \cdot \text{kg}^{-1})$			
	288.15K	298.15K	308.15K	318.15K		288.15K	298.15K	308.15K	318.15K
Sodium Nitrate + 0.00 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate					Trisodium Citrate + 0.00 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate				
0.08744	0.27775	0.30521	0.32376	0.35194	0.08734	0.28592	0.29429	0.30062	0.30642
0.18432	0.28761	0.31170	0.32961	0.35473	0.18432	0.28660	0.29604	0.30212	0.30833
0.28217	0.30058	0.31602	0.33142	0.35616	0.28550	0.28726	0.29716	0.30348	0.31016
0.39429	0.30442	0.31868	0.33670	0.35907	0.38023	0.28839	0.29838	0.30489	0.31215
0.48416	0.30507	0.32545	0.34249	0.36359	0.47605	0.28957	0.29901	0.30633	0.31407
Sodium Nitrate + 0.03 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate					Trisodium Citrate + 0.03 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate				
0.10205	0.29080	0.30746	0.32715	0.35421	0.10020	0.29805	0.30230	0.30571	0.30917
0.20083	0.29694	0.31321	0.33015	0.35517	0.19263	0.29921	0.30317	0.30671	0.31041
0.30085	0.30263	0.31676	0.33413	0.35622	0.28933	0.30037	0.30407	0.30778	0.31180
0.40169	0.30800	0.32163	0.33647	0.36003	0.39530	0.30166	0.30504	0.30892	0.31317
0.49193	0.30976	0.32261	0.33856	0.36079	0.49600	0.30292	0.30606	0.30991	0.31442
Sodium Nitrate + 0.06 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate					Trisodium Citrate + 0.06 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate				

0.09643	0.32560	0.33313	0.34058	0.34721	0.09724	0.29934	0.30343	0.30674	0.31013
0.19994	0.32874	0.33577	0.34277	0.34871	0.19724	0.30041	0.30436	0.30753	0.31086
0.31793	0.33393	0.34022	0.34620	0.35111	0.29255	0.30130	0.30521	0.30841	0.31201
0.39181	0.33710	0.34292	0.34862	0.35250	0.40389	0.30245	0.30622	0.30947	0.31339
0.48364	0.34017	0.34613	0.35114	0.35428	0.48379	0.30336	0.30692	0.31029	0.31472
Sodium Nitrate + 0.09 mol · kg⁻¹ choline salicylate					Trisodium Citrate + 0.09 mol · kg⁻¹ choline salicylate				
0.10652	0.32769	0.33373	0.34156	0.34841	0.10043	0.30213	0.30430	0.30697	0.31044
0.19729	0.33012	0.33652	0.34483	0.35105	0.19511	0.30300	0.30502	0.30780	0.31118
0.30981	0.33472	0.34070	0.34991	0.35523	0.29212	0.30388	0.30595	0.30878	0.31238
0.39501	0.33832	0.34419	0.35341	0.35897	0.39598	0.30475	0.30687	0.30969	0.31386
0.49257	0.34230	0.34785	0.35893	0.36410	0.49757	0.30568	0.30789	0.31046	0.31515

standard uncertainties u is u(m)=0.01(mol·kg⁻¹), u(T)= 0.001K, u(ASV)=0.006×10⁻³/(m³·kg⁻¹).

Table 4.47 α_p for NaNO₃ and C₆H₅Na₃O₇ in aqueous choline salicylate solutions.

$m_b / (\text{mol} \cdot \text{kg}^{-1})$	$\alpha_p \times 10^3 / (K^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate				
0.03	5.02	6.29	7.37	8.16
0.06	2.52	2.42	2.33	2.25
0.09	1.95	2.01	2.07	2.12
Trisodium Citrate				
0.03	1.56	1.32	1.09	0.86
0.06	1.47	1.24	1.02	0.80
0.09	0.65	0.79	0.92	1.02

standard uncertainties, $u(\alpha_p) = 0.032 \times 10^{-3} / (K^{-1})$, $u(T) = \pm 0.001 K$, $u(p) = 0.01 \text{ MPa}$

Relative Association (R_a)

It can be determined using the equation 4.15. The values of R_a at different molalities are presented in **Table 4.48**. From the values, it is observed that for sodium nitrate solutions, R_a increases with increasing molality across all temperatures. This increase suggests that sodium nitrate weakens the intermolecular interactions within the solvent, leading to greater solvent expansion and a rise in relative association. The structure-breaking nature of sodium nitrate results in reduced hydrogen bonding among choline salicylate molecules, thereby increasing molecular mobility. Conversely, trisodium citrate solutions exhibit a decreasing trend in R_a with increasing molality, indicating stronger solute-solvent interactions that limit molecular mobility and restrict solvent expansion. The presence of multiple carboxylate groups in sodium citrate enhances hydrogen bonding with the solvent, leading to a more structured solution. Additionally, temperature plays a significant role in influencing R_a . As temperature increases, the values of R_a generally decrease, which can be attributed to the weakening of intermolecular forces due to thermal agitation. At elevated temperatures, solute-solvent interactions are reduced, leading to greater molecular dissociation and a decrease in relative association. These observations suggest that sodium nitrate exhibits structure-breaking behaviour, whereas trisodium citrate exhibits structure-making behaviour under the investigated conditions, reinforcing the

solvent structure and reducing free volume. The observed difference mainly arises from the nature of the anions. The nitrate ion (NO_3^-) possesses a lower hydration ability and interacts more weakly with surrounding water molecules. Consequently, it disturbs the hydrogen-bonded water network, increases molecular mobility, and promotes solvent expansion, resulting in structure-breaking behaviour. In contrast, the citrate ion ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), owing to its three carboxylate groups and high charge density, exhibits stronger hydration and extensive ion–dipole interactions with water molecules. These interactions reinforce the hydrogen-bonded solvent structure, reduce free volume, and promote structure-making behaviour. Therefore, the contrasting behaviour of sodium nitrate and trisodium citrate is primarily governed by the hydration characteristics and water-structuring abilities of their respective anions. The variations in R_a suggest that the nature of solute-solvent interactions significantly influences the overall stability and organization of the solution [93,94].

Relaxation Strength (r_s)

The relaxation strength was evaluated by using the equation 4.16. The values of r_s at various molalities and temperatures are given in **Table 4.48**. The data reveal that r_s decreases with increasing molality of NaNO_3 , indicating that NaNO_3 enhances molecular motion and disrupts intermolecular interactions. The decrease in r_s suggests that NaNO_3 weakens the hydrogen-bonded network within choline salicylate, thereby reducing resistance to ultrasonic wave propagation. In contrast, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ solutions show an initial increase in r_s at lower concentrations, followed by a decreasing trend at higher concentrations. This behaviour suggests that at low concentrations, trisodium citrate increases solute-solvent interactions, which enhance relaxation strength. But at high concentrations, the development of a close molecular network decreases energy dissipation, causing smaller r_s values. Temperature also significantly affects relaxation strength. As the temperature increases, r_s decreases for all the solutions. This reduction can be explained by the weakening of intermolecular forces at higher temperatures, lowering resistance to ultrasonic perturbation and resulting in lower values of relaxation strength. A comparison of $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ and NaNO_3 solutions shows that $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ has higher r_s values than NaNO_3 , indicating stronger solute-solvent interactions and a more ordered molecular environment. The higher relaxation strength

observed for trisodium citrate originates from the combined effect of ion–dipole interactions and hydrogen bonding. The multidentate citrate ion, containing three carboxylate groups, possesses a high hydration ability and forms strong ion–dipole interactions with surrounding water molecules while simultaneously reinforcing the hydrogen-bonded solvent network. This interpretation is further supported by the FTIR results **figure 4.29**, where the pronounced broadening and red shift of the O–H stretching band together with the larger shifts in the COO^- stretching bands indicate stronger hydrogen bonding and sodium-mediated coordination in the trisodium citrate system compared with sodium nitrate. Therefore, the higher r_s values arise from the cooperative contribution of electrostatic hydration and hydrogen-bond network reinforcement rather than from a single interaction mechanism. These results show that sodium nitrate solutions allow for higher molecular mobility, which decreases relaxation strength, whereas trisodium citrate solutions create more ordered networks that are resistant to ultrasonic perturbations. The differences in relaxation strength observed point to the central role of solute characteristics in modifying solvent dynamics and demonstrate the importance of such studies in elucidating molecular interactions in complex solutions [96–99].

FTIR study

The ATR (Attenuated Total Reflectance) method was employed in the FTIR spectroscopic study to examine binary and ternary mixtures of choline salicylate over the range $400\text{--}4000\text{ cm}^{-1}$, as this technique provides insights into hydrogen bonding, ion pairing, and other molecular interactions as shown in **figure 4.29**. Peak positions were assigned based on literature values for pure aqueous choline salicylate, sodium nitrate, trisodium citrate, and water, as well as experimentally recorded spectra of the individual components (controls), to ensure accurate functional group identification [150–153]. FTIR spectra of aqueous choline salicylate at 3 concentrations (0.03 , 0.06 , and $0.09\text{ mol}\cdot\text{kg}^{-1}$) display a broad absorption band around 3400 cm^{-1} , attributed to O–H stretching vibrations of hydrogen-bonded water and solute–water complexes. With increasing choline salicylate concentration, this band broadens and shifts slightly to lower wavenumbers, indicating stronger hydrogen bonding and possible molecular aggregation; the antisymmetric COO^- stretching mode near 1600 cm^{-1} increases in

intensity, reflecting greater solute presence. In ternary mixtures containing $0.03 \text{ mol}\cdot\text{kg}^{-1}$ choline salicylate in aqueous NaNO_3 ($0.1\text{--}0.5 \text{ mol}\cdot\text{kg}^{-1}$), the O–H band narrows and decreases in intensity with increasing nitrate concentration, suggesting disruption of the hydrogen-bond network due to competition for water molecules; COO^- stretching shifts slightly to higher wavenumbers, consistent with Na^+ –salicylate ion pairing, and the nitrate band around 1384 cm^{-1} grows in intensity. By contrast, in ternary mixtures with $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ at the same molality range, the O–H band exhibits pronounced broadening and a clear red shift, indicating extensive rearrangement and strengthening of hydrogen bonding; COO^- stretching modes of both salicylate and citrate shift more markedly, implying stronger coordination via sodium-mediated bridging and hydrogen bonding due to citrate’s polyanionic, multidentate nature. These results demonstrate that NaNO_3 primarily induces ion pairing and weakens hydrogen bonding, whereas $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ causes more complex and stronger interactions, substantially perturbing the solvation structure [154,155].

Table 4.48 Values of Relative Association (R_a) and Relaxation Strength (r_s) with different molalities of salts (sodium nitrate/trisodium citrate) in choline salicylate.

$m_a/(\text{mol}\cdot\text{kg}^{-1})$	Relative Association (R_a)				Relaxation Strength (r_s)			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate in aqueous 0.000 mol·kg ⁻¹ Choline salicylate)								
0.00000	1.00000	1.00000	1.00000	1.00000	0.15981	0.12595	0.09852	0.08197
0.08744	1.00408	1.00392	1.00413	1.00456	0.15359	0.11973	0.09399	0.07725
0.18432	1.00882	1.00879	1.00876	1.00901	0.14895	0.11653	0.09018	0.07337
0.28217	1.01342	1.01337	1.01333	1.01329	0.14486	0.11222	0.08615	0.06874
0.39429	1.01880	1.01892	1.01847	1.01836	0.14053	0.10917	0.08213	0.06510
0.48416	1.02311	1.02275	1.02231	1.02200	0.13709	0.10505	0.07848	0.06097
Sodium Nitrate in aqueous 0.03 mol·kg ⁻¹ Choline salicylate								
0.00000	1.00000	1.00000	1.00000	1.00000	0.14559	0.12129	0.09571	0.07603
0.10205	1.00571	1.00515	1.00501	1.00494	0.14370	0.11716	0.09160	0.07274
0.20083	1.01097	1.00994	1.00976	1.00948	0.14146	0.11310	0.08790	0.06884
0.30085	1.01613	1.01474	1.01444	1.01390	0.13914	0.10929	0.08417	0.06443

0.40169	1.02110	1.01940	1.01897	1.01826	0.13636	0.10542	0.07985	0.06045
0.49193	1.02558	1.02354	1.02293	1.02222	0.13402	0.10166	0.07596	0.05718

Sodium Nitrate in aqueous 0.06 mol·kg⁻¹ Choline salicylate

0.00000	1.00000	1.00000	1.00000	1.00000	0.14169	0.11848	0.09223	0.07210
0.09643	1.00507	1.00474	1.00487	1.00474	0.13970	0.11504	0.08968	0.06910
0.19994	1.01030	1.00956	1.00973	1.00964	0.13720	0.11061	0.08568	0.06550
0.31793	1.01607	1.01495	1.01523	1.01512	0.13436	0.10598	0.08178	0.06161
0.39181	1.01961	1.01823	1.01837	1.01848	0.13267	0.10305	0.07823	0.05916
0.48364	1.02385	1.02216	1.02235	1.02255	0.13009	0.09911	0.07454	0.05598

Sodium Nitrate in aqueous 0.09 mol·kg⁻¹ Choline salicylate

0.00000	1.00000	1.00000	1.00000	1.00000	0.13752	0.11295	0.08640	0.06535
0.10652	1.00561	1.00547	1.00552	1.00545	0.13551	0.11041	0.08447	0.06328
0.19729	1.01028	1.00857	1.00870	1.00983	0.13380	0.10718	0.08197	0.06077
0.30981	1.01593	1.01379	1.01394	1.01520	0.13183	0.10320	0.07859	0.05826
0.39501	1.02005	1.01754	1.01779	1.01904	0.13007	0.09973	0.07597	0.05580
0.49257	1.02458	1.02175	1.02194	1.02330	0.12769	0.09584	0.07253	0.05313

Trisodium Citrate in aqueous 0.000 mol·kg⁻¹ Choline salicylate

0.00000	1.00000	1.00000	1.00000	1.00000	0.15981	0.12595	0.09852	0.08197
0.08734	1.01198	1.01176	1.01195	1.01254	0.13959	0.10469	0.07829	0.06158
0.18432	1.02479	1.02464	1.02499	1.02530	0.11612	0.08195	0.05644	0.03846
0.28550	1.03766	1.03776	1.03809	1.03834	0.09062	0.05826	0.03280	0.01497
0.38023	1.04922	1.04945	1.05034	1.05062	0.06584	0.03466	0.01254	-0.00440
0.47605	1.06070	1.06161	1.06206	1.06230	0.04122	0.01385	-0.00994	-0.02631

Trisodium Citrate in aqueous 0.03 mol·kg⁻¹ Choline salicylate

0.00000	1.00000	1.00000	1.00000	1.00000	0.14559	0.12129	0.09571	0.07603
0.10020	1.01399	1.01362	1.01375	1.01413	0.12511	0.09872	0.07357	0.05594
0.19263	1.02620	1.02577	1.02601	1.02605	0.10427	0.07730	0.05255	0.03300
0.28933	1.03859	1.03791	1.03851	1.03864	0.08207	0.05347	0.03054	0.01159
0.39530	1.05161	1.05109	1.05206	1.05225	0.05677	0.02858	0.00760	-0.01078
0.49600	1.06338	1.06371	1.06439	1.06463	0.03131	0.00735	-0.01540	-0.03321

Trisodium Citrate in aqueous 0.06 mol·kg⁻¹ Choline salicylate

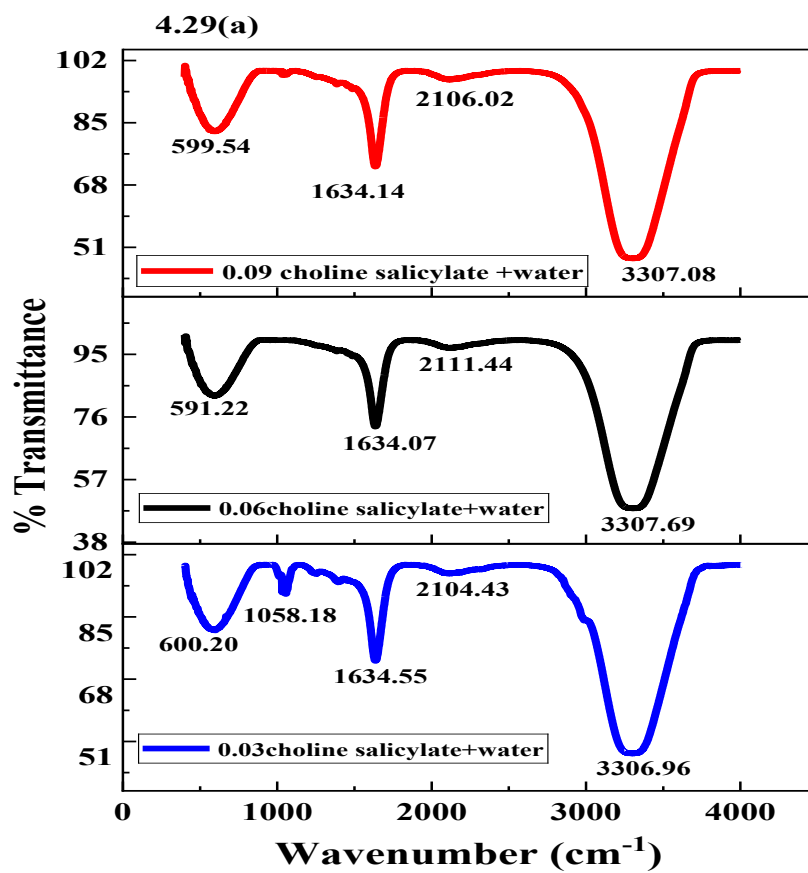
0.00000	1.00000	1.00000	1.00000	1.00000	0.14169	0.11848	0.09223	0.07210
0.09724	1.01359	1.01329	1.01336	1.01385	0.12196	0.09705	0.07092	0.05345
0.19724	1.02680	1.02624	1.02686	1.02698	0.09951	0.07300	0.04955	0.02990

0.29255	1.03895	1.03822	1.03930	1.03936	0.07736	0.04980	0.02858	0.00863
0.40389	1.05272	1.05217	1.05336	1.05372	0.05134	0.02449	0.00367	-0.01441
0.48379	1.06232	1.06214	1.06282	1.06338	0.03248	0.00740	-0.01638	-0.03292

Trisodium Citrate in aqueous 0.09 mol·kg⁻¹ Choline salicylate

0.00000	1.00000	1.00000	1.00000	1.00000	0.13752	0.11295	0.08640	0.06535
0.10043	1.01412	1.01440	1.01468	1.01494	0.11789	0.09453	0.06920	0.04962
0.19511	1.02663	1.02673	1.02737	1.02748	0.09692	0.07217	0.04852	0.02791
0.29212	1.03881	1.03886	1.03985	1.04006	0.07369	0.04825	0.02619	0.00617
0.39598	1.05190	1.05168	1.05319	1.05341	0.05084	0.02353	0.00410	-0.01559
0.49757	1.06361	1.06422	1.06512	1.06581	0.02439	0.00127	-0.02207	-0.03865

standard uncertainties u is u(m)=0.01(mol·kg⁻¹), u(T)= 0.001K, u(R_a)=0.00121, u(p)=0.01MPa.



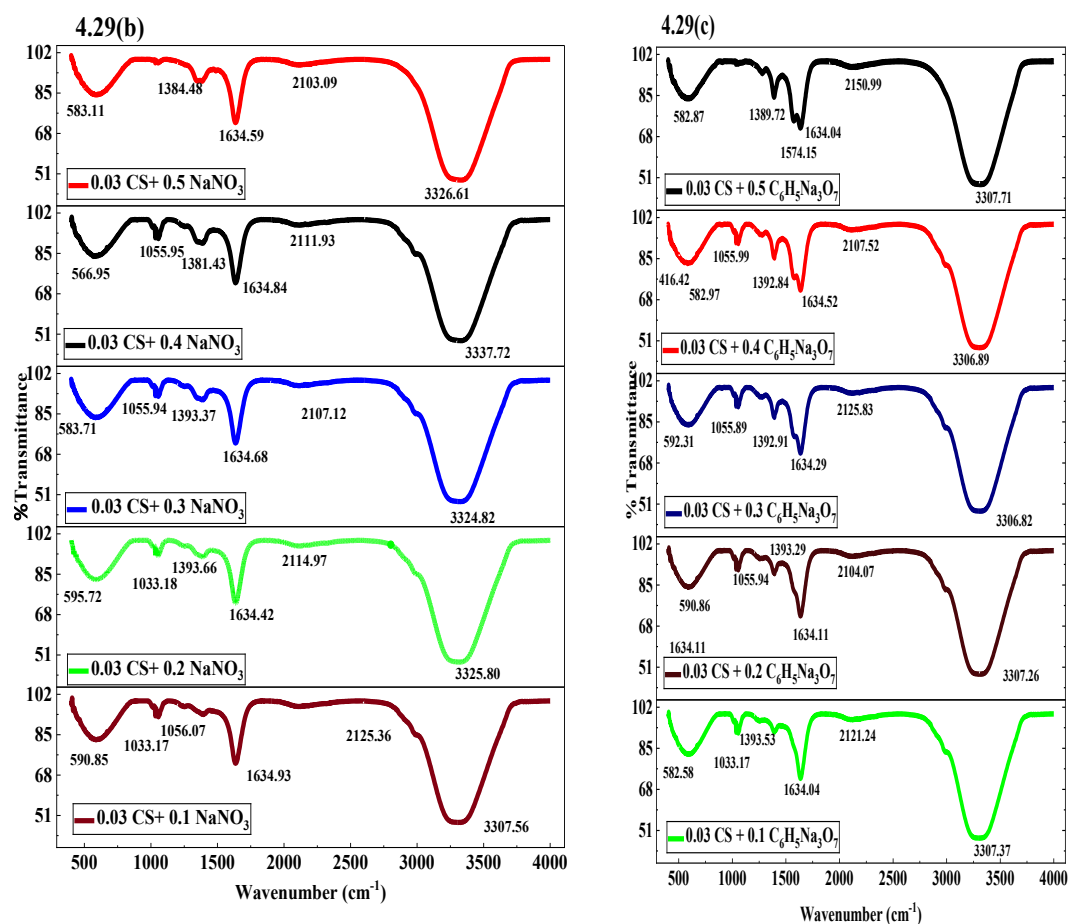


Figure 4.29 FTIR spectra for binary mixture (water + choline salicylate) at three different concentrations; 0.03 (blue), 0.06 (black) and 0.09 (red) in **4.29(a)** and **4.29(b)**, (c) are spectra of ternary mixtures of 0.02 concentration of choline salicylate in sodium nitrate and trisodium citrate at 0.1-0.5 molalities respectively.

Problem 5

Thermophysical and Acoustic Investigation of Molecular Interactions in Choline Salicylate Solutions Containing Sodium Sulphate and Sodium Bicarbonate

In this problem, densities and ultrasonic velocity were measured for the sodium bicarbonate and sodium sulphate in aqueous Choline Salicylate at different concentrations.

Density and ultrasonic velocity

The measured density and ultrasonic velocity values of choline salicylate with sodium bicarbonate and sodium sulphate are presented in **Table 4.49**. These data show that density increases with higher concentrations of choline salicylate and salts, indicating strong solute–solvent interactions as shown in **Figure 4.30**. In contrast, density decreases with increasing temperature, which is typical for aqueous systems due to thermal expansion. For comparison, the density and ultrasonic data of the binary solutions—choline salicylate + water [111,112] (**Figure 4.23(a)(b)**), sodium sulphate + water [105] [106] [107] (**Figure 4.16(a)(b)**), and sodium bicarbonate + water [53] (**Figure 4.8(b)**)—were plotted against the corresponding literature values. The observed trends in these binary systems agree well with previously reported data, confirming the reliability of the present measurements.

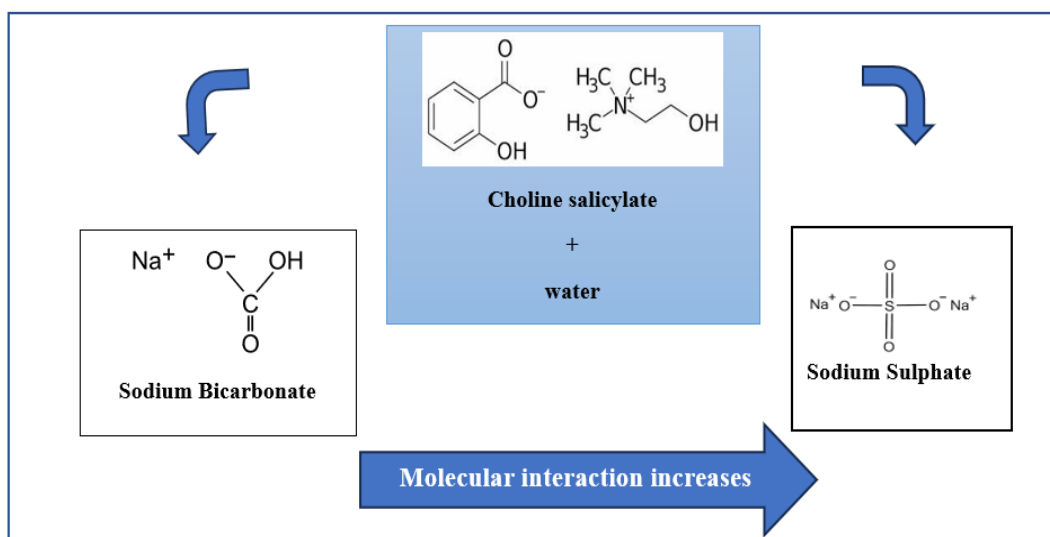


Figure 4.30: sodium bicarbonate/sodium sulphate in aqueous choline salicylate interaction

Table 4.49: Experimental data of densities, ρ and ultrasonic velocity (c), data for choline salicylate with $\text{Na}_2\text{SO}_4 / \text{NaHCO}_3$.

$^a m_A / (\text{mol} \cdot \text{kg}^{-1})$	$\rho \times 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$				$c / (\text{m} \cdot \text{s}^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium sulphate + 0.00 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate								
0.00000	0.99926	0.99704	0.99404	0.99036	1466.59	1495.85	1519.14	1536.02
0.09136	1.01068	1.00834	1.00521	1.00141	1480.92	1509.9	1532.18	1548.23
0.20034	1.02410	1.02162	1.01837	1.01445	1496.62	1523.6	1544.23	1560.09
0.30305	1.03667	1.03405	1.03069	1.02662	1511.04	1537.84	1558.04	1572.17
0.39442	1.04769	1.04496	1.04146	1.03729	1527.02	1554.15	1572.09	1585.37
0.49751	1.06004	1.05713	1.05349	1.04918	1541.01	1566.07	1584.88	1597.67
Sodium sulphate + 0.0590 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate								
0.00000	1.00178	0.99965	0.99654	0.99234	1475.32	1503.23	1526.43	1541.24
0.09413	1.01334	1.01105	1.00785	1.00352	1491.06	1515.35	1536.98	1552.54
0.19491	1.02562	1.02316	1.01986	1.01539	1506.2	1529.08	1551.29	1565.32
0.29793	1.03808	1.03543	1.03203	1.02748	1519.81	1546	1565.72	1579.64
0.38822	1.04893	1.04611	1.04262	1.03797	1533.05	1558.58	1578.49	1590.84
0.50770	1.06314	1.06014	1.05660	1.05174	1551.53	1575.54	1593.41	1605.64
Sodium sulphate + 0.0688 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate								
0.00000	1.00229	0.99998	0.99690	0.99271	1476.81	1504.83	1527.14	1542.62
0.09784	1.01422	1.01182	1.00864	1.00432	1495.64	1518.32	1539.37	1554.48

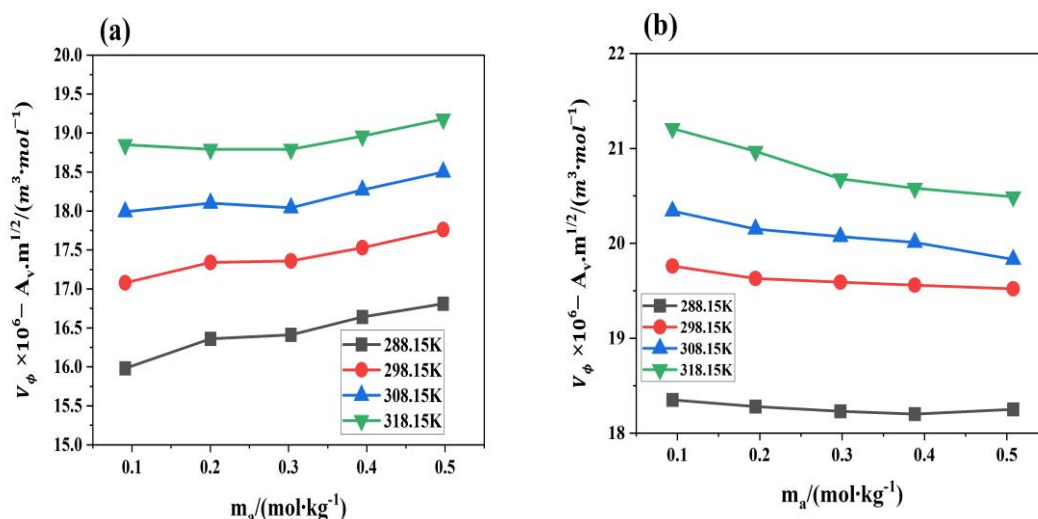
0.19991	1.02662	1.02406	1.02079	1.01633	1510.32	1533.49	1553.49	1568.48
0.29955	1.03863	1.03590	1.03254	1.02797	1525.27	1548.83	1567.99	1581.46
0.39438	1.04996	1.04705	1.04364	1.03897	1540.08	1562.91	1581.49	1593.89
0.47842	1.05992	1.05687	1.05337	1.04866	1556.54	1575.34	1592.61	1605.44
Sodium sulphate + 0.0885 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1.00318	1.00078	0.99797	0.99340	1478.92	1506.93	1529.32	1545.14
0.10946	1.01658	1.01402	1.01110	1.00636	1499.27	1522.13	1543.39	1558.64
0.20754	1.02849	1.02576	1.02276	1.01790	1514.05	1536.58	1556.35	1571.29
0.30786	1.04055	1.03767	1.03460	1.02961	1528.71	1551.46	1570.87	1584.52
0.39680	1.05117	1.04815	1.04501	1.03993	1542.49	1564.29	1583.43	1595.47
0.49283	1.06257	1.05939	1.05618	1.05101	1561.54	1578.32	1596.13	1609.21
Sodium Bicarbonate+ 0.00 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	0.99926	0.99704	0.99404	0.99036	1466.59	1495.85	1519.14	1536.02
0.10313	1.00601	1.00367	1.00058	0.99676	1475.78	1505.00	1526.73	1544.01
0.18524	1.01111	1.00868	1.00549	1.00152	1482.42	1512.09	1532.92	1549.76
0.30886	1.01842	1.01585	1.01257	1.00838	1493.35	1521.81	1542.69	1558.44
0.37932	1.02240	1.01973	1.01634	1.01212	1499.02	1526.91	1548.31	1563.69
0.45128	1.02627	1.02356	1.02003	1.01580	1505.67	1532.57	1553.10	1567.49
Sodium Bicarbonate + 0.0590 $mol \cdot kg^{-1}$ choline salicylate								
0.00000	1.00178	0.99965	0.99654	0.99234	1475.32	1503.23	1526.43	1541.24

0.09702	1.00707	1.00480	1.00198	0.99949	1483.12	1508.76	1530.69	1546.48
0.19336	1.01247	1.01003	1.00712	1.00454	1490.29	1516.26	1536.89	1552.86
0.29746	1.01821	1.01558	1.01261	1.00993	1497.45	1523.68	1544.31	1559.54
0.39665	1.02358	1.02079	1.01774	1.01498	1506.38	1531.49	1550.93	1566.29
0.49097	1.02863	1.02565	1.02256	1.01975	1512.34	1538.43	1558.26	1572.30
Sodium Bicarbonate + 0.0688 mol · kg ⁻¹ choline salicylate								
0.00000	1.00229	0.99998	0.99690	0.99271	1476.81	1504.83	1527.14	1542.62
0.10068	1.00761	1.00539	1.00260	1.00011	1485.16	1511.26	1532.72	1548.15
0.19470	1.01284	1.01047	1.00755	1.00499	1491.89	1518.79	1539.04	1554.87
0.29574	1.01837	1.01585	1.01283	1.01014	1499.91	1526.04	1546.53	1561.09
0.38527	1.02320	1.02055	1.01741	1.01465	1507.29	1533.39	1552.29	1567.49
0.49922	1.02917	1.02648	1.02314	1.02037	1515.72	1541.27	1560.74	1574.39
Sodium Bicarbonate + 0.0885 mol · kg ⁻¹ choline salicylate								
0.00000	1.00318	1.00078	0.99797	0.99340	1478.92	1506.93	1529.32	1545.14
0.09601	1.00775	1.00591	1.00311	1.00034	1486.78	1514.14	1535.04	1551.83
0.20086	1.01354	1.01153	1.00861	1.00575	1495.29	1522.49	1541.69	1557.49
0.30215	1.01906	1.01690	1.01385	1.01092	1502.98	1530.04	1548.77	1563.51
0.39478	1.02406	1.02172	1.01858	1.01557	1510.49	1537.39	1554.59	1569.59
0.48603	1.02886	1.02641	1.02312	1.02008	1516.35	1545.16	1561.91	1575.74

standard uncertainties $u_r(m) = 0.01$, $u(\rho) = 0.00130 \text{ g} \cdot \text{cm}^{-3}$, $u(V_\phi) = 0.33479 \times 10^{-6}/(\text{m}^3 \cdot \text{mol}^{-1})$, $u(T) = 0.01 \text{ K}$.

Apparent Molar volume

The density measurements were used to determine the apparent molar volume (V_ϕ) by using equation 4.1 [156,157], Where M indicates molar mass of the salts, ρ_0 = densities of solvent (water + choline salicylate), and ρ is the densities of the solutions. Densities and V_ϕ values are provided in **Table 4.50**. Furthermore, the data for the electrolytes ($V_\phi - A_V\sqrt{m}$) are shown as a function of molality in **Figure 4.31** which shows the trend of V_ϕ , graphically. Each value is positive and escalate with rising temperature, concentration, and molality of the salts. This increasing trend in V_ϕ with concentration is primarily due to enhanced solute–solute (ion–ion) interactions at higher concentrations. As more solute is added, ions come closer together, intensifying electrostatic interactions that disrupt the hydration shells surrounding the ions. This leads to a loosening of the water structure, causing water molecules to occupy a larger volume. Consequently, the solution expands, reflected in the increase in V_ϕ . The solution density increases with salt concentration due to the greater mass per unit volume but decreases with temperature due to thermal expansion and increased molecular motion. Among the studied systems, sodium sulphate showed a more pronounced increase in V_ϕ , likely due to its higher ionic strength and stronger structure-making ability compared to sodium bicarbonate [158–160].



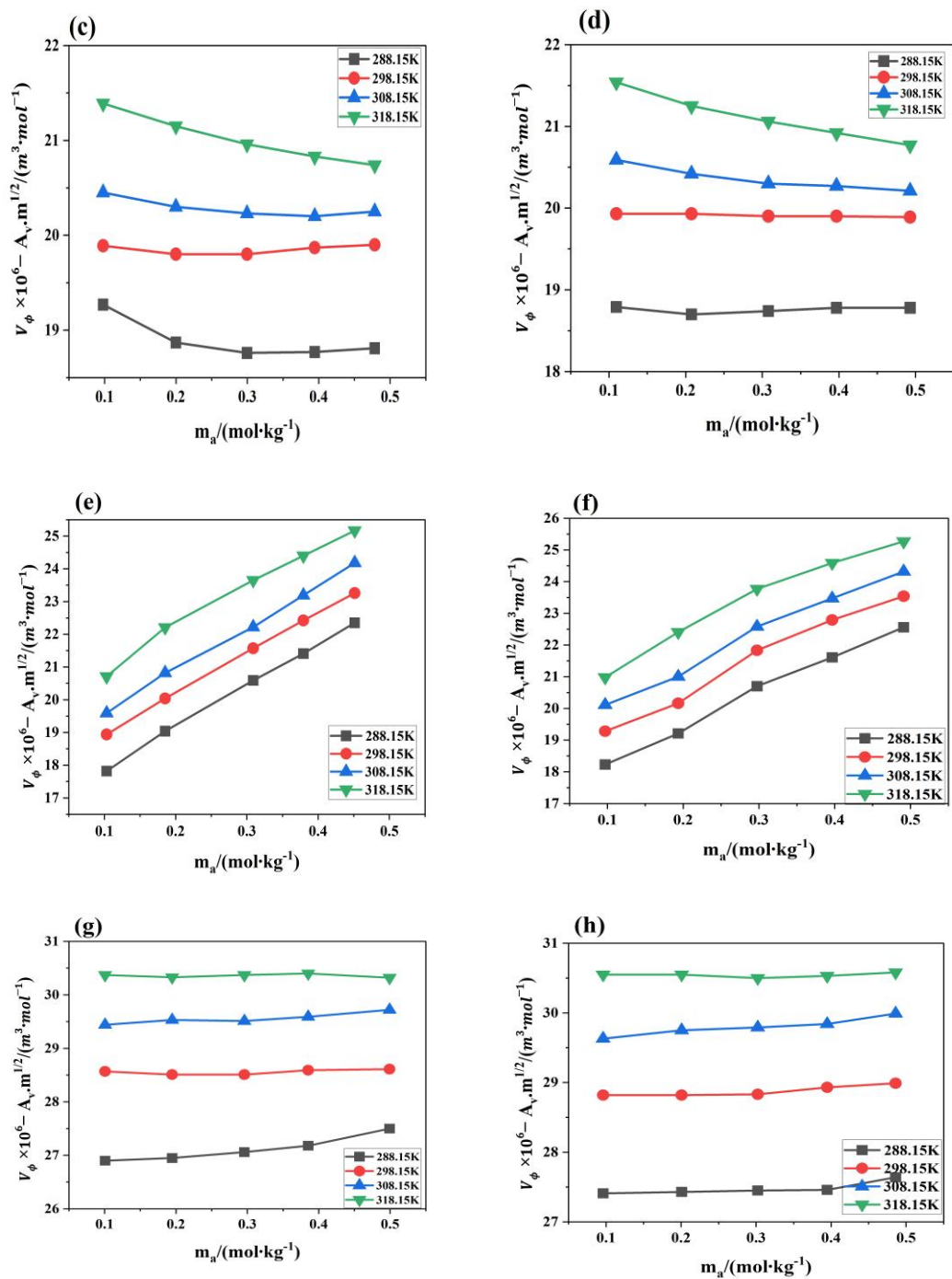


Fig. 4.31. V_ϕ versus m_a (molality) plots for: (a–d) sodium sulphate and (e–h) sodium bicarbonate in H_2O and in aqueous choline salicylate at 0.0590, 0.0688 and 0.0885 $\text{mol} \cdot \text{kg}^{-1}$.

Table 4.50: Measured V_ϕ and $K_{\phi,S}$ for choline salicylate with sodium Bicarbonate/sodium sulphate.

$^a m_A / (mol \cdot kg^{-1})$	$V_\phi \times 10^6 / (m^3 \cdot mol^{-1})$				$\kappa_{\phi,S} \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Sulphate + 0.00 $mol \cdot kg^{-1}$ Choline salicylate								
0.09136	15.98	17.08	17.99	18.85	-44.57	-42.88	-41.64	-40.79
0.20034	16.36	17.34	18.10	18.79	-43.33	-41.82	-40.71	-39.90
0.30305	16.41	17.36	18.04	18.79	-42.06	-40.62	-39.59	-38.89
0.39442	16.64	17.53	18.27	18.96	-40.79	-39.39	-38.51	-37.88
0.49751	16.81	17.76	18.50	19.18	-39.60	-38.37	-37.48	-36.89
Sodium Sulphate + 0.0590 $mol \cdot kg^{-1}$ Choline salicylate								
0.094133	18.35	19.76	20.34	21.21	-43.98	-42.59	-41.40	-40.57
0.194911	18.28	19.63	20.15	20.97	-42.82	-41.56	-40.38	-39.67
0.297928	18.23	19.59	20.07	20.68	-41.63	-40.24	-39.24	-38.56
0.388218	18.20	19.56	20.01	20.58	-40.52	-39.22	-38.25	-37.67
0.507702	18.25	19.52	19.83	20.49	-39.05	-37.90	-37.06	-36.51
Sodium Sulphate + 0.0688 $mol \cdot kg^{-1}$ Choline salicylate								
0.097843	19.27	19.89	20.45	21.39	-43.72	-42.42	-41.27	-40.47
0.199914	18.87	19.80	20.30	21.15	-42.57	-41.30	-40.25	-39.49
0.299552	18.76	19.80	20.23	20.96	-41.33	-40.09	-39.13	-38.47
0.394382	18.77	19.87	20.20	20.83	-40.13	-38.99	-38.08	-37.50
0.478417	18.81	19.90	20.25	20.74	-38.94	-38.03	-37.22	-36.64

Sodium Sulphate + 0.0885 $\text{mol} \cdot \text{kg}^{-1}$ Choline salicylate

0

0.109457	18.79	19.93	20.59	21.54	-43.49	-42.20	-41.04	-40.25
0.20754	18.70	19.93	20.42	21.25	-42.33	-41.11	-40.08	-39.32
0.307862	18.74	19.90	20.30	21.06	-41.11	-39.93	-38.95	-38.29
0.396802	18.78	19.90	20.27	20.92	-40.00	-38.91	-37.98	-37.42
0.492831	18.78	19.89	20.21	20.77	-38.63	-37.83	-37.00	-36.41

Sodium Bicarbonate + 0.00 $\text{mol} \cdot \text{kg}^{-1}$ Choline Salicylate

0.00000

0.10313	17.82	18.94	19.59	20.71	-45.16	-43.42	-42.20	-41.26
0.18524	19.04	20.04	20.82	22.21	-44.72	-42.99	-41.83	-40.94
0.30886	20.59	21.57	22.22	23.65	-43.85	-42.24	-41.11	-40.30
0.37932	21.41	22.42	23.19	24.40	-43.37	-41.82	-40.68	-39.90
0.45128	22.35	23.26	24.18	25.17	-42.85	-41.37	-40.30	-39.58

Sodium Bicarbonate + 0.0590 $\text{mol} \cdot \text{kg}^{-1}$ Choline Salicylate

0.00000

0.09702	18.23	19.28	20.11	20.98	-44.74	-43.25	-42.00	-41.07
0.19336	19.21	20.16	21.00	22.41	-44.31	-42.82	-41.67	-40.75
0.29746	20.70	21.83	22.58	23.77	-43.72	-42.25	-41.12	-40.26
0.39665	21.61	22.79	23.47	24.59	-43.01	-41.64	-40.60	-39.74
0.49097	22.56	23.54	24.32	25.27	-42.49	-41.09	-40.05	-39.28

Sodium Bicarbonate + 0.0688 $\text{mol} \cdot \text{kg}^{-1}$ Choline Salicylate								
0.10068	26.90	28.57	29.44	30.37	-44.65	-43.11	-41.90	-40.99
0.19470	26.95	28.51	29.53	30.33	-44.23	-42.67	-41.55	-40.64
0.29574	27.06	28.51	29.51	30.37	-43.59	-42.12	-41.01	-40.18
0.38527	27.18	28.59	29.59	30.40	-43.00	-41.56	-40.55	-39.71
0.49922	27.50	28.61	29.72	30.32	-42.30	-40.92	-39.91	-39.16
Sodium Bicarbonate + 0.0885 $\text{mol} \cdot \text{kg}^{-1}$ Choline Salicylate								
0.09601	27.41	28.82	29.63	30.55	-44.56	-42.94	-41.77	-40.80
0.20086	27.43	28.82	29.75	30.55	-44.04	-42.46	-41.42	-40.51
0.30215	27.45	28.83	29.79	30.50	-43.43	-41.89	-40.89	-40.06
0.39478	27.46	28.93	29.84	30.53	-42.82	-41.33	-40.43	-39.60
0.48603	27.64	28.99	29.99	30.58	-42.31	-40.75	-39.89	-39.13

standard uncertainties u is $u_r(m) = 0.01$, $u(c) = 2.26 \text{ m} \cdot \text{s}^{-1}$, $u(p) = 0.01 \text{ MPa}$, $u(T) = 0.01 \text{ K}$. Molality of choline salicylate is given as moles per kilogram of pure water.

Partial molar volume

The V_{ϕ}^0 values were obtained by extrapolating the apparent molar volume data to infinite dilution using the Redlich-Mayer equation 4.2 [76,161]. The calculated V_{ϕ}^0 are listed in **Table 4.51** and presented in **figure 4.32**. The positive V_{ϕ}^0 values at all temperatures indicate favourable solute–solvent interactions between the salts and the choline salicylate–water solvent. The observed increase in V_{ϕ}^0 with temperature may reflect a weakening of structured hydration shells and a corresponding increase in solute–solvent volume contributions. The slope S_V quantifies solute–solute (ion–ion) interactions. Its positive values suggest hydrophilic interactions, while the magnitude of S_V reflects how strongly these interactions affect the volumetric behaviour. Compared to V_{ϕ}^0 , the generally moderate S_V values indicate that both solute–solute and solute–solvent interactions are significant, though the dominance may vary with salt type and temperature. These findings align with the co-sphere overlap model, which suggests that as solute concentration increases, overlapping hydration shells and ion pairing modify the solution structure. The presence of choline salicylate further alters the local solvent environment, influencing both solvation and interionic interactions, thus leading to systematic trends in the volumetric parameters [162–164].

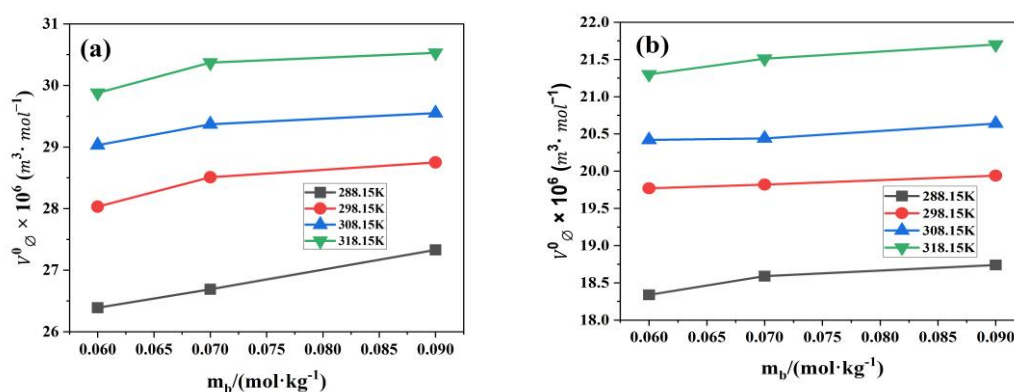


Fig. 4.32. V_{ϕ}^0 of (a) sodium bicarbonate and (b) sodium sulphate in choline salicylate solutions across different temperatures

Table 4.51: Calculated V_ϕ^0 values along with experimental slope (S_V^*) for choline salicylate with sodium Bicarbonate/sodium sulphate.

$^a m_B / (mol \cdot kg^{-1})$	$V_\phi^0 \times 10^6 (m^3 \cdot mol^{-1})$				$S_V^* \times 10^6 (m^3 \cdot kg \cdot mol^{-2})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Bicarbonate								
0.00	16.57(± 0.08)	17.71(± 0.05)	18.31(± 0.10)	19.65(± 0.24)	12.86(± 0.27)	12.39(± 0.16)	12.94(± 0.32)	12.52(± 0.77)
0.0590	26.39(± 0.03)	28.03(± 0.05)	29.03(± 0.07)	29.88(± 0.03)	1.14(± 0.09)	0.94(± 0.16)	0.06(± 0.23)	-0.25(± 0.09)
0.0688	26.69(± 0.08)	28.51(± 0.04)	29.37(± 0.04)	30.37(± 0.04)	1.45(± 0.25)	0.16 (± 0.14)	0.63(± 0.14)	-0.04(± 0.12)
0.0885	27.33(± 0.06)	28.75(± 0.04)	29.55(± 0.03)	30.53(± 0.03)	0.49(± 0.19)	0.45 (± 0.13)	0.84(± 0.11)	0.03(± 0.10)
Sodium sulphate								
0.00	15.86(± 0.08)	16.95(± 0.06)	17.83(± 0.11)	18.67(± 0.12)	1.94(± 0.25)	1.54(± 0.20)	1.17(± 0.33)	0.80(± 0.36)
0.0590	18.34(± 0.04)	19.77(± 0.03)	20.42(± 0.08)	21.30(± 0.08)	-0.27(± 0.13)	-0.55(± 0.11)	-1.15(± 0.11)	-1.77(± 0.27)
0.0688	18.59(± 0.06)	19.82(± 0.05)	20.44(± 0.07)	21.51(± 0.04)	0.09(± 0.18)	0.08(± 0.16)	-0.54(± 0.22)	-1.70(± 0.15)
0.0885	18.74(± 0.04)	19.94(± 0.01)	20.64(± 0.05)	21.70(± 0.05)	0.05(± 0.13)	-0.11(± 0.01)	-0.96(± 0.16)	-1.96(± 0.16)

standard uncertainties u is $u(m) = 0.01$, $u(V_\phi^0) = \pm 0.01 \times 10^{-6} (m^3 \cdot mol^{-1})$, $u(S_V^*) = 1.47 \times 10^{-6} (m^3 \cdot kg \cdot mol^{-2})$.

Partial molar volume of transfer (ΔV_{ϕ}^0)

This volume change can be present mathematically as in equation 4.3. These values, listed in **Table 4.52**. The consistently positive ΔV_{ϕ}^0 values indicate that the presence of choline salicylate modifies the solvent structure around the ions, likely weakening the hydration shell due to co-solute interactions. This leads to the release of tightly bound H₂O molecules into the bulk, resulting in a net increase in system volume. The increase in ΔV_{ϕ}^0 with rising temperature reflects the progressive disruption of the H-bonded network of H₂O, which amplifies the effect of choline salicylate on solvation dynamics. These observations are consistent with the co-sphere overlap model, suggesting that choline salicylate alters the immediate hydration environment of the solute via preferential interactions, promoting structural modification in the solvent [165,166].\

Table 4.52: Calculated values of ΔV_{ϕ}^0 for choline salicylate with sodium Bicarbonate/sodium sulphate.

$^a m_b / (mol \cdot kg^{-1})$	$\Delta V_{\phi}^0 \times 10^6 (m^3 \cdot mol^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Sodium Bicarbonate				
0.0590	9.81	10.33	10.72	10.22
0.0688	10.12	10.81	11.06	10.72
0.0885	10.76	11.04	11.24	10.88
Sodium Sulphate				
0.0590	2.48	2.82	2.59	2.63
0.0688	2.73	2.87	2.61	2.84
0.0885	2.88	2.99	2.82	3.03

standard uncertainties u , is $u(m_b) = 0.01$, $u(\Delta V_{\phi}^0) = 0.09 \times 10^{-6} / (m^3 \cdot mol^{-1})$, $u(p) = 0.01 \text{ MPa}$, $u(T) = 0.01 \text{ K}$.

Temperature dependent partial molar volume

The experimental V_{ϕ}^0 values were fitted to the polynomial equation 4.4. Here $T_{ref} = 298.15\text{K}$. The a, b, c for both solutes describes how the partial molar volumes vary with temperature, are provided in **table 4.53**. The fit quality was assessed by calculating the relative deviation (σ) between experimental and calculated V_{ϕ}^0 values, with very low deviations and high R^2 values confirming the reliability of the polynomial model equation 4.5, with, $Y = V_{\phi}^0$, the polynomial equation fitted to the data demonstrates very low deviation values, as indicated by the R^2 values, confirming that it accurately represents the relationship [71]. The primary objective of evaluating the V_{ϕ}^0 data is to derive the partial molar expansibilities, which are determined using the equation 4.6 [70,72]. The partial molar expansibility at infinite dilution, E_{ϕ}^0 , provides critical insights into the solute-solvent dynamics within the mixture. The ability of a solute to induce structural organization or disintegration within a solution medium can be assessed through a corresponding thermodynamic equation 4.7. The calculated E_{ϕ}^0 values for choline salicylate with both sodium bicarbonate and sodium sulphate are summarized in **Table 4.54**. To further probe the solution structure, the temperature dependence of the expansibility, $(\partial E_{\phi}^0 / \partial T)_p$, was analysed. A positive or slightly negative value of this derivative reflects structure-promoting effects, whereas strongly negative values imply disruption of the solvent structure. As shown in **Table 4.54**, the observed E_{ϕ}^0 and $(\partial E_{\phi}^0 / \partial T)_p$ values for both salt systems demonstrate predominantly structure-making characteristics for choline salicylate in these ternary mixtures, reflecting strong solute-solvent interactions and a tendency to enhance the organization of the solvent network with increasing temperature [73,74].

Table 4.53: Calculated values for empirical parameters for choline salicylate with sodium Bicarbonate/sodium sulphate.

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$a \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$	$b \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R^2	ARD
Sodium Bicarbonate					
0.0590	26.59257	0.58828	-0.02523	0.999	0.14814
0.0688	27.49992	0.60433	-0.02637	0.999	0.00000
0.0885	28.46679	0.58295	-0.02515	0.999	0.11351
Sodium Sulphate					
0.0590	19.34883	0.15774	-0.00675	0.999	0.04483
0.0688	20.00976	0.14434	-0.00596	0.999	0.00000
0.0885	20.94611	0.15404	-0.00611	0.999	0.02808

$^a m_b$ - molality of aqueous choline salicylate is given per kg of pure water.

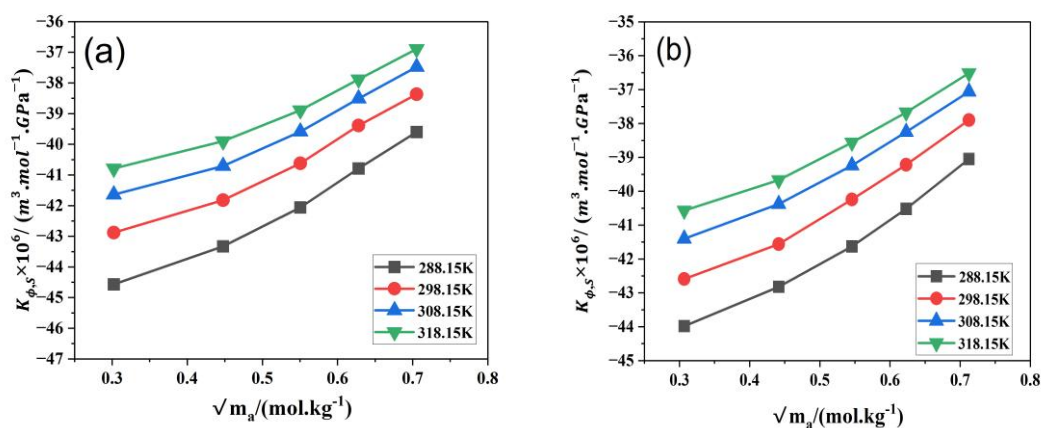
Table 4.54: Calculated E_{ϕ}^0 values for choline salicylate with sodium Bicarbonate/sodium sulphate.

$^a m_b \text{ (mol} \cdot \text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p \text{ / (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	288.15K	298.15K	308.15K	318.15K	
Sodium Bicarbonate					
0.0590	1.09283	0.58828	0.08372	-0.42083	-0.05046
0.0688	1.13170	0.60433	0.07696	-0.45041	-0.05274
0.0885	1.08602	0.58295	0.07989	-0.42317	-0.05031
Sodium Sulphate					
0.0590	0.29284	0.15774	0.02264	-0.11246	-0.01351
0.0688	0.26356	0.14434	0.02512	-0.09409	-0.01192
0.0885	0.27630	0.15404	0.03178	-0.09047	-0.01223

standard uncertainties u is $u(E_{\phi}^0) = 0.005 \times 10^{-6} / (m^3 \cdot mol^{-1} \cdot K^{-1})$, $u(\frac{\partial E_{\phi}^0}{\partial T}) = 0.00055 / (m^3 \cdot mol^{-1} \cdot K^{-2})$, $u(T) = 0.01K$.

Apparent molar isentropic compression

Using ultrasonic velocity values, the k_s (isentropic compressibility) of each solution was computed according to the Newton–Laplace equation 4.9. To further investigate solute–solvent interactions, the $K_{\phi,s}$ was computed by the equation 4.8. The measured values of the sound speed and the calculated $K_{\phi,s}$ for choline salicylate with sodium bicarbonate and sodium sulphate are presented in Table 4.50 (Figure 4.33). The results reveal a clear trend: the speed of sound increases with both increasing solute concentration and temperature, which is indicative of enhanced solute–solvent interactions and a more structured solution environment[76]. Conversely, the $K_{\phi,s}$ values become more negative with decreasing concentration, reflecting the formation of a tightly bound hydration shell around the solute ions and a decrease in the compressibility of the solution. These observations are consistent with previous literature reports on similar aqueous systems, which have shown that the addition of ionic or hydrophilic solutes typically leads to stronger cohesive forces and a more structured, less compressible solution matrix. The trends observed in this study confirm that choline salicylate, in the presence of sodium bicarbonate or sodium sulphate, significantly influences the acoustic and compressibility properties of the solution, underscoring the importance of solute–solvent interactions in determining the physicochemical behaviour of such systems [76–79].



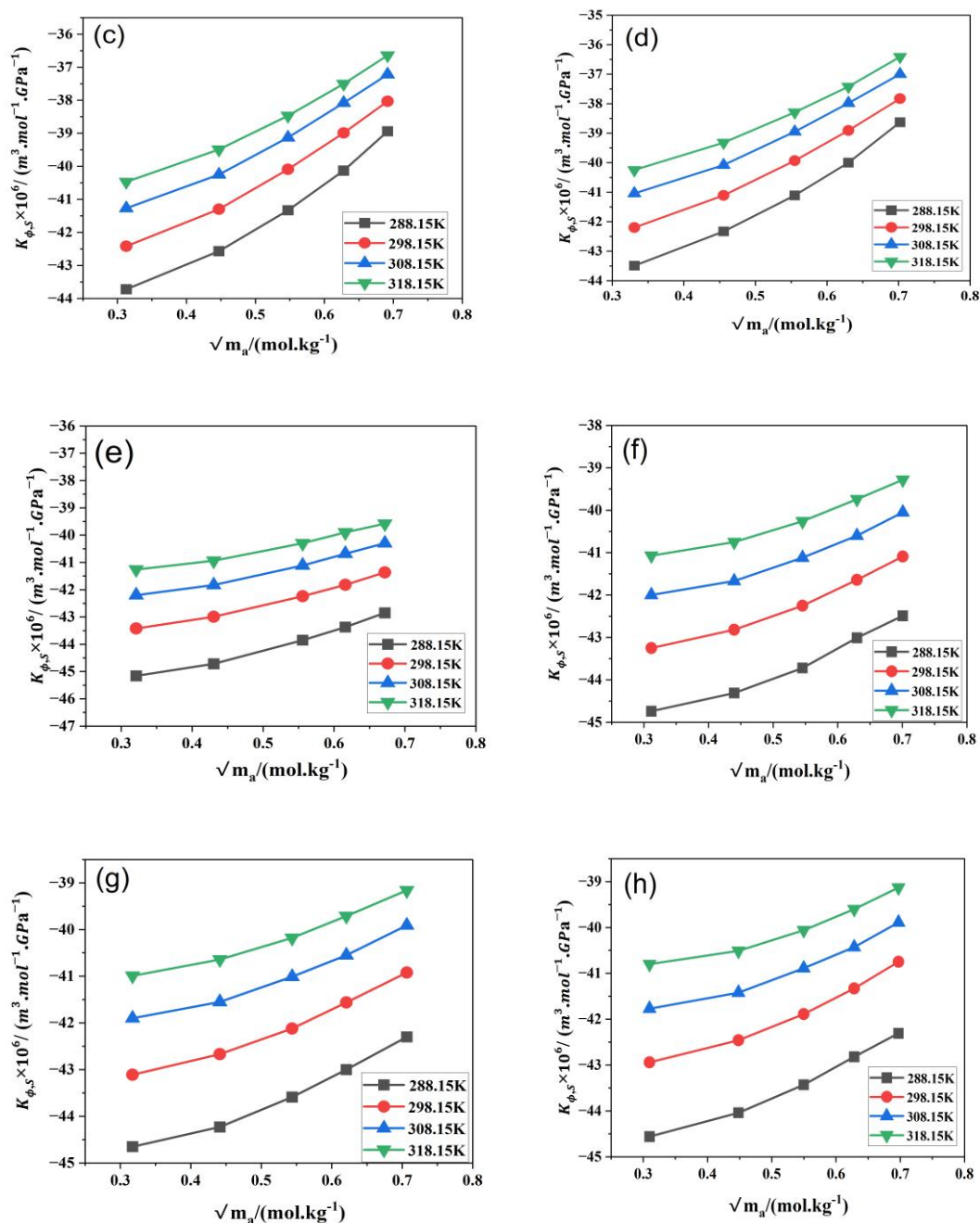


Fig. 4.33. Plots of $K_{\phi,S}$ versus molality for: (a–d) sodium sulphate and (e–h) sodium bicarbonate in H_2O and in choline salicylate aqueous solutions at 0.0590, 0.0688 and 0.0885 $\text{mol} \cdot \text{kg}^{-1}$.

Partial molar and transfer isentropic compressibility

In this study, $K_{\phi,S}^0$ (partial molar isentropic compressibility) was determined for Na_2SO_4 and $NaHCO_3$ in aqueous choline salicylate solutions by extrapolating the $K_{\phi,S}$

versus $\sqrt{m}$ (m is molality) to infinite dilution, according to the Redlich–Mayer equation 4.10. Here S_K^* is an empirical slope parameter that reflects solute–solute interactions at finite concentrations. The values presented in **table 4.55 (figure 4.34)** of $K_{\phi,s}$ thus reflects the limiting compressibility of the solute in the solvent, under conditions where solute–solute interactions are minimal and solute–solvent interactions are the primary contributors. These values provide insight into the structural effects of choline salicylate on ion hydration and compressibility behaviour in the ternary system [80–83]. To further elucidate the effect of choline salicylate on the hydration and compressibility properties of the solutes, ΔK_{ϕ}^0 was computed by equation 4.11. The data in **Table 4.56** show that ΔK_{ϕ}^0 increases with choline salicylate concentration and temperature. Because these values are evaluated at infinite dilution, the observed variations reflect changes in solute–solvent interactions rather than solute–solute associations. The positive values suggest a weakening of the structured hydration layer around the ions in the presence of choline salicylate, leading to increased compressibility of the solvation shell. This trend aligns with the co-sphere overlap model, where overlapping hydration spheres between solute and co-solute disrupt the tightly ordered water structure. At higher concentrations of choline salicylate, this disruption becomes more pronounced, contributing to an increase in ΔK_{ϕ}^0 . These findings reinforce the idea that choline salicylate acts as a structure-modifying co-solute, affecting the dynamic compressibility and hydration environment of the solute ions. [84,85].

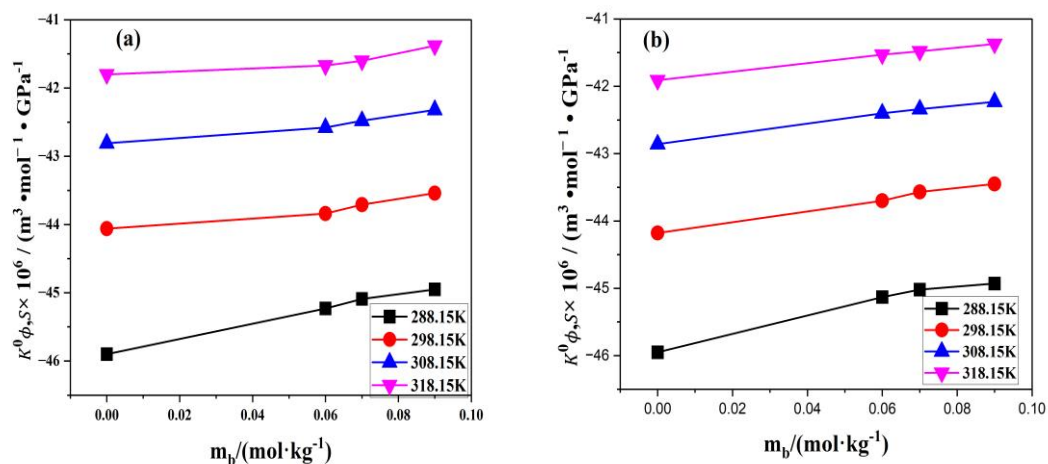


Figure 4.34 Partial molar isentropic compressions, $K^0_{\phi,s}$, plotted against molality (a) Sodium bicarbonate and (b) sodium sulphate in aqueous choline salicylate solutions at different temperatures.

Pair and triplet coefficients

Friedman and Krishnan expanded upon McMillan and Mayer's hypothesis to elucidate a solute's transfer properties in aqueous choline salicylate solution. **Table 4.57** displays the interaction coefficients. The equations 4.12,4.13 were used to compute pair and triple interaction coefficients of volume and compression. The interaction coefficients for salts in aqueous choline salicylate solutions, reveal significant trends that illuminate the molecular interactions governing these multi-component systems. These coefficients, derived using the extended McMillan-Mayer approach, quantitatively separate the contributions from direct solute–solute (pair) and cooperative (triplet) interactions, enabling a nuanced interpretation of the volumetric and compressibility data. A close examination that the V_{AB} , K_{AB} for both salts decrease progressively with temperature rising. This decrease indicates a weakening of the direct ion– co-solute and ion–solvent interactions as thermal energy disrupts the structured hydration shells around the ions and choline salicylate molecules.

Table 4.55: Values for $K_{\phi,S}^0$ and, S_K^* of Na_2SO_4 and NaHCO_3 in the aqueous choline salicylate at varying temperatures.

^a m_b (mol·kg ⁻¹)	$K_{\phi,S}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$				$S_K^* \times 10^6 / (\text{kg} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{GPa}^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Bicarbonate								
0.00	-45.90(±0.06)	-44.06(±0.02)	-42.81(±0.04)	-41.80(±0.04)	6.70(±0.09)	5.92(±0.09)	5.55(±0.14)	4.92(±0.14)
0.0590	-45.23(±0.14)	-43.84(±0.05)	-42.58(±0.07)	-41.67(±0.06)	5.50(±0.44)	5.54(±0.18)	5.02(±0.23)	4.65(±0.18)
0.0688	-45.09(±0.14)	-43.71(±0.04)	-42.48(±0.06)	-41.60(±0.04)	5.44(±0.45)	5.56(±0.15)	5.03(±0.19)	4.66(±0.14)
0.0885	-44.95(±0.15)	-43.54(±0.06)	-42.32(±0.08)	-41.38(±0.09)	5.35(±0.46)	5.65(±0.21)	4.86(±0.25)	4.35(±0.27)
Sodium Sulphate								
0.00	-45.95(±0.06)	-44.18(±0.04)	-42.86(±0.04)	-41.91(±0.03)	13.60(±0.22)	12.49(±0.12)	11.49(±0.14)	10.68(±0.12)
0.0590	-45.13(±0.03)	-43.70(±0.06)	-42.40(±0.04)	-41.53(±0.04)	11.92(±0.11)	11.47(±0.20)	10.58(±0.12)	9.91(±0.13)
0.0688	-45.02(±0.09)	-43.57(±0.03)	-42.34(±0.04)	-41.48(±0.02)	12.54(±0.29)	11.60(±0.10)	10.74(±0.12)	10.09(±0.07)
0.0885	-44.93(±0.09)	-43.45(±0.09)	-42.23(±0.02)	-41.37(±0.09)	12.61(±0.27)	11.43(±0.06)	10.65(±0.12)	10.01(±0.10)

standard uncertainties u is $u(K_{\phi,S}^0) = 0.31 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$, $u(S_K^*) = 0.50 \times 10^{-6} / (\text{kg} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{GPa}^{-1})$, $u(T) = 0.01\text{K}$, $u(p) = 0.01\text{MPa}$.

Table 4.56: $\Delta K_{\phi,S}^0$ for ternary mixes of Na_2SO_4 and NaHCO_3 in aqueous choline salicylate.

^a m_b (mol·kg ⁻¹)	$\Delta K_{\phi,S}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Bicarbonate				
0.0590	0.67	0.22	0.23	0.13
0.0688	0.82	0.34	0.33	0.21
0.0885	0.95	0.52	0.49	0.42
Sodium Sulphate				
0.0590	0.82	0.48	0.46	0.38
0.0688	0.93	0.60	0.52	0.43
0.0885	1.02	0.72	0.63	0.55

standard uncertainties u is $u(m_b) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$, $u(\Delta K_{\phi,S}^0) = 0.08 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$, $u(T) = 0.01\text{K}$, $u(p)=0.01\text{MPa}$.

At lower temperatures, the positive values of V_{AB} , K_{AB} suggest that the presence of choline salicylate enhances the ordering of water molecules, likely through Kosmotropic (structure-making) effects. As the temperature rises, these coefficients diminish or even become negative, reflecting a transition toward chaotropic (structure-breaking) behaviour, where increased molecular motion leads to a less structured solvent environment. The triplet interaction coefficients (V_{ABB} , K_{ABB}) provide further insight into the cooperative interactions involving two choline salicylate molecules and a salt ion. The values of (V_{ABB} , K_{ABB}) are generally smaller in magnitude than the pair coefficients, yet their temperature dependence is notable. For instance, positive triplet coefficients at lower temperatures imply that cooperative structuring—possibly due to enhanced hydrogen bonding or hydrophobic clustering—plays a significant role in stabilizing the local environment around the ions. Conversely, negative values at higher temperatures may indicate that such cooperative effects are diminished or that competitive interactions disrupt the local structure.

These observed trends in both pair and triplet coefficients underscore the complex interplay between electrostatic, hydrophobic, and hydrogen-bonding interactions in these systems. The systematic decrease in both V_{AB} and K_{AB} with temperature, along

with the nuanced behaviour of V_{ABB} and K_{ABB} , highlights the sensitivity of molecular organization to thermal effects and the nature of the solute and co solute present. This comprehensive analysis supports the interpretation of the volumetric and compressibility data, providing a mechanistic understanding of how choline salicylate modulates the structure and dynamics of aqueous solutions containing salts. Ultimately, these findings contribute valuable knowledge for predicting and tuning the behaviour of similar multi-component electrolyte systems in both fundamental studies and practical applications[112][139][167].

Thermal expansion coefficient

Unlike the partial molar volume or the transfer volume, which characterize the solute's contribution to the solution volume or the effect of transferring solute between solvents, respectively, α_p specifically quantifies the fractional change in apparent molar volume per degree of temperature increase. Using equation 4.14, the values of α_p for Na_2SO_4 and $NaHCO_3$ in aqueous choline salicylate mixes at various temperatures and 0.1 MPa are reported in **Table 4.58**. These results provide insight into the thermal response and molecular flexibility of the ternary mixtures, with higher α_p values indicating greater expansion of the solution volume with temperature. The observed trends in α_p thus reveal important aspects of solute–solvent interactions and the structural adaptability of these systems under thermal perturbation [90,168].

Table 4.57: V_{AB} , K_{AB} , V_{ABB} , K_{ABB} for Na_2SO_4 and NaHCO_3 in aqueous choline salicylate solutions.

T/K	$V_{AB} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg})$	$V_{ABB} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2)$	$K_{AB} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kgGPa}^{-1})$	$K_{ABB} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2 \text{GPa}^{-1})$
Sodium Bicarbonate				
288.15	101.15801	-299.50209	6.62540	-9.54625
298.15	134.60154	-543.28954	0.17535	20.14316
308.15	141.30777	-585.34352	0.55514	16.17576
318.15	134.15226	-546.23545	-1.46459	28.14653
Sodium Sulphate				
288.15	-1.14906	74.70354	9.37664	-27.12590
298.15	-2.72810	80.55637	4.31654	-1.86691
308.15	3.17979	21.51037	4.52484	-7.58652
318.15	7.63514	-8.30521	3.42862	-2.95812

^a m_B - choline salicylate molality.

Table 4.58: Values of thermal expansion for Na_2SO_4 and NaHCO_3 dissolved in aqueous choline salicylate under 0.1 MPa pressure.

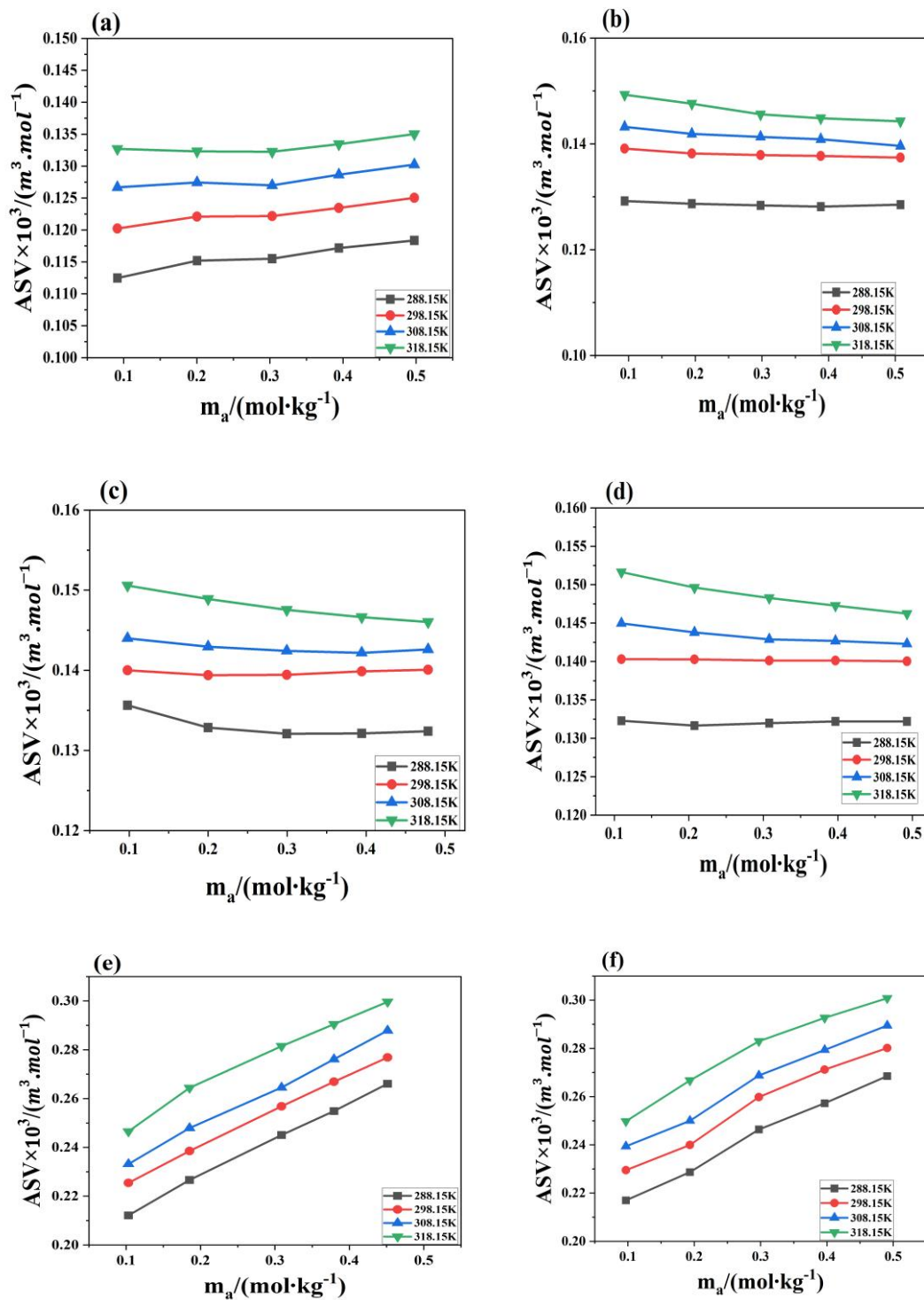
$^a m_b /$ (mol· kg ⁻¹)	$\alpha_p \times 10^3 / (K^{-1})$							
	Sodium Bicarbonate				Sodium sulphate			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
0.0590	41.42	20.99	2.88	-14.09	15.97	7.98	1.11	-5.28
0.0688	42.40	21.19	2.62	-14.83	14.18	7.28	1.23	-4.37
0.0885	39.73	20.28	2.70	-13.86	14.74	7.72	1.54	-4.17

standard uncertainties, $u(T) = 0.01K$, $u(\alpha_p) = 0.032 \times 10^{-3} / (K^{-1})$, $u(p) = 0.01\text{MPa}$

Apparent specific volume

The ASV is a fundamental thermodynamic indicator that signifies the true volume taken by the solute in a solution per unit mass. It reflects information about solute-solvent interactions and molecular organization of the system. An increased ASV usually signifies stronger solute-solvent interactions, which have an effect on numerous physicochemical properties of the solution. The ASV is determined from the **4.19** equation. The ASV data are presented in **Table 4.59** and shown in **fig. 4.35 graphically**. For sodium sulphate, ASV values generally fall within the range of 0.15 to $0.30 \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$, which is below the $0.33 \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$ threshold for the "salt" taste classification. In contrast, the ASV values for sodium bicarbonate range from approximately 0.25 to $0.50 \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$. This indicates that, depending on the specific concentration and temperature, sodium bicarbonate can fall within both the "salt" ($<0.33 \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$) and "sour" ($0.33\text{--}0.52 \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$) taste ranges [140–142]. The addition of choline salicylate does not significantly alter the ASV values for either salt, as values remain within the same taste classification ranges across all tested conditions. Thus, for sodium sulphate, the taste remains classified as "salt," while for sodium bicarbonate, the taste may be classified as "salt" or "sour" depending on the specific ASV value. These findings are consistent with existing literature, which

indicates that the taste quality of these solutes is not markedly affected in various aqueous and mixed solvent system [143–145].



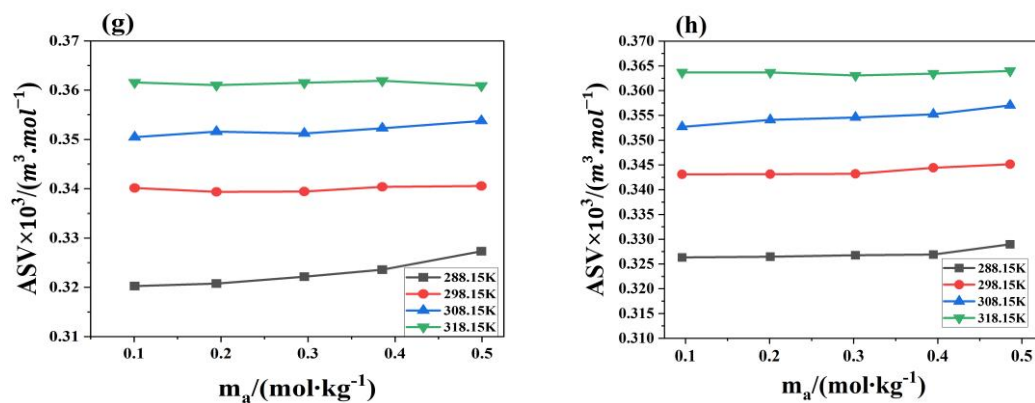


Fig 4.35. ASV plotted against molality for systems containing Na_2SO_4 and NaHCO_3 in H_2O and aqueous choline salicylate (0.0590, 0.0688 and 0.0885 mol.kg⁻¹), measured at various temperatures: (a–d) Na_2SO_4 with increasing choline salicylate concentration, (e–h) NaHCO_3 with increasing choline salicylate concentration.

Table 4.59: ASV (Apparent specific volume) for Na₂SO₄ and NaHCO₃ in aqueous solutions of choline salicylate.

$^a m_a / (mol \cdot kg^{-1})$	$ASV \times 10^3 / (m^3 \cdot kg^{-1})$				$^a m_A / (mol \cdot kg^{-1})$	$ASV \times 10^3 / (m^3 \cdot kg^{-1})$			
	288.15K	298.15K	308.15K	318.15K		288.15K	298.15K	308.15K	318.15K
Sodium Sulphate + 0.00 mol · kg⁻¹ choline salicylate					Sodium Bicarbonate + 0.00 mol · kg⁻¹ choline salicylate				
0.09136	0.11248	0.12023	0.12667	0.13269	0.10313	0.21210	0.22545	0.23319	0.24653
0.20034	0.11520	0.12210	0.12743	0.13232	0.18524	0.22665	0.23853	0.24790	0.26439
0.30305	0.11551	0.12219	0.12698	0.13226	0.30886	0.24507	0.25679	0.26452	0.28150
0.39442	0.11718	0.12344	0.12865	0.13345	0.37932	0.25489	0.26692	0.27611	0.29048
0.49751	0.11837	0.12503	0.13023	0.13502	0.45128	0.26609	0.27684	0.28788	0.29966
Sodium Sulphate + 0.0590 mol · kg⁻¹ choline salicylate					Sodium Bicarbonate + 0.0590 mol · kg⁻¹ choline salicylate				
0.09413	0.12921	0.13912	0.14321	0.14929	0.09702	0.21697	0.22947	0.23937	0.24977
0.19491	0.12869	0.13820	0.14188	0.14761	0.19336	0.22866	0.23992	0.25000	0.26673
0.29793	0.12837	0.13790	0.14132	0.14558	0.29746	0.24637	0.25984	0.26876	0.28294
0.38822	0.12813	0.13770	0.14087	0.14486	0.39665	0.25725	0.27123	0.27938	0.29268
0.50770	0.12850	0.13741	0.13961	0.14428	0.49097	0.26850	0.28017	0.28950	0.30082
Sodium Sulphate + 0.0688 mol · kg⁻¹ choline salicylate					Sodium Bicarbonate + 0.0688 mol · kg⁻¹ choline salicylate				

0.09784	0.13564	0.14001	0.14399	0.15058	0.10068	0.32026	0.34013	0.35045	0.36157
0.19991	0.13286	0.13940	0.14294	0.14891	0.19470	0.32076	0.33936	0.35158	0.36102
0.29955	0.13209	0.13943	0.14243	0.14755	0.29574	0.32215	0.33942	0.35123	0.36151
0.39438	0.13213	0.13987	0.14219	0.14664	0.38527	0.32358	0.34038	0.35227	0.36192
0.47842	0.13241	0.14008	0.14260	0.14603	0.49922	0.32731	0.34054	0.35377	0.36090
Sodium Sulphate + 0.0885 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate					Sodium Bicarbonate + 0.0885 $\text{mol} \cdot \text{kg}^{-1}$ choline salicylate				
0.10946	0.13228	0.14031	0.14497	0.15164	0.09601	0.32632	0.34311	0.35269	0.36369
0.20754	0.13165	0.14028	0.14378	0.14962	0.20086	0.32647	0.34313	0.35410	0.36367
0.30786	0.13197	0.14011	0.14288	0.14827	0.30215	0.32675	0.34320	0.35458	0.36306
0.39680	0.13220	0.14011	0.14267	0.14727	0.39478	0.32690	0.34441	0.35523	0.36345
0.49283	0.13220	0.14003	0.14230	0.14622	0.48603	0.32897	0.34514	0.35703	0.36399

standard uncertainties u is u(m)=0.01, u(T)= 0.01K, u(ASV)= $0.006 \times 10^{-3}/(\text{m}^3 \cdot \text{kg}^{-1})$.

Relative association

It reflects how the addition of a solute, such as a salt, influences the structural organization and interaction strength among the components of the solution. Higher R_a values typically indicate stronger or more extensive solute-solvent associations, often resulting from enhanced hydrogen bonding, ion pairing, or other intermolecular forces. Relative association (R_a) has been calculated by equation 4.15 [92]. The values of relative association (R_a) for aqueous choline salicylate solutions containing varying molality's of sodium bicarbonate and sodium sulphate are in **Table 4.60**. The data reveal that R_a increases with increasing salt molality at all studied temperatures for both salts. This indicates that the presence of sodium bicarbonate or sodium sulphate enhances associative interactions between choline salicylate and water molecules, likely due to increased hydrogen bonding and ion-pair formation. Additionally, R_a values are observed to increase with rising temperature, suggesting that thermal energy may facilitate greater molecular association or structural reorganization within the solution. Notably, sodium sulphate generally exhibits higher R_a values than sodium bicarbonate at equivalent molality's and temperatures, which may be attributed to the higher charge density and stronger hydration ability of the sulphate ion [93,94].

Relaxation strength

In electrolyte solutions, relaxation strength provides insight into the dynamic behaviour and mobility of solvent and solute molecules, as well as the degree of structural organization within the solution. The relaxation strength was calculated by using the equation 4.16. The relaxation strength data is mentioned in **table 4.60**. The relaxation strength data show a decreasing trend with rising molality of both sodium bicarbonate and sodium sulphate. This suggests that as the concentration of solute (salt) increases, the solution becomes less capable of dissipating energy through molecular relaxation processes, possibly due to the formation of more rigid or compact solute-solvent structures. Furthermore, relaxation strength decreases with rising temperature, which can be due to enhanced molecular motion and reduced structural organization at elevated temperatures. These findings highlight the significant influence of both salt type and concentration, as well as temperature, on the dynamic properties and molecular organization of aqueous choline salicylate solutions [96–99].

Table 4.60 Relaxation strength (r_s) and Relative association (R_a) and for aqueous choline salicylate containing varying concentrations of Na_2SO_4 and NaHCO_3 , measured across varying temperatures.

$m_a/(\text{mol}\cdot\text{kg}^{-1})$	Relaxation Strength (r_s)				Relative Association (R_a)			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Sulphate in 0.000 mol·kg⁻¹ Choline salicylate)								
0.00000	0.15981	0.12595	0.09852	0.07838	1.00000	1.00000	1.00000	1.00000
0.09136	0.14331	0.10945	0.08298	0.06367	1.00816	1.00818	1.00836	1.00849
0.20034	0.12505	0.09322	0.06850	0.04927	1.01796	1.01838	1.01890	1.01903
0.30305	0.10811	0.07619	0.05176	0.03448	1.02716	1.02758	1.02817	1.02861
0.39442	0.08914	0.05649	0.03458	0.01820	1.03445	1.03478	1.03581	1.03640
0.49751	0.07238	0.04196	0.01881	0.00291	1.04347	1.04417	1.04495	1.04559
Sodium Sulphate in 0.0590 mol·kg⁻¹ Choline salicylate								
0.00000	0.14978	0.11730	0.08985	0.07210	1.00000	1.00000	1.00000	1.00000
0.09413	0.13154	0.10301	0.07722	0.05845	1.00797	1.00870	1.00904	1.00881
0.19491	0.11381	0.08669	0.05996	0.04288	1.01675	1.01772	1.01791	1.01796
0.29793	0.09773	0.06636	0.04239	0.02529	1.02602	1.02615	1.02689	1.02696

0.38822	0.08194	0.05110	0.02671	0.01142	1.03375	1.03393	1.03462	1.03500
0.50770	0.05967	0.03034	0.00822	-0.00706	1.04359	1.04403	1.04521	1.04550

Sodium Sulphate in 0.0688 mol·kg⁻¹ Choline salicylate

0.00000	0.14806	0.11542	0.08900	0.07044	1.00000	1.00000	1.00000	1.00000
0.09784	0.12620	0.09949	0.07435	0.05609	1.00764	1.00883	1.00910	1.00911
0.19991	0.10896	0.08141	0.05729	0.03901	1.01665	1.01766	1.01814	1.01813
0.29955	0.09123	0.06294	0.03961	0.02304	1.02517	1.02601	1.02668	1.02697
0.39438	0.07350	0.04583	0.02300	0.00762	1.03302	1.03393	1.03476	1.03526
0.47842	0.05359	0.03059	0.00922	-0.00681	1.03913	1.04088	1.04197	1.04240

Sodium Sulphate in 0.0885 mol·kg⁻¹ Choline salicylate

0.00000	0.14562	0.11295	0.08640	0.06740	1.00000	1.00000	1.00000	1.00000
0.10946	0.12195	0.09497	0.06951	0.05103	1.00875	1.01162	1.01006	1.01012
0.20754	0.10455	0.07770	0.05382	0.03557	1.01724	1.02145	1.01887	1.01894
0.30786	0.08713	0.05975	0.03608	0.01926	1.02587	1.03161	1.02749	1.02779
0.39680	0.07060	0.04414	0.02061	0.00565	1.03324	1.04037	1.03507	1.03571
0.49283	0.04750	0.02692	0.00483	-0.01155	1.04019	1.04976	1.04335	1.04376

Sodium Bicarbonate in 0.00 mol·kg⁻¹ Choline salicylate

0.00000	0.15981	0.12595	0.09852	0.07838	1.00000	1.00000	1.00000	1.00000
0.10313	0.14925	0.11522	0.08949	0.06876	1.00466	1.00460	1.00490	1.00472
0.18524	0.14157	0.10687	0.08209	0.06181	1.00824	1.00803	1.00848	1.00827
0.30886	0.12887	0.09535	0.07035	0.05128	1.01305	1.01303	1.01343	1.01329
0.37932	0.12224	0.08928	0.06357	0.04487	1.01572	1.01576	1.01598	1.01591
0.45128	0.11444	0.08251	0.05777	0.04022	1.01807	1.01832	1.01861	1.01878

Sodium Bicarbonate in 0.0590 mol·kg⁻¹ Choline salicylate

0.00000	0.14978	0.11730	0.08985	0.07210	1.00000	1.00000	1.00001	1.00000
0.09702	0.14076	0.11080	0.08476	0.06578	1.00352	1.00392	1.00453	1.00607
0.19336	0.13244	0.10194	0.07733	0.05806	1.00728	1.00748	1.00833	1.00977
0.29746	0.12408	0.09312	0.06840	0.04994	1.01137	1.01137	1.01220	1.01373
0.39665	0.11360	0.08380	0.06040	0.04169	1.01469	1.01483	1.01588	1.01734
0.49097	0.10657	0.07548	0.05149	0.03433	1.01836	1.01812	1.01908	1.02082

Sodium Bicarbonate in 0.0688 mol·kg⁻¹ Choline salicylate

0.00000	0.14806	0.11542	0.08900	0.07044	1.00000	1.00000	1.00000	1.00000
0.10068	0.13840	0.10785	0.08233	0.06376	1.00343	1.00398	1.00450	1.00625

0.19470	0.13057	0.09894	0.07475	0.05562	1.00712	1.00738	1.00808	1.00970
0.29574	0.12120	0.09031	0.06572	0.04805	1.01081	1.01114	1.01171	1.01353
0.38527	0.11253	0.08153	0.05875	0.04022	1.01394	1.01419	1.01503	1.01667
0.49922	0.10258	0.07207	0.04847	0.03176	1.01796	1.01834	1.01891	1.02090

Sodium Bicarbonate in 0.0885 mol·kg⁻¹ Choline salicylate

0.00000	0.14562	0.11295	0.08640	0.06740	1.00000	1.00000	1.00000	1.00000
0.09601	0.13652	0.10445	0.07955	0.05931	1.00279	1.00353	1.00390	1.00554
0.20086	0.12660	0.09454	0.07156	0.05243	1.00663	1.00729	1.00795	1.00975
0.30215	0.11760	0.08554	0.06301	0.04509	1.01038	1.01097	1.01164	1.01364
0.39478	0.10876	0.07673	0.05596	0.03765	1.01365	1.01413	1.01509	1.01698
0.48603	0.10183	0.06738	0.04705	0.03010	1.01709	1.01708	1.01803	1.02017

standard uncertainties u is u(m)=0.01, u(T)= 0.01K, u(R_a)=0.00121, u(p)=0.01MPa.

Problem 6

Insights into Molecular Interactions of Aqueous Choline Salicylate in Potassium and Sodium Chloride Solutions via Volumetric, Acoustic, and Spectroscopic Techniques

In this problem, values of density and ultrasonic velocity were experimentally measured and then FTIR study was also conducted to validate results.

Density and Ultrasonic velocity

The data that were taken through experimentation of density and ultrasonic velocity are given in **Table 4.61**. The results indicate that density and ultrasonic velocity increase as the molality of sodium chloride/potassium chloride rises in the aqueous choline salicylate solution. This increase primarily results from the greater mass of the solution. Additionally, the rise in density and speed of sound suggests stronger solute-solvent interactions [48–50]. A comparison of these values with previously reported data [76] [104] [79] for (potassium chloride + water) is present in **Figures 4.15(a), 4.15(b)**, for (sodium chloride + water) [1–5] is presented in **Fig. 4.1(a) and 4.1(b)** and for choline salicylate + Water [111,112] is presented in **figure 4.23(a),(b)** respectively which shows experimentally obtained density and speed of sound values for potassium chloride + H₂O, sodium chloride+ H₂O and choline salicylate + water at different temperatures align well with existing literatures. **Figure 4.36** shows schematic representation of Molecular Interactions of aqueous choline salicylate in NaCl/KCl.

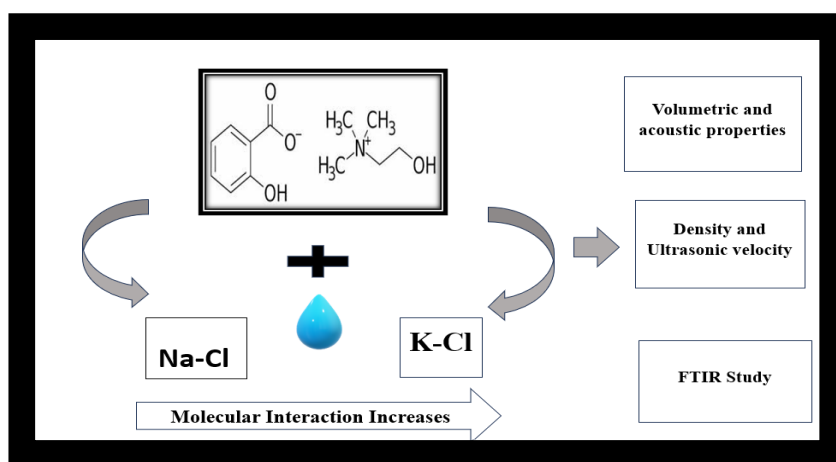


Figure 4.36: Molecular Interactions of aqueous choline salicylate in NaCl/KCl.

Table 4.61. Measured ρ and c for mixtures of Sodium chloride/ potassium chloride in choline salicylate aqueous solutions.

$^a m_a / (mol \cdot kg^{-1})$	$\rho \times 10^{-3} / (kg \cdot m^{-3})$				$c / (m \cdot s^{-1})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium chloride + 0.00000 Choline salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036	1466.59	1495.85	1519.14	1536.02
0.09669	1.00334	1.00109	0.99803	0.99431	1473.21	1502.91	1526.41	1542.35
0.19897	1.00762	1.00532	1.00221	0.99844	1478.91	1508.03	1531.23	1545.96
0.29215	1.01146	1.00913	1.00598	1.00217	1490.23	1518.23	1539.81	1555.31
0.40757	1.01617	1.0138	1.01059	1.00674	1494.53	1522.32	1542.71	1560.21
0.49242	1.0196	1.01719	1.01394	1.00919	1498.25	1525.14	1544.41	1563.73
Sodium chloride + 0.01500 Choline salicylate								
0.00000	1.00017	0.99802	0.99491	0.99101	1470.07	1499.96	1522.82	1538.23
0.09227	1.00399	1.00182	0.99869	0.99475	1476.91	1506.59	1529.09	1544.19
0.19715	1.00828	1.00607	1.00291	0.99894	1484.21	1513.78	1535.76	1550.67
0.30150	1.01248	1.01024	1.00705	1.00305	1492.34	1520.53	1542.17	1557.19
0.39763	1.01629	1.01404	1.01081	1.00678	1499.36	1526.91	1546.89	1562.89
0.49161	1.01996	1.01768	1.01444	1.01039	1505.88	1532.35	1552.40	1568.40
Sodium chloride + 0.03100 Choline salicylate								
0.00000	1.00085	0.99872	0.99559	0.99155	1473.10	1503.15	1525.01	1541.17
0.13336	1.00636	1.00419	1.00101	0.99692	1483.13	1512.03	1533.88	1550.22
0.22259	1.00998	1.00778	1.00457	1.00045	1490.03	1518.47	1539.49	1555.91
0.34307	1.01481	1.01255	1.00931	1.00516	1499.61	1526.90	1547.42	1562.88

0.42491	1.01805	1.01575	1.01249	1.00831	1505.72	1532.59	1552.02	1567.92
0.51525	1.02154	1.01925	1.01597	1.01178	1512.93	1538.81	1557.68	1572.46
Sodium chloride + 0.06000 Choline salicylate								
0.00000	1.00229	0.99998	0.99690	0.99271	1475.81	1504.83	1527.14	1542.62
0.09820	1.00632	1.00397	1.00085	0.99662	1484.14	1512.94	1534.11	1550.01
0.19243	1.01011	1.00772	1.00458	1.00031	1492.29	1520.10	1540.49	1555.93
0.29603	1.01421	1.01176	1.00860	1.00431	1500.64	1528.17	1547.33	1561.98
0.39224	1.01794	1.01543	1.01224	1.00792	1508.69	1535.39	1553.36	1568.09
0.48083	1.02132	1.01878	1.01557	1.01118	1515.70	1541.82	1558.70	1573.64
Potassium chloride + 0.00000 Choline salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036	1466.59	1495.85	1519.14	1536.02
0.10621	1.00429	1.00205	0.99900	0.99528	1472.79	1502.36	1525.07	1541.95
0.18956	1.00820	1.00593	1.00285	0.99910	1477.49	1506.92	1529.29	1545.63
0.28101	1.01243	1.01014	1.00705	1.00325	1482.79	1511.96	1533.79	1549.73
0.38281	1.01710	1.01479	1.01167	1.00781	1488.45	1516.72	1538.93	1554.11
0.46818	1.02097	1.01864	1.01551	1.01159	1493.37	1521.51	1543.17	1558.56
Potassium chloride + 0.01500 Choline salicylate								
0.00000	1.00017	0.99802	0.99491	0.99101	1470.07	1499.96	1522.82	1538.23
0.09547	1.00464	1.00247	0.99933	0.99539	1475.19	1504.42	1527.04	1542.63
0.19396	1.00915	1.00695	1.00378	0.99981	1480.49	1508.97	1531.58	1546.78
0.29203	1.01354	1.01132	1.00811	1.00411	1485.55	1513.73	1536.11	1550.85
0.39272	1.01795	1.01570	1.01246	1.00841	1490.90	1518.68	1540.96	1555.38

0.46847	1.02120	1.01893	1.01565	1.01158	1494.80	1522.32	1544.43	1558.97
Potassium chloride + 0.03100 Choline salicylate								
0.00000	1.00085	0.99872	0.99559	0.99155	1473.10	1503.15	1525.01	1541.17
0.10409	1.00568	1.00349	1.00029	0.99618	1478.49	1507.28	1529.39	1545.21
0.18604	1.00940	1.00715	1.00392	0.99974	1482.39	1510.78	1532.89	1548.39
0.32172	1.01542	1.01309	1.00978	1.00553	1488.63	1516.64	1538.86	1553.98
0.41181	1.01931	1.01692	1.01358	1.00930	1493.18	1520.49	1542.88	1557.62
0.49732	1.02293	1.02047	1.01711	1.01278	1497.01	1524.39	1546.75	1561.38
Potassium chloride + 0.06000 Choline salicylate								
0.00000	1.00229	0.99998	0.99690	0.99271	1475.81	1504.83	1527.14	1542.62
0.10574	1.00718	1.00479	1.00163	0.99737	1480.59	1509.16	1531.13	1546.73
0.20261	1.01154	1.00909	1.00588	1.00155	1484.89	1513.28	1535.13	1550.45
0.29465	1.01558	1.01307	1.00983	1.00542	1488.97	1517.34	1538.89	1554.09
0.42047	1.02096	1.01838	1.01510	1.01058	1494.59	1522.76	1544.19	1559.12
0.50400	1.02443	1.02178	1.01851	1.01392	1498.25	1526.42	1547.84	1562.49

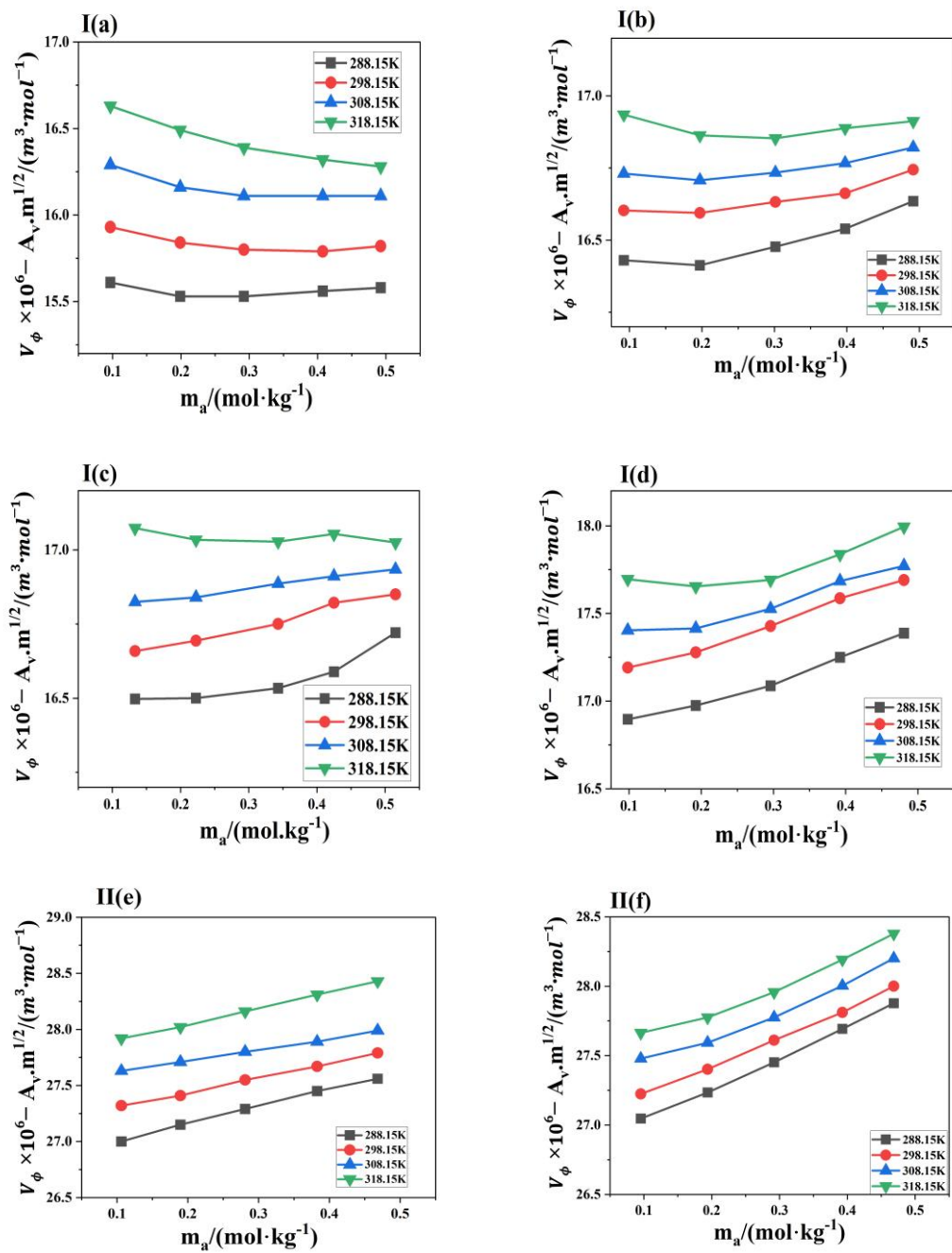
The standard uncertainties were $u(T) = 0.001$ K, $u(\rho) = 0.58$ kg·m⁻³, $u(p) = 0.01$ MPa, and $u(s) = 1.94$ m·s⁻¹.

Apparent and partial molar volumes

The V_ϕ was computed by using equation 4.1. The obtained V_ϕ values (**Table 4.62**) are positive and show an increasing trend with both temperature and salt molality. The variation of $(V_\phi - A_V\sqrt{m})$ with molality (**Figure 4.37**) exhibits a linear relationship, confirming the consistency of the experimental data. V_ϕ rises with salt content shows that solute–solute interactions (ion–ion and ion–dipole) are slowly taking over solute–solvent interactions. Choline salicylate and water molecules interact strongly in dilute environments through ion–dipole and hydrogen bonding, which creates structured hydration shells. When there is more NaCl or KCl, the ions (Na^+/K^+ , Cl^- , choline $^+$, and salicylate $^-$) interact with each other through electrostatic forces. The effects of competing hydration break apart these solvent cages. When water molecules leave the hydration shells and ions lose some of their water, the solution gets bigger. This effect is stronger for KCl than for NaCl because K^+ has a lower charge density and a bigger ionic radius. This means that it is less likely to hydrate and more likely to grow in size. The rise in V_ϕ means that the connection between the solute and the solvent is getting weaker and the connection between the ions is getting stronger [54–57,108]. V_ϕ^0 were obtained by extrapolating the experimental V_ϕ versus molality data to zero concentration using the Redlich–Meyer equation (Eq. 4.2). The Debye–Hückel limiting slope (A_V) values for sodium chloride and potassium chloride (1:1 electrolyte) at the investigated temperatures were obtained from literature sources [58,59,108]. The parameter S_V , derived experimentally, accounts for deviations from ideal behaviour at higher concentrations and represents specific ion–ion interactions [60,61]. **Table 4.63** and **Figure 4.38** show that the V_ϕ^0 values go up with temperature. This is because ions are less attracted to solvents by electrostatic forces and lose some water when the temperature goes up. This pattern shows that heating weakens the way water is ordered around ions and choline salicylate molecules, which causes the solvent structure to grow. The positive S_V values in both systems show that the ions are interacting with each other in a way that makes structures, while negative or close-to-zero values would show that the ions are breaking down structures [62–64].

Partial molar volume of transfer (ΔV_{ϕ}^0)

This quantifies the change in V_{ϕ}^0 when the salt is transferred from water to aqueous magnesium salicylate and is given by equation 4.3. The ΔV_{ϕ}^0 values (Table 4.64) are positive for NaCl across all temperatures, whereas KCl exhibits negative values at low molality and temperature that gradually become positive as both parameters increase. The negative ΔV_{ϕ}^0 values at lower temperatures indicate stronger ion–solvent interactions and a structure-making effect of KCl in the choline salicylate medium. As temperature and concentration rise, ΔV_{ϕ}^0 turns positive, reflecting disruption of the ordered hydration shell and dominance of ion–ion associations. In contrast, NaCl consistently shows positive ΔV_{ϕ}^0 values, suggesting weaker hydration and greater structure-breaking behaviour. Overall, these results confirm that KCl undergoes a structure-making to structure-breaking transition with temperature, whereas NaCl remains a structure breaker throughout the studied range. The different behaviour of KCl and NaCl in aqueous choline salicylate should be interpreted in terms of ion-specific hydration rather than assigning fundamentally different kosmotropic or chaotropic characters to the salts. Although both NaCl and KCl are conventionally classified as kosmotropic electrolytes in dilute aqueous media, the larger ionic radius and lower hydration energy of K^+ make its hydration shell more susceptible to thermal disruption than that of Na^+ . Consequently, KCl exhibits a temperature-dependent shift in ΔV_{ϕ}^0 values, reflecting a gradual change from hydration-dominated to ion–ion interaction-dominated behaviour. In contrast, NaCl retains positive ΔV_{ϕ}^0 values throughout the investigated temperature range because the more strongly hydrated Na^+ ion maintains relatively stronger ion–solvent interactions. Therefore, the observed difference represents a solvent- and temperature-dependent ion-specific effect in aqueous choline salicylate rather than a contradiction of the conventional behaviour of NaCl and KCl in pure water. [65–69,109].



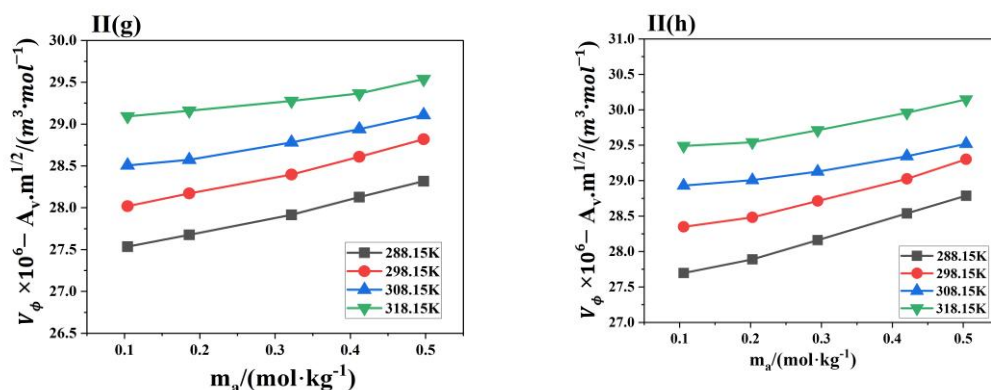


Figure 4.37 Plots of V_ϕ (I) Sodium chloride and (II) Potassium chloride from H_2O to an aqueous choline salicylate solution (a)(e) 0.000 choline salicylate, (b)(f) 0.015 choline salicylate, (c) (g) 0.031 choline salicylate, and (d) (e) 0.060 choline salicylate ($\text{mol} \cdot \text{kg}^{-1}$).

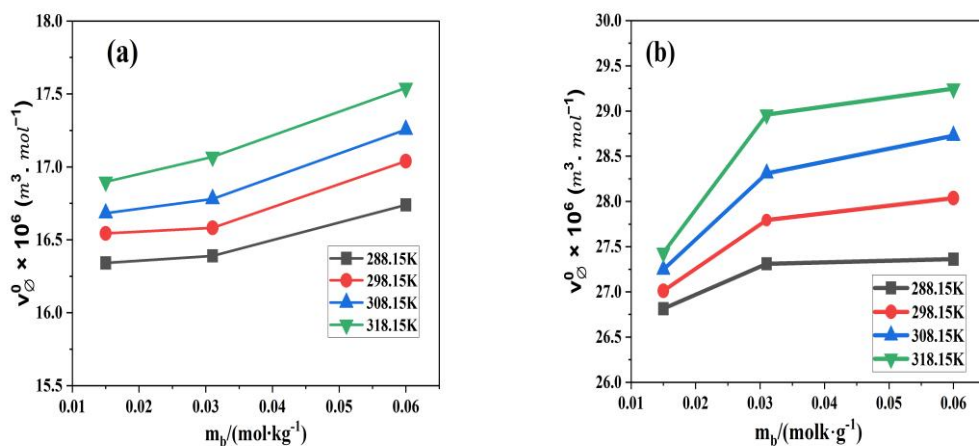


Figure 4.38 Plots of V_ϕ^0 , for sodium chloride (a) and potassium chloride (b) within a choline salicylate aqueous solution at various temperatures.

Apparent molar isentropic compressibility (K_S)

The k_s was determined from the experimentally measured ρ and c values using the Newton–Laplace equation 4.9. To gain further insight of molecular interactions, the $K_{(\phi,s)}$ was computed using the equation 4.8. The negative $K_{\phi,s}$ values (Table 4.65, Figure 4.39) for both NaCl and KCl systems decrease with rising temperature and concentration. Such negative values reflect the dominance of ion-solvent interactions, which results in electrostriction and a compact structure of solvent around ions. With

a rise in temperature, the hydration shells become looser and the magnitude of $K_{\phi,s}$ decreases, reflecting a decrease in compressibility. Of the two salts, KCl exhibits slightly more negative values than NaCl, which indicates that ion-solvent association is stronger in aqueous choline salicylate medium. These changes indicate that choline salicylate promotes ion-specific interactions and changes the local structure of water by combined hydrophilic and hydrophobic effects.

Table 4.62. V_ϕ of sodium chloride/potassium chloride in H₂O and aqueous choline salicylate.

$^am_a/$ ($mol \cdot$ kg^{-1})	$V_\phi \times 10^6/(m^3 \cdot mol^{-1})$				$^am_a/$ ($mol \cdot$ kg^{-1})	$V_\phi \times 10^6/(m^3 \cdot mol^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K		T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride + 0.00000 Choline salicylate					Potassium chloride + 0.00000 Choline salicylate				
0.09669	15.61	15.93	16.29	16.63	0.10621	27.00	27.32	27.63	27.92
0.19897	15.53	15.84	16.16	16.49	0.18956	27.15	27.41	27.71	28.02
0.29215	15.53	15.80	16.11	16.39	0.28101	27.29	27.55	27.80	28.16
0.40757	15.56	15.79	16.11	16.32	0.38281	27.45	27.67	27.89	28.31
0.49242	15.58	15.82	16.11	16.28	0.46818	27.56	27.79	27.99	28.43
Sodium chloride + 0.01500 Choline salicylate					Potassium chloride + 0.01500 Choline salicylate				
0.09227	16.43	16.60	16.73	16.94	0.09547	27.05	27.22	27.48	27.66
0.19715	16.41	16.59	16.71	16.86	0.19396	27.23	27.40	27.59	27.78
0.30150	16.48	16.63	16.73	16.85	0.29203	27.45	27.61	27.78	27.96
0.39763	16.54	16.66	16.77	16.89	0.39272	27.69	27.81	28.00	28.19
0.49161	16.63	16.74	16.82	16.91	0.46847	27.88	28.00	28.20	28.38
Sodium chloride + 0.03100 Choline salicylate					Potassium chloride + 0.03100 Choline salicylate				
0.13336	16.50	16.66	16.82	17.07	0.10409	27.53	28.02	28.51	29.09
0.22259	16.50	16.69	16.84	17.03	0.18604	27.68	28.17	28.57	29.16
0.34307	16.53	16.75	16.89	17.03	0.32172	27.92	28.40	28.78	29.28

0.42491	16.59	16.82	16.91	17.05	0.41181	28.13	28.61	28.94	29.37
0.51525	16.72	16.85	16.93	17.02	0.49732	28.32	28.82	29.11	29.54
Sodium chloride + 0.06000 Choline salicylate					Potassium chloride + 0.06000 Choline salicylate				
0.09820	16.90	17.19	17.40	17.70	0.10574	27.70	28.35	28.93	29.49
0.19243	16.97	17.28	17.41	17.65	0.20261	27.89	28.48	29.01	29.54
0.29603	17.09	17.43	17.53	17.69	0.29465	28.16	28.71	29.13	29.71
0.39224	17.25	17.59	17.69	17.84	0.42047	28.54	29.02	29.35	29.96
0.48083	17.39	17.69	17.77	17.99	0.50400	28.79	29.30	29.52	30.15

standard uncertainties are $u(T) = 0.001$ K, $u(V_\phi) = 0.45 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, and $u(p) = 0.01$ MPa.

Table 4.63: V_ϕ^0 values along with S_V^* of Sodium chloride/ potassium chloride in choline salicylate aqueous solutions.

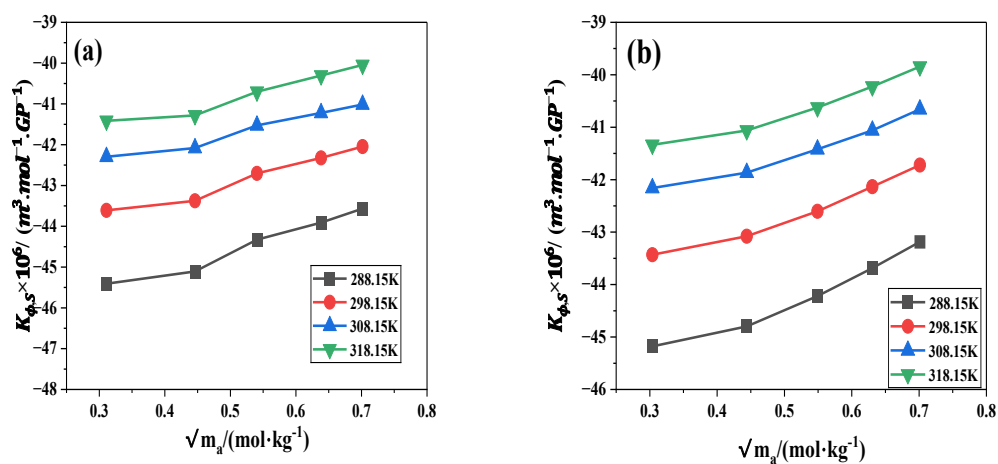
$^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$V_\phi^0 \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$				$S_V^* \times 10^6 (\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium Chloride								
0.00000	15.57(±0.04)	15.91(±0.04)	16.27(±0.05)	16.68(±0.04)	-0.03(±0.12)	-0.27(±0.13)	-0.41(±0.16)	-0.87(±0.11)
0.01500	16.34(±0.04)	16.54(±0.03)	16.68(±0.05)	18.89(±0.04)	0.53(±0.12)	0.34(±0.11)	0.23(±0.15)	-0.02(±0.13)
0.03100	16.38(±0.05)	16.58(±0.06)	16.78(±0.07)	17.06(±0.06)	0.54(±0.14)	0.52(±0.19)	0.30(±0.21)	-0.08(±0.19)
0.06000	16.73(±0.05)	17.03(±0.03)	17.25(±0.04)	17.54(±0.07)	1.30(±0.14)	1.35(±0.10)	1.04(±0.12)	0.80(±0.22)
Potassium chloride								
0.00000	26.85(±0.01)	27.17(±0.01)	27.52(±0.07)	27.76(±0.04)	1.54(±0.04)	1.30(±0.03)	0.98(±0.02)	1.42(±0.02)
0.01500	26.81(±0.01)	27.01(±0.01)	27.25(±0.04)	27.43(±0.04)	2.24(±0.06)	2.07(±0.05)	1.95(±0.15)	1.94(±0.15)
0.03100	27.31(±0.02)	27.79(±1.03)	28.31(±0.03)	28.96(±0.04)	1.98(±0.07)	2.003(±0.09)	1.54(±0.10)	1.06(±0.11)
0.06000	27.36(±0.03)	28.04(±0.05)	28.73(±0.04)	29.25(±0.05)	2.79(±0.11)	2.41(±0.17)	1.49(±0.13)	1.70(±0.17)

u is u(m) = 0.01000 mol · kg⁻¹, u (T) = ±0.001K, u (V_φ⁰) = ±0.01 × 10⁻⁶ (m³ · mol⁻¹), u (S_V^{*}) = 1.47 × 10⁻⁶ (m³ · kg · mol⁻²).

Table. 4.64. ΔV_{ϕ}^0 of Sodium chloride/ potassium chloride in aqueous choline salicylate solutions.

${}^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$\Delta V_{\phi}^0 \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$			
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K
Sodium chloride				
0.01500	0.77	0.63	0.40	0.22
0.03100	0.82	0.67	0.50	0.39
0.06000	1.17	1.12	0.98	0.86
Potassium chloride				
0.01500	-0.03	-0.16	-0.28	-0.33
0.03100	0.46	0.62	0.79	1.20
0.06000	0.51	0.86	1.20	1.49

standard uncertainties u are $u(m) = 0.01000 \text{ mol} \cdot \text{kg}^{-1}$, $u(p) = 0.01 \text{ MPa}$, $u(\Delta V_{\phi}^0) = 0.09 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1})$.



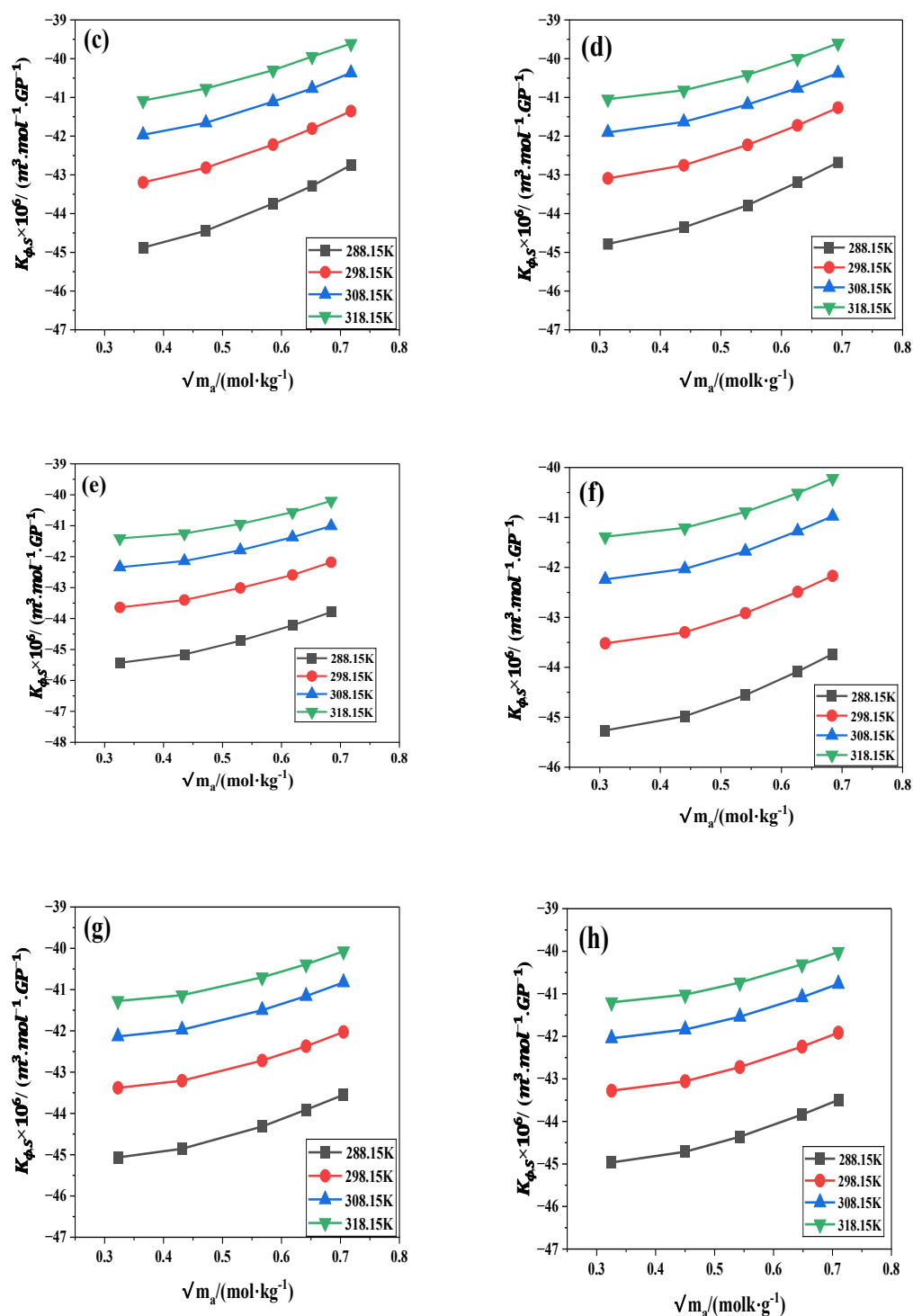


Figure 4.39 Plots of $K_{(\phi,s)}$ (a) Sodium chloride + water, (e) Potassium chloride + water, (b), (c), (d), (f), (g), (h) Sodium chloride and potassium chloride in aqueous choline salicylate solution at 0.015, 0.031, 0.060 choline salicylate ($\text{mol} \cdot \text{kg}^{-1}$) respectively.

Partial molar and transfer isentropic compressibility

The $K_{(\phi,s)}^0$ was obtained by extrapolating the $K_{(\phi,s)}$ versus $\sqrt{m_A}$ to infinite dilution using eq. 4.10, where S_K^* is an empirical slope parameter that reflects solute–solute interactions at finite concentrations. The negative value of the extrapolated $K_{\phi,s}^0$ values for both NaCl and KCl systems in **Table 4.66** and **Figure 4.40** decreases with rising temperature. Such a fall in magnitude signifies that solutions become less compressible with a rise in temperature due to weakening of electrostriction and partial disruption in hydration shells surrounding ions. The negative sign of $K_{\phi,s}^0$ points to strong ion–solvent interactions in the choline salicylate medium, but a reduction in magnitude with the rise in temperature is due to increased molecular mobility with reduced rigidity of the solvent network. The slope S_K^* parameter has a positive value for both systems, indicating that structure-making ion–ion interactions predominate at lower temperatures. To further elucidate the effect of magnesium salicylate on the hydration and compressibility properties of the solutes, ΔK_ϕ^0 was computed by equation 4.11. The ΔK_ϕ^0 values (**Table 4.67**) are negative for sodium chloride and positive for potassium chloride at all studied concentrations. The negative ΔK_ϕ^0 (-0.29×10^{-6} to $-0.14 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1}$) for NaCl suggest enhanced ion–solvent electrostriction and structure-making behaviour in aqueous choline salicylate medium, indicating stronger hydration around Na^+ ions. Conversely, the positive ΔK_ϕ^0 values (0.25×10^{-6} to $0.56 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1}$) observed for KCl indicate a structure-breaking tendency due to weaker ion–solvent interactions. For both salts, the magnitude of ΔK_ϕ^0 decreases with rising temperature, which may be attributed to thermal disruption of hydration shells and weakening of electro-strictive forces in the solvent environment.

Table 4.65. $\kappa_{\phi,S}$ of sodium chloride/potassium chloride in water and aqueous choline salicylate solutions.

$^a m_A /$ ($\text{mol} \cdot$ kg^{-1})	$\kappa_{\phi,S} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$				$^a m_A /$ ($\text{mol} \cdot$ kg^{-1})	$\kappa_{\phi,S} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K		T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride + 0.00000 choline salicylate					trisodium citrate + 0.00000 choline salicylate				
0.09669	-45.61	-43.83	-42.51	-41.63	0.10621	-45.43	-43.64	-42.34	-41.41
0.19897	-46.06	-44.26	-42.92	-42.04	0.18956	-45.16	-43.4	-42.14	-41.25
0.29215	-46.31	-44.50	-43.15	-42.26	0.28101	-44.72	-43.01	-41.79	-40.94
0.40757	-46.57	-44.75	-43.39	-42.50	0.38281	-44.22	-42.59	-41.37	-40.56
0.49242	-46.75	-44.92	-43.55	-42.62	0.46818	-43.79	-42.18	-41.01	-40.2
Sodium chloride + 0.01500 choline salicylate					Potassium chloride + 0.01500 choline salicylate				
0.09227	-45.18	-43.43	-42.16	-41.33	0.09547	-45.26	-43.52	-42.24	-41.39
0.19715	-44.80	-43.08	-41.87	-41.06	0.19396	-44.98	-43.30	-42.03	-41.21
0.30150	-44.22	-42.60	-41.42	-40.63	0.29203	-44.56	-42.92	-41.68	-40.89
0.39763	-43.69	-42.13	-41.06	-40.22	0.39272	-44.08	-42.49	-41.27	-40.51
0.49161	-43.19	-41.72	-40.66	-39.84	0.46847	-43.73	-42.17	-40.98	-40.22
Sodium chloride + 0.03100 choline salicylate					Potassium chloride + 0.03100 choline salicylate				
0.13336	-44.88	-43.20	-41.97	-41.08	0.10409	-45.07	-43.38	-42.13	-41.28
0.22259	-44.44	-42.82	-41.65	-40.77	0.18604	-44.86	-43.21	-41.97	-41.14
0.34307	-43.74	-42.22	-41.11	-40.30	0.32172	-44.32	-42.72	-41.50	-40.70

0.42491	-43.28	-41.80	-40.77	-39.95	0.41181	-43.91	-42.37	-41.16	-40.39
0.51525	-42.75	-41.35	-40.37	-39.61	0.49732	-43.55	-42.03	-40.83	-40.07
Sodium chloride + 0.0600 choline salicylate					Potassium chloride + 0.06000 choline salicylate				
0.09820	-44.78	-43.09	-41.90	-41.05	0.10574	-44.96	-43.28	-42.05	-41.20
0.19243	-44.36	-42.75	-41.63	-40.82	0.20261	-44.71	-43.06	-41.84	-41.02
0.29603	-43.78	-42.23	-41.19	-40.42	0.29465	-44.36	-42.72	-41.54	-40.74
0.39224	-43.20	-41.72	-40.76	-40.00	0.42047	-43.84	-42.24	-41.08	-40.31
0.48083	-42.68	-41.27	-40.38	-39.60	0.50400	-43.49	-41.92	-40.77	-40.02

^a m_A is the molality of NaCl / KCl in choline salicylate–water systems; standard uncertainties, u is 0.07614 mol·kg⁻¹ (for NaCl + water), 0.07592 mol·kg⁻¹ (for 0.015 choline salicylate+ NaCl), 0.07815 mol·kg⁻¹ (for 0.031 choline salicylate+ NaCl), 0.073987 mol·kg⁻¹ (for 0.060 choline salicylate+ NaCl), 0.07121 mol·kg⁻¹ (for KCl + water), 0.0753 mol·kg⁻¹ (for 0.015 choline salicylate+ KCl), 0.0748 mol·kg⁻¹ (for 0.031 Choline salicylate + KCl), 0.0761 mol·kg⁻¹ (for 0.060 choline salicylate + KCl), $u(T) = \pm 0.001 K$, $u(p) = 0.01 \text{ MPa}$.

Table 4.66: The values for $K_{\phi,S}^0$ and, S_K^* of Sodium chloride and potassium chloride in the aqueous choline salicylate solutions.

^a m_b (mol·kg ⁻¹)	$K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$S_K^* \times 10^6 / (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride								
0.00000	-45.43(±0.09)	-43.66(±0.09)	-42.34(±0.09)	-41.48(±0.09)	-2.79(±0.26)	-2.67(±0.25)	-2.55(±0.24)	-2.44(±0.26)
0.01500	-45.72(±0.07)	-43.88(±0.07)	-42.56(±0.07)	-41.75(±0.07)	5.09(±0.21)	4.36(±0.15)	3.81(±0.15)	3.82(±0.18)
0.03100	-45.66(±0.08)	-43.87(±0.08)	-42.56(±0.04)	-41.62(±0.08)	5.61(±0.09)	4.86(±0.08)	4.23(±0.09)	3.90(±0.06)
0.06000	-45.38(±0.07)	-43.63(±0.05)	-42.36(±0.05)	-41.50(±0.06)	5.56(±0.17)	4.85(±0.18)	4.07(±0.16)	3.83(±0.22)
Potassium chloride								
0.00000	-45.98(±0.05)	-44.13(±0.05)	-42.80(±0.06)	-41.84(±0.07)	4.61(±0.18)	4.07(±0.17)	3.75(±0.19)	3.40(±0.23)
0.01500	-45.73(±0.06)	-43.95(±0.07)	-42.64(±0.06)	-41.76(±0.07)	4.18(±0.21)	3.71(±0.23)	3.47(±0.21)	3.20(±0.23)
0.03100	-45.54(±0.05)	-43.81(±0.05)	-42.55(±0.05)	-41.66(±0.06)	3.93(±0.17)	3.50(±0.17)	3.39(±0.17)	3.12(±0.18)
0.06000	-45.42(±0.05)	-43.71(±0.05)	-42.46(±0.06)	-41.59(±0.06)	3.76(±0.17)	3.50(±0.17)	3.27(±0.18)	3.04(±0.17)

standard uncertainties u is $u(K_{\phi,S}^0) = 0.31 \times 10^{-6} / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$, $u(S_K^*) = 0.50 \times 10^{-6} / (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$.

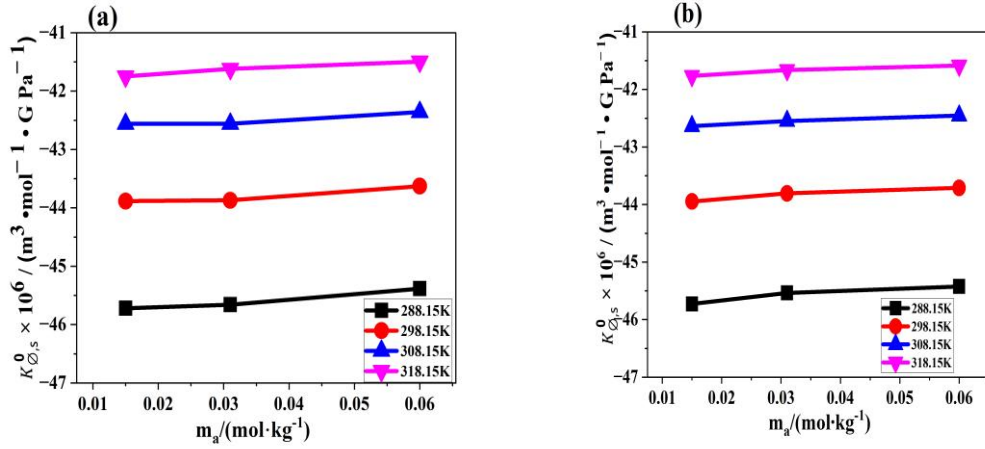


Figure 4.40: $K_{\phi,S}^0$ (a) sodium chloride and (b) Potassium chloride in aqueous solutions of choline salicylate.

Table 4.67: The $\Delta K_{\phi,S}^0$ values of the mixtures of sodium chloride and potassium chloride in aqueous choline salicylate.

^a m_b (mol·kg ⁻¹)	$\Delta K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium chloride				
0.01500	-0.29	-0.23	-0.21	-0.27
0.03100	-0.23	-0.21	-0.22	-0.14
0.06000	0.05	0.03	-0.02	-0.01
Potassium chloride				
0.01500	0.25	0.18	0.16	0.08
0.03100	0.44	0.32	0.25	0.18
0.06000	0.56	0.42	0.34	0.26

u is $u(m_b) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$, $u(\Delta K_{\phi,S}^0) = 0.08 \times 10^{-6} / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$.

Temperature dependent partial molar volume

The experimental V_{ϕ}^0 were inserted to the equation 4.4. where $T_{ref} = 298.15\text{K}$. The a, b, c, describing the temperature dependence of V_{ϕ}^0 for both solutes, are listed in **Table 4.68**. The fit quality was assessed by evaluating the relative deviation (σ) among experimental and calculated V_{ϕ}^0 values, with very low deviations and high R^2 values confirming the reliability of the polynomial model given in equation 4.5. Taking $Y = V_{\phi}^0$, the polynomial regression yielded very small deviations, with R^2 values indicating that the model effectively describes the relationship[71]. The V_{ϕ}^0 data is to evaluate the

expansibilities, which were determined by the equation 4.6 [70,72]. At infinite dilution, E_{ϕ}^0 provides valuable insights into the interaction dynamics between solute and solvent molecules. The ability of a solute to induce structural organization or disintegration within a solution medium can be assessed through a corresponding thermodynamic equation 4.7. The calculated E_{ϕ}^0 values for choline salicylate with both potassium chloride and sodium chloride are summarized in **Table 4.69**. The E_{ϕ}^0 and $(\frac{\partial E_{\phi}^0}{\partial T})_P$ values provide crucial information on solute–solvent interactions. Positive or slightly negative $(\frac{\partial E_{\phi}^0}{\partial T})_P$ values are generally indicative of structure-making (order-promoting) effects, while strongly negative values correspond to structure-breaking tendencies. As observed from **Table 4.69**, the calculated E_{ϕ}^0 and $(\frac{\partial E_{\phi}^0}{\partial T})_P$ values indicate relatively stronger solute–solvent interactions, particularly at lower concentrations. These observations are specific to the aqueous choline salicylate system and reflect ion-specific hydration behaviour rather than a universal classification of NaCl or KCl as structure-making or structure-breaking electrolytes. This suggests strong solute–solvent interactions, possibly arising from ion–dipole and hydrogen-bonding interactions between choline salicylate and water molecules. The slightly higher E_{ϕ}^0 values observed in the potassium chloride system compared to sodium chloride indicate a greater disruption of the water structure, which may be attributed to the weaker hydration and larger ionic radius of K^+ relative to Na^+ [73,74]. Overall, these findings indicate that temperature and ionic environment significantly influence the hydration structure and volumetric behaviour of choline salicylate solutions.

Table 4.68: Calculated values for empirical parameters for choline salicylate with sodium chloride and potassium chloride.

$m_B / (\text{mol} \cdot \text{kg}^{-1})$	$a \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$	$b \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R^2	ARD
Sodium chloride					
0.01500	16.52271	0.01775	0.00003	16.52271	0.00087
0.03100	16.56944	0.01996	0.00024	16.56944	0.0005
0.06000	17.01663	0.02658	-0.00004	17.01663	0.0009
Potassium chloride					
0.01500	27.02507	0.02118	-0.00003	0.99837	0.000311
0.03100	27.77862	0.05050	0.00042	0.99966	0.000358
0.06000	28.06499	0.06735	-0.00039	0.99916	0.000649

^a m_B is molality of choline salicylate (moles per kg of pure water).

Table 4.69: Calculated partial molar expansibilities, (E_{ϕ}^0) values for choline salicylate with sodium chloride and potassium chloride.

$^a m_B \text{ (mol} \cdot \text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p / \text{(m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	T = 288.15K	T = 298.15K	T = 308.15K	T = 318.15K	
sodium chloride					
0.01500	0.01710	0.01775	0.01841	0.01906	0.00007
0.03100	0.01514	0.01996	0.02478	0.02960	0.00048
0.06000	0.02733	0.02658	0.02583	0.02508	-0.00007
Potassium chloride					
0.01500	0.021806	0.021177	0.020549	0.019921	-0.00006
0.03100	0.042121	0.050502	0.058884	0.067266	0.00084
0.06000	0.075093	0.067345	0.059598	0.051851	-0.00077

standard uncertainties u is $u(E_{\phi}^0) = 0.005 \times 10^{-6} \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$, $u(\frac{\partial E_{\phi}^0}{\partial T}) = 0.00055 \text{ (m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$, $u(T) = \pm 0.001 \text{ K}$, $u(p) = 0.01 \text{ MPa}$.

Table 4.70: V_{AB} , K_{AB} , V_{ABB} , and K_{ABB} coefficients of (sodium chloride and potassium chloride) salts present in aqueous solutions of choline salicylate.

T/K	$V_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg)$	$V_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2)$	$K_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg GPa^{-1})$	$K_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2 GPa^{-1})$
Sodium chloride				
288.15	22.17042	-140.696	3.255291	-15.0909
298.15	16.89442	-86.0852	0.386905	24.67432
308.15	10.73616	-30.0325	1.633519	-1.5007
318.15	6.03080	12.24499	-1.24785	15.89047
Potassium chloride				
288.15	5.70375	-13.2906	9.76372	-56.9867
298.15	4.54538	33.5056	6.92474	-38.4146
308.15	3.86555	74.1333	5.64849	-31.0366
318.15	9.82132	36.9172	3.32992	-13.0384

^a m_B is molality of choline salicylate (moles per kg of pure water).

Pair and triplet interaction coefficient

Friedman and Krishnan extended the McMillan–Mayer theory offering a framework to understand the transfer properties of solutes in aqueous choline salicylate solutions. The equations 4.12 and 4.13 were used to compute interaction coefficients of volume and compressibility. The interaction coefficients (Table 4.70) yield quantitative information on the solute–solute and cooperative interactions in these ternary systems. Positive V_{AB} values at lower temperatures indicate important ion–solvent and solute–solvent interactions characteristic of structure-making. Negative V_{AB} values at lower temperatures reflect the fact that at higher concentrations, such solute–solute interactions caused by structural promotion led to partial disruption of the solvent structure. Similarly, the compressibility coefficients (K_{AB} and K_{ABB}) reflect the effect of ionic environment on the compressional properties of the medium. For the sodium chloride system, K_{AB} values decrease with rising temperature, indicating a loss of ion–solvent coupling and increased freedom of the molecules in solution. In contrast, higher K_{AB} values are found for the potassium chloride system in accordance with a weaker hydration ability of K^+ ions compared to Na^+ , thus, more pronounced structure-breaking effects may be expected. The general trend, therefore, appearing in the variation of volume and compressibility interaction coefficients with temperature, shows that the interactions in choline salicylate–salt–water systems are determined by a fine balance between electrostatic and hydrophobic forces. Increase in temperature, on one hand, increases solute–solute association, while on the other, reduces structuring of the solvent, and this is consistent with a transition from highly ordered to a less organized hydration environment [72,86–89].

Isobaric thermal expansion coefficients

The α_p quantifies the fractional temperature dependence of V_ϕ^0 at constant pressure. It was calculated using the equation 4.14. As shown in Table 4.71, α_p values increase with rising temperature for both sodium chloride and potassium chloride systems, indicating enhanced molecular motion and decreased structural ordering of water at elevated temperatures. The higher α_p values observed in the potassium chloride system compared to sodium chloride suggest greater expansibility and stronger structure-breaking behaviour, consistent with the lower hydration ability of K^+ ions.

Furthermore, the presence of choline salicylate slightly elevates α_p , implying that solute–solvent interactions weaken the hydrogen-bonded network of water, leading to increased compressibility and reduced cohesion within the solution.

Table 4.71 α_p for sodium chloride and potassium chloride in aqueous choline salicylate solutions at numerous temperatures.

$^a m_b /$ (mol· kg ⁻¹)	$\alpha_p \times 10^3 / (K^{-1})$							
	Sodium chloride				Potassium chloride			
	288.15	298.15	308.15	318.15	288.15	298.15	308.15	318.15
0.015	1.05	1.07	1.10	1.13	0.81	0.78	0.75	0.73
0.0310	0.92	1.20	1.48	1.73	1.54	1.82	2.08	2.32
0.0600	1.63	1.56	1.50	1.43	2.74	2.40	2.07	1.77

standard uncertainties, $u(\alpha_p) = 0.032 \times 10^{-3} / (K^{-1})$.

Hydration number

The variation of n_H with temperature and concentration provides valuable insight into the structure and dynamics of the solvation shell surrounding the ions. The n_h values for the studied liquid systems were computed using an equation proposed by Passynski [102,103], which is given in equation 4.18. The temperature rise causes, as can be seen from **Table 4.72**, a decrease in n_H for both sodium chloride and potassium chloride, indicating weakening ion-dipole interactions and partial disruption of the hydration shell by enhanced thermal motion. In aqueous choline salicylate solutions, n_H values are lower than in pure water, indicating the competition of choline salicylate molecules with water as solvation species around the ions. The constantly higher hydration numbers of sodium chloride compared with potassium chloride point to the stronger hydration of Na^+ ions due to the smaller ionic radius and higher charge density. Overall, this decrease of n_H by temperature and by solute concentration corresponds to reduced solvent structuring and a transition toward a more disordered aqueous environment.

Specific heat ratio

This was calculated by equation 4.17, As shown in Table 4.73, γ decreases slightly with increasing temperature for both sodium chloride and potassium chloride systems, reflecting enhanced molecular mobility and reduced cohesive forces within the liquid phase. In aqueous choline salicylate solutions, γ values are marginally lower than in pure water, suggesting comparatively weaker hydrogen bonding and greater molecular mobility in the investigated aqueous choline salicylate system caused by solute–solvent interactions. The potassium chloride system exhibits slightly lower γ values compared to sodium chloride, consistent with the weaker hydration and larger ionic radius of K^+ ions.

Spectroscopic study

FTIR spectroscopy was employed to investigate aqueous choline salicylate of $0.060 \text{ mol}\cdot\text{kg}^{-1}$ concentration with salts at different molalities (Figure 4.41). The FTIR spectra of choline salicylate (CS) in H_2O and in the presence of NaCl/KCl exhibit distinctive vibrational characteristics that indicate unique interaction patterns within the system. The broad band seen between 3300 and 3400 cm^{-1} in aqueous CS is due to O–H stretching vibrations of water and hydrogen-bonded hydroxyl groups of CS. The peak at 1634 – 1655 cm^{-1} is due to C=O stretching of the salicylate moiety, and the bands near 550 – 600 cm^{-1} are due to aromatic C–H out-of-plane bending. When NaCl or KCl is added, the O–H and C=O stretching regions change noticeably. The O–H band moves to 3306 – 3339 cm^{-1} and the C=O band moves to 1633 – 1643 cm^{-1} . This shows that the hydrogen-bonding network has been reorganized and that the CS anion and the added cations are interacting in ways that are specific to each ion. Samples with NaCl usually have slightly bigger peak shifts than those with KCl. This is because Na^+ is better at hydrating and structuring than K^+ . Small changes in the vibrations of the aromatic ring (560 – 590 cm^{-1}) back up the idea that the solvation environment is changing in small ways. The spectral changes show that both NaCl and KCl change the way molecules interact and how water molecules are arranged around them. This shows clear ion-specific (Hofmeister-type) effects. These FTIR observations support the findings from the volumetric and acoustic measurements, affirming significant

solute–solvent interactions and ion-specific effects that influence the hydration structure and molecular organization within the CS–water system [68].

Table 4.72 Values for Hydration number of NaCl/KCl in water and aqueous solutions of choline salicylate.

$m_a/(\text{mol.kg}^{-1})$	n_h				$m_a/(\text{mol.kg}^{-1})$	n_h			
	288.15	298.15	308.15	318.15		288.15	298.15	308.15	318.15
0.00000 choline Salicylate + sodium chloride					0.00000 choline Salicylate + potassium chloride				
0.09669	7.46770	7.68251	7.73538	6.97042	0.10621	6.99249	7.11075	6.63674	6.58137
0.19897	6.91076	6.75204	6.63211	5.80960	0.18956	6.86890	6.83942	6.41802	6.16510
0.29215	8.20680	7.77469	7.26791	6.87345	0.28101	6.81212	6.69815	6.26412	5.97785
0.40757	7.23320	6.87352	6.29791	6.34355	0.38281	6.70274	6.43403	6.17293	5.81355
0.49242	6.87431	6.44066	5.80422	5.99420	0.46818	6.65127	6.39963	6.09807	5.82623
0.015000 choline Salicylate + sodium chloride					0.01500 choline Salicylate + potassium chloride				
0.09227	6.83495	6.22041	5.96749	6.06638	0.09547	6.60558	6.01166	5.76723	5.86281
0.19715	6.42605	5.82410	5.67490	5.56057	0.19396	6.53197	5.92010	5.76843	5.65222
0.30150	6.20155	5.71505	5.54582	5.35206	0.29203	6.40268	5.90040	5.72569	5.52564
0.39763	6.25006	5.79591	5.63439	5.42263	0.39272	6.32812	5.86829	5.70476	5.49035
0.49161	5.95966	5.54647	5.38320	5.22395	0.46847	6.25403	5.82043	5.64909	5.48198
0.03100 choline Salicylate + sodium chloride					0.03100 choline Salicylate + potassium chloride				
0.13336	7.60397	6.87929	6.85904	6.91612	0.10409	6.42979	5.44426	5.54737	5.25471
0.22259	7.66594	7.00592	6.67000	6.74705	0.18604	6.22859	5.48463	5.51504	5.20428
0.34307	7.70088	6.99094	6.63490	6.46022	0.32172	6.01051	5.46443	5.47824	5.19775

0.42491	7.58291	6.94302	6.47525	6.37778	0.41181	5.98180	5.41927	5.44669	5.15734
0.51525	7.55964	6.86716	6.39050	6.16771	0.49732	5.87543	5.40730	5.41633	5.15448
0.06000 choline Salicylate + sodium chloride					0.06000 choline Salicylate + potassium chloride				
0.09820	8.19662	7.92133	7.05714	7.29072	0.10574	5.91912	5.50935	5.20485	5.23162
0.19243	8.28622	7.68709	6.88179	6.76221	0.20261	5.82080	5.50129	5.26828	5.15883
0.29603	8.07295	7.58133	6.77431	6.52451	0.29465	5.74278	5.49280	5.24553	5.12201
0.39224	8.02486	7.44973	6.62755	6.45413	0.42047	5.65485	5.42442	5.21831	5.06937
0.48083	7.90313	7.33118	6.50432	6.40425	0.50400	5.58845	5.38185	5.20493	5.03306

m_a is the molality of aqueous choline salicylate. uncertainties u is $u(m_b) = 0.01 \text{ mol}\cdot\text{kg}^{-1}$, $u(n_h) = 0.41892$, $u(T) = 0.01\text{K}$, $u(p)=0.01\text{MPa}$.

Table 4.73 Y values for potassium chloride and sodium chloride in water and aqueous choline salicylate.

$^a m_A /$ (mol·kg ⁻¹)	Specific Heat ratio (Y)				$^a m_A /$ (mol · kg ⁻¹)	Specific Heat ratio (Y)			
	288.15	298.15	308.15	318.15		288.15	298.15	308.15	318.15
0.00000 choline Salicylate + sodium chloride					0.06000 choline Salicylate + potassium chloride				
0.00000	1.38019	1.36043	1.34198	1.32470	0.00000	1.38019	1.36043	1.34198	1.32470
0.09669	1.37832	1.35859	1.34019	1.32294	0.10621	1.37788	1.35816	1.33975	1.32251
0.19897	1.37636	1.35669	1.33832	1.32112	0.18956	1.37610	1.35641	1.33804	1.32083
0.29215	1.37462	1.35498	1.33665	1.31948	0.28101	1.37418	1.35452	1.33617	1.31900
0.40757	1.37249	1.35289	1.33461	1.31748	0.38281	1.37207	1.35245	1.33414	1.31701
0.49242	1.37095	1.35139	1.33314	1.31641	0.46818	1.37034	1.35075	1.33245	1.31537
0.01500 choline Salicylate + sodium chloride					0.01500 choline Salicylate + potassium chloride				
0.00000	1.37977	1.35998	1.34158	1.32441	0.00000	1.37977	1.35998	1.34158	1.32441
0.09227	1.37802	1.35826	1.33989	1.32275	0.09547	1.37772	1.35797	1.33961	1.32246
0.19715	1.37606	1.35635	1.33801	1.32089	0.19396	1.37567	1.35595	1.33762	1.32051
0.30150	1.37416	1.35448	1.33617	1.31909	0.29203	1.37368	1.35400	1.33570	1.31862
0.39763	1.37244	1.35279	1.33451	1.31746	0.39272	1.37169	1.35205	1.33379	1.31675
0.49161	1.37079	1.35117	1.33292	1.31589	0.46847	1.37023	1.35062	1.33239	1.31537
0.03100 choline Salicylate +sodium chloride					0.03100 choline Salicylate + potassium chloride				
0.00000	1.37946	1.35967	1.34128	1.32417	0.00000	1.37946	1.35967	1.34128	1.32417
0.13336	1.37694	1.35720	1.33885	1.32179	0.10409	1.37725	1.35751	1.33918	1.32212

0.22259	1.37529	1.35558	1.33727	1.32023	0.18604	1.37556	1.35586	1.33756	1.32054
0.34307	1.37310	1.35345	1.33517	1.31817	0.32172	1.37283	1.35321	1.33497	1.31800
0.42491	1.37165	1.35203	1.33377	1.31679	0.41181	1.37108	1.35151	1.33330	1.31636
0.51525	1.37008	1.35048	1.33225	1.31529	0.49732	1.36946	1.34994	1.33175	1.31485
0.06000 choline Salicylate + sodium chloride					0.06000 choline Salicylate + potassium chloride				
0.00000	1.37880	1.35910	1.34069	1.32365	0.00000	1.37880	1.35910	1.34069	1.32365
0.09820	1.37696	1.35730	1.33892	1.32192	0.10574	1.37657	1.35693	1.33858	1.32159
0.19243	1.37523	1.35561	1.33727	1.32029	0.20261	1.37458	1.35499	1.33669	1.31975
0.29603	1.37338	1.35380	1.33549	1.31854	0.29465	1.37276	1.35322	1.33495	1.31805
0.39224	1.37170	1.35217	1.33388	1.31696	0.42047	1.37035	1.35086	1.33263	1.31580
0.48083	1.37018	1.35068	1.33243	1.31555	0.50400	1.36879	1.34936	1.33114	1.31436

m_A is the molality of salts in the aqueous solution of choline salicylate: the calculated standard uncertainties u is $U_r(m)=0.01$, $u(T)=0.001K$, $u(Y)=0.006$.

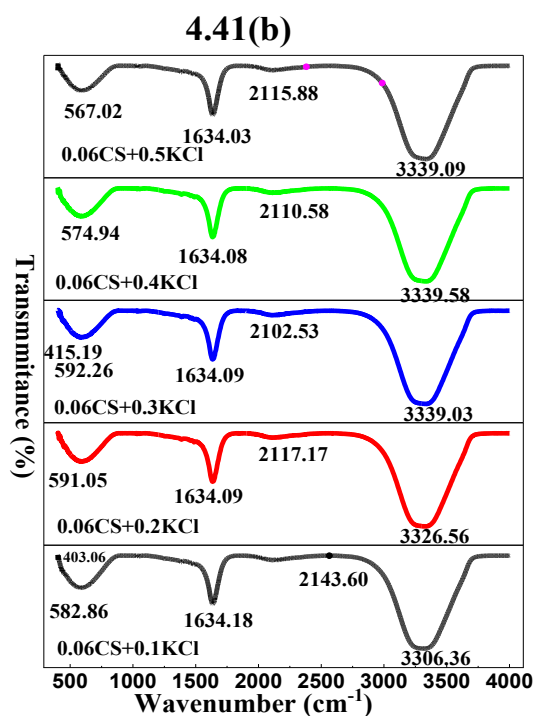
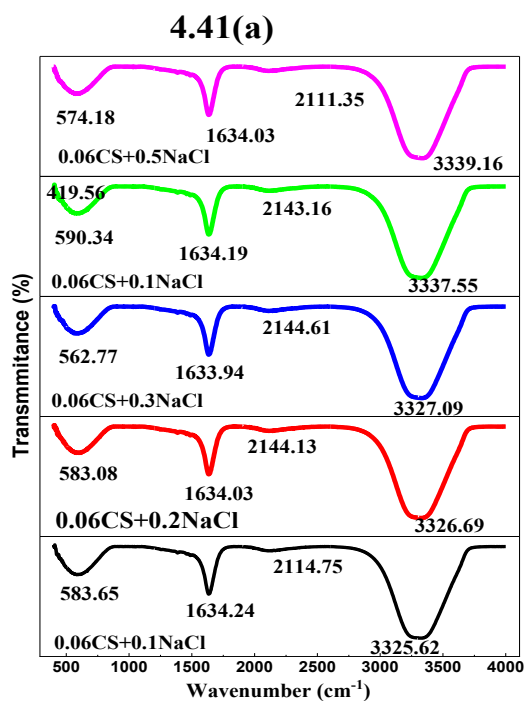
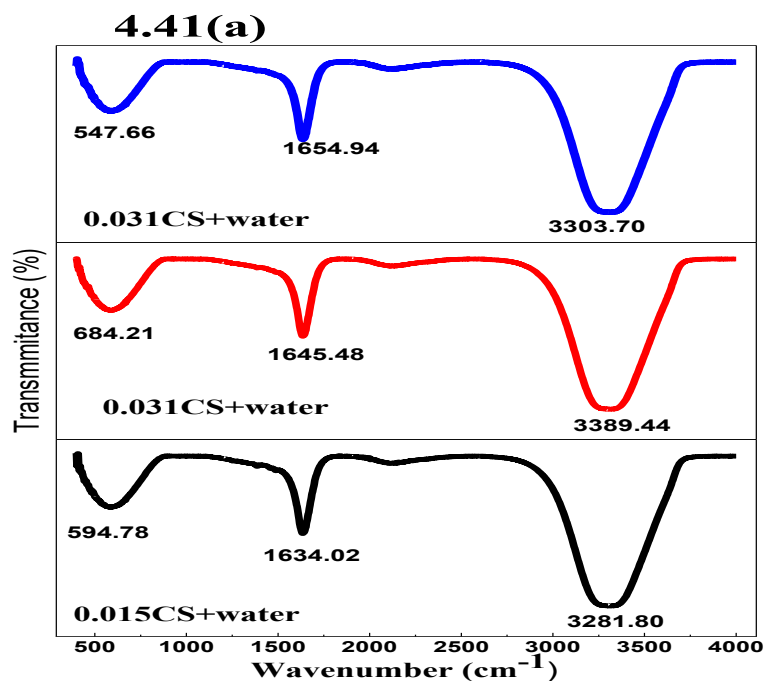


Figure 4.41: FTIR spectra for binary mixture (water + choline salicylate) at three different concentrations; in 4.41(a) and 4.41(b), (c) are spectra of ternary mixtures of 0.06 concentration of choline salicylate in sodium chloride and potassium chloride at 0.1-0.5 molalities respectively.

Section III

Problem 7: Investigation of Thermodynamic and Spectroscopic Interactions in Sodium Salicylate solutions with Sodium Salts at Varying Temperatures

In this problem, values of ρ and c were experimentally measured in sodium salicylate solutions and then FTIR spectroscopy was also conducted to validate results as shown in **figure 4.42**.

Density and ultrasonic velocity

Using experimental measured density and sound velocity, key volumetric and ultrasonic properties were calculated. The study focused on Na_2SO_4 and $NaCl$ in aqueous sodium salicylate, with concentrations from 0.010 to 0.030 mol·kg⁻¹. Readings were at four temperatures, in increments of 10 K. Analysis of the density data revealed a direct correlation with sodium salicylate concentration, showing an increase in density as concentration rises. Conversely, density values decreased with rising temperature. However, as both the concentration and the temperature of the binary mixture (water + sodium salicylate) rise, the sound velocity values also rise. The obtained values of ρ and c , as well as estimated parameters derived from these measurements, are provided in **Table 4.74 and 4.75**. A comparison plots of density and ultrasonic velocity of a binary mixtures (sodium salicylate + water) with references [169] [170] [171] [172] [173], (sodium chloride + water) [1–5] and (sodium sulphate + water) [105] [106] [107] at 0.1 MPa pressure are shown in **Figure 4.43 (a), 4.43(b)** (for density and ultrasonic velocity of sodium salicylate + water), and in **Figure 4.1(a), 4.1(b)**, (for density and ultrasonic velocity of $NaCl + H_2O$), **4.16(a), 4.16(b)**), (for density and ultrasonic velocity of $Na_2SO_4 + H_2O$) respectively. The figures clearly show that both ρ and c values agree well with those found in the literature. While previous studies have extensively reported density and sound velocity for individual binary systems (e.g., $NaCl + H_2O$, $Na_2SO_4 + H_2O$, sodium salicylate + H_2O), the present study uniquely investigates their behaviour in the presence of sodium salicylate. This comparison provides new insights into the role of sodium salicylate in modifying solute-solvent interactions, particularly in terms of hydration effects and structural rearrangements at varying temperatures. Deviations observed at higher temperatures can be attributed to increased thermal motion disrupting molecular

interactions, experimental uncertainties due to equipment sensitivity, and variations in sample purity or methodologies in the reference data. However, these variations remain consistent with trends reported in previous studies, further validating the reliability of the findings. Despite these deviations, the overall trends align well with the literature, validating the reliability of the results. Based on the observation, there is a rise in density, which is likely because of the upsurge in the chain length of the sodium chloride or sodium sulphate [174]. The observed linear rise in the sound velocity with rising temperature suggests the presence of both intermolecular and intramolecular H₂ bonds among the solute - solvent molecules [175–178]. The observed linear rise in the sound speed with rising temperature indicates changes in the structural arrangement and interactions between the solute (sodium chloride or sodium sulphate) and solvent (aqueous sodium salicylate) molecules, likely due to alterations in molecular packing and intermolecular forces. This pattern mirrors the behaviour of pure water as temperature changes. In water, the formation of monomeric water molecules and the breaking of H-bonds accelerate free molecules entering the available space, which then get trapped in a cage-shaped structure created by other water molecules. This process results in a more densely packed structure as temperature increases. Additionally, as the bonds between sodium salicylate and water molecules break, new hydrogen bonds form among *NaCl*, *Na₂SO₄*, and sodium salicylate molecules. [108,179,180].

Apparent molar volume

Equation 4.1 was used to determine the V_ϕ , m_A is the molality of the *NaCl/Na₂SO₄* per kilogram of the sodium salicylate, and ρ , ρ_0 , tells the densities of solution and the sodium salicylate + H₂O subsequently. The V_ϕ values are shown in **Table 4.74**, and the plot of $(V_\phi - A_V\sqrt{m})$ is depicted in **Figure 4.44**. For *Na₂SO₄*, V_ϕ increases with rising temperatures and decreases with increasing molality. This suggests that at higher temperatures, the structuring effect of sulphate ions weakens, allowing thermal expansion, while at higher concentrations, strong electrostatic interactions can lead to a more compact solvent arrangement. Similarly, for *NaCl* V_ϕ decreases with increasing molality, indicating strong solute-solvent interactions that restrict volume expansion. The positive V_ϕ values confirm significant solute-solvent interactions. Notably, *Na₂SO₄*, with its higher ionic charge, has a stronger effect on solvent

structuring than *NaCl*, as seen in its sharper response to temperature and concentration changes. These findings not only underscore the critical role of ionic charge and solvent interactions but also emphasize the ability of thermal energy to modulate solute-solvent dynamics. Such detailed insights provide a deeper understanding of how electrolytes interact with complex solvents, paving the way for advancements in the design of solution-based systems in chemical and industrial applications[181–183] .

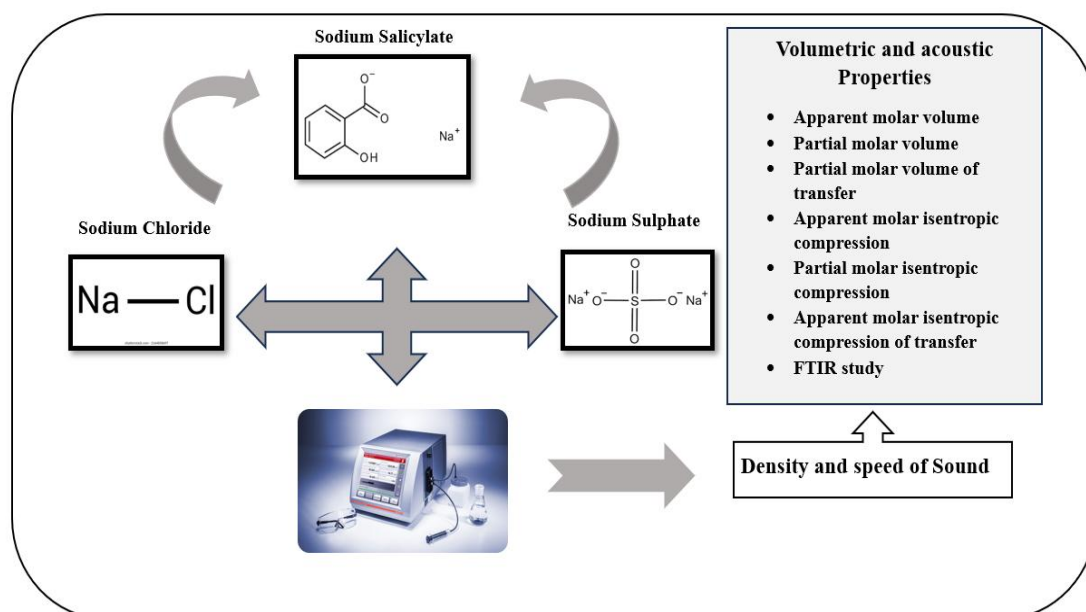


Figure 4.42: $\text{NaCl}/\text{Na}_2\text{SO}_4$ and sodium salicylate interactions

Table 4.74 Measured ρ and V_ϕ , for ternary mixes of aqueous $NaSl$ with $NaCl$ and Na_2SO_4 at multiple t temperatures.

$^a m_a / (\text{mol} \cdot \text{kg}^{-1})$	$\rho \times 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$				$V_\phi \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Chloride ($NaCl$) + H_2O								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.09669	1.00334	1.00109	0.99803	0.99431	15.61	15.93	16.29	16.63
0.19897	1.00762	1.00532	1.00221	0.99844	15.53	15.84	16.16	16.49
0.29215	1.01146	1.00913	1.00598	1.00217	15.53	15.80	16.11	16.39
0.40757	1.01617	1.01380	1.01059	1.00674	15.56	15.79	16.11	16.32
0.49242	1.01960	1.01719	1.01394	1.00919	15.58	15.82	16.11	16.28
0.01 mol·kg⁻¹ sodium salicylate + $NaCl$								
0.00000	0.99971	0.99762	0.99454	0.99091				
0.11104	1.00438	1.00228	0.99912	0.99543	15.76	15.99	16.32	16.68
0.21794	1.00882	1.00668	1.00347	0.99973	15.70	15.95	16.23	16.57
0.31387	1.01276	1.01058	1.00731	1.00353	15.69	15.93	16.24	16.54
0.41124	1.01672	1.01449	1.01117	1.00735	15.68	15.95	16.26	16.55
0.49645	1.02014	1.01789	1.01451	1.01064	15.73	15.94	16.29	16.57
0.02 mol·kg⁻¹ sodium salicylate + $NaCl$								
0.00000	1.00047	0.99843	0.99547	0.99142				
0.13357	1.00606	1.00397	1.00096	0.99685	15.87	16.14	16.38	16.71
0.20413	1.00899	1.00686	1.00383	0.99967	15.81	16.11	16.33	16.69
0.30313	1.01305	1.01088	1.00781	1.00359	15.80	16.09	16.30	16.67

0.38123	1.01622	1.01401	1.01091	1.00663	15.83	16.10	16.30	16.70
0.45398	1.01913	1.01691	1.01378	1.00946	15.88	16.11	16.30	16.70
0.03 mol·kg⁻¹ sodium salicylate + NaCl								
0.00000	1.00099	0.99914	0.99628	0.99233				
0.11030	1.00560	1.00371	1.00081	0.99681	16.05	16.29	16.54	16.87
0.19730	1.00919	1.00727	1.00435	1.00029	16.02	16.22	16.42	16.79
0.29610	1.01322	1.01127	1.00831	1.00420	16.03	16.23	16.38	16.76
0.39278	1.01712	1.01512	1.01215	1.00798	16.05	16.28	16.39	16.74
0.49499	1.02119	1.01916	1.01614	1.01192	16.11	16.32	16.45	16.77
Sodium Sulphate (Na₂SO₄) + H₂O								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.09136	1.01068	1.00834	1.00521	1.00141	15.96	17.10	18.01	18.79
0.20034	1.02410	1.02162	1.01837	1.01445	16.37	17.36	18.09	18.79
0.30305	1.03667	1.03405	1.03069	1.02662	16.40	17.35	18.02	18.77
0.39442	1.04769	1.04496	1.04146	1.03729	16.64	17.52	18.28	18.95
0.49751	1.06004	1.05713	1.05349	1.04918	16.82	17.75	18.49	19.18
0.01 mol·kg⁻¹ sodium salicylate + Na₂SO₄								
0.00000	0.99971	0.99760	0.99454	0.99124				
0.09836	1.01198	1.00972	1.00651	1.00307	16.23	17.35	18.56	19.29
0.19834	1.02427	1.02189	1.01855	1.01500	16.41	17.54	18.52	19.32
0.30305	1.03710	1.03453	1.03103	1.02737	16.53	17.61	18.58	19.30
0.41442	1.05055	1.04784	1.04419	1.04031	16.73	17.71	18.64	19.50

0.49851	1.06048	1.05773	1.05401	1.05005	17.11	17.93	18.72	19.51
0.02 mol·kg⁻¹ sodium salicylate + Na₂SO₄								
0.00000	1.00047	0.99843	0.99547	0.99142				
0.09836	1.01264	1.01047	1.00742	1.00322	17.32	18.32	18.88	19.86
0.20340	1.02556	1.02326	1.02010	1.01575	17.11	18.04	18.56	19.49
0.29805	1.03703	1.03468	1.03140	1.02689	17.30	17.98	18.58	19.55
0.40420	1.04980	1.04735	1.04402	1.03923	17.43	18.05	18.48	19.70
0.50751	1.06212	1.05949	1.05599	1.05116	17.54	18.27	18.83	19.74
0.03 mol·kg⁻¹ sodium salicylate + Na₂SO₄								
0.00000	1.00099	0.99914	0.99628	0.99233				
0.09814	1.01258	1.01043	1.00738	1.00319	17.41	18.42	18.98	19.81
0.19034	1.02391	1.02162	1.01845	1.01414	17.48	18.36	18.98	19.84
0.29305	1.03635	1.03397	1.03069	1.02625	17.55	18.33	18.96	19.86
0.40442	1.04980	1.04726	1.04380	1.03918	17.65	18.32	19.07	19.87
0.49751	1.06080	1.05820	1.05466	1.04988	17.80	18.49	19.14	19.98

^a*m*_a - molality of NaCl and Na₂SO₄ in sodium salicylate aqueous solutions. The uncertainties are *u*_r(*m*) = 0.01, *u*(*ρ*) = 0.5 kg · m⁻³, *u*(*p*)=0.01MPa, *u* (*V*_φ) = 3.15 × 10⁻⁶/(m³ · mol⁻¹), *u*(*T*)= ±0.01K.

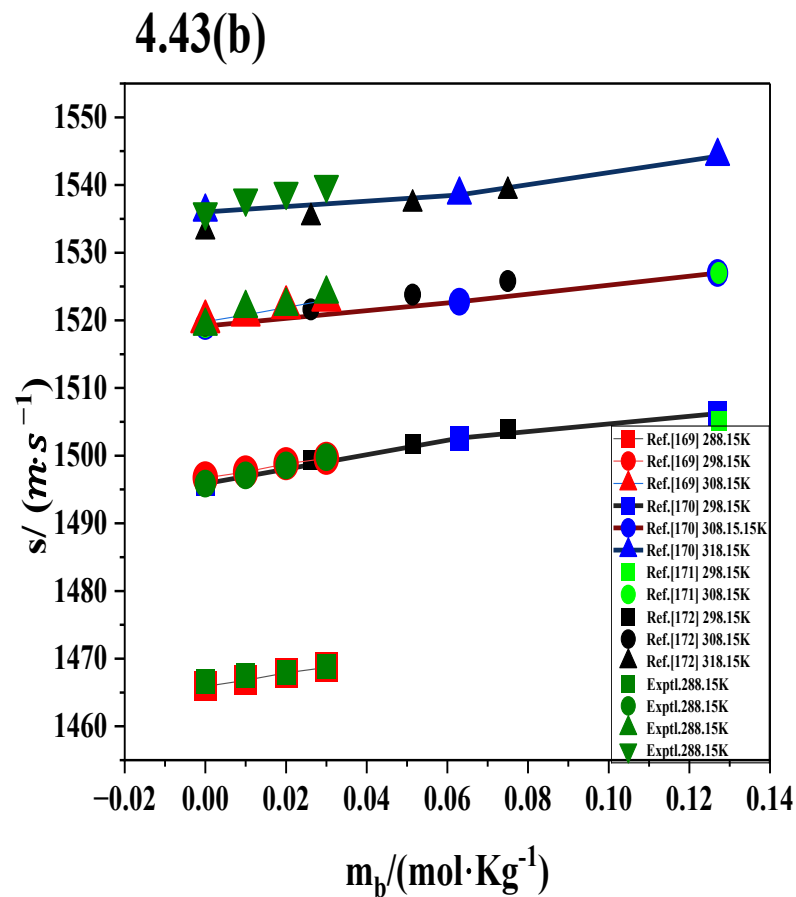
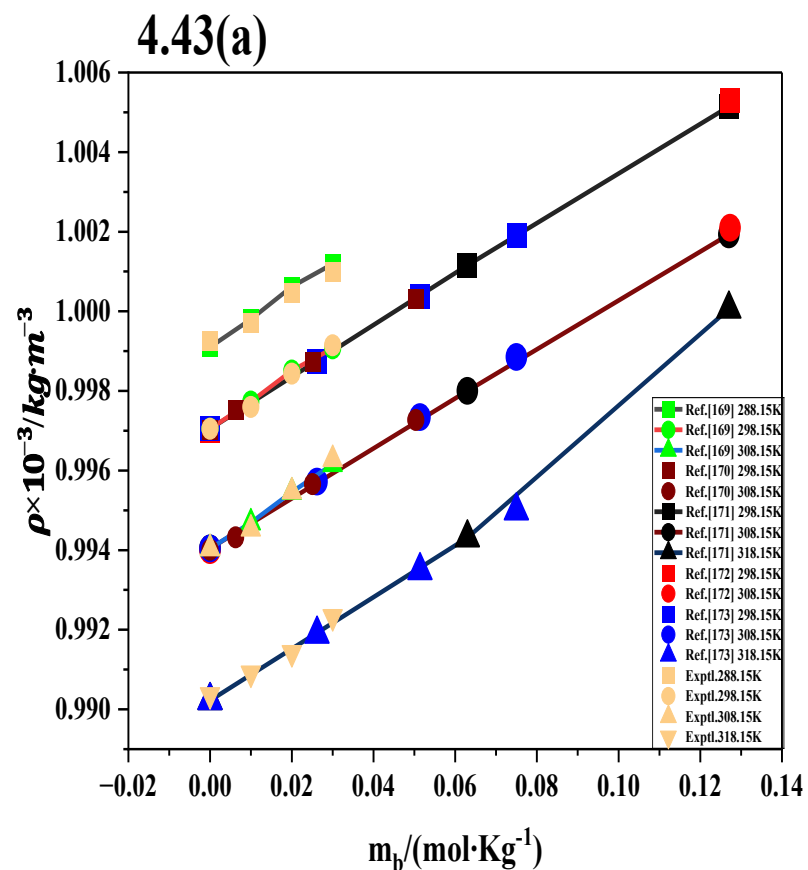


Figure 4.43: Fig. 4.43(a) ,4.43(b) depicts comparison of measured and reported values for density and sound velocity respectively, for (sodium Salicylate + H₂O) with respect to the molality (m_b) of sodium salicylate at different temperature respectively.

Table 4.75: ultrasonic velocity, c and $K_{\phi,S}$ for $NaCl$ and Na_2SO_4 in aqueous sodium salicylate.

$^a m_a / (\text{mol} \cdot \text{kg}^{-1})$ 1)	$c / (\text{m} \cdot \text{s}^{-1})$				$K_{\phi,S} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
<i>NaCl+H₂O</i>								
0.00000	1466.59	1495.85	1519.14	1536.02				
0.09669	1473.21	1502.91	1526.41	1542.35	-45.61	-43.83	-42.51	-41.63
0.19897	1478.91	1508.03	1531.23	1545.96	-46.06	-44.26	-42.92	-42.04
0.29215	1490.23	1518.23	1539.81	1555.31	-46.31	-44.50	-43.15	-42.26
0.40757	1494.53	1522.32	1542.71	1560.21	-46.57	-44.75	-43.39	-42.50
0.49242	1498.25	1525.14	1544.41	1563.73	-46.75	-44.92	-43.55	-42.62
0.01 mol·kg⁻¹ sodium salicylate + <i>NaCl</i> (in aqueous medium)								
0.00000	1467.57	1497.09	1521.78	1539.49				
0.11104	1478.27	1506.83	1531.89	1547.89	-45.33	-43.65	-42.19	-41.33
0.21794	1486.13	1513.93	1537.92	1553.21	-45.74	-44.04	-42.57	-41.70
0.31387	1493.34	1519.64	1542.48	1558.25	-45.98	-44.27	-42.79	-41.92
0.41124	1501.23	1526.07	1546.92	1563.64	-46.20	-44.48	-42.99	-42.11
0.49645	1508.18	1531.57	1550.53	1568.57	-46.37	-44.65	-43.15	-42.27
0.02 mol·kg⁻¹ sodium salicylate + <i>NaCl</i> (in aqueous medium)								
0.00000	1467.91	1498.55	1522.09	1541.04				
0.13357	1480.07	1508.08	1532.64	1548.86	-45.59	-43.79	-42.19	-41.30
0.20413	1487.12	1513.91	1537.34	1554.32	-45.84	-44.03	-42.42	-41.53

0.30313	1497.38	1521.85	1544.68	1560.24	-46.10	-44.28	-42.66	-41.76
0.38123	1506.06	1529.12	1549.03	1566.15	-46.28	-44.45	-42.82	-41.92
0.45398	1513.47	1534.42	1553.18	1571.39	-46.43	-44.60	-42.96	-42.06

0.03 mol·kg⁻¹ sodium salicylate + NaCl (in aqueous medium)

0.00000	1468.91	1499.76	1523.91	1543.07				
0.11030	1482.99	1509.15	1534.92	1550.92	-44.99	-43.50	-41.97	-41.10
0.19730	1491.34	1516.39	1541.68	1556.61	-45.34	-43.83	-42.30	-41.41
0.29610	1500.25	1523.43	1547.36	1562.7	-45.60	-44.08	-42.54	-41.65
0.39278	1510.34	1530.49	1552.08	1568.49	-45.82	-44.29	-42.73	-41.84
0.49499	1519.08	1536.49	1556.67	1574.36	-46.03	-44.49	-42.92	-42.03

Na₂SO₄+H₂O

0.00000	1466.59	1495.85	1519.14	1536.02				
0.09136	1480.92	1509.9	1532.18	1548.23	-46.51	-44.70	-43.37	-42.41
0.20034	1496.62	1523.6	1544.23	1560.09	-47.41	-45.56	-44.20	-43.22
0.30305	1511.04	1537.84	1558.04	1572.17	-48.07	-46.19	-44.81	-43.81
0.39442	1527.02	1554.15	1572.09	1585.37	-48.62	-46.72	-45.31	-44.30
0.49751	1541.01	1566.07	1584.88	1597.67	-49.22	-47.29	-45.86	-44.83

0.01 mol·kg⁻¹ sodium salicylate + Na₂SO₄ (in aqueous medium)

0.00000	1467.57	1498.21	1521.78	1539.49				
0.09836	1482.99	1514.27	1535.61	1552.67	-46.55	-44.66	-43.28	-42.28
0.19834	1500.06	1530.54	1548.32	1565.99	-47.36	-45.43	-44.02	-43.01
0.30305	1515.56	1544.98	1561.58	1577.88	-48.03	-46.07	-44.64	-43.61

0.41442	1533.43	1562.01	1576.23	1592.34	-48.70	-46.70	-45.25	-44.19
0.49851	1547.68	1575.26	1589.93	1604.99	-49.18	-47.16	-45.69	-44.63

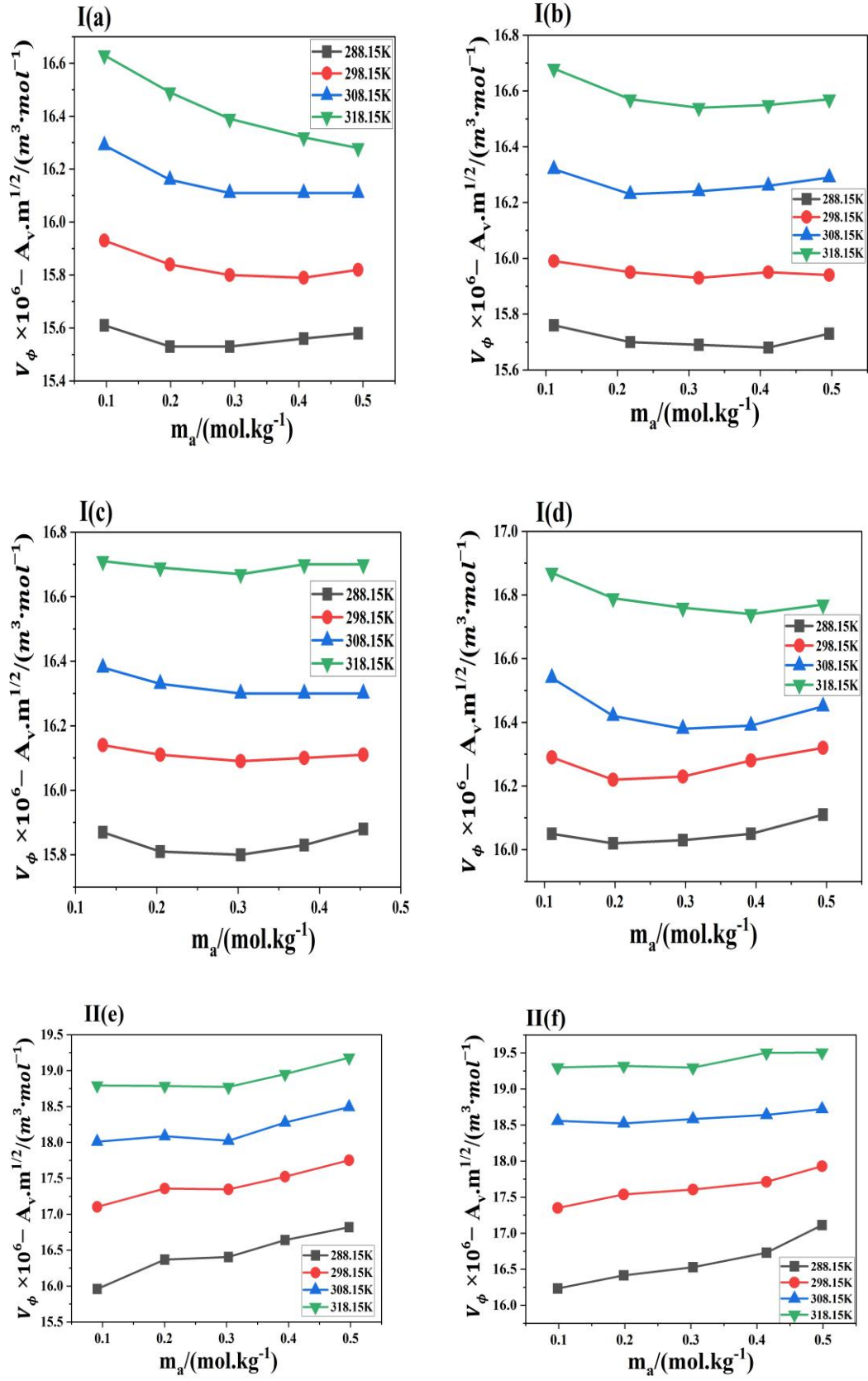
0.02 mol·kg⁻¹ sodium salicylate + Na₂SO₄ (in aqueous medium)

0.00000	1468.91	1498.55	1522.09	1541.04				
0.09836	1486.38	1511.99	1538.99	1554.67	-46.46	-44.63	-43.26	-42.19
0.20340	1502.89	1524.78	1552.06	1567.76	-47.30	-45.44	-44.04	-42.95
0.29805	1518.30	1539.44	1564.89	1579.73	-47.90	-46.01	-44.59	-43.49
0.40420	1536.32	1557.34	1580.76	1594.23	-48.54	-46.62	-45.18	-44.05
0.50751	1551.94	1572.76	1594.32	1607.41	-49.13	-47.18	-45.72	-44.58

0.03 mol·kg⁻¹ sodium salicylate + Na₂SO₄ (in aqueous medium)

0.00000	1468.91	1499.76	1523.91	1543.07				
0.08136	1489.23	1516.56	1542.53	1556.57	-46.43	-44.53	-43.12	-42.04
0.17034	1508.34	1533.93	1556.63	1570.03	-47.19	-45.24	-43.81	-42.71
0.25305	1524.43	1547.57	1570.47	1581.58	-47.85	-45.88	-44.42	-43.30
0.35442	1542.45	1560.84	1586.46	1596.91	-48.51	-46.51	-45.02	-43.89
0.43751	1558.15	1574.23	1598.66	1609.01	-49.04	-47.01	-45.51	-44.36

^a*m_A* is the molality NaCl/Na₂SO₄ in the sodium salicylate (aqueous). The uncertainties u is u_r(m) = 0.01, u (T) = 0.01K , u(p)=0.01MPa, u(s)=2.36 m · s⁻¹ and u(*K_{φ,S}*) = 0.14 × 10⁻⁶/(m³ · mol⁻¹ · GPa⁻¹).



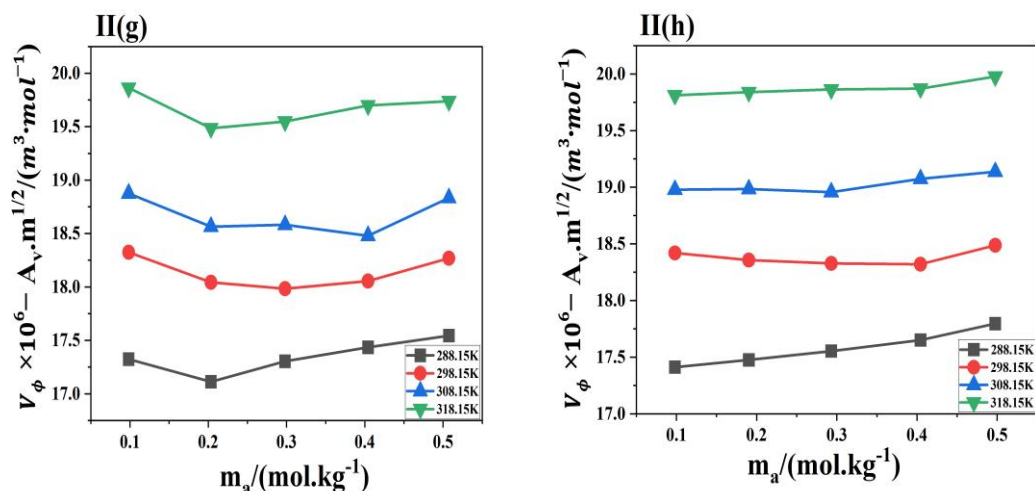


Figure 4.44 Graphical representation of V_ϕ of salts in $NaSl$ at various temperatures. Panels I (a–d) correspond to $NaCl$ with molalities of (a) 0.000, (b) 0.010, (c) 0.020, and (d) 0.03 $mol \cdot kg^{-1}$, while panels II (e–h) depict Na_2SO_4 for the same molality range.

Partial molar volume (V_ϕ^0)

The Redlich-Mayer equation 4.2 was applied to extrapolate the $\{(V_\phi - A_v \sqrt{m}) - m\}$ curve to determine the V_ϕ^0 of the electrolytes at zero concentration. S_V is an experimentally derived slope that accounts for deviations at higher concentrations. Na_2SO_4 , (1:2 electrolyte), and $NaCl$, (1:1 electrolyte), were used as solutes in this study. Na_2SO_4 dissociates into two sodium ions and one sulphate ion, leading to greater ionic strength and more pronounced ion-ion interactions than $NaCl$, which dissociates into one sodium ion and one chloride ion. The least squares approach was employed to fit the parameters for both solutes, enabling the determination of V_ϕ^0 at infinite dilution. At infinite dilution, V_ϕ^0 is assumed to be equivalent to V_ϕ [184]. **Table 4.76** provides the computed V_ϕ^0 and S_V values and the plots of V_ϕ^0 are presented in **Figure 4.45**. For $NaCl$, V_ϕ^0 values increase slightly with temperature, reflecting minor thermal expansion effects due to reduced hydrogen bonding, but decrease with increasing molality. This decrease highlights stronger solute-solvent interactions and efficient packing of ions within the solvent structure. Conversely, V_ϕ^0 values for Na_2SO_4 show a more pronounced increase with temperature, suggesting significant thermal expansion effects and weaker hydrogen bonding at higher thermal energies.

However, at higher molalities, V_{ϕ}^0 for Na_2SO_4 decreases sharply, indicating dominant electrostatic interactions and a more compact solvent structure. The stronger temperature-dependent response of V_{ϕ}^0 for Na_2SO_4 compared to NaCl highlights the critical role of ionic strength and charge in solute-solvent interactions. These trends demonstrate that Na_2SO_4 , with its higher ionic charge, exerts greater effects on solvent structuring and solvation dynamics than NaCl. Furthermore, the observed temperature-dependent increases in V_{ϕ}^0 suggest that thermal energy modulates solvation behaviour by disrupting hydrogen bonding and releasing solvent molecules from solvation layers. This is consistent with using the co-sphere overlap method, where overlapping hydration co-spheres lead to changes in volume [62–64,185].

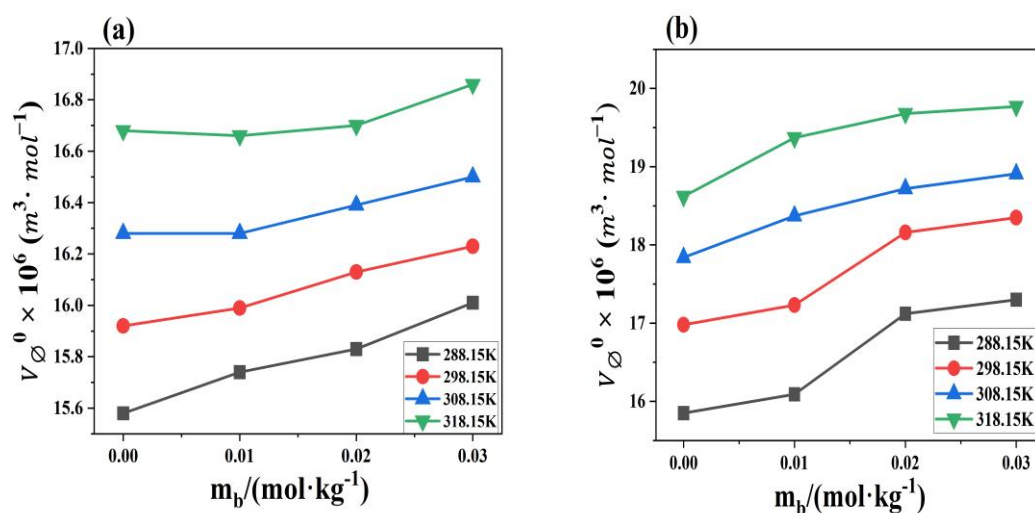


Figure 4.45: Graph of V_{ϕ}^0 , of, (a) $NaCl$ and (b) Na_2SO_4 in numerous concentrations of sodium salicylate (aqueous) solutions at four temperatures.

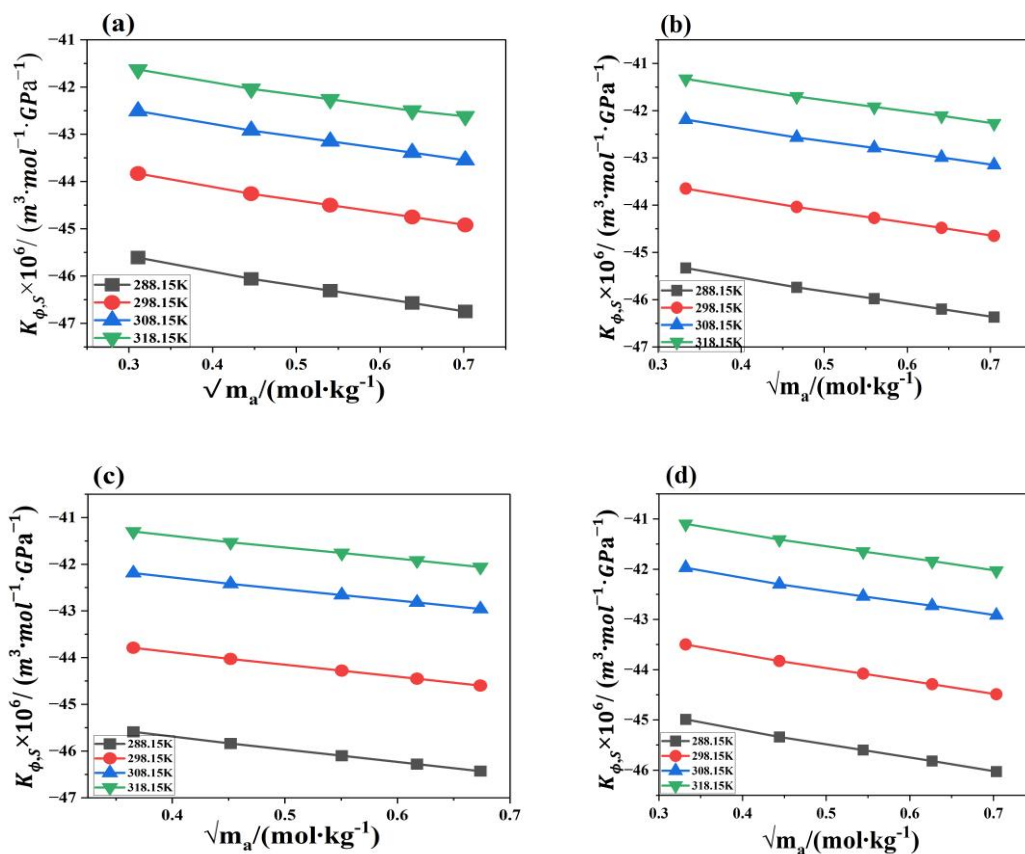
Table 4.76 V_ϕ^0 , and S_V , of salts in the sodium salicylate aqueous solutions.

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$V_\phi^0 \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$				$S_V \times 10^6 (\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2})$			
	T=288.15K	T=298.15K	T= 308K	T=318 K	T=288.15K	T=298.15K	T= 308K	T=318K
Sodium chloride								
0.00	15.58	15.92	16.28	16.68	-0.05	-0.29	-0.41	-0.86
0.01	15.74	15.99	16.28	16.66	-0.08	-0.11	-0.03	-0.26
0.02	15.83	16.13	16.39	16.70	0.05	-0.08	-0.21	-0.02
0.03	16.01	16.23	16.50	16.86	0.15	0.12	-0.20	-0.25
Sodium sulphate								
0.00	15.85	16.98	17.84	18.62	1.99	1.45	1.14	0.92
0.01	16.09	17.23	18.37	19.37	1.82	1.30	0.20	0.20
0.02	17.12	18.16	18.72	19.68	0.75	-0.09	-0.16	-0.04
0.03	17.30	18.35	18.91	19.77	0.93	0.10	0.40	0.35

$^a m_b$ - molality of sodium salicylate aqueous solutions. uncertainties u is $u(V_\phi^0) = 0.01 \times 10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$, $u(S_V^*) = 0.03 \times 10^{-6} (\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2})$.

Apparent molar isentropic compressibility (K_S)

The K_S values were derived from c measurements taken at numerous temperatures using the Newton-Laplace equation 4.9, with s denoting sound velocity and ρ representing solution's density. The computed K_S values were utilized in the equation 4.8 to evaluate the $K_{\phi,s}$. Table 4.75 (Figure 4.46) presents $K_{\phi,s}$ values under different conditions, showing consistently negative values for both salts, indicating strong solute-solvent interactions [186–189]. The negative $K_{\phi,s}$ values suggest that NaCl and Na₂SO₄ strongly shape the structural and compressibility properties of NaSl. As temperature increases, the magnitude of $K_{\phi,s}$ decreases, implying weaker interactions due to reduced hydrogen bonding in water. Additionally, absolute $K_{\phi,s}$ values decrease with increasing molality, indicating reduced compressibility as solute concentration rises, highlighting stronger interactions at lower concentrations. While both salts exhibit similar trends, differences in $K_{\phi,s}$ values suggest varying degrees of interaction with sodium salicylate [190,191].



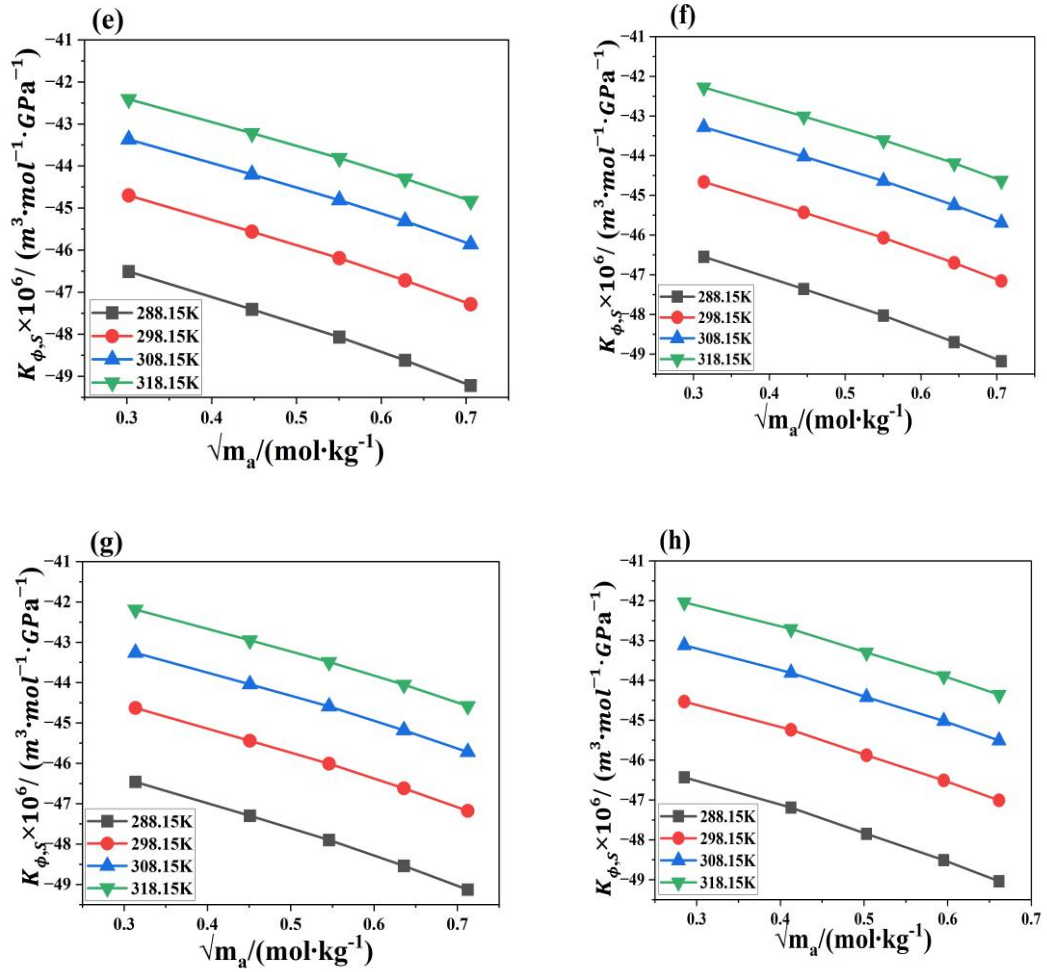


Figure 4.46. Graphs of $K_{\phi,s}$ in aqueous sodium salicylate solution. (a) 0.00 mol·kg⁻¹ NaSl + NaCl, (b) 0.01 mol·kg⁻¹ sodium salicylate + NaCl, (c) 0.02 mol·kg⁻¹ sodium salicylate + NaCl, (d) 0.03 mol·kg⁻¹ sodium salicylate + NaCl. Similarly, (e) 0.00 mol·kg⁻¹ sodium salicylate + Na₂SO₄, (f) 0.01 mol·kg⁻¹ sodium salicylate + Na₂SO₄, (g) 0.02 mol·kg⁻¹ sodium salicylate + Na₂SO₄, (h) 0.03 mol·kg⁻¹ sodium salicylate + Na₂SO₄.

Partial molar isentropic compressibility ($K_{\phi,s}^0$)

Using the least-squares technique, $K_{\phi,s}^0$ was estimated by extending the $K_{\phi,s}$ vs. $\sqrt{m}$ curve to zero concentration, as per the equation 4.10, where m_A tells the molality of the NaCl/Na₂SO₄ per kilogram of the sodium salicylate and S_K^* is experimental slope of NaCl/Na₂SO₄ and NaSl interactions. Table 4.77 contains the calculated $K_{\phi,s}^0$ values with standard errors. Since small magnitude of S_K^* , interaction between solute-solute

remain negligible at extreme dilution [192]. All the $K_{\phi,s}^0$ data is negative. The data reveals that both sodium chloride and sodium sulphate solutions exhibit decreased compressibility with escalating temperature and concentration. This is reflected by the less negative data of $K_{\phi,s}$ and S_K^* across the studied four temperatures and molalities as shown in **Figure 4.47**. Specifically, as temperature rises, the molecules kinetic energy rises, leading to greater intermolecular spacing and reduced intermolecular forces, which in turn reduces the compressibility of the solutions. As the solution exhibits enhanced resistance to compression, the ultrasonic velocity increases due to the more efficient propagation of sound waves through the denser medium. Moreover, Na_2SO_4 solutions exhibit higher compressibility than $NaCl$ solutions, likely due to variations in hydration behaviour and ionic interactions. With its larger ion size and greater ionic strength, sodium sulphate tends to disrupt the water structure more extensively, increasing compressibility relative to sodium chloride. [193,194].

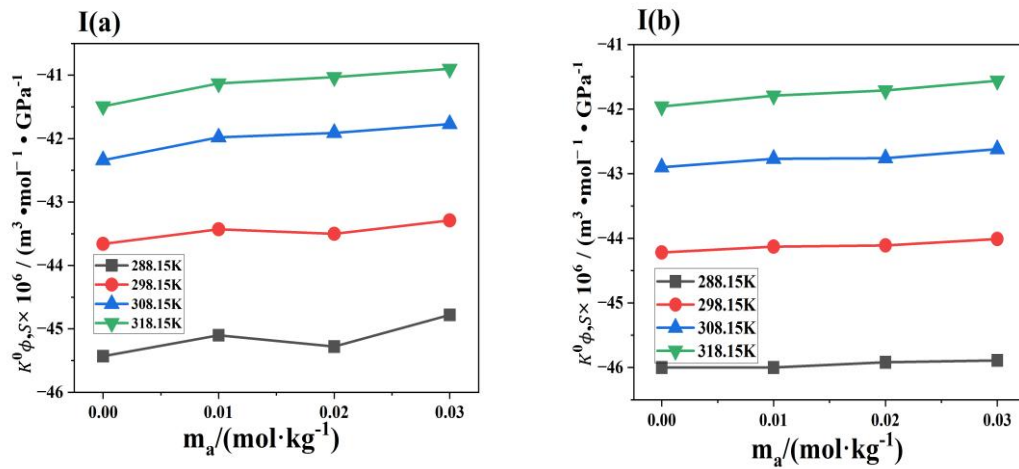


Figure 4.47: Plots of $K_{\phi,s}^0$, I(a), $NaCl$ and I(b) Na_2SO_4 , in $NaCl(aqueous)$ solutions at multiple temperatures

Table 4.77 $K_{\phi,S}^0$ and S_K^* of Na_2SO_4 and $NaCl$ in the sodium salicylate (aqueous) at four temperatures.

$m_b/(\text{mol}\cdot\text{kg}^{-1})$	$K_{\phi,S}^0 \times 10^6/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$				$S_K^* \times 10^6/(\text{kg} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{GPa}^{-1})$			
	T/K=288.15	T/K=298.15	T/K= 308.15	T/K=318.15	T/K=288.15	T/K=298.15	/K= 308.15	T/K=318.15
Sodium chloride								
0.00	-45.43	-43.66	-42.34	-41.49	-2.78	-2.66	-2.57	-2.44
0.01	-45.10	-43.43	-41.98	-41.13	-2.65	-2.54	-2.44	-2.38
0.02	-45.28	-43.50	-41.91	-41.03	-2.59	-2.48	-2.38	-2.32
0.03	-44.78	-43.29	-41.77	-40.90	-2.62	-2.51	-2.42	-2.36
Sodium sulphate								
0.00	-46.00	-44.22	-42.90	-41.96	-6.60	-6.30	-6.08	-5.91
0.01	-46.00	-44.13	-42.77	-41.79	-6.50	-6.19	-5.97	-5.79
0.02	-45.92	-44.11	-42.76	-41.71	-6.45	-6.17	-5.95	-5.76
0.03	-45.89	-44.01	-42.62	-41.56	-6.45	-6.15	-5.92	-5.74

m_b - molality of aqueous NaSl. uncertainties – u ($K_{\phi,S}^0$) = $0.01 \times 10^{-6}/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$, u (S_K^*) = $0.25 \times 10^{-6}/(\text{kg} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{GPa}^{-1})$, u(T)= 0.01K , u (p)=0.01MPa.

Partial molar volume of transfer (ΔV_{ϕ}^0)

The ΔV_{ϕ}^0 of solutes ($NaCl/Na_2SO_4$) from H_2O to solutions of NaSl solutions at extreme dilution in an aqueous medium, were calculated by the equation 4.3. **Table 4.78** contains the ΔV_{ϕ}^0 data, provide qualitative interpretation of the interactions between $NaCl/Na_2SO_4$ and NaSl molecules within the liquid mixture. For $NaCl$, at lower concentrations and temperatures, ΔV_{ϕ}^0 values are small and positive, indicating weaker interactions in solute-solvent and hydrophilic-hydrophilic interactions. As temperature rises, the ΔV_{ϕ}^0 values show a decreasing trend, indicating stronger solute-solvent interactions, higher electrostriction effects, and reduced free volume inside the solution. The transition from positive to negative values tells that hydrophilic-hydrophilic interactions at lower temperatures give way to more significant ion-hydrophilic interactions at higher temperatures and concentrations, leading to enhanced compressibility of the solution. In contrast, Na_2SO_4 exhibits uniformly negative ΔV_{ϕ}^0 values across all temperatures and concentrations, highlighting dominant ion-hydrophilic interactions and greater electrostriction effects. However, the absolute magnitude of these negative values diminishes as temperature increases, indicating that increased thermal energy weakens the compressive effects of Na_2SO_4 on the solvent structure, allowing for greater molecular mobility and reduced structuring effects. The consistently negative ΔV_{ϕ}^0 values for Na_2SO_4 demonstrate its stronger influence on the water structure compared to sodium chloride, owing to its higher ionic strength. This is further supported by its greater reduction in free volume and the significant structuring effects observed in the solution. The reduction in the magnitude of negative ΔV_{ϕ}^0 values at higher temperatures for both solutes suggests that thermal energy partially offsets the compressive effects of solute molecules on the solvent. These trends align with the co-sphere overlap model, where overlapping hydration co-spheres of solute-solvent molecules lead to changes in volume. The observed behaviours in sodium salicylate solutions can be attributed to a range of interactions, such as those between ions and hydrophilic groups, hydrophilic and hydrophilic groups, hydrophilic and hydrophobic groups, and hydrophobic and hydrophobic groups. Sodium sulphate's dominance over $NaCl$ in influencing solvent structure is evident in its stronger ion-

hydrophilic interactions, which result in significant structural changes in the solution[65–69].

Impact of Temperature partial molar volume

The relation in eq. (4.4) was utilized to examine the temperature-dependent variations in apparent molar volumes at extreme dilution. With T is temperature, a , b , c denoting empirical constants, T_{ref} is set at 298.15 K. **Table 4.79** contains empirical parameters for NaCl and Na_2SO_4 in NaSl (sodium salicylate (aqueous)). The objective of analysing V_ϕ^0 data is to assess partial molar expansibilities, as derived from eq. (4.5). **Table 4.80** contains the $E_\phi^0 = (\partial E_\phi^0 / \partial T)_P$ for the combinations of NaSl with NaCl and Na_2SO_4 across different temperatures and concentrations. For sodium chloride, E_ϕ^0 values increase consistently with temperature at all concentrations, reflecting enhanced thermal expansion and solute-solvent interactions. At $m=0.02$, E_ϕ^0 values remain relatively stable, showing minimal changes with temperature, while at $m=0.01$ and $m=0.03$, E_ϕ^0 increases more significantly, indicating varying degrees of solute-solvent interaction strength. For sodium sulphate, E_ϕ^0 values are consistently higher than those for sodium chloride, suggesting stronger solute-solvent interactions. However, E_ϕ^0 decreases with temperature across all concentrations, highlighting the disruption of structured water molecules around sulphate ions at higher temperatures. At $m=0.03$, E_ϕ^0 drops significantly from 0.09372 at 288.15 K to 0.06526 at 318.15 K, indicating a strong dependence on temperature and concentration. The positive E_ϕ^0 data indicate that sodium chloride and sodium sulphate molecules strengthen the structure-making properties of salts in sodium salicylate solutions. The decreasing trend for sodium sulphate at higher temperatures suggests a shift in solute-solvent interactions, likely due to increased thermal energy disrupting hydrogen bonding and solvation layers.

Table 4.78 ΔV_{ϕ}^0 and $\Delta K_{\phi,S}^0$ of the NaSl(aqueous) with $NaCl$ and Na_2SO_4 at varying temperatures.

$m_b / (\text{mol.kg}^{-1})$	$\Delta V_{\phi}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$				$\Delta K_{\phi,S}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15 K
Sodium chloride								
0.01	0.16	0.06	0.00	-0.02	0.33	0.23	0.36	0.36
0.02	0.25	0.21	0.11	0.02	0.15	0.16	0.43	0.45
0.03	0.43	0.31	0.22	0.18	0.66	0.37	0.57	0.58
Sodium sulphate								
0.01	0.24	0.25	0.52	0.74	0.01	0.09	0.13	0.17
0.02	1.27	1.18	0.88	1.05	0.09	0.11	0.14	0.25
0.03	1.45	1.37	1.07	1.14	0.11	0.21	0.28	0.40

m_b - aqueous sodium salicylate molality, the uncertainties are $u_r(m) = 0.01$, $u(\Delta V_{\phi}^0) = 0.09 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1})$, $u(\Delta K_{\phi,S}^0) = 0.08 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$, $u(T) = \pm 0.001\text{K}$, $u(p) = 0.01\text{MPa}$.

These trends align with Hepler's equation 4.6 where positive values are indicative of structure-making tendencies, whereas negative values point to structure-breaking behaviour[195]. The data show predominantly structure-making properties in the mixtures, with exceptions at higher temperatures and concentrations for sodium sulphate. Sodium chloride's weaker ionic interactions and greater mobility allow for more consistent thermal expansion, while sodium sulphate's higher ionic strength leads to more pronounced interactions among solute-solvent, which diminishes as temperature increases. These findings highlight the crucial role of temperature in finding the volumetric and structural characteristics of the ternary mixtures, providing deeper insights into solute-solvent interactions[196–198].

Calculation of Pair and Triplet ($V_{AB}, V_{ABB}; K_{AB}, K_{ABB}$) Coefficients

The equations 4.12, 4.13. was used to obtain the ΔV_{ϕ}^0 and ΔK_{ϕ}^0 . The parameters V_{AB} , V_{ABB} describe volumetric interactions at the binary and ternary levels, respectively. Similarly, K_{AB} and K_{ABB} indicate the isentropic compressibility interactions for two- and three-component systems. The coefficients are provided within **Table 4.81**. Based on the theory of McMillan-Mayer, the $V_{AB}, V_{ABB}; K_{AB}, K_{ABB}$ are computed by fitting the ΔV_{ϕ}^0 and ΔK_{ϕ}^0 respectively. This theoretical approach is instrumental in analysing the distinct effects of binary and ternary interactions among molecules in a liquid mixture. Detailed explorations of this theory have been conducted, with notable contributions from Friedman and Krishnan along with Franks et al. [199]. The data indicates that the interaction coefficients exhibit notable temperature dependence, which offers understanding of the behaviour of the solution at various temperatures. The coefficient V_{AB} shows positive values at lower temperatures, indicating a rise in volume due to pairwise interactions among sodium salicylate and the salts (sodium sulphate and sodium chloride). This suggests that at lower temperatures, the interactions among sodium salicylate and the salts result in a less dense structure, expanding the solution volume. However, at higher temperatures, V_{AB} turns negative, implying that these interactions promote structural compaction, leading to a decrease in solution volume.

Table 4.79 Data of empirical parameters of Eq., of $NaCl$ and Na_2SO_4 in sodium salicylate(aqueous) at multiple temperatures.

$m_b/(\text{mol}\cdot\text{kg}^{-1})$	$a \times 10^6(\text{m}^3 \cdot \text{mol}^{-1})$	$b \times 10^6(\text{m}^3 \cdot \text{mol}^{-1})$	$c \times 10^6(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R^2	ARD
Sodium chloride					
0.01	15.97975	0.02718	0.00034	0.9999	0.00029
0.02	16.11648	0.02858	0.00001	0.9999	0.00000
0.03	16.22389	0.02465	0.00035	0.9999	0.00036
Sodium sulphate					
0.01	17.25250	0.11299	-0.00035	0.9999	0.00068
0.02	18.02784	0.08441	-0.00021	0.9999	0.00000
0.03	18.23209	0.08423	-0.00047	0.9999	0.00434

uncertainties - $u(m_b) = 0.01 \text{ mol}\cdot\text{kg}^{-1}$, $u(T) = 0.01\text{K}$, $u(p) = 0.01\text{MPa}$.

Table 4.80. E_{ϕ}^0 of NaI (aqueous) with $NaCl$ and Na_2SO_4 at different temperatures, concentrations.

$m_b/(\text{mol}\cdot\text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 /(\text{m}^3 \cdot \text{mol}^{-1} \cdot K^{-1})$				$(\frac{\partial E_{\phi}^0}{\partial T})/(\text{m}^3 \cdot \text{mol}^{-1} \cdot K^{-2})$
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	
Sodium chloride					
0.01	0.02030	0.02718	0.03405	0.04092	0.00069
0.02	0.02831	0.02858	0.02885	0.02912	0.00003
0.03	0.01757	0.02465	0.03173	0.03881	0.00071
Sodium sulphate					
0.01	0.12003	0.11299	0.10595	0.09892	-0.00070
0.02	0.08858	0.08441	0.08023	0.07606	-0.00042
0.03	0.09372	0.08423	0.07475	0.06526	-0.00095
uncertainties – u (E_{ϕ}^0)= 0.003 $\times 10^{-6} /(\text{m}^3 \cdot \text{mol}^{-1} \cdot K^{-1})$, u ($\frac{\partial E_{\phi}^0}{\partial T}$) = 0.00055/($\text{m}^3 \cdot \text{mol}^{-1} \cdot K^{-2}$) , u(T)= 0.001K, u(p)=0.01MPa.					

Similarly, the K_{AB} is also positive across all taken temperatures, signifying that the interactions generally increase the compressible nature of the solution. The consistent positive value suggests that regardless of the temperature, the existence of salts and NaSl in H₂O increases the solution's ability to be compressed. The V_{ABB} , K_{ABB} provide additional insight into the complexity of these interactions. For *NaCl*, V_{ABB} shows a fluctuating trend across the temperature range, starting from 130.59 at 288.15 K, dropping to a negative value of -150.14 at 308.15 K, and returning to a positive value of 144.38 at 318.15 K. This trend suggests that triplet interactions exhibit complex volumetric effects, where the initial positive values indicate expansion due to three-body interactions, while the negative values at intermediate temperatures reflect stronger structural compaction. Similarly, for sodium sulphate, V_{ABB} demonstrates considerable variability, starting from a high value of 428.96 at 288.15 K, decreasing to 12.49 at 298.15 K, increasing to 500.64 at 308.15 K, and turning highly negative at 318.15 K (-553.12). This behaviour highlights the strong influence of triplet interactions on volumetric effects, which undergo a shift from expansion at lower temperatures to contraction at higher temperatures due to structural rearrangement. The triplet isentropic compression coefficient K_{ABB} , however, shows a more complex behaviour. For sodium chloride, K_{ABB} starts positive at 288.15 K (97.66) but becomes increasingly negative as temperature rises, reaching -202.60 at 318.15 K. This indicates that at higher temperatures, the triplet interactions reduce the solution's compressibility, leading to a more rigid structure. For sodium sulphate, K_{ABB} transitions similarly from positive values at 288.15 K (23.22) to negative values at higher temperatures (-19.80 at 318.15 K), suggesting a gradual decrease in compressibility due to stronger triplet interactions and structural rearrangement.[86–89,200].

Isobaric thermal expansion coefficient

It quantifies the fractional change in volume for each degree of temperature change at fixed pressure conditions[146]. The equation 4.14 used to determine the α_p . Table 4.82 shows the, α_p values for *NaCl* and *Na₂SO₄* in sodium salicylate solutions across different temperatures and concentrations. For *NaCl*, α_p increases with temperature at

lower molalities, reflecting significant thermal expansion effects due to weaker solute-solute interactions. However, at higher molalities, α_p remains nearly constant or increases less significantly, suggesting stronger solute-solute interactions that limit expansion. In contrast, sodium sulphate exhibits higher α_p values overall, indicating stronger interactions with water and more pronounced thermal expansion effects. As temperature rises, α_p decreases consistently for sodium sulphate across all molalities, reflecting the weakening of structured water around sulphate ions due to increased thermal energy. The distinct trends in α_p for sodium chloride and sodium sulphate provide valuable insights into solute-solvent interactions. Sodium sulphate, with its higher ionic strength, disrupts the water structure more effectively at lower temperatures, leading to larger expansion coefficients. Sodium chloride, on the other hand, shows more uniform behaviour, with less pronounced thermal effects at higher concentrations. These observations enhance our understanding of temperature-influence processes, such as solubility and transport phenomena, in sodium salicylate solutions.

FTIR Spectroscopic Analysis

FTIR analysis was conducted of aqueous *NaSl* in *NaCl/Na₂SO₄* solutions at various concentrations (**Figure 4.48(a)** for sodium salicylate with water at different concentrations). FTIR is a reliable method for identifying functional groups and analysing interactions among different compounds in a mixture [201,202]. The samples of different concentration were scanned within the range of 400-4000 cm⁻¹.

Table 4.81 V_{AB} , V_{ABB} , K_{AB} and K_{ABB}) of salts present in sodium salicylate(aqueous) exhibit variations across multiple temperatures with 0.1 MPa.

T/K	$V_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg)$	$V_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2)$	$K_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg GPa^{-1})$	$K_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2 GPa^{-1})$
Sodium chloride				
288.15	3.35	130.59	5.48	97.66
298.15	3.68	35.18	5.38	4.11
308.15	6.65	-150.14	18.21	-199.88
318.15	-3.51	144.38	18.59	-202.60
Sodium sulphate				
288.15	16.36	428.96	0.94	23.22
298.15	23.50	12.49	3.21	0.76
308.15	7.74	500.64	4.77	-5.87
318.15	43.78	-553.12	7.39	-19.80

Table 4.82. α_p for $NaCl$ and Na_2SO_4 in sodium salicylate (aqueous) at multiple temperatures and 0.1 MPa.

$m_b/(\text{mol}\cdot\text{kg}^{-1})$	$\alpha_p \times 10^3/ (K^{-1})$			
	T=288.15K	T=293.15K	T=303.15K	T=318.15K
Sodium chloride				
0.01	1.29	1.70	2.09	2.46
0.02	1.79	1.77	1.76	1.74
0.03	1.10	1.52	1.92	2.30
Sodium Sulphate				
0.01	7.46	6.56	5.77	5.11
0.02	5.17	4.65	4.29	3.87
0.03	5.42	4.59	3.95	3.30

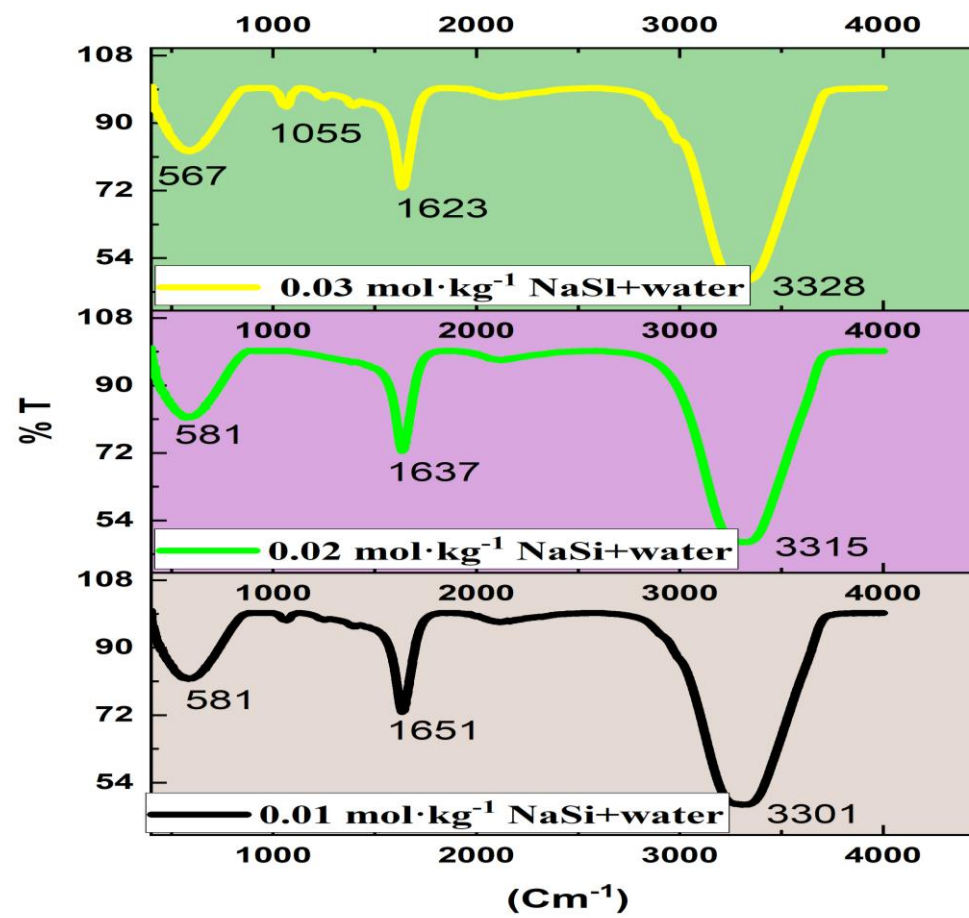
uncertainties, $u(\alpha_p) = 0.032 \times 10^{-3}/ (K^{-1})$, $u(T) = 0.001K$, $u(p) = 0.01MP$

- i Hydroxyl Groups (*O-H*): The wide absorption peak observed near 3200-3600 cm^{-1} corresponds to the *O-H* bond stretching vibrations in H_2O and sodium salicylate. The broadness and position of this band are influenced by H- bonding. In the spectra of sodium salicylate solutions **Figure 4.48(b)(c)** for sodium salicylate with Na_2SO_4 and for sodium salicylate with $NaCl$), a shift in the *O-H* stretching band is observed with increasing concentrations of sodium salicylate, Na_2SO_4 , and $NaCl$). This shift indicates changes in hydrogen bonding interactions. For instance, the presence of Na_2SO_4 causes a shift in the *O-H* stretching band towards higher wavenumbers, which suggests that the sulphate ions are breaking the hydrogen bonds among water molecules through their interactions. Similar effects are noted with sodium chloride, where the interaction with chloride ions leads to shifts in the *O-H* stretching band, reflecting alterations in the hydrogen-bonding network among water molecules[201,202].
- ii Carboxylate Groups (COO^-): The carboxylate groups (COO^-) in sodium salicylate are characterized by two distinct bands: an asymmetric stretching vibration around 1550-1650 cm^{-1} and a symmetric stretching vibration around 1400-1450 cm^{-1} (**Figure 4.48(d), (e)**). These bands are indicative of the carboxylate functionality, with the asymmetric stretch appearing at a higher wavenumber than the symmetric stretch. In the FTIR spectra, shifts in these bands are observed with

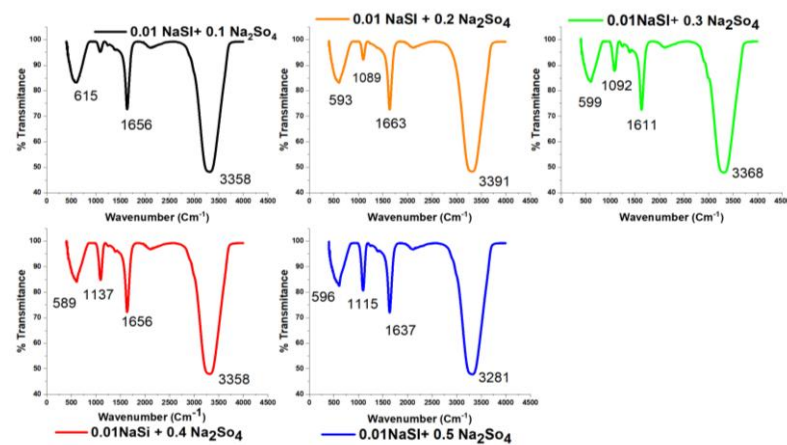
varying concentrations of sodium salicylate and the addition of salts. The presence of $NaCl$ and Na_2SO_4 affects the band locations and intensities, indicating modifications in the microenvironment of the carboxylate groups. For example, a rise in sodium sulphate concentration causes a shift in the asymmetric stretching vibration to higher wavenumbers, indicating stronger interactions between the carboxylate groups and sulphate ions. Similar interactions are observed with sodium chloride, though the shifts are less pronounced compared to sodium sulphate [201,202].

- iii Sulphate Groups (SO_4^{2-}): The sulphate groups (SO_4^{2-}) exhibit characteristic stretching vibrations around $1100\text{-}1200\text{ cm}^{-1}$, specific to the sulphate ions in sodium sulphate. (**Figure 4.48(f)(g)**). These bands confirm the presence of sulphate ions in the sodium sulphate-containing samples. Variations in the position and intensity of these bands with changes in concentration indicate interactions between sulphate ions and the surrounding water molecules or sodium salicylate. At higher concentrations of sodium sulphate, the SO_4^{2-} stretching bands shift towards higher wavenumbers, suggesting increased interactions between sulphate ions and sodium salicylate molecules. This is evident in the FTIR spectra, where the intensity of the SO_4^{2-} bands increase with higher sodium sulphate concentrations, indicating a higher degree of interaction within the solution [201,202].
- iv Chloride Interactions (Cl^-): Chloride interactions (Cl^-) are observed through subtle changes around $600\text{-}800\text{ cm}^{-1}$ in the IR spectra (**Figure 4.48(h)(i)**). Although chloride ions do not have strong IR-active bands, their interactions with water and sodium salicylate can cause noticeable shifts in this region. In the spectra, the presence of sodium chloride results in shifts in the bands within this range, reflecting changes in the hydration sphere of chloride ions. For example, increasing the concentration of sodium chloride causes the bands to shift towards higher wavenumbers, indicating stronger interactions between chloride ions and water or sodium salicylate molecules. These shifts provide insights into the solvation and interaction mechanisms of chloride ions within the mixture, revealing their role in the overall molecular dynamics of the solution [201].

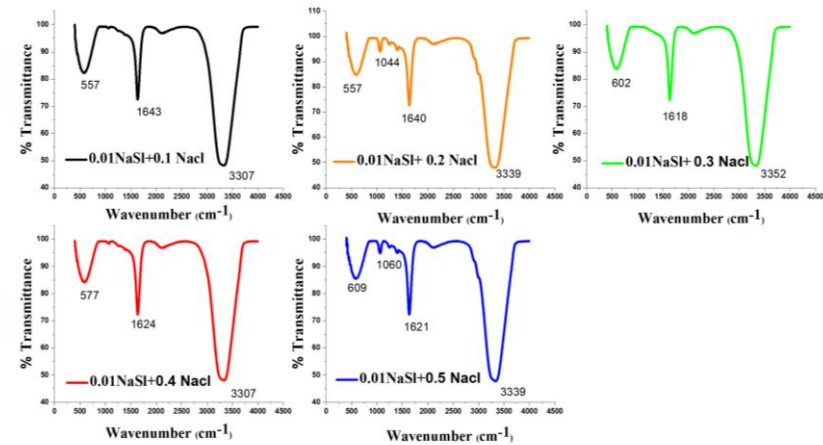
(a)



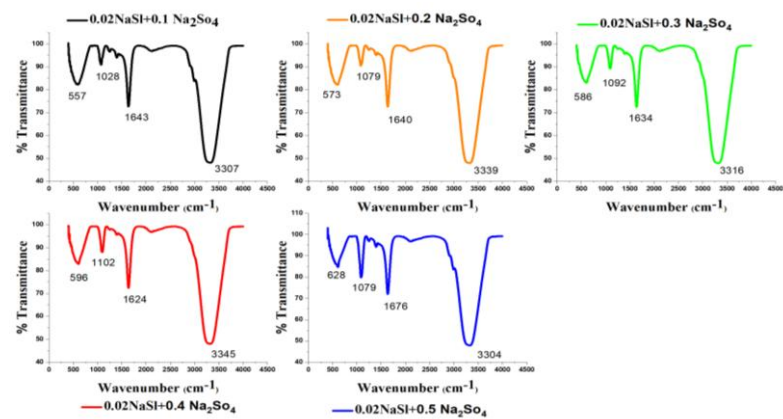
(b)



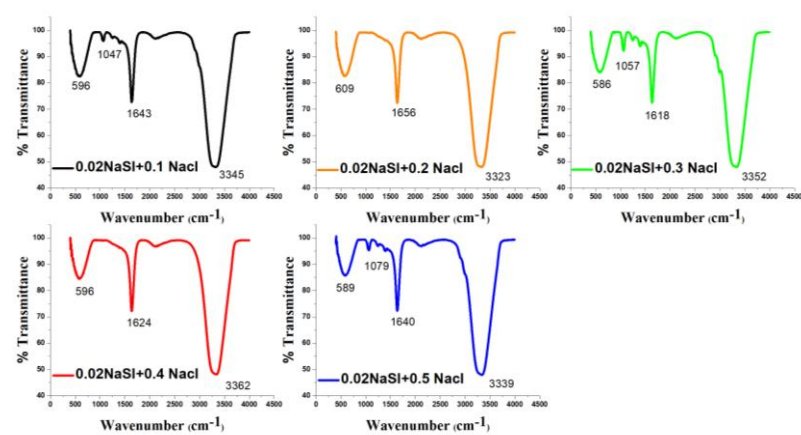
(c)



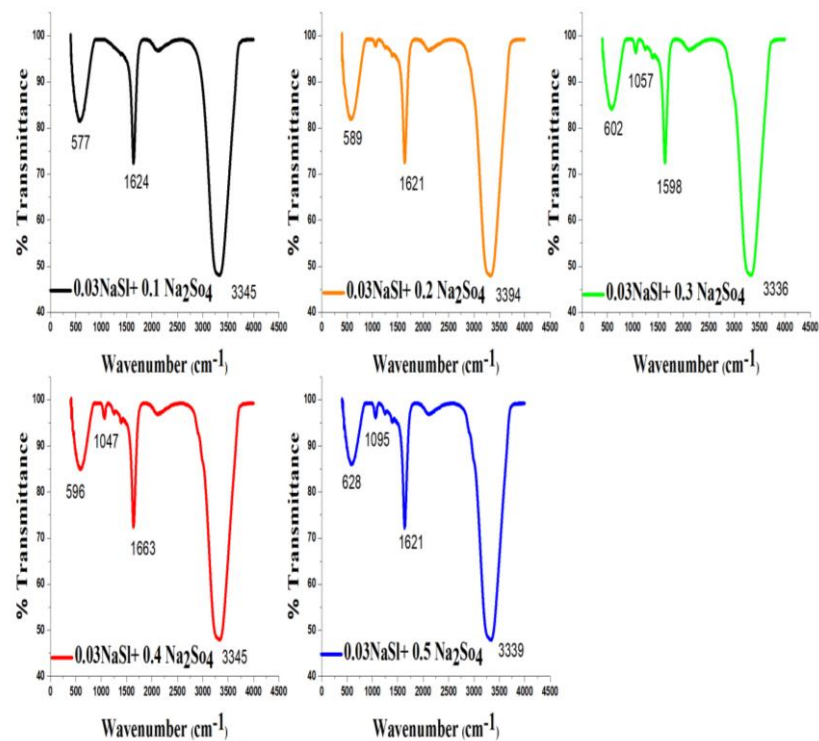
(d)



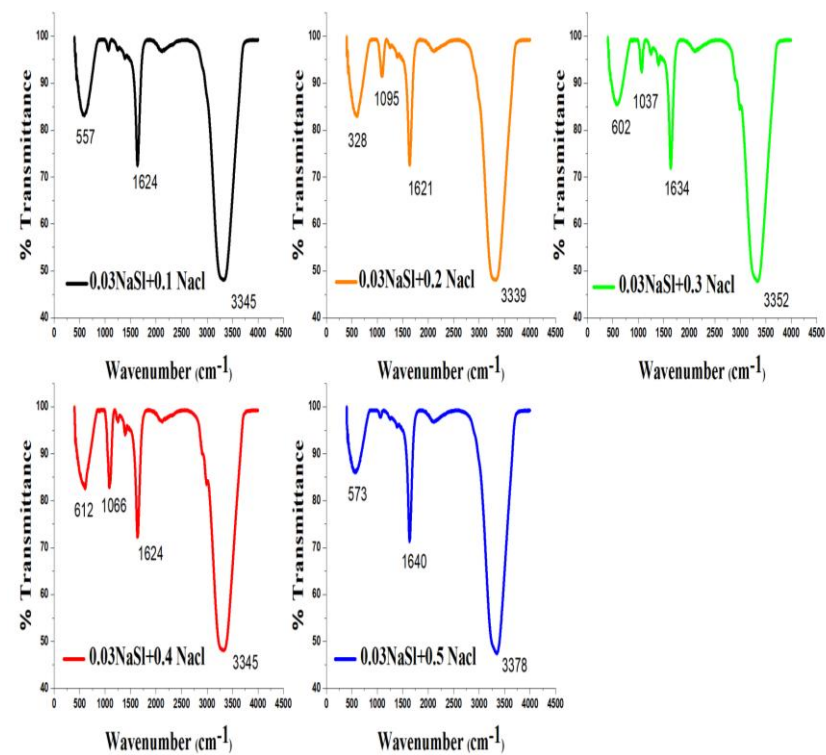
(e)



(f)



(g)



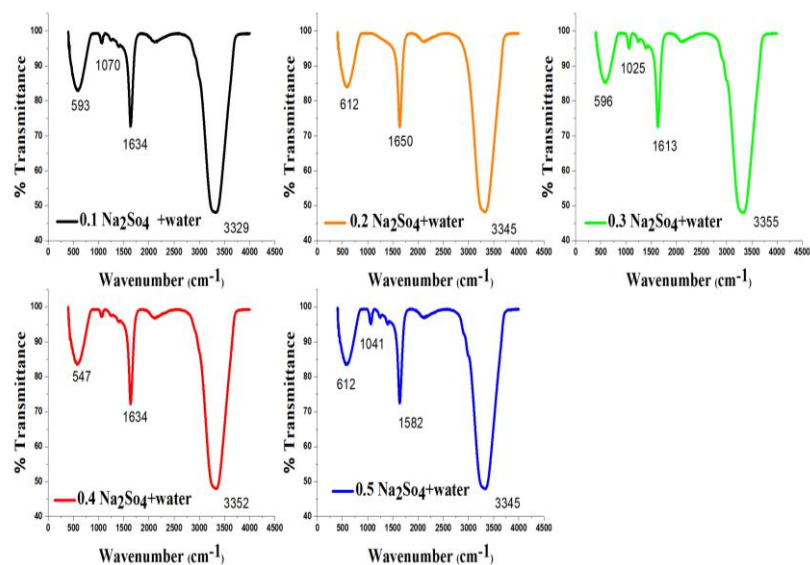
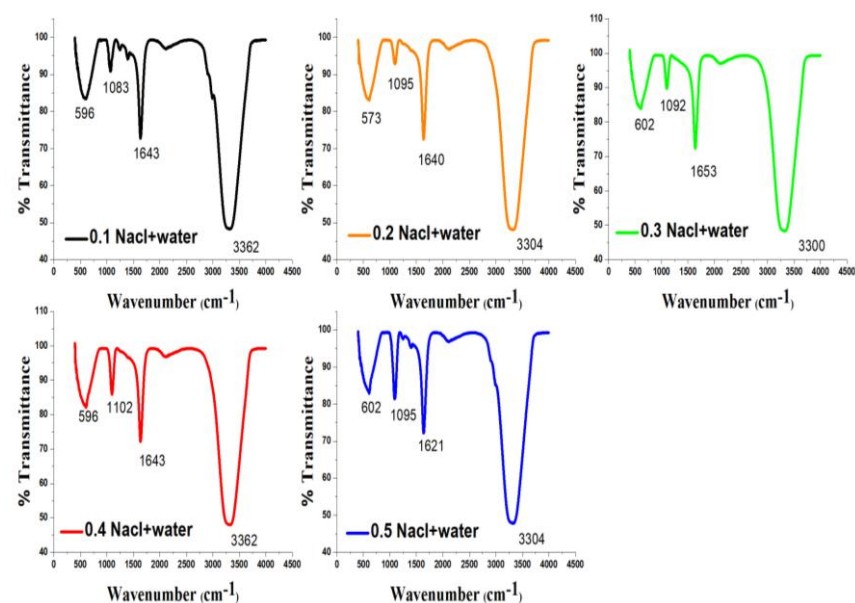
(h)**(i)**

Figure 4.48. FTIR spectra of sodium salicylate with and without salts: (a) Sodium salicylate in water at 0.01, 0.02, and 0.03 $\text{mol}\cdot\text{kg}^{-1}$; (b, c) Sodium salicylate (0.01 $\text{mol}\cdot\text{kg}^{-1}$) with NaCl and Na_2SO_4 at 0.1–0.5 $\text{mol}\cdot\text{kg}^{-1}$; (d, e) Sodium salicylate (0.02 $\text{mol}\cdot\text{kg}^{-1}$) with NaCl and Na_2SO_4 at 0.1–0.5 $\text{mol}\cdot\text{kg}^{-1}$; (f, g) Sodium salicylate (0.03 $\text{mol}\cdot\text{kg}^{-1}$) with NaCl and Na_2SO_4 at 0.1–0.5 $\text{mol}\cdot\text{kg}^{-1}$; (h, i) FTIR spectra of NaCl and Na_2SO_4 in water at 0.1–0.5 $\text{mol}\cdot\text{kg}^{-1}$.

Table 4.83. Characteristic FTIR band assignments of sodium salicylate systems and corresponding literature references.

Functional group	Assignment	Wavenumber (cm ⁻¹)	Reference
O–H	Stretching vibration	3200–3600	[201,202]
COO ⁻	Asymmetric stretching	1550–1650	[201,202]
COO ⁻	Symmetric stretching	1400–1450	[201,202]
SO ₄ ²⁻	Stretching vibration	1100–1200	[201,202]
Cl ⁻	Hydration-induced changes	spectral 600–800	[201]

Problem 8

Temperature-Dependent Physicochemical interactions and Spectroscopic characterization of Sodium Nitrate/sodium Citrate in aqueous sodium Salicylate solutions

This problem investigates the thermodynamic properties of ternary solutions comprising sodium nitrate or sodium citrate in sodium salicylate solutions by taking measurements of density and ultrasonic velocity. Further, an FTIR spectroscopic study of the mixtures (sodium salicylate + water) as well as (sodium Nitrate/sodium Citrate+ water) was conducted to provide further insight into the interactions of solutes and solvents.

Density

Table 4.84 shows, the densities of ternary mixtures (Sodium Salicylate + Sodium Nitrate/Sodium Citrate+ H₂O) and binary mixtures (H₂O + Sodium Salicylate). The binary solutions of sodium salicylate were dissolved in water of 0.000, 0.010, 0.020, and 0.030 mol·Kg⁻¹ concentrations and the ternary solutions were formulated by adding the salts (sodium Nitrate/Sodium Citrate) to Sodium Salicylate aqueous solutions. Upon examining the density, it was noticed that density of solutions decreases with escalating temperature at a constant sodium salicylate concentration. Conversely, as the sodium nitrate or sodium citrate molality escalates increases, the density rises. Furthermore, higher concentrations of sodium salicylate result in a corresponding increase in density. A comparison of density for experimental values of a binary mixture (Sodium Citrate + H₂O), (sodium Nitrate + H₂O) and (sodium salicylate + H₂O) with literature [5–7] (for sodium citrate),[51][52] (for sodium nitrate) and [169] [170] [171] [172] [173] (for sodium salicylate +H₂O) at 0.1 MPa is depicted in **Figure 4.1(c), 4.8(b) and 4.43(a) respectively**. Figures clearly shows that density correlate well with existing values of literature. The density of all binary systems exhibits a linear increase as the concentration rises and a decrease as the temperature goes up. When the temperature increases, the molecules gain kinetic energy, leading to more vigorous molecular motion. This heightened activity causes the volume to expand, resulting in a lower density of the solution. Upon close examination of the

values, it is evident that the density of the solutions escalates with both sodium nitrate/sodium citrate concentration in water. These stronger interactions cause a lead to a reduction in the net available volume, thereby causing a rise in density. Additionally, the observed density decreases with escalating temperature because of the solution's thermal expansion, which rises the kinetic energy and molecular motion, resulting in a lower density [203–205]. A schematic representation is shown in **figure 4.49**.

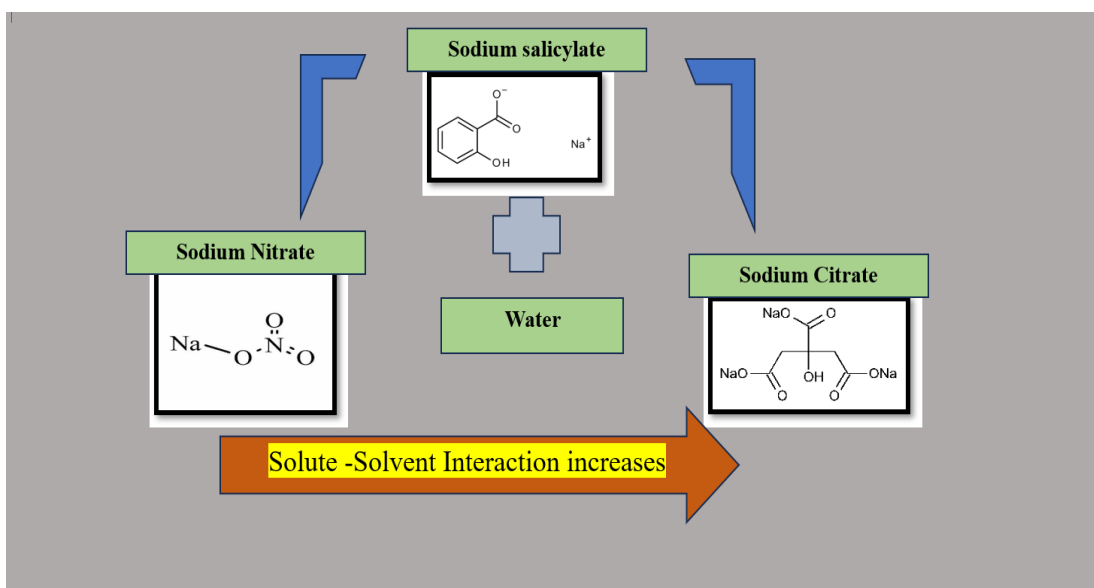
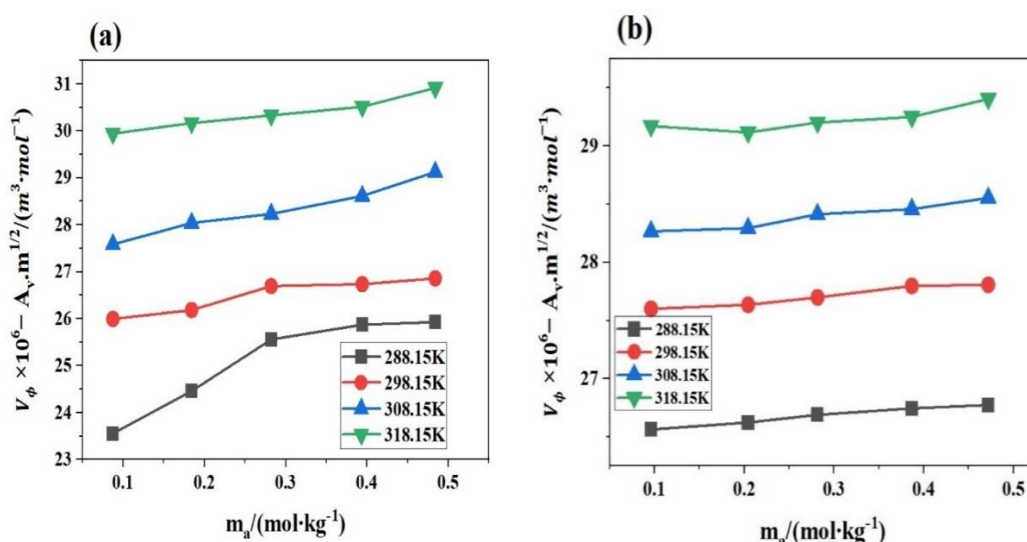


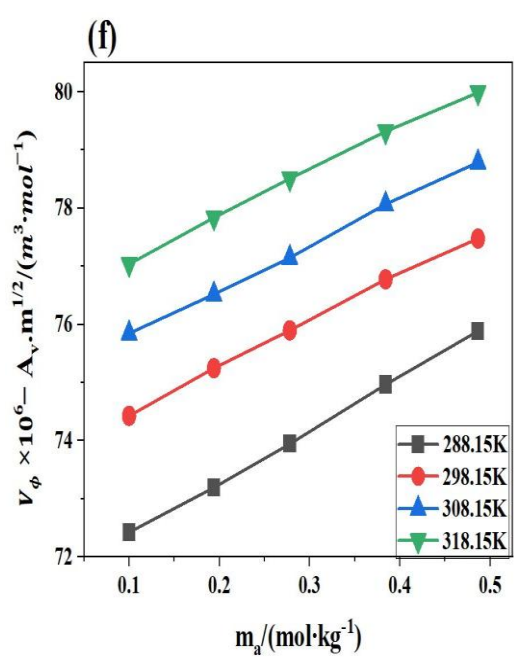
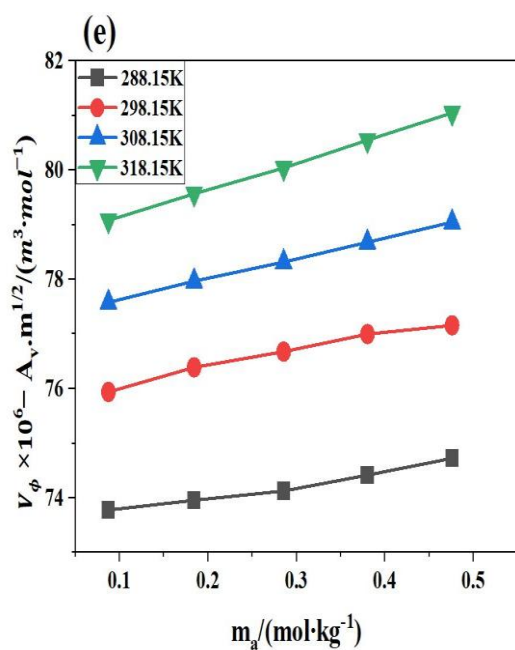
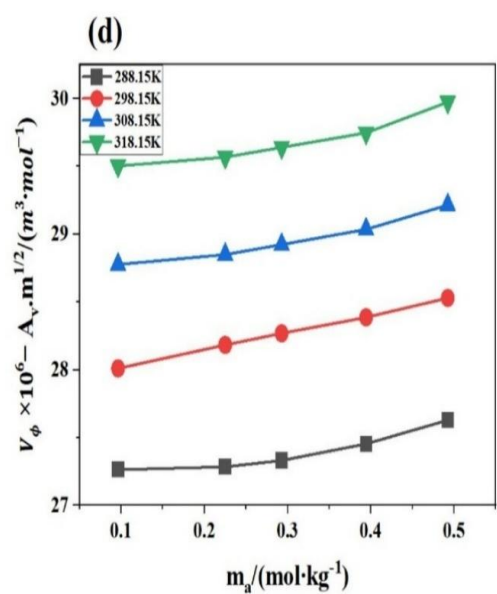
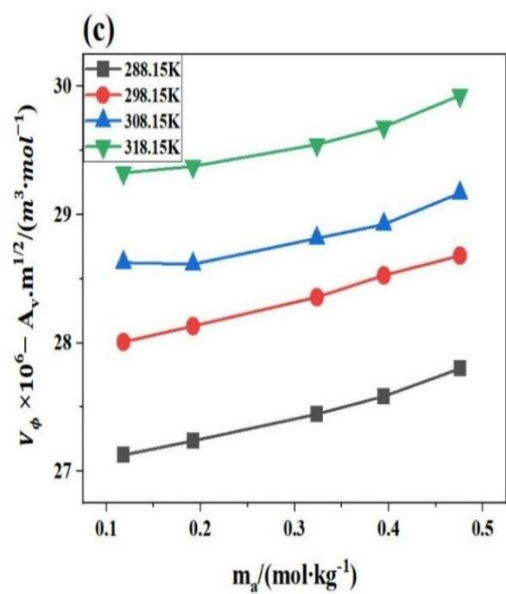
Figure 4.49: sodium Nitrate/ sodium Citrate and sodium salicylate interactions.

Apparent molar volume (V_ϕ)

The V_ϕ values were measured by the density data with the following equation 4.1 [76], m_A is the molality of the sodium nitrate/ sodium citrate solutes per kg of the sodium salicylate, and ρ , ρ_0 , represents solution's densities and the solvent (aqueous sodium salicylate) subsequently. The V_ϕ data is shown in **Table 4.84**. Being electrolytes ($V_\phi - A_V\sqrt{m}$) values are plotted as depicted in **Figure 4.50**. Our results reveal significant insights into the solute(salts)-solvent (aqueous sodium salicylate) interactions and structural changes in the mixtures. For sodium nitrate solutions, V_ϕ values generally escalate with both concentration and temperature, implying enhanced solute and solvent interactions and structural rearrangements at higher temperatures and concentrations. This trend indicates that sodium nitrate

influences the hydration structure of sodium salicylate, that leads to a rise in apparent molar volume. Similarly, V_ϕ was found to be increased with temperature as well as concentration in the sodium citrate solutions. Hence, there arises the necessity of considering the influence of the trivalent citrate ion on the hydration structure of sodium salicylate as considerable. The, V_ϕ in the sodium citrate solutions were greater than the values obtained in the sodium nitrate solutions. It is possible that the citrate ion itself is much larger and has a higher charge density than the salicylate, which leads to stronger perturbations of the solvent structure. This work reports important findings about solvation behavior and structural characteristics of aqueous sodium salicylate solutions, quite pertinent to pharmaceutical formulations, where drug solubility and hence stability are crucially dependent on interactions with additives. Such information is crucial since it allows for an understanding of solvation behaviour and structural characteristics in water-rich environments, which happens to be of importance when it applies to pharmaceutical formulations in which interaction with additives would affect drug solubility stability [15–17,109]. .





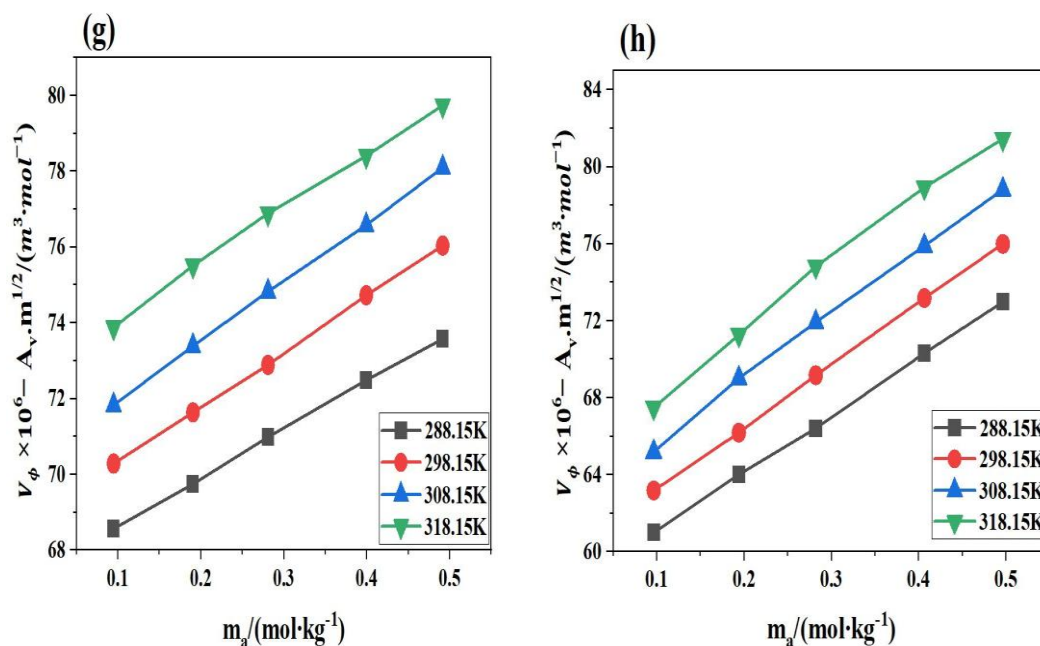


Figure 4.50. Plots representing the, V_{ϕ} , against the molality (m_a) of Sodium nitrate/sodium citrate in aqueous Sodium Salicylate; [(a) NaNO_3 +water, (b) $0.01 \text{ mol} \cdot \text{kg}^{-1}$ sodium salicylate+ sodium nitrate, (c) $0.02 \text{ mol} \cdot \text{kg}^{-1}$ sodium salicylate+ sodium nitrate (d) $0.03 \text{ mol} \cdot \text{kg}^{-1}$ sodium salicylate+ sodium nitrate,], e) sodium Citrate +water, (f) $0.01 \text{ mol} \cdot \text{kg}^{-1}$ sodium salicylate+ sodium citrate, (g) $0.02 \text{ mol} \cdot \text{kg}^{-1}$ sodium salicylate+ sodium citrate (h) $0.03 \text{ mol} \cdot \text{kg}^{-1}$ sodium salicylate+ sodium citrate,] at multiple temperature.

Partial molar volume at infinite dilution (V_{ϕ}^0)

The partial molar volumes of the electrolytes have been determined by extrapolating $\{(V_{\phi} - A_v \sqrt{m}) - m\}$ curve to zero concentration according to Redlich-Mayer equation 4.2 [206]. In this study, sodium citrate (a 1:3 electrolyte) and sodium nitrate (a 1:1 electrolyte) have been used as solutes. Sodium citrate, with three negatively charged citrate ions, contributes to a higher ionic strength and stronger ion-ion interactions compared to sodium nitrate. Consequently, the A_v values for sodium citrate are expected to differ significantly from those of sodium nitrate due to the variation in charge distribution and the resulting differences in ion-solvent and ion-ion interactions.[161][184].

Table 4.84 Measured densities, ρ and V_ϕ in the of sodium salicylate with Sodium Nitrate and sodium Citrate.

$a m_a / (\text{mol} \cdot \text{kg}^{-1})$	$\rho \times 10^{-3} / (\text{kg} \cdot \text{m}^{-3})$				$V_\phi \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
Sodium Nitrate in 0.000 mol·kg⁻¹ sodium salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.08744	1.00457	1.00214	0.99898	0.99508	23.56	26.00	27.58	29.94
0.18432	1.01023	1.00761	1.00429	1.00019	24.46	26.19	28.04	30.17
0.28217	1.01565	1.01301	1.00958	1.00526	25.56	26.70	28.23	30.33
0.39429	1.02190	1.01914	1.01545	1.01095	25.87	26.74	28.62	30.52
0.48416	1.02691	1.02376	1.01995	1.01531	25.93	26.86	29.13	30.92
Sodium Nitrate in 0.010 mol·kg⁻¹ sodium salicylate								
0.00000	0.99971	0.99760	0.99454	0.99091				
0.09598	1.00534	1.00314	0.99999	0.99620	26.56	27.60	28.27	29.17
0.20420	1.01150	1.00917	1.00593	1.00203	26.62	27.64	28.30	29.12
0.28168	1.01584	1.01343	1.01010	1.00613	26.69	27.70	28.41	29.20
0.38670	1.02168	1.01911	1.01571	1.01164	26.74	27.80	28.46	29.25
0.47192	1.02637	1.02371	1.02019	1.01599	26.77	27.81	28.55	29.41
Sodium Nitrate in 0.020 mol·kg⁻¹ sodium salicylate								
0.00000	1.00047	0.99843	0.99547	0.99142				
0.11809	1.00721	1.00503	1.00192	0.99785	27.13	28.01	28.63	29.33
0.19192	1.01135	1.00909	1.00595	1.00181	27.24	28.13	28.61	29.38
0.32357	1.01861	1.01620	1.01298	1.00871	27.44	28.36	28.82	29.55

0.39478	1.02247	1.01996	1.01671	1.01237	27.58	28.53	28.92	29.69
0.47564	1.02676	1.02419	1.02085	1.01642	27.80	28.68	29.17	29.93
Sodium Nitrate in 0.030 mol·kg⁻¹ sodium salicylate								
0.00000	1.00099	0.99914	0.99628	0.99233				
0.09613	1.00648	1.00445	1.00139	0.99734	27.26	28.01	28.78	29.50
0.22495	1.01372	1.01154	1.00838	1.00421	27.29	28.18	28.85	29.57
0.29284	1.01748	1.01521	1.01200	1.00777	27.33	28.27	28.92	29.64
0.39426	1.02302	1.02064	1.01734	1.01301	27.45	28.39	29.04	29.75
0.49245	1.02828	1.02580	1.02239	1.01795	27.63	28.53	29.21	29.97
Sodium Citrate in 0.000 mol·kg⁻¹ sodium salicylate								
0.00000	0.99926	0.99705	0.99404	0.99036				
0.08734	1.01524	1.01282	1.00964	1.00580	73.78	75.94	77.58	79.08
0.18432	1.03272	1.03001	1.02665	1.02261	73.96	76.39	77.97	79.57
0.28550	1.05066	1.04764	1.04407	1.03979	74.13	76.68	78.32	80.04
0.38023	1.06713	1.06382	1.06005	1.05551	74.42	77.00	78.68	80.55
0.47605	1.08350	1.07998	1.07590	1.07109	74.73	77.16	79.05	81.05
Sodium Citrate in 0.010 mol·kg⁻¹ sodium salicylate								
0.00000	0.99971	0.99759	0.99454	0.99091				
0.09987	1.01811	1.01577	1.01348	1.00908	72.43	74.43	75.85	77.04
0.19386	1.03504	1.03247	1.03005	1.02548	73.20	75.25	76.52	77.84
0.27802	1.04986	1.04712	1.04458	1.03985	73.95	75.90	77.15	78.51
0.38410	1.06805	1.06514	1.06242	1.05754	74.97	76.78	78.07	79.32

0.48651	1.08517	1.08215	1.07926	1.07424	75.89	77.48	78.79	79.99
Sodium Citrate in 0.020 mol·kg⁻¹ sodium salicylate								
0.00000	1.00047	0.99843	0.99547	0.99142				
0.09470	1.01830	1.01608	1.01376	1.00966	68.57	70.29	71.83	73.88
0.19030	1.03584	1.03339	1.03086	1.02651	69.75	71.64	73.39	75.51
0.28080	1.05198	1.04933	1.04656	1.04200	70.99	72.89	74.83	76.89
0.39933	1.07250	1.06945	1.06646	1.06169	72.49	74.73	76.58	78.41
0.49147	1.08799	1.08459	1.08129	1.07642	73.58	76.04	78.10	79.74
Sodium Citrate in 0.030 mol·kg⁻¹ sodium salicylate								
0.00000	1.00099	0.99914	0.99628	0.99233				
0.09631	1.01987	1.01778	1.01448	1.01148	61.00	63.19	65.19	67.49
0.19387	1.03817	1.03584	1.03215	1.02889	64.02	66.19	69.02	71.28
0.28197	1.05407	1.05135	1.04739	1.04372	66.42	69.18	71.93	74.83
0.40649	1.07523	1.07208	1.06774	1.06362	70.32	73.19	75.90	78.93
0.49644	1.08970	1.08620	1.08152	1.07730	72.98	76.00	78.83	81.46

$u(\rho) = 0.15 \text{ kg} \cdot \text{m}^{-3}$, Uncertainties in V_ϕ are $0.50 \times 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ for $\text{NaNO}_3 + \text{H}_2\text{O}$ and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$. For $\text{NaSal} + \text{NaNO}_3$, values are 0.25, 0.22, and $0.23 \times 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ at 0.01, 0.02, and 0.03 mol·kg⁻¹, respectively. For $\text{NaSal} + \text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, they are 0.45, 0.68, and $0.23 \times 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ at the same molalities.

Table 4.85 shows computed V_{ϕ}^0 values for different concentrations and temperatures, along with their respective standard errors. Additionally, S_V^* values along with errors are also given in the same table. These V_{ϕ}^0 are shown graphically in **Figure 4.51(a) and 4.51(b)**. The results demonstrate that the V_{ϕ}^0 of sodium nitrate in aqueous sodium salicylate solutions generally escalate with temperature. This pattern indicates that interactions of solute-solvent become more pronounced at higher temperatures, which can be related to the increased kinetic energy, which promotes greater molecular motion and interaction. Additionally, higher temperatures can disrupt the solvent structure, allowing solute molecules to occupy more space and further increase V_{ϕ}^0 [207–210]. However, the V_{ϕ}^0 values for sodium citrate display a different behaviour (**Figure 4.51(b)**). While V_{ϕ}^0 increases with temperature at zero molality, at higher molalities, the V_{ϕ}^0 values decrease as the temperature escalates. This can be understood in terms of greater interactions of solutes at higher concentration levels, which could better pack the ions of citrate within the solution. At higher temperatures, partial dehydration of citrate ions could occur together with behaviour related to aggregation changes, so these might explain the observed V_{ϕ}^0 decrease. All these results in a contraction of the volume occupied by the citrate ions and thus V_{ϕ}^0 decreases with temperature. The slopes S_V^* i.e experimental values, which relate the V_{ϕ}^0 to the changes in molality of the solute, also display temperature dependence. This indicates that the molecules of solute exert an influence on the volumetric properties of the solution, which is different at various temperatures. Thus, variation in value can be obtained due to differences in interaction dynamics of solute-solvent as well as due to variations in aggregation behaviour of the solute at distinct temperatures. Optimizing the chemical processes and applications dealing with such solutions is essential as this gives insight into changes in solute-solvent interaction with a change in temperature [156,211,212].

Change in partial volume of transfer per mole (ΔV_{ϕ}^0)

The ΔV_{ϕ}^0 of solutes (sodium Nitrate and sodium Citrate) from H_2O to sodium salicylate solutions at immense dilution in an aqueous medium, the equation 4.3 was used [24] [25].

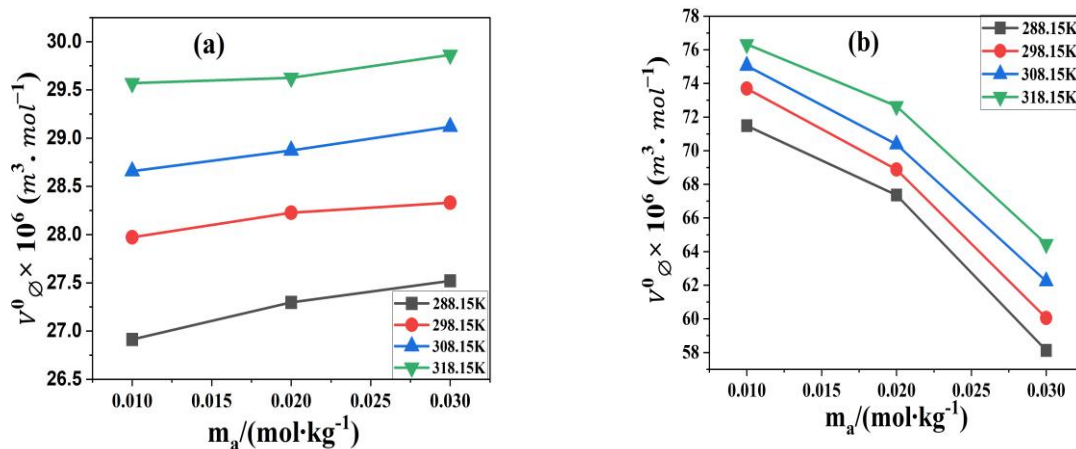


Figure 4.51: Variation of, V_{ϕ}^0 , of, 4.51 (a) sodium Nitrate and 4.51 (b) sodium Citrate in various concentration of sodium salicylate solutions at numerous temperatures.

Table 4.86 contains the ΔV_{ϕ}^0 data, provide qualitative interpretation between solute sodium Nitrate and sodium Citrate and solvent sodium salicylate molecules interactions inside the liquid mixture. These values provide qualitative details regarding solute and solvent interactions within the liquid system, excluding solute-solute interactions. For sodium nitrate, the ΔV_{ϕ}^0 values were positive at lower temperatures (288.15, 298.15, 308.15) K, indicating that the presence of sodium salicylate led to an expansion of the solution structure. This expansion is likely due to interactions involving hydrophilic groups and ion-hydrophilic bonding, which reduce the electrostriction of H_2O molecules around the sodium nitrate, causing some H_2O molecules to be dispersed in the main solution. However, at higher temperatures (318.15 K), the ΔV_{ϕ}^0 values became negative, suggesting a contraction in the solution structure, possibly due to the weakening or breakdown of these interactions at elevated temperatures. [213,214]. In contrast, sodium citrate consistently exhibited negative ΔV_{ϕ}^0 values, indicating a contraction in the solution structure upon transfer. This contraction can be associated to robust ion-hydrophilic interactions involving the citrate ions and the sodium salicylate molecules, which lead to significant structural changes in the solution.

Table 4.85 V_ϕ^0 , and S_V^* , of salts in the aqueous sodium salicylate at numerous temperatures.

^a m_b (mol·kg ⁻¹)	$V_\phi^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$				$S_V^* \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-2})$			
	288.15 K	298.15 K	308.15 K	318.15 K	288.15 K	298.15 K	308.15 K	318.15 K
Sodium Nitrate								
0.000	23.32(±0.44)	25.84(±0.17)	27.27(±0.10)	29.72(±0.07)	6.12(±1.39)	2.26(±0.54)	3.63(±0.32)	2.27(±0.23)
0.010	26.51(±0.04)	27.53(±0.04)	28.17(±0.04)	29.04(±0.03)	0.26(±0.14)	0.61(±0.12)	0.78(±0.12)	0.62(±0.11)
0.020	26.88(±0.02)	27.77(±0.02)	28.37(±0.05)	29.08(±0.05)	1.83(±0.06)	1.89(±0.05)	1.50(±0.16)	1.62(±0.14)
0.030	27.11(±0.03)	27.88(±0.04)	29.63(±0.02)	29.33(±0.03)	0.92(±0.09)	1.29(±0.12)	1.09(±0.05)	1.15(±0.09)
Sodium Citrate								
0.000	73.51(±0.06)	75.74(±0.08)	77.25(±0.01)	78.62(±0.02)	2.41(±0.21)	3.13(±0.28)	3.74(±0.04)	5.05(±0.06)
0.010	71.48(±0.04)	73.68(±0.05)	75.04(±0.04)	76.33(±0.06)	9.02(±0.13)	7.90(±0.18)	7.71(±0.15)	7.64(±0.21)
0.020	67.36(±0.04)	68.87(±0.05)	70.37(±0.05)	72.64(±0.14)	12.72(±0.14)	14.55(±0.16)	15.67(±0.17)	14.55(±0.44)
0.030	58.12(±0.10)	60.04(±0.07)	62.23(±0.26)	64.44(±0.4)	29.89(±0.31)	32.20(±0.23)	33.68(±0.02)	35.08(±0.80)

standard uncertainties u is $u(m_b) = 0.006 \text{ mol} \cdot \text{kg}^{-1}$, $u(T) = \pm 0.001 \text{ K}$, $u(p) = 0.01 \text{ MPa}$, $u(V_\phi^0) = 3.87 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ and $u(S_V^*) = 1.73 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-2})$.

The larger size and greater charge density of the citrate ion result in more pronounced perturbations in the solvent structure. Furthermore, the ΔV_{ϕ}^0 values for sodium citrate were found to decrease further with increasing temperature, indicating an intensification of these interactions at higher temperatures [215,216] The observed trends in ΔV_{ϕ}^0 values can be examined through the model of co-sphere overlap, which describes the interactions within the ternary mixtures:[217]

- i) Hydrophilic-hydrophilic interactions: Between sodium salicylate and sodium nitrate, leading to structural expansion at lower temperatures.
- ii) Ion-hydrophilic interactions: Dominant in sodium citrate solutions, causing significant structural contraction.
- iii) Ion-hydrophobic interactions: Present but less pronounced compared to interactions of ion-hydrophilic.

Table 4.86 ΔV_{ϕ}^0 of sodium nitrate and sodium citrate in solution of sodium salicylate.

^a m_b (mol·kg ⁻¹)	$\Delta V_{\phi}^0 \times 10^6 / (m^3 \cdot mol^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Nitrate				
0.010	3.19	1.68	0.89	-0.67
0.020	3.57	1.92	1.10	-0.64
0.030	3.79	2.04	1.35	-0.38
Sodium citrate				
0.010	-2.04	-2.06	-2.21	-2.30
0.020	-6.15	-6.87	-6.88	-5.98
0.030	-15.39	-15.70	-15.02	-14.18

uncertainties u is $u(T) = \pm 0.001K$, $u(p) = 0.01MPa$, and $u(\Delta V_{\phi}^0) = 1.28 \times 10^6 / (m^3 \cdot mol^{-1})$.

Temperature- dependent Partial molar Volume

The equation 4.4 was applied to find how V_{ϕ}^0 at immense dilution vary with temperature [25] .**Table 4.87** lists empirical parameters for sodium Nitrate/sodium Citrate in an aqueous solution of sodium salicylate. The minimal discrepancies among

the calculated and observed V_{ϕ}^0 data, indicating an excellent fit with the polynomial equation, as evidenced by high R^2 values[218]. The main purpose of analysing the V_{ϕ}^0 values is to derive partial molar expansibilities, which are calculated using the equation 4.5 [25]. **Table 4.88** contains the $E_{\phi}^0 = (\partial E_{\phi}^0 / \partial T)_P$ (partial molar expansibilities) for the mixtures of sodium salicylate with Sodium Nitrate and Sodium Citrate at various temperatures and concentrations. The study reveals that for sodium nitrate, the partial molar expansibilities (E_{ϕ}^0) decrease with increasing temperature. At 288.15 K, the (E_{ϕ}^0) values are higher, indicating greater expansibility, which diminishes progressively at higher temperatures. This pattern signifies that the interaction amongst sodium nitrate and sodium salicylate in the aqueous solution becomes less expansive as the temperature escalates. This contraction behaviour as temperature increases is affirmed by the negative value of $(\partial E_{\phi}^0 / \partial T)_P$. The trend of sodium citrate also decreases with increasing temperature. However, for sodium citrate is an order of magnitude greater than that for sodium nitrate, which implies greater interaction and higher expansibilities in the solution. The negative values for sodium citrate are stronger, particularly at higher concentrations, indicating a significant contraction in the solution structure with the escalate of temperature. These findings suggests that sodium citrate has interaction strength greater with sodium salicylate than with sodium nitrate in the aqueous solution, and hence volumetric properties change to a greater degree based on the changes in the temperature [168,219,220].

Table 4.87 Calculation of empirical constants of salts in aqueous solution of sodium salicylate.

$^a m_b /$ (mol·kg ⁻¹)	$a \times$ $10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	$b \times$ $10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \times 10^6 /$ ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$)	R^2	ARD
Sodium Nitrate					
0.010	27.4392	0.0860	-0.0004	0.9999	0.0021
0.020	27.7145	0.0763	-0.0004	0.9999	0.0014
0.030	27.8890	0.0757	-0.0002	0.9999	0.0001
Sodium Citrate					
0.010	73.6609	0.1820	-0.0022	0.9999	0.0252
0.020	68.7593	0.1543	0.0019	0.9999	0.0011

0.030	60.0842	0.2041	0.0007	0.9999	0.0003

Table 4.88 Expansibilities, E_{ϕ}^0 for the sodium salicylate in aqueous solutions of Sodium Nitrate and sodium Citrate at 0.1MPa.

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_{\phi}^0 / \partial T)_p / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	288.15 K	298.15 K	308.15 K	318.15K	
Sodium Nitrate					
0.010	0.0931	0.0860	0.0789	0.0718	-0.0007
0.020	0.0851	0.0763	0.0675	0.0587	-0.0009
0.030	0.0789	0.0757	0.0724	0.0692	-0.0003
Sodium Citrate					
0.010	0.2279	0.1820	0.1362	0.0903	-0.0046
0.020	0.1162	0.1543	0.1923	0.0230	-0.0038
0.030	0.1896	0.2041	0.2186	0.2331	-0.00145

Isobaric Thermal Expansion coefficient at fixed pressure

This α_p , describes how volume changes of a material whenever the temperature deviates while keeping a constant pressure. It is simply a measure of how much in percentage the volume changes per degree of temperature for constant uniform pressure parameters [146]. The formula for determining the isobaric thermal expansion coefficient is given in equation 4.14 [76]. From **table 4.89**, it is evident that in case of sodium nitrate, α_p generally lowers with increasing temperature especially at lower molalities. This trend indicates the lesser thermal expansion of the solution with rising temperature indicating lesser sensitivity towards temperature fluctuations in terms of volume. Probably, this would be due to the interaction of the sodium nitrate-sodium salicylate interaction wherein the solvating shell surrounding the solute is disorganized by rising temperature and thus the volume expansion becomes less when temperature increases. On the other hand, sodium citrate exhibits anomalous thermal expansion behaviour of its kind, and α_p values are generally smaller in comparison to sodium

nitrate for similar molalities. The relation of α_p with increasing temperature is in contrast for sodium citrate solutions compared to sodium nitrate solutions. Different interaction dynamics of sodium citrate with the solvent are responsible for this trend. Complex hydration nature of the chemical properties of the citrate anion-triprotic ion- could be important factors in this respect. Lower values of sodium citrate signify weaker thermal expansion effects, which can be ascribed to the strong electrostatic interactions amongst molecules of H₂O and citrate anion that stabilize more stable solvation structures less sensitive to the changes within temperature. Useful in gaining insight into the behaviour of salts and sodium salicylate interactions in these solutions are the concentration and temperature dependencies of α_p . The closer concentration becomes, the more important solute-solute interaction becomes and results in such complicated behavior in the α_p values. Knowledge of such thermal expansion coefficients becomes important for any applications involving temperature-dependent processes, such as solubility, reactions in chemicals or any transport processes in solutions. The analysis refines our discussion on the thermodynamic properties and interactions in sodium salicylate solutions by providing a more nuanced understanding of how such solutes might affect solution behaviour under a range of thermal conditions.

Table 4.89. α_p for sodium Nitrate and sodium Citrate in aqueous sodium salicylate

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$\alpha_P \times 10^3 / (K^{-1})$			
	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate				
0.01	3.63	3.23	2.89	2.56
0.02	3.28	2.86	2.49	2.13
0.03	3.02	2.82	2.63	2.45
Sodium Citrate				
0.01	3.19	2.47	1.82	1.18
0.02	1.73	2.24	2.73	0.32
0.03	3.26	3.40	3.51	3.62

Ultrasonic velocity (c)

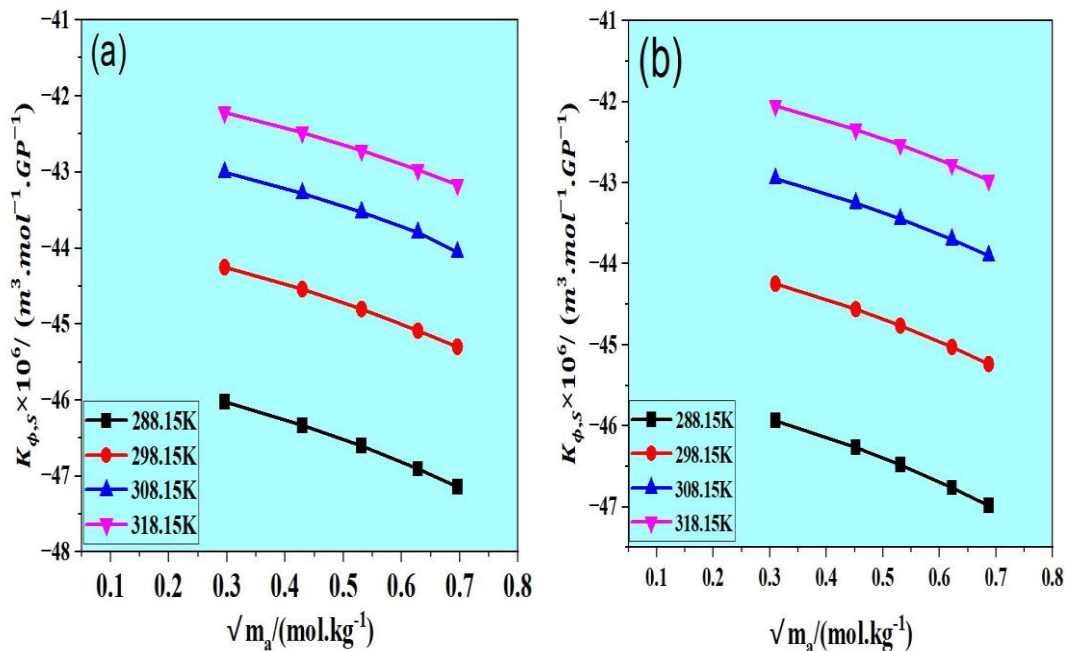
The c for the mixture (Sodium Salicylate + H₂O + Sodium Nitrate/Sodium Citrate) at 0.1MPa, and various temperatures with a difference of 10 K and different sodium salicylate concentrations, are mentioned in **Table 4.90**. A comparison graph of velocity of sound for experimental data of a binary mixture with literature[75][52](for sodium nitrate +water),[52,221,222] (for sodium citrate +water) and [223][224] [225][226](for sodium salicylate + water) with literature at 0.1 MPa pressure is depicted in **Figure 4.12, 4.1(d) and 4.43(b) respectively**. Figures clearly shows that ultrasonic velocity correlate well with existing values of literature. when the molalities of salts (sodium nitrate and sodium citrate) increases, the molecules pack closer together, allowing sound waves to travel faster. This results in higher sound velocities. Additionally, raising the temperature further boosts the sound speed because the heat disrupts the solvent structure, making it easier for sound to propagate. Therefore, both increased concentration and higher temperatures lead to faster sound travel in these solutions [227–229].

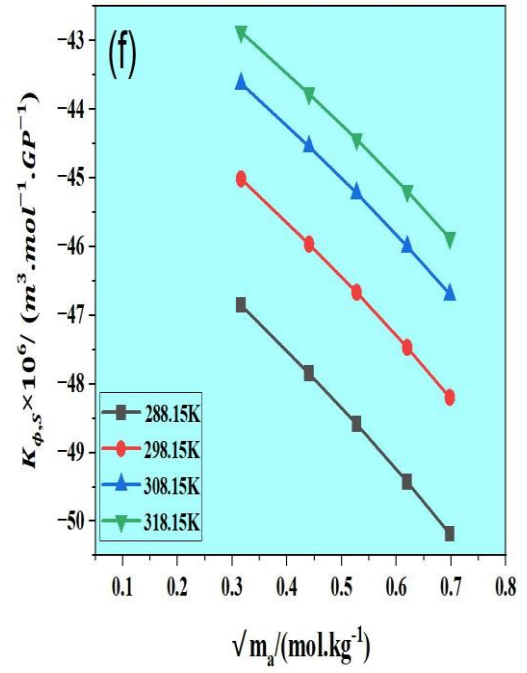
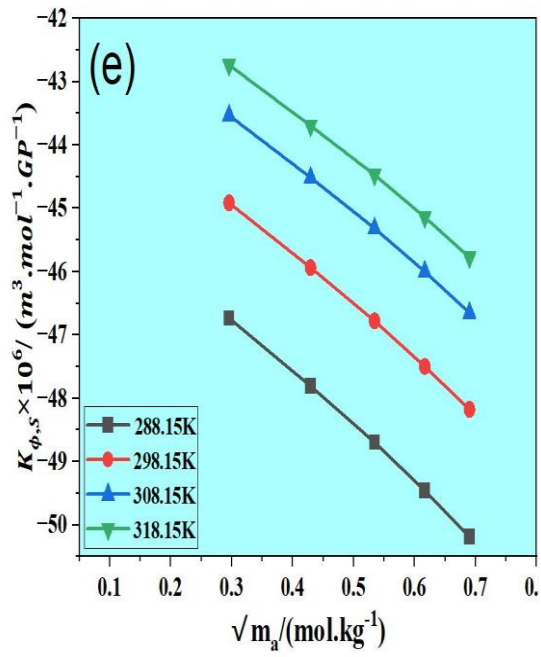
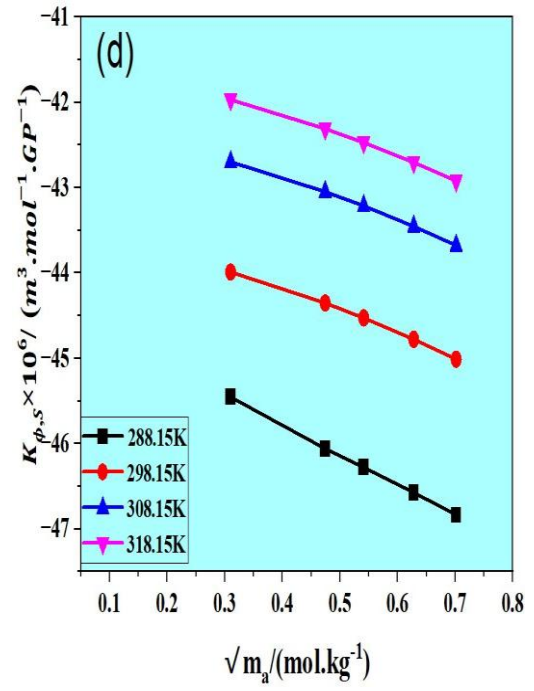
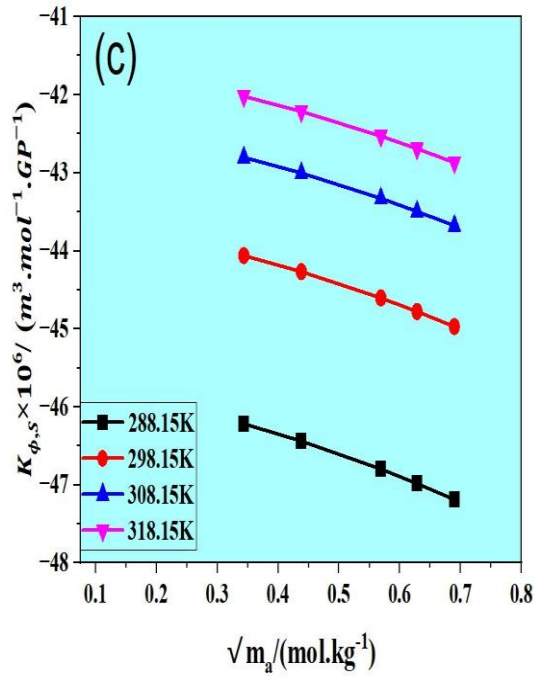
Apparent isentropic compression per mole ($K_{\phi,s}$)

The values of K_s , were obtained by employing experimentally recorded ultrasonic velocity data at different temperatures and applying Newton-Laplace formula given in equation 4.9 [230,231]. The calculated data of K_s , was used in the equation 4.8 to assess the $K_{\phi,s}$,[232]. In the prior formula, K_s and $K_{s,0}$ tells the solutions and sodium salicylate isentropic compressibility, and m_a is molality of the sodium Nitrate/Sodium Citrate per kg of the sodium salicylate. The $K_{\phi,s}$ of Sodium Nitrate/Sodium Citrate in water soluble sodium salicylate solutions were examined across a range of temperatures (288.15 Kelvin to 318.15 Kelvin) and molalities ($0.000\text{mol} \cdot \text{kg}^{-1}$ $0.01\text{mol} \cdot \text{kg}^{-1}$, $.02\text{mol} \cdot \text{kg}^{-1}$ and $.03\text{mol} \cdot \text{kg}^{-1}$. **Table 4.90 (Figure 4.52)** shows across all conditions, the $K_{\phi,s}$ data for each salt is negative, illustrating strong solute-solvent interactions [186–189]. The data for sodium nitrate and sodium citrate in aqueous sodium salicylate solutions reveal several key trends:

- i) The negative $K_{\phi,s}$ values across all temperatures and molalities indicate robust solute-solvent interactions. This negativity implies that the existence of both the salts considerably impacts the structure and compressible nature of sodium salicylate.

- ii) The escalation in temperature results to a decrease in the negative extent of $K_{\phi,s}$. This trend shows that solute-solvent interactions weaken with rising temperature, likely due to the reduced structuring of H_2O molecules at higher temperatures.
- iii) Higher molalities correlate with decreased absolute $K_{\phi,s}$ values. This reduction in compressibility as more solute is added points to stronger interactions at minimal concentrations. As molality increases, the compressibility of the solution diminishes, indicating more robust solute(salts)- solvent (sodium salicylate) interactions at minimal solute concentrations.
- iv) Sodium citrate exhibits more negative $K_{\phi,s}$ values than sodium nitrate, indicating stronger interactions with sodium salicylate. Despite differences in magnitude, the consistent trends observed for both salts underscore the effective interaction facilitation by sodium salicylate. This study highlights that both sodium nitrate and sodium citrate significantly influence the structural and compressible properties of sodium salicylate solutions. The data reveal that sodium citrate demonstrates stronger interactions compared to sodium nitrate [233,234].





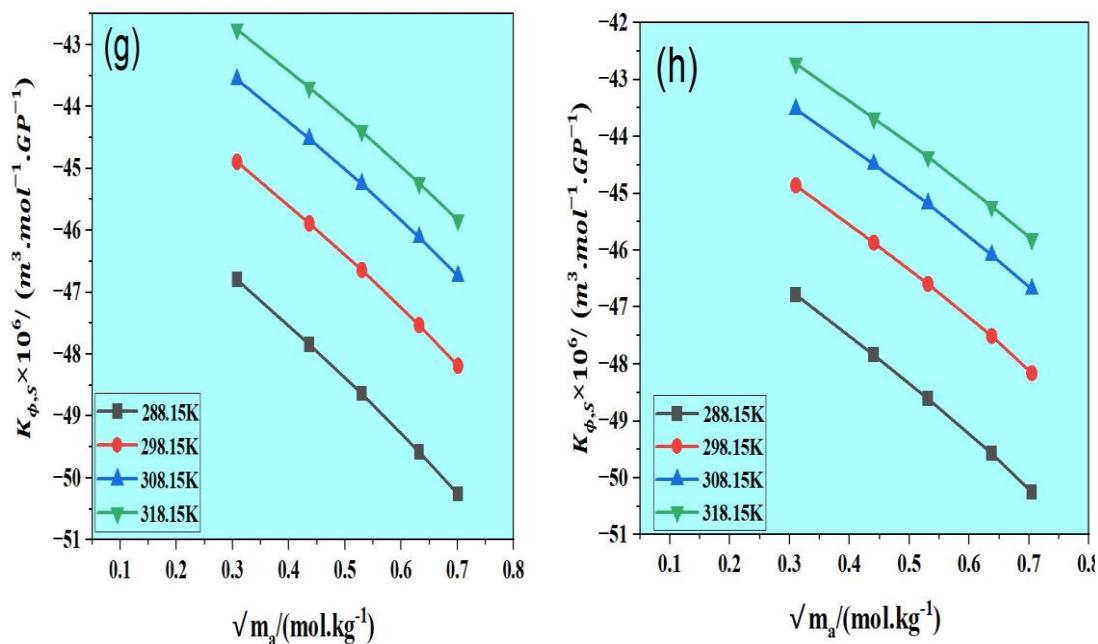


Figure 4.52: Plots representing the, $K_{\phi,S}$, against the molality (m_a) of Salts in Sodium Salicylate at various temperatures. (a) (Sodium Nitrate+ water) (b) (0.010 sodium salicylate+ Sodium Nitrate) (c) (0.020 sodium salicylate+ Sodium Nitrate) (d) (0.030 sodium salicylate+ Sodium Nitrate) and (e) (Sodium Citrate + water) (f) (0.010 sodium salicylate+ Sodium Citrate) (g) (0.020 sodium salicylate+ Sodium Citrate) (h) (0.030 sodium salicylate+ Sodium Citrate).

Table 4.90: ultrasonic velocity and $K_{\phi,S}$ for NaNO_3 and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ in aqueous sodium salicylate solutions.

$m_a/(\text{mol}\cdot\text{kg}^{-1})$	$s/(m\cdot s^{-1})$				$K_{\phi,S} \times 10^6/(\text{m}^3\cdot\text{mol}^{-1}\cdot\text{GP}^{-1})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate in aqueous $0.000\text{ mol}\cdot\text{kg}^{-1}$ sodium salicylate								
0.00000	1466.59	1495.85	1519.14	1533.02				
0.08743	1472.01	1501.16	1522.95	1536.96	-46.02	-44.25	-43.00	-42.22
0.18432	1476.04	1503.89	1526.15	1540.19	-46.33	-44.54	-43.28	-42.48
0.28217	1479.58	1507.55	1529.53	1544.03	-46.60	-44.80	-43.53	-42.72
0.39429	1483.32	1510.14	1532.89	1547.04	-46.90	-45.09	-43.79	-42.97
0.48416	1486.29	1513.63	1535.93	1550.46	-47.14	-45.30	-44.05	-43.16
Sodium Nitrate in aqueous $0.010\text{ mol}\cdot\text{kg}^{-1}$ sodium salicylate								
0.00000	1467.57	1497.09	1521.78	1538.04				
0.09598	1473.01	1502.86	1524.65	1539.36	-45.93	-44.24	-42.95	-42.05
0.20420	1477.48	1507.89	1528.32	1543.21	-46.26	-44.56	-43.25	-42.34
0.28168	1480.18	1510.50	1530.43	1546.03	-46.48	-44.76	-43.44	-42.53
0.38670	1483.59	1513.83	1533.92	1549.49	-46.76	-45.03	-43.70	-42.78
0.47192	1486.49	1516.63	1537.18	1552.46	-46.98	-45.24	-43.90	-42.97
Sodium Nitrate in aqueous $0.020\text{ mol}\cdot\text{kg}^{-1}$ sodium salicylate								
0.00000	1467.91	1498.55	1521.09	1539.04				
0.11809	1475.96	1504.15	1526.19	1540.30	-46.22	-44.06	-42.80	-42.02
0.19192	1479.92	1509.31	1529.81	1544.62	-46.44	-44.27	-43.00	-42.21

0.32357	1483.07	1512.11	1532.37	1547.31	-46.80	-44.60	-43.33	-42.53
0.39478	1486.72	1516.10	1535.81	1550.83	-46.98	-44.78	-43.49	-42.69
0.47564	1489.95	1519.29	1538.61	1553.98	-47.19	-44.97	-43.68	-42.87
Sodium Nitrate in aqueous 0.030 mol·kg ⁻¹ sodium salicylate								
0.00000	1468.91	1499.76	1523.91	1540.07				
0.096129	1475.33	1505.25	1527.37	1541.07	-45.45	-43.99	-42.70	-41.97
0.22495	1481.02	1511.63	1531.43	1546.01	-46.06	-44.35	-43.05	-42.31
0.29284	1483.97	1514.64	1533.82	1548.38	-46.28	-44.53	-43.21	-42.47
0.394255	1488.13	1518.32	1537.43	1551.93	-46.57	-44.78	-43.45	-42.70
0.492445	1492.06	1521.98	1540.80	1555.54	-46.83	-45.01	-43.68	-42.92
Sodium Citrate in aqueous 0.000 mol·kg ⁻¹ sodium salicylate								
0.00000	1466.59	1495.85	1519.14	1533.02				
0.08734	1484.13	1513.93	1536.09	1549.95	-47.24	-45.40	-44.01	-43.21
0.18432	1504.24	1533.04	1554.19	1568.93	-48.05	-46.17	-44.75	-43.94
0.28550	1525.78	1552.69	1573.54	1587.98	-48.88	-46.96	-45.51	-44.67
0.38023	1546.43	1572.03	1589.94	1603.52	-49.65	-47.68	-46.21	-45.35
0.47605	1566.68	1588.88	1607.93	1620.91	-50.41	-48.41	-46.90	-46.02
Sodium Citrate in aqueous 0.010 mol·kg ⁻¹ sodium salicylate								
0.00000	1467.57	1497.09	1521.58	1538.04				
0.09987	1487.83	1518.64	1540.16	1554.18	-47.28	-45.43	-44.03	-43.26
0.19386	1507.12	1536.62	1557.78	1572.72	-48.07	-46.18	-44.75	-43.96
0.27802	1525.13	1552.80	1574.03	1588.11	-48.76	-46.83	-45.38	-44.58

0.38410	1548.92	1574.82	1592.98	1606.03	-49.60	-47.64	-46.16	-45.33
0.48651	1569.91	1592.44	1610.95	1625.04	-50.40	-48.40	-46.89	-46.05
Sodium Citrate in aqueous 0.020 mol·kg ⁻¹ sodium salicylate								
0.00000	1467.91	1498.55	1521.09	1539.04				
0.09470	1489.00	1520.40	1541.98	1555.50	-47.24	-45.32	-43.98	-43.17
0.19029	1508.13	1538.2	1559.25	1574.92	-48.05	-46.09	-44.72	-43.89
0.28080	1527.71	1556.07	1576.96	1590.79	-48.80	-46.80	-45.40	-44.55
0.39933	1553.92	1579.52	1596.96	1609.87	-49.75	-47.70	-46.26	-45.40
0.49147	1572.68	1596.21	1613.89	1627.59	-50.47	-48.37	-46.91	-46.02
Sodium Citrate in aqueous 0.030 mol·kg ⁻¹ sodium salicylate								
0.00000	1468.91	1499.76	1523.91	1540.07				
0.09631	1491.41	1523.58	1544.01	1557.93	-47.22	-45.29	-43.94	-43.16
0.19387	1510.82	1540.91	1561.85	1577.93	-48.07	-46.09	-44.71	-43.90
0.28197	1529.81	1558.83	1578.91	1593.13	-48.80	-46.78	-45.37	-44.53
0.40649	1556.82	1582.39	1599.92	1612.65	-49.78	-47.70	-46.25	-45.38
0.49644	1575.46	1599.88	1617.12	1630.87	-50.45	-48.33	-46.85	-45.96

^a m_A is salts molality in the aqueous Sodium salicylate solution. uncertainties u is $u(m) = 0.02425 \text{ mol·kg}^{-1}$, $u(T) = \pm 0.001K$, $u(p) = 0.01 \text{ MPa}$, $u(s) = 2.79 \text{ m} \cdot \text{s}^{-1}$ u ($K_{\phi,s}$) = $0.166 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GP}^{-1})$.

Partial Isentropic Compression per mole ($K_{\phi,s}^0$)

The values of $K_{\phi,s}^0$, was computed by the extrapolation of $K_{\phi,s}$ against $\sqrt{m}$ to zero concentration the least square fitting method, using the equation 4.10 [25]. **Table 4.91** lists the calculated $K_{\phi,s}^0$ values together with associated standard errors. Because of small magnitude of S_K^* , the solute-solute interaction is minimal at immense dilution [192]. The data reveal that all values of $K_{\phi,s}^0$ are negative, signifying strong solute-solvent interactions. The compressibility of both sodium nitrate and sodium citrate solutions decreases with rising temperature and concentration, as evidenced by less negative $K_{\phi,s}$ and S_K^* values (**Figure 4.53(a) and (b)**). Increasing temperature raises molecular kinetic energy, which expands intermolecular spacing and weakens intermolecular forces, thereby reducing compressibility. Similarly, higher concentrations increase solute particles, reducing free volume and enhancing the solution's resistance to compression. This increased resistance enhances sound velocity through the solution as sound waves travel more efficiently in a denser medium. Sodium citrate solutions are generally more compressible than sodium nitrate solutions due to differences in ionic interactions and hydration effects. Sodium citrate, with higher ionic strength and larger ion size, disrupts water structure more significantly, leading to higher compressibility compared to sodium nitrate[235,236].

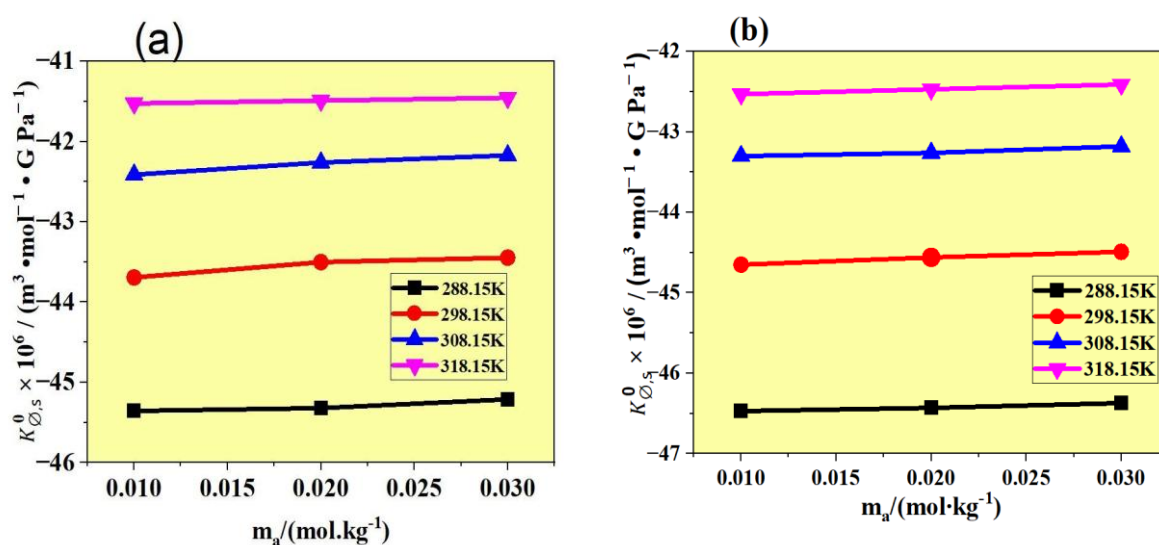


Figure 4.53: Graph of, $K_{\phi,s}^0$, of (a), Sodium Nitrate and (b) Sodium Citrate, in aqueous sodium salicylate solutions at numerous temperatures.

Table 4.91 Values of $K_{\phi,S}^0$ and, S_K^* of Sodium nitrate/sodium citrate in the aqueous sodium salicylate.

^a	m_b	$K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$				$S_K^* \times 10^6 / (kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1})$			
(mol·kg ⁻¹)		288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate									
0.000	-46.45(±0.10)	-43.70(±0.10)	-42.45(±0.08)	-41.70(±0.09)	-3.58(±0.30)	-3.38(±0.30)	-3.38(±0.24)	-3.10(±0.29)	
0.010	-45.35(±0.09)	-43.69(±0.08)	-42.41(±0.08)	-41.53(±0.08)	-3.51(±0.27)	-3.33(±0.26)	-3.21(±0.26)	-3.11(±0.26)	
0.020	-45.32(±0.06)	-43.50(±0.06)	-42.26(±0.06)	-41.49(±0.06)	-3.30(±0.18)	-3.11(±0.17)	-3.00(±0.17)	-2.92(±0.17)	
0.030	-45.21(±0.09)	-43.45(±0.09)	-42.17(±0.09)	-41.45(±0.09)	-3.43(±0.28)	-3.25(±0.27)	-3.13(±0.26)	-3.05(±0.26)	
Sodium Citrate									
0.000	-46.53(±0.01)	-44.73(±0.01)	-43.37(±0.01)	-42.59(±0.01)	-8.17(±0.05)	-7.74(±0.04)	-7.43(±0.04)	-7.22(±0.05)	
0.010	-46.50(±0.02)	-44.68(±0.01)	-43.31(±0.01)	-42.55(±0.01)	-8.05(±0.06)	-7.68(±0.06)	-7.39(±0.06)	-7.22(±0.05)	
0.020	-46.49(±0.02)	-44.61(±0.02)	-43.30(±0.02)	-42.51(±0.02)	-8.14(±0.07)	-7.70(±0.08)	-7.38(±0.08)	-7.19(±0.07)	
0.030	-46.48(±0.04)	-44.60(±0.04)	-43.28(±0.04)	-42.52(±0.03)	-8.07(±0.13)	-7.60(±0.13)	-7.25(±0.12)	-7.00(±0.12)	

standard uncertainties u is $u(K_{\phi,S}^0) = 0.32 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$, $u(T) = \pm 0.001 K$, $u(p) = 0.01 MPa$.

Partial Molar Isentropic Compression of transfer ($\Delta K_{\phi,s}^0$)

The $\Delta K_{\phi,s}^0$ is determined using the equation 4.11 for the transition from H₂O to Sodium Salicylate aqueous solutions [237]. The estimated $\Delta K_{\phi,s}^0$ values are positive in nature in all the sodium salicylate concentrations and measured temperatures which are in **Table 4.92**. The $\Delta K_{\phi,s}^0$ increase as the Sodium Salicylate proportion rises. The co-sphere overlap concept advanced by Krishnan and Friedman [238] elucidates this phenomenon. This model enlightens how interactions in solutes and solvents cause volume to expand and contract. These values provide an understanding of how the compressibility of the solutes varies when shifted from H₂O to sodium salicylate solutions at all temperatures and molalities. The $\Delta K_{\phi,s}^0$ values for sodium nitrate are negative, indicating a decrease in compressibility when sodium nitrate is transferred from water to sodium salicylate solutions. The $\Delta K_{\phi,s}^0$ values change slightly with temperature but remain largely positive. At the higher concentrations of sodium nitrate, the more positive values of $\Delta K_{\phi,s}^0$ are obtained indicating stronger interactions of the salts with the sodium salicylate at the higher concentration of salts. On the contrary, $\Delta K_{\phi,s}^0$ data for sodium citrate are temperature and concentration-dependent, though generally less positive, or even close to zero with respect to sodium nitrate. At lower temperatures and concentrations, the $\Delta K_{\phi,s}^0$ values become a little negative or near zero; thus, there will be only a minimum change or even an increase in compressibility when sodium citrate is transferred from water to sodium salicylate solutions. As the temperature and concentration increase, $\Delta K_{\phi,s}^0$ values for sodium citrate are slightly positive; thus, compressibility decreases as the solute concentration increases. These results show that the positive $\Delta K_{\phi,s}^0$ values of sodium nitrate produce very strong solute-solvent interactions in sodium salicylate solutions, so compressibility is lower than that in pure water. For sodium citrate, +slight positive or nearly zero values of $\Delta K_{\phi,s}^0$ imply that it interacts less with sodium salicylate than sodium nitrate; hence, the least compressibility change is found to exist. The trends point out that sodium nitrate has stronger interaction with sodium salicylate, resulting in more drastic compression reductions, and in contrast to this, sodium citrate has relatively weaker interplays, and the compressibility is little different from that in the solvent. These insights provide a

comprehensive view of sodium nitrate and sodium citrate interaction with sodium salicylate solutions, thus influencing their compressibility properties at numerous temperatures and concentrations.

Table 4.92 $\Delta K_{\phi,S}^0$ of Sodium chloride and sodium sulphate in aqueous sodium salicylate.

^a m_b (mol·kg ⁻¹)	$\Delta K_{\phi,S}^0 \times 10^6 / (m^3 \cdot mol^{-1} \cdot GPa^{-1})$			
	T=288.15K	T=298.15K	T=308.15K	T=318.15K
Sodium Nitrate				
0.010	0.09	0.01	0.04	0.17
0.020	0.13	0.20	0.19	0.21
0.030	0.23	0.25	0.27	0.25
Sodium Citrate				
0.010	0.04	0.05	0.06	0.05
0.020	0.05	0.12	0.07	0.09
0.030	0.05	0.14	0.09	0.08

Pair and Triplet Coefficients

The equation 4.12, 4.13 was employed to calculate the ΔV_{ϕ}^0 and ΔK_{ϕ}^0 , [239][240]. The coefficients V_{AB} and V_{ABB} denotes the interaction coefficients for volume at both the pair and triplet level respectively. Similarly, K_{AB} and K_{ABB} denotes the interaction coefficients for isentropic compression at these levels. The coefficients are given in Table 4.93. According to the theory of McMillan-Mayer, V_{AB} , V_{ABB} and K_{AB} , K_{ABB} , are evaluated by fitting the ΔV_{ϕ}^0 and ΔK_{ϕ}^0 respectively. This theoretical method proves useful for studies on binary as well as ternary molecular interactions. In fair detail, Friedman and Krishnan and by Franks et al. [241] applied the theory. The results are quite candid in stating that the coefficients of interaction are strongly temperature dependent, yielding further insight into the behaviour of solutions at different temperatures. For sodium nitrate, V_{AB} , V_{ABB} gives positive data at 288.15 K and 298.15 K, indicating an expansion in volume because of the pairwise interactions between the solvent and the salt. Therefore, at lower temperatures these interactions present less dense structures and produce an expanded solution volume. But at 318.15 K, V_{AB} , V_{ABB} becomes negative, meaning that the interactions will result in a more compact structure, thus lowering the

volume of the solution. Similarly, for sodium nitrate, K_{AB} , K_{ABB} are positive at all temperatures studied; this is an indication that interactions generally enhance the compressible nature of the solution. This does mean a steadily positive value indicates that sodium salicylate and sodium nitrate in water increase the compressibility of the solution, independently of temperature. For sodium citrate, V_{AB} , V_{ABB} is negative at all temperatures, meaning that pairwise interactions give a more tightly structured system. The K_{AB} , K_{ABB} values change, with negative ones at 288.15, 318.15 K, which means that interactions reduce compressibility.

The triplet interaction coefficients further explain the intricacies of these interactions. For sodium nitrate, V_{AB} , V_{ABB} is negative at 288.15, 298.15, and 308.15 K which explains the fact that triplet interactions lead to a more structured co-sphere as compared to the solvent, thus lowering the solution volume. However, at 318.15 K, V_{AB} , V_{ABB} becomes positive, which shows an expansion in volume due to triplet interactions in the mixture at this temperature. The triplet isentropic compression coefficient K_{AB} , K_{ABB} for sodium nitrate is mainly negative, indicating that triplet interactions generally decrease compressibility in solution. These are negative values at 288.15, 308.15, and 318.15 K, indicating that the solution has become stiffer in structure due to the triplet interactions; thus, it has become less compressible. At 298.15 K, K_{AB} , K_{ABB} is positive; thus, at that temperature, triplet interactions have increased the compressibility of the solution. For sodium citrate, V_{AB} , V_{ABB} all are negative for all the temperatures, suggesting that the interaction in triplet has led to a more packed structure. Values of K_{AB} , K_{ABB} for sodium citrate vary with temperature, showing that compressibility changes due to the triplet interaction at different temperatures.

Table 4.93 V_{AB} , K_{AB} and V_{ABB} , K_{ABB} of (sodium sulphate and sodium chloride) salts present in aqueous solutions of sodium salicylate.

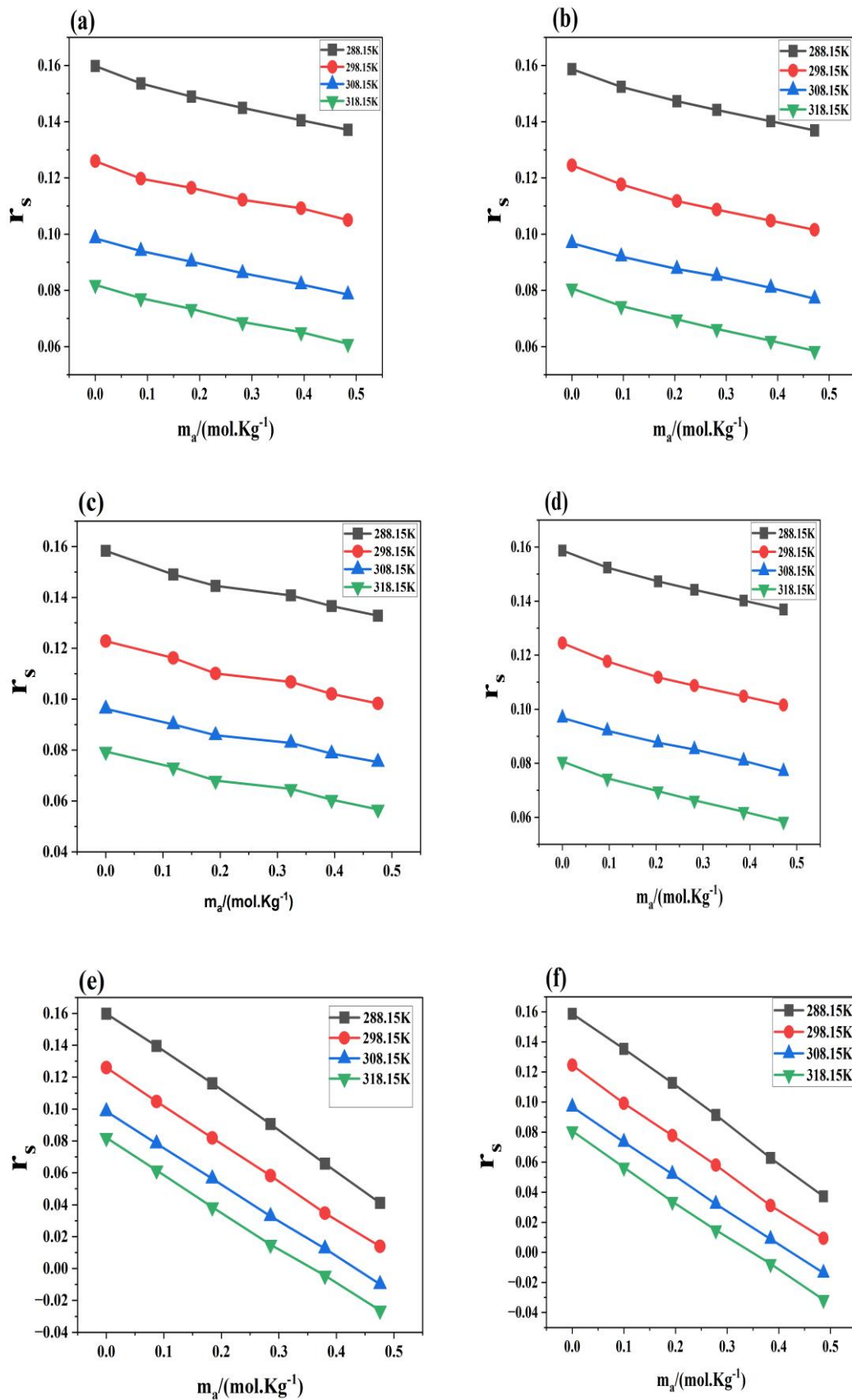
T/K	$V_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg)$	$V_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2)$	$K_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg GPa^{-1})$	$K_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2 GPa^{-1})$
Sodium Nitrate				
288.15	177.31	-2586.91	3.38	9.40
298.15	94.18	-1363.11	2.14	53.02
308.15	47.30	-564.95	2.36	52.73
318.15	-41.75	795.24	9.46	-122.06
Sodium Citrate				
288.15	-16.24	-5230.24	2.02	-25.61
298.15	-32.98	-5015.53	3.63	-28.73
308.15	-49.64	-4406.25	3.28	-39.89
318.15	-40.72	-4244.05	3.33	-44.35

Relative Association (R_a):

The solvation process yields valuable findings about how extensive and what kind of interactions between the particles in the system are. Relative association (R_a) has been calculated using the equation 4.15 [242]. Where ρ_0 and ρ represents densities and s_0 and s are the sound speeds of the aqueous sodium salicylate and ternary solution, respectively. The data in **table 4.94** reveals that the R_a values generally escalate with increasing molality of salts (sodium nitrate or sodium citrate) in sodium salicylate + water solutions. However, R_a values decrease as the temperature rises across all concentrations. This trend indicates that, at lower temperatures, the solvation of the solutes by the solvent (sodium salicylate + water) is more pronounced, leading to stronger molecular interactions. Conversely, at elevated temperatures, the disruption of the solvent structure appears to outweigh solvation effects, resulting in lower R_a values.[93][94]

Relaxation Strength (r_s)

The relaxation strength was calculated by using the equation 4.16 [95]. Here s is the ultrasonic velocity and the value of s_∞ is constant, set at $1600 \text{ m}\cdot\text{s}^{-1}$ [95]. The data of relaxation strength are mentioned in **table 4.94** (graphically present in **Figure 4.54**) and was found to decrease with the increase of molality of sodium nitrate/sodium citrate to the sodium salicylate + water solution. Additionally, relaxation strength decreases with increasing temperature. At lower mole fractions of salts, relaxation strength is more pronounced compared to higher mole fractions. This trend suggests that both increased salt concentration and rising temperatures reduce molecular interactions within the system [96]. These findings have significant implications for understanding molecular interactions in complex solutions. The decrease in relaxation strength highlights the delicate balance between solute-solvent interactions, providing insights into the thermodynamic stability and transport properties of such systems. This understanding is crucial for applications in pharmaceuticals, where solvation dynamics and molecular interactions play a pivotal role in drug formulation and delivery mechanisms.



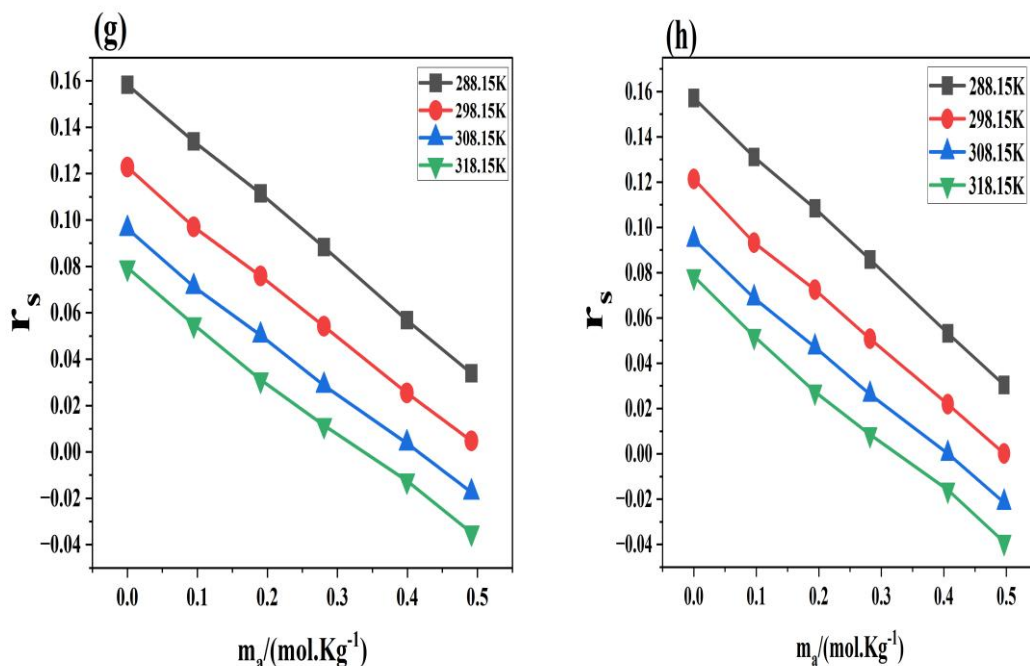


Figure 4.54: Plots representing the Relaxation Strength (r_s) against the molality (m_a) of Salts in Sodium Salicylate at various temperatures. (a) (Sodium Nitrate+ water) (b) (0.01 sodium salicylate+ Sodium Nitrate) (c) (0.02 sodium salicylate+ Sodium Nitrate) (d) (0.03 sodium salicylate+ Sodium Nitrate) and (e) (Sodium Citrate + water) (f) (0.01 sodium salicylate+ Sodium Citrate) (g) (0.02 sodium salicylate+ Sodium Citrate) (h) (0.03 sodium salicylate+ Sodium Citrate).

ATR-FTIR Analysis

FTIR spectra of binary mixtures of sodium salicylate + water (**figure 4.55(a)**), sodium citrate + water (**4.55(b)**) and sodium nitrate + water **4.55(c)**, show substantial changes in the vibrational frequencies of major peaks, indicating molecular interaction in these solutions. In the case of sodium salicylate in water, the characteristic peaks appeared at 581 cm^{-1} , 1637 cm^{-1} , and 3328 cm^{-1} corresponding to the aromatic ring bending, C=O stretching, and O-H stretching vibrations, respectively. As the concentration of sodium salicylate increases, those peaks shift to lower wavenumbers. As such, the C=O stretching peak shifts from 1637 cm^{-1} to 1623 cm^{-1} while indicating an increase in the H-bonding between the carboxylate groups of sodium salicylate and the water molecules.

Table 4.94 Values of R_a and r_s with different molalities of salts (sodium nitrate/sodium citrate) in sodium salicylate at numerous temperatures.

$m_a/(\text{mol}\cdot\text{kg}^{-1})$	R_a				r_s			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Sodium Nitrate in aqueous 0.000 mol·kg⁻¹ sodium salicylate								
0.00000	1.0000	1.0000	1.0000	1.0000	0.1598	0.1260	0.0985	0.0820
0.08744	1.0041	1.0039	1.0041	1.0039	0.1536	0.1197	0.0940	0.0772
0.18432	1.0088	1.0088	1.0088	1.0084	0.1489	0.1165	0.0902	0.0734
0.28217	1.0134	1.0134	1.0133	1.0126	0.1449	0.1122	0.0861	0.0687
0.39429	1.0188	1.0189	1.0185	1.0177	0.1405	0.1092	0.0821	0.0651
0.48416	1.0231	1.0227	1.0223	1.0213	0.1371	0.1050	0.0785	0.0610
Sodium Nitrate in aqueous 0.010 mol·kg⁻¹ sodium salicylate								
0.00000	1.0000	1.0000	1.0000	1.0000	0.1587	0.1245	0.0968	0.0807
0.09598	1.0043	1.0042	1.0045	1.0042	0.1524	0.1177	0.0920	0.0744
0.20420	1.0094	1.0091	1.0096	1.0092	0.1473	0.1118	0.0876	0.0697
0.28168	1.0132	1.0127	1.0134	1.0127	0.1442	0.1087	0.0851	0.0663

0.38670	1.0182	1.0177	1.0182	1.0175	0.1402	0.1048	0.0809	0.0621
0.47192	1.0222	1.0216	1.0220	1.0212	0.1369	0.1015	0.0770	0.0585

Sodium Nitrate in aqueous 0.020 mol·kg⁻¹ sodium salicylate

0.00000	1.0000	1.0000	1.0000	1.0000	0.1583	0.1228	0.0962	0.0794
0.11809	1.0049	1.0054	1.0054	1.0054	0.1490	0.1162	0.0901	0.0732
0.19192	1.0081	1.0083	1.0087	1.0084	0.1445	0.1101	0.0858	0.0680
0.32357	1.0147	1.0148	1.0152	1.0148	0.1408	0.1068	0.0828	0.0648
0.39478	1.0177	1.0176	1.0182	1.0177	0.1366	0.1021	0.0786	0.0605
0.47564	1.0212	1.0211	1.0217	1.0211	0.1328	0.0983	0.0753	0.0567

Sodium Nitrate in aqueous 0.030 mol·kg⁻¹ sodium salicylate

0.00000	1.0000	1.0000	1.0000	1.0000	0.1571	0.1214	0.0946	0.0783
0.09613	1.0040	1.0042	1.0042	1.0042	0.1498	0.1149	0.0887	0.0723
0.22495	1.0099	1.0098	1.0104	1.0100	0.1432	0.1074	0.0839	0.0663
0.29284	1.0130	1.0128	1.0135	1.0131	0.1398	0.1039	0.0810	0.0635
0.39426	1.0176	1.0174	1.0180	1.0176	0.1349	0.0995	0.0767	0.0592
0.49245	1.0219	1.0218	1.0223	1.0217	0.1304	0.0951	0.0726	0.0548

Sodium Citrate in aqueous 0.000 mol·kg⁻¹ sodium salicylate

0.00000	1.0000	1.0000	1.0000	1.0000	0.1598	0.1260	0.0985	0.0820
0.08734	1.0120	1.0118	1.0119	1.0119	0.1396	0.1047	0.0783	0.0616
0.18432	1.0248	1.0246	1.0250	1.0246	0.1161	0.0819	0.0564	0.0385
0.28550	1.0377	1.0378	1.0381	1.0377	0.0906	0.0583	0.0328	0.0150
0.38023	1.0492	1.0495	1.0503	1.0499	0.0658	0.0347	0.0125	-0.0044
0.47605	1.0607	1.0616	1.0621	1.0616	0.0412	0.0139	-0.0099	-0.0263

Sodium Citrate in aqueous 0.010 mol·kg⁻¹ sodium salicylate

0.00000	1.0000	1.0000	1.0000	1.0000	0.1587	0.1245	0.0968	0.0807
0.09987	1.0138	1.0134	1.0138	1.0136	0.1353	0.0991	0.0734	0.0565
0.19386	1.0262	1.0260	1.0264	1.0260	0.1127	0.0777	0.0521	0.0338
0.27802	1.0368	1.0369	1.0373	1.0370	0.0914	0.0581	0.0322	0.0148
0.38410	1.0493	1.0498	1.0508	1.0507	0.0628	0.0312	0.0088	-0.0076
0.48651	1.0614	1.0627	1.0635	1.0631	0.0373	0.0094	-0.0137	-0.0315

Sodium Citrate in aqueous 0.020 mol·kg⁻¹ sodium salicylate

0.00000	1.0000	1.0000	1.0000	1.0000	0.1583	0.1228	0.0962	0.0794
0.09470	1.0130	1.0128	1.0129	1.0129	0.1339	0.0970	0.0712	0.0549

0.19029	1.0261	1.0261	1.0262	1.0256	0.1115	0.0758	0.0503	0.0311
0.28080	1.0376	1.0379	1.0379	1.0376	0.0883	0.0542	0.0286	0.0115
0.39933	1.0518	1.0525	1.0532	1.0530	0.0568	0.0254	0.0038	-0.0124
0.49147	1.0628	1.0637	1.0641	1.0637	0.0339	0.0047	-0.0174	-0.0348

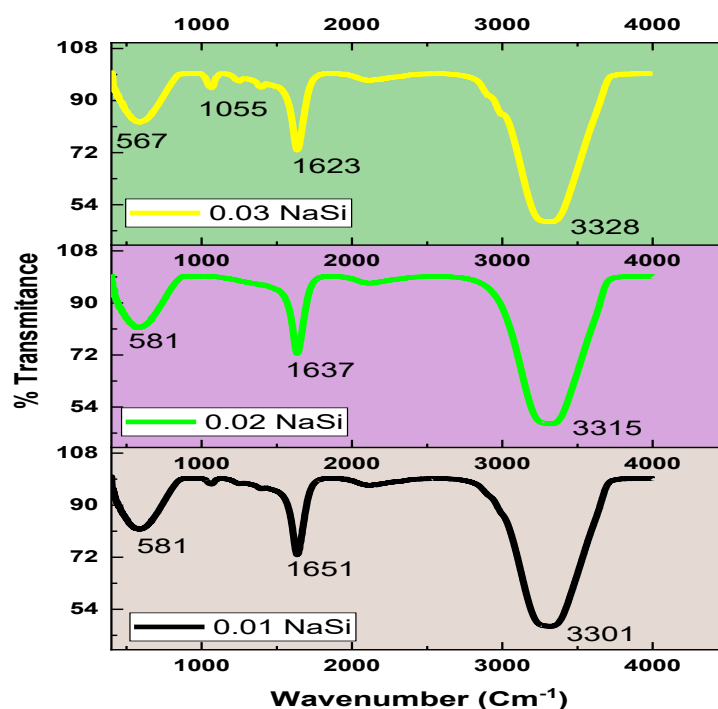
Sodium Citrate in aqueous 0.030 mol·kg⁻¹ sodium salicylate

0.00000	1.0000	1.0000	1.0000	1.0000	0.1571	0.1214	0.0946	0.0783
0.09631	1.0137	1.0133	1.0137	1.0135	0.1311	0.0932	0.0688	0.0519
0.19387	1.0275	1.0274	1.0274	1.0266	0.1084	0.0725	0.0471	0.0274
0.28197	1.0389	1.0388	1.0388	1.0380	0.0858	0.0508	0.0262	0.0086
0.40649	1.0536	1.0540	1.0544	1.0535	0.0532	0.0219	0.0001	-0.0159
0.49644	1.0635	1.0640	1.0642	1.0631	0.0304	0.0001	-0.0215	-0.0390

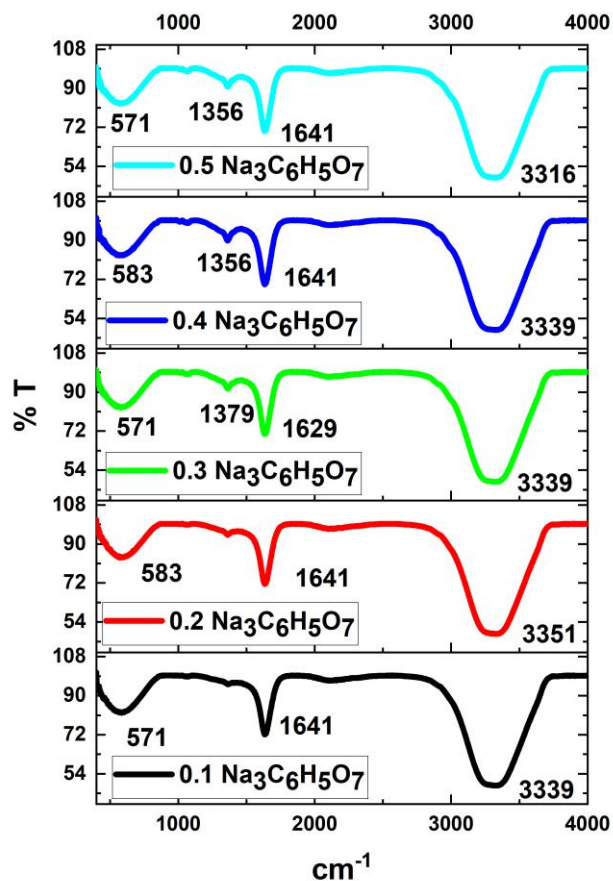
standard uncertainties u is $u(m_a) = 0.02425 \text{ mol}\cdot\text{kg}^{-1}$, $u(T) = \pm 0.001 K$, $u(R_a) = 0.0013$ and $u(p) = 0.01 \text{ MPa}$.

The shifts in the O-H stretching peak are also slight with changes in the hydrogen bonding network as the solvation dynamics evolve with higher salt concentrations. In the case of sodium citrate + water, FTIR spectra show peaks at around 571 cm^{-1} and 1629 cm^{-1} . With increasing concentration of citrate, these peaks shift gradually, indicating stronger hydrogen bonding and even more complex interactions in the solution. The shifts correspond to the system's adaptation to higher ionic strength and the tendency for aggregation or complexation of ions. Similar trends can be observed for the system sodium nitrate + water. The FTIR spectra of the peaks, particularly those corresponding to nitrate ions, show concentration-dependent shifts, which are indicative of changes in the hydrogen-bonding environment and electrostatic interactions as the ionic strength of the solution increases. These FTIR spectra, overall, depict the interplay of concentration of solutes with the molecular interactions present within the aqueous phase. The vibrational frequency shifts recorded here are consistent with the dynamic changes in the solvent and hydrogen bonding that possibly result in ionic association, thus revealing how the behaviour and stability of the given systems change under varied concentration.

4.55(a)



4.55(b)



4.55(c)

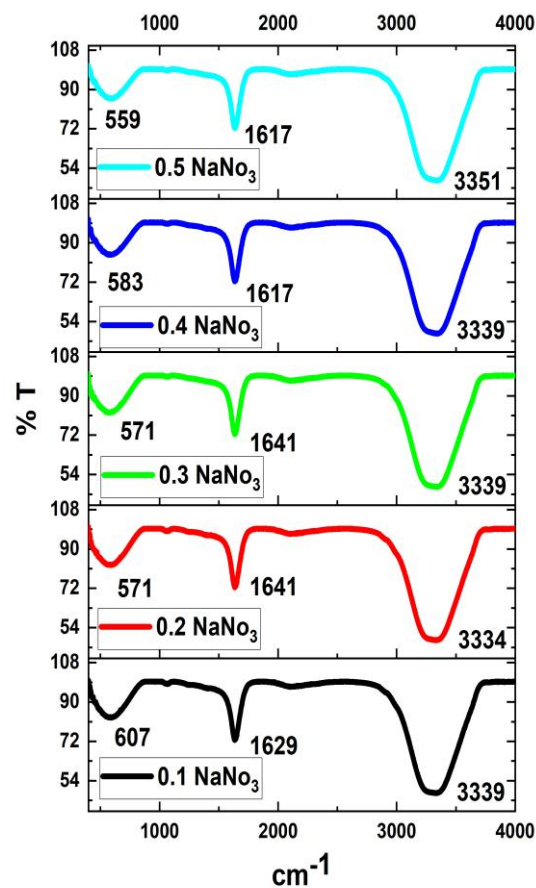


Figure 4.55: 4.55 (a) spectra of sodium salicylate in water at 0.010,0.020,0.030 concentration. 4.61(b) and 4.61(c) are the spectra of sodium Citrate and sodium Nitrate with water at different concentrations.

Problem 9

Acoustic and Spectroscopic Investigation of Sodium Salicylate with Potassium Chloride/Sodium bicarbonate: A Volumetric and Thermodynamic Study

This problem investigates the thermodynamic properties of ternary solutions comprising potassium chloride/sodium bicarbonate in sodium salicylate solutions by taking measurements of density and ultrasonic velocity.

Density and ultrasonic velocity

Volumetric, ultrasonic characteristics were obtained from experimental ultrasonic velocity and density values. At $T = 288.15\text{--}308.15\text{K}$, (with gap of 10K), the densities and ultrasonic velocity for KCl and NaHCO_3 of $(0.01, 0.02, 0.03) \text{ mol}\cdot\text{kg}^{-1}$ sodium salicylate water-based solutions were measured. The density results clear that values increase as sodium salicylate concentration rises and decrease as temperature rises. However, as both the concentration and the temperature of the binary mixture (water + sodium salicylate) rise, the data of the sound velocity also rise. The data that were taken through experimentation of density and ultrasonic velocity are presented in **Table 4.95**. The plots of comparison of density and sound velocity of literatures [169] [170] [171] [172] [173] with experimental values of a (sodium salicylate + water), sodium bicarbonate + water [53] and [76] [104] [79] for (potassium chloride + water) is present in **Figures 4.43(a), 4.8(b), 4.15(a)** for density and **4.43(b), 4.15(b)** for speed of sound of sodium salicylate + water and potassium chloride + water respectively. The density increases with concentration for both the salts. It can be explained by adding ions to the solution as the concentration increases, thereby raising density. The sound velocity escalates with concentration, reflecting the increased rigidity of the mixture due to stronger ion-solvent interactions. With temperature rising, the density and, consequently, the ultrasonic velocity increase also, a behaviour that is explained by thermal expansion of the solvent and the weakening of intermolecular forces. The escalation of density with concentration can be ascribed to the ion hydration effect, which decreases the free volume with tight binding of layers of H_2O molecules around the ions. In contrast, the enhancement of velocity of sound with concentration comes

from the rise in the compressibility of the solution, for which the ion-induced ordering of the medium increases its stiffness. The temperature-dependent trends favour the fact that high temperatures induce interference of interactions of solute and solvent. It also means less energy in propagation of sound along with lower density [76] [243]. Schematic representations of the systems is shown in **figure 4.56**.

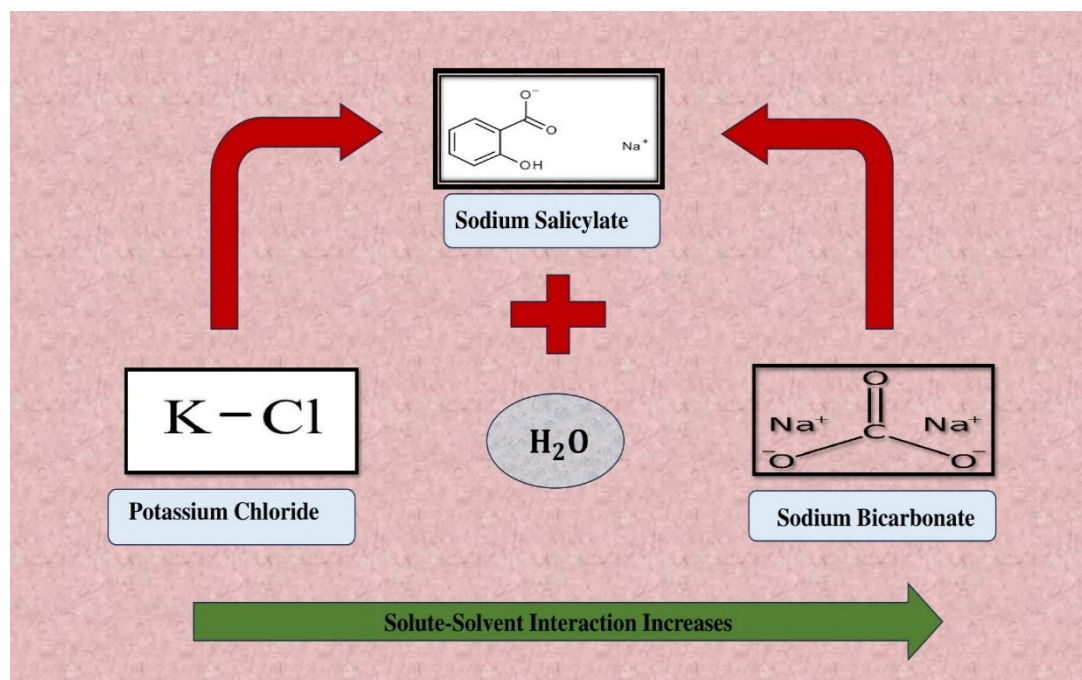
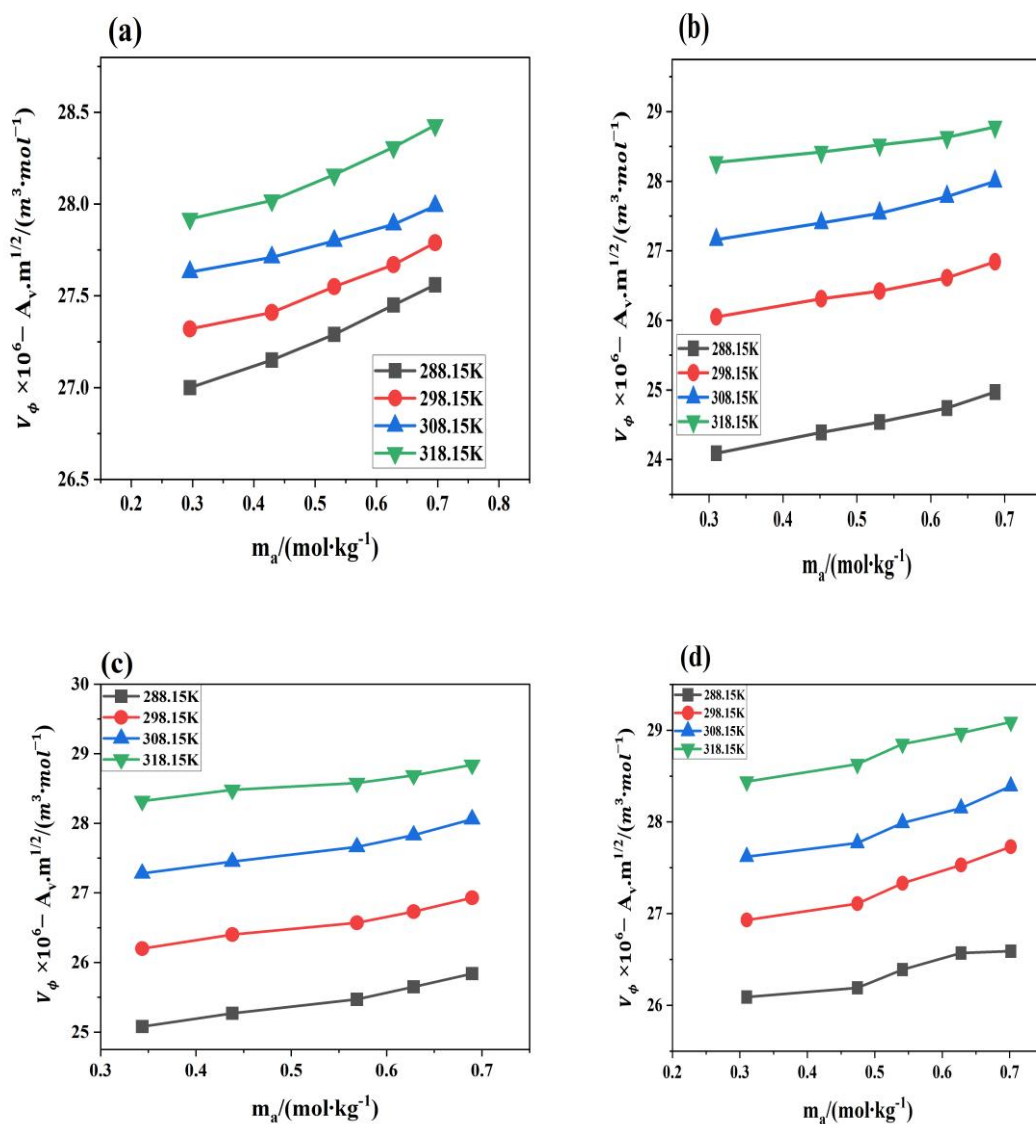


Figure 4.56: Sodium bicarbonate/ potassium chloride and sodium salicylate interactions.

Apparent molar volume

The V_ϕ for solvent (aqueous sodium salicylate) with NaHCO_3 and KCl was derived from the experimentally measured density values. The V_ϕ values were computed using the equation 4.1. Here M , molecular mass of sodium bicarbonate/potassium chloride, m_A is molality of the KCl / NaHCO_3 solutes per kilogram of the aqueous NaSl , and ρ_0, ρ represents and the solvent aqueous sodium salicylate and the solution's densities (ternary) subsequently. The obtained V_ϕ shown in **Table 4.96**, and **figure 4.57 (a, b, c, d for potassium chloride and e, f, g, h for sodium bicarbonate)**. The reported molar volume (V_ϕ) values for potassium chloride (KCl) and sodium bicarbonate (NaHCO_3) in water solutions of sodium salicylate exhibit a consistent increase with rising solute concentration and temperature. This rise is mainly due to

the enhancement of ion-ion (solute-solute) interactions at elevated concentrations, which results in the progressive breakage of the hydration shells around the ions. Ions are closely sheathed by hydration shells of an ordered structure in dilute solutions, but upon increasing the concentration of the solute, cluster formation and pairing of ions bring about the collapse of this structure of hydration. In addition, the monotonically increasing V_ϕ with temperature is an indicative of the compromised ion-solvent interactions brought about by thermal expansion and diminishing hydration strength with increasing temperature [78,244].



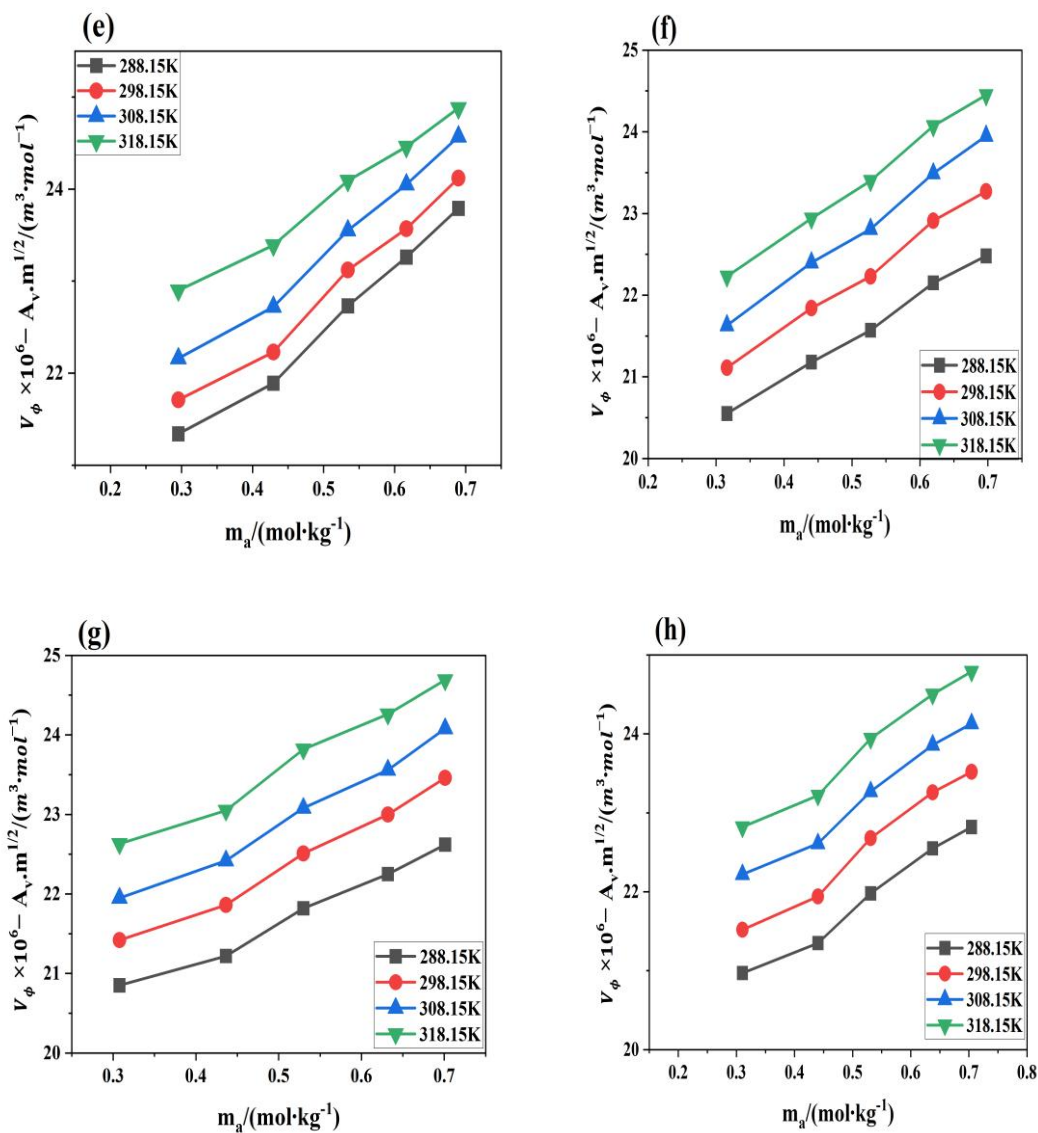


Figure 4.57: Variation of V_ϕ with salt molality (m_a): (a) (KCl + water), (b-d) – Potassium chloride in sodium salicylate solution at 0.01, 0.02 and 0.03 $\text{mol} \cdot \text{kg}^{-1}$ respectively; (e) $\text{NaHCO}_3 + \text{water}$, (f-h) – sodium bicarbonate in sodium salicylate at 0.01, 0.02 and 0.03 $\text{mol} \cdot \text{kg}^{-1}$ respectively.

Table 4.95 Measured densities (ρ) and ultrasonic velocity (c) of sodium salicylate–based ternary solutions containing potassium chloride and sodium bicarbonate.

^a $m_a/(\text{mol} \cdot \text{kg}^{-1})$	$\rho/(\text{kg} \cdot \text{m}^{-3})$				$c/(\text{m} \cdot \text{s}^{-1})$			
	288.15	298.15	308.15	318.15	288.15	298.15	308.15	318.15
Potassium Chloride + water								
0.00000	999.26	997.05	994.04	990.36	1466.59	1495.85	1519.14	1536.02
0.10621	1004.29	1002.05	999.00	995.28	1472.79	1502.36	1525.07	1541.95
0.18956	1008.20	1005.93	1002.85	999.10	1477.49	1506.92	1529.29	1545.63
0.28101	1012.43	1010.14	1007.05	1003.25	1482.79	1511.96	1533.79	1549.73
0.38281	1017.10	1014.79	1011.67	1007.81	1488.45	1516.72	1538.93	1554.11
0.46818	1020.97	1018.64	1015.51	1011.59	1493.37	1521.51	1543.17	1558.56
0.01 ($\text{mol} \cdot \text{kg}^{-1}$) sodium salicylate (NaSl) + Potassium Chloride (in aqueous medium)								
0.00000	999.71	997.60	994.54	990.91	1467.57	1497.09	1521.78	1538.04
0.08697	1004.18	1001.92	998.74	994.94	1473.18	1502.47	1525.65	1541.93
0.20408	1009.99	1007.49	1004.19	1000.27	1479.80	1508.92	1531.14	1546.89
0.26827	1013.13	1010.52	1007.13	1003.16	1483.18	1512.20	1534.17	1550.03
0.36285	1017.72	1014.92	1011.41	1007.37	1488.92	1517.03	1538.93	1554.39
0.47627	1023.14	1020.13	1016.48	1012.37	1494.89	1522.58	1544.34	1559.74
0.02 ($\text{mol} \cdot \text{kg}^{-1}$) sodium salicylate (NaSl) + Potassium Chloride (in aqueous medium)								
0.00000	1000.47	998.43	995.47	991.42	1467.91	1498.55	1521.09	1539.04
0.08506	1004.67	1002.50	999.39	995.33	1474.14	1503.61	1526.22	1542.67
0.18569	1009.58	1007.30	1004.07	999.90	1479.72	1508.59	1531.12	1547.09

0.28869	1014.54	1012.14	1008.79	1004.54	1485.70	1514.49	1535.71	1551.69
0.38025	1018.89	1016.39	1012.94	1008.61	1490.92	1519.29	1540.12	1555.75
0.47100	1023.14	1020.54	1016.96	1012.59	1495.33	1523.94	1544.39	1559.99
0.03 (mol·kg ⁻¹) sodium salicylate (NaSl) + Potassium Chloride (in aqueous medium)								
0.00000	1000.99	999.14	996.28	992.33	1468.91	1499.76	1523.91	1540.07
0.10774	1006.20	1004.16	1001.11	997.04	1476.82	1505.33	1529.14	1544.92
0.18250	1009.78	1007.66	1004.56	1000.42	1481.12	1509.29	1532.37	1548.29
0.29139	1014.92	1012.69	1009.51	1005.27	1487.70	1515.19	1537.31	1553.19
0.37361	1018.75	1016.43	1013.20	1008.91	1491.92	1519.79	1540.82	1556.95
0.48510	1023.97	1021.45	1018.13	1013.79	1497.63	1525.76	1545.94	1561.46
Sodium Bicarbonate + water								
0.00000	999.26	997.05	994.04	990.36	1466.59	1495.85	1519.14	1536.02
0.10313	1005.91	1003.96	1000.78	996.81	1475.78	1505.00	1526.73	1544.01
0.18524	1010.83	1008.59	1005.49	1001.44	1482.42	1512.09	1532.92	1549.76
0.30886	1018.17	1015.94	1012.57	1008.29	1493.35	1521.81	1542.69	1558.44
0.37932	1022.13	1019.73	1016.23	1011.97	1499.02	1526.91	1548.31	1563.69
0.45128	1026.27	1023.56	1020.03	1015.80	1505.67	1532.57	1553.10	1567.49
0.01 (mol·kg ⁻¹) sodium salicylate (NaSl) + Sodium Bicarbonate (in aqueous medium)								
0.00000	999.71	997.60	994.54	990.91	1467.57	1497.09	1521.78	1538.04
0.10555	1006.76	1004.49	1001.52	997.41	1477.37	1506.32	1527.98	1544.89
0.22273	1013.84	1011.47	1008.29	1003.92	1487.02	1515.92	1536.93	1552.92
0.29577	1018.15	1015.84	1012.56	1007.91	1493.16	1521.8	1542.94	1558.08

0.40064	1024.32	1021.93	1018.14	1013.44	1502.03	1529.42	1550.62	1565.93
0.46434	1028.02	1025.25	1021.66	1016.80	1507.63	1535.09	1555.30	1569.91
0.02 (mol·kg ⁻¹) sodium salicylate (NaSl) + Sodium Bicarbonate (in aqueous medium)								
0.00000	1000.47	998.43	995.47	991.42	1467.91	1498.55	1521.09	1539.04
0.10080	1006.96	1005.08	1001.80	997.85	1477.89	1507.14	1528.98	1545.51
0.17798	1011.92	1009.53	1006.29	1002.52	1484.32	1513.32	1534.91	1550.92
0.30352	1019.28	1017.33	1013.61	1009.46	1494.66	1523.26	1544.89	1559.38
0.39069	1024.53	1022.25	1018.14	1014.58	1501.92	1529.92	1550.92	1565.91
0.47582	1029.76	1027.17	1022.78	1019.31	1509.50	1536.86	1557.15	1571.92
0.03 (mol·kg ⁻¹) sodium salicylate (NaSl) + Sodium Bicarbonate (in aqueous medium)								
0.00000	1000.99	999.14	996.28	992.33	1468.91	1499.76	1523.91	1540.07
0.10263	1007.69	1005.69	1002.57	998.45	1479.32	1508.79	1530.67	1546.93
0.17745	1012.65	1010.33	1006.85	1003.12	1485.53	1514.79	1536.23	1551.89
0.30860	1020.33	1018.23	1014.33	1010.36	1496.32	1524.93	1546.54	1560.52
0.41533	1026.93	1024.57	1020.14	1016.53	1505.39	1533.13	1554.54	1568.84
0.46362	1029.90	1027.18	1022.75	1019.44	1509.98	1536.93	1557.84	1572.85

For the ternary system, aqueous sodium salicylate solutions were used as solvents, and the molality of the added salts (m_a) was calculated using 1 kg of the respective NaSl solution. The Calculated uncertainties $u(m) = 0.01$, $u(\rho) = 0.60 \text{ kg} \cdot \text{m}^{-3}$, $u(u) = 1.98 \text{ m} \cdot \text{s}^{-1}$, $u(T) = \pm 0.001 \text{ K}$.

Table 4.96: V_ϕ and $K_{\phi,S}$ for KCl and $NaHCO_3$ in sodium salicylate aqueous solutions.

$^a m_a / (\text{mol} \cdot \text{kg}^{-1})$	$V_\phi \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$				$K_{\phi,S} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
T/K	288.15	298.15	308.15	318.15	288.15	298.15	308.15	318.15
Potassium Chloride + water								
0.10621	27.00	27.32	27.63	27.92	-45.43	-43.64	-42.34	-41.41
0.18956	27.15	27.41	27.71	28.02	-45.16	-43.40	-42.14	-41.25
0.28101	27.29	27.55	27.80	28.16	-44.72	-43.01	-41.79	-40.94
0.38281	27.45	27.67	27.89	28.31	-44.22	-42.59	-41.37	-40.56
0.46818	27.56	27.79	27.99	28.43	-43.79	-42.18	-41.01	-40.20
0.01 (mol·kg ⁻¹) sodium salicylate (NaSl) + Potassium Chloride (in aqueous medium)								
0.08697	24.09	26.05	27.16	28.27	-45.34	-43.57	-42.24	-41.36
0.20408	24.39	26.31	27.40	28.42	-44.97	-43.26	-42.02	-41.18
0.26827	24.54	26.42	27.54	28.52	-44.68	-43.00	-41.78	-40.95
0.36285	24.74	26.61	27.78	28.63	-44.18	-42.58	-41.39	-40.60
0.47627	24.97	26.84	28.00	28.78	-43.63	-42.09	-40.93	-40.15
0.02 (mol·kg ⁻¹) sodium salicylate (NaSl) + Potassium Chloride (in aqueous medium)								
0.08506	25.08	26.20	27.28	28.32	-45.28	-43.50	-42.21	-41.35
0.18569	25.27	26.40	27.45	28.48	-45.01	-43.30	-42.04	-41.22
0.28869	25.47	26.57	27.66	28.58	-44.51	-42.85	-41.68	-40.87
0.38025	25.65	26.73	27.83	28.69	-44.05	-42.43	-41.31	-40.53

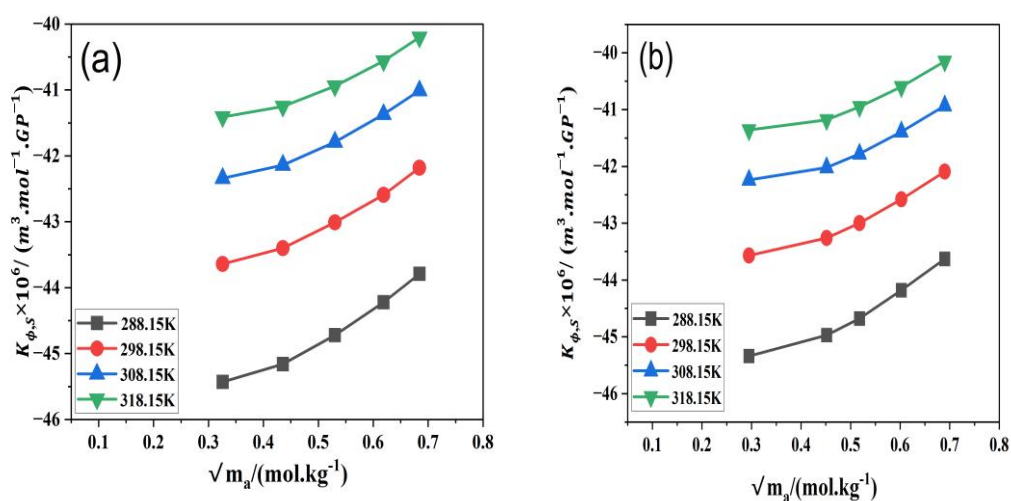
0.47100	25.84	26.93	28.06	28.84	-43.63	-42.03	-40.94	-40.17
0.03 (mol·kg ⁻¹) sodium salicylate (NaSl) + Potassium Chloride (in aqueous medium)								
0.10774	26.09	26.93	27.62	28.44	-45.18	-43.48	-42.13	-41.43
0.18250	26.19	27.11	27.77	28.63	-44.93	-43.27	-41.98	-41.29
0.29139	26.39	27.33	27.99	28.85	-44.40	-42.82	-41.60	-40.92
0.37361	26.57	27.53	28.15	28.97	-44.02	-42.43	-41.29	-40.61
0.48510	26.59	27.73	28.39	29.09	-43.49	-41.92	-40.85	-40.21
Sodium Bicarbonate + water								
0.10313	21.34	21.71	22.16	22.90	-45.17	-43.43	-42.20	-41.26
0.18524	21.89	22.23	22.72	23.39	-44.74	-43.00	-41.84	-40.94
0.30886	22.73	23.12	23.55	24.09	-43.86	-42.24	-41.11	-40.29
0.37932	23.26	23.57	24.05	24.46	-43.39	-41.82	-40.68	-39.88
0.45128	23.79	24.12	24.57	24.88	-42.85	-41.37	-40.29	-39.55
0.01 (mol·kg ⁻¹) sodium salicylate (NaSl) + Sodium Bicarbonate (in aqueous medium)								
0.10555	20.55	21.11	21.63	22.23	-45.07	-43.35	-42.14	-41.23
0.22273	21.18	21.84	22.40	22.94	-44.39	-42.72	-41.56	-40.73
0.29577	21.57	22.23	22.81	23.40	-43.88	-42.25	-41.11	-40.34
0.40064	22.15	22.91	23.49	24.07	-43.14	-41.62	-40.50	-39.74
0.46434	22.48	23.27	23.95	24.45	-42.68	-41.18	-40.13	-39.41
0.02 (mol·kg ⁻¹) sodium salicylate (NaSl) + Sodium Bicarbonate (in aqueous medium)								
0.10080	20.85	21.42	21.95	22.63	-45.04	-43.31	-42.08	-41.23
0.17798	21.22	21.86	22.42	23.05	-44.63	-42.94	-41.75	-40.93

0.30352	21.82	22.51	23.08	23.82	-43.79	-42.17	-41.00	-40.29
0.39069	22.25	23.00	23.56	24.26	-43.18	-41.62	-40.51	-39.79
0.47582	22.62	23.46	24.08	24.69	-42.56	-41.07	-40.02	-39.32
0.03 (mol·kg ⁻¹) sodium salicylate (NaSl) + Sodium Bicarbonate (in aqueous medium)								
0.10263	20.97	21.52	22.22	22.82	-44.95	-43.09	-42.00	-41.16
0.17745	21.35	21.94	22.61	23.22	-44.56	-42.74	-41.68	-40.89
0.30860	21.98	22.68	23.27	23.94	-43.68	-41.95	-40.91	-40.23
0.41533	22.55	23.26	23.86	24.50	-42.93	-41.28	-40.28	-39.60
0.46362	22.82	23.52	24.13	24.79	-42.56	-40.98	-40.02	-39.31

^am_a represents the molality of the added salt in the aqueous sodium salicylate , Uncertainties in apparent molar properties ($\times 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$) vary with solute concentration and are given for each composition as follows: Potassium Chloride + water (0.08), 0.01 mol·kg⁻¹ NaSl + Potassium Chloride (0.35), 0.02 mol·kg⁻¹ NaSl + Potassium Chloride (0.27), 0.03 mol·kg⁻¹ NaSl + Potassium Chloride (0.21), Sodium Bicarbonate + water (0.23), 0.01 mol·kg⁻¹ NaSl + Sodium Bicarbonate (0.24), 0.02 mol·kg⁻¹ NaSl + Sodium Bicarbonate (0.23), and 0.03 mol·kg⁻¹ NaSl + Sodium Bicarbonate (0.23) and $u(K_{\phi,S}) = 0.12 \times 10^{-6} / (m^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$.

Isentropic apparent molar compressibility ($K_{\phi,s}$)

The $K_{\phi,s}$ data is placed in **table 4.96** and presented in **figure 4.58**. All measured $K_{\phi,s}$ values were negative across the studied temperatures and concentrations for both sodium bicarbonate and potassium chloride in aqueous sodium salicylate solutions. This negativity reveals strong solute–solvent interactions and suggests a greater ordering of solvent molecules around the solute ions, resulting in a compressed hydration shell. Furthermore, a decrease in the magnitude of $K_{\phi,s}$ with rising temperature implies a gradual weakening of these interactions, likely due to thermal disruption of structured water layers. Similar consistent trends have been observed in other ternary electrolyte solutions, where negative compressibility values denote the existence of ion–solvent interactions and reduced compressibility of the overall system [245] [246][247].



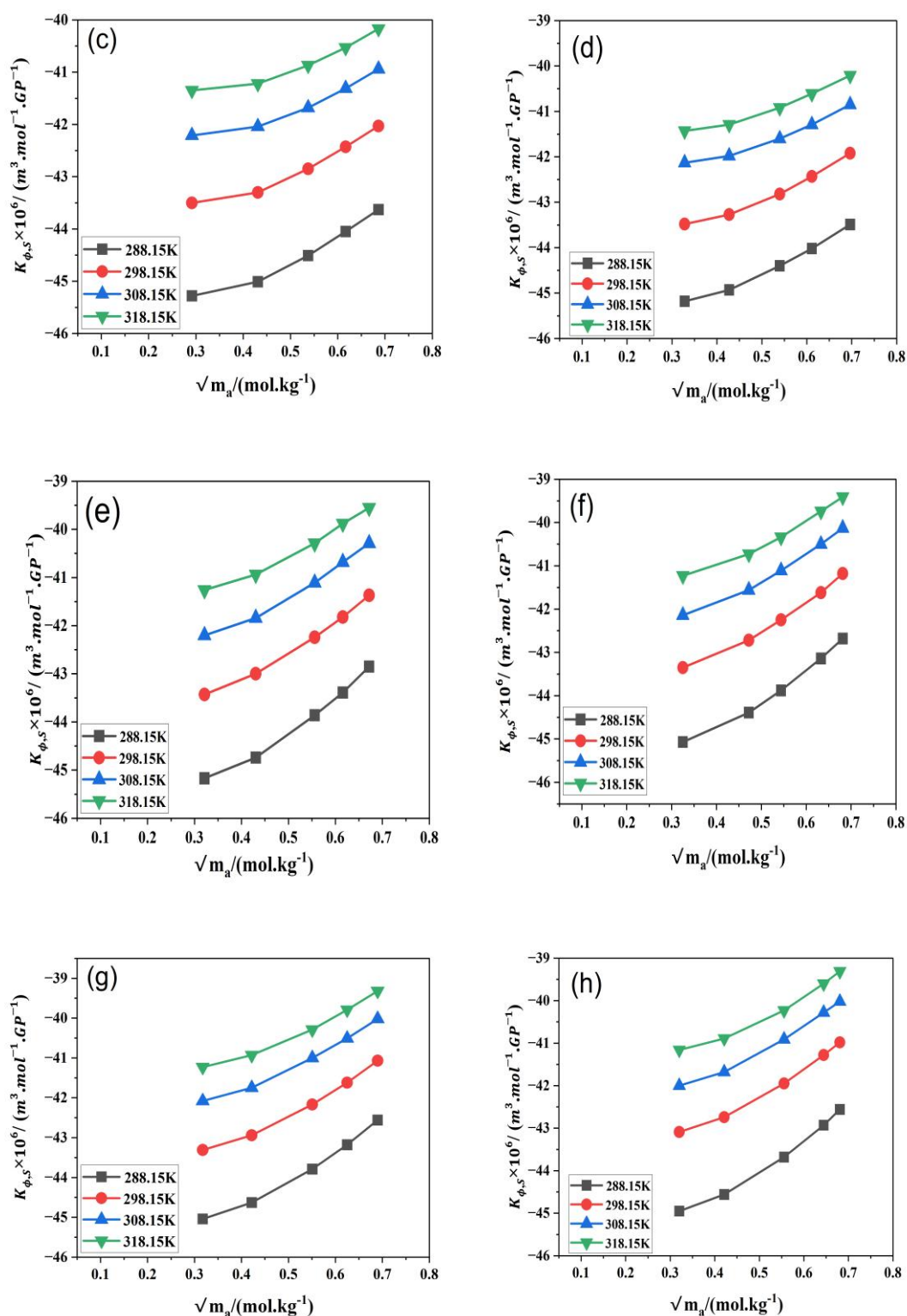


Figure 4.58: $K_{\phi,S}$ with salt molality (m_a) (a) (KCl + water), (b-d) – KCl in sodium salicylate solution at 0.01, 0.02 and 0.03 $\text{mol} \cdot \text{kg}^{-1}$ respectively; (e) NaHCO_3 + water, (f-h) – NaHCO_3 in sodium salicylate solution at 0.01, 0.02 and 0.03 $\text{mol} \cdot \text{kg}^{-1}$ respectively.

Partial molar volume

The V_{ϕ}^0 values were computed by applying the eq. 4.2. Estimated V_{ϕ}^0 and S_V^* values with errors are compiled in **Table 4.97** and **Figure 4.59** depicts the variation of V_{ϕ}^0 across conditions. The data shows that V_{ϕ}^0 increases with concentration and temperature for both salts, which gives evidence of the influence of interactions in solute-solvent. At lower concentrations, the partial molar volume value is smaller because of the strong hydration shells formed around the ions, which limit the effective volume occupied by the salt. As the concentration increases, hydration shells are saturated and more and more solute molecules start to interact more with other solute molecules rather than the solvent, thereby leading to a rise in V_{ϕ}^0 . Temperature dependence shows that V_{ϕ}^0 increases as the temperature escalates. This relates to the reduction of solute and solvent interactions at the elevated temperatures as well due to the reduced intensity of the H-bonding among the H_2O molecules and the ions because of the increased K.E of the molecules, thereby enabling the solute to occupy a larger effective volume in the solution. The experimental slopes S_V^* provide the rate of variation of the partial molar volumes regarding concentration and offer further perception into the influence of solute-solvent interactions. The general trend found for potassium chloride is that the slopes are smaller than those of sodium bicarbonate, suggesting an interaction with water molecules weaker than its counterpart. In terms of the values of slopes, there is some variation with temperature but within limits so that the amount of hydration seems to vary moderately with temperature. With the sodium bicarbonate, the slopes were larger especially at lower concentrations, and this suggests stronger ion-solvent interactivity in comparison to the corresponding compound, potassium chloride. This can be expected given that the charge density of bicarbonate ions is higher as compared to chloride ions and thus can be expected to attract more water molecules towards them, resulting in a strong hydration shell. The slopes steeply decline with increasing temperatures due to an inability of the bicarbonate ions at high temperatures to maintain strong hydration shells [62–64,185].

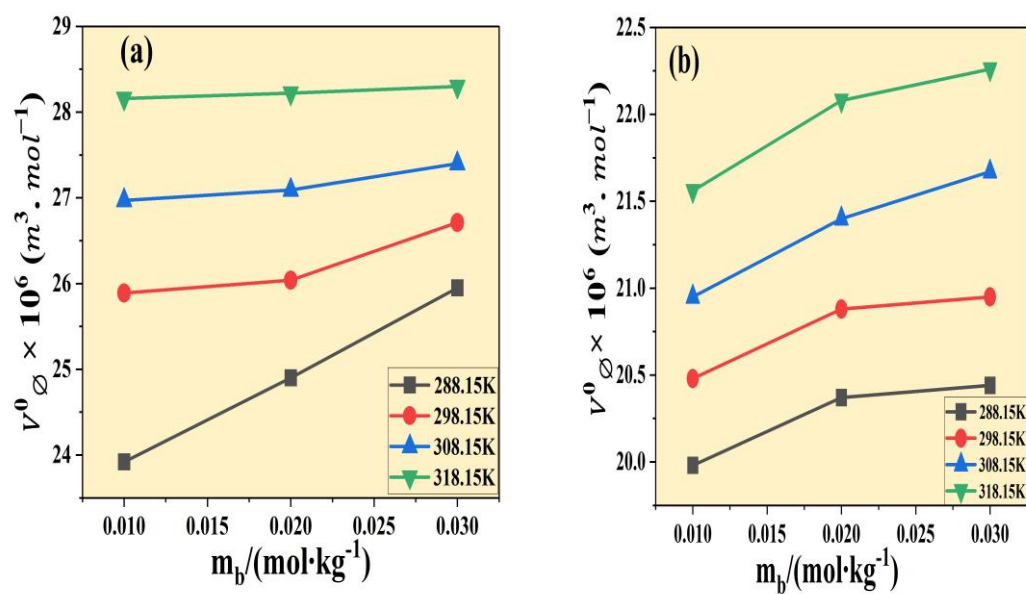


Figure 4.59: variations of V_{ϕ}^0 , of, (a) KCl and (b) NaHCO₃ in varying concentration of NaI aqueous solutions.

Table 4.97 Standard V_{ϕ}^0 and S_V^* of salts in the sodium salicylate water-based solution at 0.1MPa.

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$V_{\phi}^0 \times 10^6 (\text{m}^3 \cdot \text{mol}^{-1})$				$S_V^* \times 10^6 (\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2})$			
	288.15K	298.15K	308.15K	318.15K	288.15K	298.15K	308.15K	318.15K
Potassium chloride								
0.00	26.85	27.17	27.52	27.76	1.55	1.30	0.99	1.41
0.01	23.92	25.89	26.97	28.16	2.24	2.01	2.18	1.32
0.02	24.90	26.04	27.09	28.22	1.99	1.84	2.01	1.30
0.03	25.95	26.71	27.40	28.30	1.45	2.13	2.04	1.72
Sodium Bicarbonate								
0.00	20.60	20.98	21.44	22.33	7.02	6.91	6.91	5.64
0.01	19.98	20.48	20.95	21.56	5.39	6.01	6.41	6.23
0.02	20.37	20.88	21.40	22.08	4.76	5.42	5.61	5.54
0.03	20.44	20.95	21.67	22.26	5.08	5.55	5.28	5.43

standard uncertainties u is $u(V_{\phi}^0) = 0.54 \times 10^{-6} (\text{m}^3 \cdot \text{mol}^{-1})$, $u(T) = \pm 0.001 \text{K}$, $u(S_V^*) = 0.38 \times 10^{-6} (\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2})$, $u(p) = 0.01 \text{MPa}$.

Partial molar isentropic compressibility ($K_{\phi,s}^0$)

Using the least-squares technique, $K_{\phi,s}^0$ was computed by extending the $K_{\phi,s}$ vs. $\sqrt{m}$ curve to zero concentration, as per the equation 4.10. **Table 4.98** (graphically presents in **Figure 4.60**) lists the calculated $K_{\phi,s}^0$ values along with their corresponding standard errors. Due to the small value of S_K^* , minimal solute–solute interaction is observed at infinite dilution [192]. As temperature increases, the $K_{\phi,s}^0$ become less negative, reflecting weaker solute-solvent interactions due to thermal expansion. Additionally, $K_{\phi,s}^0$ increases (becomes less negative) with concentration, suggesting that higher concentrations result in a more saturated solute-solvent interaction, thus reducing the solute's impact on compressibility. The experimental slopes S_k^* show how compressibility changes with concentration. Sodium bicarbonate exhibits larger slopes, indicating stronger interactions with the solvent compared to potassium chloride. As temperature rises, these slopes decrease, signifying that solute-solvent interactions weaken with increasing temperature, especially for sodium bicarbonate, which has more structured interactions with the solvent [193,194].

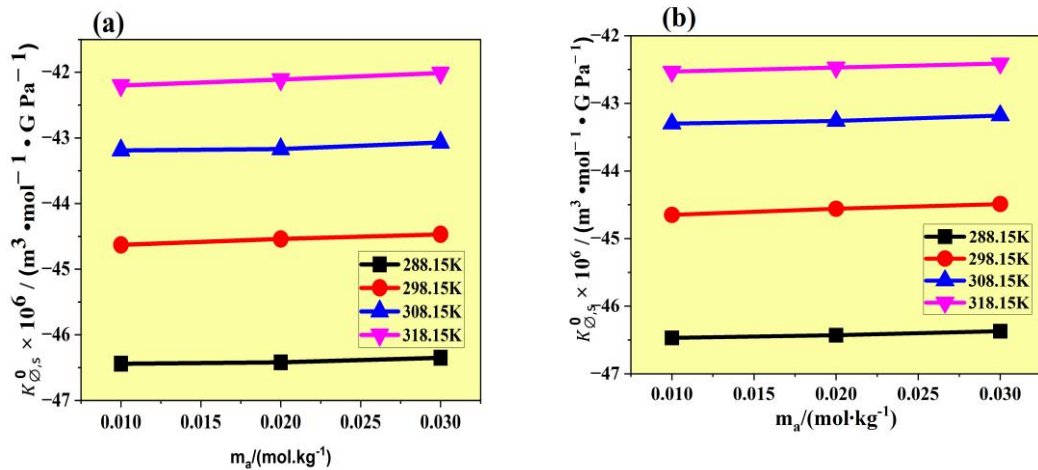


Figure 4.60: Variation of, $K_{\phi,s}^0$, of (a), potassium chloride and (b) Sodium bicarbonate, in sodium salicylate solutions.

Table 4.98 $K_{\phi,S}^0$ and (S_K^*) of Potassium chloride and Sodium bicarbonate in the aqueous sodium salicylate solution temperatures and 0.1 MPa.

$a_{m_b}/(\text{mol}\cdot\text{kg}^{-1})$	$K_{\phi,S}^0 \times 10^6/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$				$S_K^* \times 10^6/(\text{kg} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{GPa}^{-1})$			
	T=288.15K	T=298.15K	T= 308.15K	T=318.15 K	T=288.15K	T=298.15K	T= 308.15K	T=318.15 K
Potassium chloride								
0.00	-45.98	-44.15	-42.83	-41.87	4.61	4.11	3.82	3.45
0.01	-45.82	-44.01	-42.68	-41.79	4.49	3.93	3.54	3.30
0.02	-45.74	-43.96	-42.63	-41.76	4.39	3.99	3.45	3.22
0.03	-45.72	-44.01	-42.59	-41.89	4.56	4.23	3.51	3.39
Sodium bicarbonate								
0.00	-45.92	-44.06	-42.80	-41.78	6.72	5.93	5.56	4.96
0.01	-45.83	-44.03	-42.77	-41.83	6.70	6.05	5.65	5.17
0.02	-45.77	-43.96	-42.69	-41.80	6.66	6.01	5.57	5.15
0.03	-45.69	-43.74	-42.62	-41.77	6.67	5.91	5.59	5.20

uncertainties u is u ($K_{\phi,S}^0$) = $0.27 \times 10^{-6}/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$, u (S_K^*)= $0.05 \times 10^{-6}/(\text{kg} \cdot \text{m}^3 \cdot \text{mol}^{-2} \cdot \text{GPa}^{-1})$, u(T)= $\pm 0.001\text{K}$, u (p)=0.01MPa.

Partial molar volume of transfer

The ΔV_{ϕ}^0 of solutes (potassium chloride and sodium bicarbonate) from H_2O to solutions of sodium salicylate solutions at immense dilution in an aqueous medium, the equation 4.3 was used. **Table 4.99** contains the ΔV_{ϕ}^0 data, provide qualitative interpretation of the interactions between salts and sodium salicylate molecules inside the liquid mixture. This parameter reveals how the presence of sodium salicylate, acting as a co-solute, modifies the solvation behaviour of potassium chloride and sodium bicarbonate at infinite dilution. The ΔV_{ϕ}^0 values for KCl are negative at lower temperatures, indicating that the ion–solvent interactions in sodium salicylate solution are more compact and structured than in pure water. At higher temperatures, these values become positive, suggesting a shift toward reduced solute–solvent interactions and a more expanded solvation shell in the co-solute medium. For sodium bicarbonate, the ΔV_{ϕ}^0 values remain largely negative across all temperatures, reflecting strong ion–solvent interactions even in the presence of sodium salicylate. This suggests that $NaHCO_3$ maintains or enhances the structuring of the solvent environment, especially at lower temperatures. The observed variation in ΔV_{ϕ}^0 with temperature indicates that sodium salicylate influences the extent of solvation and hydration structure around the added salts, especially through hydrogen bonding and ionic interactions [65–69].

Partial molar isentropic compression of transfer

The ΔK_{ϕ}^0 is computed by the equation 4. 11 from H_2O to aqueous sodium salicylate solutions. The ΔK_{ϕ}^0 values in **table 4.99** tells the compressibility of the solution changes when potassium chloride/sodium bicarbonate is transferred from water to the sodium salicylate solution. ΔK_{ϕ}^0 provides insights into how the compressibility of the medium changes due to the presence of sodium salicylate. For KCl, the positive ΔK_{ϕ}^0 values across all temperatures suggest that the medium becomes more compressible, indicating a disruption in the solvent structure and weaker solute–solvent interactions in the sodium salicylate solution compared to water. At higher temperature, the values rise further, showing enhanced thermal motion weakening any residual structure. In

contrast, sodium bicarbonate exhibits small or slightly positive ΔK_{ϕ}^0 values. This implies that NaHCO_3 maintains a relatively structured and less compressible environment, even in the sodium salicylate solution. This behaviour reflects its strong hydration capacity and persistent solute–solvent interactions, which resist compression and reduce the influence of temperature compared to KCl.

Temperature- dependent partial molar volume

The equation 4.4 was applied to find how V_{ϕ}^0 at immense dilution vary with temperature, with constants as a, b, c and $T_{ref} = 298.15\text{K}$. **Table 4.100** also illustrates the deviations between the computed and observed V_{ϕ}^0 values, which are assessed using the equation 4.5, with, $Y = V_{\phi}^0$, the polynomial equation fitted to the data demonstrates very low deviation values, as indicated by the R^2 values, confirming that it accurately represents the relationship

The minimal discrepancies among the calculated and observed V_{ϕ}^0 data, indicating excellent fit with the polynomial equation, as evidenced by high values of R^2 [69]. The solute's capacity to form or disrupt structures in solution can be evaluated using the following thermodynamic equation 4.100. **Table 4.101** contains the $E_{\phi}^0 = (\partial E_{\phi}^0 / \partial T)_P$ values for the mixtures of aqueous sodium salicylate with potassium chloride/sodium bicarbonate at numerous temperatures and concentrations. Based on Hepler's criterion, sodium bicarbonate exhibits positive $2c$ values at all concentrations, indicating structure-making behaviour. In contrast, potassium chloride shows a negative $2c$ value at 0.01 mol/kg, suggesting structure-breaking nature at lower concentrations, while shifting to structure-making at higher concentrations. These observations reflect the salt's varying ability to organize or disrupt the water structure with concentration. Furthermore, the positive E_{ϕ}^0 values shows that the solutes increase the expansion of the sodium salicylate solution as the thermal motion breaks down the network within the solvent.

Table 4.99 ΔV_{ϕ}^0 and $\Delta K_{\phi,S}^0$ of sodium salicylate in water-based solutions with Potassium chloride and sodium bicarbonate.

$^a m_b / (\text{mol.kg}^{-1})$	$\Delta V_{\phi}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$				$\Delta K_{\phi,S}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	T= 288.15 K	T= 298.15K	T= 308.15 K	T= 318.15 K	T= 288.15 K	T= 298.15 K	T= 308.15 K	T= 318.15 K
Potassium chloride								
0.01	-2.93	-1.29	-0.55	0.39	0.17	0.14	0.15	0.08
0.02	-1.95	-1.13	-0.43	0.45	0.25	0.19	0.21	0.12
0.03	-0.90	-0.46	-0.12	0.53	0.26	0.14	0.24	-0.01
Sodium bicarbonate								
0.01	-0.62	-0.50	-0.49	-0.77	0.09	0.03	0.03	-0.05
0.02	-0.23	-0.09	-0.04	-0.25	0.15	0.09	0.11	-0.02
0.03	-0.16	-0.02	0.23	-0.07	0.23	0.31	0.18	0.02

$^a m_b$ is the aqueous sodium salicylate molality calculated as the number of moles of sodium salicylate per kilogram of water, standard uncertainties u is $u_r(m) = 0.01$, $u(\Delta V_{\phi}^0) = 0.15 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1})$, $u(\Delta K_{\phi,S}^0) = 0.01 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$, $u(T) = \pm 0.001\text{K}$, $u(p) = 0.01\text{Ma}$

Table 4.100 Data of empirical constants of salts in aqueous sodium salicylate.

$^a m_b / (\text{mol} \cdot \text{kg}^{-1})$	$a \times 10^6 (m^3 \cdot \text{mol}^{-1})$	$b \times 10^6 (m^3 \cdot \text{mol}^{-1})$	$c \times 10^6 (m^3 \cdot \text{mol}^{-1} \cdot K^{-2})$	R^2	ARD
Potassium chloride					
0.01	25.7365	0.1574	-0.0019	0.9999	0.0038
0.02	26.0162	0.1104	0.0000	0.9999	0.0007
0.03	26.6675	0.0737	0.0004	0.9999	0.0011
Sodium Bicarbonate					
0.01	20.6633	-0.0109	0.0014	0.9999	0.0229
0.02	21.1138	-0.0076	0.0019	0.9999	0.0206
0.03	21.8078	-0.0206	0.0024	0.9999	0.0330

$^a m_b$ is the molality of aqueous sodium salicylate calculated as the number of moles of sodium salicylate per kilogram of water.

Table 4.101 E_{ϕ}^0 for the sodium salicylate aqueous solutions with salts.

$m_b/(\text{mol} \cdot \text{kg}^{-1})$	$E_{\phi}^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\frac{\partial E_{\phi}^0}{\partial T})/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	T=288.15K	T=298.15K	T=308.15K	T=318.15K	
Potassium chloride					
0.01	0.1963	0.1574	0.1186	0.0797	-0.0039
0.02	0.1111	0.1104	0.1097	0.1090	-0.0001
0.03	0.0666	0.0737	0.0808	0.0878	0.0007
Sodium bicarbonate					
0.01	-0.0393	-0.0109	0.0176	0.0460	0.0028
0.02	-0.0457	-0.0076	0.0305	0.0687	0.0038
0.03	-0.0679	-0.0206	0.0267	0.0740	0.0047

uncertainties u is $u(E_{\phi}^0) = 0.0135 \times 10^{-6} / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$, $u(\frac{\partial E_{\phi}^0}{\partial T}) = 0.00128 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$, $u(T) = \pm 0.001\text{K}$, $u(p) = 0.01\text{MPa}$.

Pair and triplet coefficients

The equations 4.12 and 4.13 were employed to calculate the ΔV_{ϕ}^0 and ΔK_{ϕ}^0 . The V_{AB}, V_{ABB} represents the interaction coefficients for volume at both the pair and triplet levels respectively. Similarly, K_{AB} and K_{ABB} denote the interaction coefficients for isentropic compression at these levels. The coefficients are provided within **Table 4.102**. As per the McMillan- Mayer, the $V_{AB}, V_{ABB}; K_{AB}, K_{ABB}$ are computed by fitting the ΔV_{ϕ}^0 and ΔK_{ϕ}^0 respectively. This theoretical approach is instrumental in analyzing the distinct effects of binary and ternary interactions among molecules in a liquid mixture. Detailed explorations of this theory have been conducted by Friedman and Krishnan along with Franks et al. [199]. V_{AB} describes how one solute molecule interacts with the solvent, reflecting the direct solute-solvent interaction. The negative values for KCl and NaHCO₃ at low temperature mean a strong solute-solvent attraction where the solvent structure is significantly influenced by the solute molecules. With rising temperature, the weakening of the said interaction via thermal agitation leads to positive values of V_{AB} and indicates less influence by the sodium salicylate in terms of the salt's molecules. Conversely, V_{ABB} is more concerned about the effect that the presence of an additional solute has on this interaction. V_{ABB} focuses on cooperation among the molecules of the solute in the background presence of the sodium salicylate that pairing interactions themselves do not contact. Positive values for V_{ABB} suggest that as more of the solute is added to the solution, then the molecules in solution go on to interact with each other and hence are subjected to cooperative expansion of the solution, especially at larger concentrations. This is a transition from solute-solvent dominance at low concentration to more significant solute-solute forces as the concentration rises. In the case of isentropic compression, K_{AB} becomes positive at lower temperatures, meaning the solute-solvent system is less compressible due to tighter forces. Negative values at elevated temperatures mean that the solution becomes more compressible because thermal motion breaks these forces. Thus, the triplet coefficient K_{ABB} captures ternary contributions to compressibility but with a greater contribution coming from interactions among solute molecules themselves in the solvent medium with the rise in temperature.

Isobaric thermal Expansion Coefficient

Essentially, it quantifies the fractional change in volume for each degree of temperature change under these uniform pressure parameters [146] [147]. Equation 4.14 used for determining the α_p . **Table 4.103** shows, α_p values. The α_p represents the variation in the volume of potassium chloride and sodium bicarbonate solutions in sodium salicylate with the variation of temperature. For potassium chloride, α_p decreases with increasing temperature at lower concentrations, indicating that the solution expands more at lower temperatures, probably because the interactions between salts and sodium salicylate are stronger compared to the situation at higher temperatures, when thermal agitation weakens them. At higher concentrations, the trend stabilizes, indicating that solute-solute interactions begin to dominate, leading to more uniform expansion. In contrast, sodium bicarbonate initially gives a negative α_p values at low temperatures, displaying contraction due to strong structuring of both the salts and the sodium salicylate. For these interactions at higher temperatures, α_p may have to turn positive to reflect expansion from the previously dominant thermal motion that overcame the sodium salicylate structural influence by the salts [148,149].

Relative Association (R_a):

Relative association (R_a) reflects the extent to which the structure of a solvent is altered by the presence of a solute and the associated solvation process of ions within the medium. This parameter offers insights into both the magnitude and nature of interactions occurring between the species in solution. The value of R_a is determined using the equation 4.15, As presented in **Table 4.104**, R_a tends to increase with the molality of added salts (NaHCO_3 or KCl) in sodium salicylate + water mixtures. This behaviour implies that higher salt concentrations enhance molecular association within the system. On the other hand, a consistent decrease in R_a values is observed with rising temperature at all molalities. This inverse relationship suggests that stronger solute-solvent interactions are favoured at lower temperatures, possibly due to enhanced solvation. At higher temperatures, thermal agitation disrupts the organized solvent structure, thereby diminishing the extent of relative association [93,248][94].

Table 4.102 V_{AB} , V_{ABB} , K_{AB} and K_{ABB} of salts present in aqueous sodium salicylate.

T/K	$[V_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kg)]$	$[V_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2)]$	$[K_{AB} \times 10^6 / (m^3 \cdot mol^{-2} \cdot kgGPa^{-1})]$	$K_{ABB} \times 10^6 / (m^3 \cdot mol^{-3} \cdot kg^2GPa^{-1})$
Potassium chloride				
288.15	-158.55	3258.51	2.42	-0.97
298.15	-76.38	1536.56	3.88	-0.31
308.15	-32.47	682.27	6.40	-47.06
318.15	20.32	-260.69	9.69	-75.02
Sodium bicarbonate				
288.15	-29.81	630.15	2.55	-1.09
298.15	-23.04	527.59	4.74	-10.68
308.15	-25.94	684.34	3.61	-7.97
318.15	-38.46	859.78	3.09	-0.36

Table 4.103 α_p for KCl and NaHCO₃ in aqueous Sodium salicylate at 0.1 MPa.

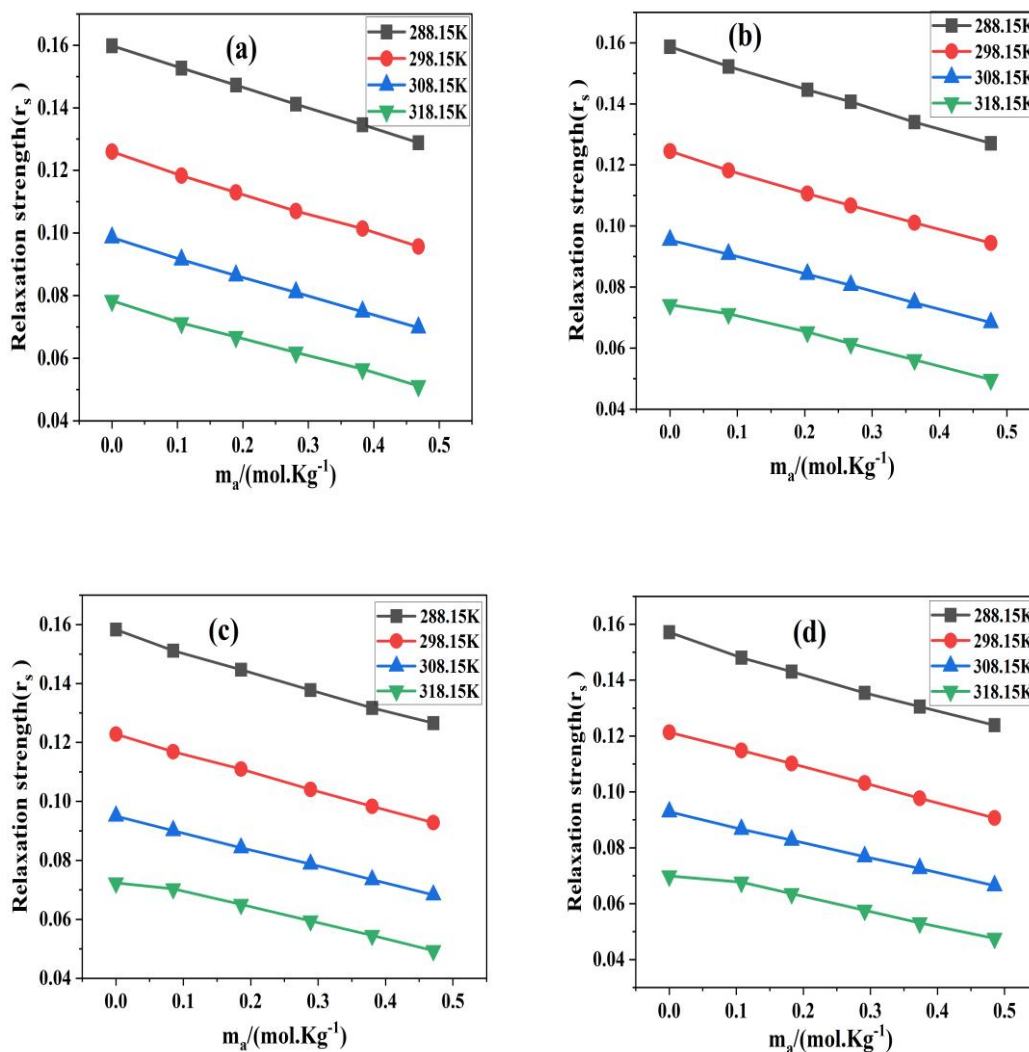
$m_b/(\text{mol}\cdot\text{kg}^{-1})$	$\alpha_p \times 10^3/ (K^{-1})$			
	T=288.15K	T=293.15K	T=303.15K	T=318.15K
Potassium chloride				
0.01	8.21	6.08	4.40	2.83
0.02	4.46	4.24	4.05	3.86
0.03	2.57	2.76	2.95	3.10
Sodium Bicarbonate				
0.01	-1.97	-0.53	0.84	2.13
0.02	-2.25	-0.36	1.43	3.11
0.03	-3.32	-0.98	1.23	3.32

$u(\alpha_p)=0.55 \times 10^{-3}/ (K^{-1})$, $u(p)=0.01\text{MPa}$.

Relaxation Strength (r_s)

The relaxation strength was determined using the equation **4.16**. The r_s are presented in **Table 4.104** and illustrated in **Figure 4.61**. A declining trend in relaxation strength was observed with increasing molality of sodium bicarbonate or potassium chloride in the sodium salicylate + water system. Furthermore, r_s also decreases as temperature increases. Notably, relaxation strength is more significant at lower salt concentrations compared to higher ones. This pattern implies that both elevated salt levels and higher temperatures tend to weaken molecular interactions within the mixture [96]. However, this tendency arises mainly because of the formation of complexes among the salts and sodium salicylate molecules. In this system, salt molecules surround the solvent molecules, thus enhancing molecular interaction. As the concentration of sodium nitrate and sodium citrate is increased, the solute molecules impose a limitation on the solvent molecule's movement; therefore, they absorb lesser energy that further lowers the relaxation strength. This trend proves greater solute-solvent interaction for higher concentrations as the structural arrangement among the solvent molecules is shown by the solute molecules. In addition, with temperature relaxation strength declines. The reason, at elevated temperatures, interactions in solute-solvent become weaker since the molecules possess greater kinetic energy. With increased temperature, thermal motions generate disordered structures in the solution instead of falling under a more

organized structure dictated by interactions between the salts and sodium salicylate. Thus, this loss in rigid molecules within the solution dissipates less energy during relaxation, therefore having lower relaxation strength. The behaviour under observation is thus in line with similar systems, where raising temperature has decreased the importance of solute molecules towards solvent structure relaxation strength[97][98][99].



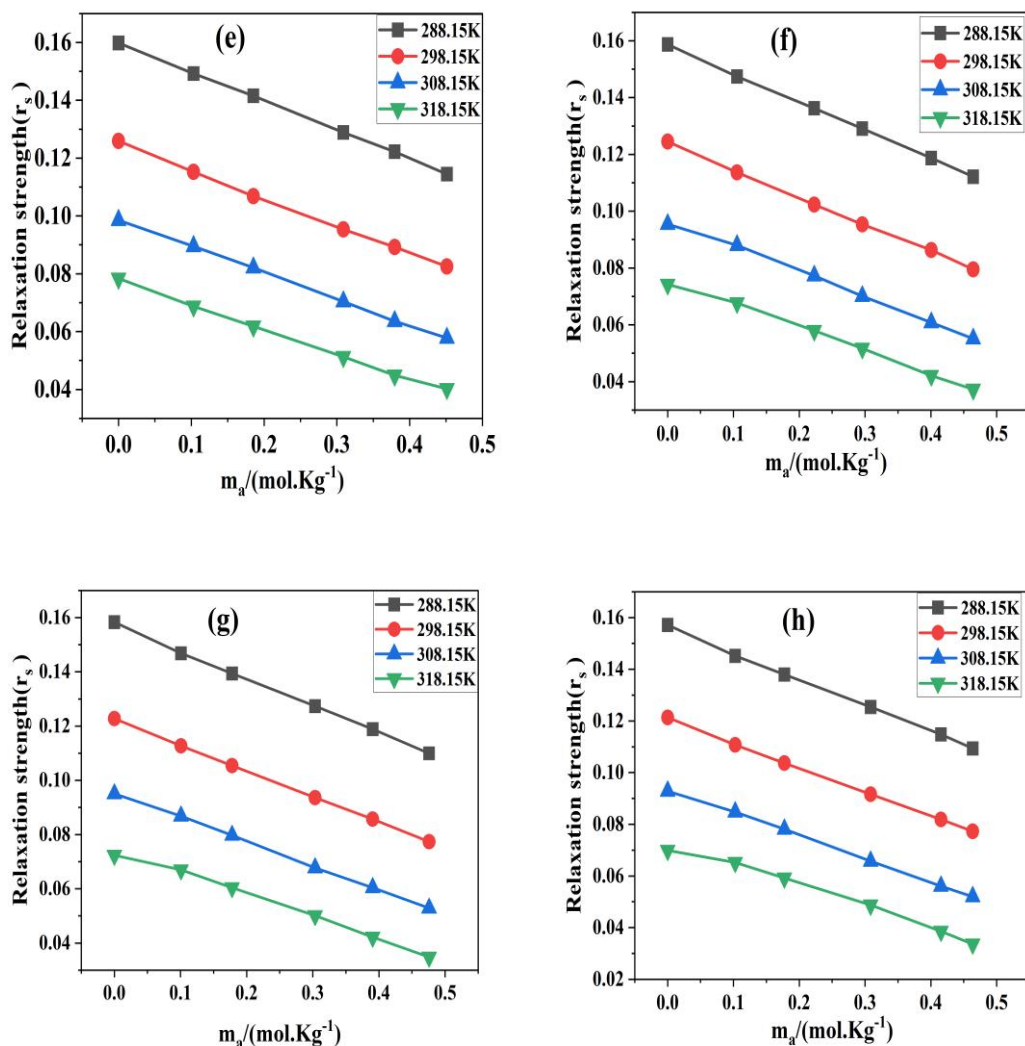


Figure 4.61: Variation of Relaxation Strength (r_s) with salt molality (m_a) (a) (Potassium chloride + water), (b-d) – Potassium chloride in sodium salicylate solution at 0.01,0.02 and 0.03 mol·kg⁻¹ respectively;(e) sodium bicarbonate + water, (f-h) – sodium bicarbonate in sodium salicylate solution at 0.01,0.02 and 0.03 mol·kg⁻¹ respectively.

FTIR Analysis

The FTIR spectra of sodium salicylate in H₂O, sodium salicylate with potassium chloride, and sodium bicarbonate across varying concentrations reveal significant shifts in key vibrational frequencies, reflecting the complex molecular interactions within these systems. In **Figure 4.62**, spectra of sodium salicylate in water and with varying concentrations of sodium bicarbonate and potassium chloride are shown. For

sodium salicylate in aqueous solution, prominent absorption peaks are observed at 581 cm^{-1} , 1637 cm^{-1} , and 3328 cm^{-1} , which correspond to aromatic ring bending, C=O stretching, and O–H stretching vibrations, respectively. With increasing sodium salicylate concentration, these peaks exhibit a shift toward lower wavenumbers — most notably, the C=O stretching band shifts from 1637 cm^{-1} to 1623 cm^{-1} . This redshift indicates enhanced H - bonding interactions among the carboxylate groups of sodium salicylate and surrounding H_2O molecules, due to the greater availability of salt molecules facilitating such interactions. The O-H stretching peak, indicative of the hydrogen bonding network in the solution, also shifts slightly, signalling changes in the solvation dynamics as the concentration increases. In the sodium salicylate + potassium chloride system, the stretching band of COO^- is displaced due to ion-dipole forces involving the potassium ions and salicylate anions while a slight shift of the OH stretch reflects interference in the H-bonding inside the solvent structure. For sodium salicylate + sodium bicarbonate, the spectrum shows broader shifts in the COO^- stretch suggesting that the bicarbonate ions interact more strongly with sodium salicylate. In addition, there are some absorption bands associated with the interactions of the bicarbonate ions with water, indicating the interaction changes associated with sodium bicarbonate are not the same as potassium chloride, which is likely related to stronger hydrogen bonding.

4.62(a)

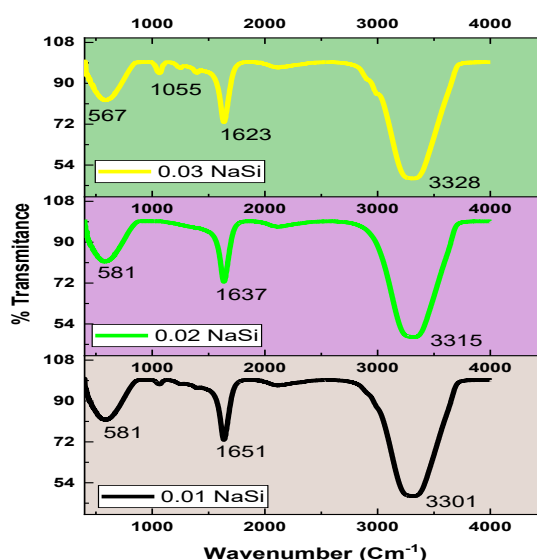


Table 4.104 Relative Association (R_a) and Relaxation Strength (r_s) for ternary mixtures of sodium salicylate in KCl and $NaHCO_3$.

$m_a/(\text{mol}\cdot\text{kg}^{-1})$	Relative Association (R_a)				Relaxation Strength (r_s)			
	(288.15) K	(298.15) K	(308.15) K	(318.15) K	(288.15) K	(298.15) K	(308.15) K	(318.15) K
Potassium chloride + water								
0.00000	1.00000	1.00000	1.00000	1.00000	0.15981	0.12595	0.09852	0.07838
0.10621	1.00363	1.00356	1.00368	1.00368	0.15269	0.11833	0.09147	0.07125
0.18956	1.00646	1.00643	1.00663	1.00673	0.14727	0.11297	0.08643	0.06681
0.28101	1.00948	1.00952	1.00985	1.01002	0.14115	0.10702	0.08105	0.06185
0.38281	1.01284	1.01310	1.01335	1.01365	0.13458	0.10139	0.07488	0.05654
0.46818	1.01558	1.01588	1.01626	1.01649	0.12885	0.09571	0.06978	0.05113
0.01 ($\text{mol}\cdot\text{kg}^{-1}$) sodium salicylate + Potassium Chloride (in aqueous medium)								
0.00000	1.00000	1.00000	1.00000	1.00000	0.15869	0.12450	0.09539	0.07421
0.08697	1.00319	1.00313	1.00338	1.00321	0.15224	0.11820	0.09078	0.07127
0.20408	1.00749	1.00728	1.00764	1.00750	0.14461	0.11061	0.08422	0.06529
0.26827	1.00985	1.00957	1.00993	1.00973	0.14069	0.10674	0.08059	0.06149
0.36285	1.01312	1.01289	1.01317	1.01302	0.13403	0.10102	0.07488	0.05620
0.47627	1.01716	1.01685	1.01706	1.01688	0.12707	0.09443	0.06836	0.04969
0.02 ($\text{mol}\cdot\text{kg}^{-1}$) sodium salicylate + Potassium Chloride (in aqueous medium)								
0.00000	1.00000	1.00000	1.00000	1.00000	0.15830	0.12279	0.09502	0.07234

0.08506	1.00278	1.00295	1.00304	1.00258	0.15114	0.11686	0.09010	0.07038
0.18569	1.00641	1.00663	1.00666	1.00622	0.14470	0.11100	0.08425	0.06504
0.28869	1.01000	1.01016	1.01038	1.00989	0.13777	0.10403	0.07875	0.05948
0.38025	1.01314	1.01333	1.01356	1.01310	0.13170	0.09834	0.07345	0.05455
0.47100	1.01637	1.01643	1.01665	1.01618	0.12656	0.09282	0.06830	0.04939

0.03 (mol·kg⁻¹) sodium salicylate + Potassium Chloride (in aqueous medium)

0.00000	1.00000	1.00000	1.00000	1.00000	0.15715	0.12137	0.09285	0.06990
0.10774	1.00341	1.00378	1.00369	1.00334	0.14805	0.11484	0.08661	0.06766
0.18250	1.00600	1.00639	1.00644	1.00601	0.14308	0.11017	0.08275	0.06359
0.29139	1.00963	1.01010	1.01032	1.00983	0.13545	0.10320	0.07683	0.05766
0.37361	1.01248	1.01281	1.01325	1.01266	0.13054	0.09775	0.07261	0.05309
0.48510	1.01637	1.01648	1.01705	1.01658	0.12387	0.09065	0.06643	0.04759

Sodium Bicarbonate + water

0.00000	1.00000	1.00000	1.00000	1.00000	0.15981	0.12595	0.09852	0.07838
0.10313	1.00436	1.00410	1.00471	1.00457	0.14925	0.11522	0.08949	0.06876
0.18524	1.00785	1.00750	1.00829	1.00823	0.14157	0.10687	0.08209	0.06181
0.30886	1.01268	1.01260	1.01337	1.01353	0.12887	0.09535	0.07035	0.05128
0.37932	1.01542	1.01549	1.01613	1.01640	0.12224	0.08928	0.06357	0.04487
0.45128	1.01793	1.01823	1.01906	1.01958	0.11444	0.08251	0.05777	0.04022

0.01 (mol·kg⁻¹) sodium salicylate + Sodium Bicarbonate (in aqueous medium)

0.00000	1.00000	1.00000	1.00000	1.00000	0.15869	0.12450	0.09539	0.07421

0.10555	1.00445	1.00456	1.00528	1.00501	0.14741	0.11367	0.08800	0.06770
0.22273	1.00949	1.00957	1.01040	1.01030	0.13624	0.10234	0.07728	0.05798
0.29577	1.01250	1.01262	1.01340	1.01345	0.12909	0.09536	0.07005	0.05171
0.40064	1.01667	1.01700	1.01774	1.01773	0.11871	0.08628	0.06077	0.04213
0.46434	1.01909	1.01937	1.02026	1.02042	0.11213	0.07949	0.05509	0.03726

0.02 (mol·kg⁻¹) sodium salicylate + Sodium Bicarbonate (in aqueous medium)

0.00000	1.00000	1.00000	1.00000	1.00000	0.15830	0.12279	0.09502	0.07234
0.10080	1.00408	1.00436	1.00465	1.00421	0.14681	0.11271	0.08680	0.06695
0.17798	1.00739	1.00770	1.00803	1.00767	0.13937	0.10542	0.07971	0.06041
0.30352	1.01263	1.01298	1.01328	1.01317	0.12734	0.09362	0.06770	0.05013
0.39069	1.01612	1.01657	1.01698	1.01673	0.11884	0.08568	0.06041	0.04216
0.47582	1.01935	1.01986	1.02038	1.02019	0.10993	0.07737	0.05285	0.03479

0.03 (mol·kg⁻¹) sodium salicylate + Sodium Bicarbonate (in aqueous medium)

0.00000	1.00000	1.00000	1.00000	1.00000	0.15715	0.12137	0.09285	0.06990
0.10263	1.00409	1.00429	1.00464	1.00421	0.14516	0.11076	0.08478	0.06524
0.17745	1.00729	1.00752	1.00795	1.00761	0.13797	0.10368	0.07812	0.05923
0.30860	1.01275	1.01307	1.01344	1.01340	0.12540	0.09164	0.06571	0.04874
0.41533	1.01693	1.01741	1.01779	1.01765	0.11477	0.08184	0.05602	0.03857
0.46362	1.01865	1.01930	1.01977	1.01945	0.10936	0.07728	0.05201	0.03365

Uncertainties u is $u_r(m) = 0.01$, $u(T) = \pm 0.001K$, $u(R_a) = 0.00045$, $u(r_s) = 0.00235$ and $u(p) = 0.01M$

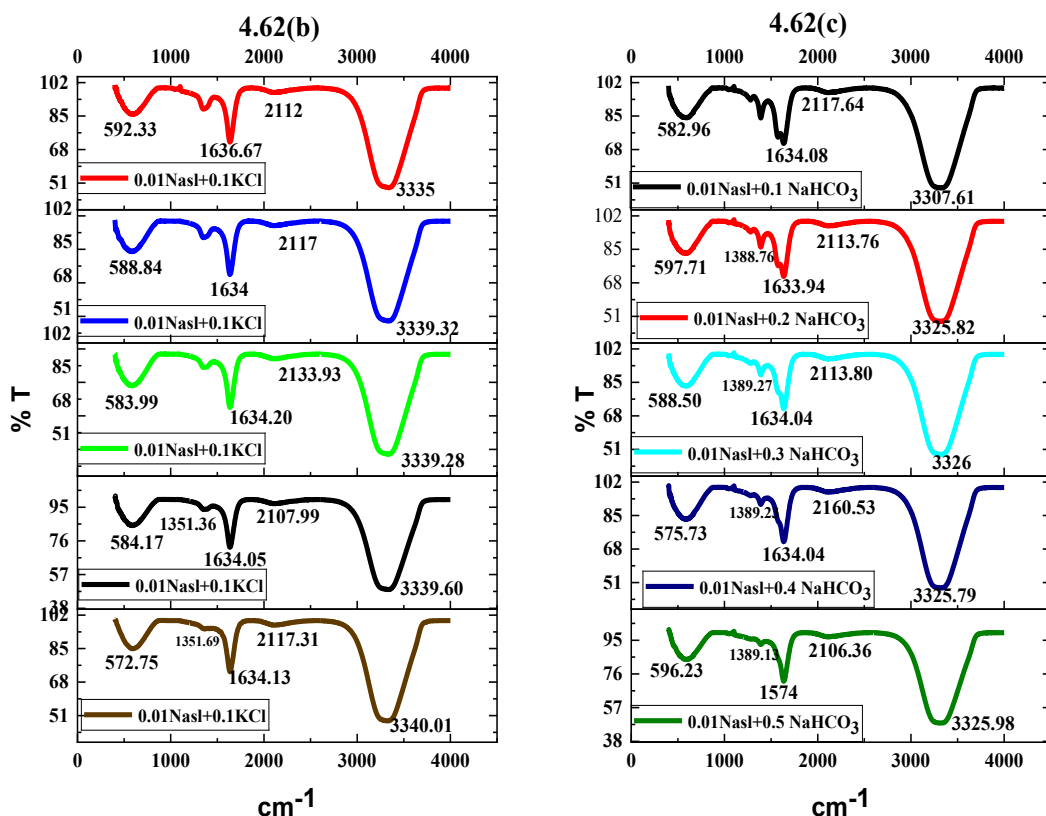


Figure 4.62: 4.62(a) Spectra of sodium salicylate with H₂O at 0.01,0.02 and 0.03 mol · kg⁻¹. 4.62(b) ,4.62(c), are spectra of 0.01 concentration of sodium salicylate with water and sodium bicarbonate/potassium chloride at different (0.1,0.2,0.3,0.4,0.5 mol · kg⁻¹) concentrations respectively.

Chapter Summary

This chapter presents the experimental density and ultrasonic velocity data for the investigated binary and ternary salicylate-based aqueous systems over a range of concentrations and temperatures. The variation of volumetric, acoustic, and thermodynamic parameters is analysed to understand solute–solvent and solute–solute interactions. The results are interpreted using fundamental thermodynamic concepts and established theoretical models to elucidate hydration behaviour, molecular association, and structural effects in the studied systems.

SUMMARY AND CONCLUSIONS

The present thesis entitled “**Study of Thermodynamical properties of Salicylates in aqueous Salt solutions: volumetric-acoustical approach**” provides a comprehensive understanding of the volumetric, acoustic, and spectroscopic behaviour of ternary systems involving salicylates and various inorganic salts. Density and ultrasonic velocity measurements were carried out over the temperature range 288.15–318.15 K and at 0.1 MPa, and from these measurements several important thermodynamic parameters—apparent and partial molar volumes, isentropic compressibilities, expansibilities, relaxation strength, relative association, transfer properties, and hydration numbers—were derived. These parameters have been used to interpret the molecular interactions, solvation dynamics, and structure-making or structure-breaking tendencies that govern the physicochemical behaviour of these systems. FTIR spectroscopy further strengthened the conclusions by providing direct evidence of hydrogen bonding, ion–dipole interactions, and solute–solvent association. In **Section I**, three magnesium salicylate systems were studied. The volumetric and acoustic analysis of magnesium salicylate with trisodium citrate and sodium chloride demonstrated strong solute–solvent interactions, positive apparent molar volumes, and negative isentropic compressibilities which became less negative with temperature, indicating enhanced molecular association and structure-making behaviour. FTIR shifts, particularly in the O–H stretching region, confirmed intermolecular hydrogen bonding. In the second problem, the systems containing magnesium salicylate with sodium bicarbonate and sodium nitrate showed ion-specific differences in hydration and compressibility. Thermodynamic derivative parameters clearly indicated that bicarbonate exhibited comparatively weaker hydration than nitrate, and the strength of solute–solvent interactions decreased with temperature. The third magnesium salicylate system, with potassium chloride and sodium sulphate, showed that sulphate ions induced stronger solvation and greater structure-making behaviour due to higher charge density and stronger hydration capability. Positive Hepler values confirmed structure-making tendencies, and FTIR supported hydrogen-bonding and ion–solvent association. In **Section II**, the choline salicylate systems exhibited significant thermoacoustic sensitivity. In mixtures with trisodium citrate and sodium nitrate, strong solute–solvent coupling was reflected in increased density and ultrasonic velocity,

reduced compressibility, and higher relaxation strength. The presence of choline salicylate promoted structural reorganization and aggregation, supported by FTIR evidence of hydrogen bonding and dipolar interactions. The choline salicylate + sodium sulphate/sodium bicarbonate systems showed that sulphate had a much stronger structuring effect than bicarbonate due to strong electrostatic and hydration interactions. Transfer properties and derivative thermodynamic parameters suggested dominant hydrophilic–hydrophilic interactions that stabilized the ternary mixtures. In the system with potassium chloride and sodium chloride, cation-specific effects were clearly evident: Na^+ enhanced hydration and compressibility more strongly than K^+ , reflecting differences in ionic radius and hydration energy. FTIR spectra showed clear shifts associated with hydrogen bonding and ion association. In **Section III**, sodium salicylate systems were examined with a variety of salts. The interaction behaviour of sodium salicylate with sodium chloride and sodium sulphate showed temperature-dependent variations in molecular packing, with sodium sulphate exhibiting stronger solute–solvent association than chloride. Apparent and partial molar parameters showed structure-making at low temperature and structure-breaking at high temperature. In the sodium salicylate + sodium nitrate/sodium citrate systems, density and sound speed increased with salicylate concentration, indicating strengthened solvation at low temperature. Relaxation strength and relative association decreased with temperature, showing weaker solute–solvent coupling. FTIR band shifts confirmed hydrogen-bond rearrangements and ion–pair formation. The final system involving sodium salicylate with potassium chloride and sodium bicarbonate showed distinct solvation behaviour: both salts induced positive volumetric parameters at lower temperatures, confirming structure-making effects, whereas temperature rise led to dehydration of solvation shells. Negative isentropic compressibility values that became less negative demonstrated changes in packing and molecular ordering. FTIR findings validated the presence of hydrogen bonding and solute–solvent association. Overall, the combined volumetric, acoustic, and spectroscopic results across all nine problems show that salicylate systems exhibit strong ion-specific solvation, cooperative hydration, and significant molecular association. The presence of multivalent anions (SO_4^{2-} , citrate^{3-}) strengthens structural organization, while monovalent ions exhibit moderate to weak structure-making behaviour depending on temperature. Temperature

plays a crucial role: lower temperatures favour enhanced hydration, compact molecular packing, and stronger solute–solvent coupling, whereas higher temperatures promote dehydration and structure-breaking tendencies. The FTIR analysis validates these findings by providing molecular-level evidence of hydrogen bonding and solvation effects. Collectively, the thesis establishes a complete understanding of how salicylates interact with different inorganic salts, offering valuable insights for solution chemistry, pharmaceutical formulations, electrolyte design, and modelling of complex aqueous mixed systems.

Future Scope of the Present Work

The present investigation provides valuable understanding of the temperature-dependent physicochemical and spectroscopic behaviour of magnesium, choline, and sodium salicylate systems in the presence of inorganic salts. Based on the outcomes of this work, future studies can be extended in several important directions. Computational approaches such as molecular dynamics simulations and quantum chemical calculations may be employed to support the experimental results and to obtain molecular-level insight into solvation structure, ion association, and hydrogen bonding. Pressure-dependent and high-frequency ultrasonic studies may further be carried out to examine relaxation processes and compressibility behaviour over wider thermodynamic ranges. Future investigations may also include mixed solvent systems such as deep eutectic solvents and ionic liquids to understand solvent polarity and cooperative hydration effects. In addition, advanced spectroscopic techniques such as Raman and NMR may be incorporated to strengthen the interpretation of solute–solvent interactions. The salicylate-based electrolyte systems investigated in this work have potential applications in pharmaceutical formulation development, green solvent engineering, and electrochemical systems, where controlled solvation and hydrogen bonding are of critical importance. Overall, these extensions will broaden the scientific and industrial relevance of volumetric and ultrasonic investigations of complex liquid systems.

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CURRICULUM VITAE

Name: Mashahid Hussain Choudhary

Email: mashahid0249@gmail.com

Google Scholar: <https://scholar.google.com/citations?hl=en&user=NfVCggoAAAAJ>

ORCID iD: <https://orcid.org/0009-0006-6222-8678>

Educational Qualifications

PhD Physics (2026) – Lovely Professional University

M.Sc. Physics (2021) – Shri Mata Vaishno Devi University, Katra, Jammu

B.Sc. (Non-Medical)(2019) – University of Jammu, Jammu

Publications

1. M.H. Choudhary, N. Chakraborty, Harmonizing Molecular Mysteries: A Comprehensive Review of Ultrasonic, Acoustic, and Volumetric Studies in Complex Solutions, E3S Web of Conferences 453 (2023) 01049.

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- 8. M.H. Choudhary**, N. Chakraborty, K.C. Juglan, Thermophysical and Acoustic Investigation of Molecular Interactions in Choline Salicylate Solutions Containing Sodium Sulphate and Sodium Bicarbonate. *Int J Thermophys* **47**, 6 (2026). <https://doi.org/10.1007/s10765-025-03673-8>.
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- 10. M.H. Choudhary**, N. Chakraborty, K.C. Juglan, R. Kamboj, Thermoacoustic and spectroscopic studies of aqueous magnesium salicylate in potassium chloride and sodium sulphate, *J. Chem. Thermodyn.* **218** (2026) 107674. <https://doi.org/10.1016/j.jct.2026.107674>.

Conferences / Workshops

Short-Term Course on Advanced Materials Characterization Techniques: Hands-on Training and Data Interpretation, Lovely Professional University, Phagwara, Punjab, 09–16 December 2024 (Grade A)

Recent Advances in Fundamental and Applied Sciences, LPU Phagwara, April 2024.

Recent Advances in Fundamental and Applied Sciences, LPU Phagwara, March 2025.

9th National Symposium on Advances in Chemical Sciences, GNDU Amritsar 2025.