THERMO-ACOUSTICAL STUDY OF TERNARY LIQUID MIXTURES OF N-ALKYL PARABENS WITH DIFFERENT ORGANIC SOLVENTS

A Thesis
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CERTIFICATE

This is to certify that Ashima has completed Ph.D. Thesis titled "**Thermo-acoustical study of ternary liquid mixtures of n-alkyl parabens with different organic solvents**" under my Guidance and supervision. To the best of my knowledge, the present work is the result of her original investigation and study. No part of the project has ever been submitted for any other Degree or Diploma at any University.

The Project is fit for the submission and the partial fulfillment of the conditions for the award of Doctor of Philosophy in Physics.

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DECLARATION

I hereby declare that thesis "**Thermo-acoustical study of ternary liquid mixtures of n-alkyl parabens with different organic solvents**" submitted by me for the degree of **Doctor of Philosophy** in **Physics** to the Lovely Professional University Phagwara is the result of my original and independent work under the guidance of **Dr. Kailash Chandra Juglan**. This work has not previously formed the basis for the award of any degree, fellowship, diploma or other similar titles in this or any other University.

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ABSTRACT

The thesis entitled "**Thermo-acoustical study of ternary liquid mixtures of n-alkyl parabens with different organic solvents**" deals with the study of acoustical and thermodynamic properties of the liquid mixtures comprising of glycols. The acoustic method is widely considered as the simple tool in order to infer the thermodynamic properties of compressed solutions for the last 10 decades. The information regarding thermodynamic properties of liquid mixtures has become the object of interest for researchers in the recent days. The thermophysical and thermodynamic nature of liquid mixtures is of great importance for designing processes in pharmaceutical, petrochemical, chemical along with the development of model. The investigated mixtures were taken with the aim to get the knowledge concerning molecular interactions prevailing in their components. The awareness of different thermodynamic properties like ultrasonic velocity, density, apparent and partial molar properties is very useful as solute solvation in different solvents and blending consequence of solution mixtures employed in the industry is very hard to understand. The thermo- acoustical investigation has been done in order to study the molecular interaction of glycols in the aqueous and non –aqueous solutions. The molecular interaction among glycols and parabens has been inspected by evaluating volumetric and acoustic properties via Anton Paar 5000 M density and velocity meter. The densities and sound velocity of ethylene glycol, propylene glycol, and hexylene glycol in (0.00, 0.01, 0.03, 0.05) mol·kg^{-1} methanol mixture of methylparaben (methyl 4-hydroxybenzoate) have been determined at four different temperatures namely, 293.15, 298.15, 303.15, 308.15 K and p = 0.1MPa. The apparent and partial molar properties have been computed from density and sound velocity data. The apparent molar volume (V_ϕ) and partial molar volume (V_ϕ^o) is estimated from the density data whereas; the apparent molar isentropic compression ($K_{\phi,s}$) and partial molar isentropic compression ($K_{\phi,s}^o$) is determined from the measured sound velocity data. The isentropic compressibility (β_s) and partial molar expansibility $\left(E_\phi^0\right)$ are also computed. From the inspection of these parameters the results are explained in the form of associations midst solute and solvent fragments occurring in the inspected liquid mixtures together with the dominance of solute intrinsic compressibility over

solvent intrinsic compressibility. The nature of interaction of propylparaben (propyl 4-hydroxybenzoate) with two glycols namely, ethylene glycol and propylene glycol in methanol medium have been evaluated at 293.15, 298.15, 303.15, and 308.15 K and p = 0.1 MPa experimental pressure. The density data is employed to compute the apparent molar volume (V_{ϕ}) and partial molar volume (V_{ϕ}^{o}) on the other hand; the ultrasonic velocity data have been utilized to determine the apparent molar isentropic compression ($K_{\phi,s}$) and partial molar isentropic compression ($K_{\phi,s}^{o}$). The partial molar expansibilities and isentropic compressibility are also examined. From the analysis of these properties, the interpretation is given with regard to physicochemical associations occurring midst the solute and solvent molecules along with the supremacy of penetration effect upon solvent intrinsic effect. Further, volumetric and acoustic analysis is employed to inspect the molecular associations of ethylene glycol, propylene glycol and hexylene glycol with sodium ethylparaben as a temperature function. The data of densities and speed of sound of ethylene, propylene and hexylene glycol in 0.00, 0.01, 0.03, 0.05 mol·kg^{-1} sodium ethylparaben solutions in water medium are measured at four working temperatures i.e. 293.15, 298.15, 303.15, 308.15 K and atmospheric pressure p = 0.1 MPa. By using density measurement, the apparent molar volume and partial molar volume (V_{ϕ} and V_{ϕ}^{o}) are determined and by utilizing measurement of ultrasonic velocity, the apparent molar isentropic compression and partial molar isentropic compression ($K_{\phi,s}$ and $K_{\phi,s}^{o}$) are investigated. The pair and triplet coefficients are evaluated from partial molar volume of transfer and partial molar isentropic compression of transfer (ΔV_{ϕ}^{o} and $\Delta K_{\phi,s}^{o}$). The partial molar expansibility (E_{ϕ}^{0}) together with the $(\partial^{2}V_{\phi}^{0}/\partial T)_{P}$ are also studied. Through the analysis of computed parameters, the interpretations are made on the basis of co-solutes and solvents associations occurring in solution mixture together with structure erecting/structure rupturing nature of glycols in aqueous solutions of sodium ethylparaben. Moreover, the density and sound velocity measurements have been employed to estimate the nature of interactions prevailing among two polyethylene glycols with the molecular weight 200 and 600 in 0.00, 0.01, 0.03, 0.05 mol·kg^{-1} sodium methylparaben in water at several temperatures ranging from (293.15 to 308.15)K and p = 0.1 MPa. The apparent molar volumeV_{ϕ}, partial molar

volume V_{ϕ}^{0} and partial molar volume of transfer ΔV_{ϕ}^{0} is inspected by making use of density data. The apparent molar isentropic compression $K_{\phi,s}$, partial molar isentropic compression $K_{\phi,s}^{0}$ and partial molar isentropic compression of transfer $\Delta K_{\phi,s}^{0}$ is investigated with the addition of ultrasonic velocity data. McMillan and Mayer theory of liquids has been employed to estimate the pair and triplet coefficients from the measured data. The partial molar expansibilities E_{ϕ}^{0} along with $(\partial E_{\phi}^{0}/\partial T)_P$ are also computed. By the scrutiny of these evaluated properties, the interpretation is done on the basis of physicochemical co-solute-solvent associations present in the examined ternary system. Furthermore, the intermolecular inspection of polyethylene glycols viz. polyethylene glycol 200 and polyethylene 600 with butylparaben in methanol medium at 293.15 to 308.15 K temperature and at p = 0.1 MPa experimental pressure has been done. The various physical parameters such as V_{ϕ}, apparent molar volume; $K_{\phi,s}$, apparent molar isentropic compression; V_{ϕ}^{0}, apparent molar volume at infinite dilution; $K_{\phi,s}^{0}$, apparent molar isentropic compression at infinite dilution are estimated from the measure density and sound velocity data. The parameters E_{ϕ}^{0}, limiting apparent molar expansibilities and k_s, isentropic compressibility are also investigated. The results are elucidated in respect of associations amid solute and co-solute fragments existing in the inspected ternary system along with the pre-eminence of negative effect upon positive effect.

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(Ashima)

TABLE OF CONTENTS

List of Tables
List of Figures
Glossary of Symbols

Chapter No

1. **Introduction**
   - **1.1.** Ultrasonic techniques
   - **1.2.** Linear and non-linear ultrasonic techniques
   - **1.3.** Ultrasonic testing
   - **1.4.** Density and sound velocity meter
   - **1.5.** Chemistry of parabens
   - **1.6.** Glycols
   - **1.7.** Methanol (methyl alcohol)
   - **1.8.** Water molecule
   - **1.9.** Volumetric properties

2. **Review of Literature**
   - **2.1** Brief review of relevant literature

3. **Objectives and Experimental Procedures**
   - **3.1** Objectives
   - **3.2** Research methodology
   - **3.3** Structure of chemicals utilized in the research
   - **3.4** Description of the chemicals utilized in the work
   - **3.5** Experimental methods employed in the research
   - **3.6** Different ultrasonic parameters
   - **3.7** Apparent molar and partial molar properties

4. Result and Discussion

4.1 Part I

Ethylene, propylene and hexylene glycols + methyl paraben

4.2 Part II

Ethylene and propylene glycols + sodium ethylparaben

4.3 Part III

Ethylene and propylene glycols + propylparaben

4.4 Part IV

Polyethylene glycols + sodium methylparaben

4.5 Part V

Polyethylene glycols + butylparaben

5. Summary and Conclusions

6. List of publications and conferences attended

LIST OF TABLES

Table No	Caption of Tables
3.1	Description of chemicals utilized in the research.
4.1	Comparison of Experimental densities (ρ) and ultrasonic velocities (u) with literature values for pure chemicals at different temperatures
4.2	Densities (ρ), and speed of sound (u) of (EG/PG/HG+ MePB-MeOH) ternary systems at different temperatures.
4.3	Apparent molar volume (V_ϕ) and apparent molar isentropic compressibility ($K_{\phi,s}$) of EG, PG and HG in MeOH solution of MePB ternary systems at different temperatures.
4.4	Limiting partial molar volume, V_ϕ^0 and experimental slopes, S_v of EG, PG and HG in MeOH solution of MePB at different temperatures.
4.5	Limiting partial molar isentropic compressibility ($K_{\phi,s}^0$) and experimental slope S_k of EG, PG and HG in MeOH solution of MePB at different temperatures.
4.6	Empirical parameters of Eq. (5) for EG, PG and HG in MePB—MeOH solution at different concentrations.
4.7	The infinite dilution apparent molar expansion, E_ϕ^0 of EG/PG/HG in MeOH solution of MePB at different temperatures and at atmospheric pressure.
4.8	Comparison of density (ρ) and speed of sound (u) of pure compounds with literature at temperature from T= (293.15 to 308.15) K at pressure, p=0.1 MPa.
4.9	Densities, ρ and apparent molar volumes, V_ϕ of ternary system (glycols + SEP + water) at various temperatures and atmospheric pressure p=0.1 MPa.

4.10	Partial molar volumes, (V_{ϕ}^{0}), experimental slopes, S_v of EG and PG in SEP solutions of water at various temperatures
4.11	Limiting partial molar volume of transfer, $\Delta_{tr}V_{\phi}^{0}$ of glycols in aqueous SEP solutions at different temperatures.
4.12	Values of **e**mpirical parameters of eq (3) for EG and PG in aqueous SEP solutions at different concentrations
4.13	Apparent molar expansion at infinite dilution, E_{ϕ}^{0} of EG and PG in aqueous solutions of SEP at different temperatures, T/K= (293.15 to 308.15), Hepler constant $(\partial E_{\phi}^{0}/\partial T)_P = 2c$ and α , thermal expansion coefficient at T = 298.15 K
4.14	Speed of sound, u and apparent molar isentropic compression, ($K_{\phi,s}$) of ternary system (glycol + SEP + water) at various temperatures and atmospheric atmosphere, p = 0.1MPa.
4.15	Limiting apparent molar isentropic compression, ($K_{\phi,s}^{0}$) and experimental slope, S_k of EG and PG in aqueous solution of SEP at different temperatures.
4.16	Comparison of partial molar volume and partial molar isentropic compression obtained in this work with literature data.
4.17	Pair (V_{AB} and K_{AB}) and triplet (V_{ABB} and K_{ABB}) interaction coefficients for EG and PG in aqueous solutions of SEP at T = (293.15 K to 303.15) K.
4.18	Comparison of experimental and literature values of pure compounds used in this work.
4.19	Densities (ρ), and speed of sound (u) for ethylene glycol/propylene glycol in methanol solutions of propylparaben ternary systems at different temperatures and experimental pressure p=0.1 MPa.
4.20	Apparent molar volume (V_{ϕ}) and apparent molar isentropic compression ($K_{\phi,s}$) of ethylene glycol/propylene glycol in methanol solution of propylparaben at different temperatures.

4.21	Limiting apparent molar volumes, (V_ϕ^0), experimental slopes, S_v, limiting apparent molar isentropic compression ($K_{\phi,s}^0$) and experimental slope S_k of ethylene glycol/ propylene glycol in methanol solution of propylparaben at different temperatures.
4.22	Empirical parameters of eq (4.6) for ethylene glycol and propylene glycol in methanol solution of propylparaben at different concentrations
4.23	Limiting molar expansivity, E_ϕ^0 of ethylene glycol/propylene glycol in methanol solution of propylparaben at different temperatures.
4.24	Values of experimental densities, ρ and speeds of sound, u of PEGs in aqueous solutions of sodium methylparaben at several temperatures and experimental pressure p = 0.1 MPa.
4.25	Values of apparent molar volume, V_ϕ and apparent molar isentropic compression, $K_{\phi,s}$ of PEGs in aqueous solutions of SMP at several temperatures and experimental pressure, p = 0.1 MPa.
4.26	Limiting apparent molar volumes, V_ϕ^0 and experimental slopes, S_v of PEGs in aqueous solution of SMP at several temperatures and experimental pressure, p = 0.1 MPa.
4.27	Limiting apparent molar isentropic compression, $K_{\phi,s}^0$ and experimental slope, S_k of PEGs in aqueous solution of SMP at different temperatures and experimental pressure, p = 0.1 MPa.
4.28	Partial molar volume of transfer, ΔV_ϕ^0 and partial molar isentropic compression of transfer, $\Delta K_{\phi,s}^0$ of PEGs in aqueous solution of SMP at different temperatures and experimental pressure, p = 0.1 MPa.
4.29	Values of **e**mpirical parameters of eq (8) for PEGs in aqueous SMP solutions at experimental pressure, p = 0.1 MPa
4.30	Limiting apparent molar expansibilities, E_ϕ^0 for PEGs in aqueous solutions of SMP at different temperatures and experimental pressure, p = 0.1 MPa.
4.31	Pair (V_{AB} and K_{AB}) and triplet (V_{ABB} and K_{ABB}) interaction coefficients for

	PEGs in aqueous solutions of SMP at different temperatures and experimental pressure, p = 0.1 MPa.
4.32	The values of densities, ρ and sound velocity, u of (polyethylene glycols +methanol +BuPB) ternary solutions at different temperature and experimental pressure, p = 0.1 MPa.
4.33	The values of apparent molar volume, V_ϕ and apparent molar isentropic compression, $K_{\phi,s}$ of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p = 0.1 MPa.
4.34	The values of limiting apparent molar volumes, V_ϕ^0 and experimental slopes, S_v of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p =0.1MPa.
4.35	The values of limiting apparent molar isentropic compression, $K_{\phi,s}^0$ and experimental slope, S_k of (polyethylene glycols+methanol+BuPB) ternary solutions at various temperatures and experimental pressure, p = 0.1 MPa.
4.36	Values of **e**mpirical parameters of equation (6) for (polyethylene glycols +methanol +BuPB) ternary solutions at several temperatures and experimental pressure p = 0.1 MPa.
4.37	The values of temperature dependent limiting apparent molar volumes, $V_\phi^0(T)$ of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p =0.1MPa.
4.38	The values of limiting apparent molar expansion, E_ϕ^0 for (polyethylene glycols +methanol +BuPB) at various temperatures and experimental pressure p = 0.1 MPa.
4.39	Computed values of acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), Gibb's free energy (ΔG) and relative association (R_A) for ternary liquid mixture at 25^0C
4.40	Computed values of viscosity (η), relaxation time (τ) and ultrasonic

	attenuation (α/f^2) for ternary liquid mixture at 25^0C
4.41	Computed values of η_0 / η and concentration for ternary liquid mixture at 25^0C
4.42	Calculated parameters of Jon-Dole's equation for ternary liquid mixture at 25^0C
4.43	Computed Values of Acoustic impedance (Z) for ternary liquid mixture at different temperatures.
4.44	Computed values of Adiabatic compressibility (β) for ternary liquid mixture at different temperatures
4.45	Computed values of Intermolecular free length (L_F) for ternary liquid mixture at different temperatures.
4.46	Computed values of viscosity (η)for ternary liquid mixture at different temperatures.
4.47	Computed Values of Relaxation time (τ) for ternary liquid mixture at different temperatures.
4.48	Computed Values of Ultrasonic attenuation (α/f^2) for ternary liquid mixtures at different temperatures.
4.49	Computed values of Gibbs free energy (ΔG) for ternary liquid mixture at different temperatures.
4.50	Computed Values of relative viscosity (η_0 / η) and concentration for ternary liquid mixtures at different temperatures

LIST OF GRAPHS

Graph No	Caption of Graph
4.1	Plot of experimental and literature values [3, 4] of density for EG + methanol mixtures at different temperatures.
4.2	Plot of experimental and literature values [5] of density for PG + methanol at different temperatures.
4.3	Plot of experimental and literature values [6] of density for methylparaben +methanol at T= 298.15K.
4.4	Plot of isentropic compressibility, β_S against molality ^{a}m for (a) EG (b) PG and (c) HG at different temperatures. (Cube, T = 293.15 K; Circle, T = 298.15 K; Diamond, T = 303.15 K; Triangle, T = 308.15 K) (Purple, 0.01 $mol{\cdot}kg^{-1}$; Orange, 0.03 $mol{\cdot}kg^{-1}$; Wine, 0.05 $mol{\cdot}kg^{-1}$)
4.5	Apparent molar volume V_{ϕ} against molality ^{a}m for EG, PG and HG in (a) 0.01$mol{\cdot}kg^{-1}$ MeOH solution of MePB (Cube EG , Dot PG , Sphere HG); (b) 0.03 $mol{\cdot}kg^{-1}$MeOH solution of MePB (Cube EG , Dot PG , Sphere HG); (c) 0.05 $mol{\cdot}kg^{-1}$MeOH solution of MePB (Cube EG , Dot PG , Sphere HG) at different temperatures.
4.6	Graph of experimental (*empty square*) and literature data (*filled triangle* [1]; *filled circle* [2]; *filled square* [3]) of densities for mixtures of (EG + water) at various temperatures [*black*, 293.15 K; *red*, 298.15 K; *green*, 303.15 K; *blue*, 308.15 K]. (Solid lines, experimental data; dotted lines, literature data)
4.7	Graph of experimental (*empty square*) and literature values (*filled square* [4]; *filled triangle* [5]; *filled star* [6]; *filled diamond* [7] *filled circle* [8]) of densities for mixtures of (PG + water) at 298.15K temperature. [Solid lines, experimental data; dotted lines, literature data]
4.8	Graph for V_{ϕ}, apparent molar volume versus ^{a}m, concentration of EG and

	PG in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1}aqueous SEP solution (Sphere EG and Cube PG) at various temperatures.
4.9	Graph of V_{ϕ}^{0}, partial molar volume at infinite dilution for EG and PG in various concentration of aqueous SEP solution at different temperatures (dot, EG; cube, PG).
4.10	Graph of experimental (*empty square*) and literature values (*filled circle* [1]; *filled triangle* [3]) of speed of sound for mixtures of (EG + water) at various temperatures. [*black*, 293.15 K; *red*, 298.15 K; *green*, 303.15 K; *blue*, 308.15 K]. [Solid lines, experimental data; dotted lines, literature data]
4.11	Graph of experimental (*filled square*) and literature values (*filled circle* [4]; *filled triangle* [5] *filled star* [6]) of speed of sound for mixtures of (PG + water) at 298.15K temperature.
4.12	Graph.of $K_{\phi,s}^{0}$, partial molar isentropic compression for (a) EG (b) PG in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} SEP solutions of water at various temperatures.
4.13	Plot of experimental and literature values [1] of density for EG+methanol mixtures at T=293.15K.
4.14	Plot of experimental and literature values [2] of density for EG+methanol mixtures at different temperatures**.**
4.15	Plot of experimental and literature values [3] of density for PG+methanol at different temperatures.
4.16	3D - plots of isentropic compressibilityk_s against molality m of EG in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1} methanol solution of propylparaben at different temperatures.
4.17	3D - plots of isentropic compressibility k_s against molality m of PG in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1} methanol solution of propylparaben at different temperatures.

4.18	Representation of measured and values reported in literature [1, 2] of densities for (PEG-200+water) at various temperatures.
4.19	Representation of measured and values reported in the literature [2-4] of densities for (PEG-600+water) at various temperatures
4.20	Representation of measured and values reported in the literature [2] of speed of sound for (PEG- 200+water) at various temperatures.
4.21	Representation of measured and values reported in the literature [2, 4] of speed of sound for (PEG-600+water) at various temperatures.
4.22	Graph of partial molar volume V_{ϕ}^{0} for PEG-200 (cube) and PEG-600 (dot) in various concentration of SMP solutions in water at different temperatures.
4.23	Graphs of partial molar isentropic compression $K_{\phi,s}^{0}$ for (a) PEG-200 (b) PEG-600 against temperature in various concentrations of SMP solutions in water. [cube, 0.00 mol·kg^{-1}; triangle, 0.01 mol·kg^{-1}; diamond, 0.03 mol·kg^{-1}; circle, 0.05 mol·kg^{-1}]
4.24	Graph of V_{ϕ} versus ^{a}m for polyethylene glycol 200 in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1}; (c) 0.05 mol·kg^{-1} methanol-BuPB solution at several temperatures. (black, 293.15K; red, 298.15K; blue, 303.15K; green, 308.15K)
4.25	Graph of V_{ϕ} versus ^{a}m for polyethylene glycol 600 in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1}; (c) 0.05 mol·kg^{-1} methanol-BuPB solution at several temperatures. (black, 293.15K; red, 298.15K; blue, 303.15K; green, 308.15K)
4.26	Graph of ks versus ^{a}m for (a) polyethylene glycol 200 and (b) polyethylene glycol 600 at several temperatures. (dot, 0.01 mol·kg^{-1}; diamond, 0.03 mol·kg^{-1}; triangle, 0.05 mol·kg^{-1})
4.27	Graph of V_{ϕ}^{0} versus temperature for (a) polyethylene glycol 200 (b) polyethylene glycol 600 in different methanol-BuPB concentration. (circle, 0.00 mol·kg^{-1}; triangle, 0.01 mol·kg^{-1}; square, 0.03 mol·kg^{-1}; diamond, 0.05

	mol$\cdot$kg^{-1})
4.28	Plots of acoustic impedance versus concentration for (PEGs+ water+ sodium methylparaben) at 25^{0}C
4.29	Variation of acoustic impedance with molal concentration of (glycols+ methanol+ methylparaben) at 25^{0}C.
4.30	Variation of adiabatic compressibility against molality of (glycols+ methanol+ methylparaben) at 25^0 C.
4.31	Variation of intermolecular free length versus molality of (glycols+ methanol+ methylparaben) at 25^{0}C .
4.32	Variation of relative viscosity versus concentration of (glycols+ methanol+ methylparaben) at 25^{0}C.
4.33	Variation of $\sqrt{C}$ and $(\eta_0 / \eta - 1)/\sqrt{C}$ for (PEGs+ water+ sodium methylparaben) at 25^{0}C.

u	Speed of sound
F	Frequency of particle vibration
ρ	Density of material
η	viscosity
w_1	Weight of the distilled water
w_2	Weight of the experimental liquid
ρ_1	Density of water
ρ_2	Density of Experimental liquid
Z	Acoustic impedance
τ	Relaxation time for binary mixture
β	Adiabatic compressibility
α	Ultrasonic Attenuation
τ	Relaxation time
ΔG	Gibb's Free Energy
V_{ϕ}	Apparent molar volume
m_A	Molality of the glycols
V_{ϕ}^{0}	Partial molar volume
ΔV_{ϕ}^{0}	Partial molar volume of transfer
E_{ϕ}^{0}	Partial molar expansibility
$K_{\phi,s}$	Apparent molar isentropic compression

k_s	Isentropic compressibility
$K^{o}_{\phi,s}$	Partial molar isentropic compression
$\Delta K^{o}_{\phi,s}$	Partial molar isentropic compression of transfer
V_{AB}	Pair interaction coefficient for volume
V_{ABB}	Pair interaction coefficient for isentropic compression
K_{AB}	Triplet interaction coefficient for volume
K_{ABB}	Triplet interaction coefficient for isentropic compression
EG	Ethylene Glycol
PG	Propylene Glycol
HG	Hexylene Glycol
PEG200	Polyethylene Glycol-200
PEG600	Polyethylene Glycol-600
MePB	Methyl paraben
SMP	Sodium methylparaben
SEP	Sodium ethylparaben
BuPB	Butylparaben

INTRODUCTION

1. INTRODUCTION

1.1. ULTRASONIC TECHNIQUES

The travelling of ultrasonic waves in liquid is a very useful technique used by researcher to explore the properties of liquid. One can study the physical and chemical properties of solution and its molecular interaction by estimating density, viscosity and ultrasonic speed. Through literature survey it is found that the ultrasonic study is very beneficial to understand the behavior and strength of interactions between the molecules in the binary or ternary mixtures [1-4]. Different kind of liquid mixtures show various usual or unusual characteristics which gains substantial attention. Surface tension investigation of polar and nonpolar components of liquid mixture is very helpful in understanding intermolecular interaction between molecules as it has wide application in various area of industry and technology [5].

Volumetric study determines the molecular property taken as a solution function that also includes its role in solvation. In order to get the information regarding the interaction between the hydrogen bonding and various forces in ions, dipoles in liquid is extracted when ultrasonic speed, density and viscosity are measured together [6, 7]. The ultrasound studies used in oil and gas pipeline plants helps to know how to use this technology in combination with other techniques for the development and improvement of quality of analysis [8]. In medical science, the waves are being used for medical diagnosis, for detection of cancer tumors, bone fractures and physiotherapy, gynecology, bloodless surgery, cardiology, etc [9, 10]. In recent years a lot of work is done in order to relate the experimental data of ultrasonic velocities with the theoretical values using empirical and semi empirical relations [11].

Due to simplicity and accuracy of the ultrasonic technique it is being most widely used in the study of liquid state among the three states of matters [12]. The study of various types of associations midst solute and solvent fragments is of vast interest in various branches of physics and chemistry that help us to know whether solute disrupts or modifies the solvent [13]. Hydrogen bonding systems are considered to be very interesting as they are widely applicable in chemical, physical and biological process [14]. Measurements over wide range of temperatures provide the detailed information about the electrostatic attractions that exists between polar molecules like alcohols which combine with each other and there is formation of hydrogen bond. In recent years the acoustical properties of the binary liquid mixtures that contain aromatic hydrocarbon have gained a considerable attention [15]. The excess thermodynamic properties get affected by the type of molecular interaction, molecular size and the polarity that exist in the mixture [16]. It is known that the properties of anion and cation surfactant are mainly affected by different type of non electrolytes present in the mixture [17]. In the recent years ultrasonic study of miscibility and molecular interaction in polymer is of great importance for engineering applications as they provide meaningful information on the process that involves polymer production and its uses. [18]. The mechanism of transport processes can be understood with the help of viscous properties of molecules present in mixture. The parameters of viscosity give the useful data about the molecular size and shape [19].

As a result of sturdy electrostrictive forces there exists the compressibility loss of neighboring fragments of co-solute that cause electrostrictive solvation. In other words, through the application of pressure the medium is little compressed and a tight salvation is formed around the ion [20]. The theory of transition state is applied to find the free activation energy per mole of solvent simply called as activation parameters of viscous flow [21]. In living systems the derangement of water and electrolyte balance leads to wide variety of health problems. The results will enable us to know the effect of particular interaction on the excess properties of mixtures and the effect of temperature on composition dependent behavior of mixtures. Ultrasonic measurements are very beneficial in food and chemical process, to test the materials, underwater ranging and cleaning, pharmaceuticals and are mainly used in machinery of materials [22, 23].

An ultrasonic velocity measurement is done widely to detect weakness and strongness interactions of molecule in binary and ternary liquid mixtures because solvents that are mixed has wide applications in several processes of industry and chemicals. The interaction parameter showing negative value tells the existence of week dipole-dipole interaction when the temperature is increased [24] when a polar and non polar liquid is mixed there exists induced dipole induced dipole, dipole-dipole, dipole induced dipole interactions [25]. Internal pressure measures the cohesion property of molecule and derivative of volume which is instant of the cohesive energy linked with an expansion of liquid at constant temperature because this is result of different forces between the molecule [26]. The study of non electrolytic components in aqueous and non aqueous solution has been increasing day by day [27] when electrolyte go in the water the position of fragments of water gets effected with robust ions of electric field . Due to this behavior electrolytes are classified as structure makers or breaker and it is extensively used to understand the electrolytes effect on the proteins [28]. Ultrasonic wave passes through materials under the influence of pressure of sound and hence its velocity is controlled with the help of moduli of elasticity and material density which in turn are carried by the various phases and the damage in the material [29]. Both spectroscopic and non spectroscopic techniques are used to study the molecular interaction that involves measurement of ultrasonic speed and viscosity because it is widely applicable in the field of structural studies [30]. Measurement of ultrasonic speed is used to study the ion- solvent interaction by several researchers. The thermo-acoustical parameters of aqueous vitamins provide the useful information regarding chemical analyses, association, dissociation and complex structure of vitamins molecules [31]. Some of the solute- solvent interactions have wide application in many biochemical and physiological processes in the living system [32]. Information about relaxation process is extracted from the absorption and dispersion of ultrasonic waves in liquid [33].

1.2. LINEAR AND NON-LINEAR ULTRASONIC TECHNIQUES

Ultrasonic technique is employed extensively as the non-destructive inspection of harm occurring in the arrangement throughout the service for controlling the condition as well as residual life estimation of in-service structures. Nevertheless, many of the ubiquitous methods constituting ultrasonic properties in the linear elastic part is less responsive to micro damage whereas; reactive to gross defeats only. To overcome this problem, the ultrasonic method which make use of nonlinear ultrasonic properties like non-linear resonance, sub-harmonic and higher harmonic generation, mixed frequency response has been inspected to be the positive technique. The traditional non-destructive ultrasonic method is dependent on linear theory and applies on evaluating specific parameters like reflection and transmission coefficients, attenuation and sound velocity in order to detect the defects and to estimate the elastic characteristics of materials [34]. The main difference midst the linear and non-linear non–destructive method is that the properties and occurrence of defects in the non-linear NDT is related to the ultrasonic signal in which frequency varies from the input signal. In this method, high power radiation and finite amplitude ultrasound interacts with the various discontinuities like interfaces, cracks and voids. Recently, much attention is focused on the application of non-linear ultrasonic method as non- linear mechanical behaviour leads to the damage of material and material failure [35, 36]. The linear ultrasonic technique deals with the dissipation of vibrations from the medium. The propagating ultrasonic wave is having less intensity and amplitude as the deviations caused by these vibrations from the equilibrium state of medium are quite small. The propagation of ultrasonic waves with finite amplitude is accomplished by the various factors whose magnitude is dependent upon amplitude vibration.

1.3. ULTRASONIC TESTING

Ultrasonic testing is basically a non-destructive method, which is based on the transmission of ultrasonic waves in material tested. With the aim to find the material properties or to identify the internal imperfection; the ultrasonic wave pulse of frequency 50 MHz is transmitted in to materials whereas, short ultrasonic wave pulse with the range of frequency (0.1 to 0.5 MHz) has been employed in common ultrasonic testing. Ultrasonic testing is employed in many sectors such as aerospace, metallurgy, aluminum and steel construction, transportation. This testing can be performed on wood, composites, steel, metals, alloy, and concrete with low resolutions.

WORKING OF ULTRASONIC TESTING

The apparatus, ultrasonic transducer is attached to a detector which is placed upon the material investigated in the ultrasonic testing. This transducer is separated by water or oil which acts as an couplant. No couplant is needed in case when inspection of ultrasonic waves is carried by electromagnetic transducer which is based on acoustic waves. The ultrasonic wave is received in two ways: one is the reflection and other is the attenuation. In the reflection method, transducer sends as well as receives the pulsed waves due to the reflection of acoustic wave to the apparatus. Ultrasonic wave comes from the interface such as imperfection occurs in substance. The detector indicates the interpretation in the form of signal w.r.t. distance stating the arriving time of the reflection; on the hand amplitude showing the reflection intensity. In the second method (attenuation) one transducer sends the pulse wave from one surface and other transducer receives those waves after passing from the medium. The presence of imperfections and other factors reduce the quantity of the propagating sound wave. By making the use of couplant, the efficiency of sound wave is elevated which results in the reduction of ultrasonic wave energy.

Features:

- Portable and extremely automated operation.
- Possess higher accuracy as compared other harmless technique in case of evaluating width of parts and internal defects of materials.
- Tendency to determine the shape, size and nature of materials and also to investigate the shape and structure of alloys by utilizing different acoustical properties.
- Greater penetration power that causes the estimation of defects deeply in the material tested.
- Instantaneous decisions can be made as the results are immediate.
- Highly responsive.

1.4. DENSITY AND SOUND VELOCITY METER

Anton Paar 5000 M density and velocity meter simultaneously measures both density and velocity under same conditions, at same time in a single step. It is the most convenient method to investigate the thermodynamic properties as it contains wide range of temperature and have the capability to change the temperature quickly. With its unique evaluating system, it increases the accuracy for investigating the concentrations of binary mixtures. DSA 5000 M is commonly utilized for paints, inks, as well ternary solutions. The typical application of this instrument is found in food, petroleum, cosmetics, pharmaceutical, semiconductor sectors.

Excellent features:

- Provides greatest repeatability and reproducibility
- The most accurate density and sound velocity results.
- Precise and quick evaluation of small volume samples.
- No errors caused due to temperature dependent investigations.
- To get the accurate results, the steady state controlling system is being applied which is not effected by outer factors.
- The sample’s viscosity is also measured by this instrument.
- It provides the most adequate correction of viscosity.
- Diagnose the gas bubbles prevailing within the sample and displays the foiling error on the screen.
- Filling and cleansing of the measuring cells is done simultaneously ad automatically.

1.5. CHEMISTRY OF PARABENS

Alkyl esters of para-hydroxy benzoate, also called as parabens are a group of substane mainly utilized to preserve the food and cosmetic products and also in toiletries, preparing pharmaceutical products, beverages and medications because of their antifungal and antimicrobial properties, good stability, less cost and low toxicity [37-42]. In order to inhibit the augmentation of micro-organisms, class of parabens namely methylparaben, ethylparaben, propylparaben, and butylparaben is widely employed as ingredient in cosmetics [43]. As alkyl group chain length elevates from methyl to butyl, the antifungal properties of paraben surges and become lipophilic in nature [44, 45]. As parabens posses low toxicity and are widely employed as a preservative; so these are considered as safe compounds. As per recent study, in addition to antimicrobial activity in vitro and vivo, the class of parabens is examined as having an estrogenic impact [46-48].

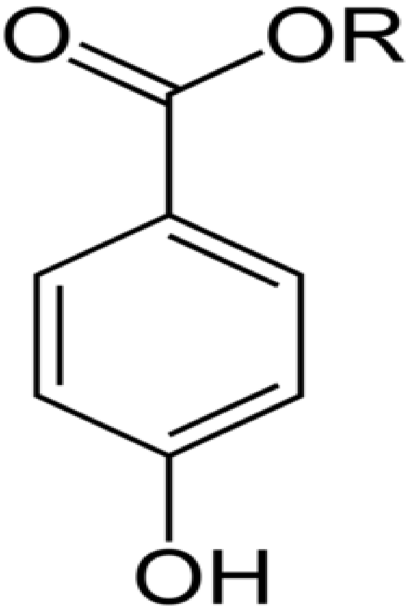
1.5.1. METHYLPARABEN AND ETHYLPARABEN

Methylparaben is the methyl ester of parahydroxybenzoates, acts as an anti-fungal agent in different variety of personal-care products and cosmetics. It is also employed as food preservatives in foods. Methylparaben has estrogenic effect and is toxic at higher concentrations. Methyl parahydroxybenzoate is readily absorbed through the skin. Methyl parahydroxybenzoate is promptly consumed through the skin. It is hydrolyzed to p-hydroxybenzoic corrosive and quickly discharged in urine without aggregating in the body. Acute poisonous quality investigations have demonstrated that methylparaben is practically non-toxic by both oral and parenteral organization in animals. In a population with typical skin, methylparaben is essentially non-aggravating and non-sharpening; notwithstanding, however, allergic responses to ingested parabens have been reported. Studies demonstrate that methylparaben consumed on the skin may respond with UVB, prompting expanded skin maturing and leads to harm DNA.

Ethylparaben is the ethyl ester of parahydroxybenzoates. It is employed as preservative in foods and cosmetics. Ethylparaben forms white powder or little colorless crystals. Ethylparaben was considered as a skin irritant in human. In human research it provides no proof of sensitizing potential. The paraben esters as a non-excusive group are rare sensitizers when consumed to the intact skin of man. Implementation to the harmed skin is an increasingly basic reason of sensitization. Ethylparaben was examined as an eye irritant in rabbits. The intake of ethylparaben produces cell proliferation in the forestomach of rats.

1.5.2. SYNTHESIS OF PARABENS

All the industrially consumed parabens are synthetically manufactured, even some of them are consistent with those occur in nature. They are manufactured by the etherification of para-hydroxy benzoate with suitable liquor like methanol, ethanol, and propanol. The parahydroxybenzoates (parabens) are industrially manufactured by the modification of Kolbe-Schmitt reaction with the help of carbon-dioxide and potassium phenoxide. The general chemical structure of parahydroxybenzoates (parabens) is shown below:



Structure of parabens

Where R represents the alkyl group like methyl, ethyl, propyl and butyl.

1.6. GLYCOLS

Glycols belong to alcohol class and obtain two classes of hydroxyl in each atom. Numerous scientists found the investigation of glycols an exceptionally intrigrued region because of its extensive uses in biotechnology, beverages, cosmetic and pharmaceutical industry [49-53]. There have been numerous studies on the thermo-physical properties on glycols schemes in water besides ether, amides, alcohols and glycerol [54-61]. A extensive application has been found for fluid glycol arrangements, for example, making of conditioning agents, greases, solvents and hygroscopic operators [62]. Glycol's viscosities change conversely with respect to temperature. At large temperature, atoms of glycols move openly and as the particles of glycol cool, their viscosity continues increasing until their last settlement and failure of development of particles. These are much liquid than the greater part of the solvents and plastizers possessing high boiling points. On account of this reason, to diminish the viscosities of fluid structures, glycols are as often as possible pushed off either alone or in relationship with different liquids.

1.6.1. ETHYLENE GLYCOL

Ethylene glycols are solvents that constitute two hydroxyl members in each atom in which inter and intra sub-atomic hydrogen bonds were arranged between –O- and –OH groups [63]. The fluids namely, ethylene glycol and monoalcohols are the fundamental fluids as they discover the diversity of utilization in beauty care products, pharmaceuticals, etc. Ethylene glycols with the general formula $H(OCH_2CH_2)_nOH$, where n is from 1–5 termed as the series of synthetic linear oligomers of escalating oxyethylene units each molecule [64]. Ethylene glycol is employed as the main constituent in the usually available automotive antifreeze products [65-68].

1.6.2. PROPYLENE GLYCOL

Propylene glycol is hygroscopic in nature and acts as prevalent humectants, with capacity of saving moisture over a wide scope of moistness [69, 70]. Propylene glycol is commonly employed as a vehicle for topical arrangements in makeup and remedial items [71]. Propylene glycol (PG) is self associated to inter and intra hydrogen bonding. The disturbance of related particles is noted and some association happens between unlike molecules via intra hydrogen association on mixing propylene glycol with methanol and ethanol [72].

1.6.3. HEXYLENE GLYCOL

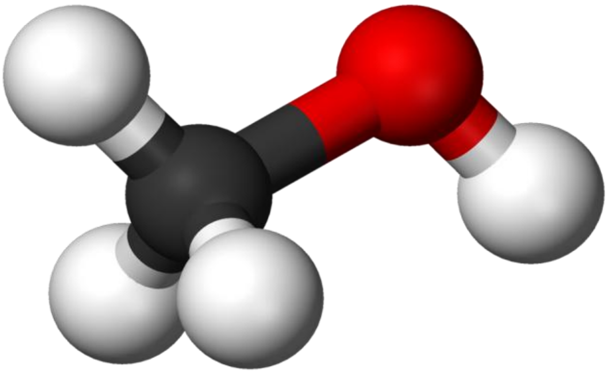
Hexylene glycol is considered as an extremely intriguing fluid because of its widespread usage in numerous purposes. It behaves like a solvent of the fact that it gets effectively broke split in to water and natural solvents that help it to deliver fat and water-soluble substances [73]. It is additionally used for organic crystallisation biomolecules [74]. Hexylene glycol (2-methyl-2,4-pentanediol) is a chiral diol, and it has two enantiomers (4R) – (−) and (4S) – (+). Monetarily, it is called as MPD. It is stabilised by constructive arrangements of substituents on neighboring carbons and development of intra-molecular hydrogen bond. Hexylene glycol is so profitable in protein crystallography as a result of its amphiphilic nature and little adaptable structure that enables it to tie to a few unique areas on a protein structure.

1.6.4. POLYETHYLENE GLYCOL 200 and 600

In many research and technology fields poly (ethylene) glycols of different molar masses are used. These are of great therapeutic use on the basis of multiple laxatives and skin creams, due to their low toxicity[75,76].Polyethylene glycol (PEG) is the most significant, widely used nonionic polymer in industry. Bioavailability of the drugs to improve the biochemical activity of proteins[77],Polyethylene glycols are commonly used as reaction process regulators of biological macromolecules.PEG also functions as a crowding agent in macromolecules.From the toxicological studies and environmental characteristics it has been established that polyethylene glycol is eatable, biodegradable, and harmless.The liquid form of PEGs and its monomer are good solvents and highly polar.

METHANOL (METHYL ALCOHOL)

Methanol also abbreviated as MeOH, is a compound with the chemical formula CH_3OH. Methyl alcohol is considered as the simplest alcohol, where methyl group is attached to the hydroxyl group. MeOH is more toxic than the ethanol. Methanol is light, having odor such as ethanol, constituting no colour, volatile and flammable liquid. Is is also employed as precursor to other chemicals like acetic acid, methyl-tert-butyl ether, formaldehyde etc. Methanol is produced in anaerobic metabolism of different varieties of bacteria naturally and is usually exists in little quantity in the atmosphere. Due to which, the atmosphere constitute small amount of methanol vapor. Methanol has low intense harmfulness in people however is hazardous on the basis that, together with ethanol, it is occasionally ingested in huge volumes. Methanol is randomly employed as denaturant additive for ethanol which is made for industrial applications due to its toxic properties. The structure of methanol is given below:



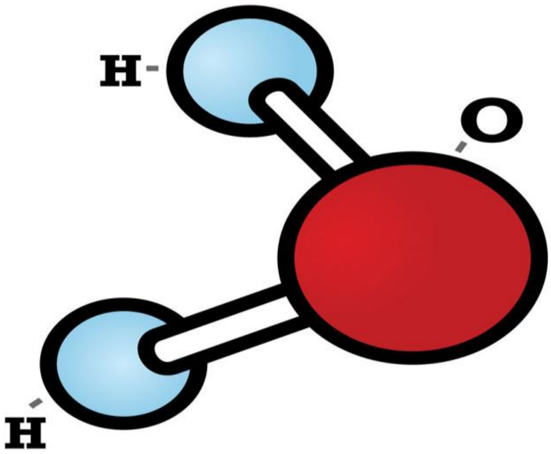
Methanol

1.7. WATER MOLECULE

Water comprises of little polar V-molded particles with atomic mass H_2O. Water is a minor twisted particle constitute the molecular formula H_2O which composed of two light hydrogen molecules appended to each 16-fold stronger oxygen atom. Each atom is however polar in terms of electric impartiality, with the center point of p ositive and negative charges located in different locations. Every hydrogen molecule has a core comprising of a singly charged proton encompassed by a 'cloud' of single negative charged electron and the oxygen molecule has a core comprising of eight positively charged protons and eight uncharged neutrons encompassed by a 'cloud' of eight negatively charged electrons.

On the creation of particles, the ten electrons pair up into five orbital sets closely linke d to the oxygen molecule, two sets connected to the oxygen atoms as external electron s and two sets forming each of the two inseparable O-H covalent bonds

The atom is V- shaped as it possess two hydrogen molecules and one oxygen molecule and is considered as a polar molecule. This is due to the fact that the oxygen atom os molecule in the middle is negatively charged and the hydrogen molecules at the end are positively charged. The water molecule is bent because of 105^0 bond in the angles midst the oxygen atom in the centre and hydrogen atom on the both sides of the molecule. Due to this, molecule constitutes non-linear shape. It contains two pairs of unshared lone pairs and two pairs of bonded electrons. The water molecules are largely attracted towards each other due to polarity and this shape. The structure of water molecule is given as:



Water molecule

1.9.VOLUMETRIC PROPERTIES

The volumetric properties give the significant data with respect to the procedures of solvation in arrangements together with the packing of system structure. Various investigations demonstrate the affectability of volumetric characteristics to solute + dissolvable connections [78]. The investigations of volumetric characteristics inside the broad scope of temperature are basic, since these characteristics enable to understand the different procedures happening in the solution mixtures. The impact of temperature on the idea of volumetric properties of watery arrangements is often used for data discovery regarding solute structural consequences on water structure. The temperature reliance of limiting partial molar volume is contended in arrangement of solute hydration and balance among hydrophilic and hydrophobic connections among water and solute [79-82]. Partial molar volume at infinite dilution rely on a few factors, for example, solute-solvent and solute-solute associations along with the atomic shape and relative size of solute particles. The partial molar volume provides the data concern solute and solvent associations; concentration dependence of limiting partial molar volume gives the useful data about solute-solute associations.

1.10. VISCOSITY MEASUREMENT

Viscosity is the property of the fluid that deforms that deforms under stress from the shear. Its commonly perceived as conducting flows or gasping resistance. Viscosity describes a internal fluid flow resistance and may be considered as measure of friction with air. Viscosity for certain liquids is a material constant, dependent on temperature and pressure. This category of material is called as Newtonian liquids. All liquid and gases possess viscosity to certain extent. Viscosity assessment is an important means in examining the properties of matter or fluids. It plays a big part in quality control and multiple research and stages of development for a variety of industries including cosmetic, pharmacy and pharmaceutical etc.

Viscosity also termed as coefficient of viscosity is measure of fluids resistance to flow. It is a persistent material indicating the fluidity magnitude of a liquid. Viscosity is usually correlated with the liquid.

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REVIEW OF LITERATURE

2. Review of Literature

Hout *et al.* (1988)[1] had done the thermodynamic study of ethylene glycol with water at the temperature namely, 5, 25 and 45^0 C. The acoustical parameters like isobaric hest capacity and densities were computed from the apparatus called micro calorimeter and flow densimeter. The excess and apparent along with the partial molar properties were being determined from the compute density data. The negative impact of the hydroxyl group leads to the negatives excess values on the other hand, methylene group leads to positive contribution. The magnitude of excess enthalpies showed that exothermic mixing of water-ethylene glycol was significantly conquered by interactions including the hydroxyl group of ethylene glycol. The constant variation in different higher order acoustic properties were found in terms of rise in connectivity midst fragments of ethylene glycol.

Lee and Hong (1990)[2] had inspected the excess molar properties of ethylene glycol, water and methanol binary and ternary mixtures with the help of density measurement. The apparatus Anton Paar DMA was utilized to measure the density of ethylene glycol with water and methanol and methanol with water at various temperatures like 283.15, 293.15 and 303.15K. The values of excess molar volumes were found to be negative for all the investigated ternery and binary mixtures which were obtained from the calculation of density data. Furthermore, A and B coefficients were calculated with the help of Redlich-Kister equation by utilizing least square technique.

Douheret *et al.* (1991)[3] The measurement of densities, sound velocities and isobaric heat capacities for the aqueous ethylene glycol mixtures were done at various temperatures. The isentropic compressibility and excess molar volume were computed from the data of speed of sound and density. From the measured parameters the Isobaric and isentropic expansivities were also evaluated. The excess molar parameters were obtained with the help of a segmented-composition model. The scrutiny of the parameters suggested the formation of the highly irregular bunches which constitute high range of hydrophobic gathering.

Reddy *et al.* (1994)[4] The data of sound velocity, excess volume along with the viscosity had been investigated for the binary mixtures of ethylene glycol+water, 2-ethoxyethanol+water, 2- methoxyethanol+water and 2- butoxyethanol+water at 308.15 K. The acoustical parameters density and isentropic compressibility were computed from the measured parameters. The excess volume deviations were negative whereas, viscosity deviations were coming out to be positive. The obtained results were explained in regard of the existence of associations among like and unlike compounds.

Rajulu and Sab (1995)[5] had inspected and determined the various acoustical properties of aqueous polyethylene glycol at 303 K temperature. The components utilized in the research were vacumm dried at 338.15K temperature. The sound velocity was measured by employing variable path interferometer which works at the frequency of 2MHz whereas; density was computed with the help of density bottle. There was a non-linear relationship among the various parameters which further signifies the occurrence of association midst polyethylene glycols with water.

Rajulu and Sab (1995)[6] had evaluated the different acoustical parameters of polyethylene glycol and water binary mixtures at 30ºC temperature. The chemicals employed in this work were vacumm dried at 65ºC. The density and sound velocity was computed with the help of density bottle and variable path interferometer that works at the frequency of 2MHz. There was a non-linear association among polyethylene glycols and water.

Kirincic and Klofutar (1998)[7] had studied the densities of polyethylene glycols with water at 298.15K temperature. The calculated data was further utilized to evaluate the parameters such as apparent specific volume of solute along with the partial specific volume of solvent and solute. There was rise in the concentration with the reduction in the partial specific volume of solute. On the other hand, this parameter i.e. partial specific volume of the solvent escalates with respect to escalation in the concentration of the solute.

Henni *et al.* (1999)[8] had done the experimental work in order to determine the density and viscosity of triethylene glycol monomethyl ether. They utilized Helper's method of Studies which further signifies that there was no effect on the structure of triethylene glycol monomethyl ether on the addition of water to it. The positive values were computed for Grunberg-Nissan.

Orge *et al.* (2001)[9] had reported the experimental values of density, sound velocity as well as refractive index of methanol/ acetone with ethylene glycol, propylene glycol, 1, 3-propanediol, 3- methyl, 1 butanol, 2- methyl, 1 propanol constituting mole fraction as a function at atmospheric pressure and 298.15K temperature. Various excess parameters such as excess molar volume, isentropic compressibility after mixing, and refractive index after mixing were evaluated from the experimentally obtained density and speed of the sound. For the enclosed structure of the branched alcohols mixtures the increased trend was obtained. Different degree polynomials were fitted in to the results of the work. The partial molar volume determines the effect of hydroxyl group on the non-ideal nature of these binary studied mixtures.

Branca *et al.* (2002)[10] done the investigation of variation of viscosity with regard to sound velocity measurements and concentration of the solute and hence indexed the hydration numbers. Due to the acoustical and viscosity measurements elevation, the calculated hydration numbers surges instantly and because of that there was rise in the degree of polymerization. Moreover, it was interpreted that the temperature increase cause reduction in the strength of the association among polymer and water reduces which leads to loss of water fragments that are not tightly associated to each other.

Karunakar Kar *et al.* (2002)[11] had studied the interaction of calcium chloride with chymotrypsin. The thermal unfolding of chymotrypsin had been studied in presence of calcium by using uv-visible spectrophotometry and differential scanning calorimetry. Quantitative thermodynamic parameters carrying the thermal transitions had been calculated. The values of surface tension of calcium chloride that was a aqueous solution were measured and it was found that surface tension was not the factor to provide thermal stability of the protein.

Zhenning Yan *et al.* (2003)[12] had estimated the effect of temperature on the viscometric and volumetric property of some amino acids in the aq. solution of calcium chloride. Some amino acids density and viscosity in the solution of calcium chloride had been measured at 278.15, 288.15.298.15 and 308.15K temperatures. Viscosity B coefficients and Apparent molar properties of amino acids had been calculated. At different temperatures standard partial molar volume and hydration number had determined. Free energies of activation had been obtained by using transition state theory. The effect of the amino acids structure had been studied through viscosity data.

Sun *et al.* (2003)[13] had computed the density, thermal conductivity and viscosity of ethylene glycol, diethylene glycol, and triethylene glycol in water mixtures at different temperatures that ranges from 290 to 450 K and at different concentrations that varies from 25 mol % to 100 % of mol of glycol. The experimentally computed data was in coherence with the data available in the literature and this data was further correlated by employing generalized corresponding principle together with the empirical expression. The extrapolation of density data and transport property data was done with the help of two adjustable parameters and generalized corresponding principle method.

Sanjeev Maken *et al.* (2005)[14] had done the investigation of molecular interaction of binary liquid mixtures thermodynamically and topologically. The excess properties such as molar excess volume and molar excess enthalpies of binary mixtures of butyl acetate with benzene, cyclohexane and toluene had measured calorimetrically at 308.15K temperature. Excess molar volume was analyzed through graphical approach which tells that the butyl acetate remain as associated entity in its pure state. It was found that the value of excess molar volume and excess molar enthalpies calculated by this graphical approach fitted well in the experimental data.

Tuhina Banerjee and Nand Kishore (2005)[15] studied the interactions of tetraethyl ammonium bromide with some amino acids at 298.15K. The apparent molar volume of some amino acids had measured in the aq. solution of TEAB at different concentration and at temperature of 298.15K by using density measurement. A parameter called standard partial molar volume was classified as very sensitive that it changed the structure in solution. The amount of water molecules increases as the hydrophobic content in the amino acid increases which shows the presence of interaction namely hydrophobic between amino acid and TEAB solution.

Tuhina Banerjee and Nand Kishore (2006)[16] had studied the interaction of aq. solution of tetraethyl ammonium bromide with peptides and lysozyme at temperature of 298.15K.The apparent molar volume of peptides and partial specific volume of lysozyme had measured in the aq. solution of tetraethyl ammonium bromide by using density measurement at 298.15K.The lysozyme that had specific volume of transfer from water to solution of tetraethyl ammonium bromide indicate the presence of hydrophobic interactions. The partial specific volume of proteins Decreases due to increase in the TEAB concentration.

Ali, A *et al.* (2006)[17] had studied the physiochemical behavior of amino acids in the aq. Solution of caffeine at temperatures like 25, 30, 35 and 40^0C. Various parameters such as density, refractive index and viscosity of amino acids had measured in aq. solution of caffeine at different temperatures. The partial molar volume and the viscosity data analyzed by using Masson's equation and Jones Doles equation. The solute- solute and solute-solvent interaction were interpreted from the obtained values of Falkhengan coefficient and Jones Dole coefficient. Transition state theory was also applied and refractive index calculated the molar refractivity of mixtures.

H. Iloukhani and K. Khanlarzadeh (2006)[18] had measured the refractive indices, viscosities, densities for binary and ternary mixtures of Ethyl acetate, 2-methylbutan-2-ol and n,n-Dimethylacetamide for the region in liquid at 298.15K temperature. The deviation in excess molar volume, refractive indices and viscosity had calculated from the experimentally verified data. Redlich-Kister and the Cibulka equations were used to correlate the binary and ternary data. Nature and strength of intermolecular interaction in these mixtures were estimated from binary, ternery and experimental system collectively.

Amalendu Pal and Rekha Gaba (2008)[19] had determined the thermodynamic properties of mixtures that contain alkoxy propanol and n- alkanols. Densities for the binary liquid mixtures containing propanols and n- alkanols had been measured by using Antan Paar DSA 5000 densimeter at different temperatures. The calculated parameters were applied to measure the volume expansivity and excess molar volume at 298.15K temperature. The obtained result was compared by using values calculated from theory of liquid mixtures. The effect of particular interactions on the excess property because of rise in the temperature was studied.

Stephanie L. Outcalt *et al.* (2009)[20] had measured the density and sound of 1 and2-butanol by using two instruments that had vibrating tube sensors for measuring density. Speed of sound and Density was measured from 278.15 K to 343.15 K and at 83Kpa pressure. Adiabatic compressibility was measured from data obtained by density and speed of sound.. The modified Tait equation was used to correlate the calculated density data that gives the idea for extensive comparison of data with literature extensively. The isomers that had measured differences in macroscopic properties were related to molecular level differences.

Yasmin Akhtar and S.F. Ibrahim (2010)[21] had determined the ultrasonic and thermo dynamical study of glycine in aq. solution of various electrolytes at 303K temperature. Densities and ultrasonic velocities of glycine had measured in the aq. solution of electrolytes namely magnesium chloride and sodium chloride at 303K temperature. Adiabatic compressibility, both partial and apparent molar properties had calculated from the data that was obtained experimentally for all the ternary systems. The data was estimated in terms of solute-solute and solvent-solvent interaction. There was strong dipole- dipole and ion solvent interaction in glycine and magnesium chloride electrolyte.

Outcault *et al.* (2010)[22] had done the experimental work to find the density and sound velocity of 1 and 2 butanol . The experimental work was done with the help of two instruments that used vibrating tube sensors in order to measure the density. The sound velocity and densioty were computed from 278.15 K to 343.15 K at 83 kPa. The density and sound velocity data were evaluated from the measurement of density and sound velocity. The density of compressed liquid mixtures was computed in the other instrument whose temperature varies from 270 K to 470 K and pressure from

0.5 MPa to 50 MPa. The tait equation was being utilized in order to associate the density along with its error. There was the comparison of macroscopic properties of the investigated mixtures with the microscopic level differences.

Chandra Bhan Singh *et al.* (2012)[23] had studied the interaction between the molecules of binary liquid mixture of benzene with methyl salicylate and benzene at three different temperatures. The acoustical parameters and excess parameters were determined at 303 K, 308K and 313K temperature from the calculated value of density, ultrasonic speed and viscosity. The negative interaction between the molecules indicates weak dipole dipole interaction due to the increase of temperature.

Ramteke (2012)[24] had studied the sound velocities of alpha-picolin with ethanol mixtures at various temperatures. The hydrostatic sinker technique was being employed in order to compute the densities of binary components and pure components which in turn provides the interest to evade the solution mixture vapourisation. The preparation of the mixture was done in terms of the mole fraction for various concentrations. For the pure components and mixtures the temperature was kept constant with the help of thermostat. From the interpretation of the parameters such as sound velocity, density, viscosity and other acoustical parameters over the whole range of concentration, it was found that strong intermolecular interaction occurs in the investigated binary mixtures.

E.J. Gonzalez *et al.* (2012)[25] had determined the excess and thermophysical properties of binary mixtures containing ionic liquid and alcohol at 298.15 K temperature. Different parameters such as density, ultrasonic velocity and refractive index of the mixtures were calculated. Many cations, anions and alkyl side chain were presented in ionic liquids. Many excess properties were calculated and were well fit by using Redlich Kister equation. The property that was calculated in this work depends on the ionic liquids structure mainly on the anions. Alkyl side chain and cation had less effect on excess properties of mixtures.

Kaur *et al.* (2013)[26] had computed the acoustical parameters of polyvinyl acetate with acetic acid by the virtue of acoustic method. The chemicals constituting 100% purity were employed as such without any purification. The mixture was prepared by them by adding polyvinyl acetate in the acetic acid whose volume was kept constant. In order to weight the samples, the electronic weighing balance was employed. The degassed water was used for the preparation of solution. The sound velocity was computed by using variable path interferometer which works at 2 MHz frequency and at room temperature. It was concluded that the obtained parameters surges with escalation in the concentration. Moreover, it was concluded that the major cause for the transmission of energy was the large amount of molecules which leads to rise in the sound velocity.

Moattar and Tohidifar (2013)[27] had inspected the influence of temperature on volumetric and transport properties of poly ethylene glycol di-methyl ether 2000 + polyethylene glycol 400 in water at the temperature that varies from 293.15 to 313.15 K. The density, sound velocity and viscosity data was utilized in order to compute various excess parameters like excess Gibb's free energy, excess volume, deviation of the viscous flow, and excess molar isentropic compression. At infinite dilution the apparent molar volume was determined by the means of density which further gives the information regarding co-solute-solute and solute-solvent fragments.

Sannaningannavar *et al.* (2013)[28] had studied and investigated the thermo-physical parameters of PEG -400 at two temperatures namely, 299 and 363K. The pycnometer was employed to measure the density on the other hand; the speed of the sound measurements was done with the help of ultrasonic interferometer which works at the frequency range of 3MHz. In order to maintain the temperature, the thermostatic water bath was employed to keep the temperature constant. It was inferred from the parameters that due to the increase in temperature, the volume of polyethylene glycol-400 surges and the structure of the solution mixture gets destroyed. It was also established that when temperature was increased with respect to decrease in the intermolecular forces the expansion of chain and unfolding take place. The dependence of temperature of the elastic and inertial characteristics of the mixtures was also determined.

Amalendu Pal *et al.* (2013)[29] had studied the densities and ultrasonic speeds of alkyl acetate and dipropylene by using Anton Paar DSA densimeter at different temperatures. The excess properties such as excess molar volume and deviation in isentropic compressibility which had calculated were fitted in the Redlich–Kister type polynomial equation to get their coefficients and standard deviations. Mixtures that tell the negative value of excess molar volume and value of isotropic compressibility become more positive than the pure components.

Amalendu Pal *et al.* (2013)[30] had carried out the study of the densities and the speeds of sound of butanol , propanol with 1,4-dioxane by using Anton Paar DSA densimeter for the binary liquid mixtures at different temperatures. Excess molar volumes values and excess molar isentropic compressibility values were fitted to Redlich–Kister equation to find out the coefficients and standard error values. Excess partial molar isentropic compression of components and their limits was obtained using Redlich–Kister type equations analytically. The value of excess molar volume was positive and hence its value increases with increase in temperature .It was found that excess molar isentropic compressibility was negative at all temperatures. Negative value indicates the specific interaction among the 1, 4-dioxane binary mixtures with alkanol molecules.

J.Balakrishnan *et al.* (2013)[31] used the ultrasonic technique to study the molecular interaction of binary mixture of spindle oil with ethanol system at 303K temperature and at different temperatures. Various thermo acoustical parameters such as relaxation time, free volume, free length, acoustic impedance and relative association were calculated hence they used to determine the correlation between the binary mixtures. Because of weakening of intermolecular interactions whole volume of solution increases with rise in the temperature. The study of ultrasonic parameters and excess functions for the binary mixture of spindle oil and ethanol at various concentrations and hydrogen bonding among solute and solvent.

Saxena (2013)[32] had studied the acoustic properties of polyethylene glycol in water medium. There was a formation of transparent liquid on the addition of polyethylene glycol to the water having constant volume. With the help of ultrasonic interferometer, various acoustic parameters such as ultrasonic absorption and acoustic were determined at a frequency of 1MHz and at 308.15 K temperature. For the measurement of density, the density bottles were pre-calibrated and the temperature was controlled by utilizing thermostatic water bath. The parameters like sound velocity and viscosity were measured at various temperatures and concentrations. Whereas, other parameters were computed by further utilizing standard relations. By using standard relations other parameters were also calculated. The results were concluded in such a way that the obtained volume reduces with escalation in electrostriction; on the other hand, other parameters like density, viscosity, sound velocity and acoustic impedance surges with increase in the concentration.

Singla *et al.* (2014)[33] had done the volumetric and acoustic studies in order to determine the interaction occurring among dipepetides of glycine with amoxicillin solution in water medium by utilizing density and sound velocity measurements at the temperature namely, 305.15, 310.15 and 315.15 K. The UV absorption studies were also included in the work. The various apparent and partial molar properties of depepetides with the antibacterial amoxicillin were inspected from the data of sound velocity and density. The pair and triplet coefficients were also evaluated by the virtue of transfer properties of apparent molar volume and apparent molar isentropic compression. Moreover the results are interpreted on the basis of the associations amidst solute and solvent fragments.

Harsh Kumar *et al.* (2014)[34] had studied the interaction of aq. Triammonium citrate solution with amino acids at various temperatures. Due to rise in temperature and concentration of triammonium citrate the value of viscosity of amino acid changes which leads to amino acid–triammonium citrate interactions. Using Jones–Dole equation and theory of transition state the parameters such as viscosity and B-coefficients interaction were found which further used to interpret the interaction between ions of triammonium citrate and amino acids. The value of B-coefficients that was having great values in L-valine case was compared to other amino acids tells that there was more solute solvent interactions in L-valine TAC and water mixtures as compared to other amino acids.. This shows that ground state solute solvent interactions were quite stronger than in transition state.

S. Grace Sahaya Sheba and R. Omegala Priakumari (2014)[35] had done the investigation by using ultrasonic techniques of ethanol and polyethylene glycol molecules in binary liquid mixture at different temperature. Some thermo acoustical properties such as viscosity, Ultrasonic velocity, density were estimated at different molar fraction but at room temperature. Acoustical parameters such as free volume, internal pressure, relaxation time, intermolecular free length, acoustic impedance and adiabatic compressibility were also obtained. They found out that the interaction between the molecules of solute and solvent is quite weak.

J. A. Schroeder *et al.* (2014)[36] had studied the equation of ethanol that was in the Helmholtz energy form where density and temperature were taken as function. To improve the behavior of fundamental equation new non linear fitting techniques and new experimental data were presented. Ancillary equations, heat capacity for ideal gas, vapor pressure equation, saturated liquid density, saturated vapor density were developed. Experimentally verified data was used for the calibration of fundamental and ancillary equations. For single phase and saturation states for pressure up to 280 MPa and temperatures from 160 to 650 K this fundamental equation is valid.

Upasna Magotra *et al.* (2014)[37] had volumetrically and viscometrically studied the interactions of non ionic, anionic, cationic surfactants with L-alanine at several temperatures. The viscosity and densities of L-alanine had measured in the aq. solution of sodium dodecyl sulphate surfactant at different temperatures. Viscosity data was used to found the Falkenhagen coefficient a and Jones-Dole coefficient b by using Jones Doles equation. The behavior of calculated parameter indicates the existence of interaction between solute and solvent.

V. G. Badelin and V. I. Smirnov (2014)[38] had studied the thermodynamics of DL-Alalnyl-DL-Asparagine Dissolution (AlaAsn) in water–organic mixtures at 298.15 K temperature. Enthalpies of dissolution of AlaAsn were measured in aqueous solutions of organic mixtures such as 1, 4-dioxane, acetone, and dimethyl sulfoxide ay at T = 298.15 K. the value of Standard enthalpy of dissolution transfer property of AlaAsn from water into solvent were calculated with the help of experimental data. Both the mixtures were hydrated well in this range of concentrations and the energy consumed for dehydration of AlaAsn and molecules of organic solvent was greater than the energy released during direct interaction between them.

Golamari Siva Reddy and Mallu Maheswara Reddy (2015)[39] had studied various Thermophysical and acoustical properties such as refractive index , Surface tension of benzene with benzyl parabens for binary mixtures at several temperatures and different molefractions. The value of viscosity was correlated with equations of Krishnan-Laddha and McAllister and the excess values were related by using Redlich-Kister polynomial equation to found the standard deviation values. The interactions which result from interstitial accommodation of benzene in to benzylparaben were the main factor over dipole–dipole and dipole induced–dipole interaction.

Sherif, N. Afsar and S. Narayanan (2015)[40] studied the molecular interaction of certain zinc electrolytes in polyethylene glycol by using ultrasonic method. Measurement of some thermo acoustical properties like ultrasonic velocity, density and viscosity had done for various zinc electrolyte system at 303K and different concentrations. Several acoustical parameters were calculated from experimental data and were helpful in determining the interaction in terms of solute- solvent, ion - solvent of electrolytic solution. The trends indicated the interaction occurred at low and high concentration for the certain weak and strong electrolyte.

Suresh Kumar Sharma *et al.* (2016)[41] had studied the viscometric properties that were viscometric of L valine, L alanine and glycine aliphatic amino acids due to the temperature effect in aq. solutions of tetraethyl ammonium iodide. By making use of Jones dole equation the viscosity b coefficients for the amino acids had been measured and were taken as molality function of amino acids at different temperatures. Variations that occurred in amino acids due to rise in molal concentration of tetraethyl ammonium iodide solution and with temperature rise determined the interactions in solute and solvent in the solution. Because of stronger hydrophobic interaction at longer alkyl chain of amino acid there was increase in viscosity values and hence order was as: L-valine.> L analine> glycine.

Harsh Kumar *et al.* (2016)[42] had studied the thermodynamic properties of aq. Alkoxyalkanols solution with surfactant sodium dodecyl sulphate at various temperature. Many parameters like transfer volume, apparent molar volume. Partial molar expansibility, limiting apparent molar volume was very beneficial in studying the interactions and aggregation behavior of alkoxy alkanols. The magnitude of apparent molar volume shows the interaction that was hydrophobic or hydrophilic contained in the mixtures. The positive values of apparent molar volume show the presence of hydrophilic interactions and negative values tells the presence of hydrophobic interactions. The negative value of apparent molar compressibility for the alkoxy alkanols in surfactant sodium dodecyl sulphate shows the property of miscibility.

Kaur *et al.* (2016)[43] had investigated and studied the sound velocity in the binary mixture of methanol with chloroform. The speed of the sound evaluation was done at 295K by employing ultrasonic interferometer that works at 2MHz frequency. Further by utilizing Junjie's relation, Nomoto's relation, Van Dael-Vangeel, Rao's specific velocity relation, and Ideal mixture relation the sound velocities were correlated and estimated for the inspected mixture of methanol with chloroform. As per their result Junjie's relation was considered to be the best relation for determining the sound velocity. The results were concluded in terms of the deviation observed in the obtained parameters that further represents the existence of interactions midst the fragments of the mixture.

Vigneswaril et al. (2016)[44] had studied and inspected the nature of intermolecular interactions of poly vinyl alcohol mixtures. The apparatus required to measure the density and sound velocity by them were specific gravity bottle and ultrasonic interferometer that works at the frequency of 1MHz. The computed thermodynamic and acoustical parameter signifies the occurrence of molecular associations. The association was stronger in case of the binary mixtures in comparison to the inspected ternary mixtures. There was the formation of competitive mechanism which was utilized to establish the hydrogen bonding among the solute and solvent fragments.

Kaur *et al* (2017)[45] had utilized the volumetric and ultrasonic studies in order to inspect the molecular interaction among (ethylene, diethylene, triethylene) glycols with respect to sorbitol as the temperature function at the temperature ranges from 288.15, 298.15, 308.15 and 318.15 K and atmospheric pressure. From the measured data of density, the values of apparent molar volume, partial molar volume, and partial molar volume of transfer were evaluated and also with the help of the sound velocity data the parameters such as apparent molar isentropic compression, partial molar isentropic compression along with the transfer partial isentropic compression were computed. The partial molar expansibility and its second order derivative were also estimated. The partial transfer molar volume and partial transfer isentropic compression were computed from the data of pair and triplet coefficients. Further the results are explained on the basis of structure forming and destroying capacity of solutes in the aqueous mixtures of solvent along with the solute-solute and solute-solvent associations occurring in the ternary solution mixtures.

Kaur *et al.* (2018)[46] had examined the various temperature dependent thermo-physical properties such as apparent and partial molar properties from the measurement of density and speed of the sound. The nature of interaction among two glycols i.e. polyethylene glycol 400 and polyethylene 4000 in aqueous solution of sorbitol had been inspected at different temperatures viz. 288.15 to 388.15 K and experimental pressure p=0.1 MPa. Apparent molar volume and partial molar volume parameters were determined from the density measurements whereas apparent molar isentropic compression and partial isentropic compression parameters were evaluated from the speed of the sound measurements. Pair and triplet coefficients were also calculated from the transfer volume and transfer isentropic compression data. The partial molar expansibility along with its first order derivatives was also evaluated. Further, the results were explained in terms of various physico-chemical interactions prevailing in the liquid mixtures.

Kaur *et al.* (2018)[47] had done the volumetric and acoustic investigation of polyethylene glycols with the molecular weight 400 and 4000 among glycerol in the aqueous medium at atmospheric pressure and in the temperature ranges from 293.15 to 308.15 K. The density data was utilized to compute the apparent molar volume, partial molar volume and transfer volume properties, on the other hand the sound velocity data was employed to evaluate the apparent molar isentropic compression, partial molar isentropic compression, and transfer isentropic compression properties. From the data of partial molar transfer properties of volume and isentropic compression, the pair and triplet coefficients were determined. From the scrutiny of these calculated parameters, the results are interpreted in terms of solute-solvent interactions occurring in the investigated ternary mixtures.

Kaur *et al.* (2018)[48] had studied the interaction of glycols i.e. ethylene glycol, diethylene glycol and triethylene glycol with glycerol in medium of water in the temperature range namely 293.15, 298.15, 303.15 and 308.15 K and at atmospheric temperature viz. 0.1 MPa. Densities and sound velocity measurements have been utilized to compute the various acoustical properties such as apparent molar volume, apparent molar volume at infinite dilution, apparent molar transfer volume at infinite dilution, apparent molar isentropic compression, apparent molar isentropic at infinite dilution, and apparent molar transfer isentropic compression at infinite dilution. The data of limiting apparent molar expansibility and its first order derivative were also determined from the calculated parameters. The examination of pair and triplet interaction coefficients had been done through the partial molar transfer properties of volume and isentropic compression. The results were analyzed through the co-solute-solvent interactions existing in the ternary liquid mixtures together with the structure building and destroying capacity of glycols in the glycerol in water medium.

Chakraborty et al. (2018)[49] had inspected the interaction of ternary mixtures of glycols viz. ethylene, diethylene and triethylene glycols midst D- panthenol with the aid of density and ultrasonic velocity measurements at the temperatures (T=293.15 to 308.15 K) and experimental pressure. From the experimental density data, partial molar transfer of volume and partial volume had been determined. Whereas, partial molar transfer of isentropic compression and partial molar isentropic compression were computed from the sound velocity measurement. The pair and triplet interaction coefficient had been estimated from the calculated data of transfer molar properties.

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OBJECTIVES AND RESEARCH METHODOLOGY

3. Objectives and research methodology

3.1 OBJECTIVES

Objectives of the research are

1) To find the ultrasonic speed, density and viscosity of ternary liquid mixtures containing parabens at different temperatures.
2) To study various acoustical parameters of liquid mixtures containing parabens at different temperatures.
3) To study apparent molar properties of ternery liquid mixtures containing parabens at different temperatures.

3.2 RESEARCH METHODOLOGY

Speed of the sound and densities of liquid mixtures will automatically and simultaneously measure by instrument named Anton Paar DSA 5000 M density and sound velocity meter. The viscosity of the liquid mixtures is done with the help of Oswald's viscometer. The instrument will be calibrated with the double distilled water and the mixtures to be used before the experiment. To avoid evaporation the liquid mixtures will be ready by mass and will placed in air tight stoppered glass bottles. The mixtures will weighed on Sartorius CPA 225D balance having accuracy of $\pm$ 0.00001g. Triple distilled and degassed water will be used as a standard liquid having specific conductance $<10^{-6}$ $S \cdot cm^{-1}$. The measurement of the density and sound velocity was done for the ternary mixture of glycols in methanol and aqueous solution of parabens at various concentrations and temperatures at atmospheric pressure viz. 0.1 MPa.

PART I

Ethylene glycol		

Propylene glycol	+ methylparaben	+ methanol
Hexylene glycol		

PART II

Ethylene glycol	+ sodium ethylparaben	+ water
Propylene glycol		

PART III

Ethylene glycol	+ propylparaben	+ methanol
Propylene glycol		

PART IV

Polyethylene glycol 200	+ sodium methylparaben	+ water
Polyethylene glycol 600		

PART V

Polyethylene glycol 200	

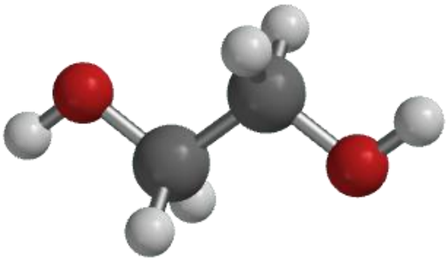
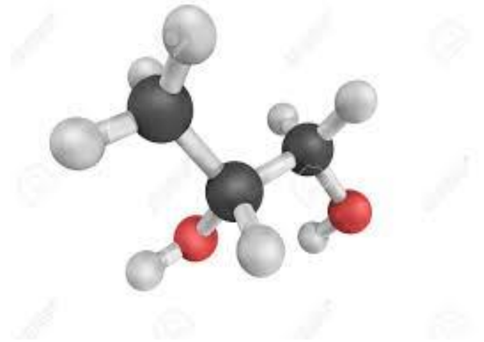
Polyethylene glycol 600	+ butylparaben + methanol

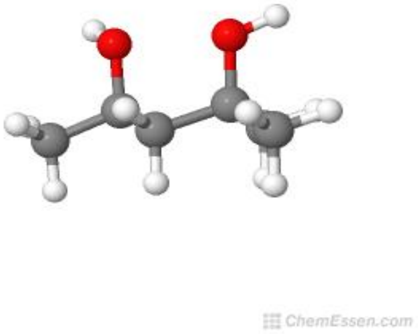
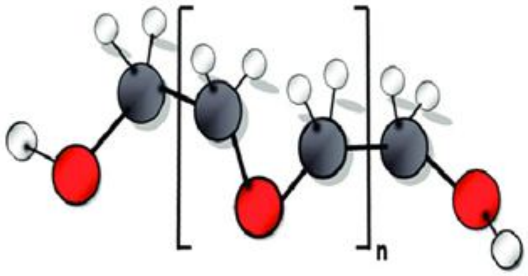
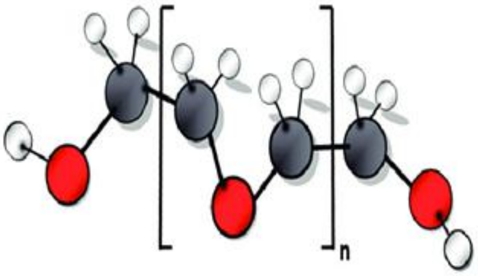
PART VI

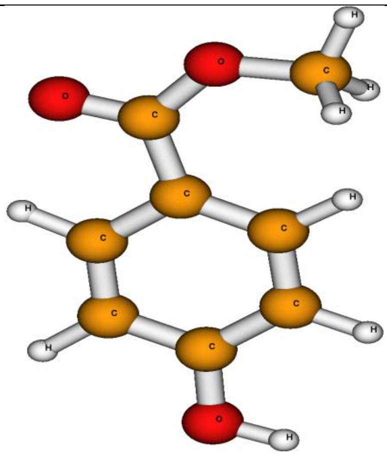
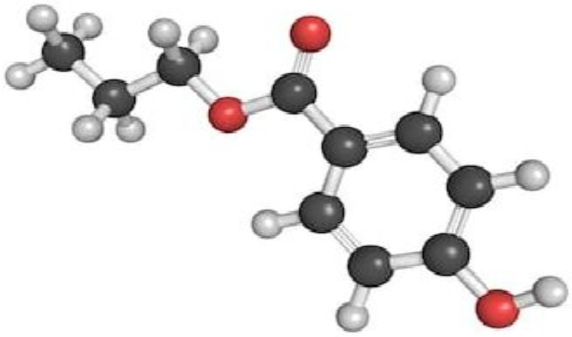
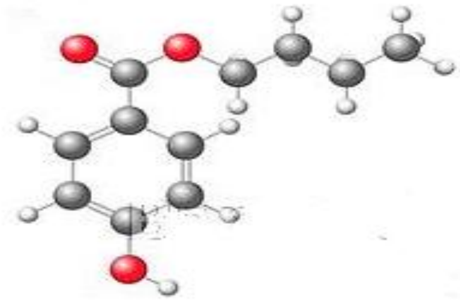
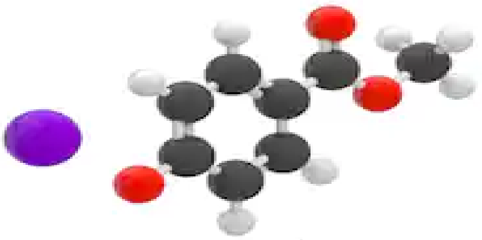
Ethylene glycol	+ Methanol + methylparaben
Propylene glycol	

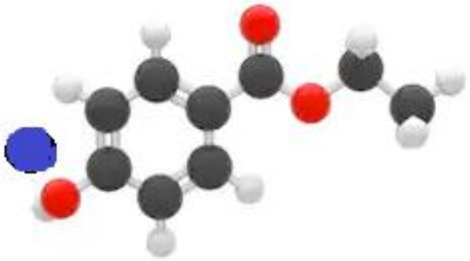
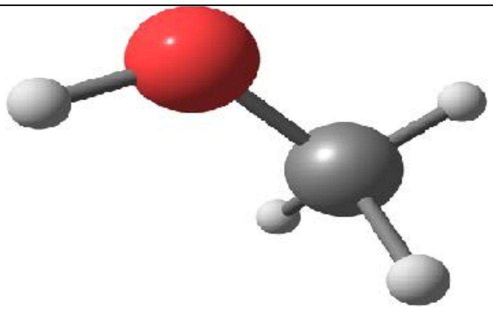
Polyethylene glycol-200	+ water + Sodium methylparaben
Polyethylene glycol-600	

3.3 STRUCTURE OF CHEMICALS UTILIZED IN THE RESEARCH

Ethylene glycol	
Propylene glycol	

Hexylene glycol	
Polyethylene glycol 200	
Polyethylene glycol 600	

Methylparaben	
Propylparaben	
Butylparaben	
Sodium methylparaben	

Sodium ethylparaben	
Methanol	

3.4 DESCRIPTION OF THE CHEMICALS EMPLOYED IN THE WORK

The following table provides the information of the chemicals employed in the research as:

Table 3.1 Description of the chemicals utilized in the research

S. No.	Chemical	Supplier	Purification method	Purity(mass fraction)
1.	Ethylene glycol	Loba Chemie Pvt. Ltd, India	None	0.995
2.	Propylene glycol	Loba Chemie Pvt. Ltd, India	None	≥0.995
3.	Hexylene glycol	Loba Chemie Pvt. Ltd, India	None	≥ 0.99
4.	Polyethylene glycol 200	Loba Chemie Pvt. Ltd, India	None	≥ 0.99
5.	Polyethylene glycol 600	Loba Chemie Pvt.	None	≥ 0.99

		Ltd, India		
6.	Methanol	Loba Chemie Pvt. Ltd, India	None	≥ 0.99
7.	Methylparaben	Loba Chemie Pvt. Ltd, India	None	≥ 0.99
8.	Propyl paraben	Loba Chemie Pvt. Ltd, India	None	≥ 0.99
9.	Butyl paraben	Loba Chemie Pvt. Ltd, India	None	≥ 0.99
10.	Sodium methylparaben	Loba Chemie Pvt. Ltd, India	Vacumm drying	≥ 0.99
11.	Sodium ethylparaben	Loba Chemie Pvt. Ltd, India	Vacumm drying	0.99

3.5 EXPERIMENTAL METHODS EMPLOYED IN THE RESEARCH

3.5.1 Different techniques employed in the recent research are given below:

- ✓ **Measurement of density and sound velocity:** The density as well as sound velocity of the ternary mixtures was computed with the help of Anton Paar DSA 5000M density and velocity meter simultaneously.
- ✓ **Measurement of viscosity:** An Oswald’s viscometer was being utilized in order to measure the viscosity of the studied liquid mixtures.

3.5.2 Working of the instruments utilized in the recent research

(i) Anton paar DSA 5000M density and velocity meter

The mixtures are made by mass with the help of Sartorius CPA 225D balance with the accuracy of ± 0.00001g. To ready the solution the degassed and newly prepared triple distilled water acquiring specific conductance ($< 10^{-6}$ S. cm^{-1}) is exercised. The density and speed of sound computation is achieved by Anton Paar DSA 5000 M density and velocity meter. The density and speed of sound are quite responsive to temperature, for that reason the temperature of the instrument was managed with the built-in Peltier device up to $\pm 1 \times 10^{-3}$ K. Anton Paar density and sound velocity analyzer measures both the two acoustical independent characteristics i.e. sound velocity and density at the same time with the one sample (Fig. 3.1 and 3.2) The time propagation methodology has been practiced to determine the speed of sound computation. Speed of the sample is obtained via dividing the familiar distance amidst receiver and transducer by the acquired prolongation time of acoustic wave. The sample is introduced among two transducers by sample filled cavity, one of which emits the acoustic waves at frequency of approximately 3MHz and other collects those released sound waves. The uncertainty of the instrument assimilates to precision in density and speed of sound measurements of 1×10^{-3} kg·m^{-3} and $1{\times}10^{-2}$ m·s^{-1}. For the different concentration computed models that are built in Anton Paar DSA density and velocity meter, the values of these parameters along with their derived parameters are quite helpful. The densities and sound velocity of the ternary mixtures of parabens with aqueous solutions of glycols has been measured through Anton Paar DSA 5000M density and velocity meter in the temperature range from 293.15, 298.15, 303.15 and 308.15 K and at experimental pressure 0.1 MPa.

Fig. 3.1 Anton Paar DSA 5000 M density and velocity meter

Anton Paar density and sound velocity analyzer measures both the two acoustical independent characteristics i.e. sound velocity and density at the same time with the one sample (Figs. 3.1 and 3.2) The instrument is the combination of the two cells; one is the density cell and other is the sound velocity cell which works along with the oscillating U-tube method together with the precise measurement of speed of sound. These constructed cells are kept at constant temperature by the use of in built Peltier thermostat. For the different concentration computed models that are built in Anton Paar DSA density and velocity meter, the values of these parameters along with their derived parameters are quite helpful.

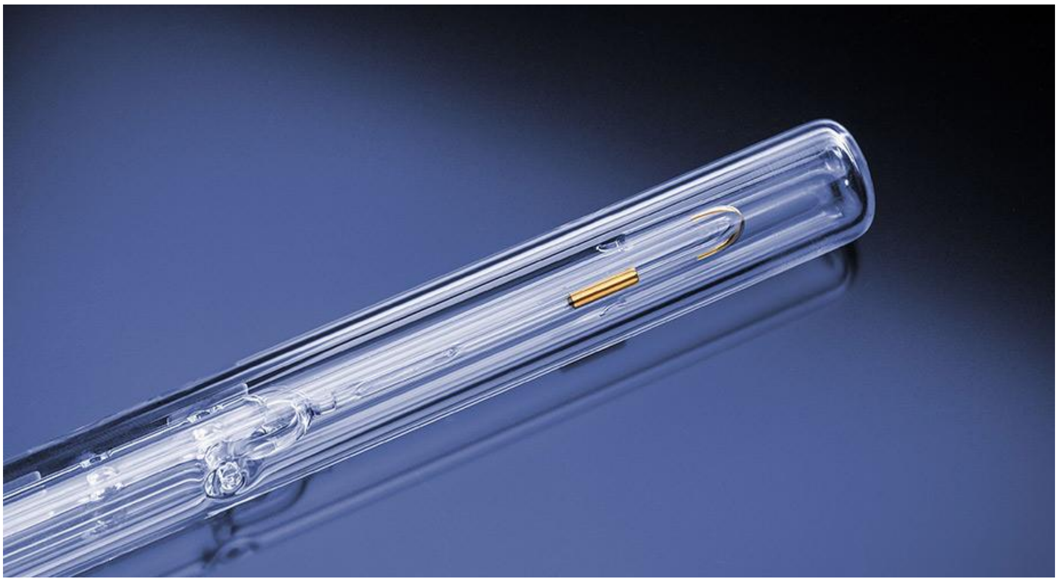


Fig. 3.2 Oscillating U-tube technique

The glass tube is U shaped and is made up of borosilicate where the prepared sample is being inserted into it as shown in the Fig. 3.3 At some frequency the inserted sample is allowed to vibrate electronically. The variation in the frequency is mostly dependent on the sample density. The density of the inspected mixture can be computed from the accurate calculation of specific frequency and the mathematical conversion.

Figure 3.3 Determination of speed of sound

The speed of sound cell comprises of transmitter on the one side and receiver on the other side and hence the mixture is inserted in to this measuring cell. The role of the transmitter is to transmit the sound waves of known time among the mixtures whereas, receiver takes those waves. The sound velocity is being computed via. Time of the received sound waves and distance among the receiver and transmitter.

Calibration Process:

First of all do the water check. Clean and then dry the density and speed of sound cell. Select the temperature to 20^0C. Now open the bottle with the liquid density standard. After that immediately inject the liquid in to Anton Paar 5000 M density and velocity meter. Now perform the measurement and hence after finishing the measurement print the result.

Precautions:

1) Before starting the measurement or cleaning process, check the injection adaptors for leak tightness.
2) Prior to starting a measurement or cleaning procedure, make sure that all parts that come into contact with fluids, especially the measuring cell, the injection adapters, hoses and waste container, are properly connected and in good condition.
3) Keep any sources of ignition, like sparks and open flames, at a safe distance from DSA 5000 M.

4) Do not spill sample/cleaning agents or leave their containers uncovered. Immediately remove spilled sample/cleaning agents.

(ii) Ostwald’s viscometer

The Ostwald’s viscometer is the apparatus required for the measurement of viscosity of the mixtures as shown in Figure 3.4. There are two bulbs situated in the arms of the instrument. One bulb is above the arm while other bulb is down the arm. The mixture is inserted from the upper bulb and the investigated liquid is allowed to get down to the lower bulb by the path of capillary. The two marks denote the known volume. The time of period of the mixture to reach down the another mark is proportional to viscosity. With the help of fluid whose properties are known, the calibration is being done. The time was measured with the precision of 0.01 s and the uncertainty was estimated to be less than 0.0003mPa.s.

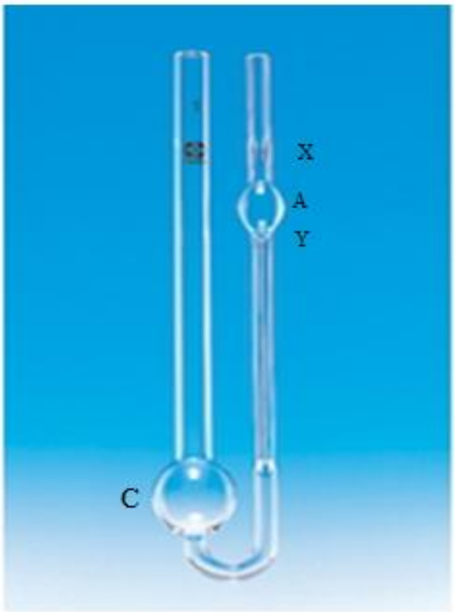


Figure 3.4 Ostwald’s viscometer

The viscosity coefficient of the investigated mixture is calculated from the following relation:

$$\eta_2 = \eta_1 (t_2/t_1) (\rho_2/\rho_1)$$

Where ρ_1 is the density of water, ρ_2 is the density of mixture, η_1 is the viscosity of water, η_2 is the viscosity of mixture, t_1 is the time of flow of water and t_2 is the time of flow of mixture.

Precautions:

1) During the flow of liquid the viscometer must be held in the vertical position.
2) There should be no formation of air bubble inside the capillary tube during sucking of liquids.
3) The volume of the liquids taken in the lower bulb (C) must be that much that when sucked up to the mark (x), it should fill the upper bulb (A) and small amount should be left in lower bulb (C).

3.6 DIFFERENT ULTRASONIC PARAMETERS

The different ultrasonic parameters derived from the density, sound velocity and viscosity are given as:

3.6.1 Acoustic impedance (Z)

Given to the transmission of sound wave in the liquid medium is known as acoustic impedance which is further termed as the product of sound velocity and density of the liquid medium. Mathematically, the acoustic impedance can be written as:

$$Z = \rho \times U \qquad (3.1)$$

Where Z denotes the acoustic impedance, U is the sound velocity and ρ is

the density of the medium.

3.6.2 Adiabatic compressibility (β)

Adiabatic compressibility is defined as the ratio of volume decrease per unit rise in the pressure when there is no flow of heat inside and outside the surrounding. The given thermodynamic relation provides the change of compressibility in liquid medium as given below:

$$\beta = (1/V)\ (dV/\ dP) \qquad (3.2)$$

Another relation among ultrasonic velocity (U) and density (ρ) of the medium to compute the adiabatic compressibility is given as:

$$\beta = 1/\ (U^2 \times \rho) \qquad (3.3)$$

3.6.3 Intermolecular free length (L_f)

An empirical formula to compute the intermolecular free length of liquids is being recommended by the Jacobson in 1952. As per the Jacobson research the intermolecular free length (L_f) is written as:

$$L_f = K_T \times \beta^{1/2} \qquad (3.4)$$

Where, β is the compressibility of the liquid and K_T is the Jacobson

constant whose value is 2.0965×10^{-6}

In terms of sound velocity and density the intermolecular free length can also be represented as:

$$L_f = K/\ (U \times \rho^{1/2}) \qquad (3.5)$$

Where, U is the sound velocity of experimental liquid

ρ is the density of liquid of experimental liquid.

3.6.4 Ultrasonic Attenuation (α)

The rate of decay of the energy due to the ultrasonic transmission in the medium is termed as ultrasonic attenuation. The factors which leads to the loss in the ultrasonic waves are scattering, refraction, reflection, absorption etc. The reduction in the ultrasonic wave intensity is defined by the ultrasonic wave attenuation coefficient (α) as:

$$\alpha/f^2 = 8\pi^2\eta\ /3\rho U^3 \qquad (3.6)$$

Where, f is the frequency of the wave.

As the ultrasonic attenuation is dependent on the square of the frequency of the wave hence it escalates with escalation in the frequency of the wave.

3.6.5 Relaxation Time (τ)

Relaxation time is defined as time taken by the fragments to come to their equilibrium position in the medium. Hence, is the relaxation time is higher, large is the energy absorption. The relation signifying the relaxation time is given as:

$$\tau = 4\beta\eta/3 \qquad (3.7)$$

The relaxation time can also be computed from the relation as:

$$\tau = 4\eta/3\rho U^2 \qquad (3.8)$$

3.6.6 Gibb's Free Energy

The energy required to do work is termed as Gibb's free energy. This energy is related to the chemical reaction which is further utilized to do work. The variation in this energy is being computed as:

$$\Delta G = K_B T \ln (K_B T \tau / h) \qquad (3.9)$$

Where K_B is the Boltzmann's constant whose value is 1.38×10^{-23}, h is the Planck's constant with the value of 6.634×10^{-34}. T is the absolute temperature i.e. 295 K, τ is the relaxation time.

3.6.7 Jone-Dole's equation

Jone-Dole's equation has been employed to study the interaction parameter as follows:

$$(\eta_0 / \eta - 1)/\sqrt{C} = A + B\sqrt{C} \qquad (3.10)$$

Where C is the molar concentration, A and B are the coefficients of the solute-solute and solute-solvent interaction. The B values were attained from the linear plot among $\sqrt{C}$ and $(\eta_0 / \eta - 1)/\sqrt{C}$

3.7 APPARENT MOLAR AND PARTIAL MOLAR PROPERTIES

3.7.1. Apparent molar volume

Apparent molar volume is termed as the difference in the volume of pure solvent per mole of solute and volume of solution. When the whole compound is added to the solution it shows the variation with respect to property of the solution hence, apparent molar volume is this property of the solution. The formula for calculation of the apparent molar volume is given by:

$$V_{\phi} = M/\rho - (\rho - \rho_0)/m_A \, \rho\rho_0 \qquad (3.11)$$

3.7.2. Limiting partial molar volume at infinite dilution

When there is no variation in the whole concentration of the solution at constant pressure, temperature and number of molecules due to the difference in the solution volume because of the addition of the solute in the whole amount of the solution is defined as the partial molar volume. It is also defined as the volume difference per mole of the component added to the solution. The equation for the partial molar volume is represented as:

$$V_{\phi} = V_{\phi}^{0} + S_V^{*} m_A \qquad (3.12)$$

3.7.3. Limiting apparent molar volume of transfer at infinite dilution

At infinite dilution, the transfer volume of solute from water to the pure solvent was evaluated through the following equation:

$$\Delta V_{\phi}^{0} = V_{\phi}^{0} \text{ (in pure solvent)} - V_{\phi}^{0} \text{ (in water)} \qquad (3.13)$$

3.7.4. Temperature dependent partial molar volume

At infinite dilution, the variation of apparent molar volume with respect to temperature
is represented as:

$$V_{\phi}^{0} = a + b(T - T_{ref}) + c(T - T_{ref})^2 \qquad (3.14)$$

Where *a*, *b* and *c* represent the empirical constants and *T* is the temperature i.e. 298.15K. These parameters were used to calculate V_{ϕ}^{0} and deviations attained from calculated and experimental values. The deviations are calculated from the following equation:

$$\sigma = (1/n)\ \Sigma[abs((Y_{exptl.} - Y_{calc.})/Y_{exptl.})] \quad (3.15)$$

where Y = V_ϕ^0 (apparent molar volume at infinite dilution).

At infinite dilution, the temperature dependence of partial molar volume (V_ϕ^0) can be uttered in terms of absolute temperature (*T*) by the following equation (6). The same equation (6) is used to calculate partial molar expansibilities as follows:

$$E_\phi^0 = (\partial V_\phi^0/\partial T)_p = b + 2c(T - T_{ref}) \quad (3.16)$$

The following thermodynamic expression determined the structure making and breaking ability of solute in solvent using the following equation:

$$(\partial E_\phi^0/\partial T)_p = (\partial^2 V_\phi^0/\partial T^2)_p = 2c \quad (3.17)$$

3.7.5. Apparent molar isentropic compression

By using the following equation, apparent molar isentropic compression of solute in the aqueous solution of a chemical sample is calculated

$$K_{\phi,s} = (M\beta_s/\rho) - (\beta_s\rho_0 - \beta_{s,0}\rho)m_A\rho\rho_0 \quad (3.18)$$

Where $m_A, M, \rho, \rho_o, \beta_{s,0}$ and β_s are the molality of solute, the molar mass of the solute, density of the solvent and the solution, isentropic compressibility of the pure solvent and the solution accordingly. The isentropic compressibility is determined by the following expression-

$$\beta s = 1/u^2\rho \quad (3.19)$$

Where ρ and u are the density and ultrasonic velocity of the solution respectively.

3.7.6. Limiting molar isentropic compression at infinite dilution

By the following equation, the change in apparent molar isentropic compression $K_{\phi,s}$ with the molar concentration is given as

$$K_{\phi,s} = K_{\phi,s}^o + S_K^* m_A \quad (3.20)$$

Where, S_K^* is an experimental slope suggestive of solute-solute interactions.

3.7.7. Limiting molar isentropic compression of transfer at infinite dilution

At infinite dilution, the partial molar isentropic compressions $\Delta K_{\phi,S}^{0}$ of glycols in aqueous solution of chemical sample is calculated with the following equation

$$\Delta K_{\phi,s}^{o} = K_{\phi,s}^{o} \text{ (in aqueous chemical sample)} - K_{\phi,s}^{o} \text{ (in water)} \tag{3.21}$$

3.7.8. Pair and triplet interaction coefficients

From the following relation, the partial molar volume of transfer and the partial molar isentropic compression of transfer can be obtained

$$\Delta V_{\phi}^{0}\text{(water to aqueous chemical sample solution)} = 2V_{AB}m_B + 3V_{ABB}m_B^2 \tag{3.22}$$

$$\Delta K_{\phi,s}^{o}\text{(water to aqueous chemical sample solution)} = 2K_{AB}m_B + 3K_{ABB}m_B^2 \tag{3.23}$$

Where A represent glycols and B represent chemical sample and m_B denotes the molality of the aqueous chemical sample solutions. The pair and triplet interaction coefficient are represented by the parameters V_{AB} and V_{ABB} for volume, and K_{AB}, K_{ABB} for isentropic compression.

RESULT AND DISCUSSION

4. Result and discussion

PART I

In this part, we have reported the densities, ρ and speed of sound u of ethylene glycol (EG), propylene glycol (PG), and hexylene glycol (HG) in (0.00, 0.01, 0.03, 0.05) mol·kg^{-1} methanol solutions of methylparaben at temperatures T = (293.15, 298.15, 303.15, 308.15) K.

Analysis of density and speeds of sound data

The upsurge in density also implies the escalation in the solvent—solvent and solute—solvent interactions [2]. The experimental values of density for EG + methanol, PG + methanol, and methylparaben + methanol at different temperatures are in good agreement with the literature values [3—6], as shown in **Figure 1—3**. From the scrutiny of figures, it is observed that the experimental densities for the mixture under investigation show the same trend as literature densities. The data of the speed of sound in the solution mixture gives important information concerning ion—solvent, solvent—solvent, and ion—ion interactions [7, 8]. The greater association results due to intermolecular hydrogen bonding among solute and solvent molecule and intra molecular hydrogen bonding among solute molecules alone [9, 10]. It can be seen that the values of speed of sound increases with MePB—MeOH molality for all the concentrations of EG, PG, and HG but decreases with increase in temperature.

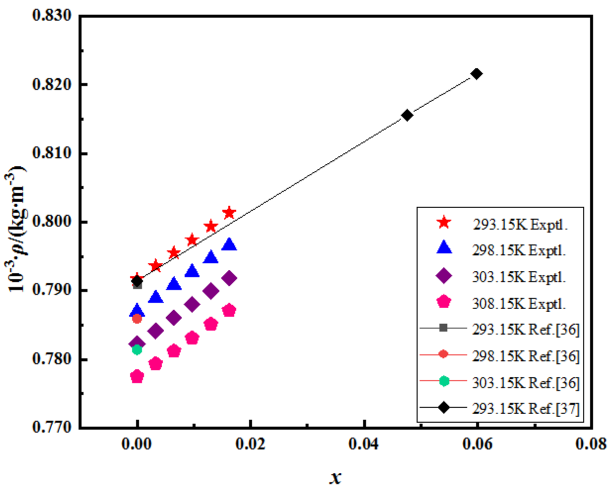


Figure 1: Plot of experimental and literature values [3, 4] of density for EG + methanol mixtures at different temperatures**.**

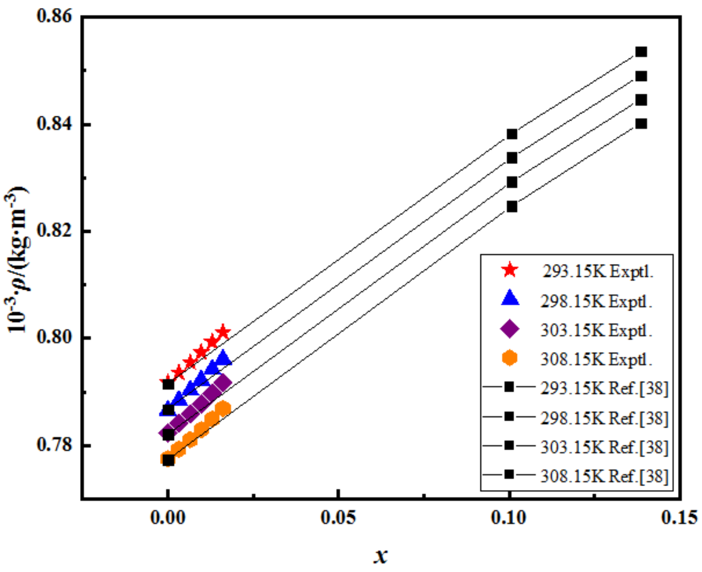


Figure 2: Plot of experimental and literature values [5] of density for PG + methanol at different temperatures.

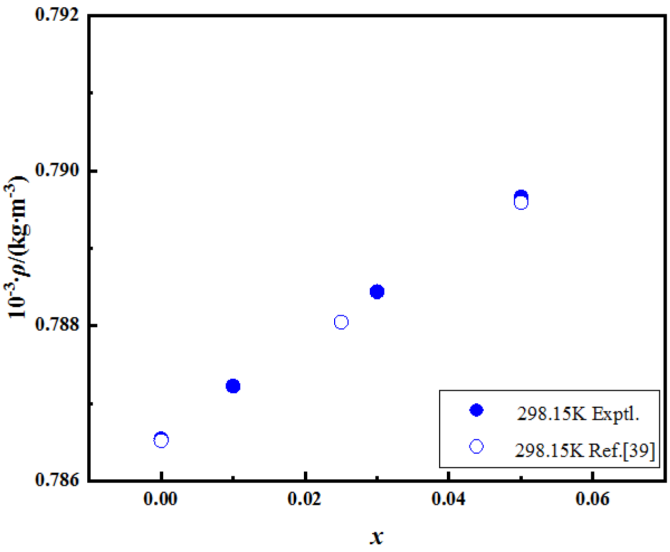


Figure 3: Plot of experimental and literature values [6] of density for methylparaben +methanol at T= 298.15K.

The experimental density and speed of sound data for the pure chemicals used in this study were compared with the literature values and listed in **Table 4.1**.

Table 4.1 Comparison of Experimental densities (ρ) and ultrasonic velocities (u) with literature values for pure chemicals at different temperatures

Chemicals	T / K	$10^{-3} \cdot \rho$ / (kg·m^{-3})		u / (m·s^{-1})	
		Experimental	Literature	Experimental	Literature
Methanol	293.15	0.791666	0.791786[30] 0.79145[37] 0.7910[36]	1120.07	1118.91[30] 1119.0[40]
	298.15	0.786968	0.786548[30] 0.7866[31] 0.78657[32]	1103.59	1102.62[30] 1105.1[33]
	303.15	0.782246	0.78185[32] 0.782286[30] 0.7814[36]	1087.2	1086.0[73] 1086.03[30]
	308.15	0.777507	0.77728[33] 0.77710[32]	1071.06	1069.80[30]
Ethylene glycol	293.15	1.112856	1.11323[35]	1667.64	1669.5[34]
	298.15	1.109359	1.1097[31]	1655.94	1656.4[34] 1660.7[33]
	303.15	1.105854	1.10546[35]	1644.26	1645.2[34]

	308.15	1.102341	1.10250[35]	1632	1633.0[34]
Propylene glycol	293.15	1.036381	1036.214[37]	1524.95	1509.3[34] 1522.42[37]
	298.15	1.03271	1.0325[31] 1.03261[32]	1511.23	1508.41[37] 1500.6[34]
	303.15	1.028998	1.02902[36] 1.02890[32]	1497.31	1494.33[37] 1495.5[34]
	308.15	1.025253	1.02540[36] 1.02516[32]	1483.39	1480.19[37] 1489.2[34]
Hexylene glycol	293.15	0.929898	921.676[1] 0.9218[38]	1480.78	1404[39]
	298.15	0.91824	918.110[1]	1470.34	
	303.15	0.918596	914.548[1] 0.9145[38]	1463.12	
	308.15	0.908378	910.981[1]	1450.98	

Standard uncertainties u are $u(T) = 0.01$ K, $u(\rho) = 0.7$ kg·m^{-3}, $u(u) = 1.0$ m·s^{-1}

Most of the experimental data show satisfactory agreement with those reported in the literature. The speed of the sound and density values that are experimentally obtained for glycols (EG, PG, and HG) in (0.00, 0.01, 0.03, and 0.05) mol·kg^{-1} of MePB—MeOH solutions at T = (293.15, 298.15, 303.15, and 308.15) K are presented in **Table 4.2**.

Table 4.2 Densities (ρ), and speed of sound (u) of (EG/PG/HG+ MePB-MeOH) ternary systems at different temperatures.

^{a}m /(mol·kg^{-1})	$10^{-3} \cdot \rho$ / (kg·m^{-3})				u / (m·s^{-1})			
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
EG + 0.00 mol·kg^{-1} MePB								
0.00000	0.791666	0.786540	0.782246	0.777507	1120.07	1103.59	1087.20	1071.06
0.10204	0.793604	0.788471	0.784132	0.779387	1123.86	1107.57	1090.82	1075.34
0.20198	0.795491	0.790370	0.785969	0.781226	1127.52	1111.34	1094.71	1079.32
0.30198	0.797371	0.792252	0.787885	0.783100	1131.09	1114.99	1098.59	1083.34
0.40608	0.799313	0.794196	0.789899	0.785082	1134.85	1118.96	1102.42	1087.57
0.50607	0.801237	0.796130	0.791828	0.786980	1138.36	1122.65	1106.05	1091.49
EG + 0.01 mol·kg^{-1} MePB								
0.00000	0.792305	0.787220	0.782874	0.778169	1121.61	1105.05	1088.57	1072.72
0.09986	0.794197	0.789101	0.784712	0.780004	1125.48	1108.92	1092.42	1076.86
0.19552	0.796003	0.790923	0.786476	0.781753	1128.99	1112.45	1096.16	1080.59
0.30041	0.797976	0.792898	0.788475	0.783688	1132.61	1116.34	1100.11	1084.89
0.39780	0.799790	0.794712	0.790362	0.785537	1135.99	1119.96	1103.58	1088.78
0.49906	0.801723	0.796668	0.792312	0.787429	1139.56	1123.73	1107.16	1093.12
EG + 0.03 mol·kg^{-1} MePB								
0.00000	0.793618	0.788440	0.784119	0.779393	1124.43	1107.82	1091.34	1075.61
0.10375	0.795574	0.790389	0.786017	0.781287	1127.91	1111.66	1094.99	1080.05
0.20032	0.797392	0.792218	0.787800	0.783048	1131.34	1115.14	1098.58	1084.05
0.30210	0.799302	0.794127	0.789727	0.784923	1134.87	1118.77	1102.28	1088.02
0.39976	0.801119	0.795941	0.791609	0.786770	1138.23	1122.23	1105.79	1091.78

0.50190	0.803067	0.797890	0.793578	0.788678	1141.61	1126.01	1109.32	1095.82
EG + 0.05 mol·kg^{-1} MePB								
0.00000	0.794830	0.789660	0.785386	0.780643	1127.08	1110.42	1093.99	1078.62
0.09789	0.796660	0.791487	0.787175	0.782429	1130.11	1113.91	1097.41	1082.32
0.19932	0.798570	0.793389	0.789027	0.784281	1133.46	1117.44	1101.25	1086.49
0.30200	0.800481	0.795320	0.790975	0.786090	1136.80	1121.11	1105.02	1090.59
0.40096	0.802320	0.797158	0.792864	0.788041	1140.11	1124.55	1108.79	1094.74
0.50218	0.804260	0.799100	0.794848	0.789919	1143.48	1128.31	1112.38	1098.89
PG + 0.00 mol·kg^{-1} MePB								
0.00000	0.791666	0.786540	0.782246	0.777507	1120.07	1103.59	1087.20	1071.06
0.10182	0.793556	0.788399	0.784100	0.779268	1124.29	1107.93	1091.39	1075.71
0.20630	0.795483	0.790309	0.785900	0.781057	1128.07	1111.87	1095.36	1080.29
0.30600	0.797360	0.792207	0.787721	0.782901	1131.64	1115.74	1099.20	1084.48
0.40701	0.799282	0.794186	0.789689	0.784888	1135.32	1119.66	1102.98	1088.67
0.50498	0.801099	0.796077	0.791709	0.786883	1138.99	1123.63	1106.32	1092.99
PG + 0.01 mol·kg^{-1} MePB								
0.00000	0.792305	0.787220	0.782874	0.778169	1121.61	1105.05	1088.57	1072.72
0.10096	0.794154	0.789041	0.784658	0.779909	1125.59	1109.29	1093.11	1077.24
0.19642	0.795886	0.790804	0.786292	0.781544	1129.45	1112.92	1096.86	1081.23
0.29903	0.797790	0.792732	0.788207	0.783418	1133.29	1116.85	1100.80	1085.56
0.40085	0.799717	0.794710	0.790172	0.785430	1136.78	1120.88	1104.48	1089.78
0.49594	0.801525	0.796571	0.792158	0.787363	1140.45	1124.58	1107.83	1093.83
PG + 0.03 mol·kg^{-1} MePB								
0.00000	0.793618	0.788440	0.784119	0.779393	1124.43	1107.82	1091.34	1075.61

0.10151	0.795461	0.790265	0.785898	0.781120	1128.11	1112.22	1095.22	1080.31
0.20210	0.797287	0.792086	0.787618	0.782851	1131.93	1115.99	1099.24	1084.57
0.30056	0.799082	0.793883	0.789442	0.784651	1135.44	1119.79	1102.77	1088.54
0.39985	0.800919	0.795891	0.791336	0.786617	1138.98	1123.53	1106.28	1092.59
0.49429	0.802773	0.797718	0.793282	0.788530	1142.68	1127.02	1110.08	1096.59
PG + 0.05 mol·kg^{-1} MePB								
0.00000	0.794830	0.789660	0.785386	0.780643	1127.08	1110.42	1093.99	1078.62
0.10144	0.796664	0.791399	0.787056	0.782326	1130.63	1114.51	1097.98	1082.97
0.19964	0.798441	0.793224	0.788833	0.784029	1134.10	1118.19	1101.42	1087.22
0.30039	0.800272	0.795085	0.790693	0.785852	1137.69	1122.18	1105.47	1091.48
0.39829	0.802028	0.797014	0.792532	0.787698	1141.15	1125.98	1109.01	1095.59
0.49844	0.804018	0.798979	0.794568	0.789634	1144.87	1129.88	1113.06	1100.00
HG + 0.00 mol·kg^{-1} MePB								
0.00000	0.791666	0.786540	0.782246	0.777507	1120.07	1103.59	1087.20	1071.06
0.10095	0.793485	0.788395	0.784094	0.779159	1124.40	1108.09	1091.45	1075.97
0.19767	0.795208	0.790198	0.785854	0.780722	1128.23	1111.98	1095.50	1080.34
0.29889	0.797038	0.792099	0.787654	0.782325	1132.26	1116.24	1099.78	1084.78
0.39935	0.798941	0.794070	0.789490	0.783888	1136.19	1120.36	1103.89	1089.19
0.49163	0.800694	0.795883	0.791309	0.785308	1139.85	1123.99	1107.77	1093.17
HG + 0.01 mol·kg^{-1} MePB								
0.00000	0.792310	0.787220	0.782874	0.778169	1121.61	1105.05	1088.49	1071.93
0.09994	0.794105	0.789035	0.784569	0.779709	1125.94	1109.48	1093.02	1076.56
0.20005	0.795879	0.790858	0.786276	0.781334	1130.09	1113.70	1097.31	1080.92
0.29956	0.797710	0.792699	0.788114	0.782978	1133.99	1117.83	1101.67	1085.51

0.39624	0.799578	0.794622	0.789889	0.784477	1137.88	1121.94	1105.66	1090.51
0.48700	0.801298	0.796368	0.791729	0.785868	1141.65	1125.49	1109.54	1094.52
HG + 0.03 mol·kg^{-1} MePB								
0.00000	0.793618	0.788440	0.784119	0.779393	1124.43	1107.82	1091.34	1075.61
0.10151	0.795410	0.790265	0.785811	0.780916	1128.38	1112.28	1095.49	1080.35
0.20210	0.797203	0.792076	0.787508	0.782551	1132.43	1116.45	1099.85	1084.69
0.30056	0.799001	0.793928	0.789302	0.784151	1136.35	1120.42	1104.15	1088.88
0.39985	0.800886	0.795802	0.791106	0.785677	1140.46	1124.57	1108.33	1093.18
0.49429	0.802667	0.797658	0.792862	0.787130	1144.38	1128.63	1112.55	1096.93
HG + 0.05 mol·kg^{-1} MePB								
0.00000	0.794830	0.789660	0.785386	0.780643	1127.08	1110.42	1093.99	1078.62
0.10291	0.796622	0.791479	0.786984	0.782169	1131.25	1114.65	1098.29	1083.21
0.19788	0.798311	0.793198	0.788530	0.783694	1134.97	1118.46	1102.33	1087.31
0.29985	0.800148	0.795073	0.790398	0.785355	1138.99	1122.88	1106.82	1091.62
0.40048	0.802009	0.796848	0.792299	0.786885	1142.98	1127.26	1111.18	1095.71
0.50399	0.803922	0.798835	0.794222	0.788440	1147.09	1131.93	1115.45	1100.02

Apparent molar properties

The apparent molar volume V_ϕ and the apparent molar isentropic compressibility $K_{\phi,s}$ can be calculated by using the following equations:

$$V_\phi = (M/\rho) - (\rho - \rho_0)/\ m\rho\rho_0 \qquad (4.1)$$

$$K_{\phi,s} = (M\beta_s/\rho) - (\beta_s\rho_0 - \beta_{s,0}\rho)m\rho\rho_0 \qquad (4.2)$$

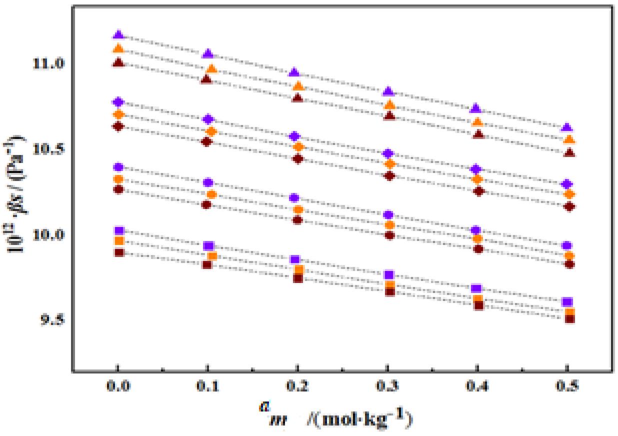
where M represents the molar mass ($\text{kg}\cdot\text{mol}^{-1}$) of the solute, m states the molality ($\text{mol}\cdot\text{kg}^{-1}$) of the solution, that is, the quantity of the solute (EG, PG, and HG) per kilogram of solvent (MePB—MeOH), and ρ_0 and ρ are the densities ($\text{kg}\cdot\text{m}^{-3}$) of the solution mixture and the pure solvent, respectively. β_s and $\beta_{s,0}$ are the isentropic compressibility of the solution and the solvent respectively.

Laplace – Newton's equation explains the isentropic compressibility [11] as follows:

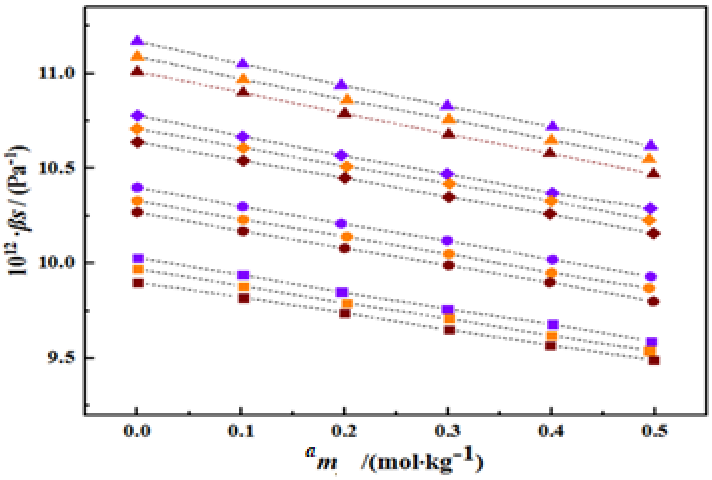
$$\beta_s = 1/(u^2\rho) \qquad (4.3)$$

where u is speed of sound and ρ is the density of the solution.

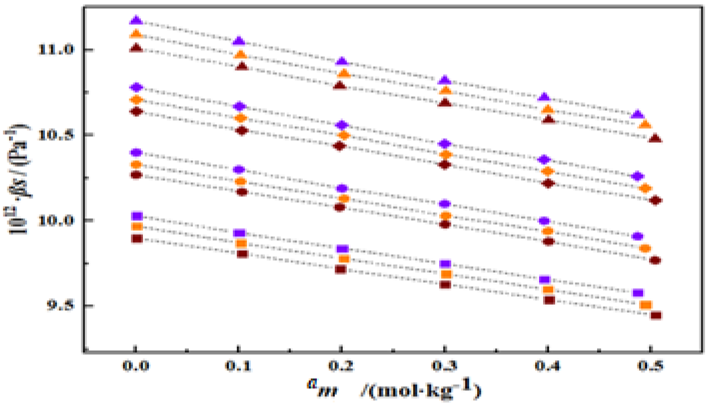
The isentropic compressibility β_s is defined as : solute intrinsic isentropic compressibility, which arises due to the hydration shell of solute (glycols) compression and solvent intrinsic compressibility, which results because of solvent molecules compression. The plot of isentropic compressibility versus molality for EG, PG and HG at different temperatures are shown in **Figure 4**.



(a)



(b)



(c)

Figure 4: Plot of isentropic compressibility, β_S against molality ${}^am$ for (a) EG (b) PG and (c) HG at different temperatures. (Cube, T = 293.15 K; Circle, T = 298.15 K; Diamond, T = 303.15 K; Triangle, T = 308.15 K) (Purple, 0.01 mol·kg^{-1}; Orange, 0.03 mol·kg^{-1}; Wine, 0.05 mol·kg^{-1})

In the present investigated system, β_s values decrease with increase in the solute concentration due to the combined effect of hydration of solute and disruption of solvent molecules structure because β_s (solute intrinsic) dominates over β_s (solvent intrinsic) effect. The same trend has been observed in the (BMIMBr + methanol) system [12].

Table 4.3 Apparent molar volume (V_{ϕ}) and apparent molar isentropic compressibility ($K_{\phi,s}$) of EG, PG and HG in MeOH solution of MePB ternary systems at different temperatures.

^{a}m /(mol·kg^{-1})	$10^{6}\cdot V_{\phi}$ / (m^{3}·mol^{-1})				$10^{6}\cdot K_{\phi,s}$ / (m^{3}·mol^{-1}·GPa^{-1})			
	T =293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T =293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
EG + 0.00 mol·kg^{-1} MePB								
0.10204	48.05	48.21	49.03	49.24	-78.67	-81.02	-83.46	-85.98
0.20198	47.99	48.03	49.00	49.14	-79.47	-81.86	-84.33	-86.88
0.30198	47.94	47.99	48.49	48.84	-79.87	-82.27	-84.76	-87.33
0.40608	47.91	47.97	48.09	48.50	-80.17	-82.59	-85.10	-87.67
0.50607	47.66	47.70	47.83	48.28	-80.43	-82.85	-85.37	-87.96
EG + 0.01 mol·kg^{-1} MePB								
0.09986	48.12	48.34	49.14	49.31	-78.42	-80.77	-83.22	-85.68
0.19552	48.03	48.06	49.00	49.27	-79.22	-81.61	-84.08	-86.58
0.30041	47.95	48.00	48.52	49.08	-79.64	-82.05	-84.54	-87.05
0.39780	47.93	48.00	48.11	48.72	-79.93	-82.35	-84.86	-87.37
0.49906	47.73	47.73	47.85	48.54	-80.19	-82.62	-85.14	-87.66
EG + 0.03 mol·kg^{-1} MePB								
0.10375	47.19	47.22	47.50	48.01	-78.08	-80.43	-82.85	-85.28
0.20032	47.20	47.24	47.55	48.13	-78.85	-81.22	-83.68	-86.14
0.30210	48.38	48.39	48.27	48.18	-79.25	-81.64	-84.12	-86.59
0.39976	49.46	49.45	49.38	49.37	-79.53	-81.94	-84.43	-86.91
0.50190	51.05	51.07	51.05	51.06	-79.79	-82.20	-84.71	-87.19

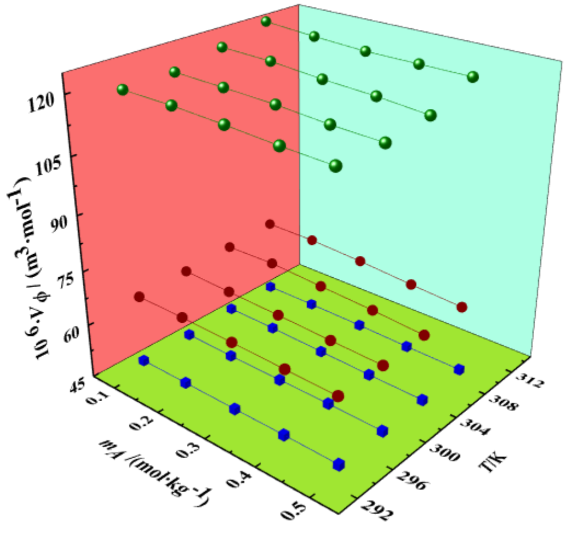
EG + 0.05 mol·kg^{-1} MePB								
0.09789	48.39	48.56	49.29	49.46	-77.63	-79.97	-82.37	-84.72
0.19932	48.16	48.37	49.19	49.33	-78.47	-80.84	-83.27	-85.65
0.30200	48.13	48.20	48.68	49.57	-78.87	-81.26	-83.71	-86.09
0.40096	48.07	48.16	48.34	48.77	-79.16	-81.55	-84.02	-86.42
0.50218	47.80	47.88	47.91	48.62	-79.41	-81.82	-84.30	-86.70
PG+ 0.00 mol·kg^{-1} MePB								
0.10182	66.41	67.07	67.36	69.10	-78.66	-81.00	-83.45	-85.96
0.20630	66.30	66.89	68.02	69.08	-79.48	-81.86	-84.33	-86.88
0.30600	65.97	66.33	67.57	68.23	-79.87	-82.27	-84.75	-87.31
0.40701	65.64	65.74	66.76	67.23	-80.17	-82.59	-85.07	-87.65
0.50498	65.54	65.42	65.86	66.35	-80.41	-82.85	-85.36	-87.94
PG + 0.01 mol·kg^{-1} MePB								
0.10096	66.79	67.40	68.21	69.17	-79.67	-82.07	-84.57	-87.08
0.19642	66.73	66.91	68.50	69.11	-79.84	-82.25	-84.75	-87.27
0.29903	66.38	66.45	67.63	68.33	-80.03	-82.45	-84.95	-87.48
0.40085	65.98	65.88	66.86	67.24	-80.22	-82.66	-85.17	-87.70
0.49594	65.67	65.45	65.87	66.38	-80.41	-82.85	-85.38	-87.92
PG + 0.03 mol·kg^{-1} MePB								
0.10151	66.92	67.43	68.38	69.47	-79.27	-81.66	-84.14	-86.61
0.20210	66.76	67.18	68.57	69.15	-79.45	-81.85	-84.32	-86.81
0.30056	66.57	66.91	67.77	68.37	-79.63	-82.03	-84.52	-87.01
0.39985	66.28	65.91	67.07	67.26	-79.81	-82.24	-84.72	-87.23

0.49429	65.72	65.54	66.12	66.42	-80.00	-82.43	-84.93	-87.44
PG + 0.05 mol·kg^{-1} MePB								
0.10144	66.96	68.71	70.04	70.09	-78.89	-81.27	-83.72	-86.13
0.19964	66.80	67.42	68.59	69.34	-79.07	-81.46	-83.91	-86.32
0.30039	66.60	66.94	67.78	68.56	-79.25	-81.65	-84.11	-86.52
0.39829	66.52	66.13	67.18	67.79	-79.42	-81.85	-84.30	-86.72
0.49844	65.79	65.60	66.24	67.10	-79.62	-82.05	-84.52	-86.93
HG+ 0.00 mol·kg^{-1} MePB								
0.10095	118.34	120.26	120.87	124.66	-79.88	-82.28	-84.78	-87.34
0.19767	117.08	119.78	120.69	124.57	-80.05	-82.47	-84.98	-87.51
0.29889	116.66	119.34	120.67	124.56	-80.24	-82.67	-85.17	-87.69
0.39935	116.40	118.30	120.31	124.54	-80.43	-82.88	-85.37	-87.87
0.49163	116.14	118.13	119.56	124.50	-80.60	-83.07	-85.57	-88.03
HG + 0.01 mol·kg^{-1} MePB								
0.09994	120.27	120.54	123.01	126.17	-79.65	-82.06	-84.55	-87.06
0.20005	120.19	120.22	122.67	125.23	-79.83	-82.25	-84.74	-87.24
0.29956	119.62	119.77	121.60	124.58	-80.02	-82.45	-84.94	-87.42
0.39624	118.84	118.86	120.98	124.56	-80.21	-82.65	-85.13	-87.59
0.48700	118.41	118.43	119.93	124.53	-80.38	-82.83	-85.33	-87.74
HG + 0.03 mol·kg^{-1} MePB								
0.10151	120.64	120.69	123.33	126.69	-79.26	-81.65	-84.13	-86.59
0.20210	120.22	120.39	122.91	125.39	-79.43	-81.84	-84.31	-86.77
0.30056	119.67	119.68	121.86	124.80	-79.61	-82.03	-84.50	-86.95

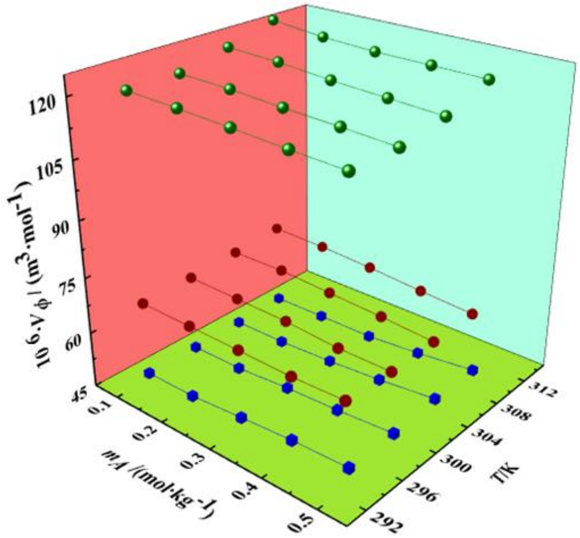
0.39985	118.97	119.15	121.21	124.75	-79.80	-82.23	-84.69	-87.12
0.49429	118.50	118.50	120.60	124.62	-79.98	-82.42	-81.92	-87.28
HG + 0.05 mol·kg^{-1} MePB								
0.10291	120.85	121.03	125.04	126.80	-78.88	-81.27	-83.71	-86.10
0.19788	120.31	120.44	124.21	125.59	-79.05	-81.45	-83.87	-86.27
0.29985	119.81	119.88	122.59	124.84	-79.23	-81.64	-84.07	-86.46
0.40048	119.23	119.78	121.42	124.81	-79.42	-81.82	-84.27	-86.62
0.50399	118.77	119.08	120.69	124.75	-79.61	-82.03	-84.48	-86.80

[a] m represents the molality of EG, PG and HG in MeOH solution of MePB, p = 0.1MPa states the experimental pressure. Standard uncertainties u are $u_r(m)$ = 1%, u (T) = 0.01 K and u (p) = 0.01MPa.

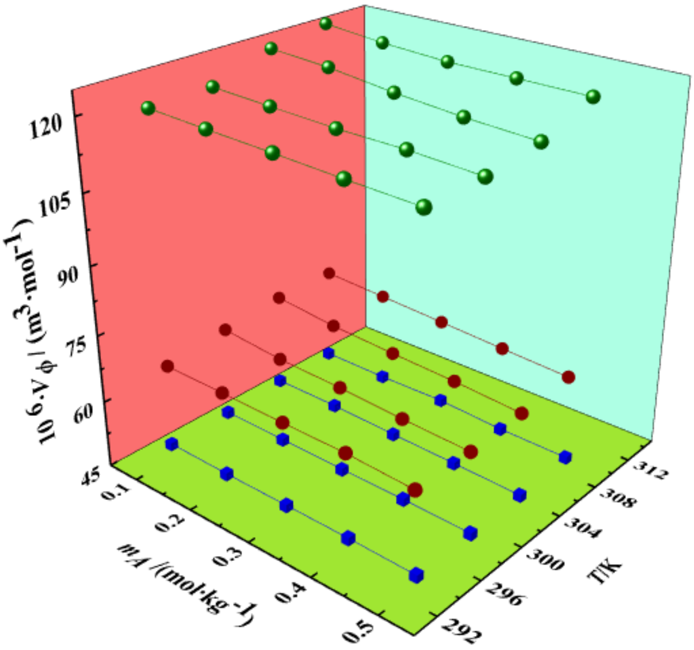
Figure 5 allocates the graphical representation of the V_ϕ values for EG, PG, and HG in (0.01, 0.03, and 0.05) mol·kg^{-1} of the MePB—MeOH solution.



(a)



(b)



(c)

Figure 5: Apparent molar volume V_ϕ against molality m_A for EG, PG and HG in (a) 0.01mol·kg^{-1} MeOH solution of MePB (Cube EG , Dot PG , Sphere HG); (b) 0.03 mol·kg^{-1}MeOH solution of MePB (Cube EG , Dot PG , Sphere HG); (c) 0.05 mol·kg^{-1}MeOH solution of MePB (Cube EG , Dot PG , Sphere HG) at different temperatures.

The value of V_ϕ in general escalates with upsurge in temperature along with the MePB concentration for all the inspected ternary systems except for EG in 0.03 mol·kg$^{—1}$ of MePB—MeOH solutions and 0.05 mol·kg$^{—1}$ of MePB—MeOH solutions. From the data, it can be seen that the V_ϕ values are positive, which infers the occurrence of strong solute—solvent interactions. Moreover, the positive V_ϕ values represents greater solute—solvent interactions that further increases from EG to PG to HG at all temperatures. The same trend of increasing V_ϕ values with increase in temperature have been observed in the V_ϕ values of glycol in the aqueous solution of sorbitol [13] and DEEAP + H_2O system [14]. Furthermore, the $K_{\phi,s}$ value obtained from Eq. (2) is negative at all temperature and concentration for all the investigated ternary system. The negative $K_{\phi,s}$ values specify the manifestation of strong attractive interaction among solvent and solute as a result of solvation of the solute [15]. It can be noticed from the data that the apparent molar isentropic compressibility decreases with increase in the concentration of solute (glycols) and temperature for all the studied system at fixed temperature. The solute—solvent interaction for HG in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} of the MePB—MeOH system are greater than EG and PG in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} of the MePB—MeOH system. The same trend of negative $K_{\phi,s}$ values has also been detected in the solution of electrolytes with methanol [16] at different temperatures.

The apparent molar volume V_{ϕ} and the apparent molar isentropic compressibility $K_{\phi,s}$ were correlated through the following equation:

$$V_{\phi} = V_{\phi}^{0} + S_{v} m_{A} \tag{4.4}$$

$$K_{\phi,s} = K_{\phi,s}^{0} + S_{k}\, m_{A} \tag{4.5}$$

where V_{ϕ}^{0} and $K_{\phi,s}^{0}$ are the limiting partial molar volume and limiting partial molar isentropic compressibility at infinite dilution. S_v and S_k are the experimental slopes (volumetric and ultrasonic virial coefficients), which represents the solute—solute interactions.

The limiting partial molar volume is considered as an essential tool for explaining different types of interactions occurring in aqueous as well as non-aqueous solutions such as solute—solvent, ion—ion and ion—solvent interactions [17, 18]. The V_{ϕ}^{0} values measures only interactions among solute—solvent despite solute—solute interactions at infinite dilution [19, 20]. The magnitude of limiting partial molar volume (V_{ϕ}^{0}) is found to be positive for all the investigated systems, availing the existence of strong interactions between the solute and the solvent [21, 22].

These computed values along with the standard errors are derived by the method of least square fitting of V_{ϕ} and $K_{\phi,s}$ values that belong to Eqs. (4) and (5). These parameters with their standard errors are reported in **Tables 4.4** and **4.5**.

Table 4.4 Limiting partial molar volume, V_ϕ^0 and experimental slopes, S_v of EG, PG and HG in MeOH solution of MePB at different temperatures.

$^a m_B$ /(mol·kg^{-1})	T = 293.15K	T = 298.15K	T = 303.15K	T = 308.15K
Ethylene glycol				
$10^6 \cdot V_\phi^0$ / (m^3·mol^{-1})				
0.00	48.16(±0.07)	48.30(±0.08)	49.48(±0.13)	49.56(±0.07)
0.01	48.21(±0.05)	48.40(±0.09)	49.55(±0.09)	49.60(±0.09)
0.03	48.46(±0.15)	48.67(±0.08)	49.68(±0.05)	49.77(±0.08)
0.05	48.48(±0.07)	48.70(±0.05)	49.75(±0.11)	49.81(±0.28)
$10^6 \cdot S_V$ / (m^3·kg·mol^{-2})				
0.00	-0.82(±0.22)	-1.05(±0.24)	-3.28(±0.40)	-2.52(±0.22)
0.01	-0.88(±0.15)	-1.29(±0.29)	-3.46(±0.28)	-2.07(±0.29)
0.03	-1.76(±0.45)	-1.56(±0.26)	-3.54(±0.16)	-2.31(±0.24)
0.05	-1.25(±0.23)	-1.55(±0.17)	-3.58(±0.35)	-2.20(±0.86)
Propylene glycol				
$10^6 \cdot V_\phi^0$ / (m^3·mol^{-1})				
0.00	66.70(±0.09)	67.64(±0.14)	68.40(±0.60)	70.22(±0.37)
0.01	67.21(±0.11)	67.89(±0.03)	69.31(±0.45)	70.28(±0.35)
0.03	67.33(±0.16)	68.13(±0.25)	69.41(±0.41)	70.57(±0.27)
0.05	67.37(±0.21)	69.23(±0.25)	70.69(±0.27)	70.85(±0.03)
$10^6 \cdot S_V$ / (m^3·kg·mol^{-2})				
0.00	-2.37(±0.26)	-4.41(±0.41)	-4.20(±1.80)	-7.28(±1.10)
0.01	-3.00(±0.34)	-4.94(±0.09)	-6.36(±1.36)	-7.48(±1.06)
0.03	-2.92(±0.48)	-5.13(±0.78)	-6.11(±1.25)	-8.13(±0.83)
0.05	-2.65(±0.64)	-7.57(±0.77)	-9.07(±0.84)	-7.60(±0.09)
Hexylene glycol				
$10^6 \cdot V_\phi^0$ / (m^3·mol^{-1})				
0.00	118.46(±0.38)	120.91(±0.21)	121.32(±0.27)	124.67(±0.02)
0.01	121.01(±0.23)	121.26(±0.19)	124.04(±0.24)	126.23(±0.39)
0.03	121.28(±0.08)	121.39(±0.13)	124.16(±0.16)	126.71(±0.48)
0.05	121.36(±0.03)	121.41(±0.16)	126.23(±0.27)	126.81(±0.51)
$10^6 \cdot S_V$ / (m^3·kg·mol^{-2})				
0.00	-5.16(±1.17)	-5.86(±0.64)	-3.03(±0.83)	-0.36(±0.07)
0.01	-5.21(±0.71)	-5.73(±0.60)	-8.08(±0.75)	-4.11(±1.21)
0.03	-5.63(±0.27)	-5.70(±0.39)	-7.28(±0.49)	-4.88(±1.47)
0.05	-5.21(±0.11)	-4.54(±0.50)	-11.45(±0.83)	-4.83(±1.54)

$^a m_B$ states the molality of methanol solutions of methylparaben. Standard uncertainties u are u (T) = 0.01 K and u (p) = 0.01MPa and p = 0.1MPa states the experimental pressure.

Table 4.5 Limiting partial molar isentropic compressibility ($K^0_{\phi,s}$) and experimental slope S_k of EG, PG and HG in MeOH solution of MePB at different temperatures.

$^a m_B$ /(mol·kg^{-1})	T=293.15K	T=298.15K	T=303.15K	T=308.15K
		Ethylene glycol		
		$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})		
0.00	-78.45(±0.21)	-80.80(±0.21)	-83.23(±0.22)	-85.74(±0.23)
0.01	-78.21(±0.21)	-80.56(±0.22)	-82.99(±0.22)	-85.45(±0.23)
0.03	-77.86(±0.20)	-80.20(±0.21)	-82.61(±0.21)	-85.04(±0.22)
0.05	-77.45(±0.21)	-79.77(±0.22)	-82.16(±0.23)	-84.51(±0.24)
		$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})		
0.00	-4.17(±0.62)	-4.34(±0.65)	-4.53(±0.67)	-4.68(±0.70)
0.01	-4.23(±0.64)	-4.42(±0.67)	-4.61(±0.69)	-4.74(±0.72)
0.03	-4.11(±0.60)	-4.28(±0.63)	-4.47(±0.64)	-4.59(±0.67)
0.05	-4.20(±0.65)	-4.38(±0.68)	-4.57(±0.70)	-4.70(±0.73)
		Propylene glycol		
		$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})		
0.00	-78.44(±0.21)	-80.78(±0.21)	-83.21(±0.21)	-85.71(±0.22)
0.01	-79.47(±0.00)	-81.86(±0.00)	-84.35(±0.01)	-86.85(±0.01)
0.03	-79.07(±0.00)	-81.45(±0.00)	-83.92(±0.01)	-86.39(±0.01)
0.05	-78.70(±0.00)	-81.07(±0.00)	-83.51(±0.00)	-85.91(±0.00)
		$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})		
0.00	-4.18(±0.62)	-4.39(±0.64)	-4.53(±0.64)	-4.72(±0.67)
0.01	-1.88(±0.01)	-1.99(±0.01)	-2.05(±0.04)	-2.11(±0.04)
0.03	-1.85(±0.01)	-1.97(±0.02)	-2.02(±0.03)	-2.10(±0.04)
0.05	-1.83(±0.02)	-1.96(±0.01)	-2.01(±0.02)	-2.03(±0.02)
		Hexylene glycol		
		$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})		
0.00	-79.68(±0.00)	-82.08(±0.00)	-84.58(±0.00)	-87.16(±0.00)
0.01	-79.46(±0.00)	-81.86(±0.00)	-84.35(±0.01)	-86.88(±0.00)
0.03	-79.06(±0.00)	-81.45(±0.00)	-85.11(±1.15)	-86.41(±0.00)
0.05	-78.69(±0.00)	-81.08(±0.00)	-83.50(±0.01)	-85.93(±0.00)
		$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})		
0.00	-1.86(±0.01)	-2.01(±0.01)	-1.99(±0.02)	-1.77(±0.01)
0.01	-1.87(±0.01)	-1.98(±0.01)	-1.99(±0.03)	-1.78(±0.01)
0.03	-1.85(±0.01)	-1.95(±0.01)	4.02(±3.49)	-1.76(±0.01)
0.05	-1.80(±0.00)	-1.88(±0.01)	-1.94(±0.02)	-1.73(±0.01)

$^a m_B$ states the molality of methanol solutions of methylparaben. Standard uncertainties u are u (T) = 0.01 K and u (p) = 0.01MPa, p = 0.1MPa states the experimental pressure.

From **Table 4.4,** it can be noticed that the value of V_ϕ^0 increases at each temperature with increase in the molar mass of glycols resulting in large V_ϕ^0 values in case of HG, which suggests the predominance of solute—solvent interactions in HG as compared to the interaction of PG and EG. In accordance with co-sphere overlap model [23, 24], The effect of hydrophilic—hydrophilic interaction on limiting partial molar volume of glycols depends on the strength of bond between glycols and MePB. The limiting partial molar volume of glycols increases with increase in the concentration of glycols if strength of the bond between glycols and MePB is weaker than those of glycols and methanol. Probably, the hydrogen bond between glycols and MePB is weaker than hydrogen bond between glycols and methanol. Hydrophobic□hydrophobic interactions between glycols and MePB cause reduction in the interactions of glycols and methanol solution of MePB. As a result, the limiting partial molar volume of glycol increases with increase in the concentration of MePB.

The limiting partial molar isentropic compressibility at infinite dilution ($K_{\phi,s}^0$) is mainly due to positive effect also known as solvent intrinsic compressibility that arises due to intermolecular free space by making the solution more compressible [25] and negative effect also called the penetration of solvent molecules into intra—ionic free space due to the interaction of the solute with the neighboring solvent molecules. The negative limiting partial molar isentropic compressibilities are attributed to the increase in the compressibility of the pure solvent as compared to the solution mixture. The resulting negative $K_{\phi,s}^0$ value is due to the preponderance of the negative effect upon the positive effect. The values of $K_{\phi,s}^0$ increase with increase in the concentration of MePB, and the values decrease with increase in temperature. Consequently, the solute—solvent interaction escalates with the increase in the concentration of MePB. In this study, the values of S_v are negative and are smaller thanV_ϕ^0, which infers the pre-eminence of solute—solvent interactions over solute—solute interactions. The data of S_v does not show a very regular trend, which implies that solute—solute interactions are affected by the other factors [26]. **Table 4.5** reported the $K_{\phi,s}^0$ values for EG, PG, and HG in (0.00, 0.01, 0.03, and 0.05) mol·kg^{-1} methanol solution of (MePB).

Table 4.5 Limiting partial molar isentropic compressibility ($K^0_{\phi,s}$) and experimental slope S_k of EG, PG and HG in MeOH solution of MePB at different temperatures.

$^{a}m_B$ /(mol·kg^{-1})	T=293.15K	T=298.15K	T=303.15K	T=308.15K
Ethylene glycol				
$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})				
0.00	-78.45(±0.21)	-80.80(±0.21)	-83.23(±0.22)	-85.74(±0.23)
0.01	-78.21(±0.21)	-80.56(±0.22)	-82.99(±0.22)	-85.45(±0.23)
0.03	-77.86(±0.20)	-80.20(±0.21)	-82.61(±0.21)	-85.04(±0.22)
0.05	-77.45(±0.21)	-79.77(±0.22)	-82.16(±0.23)	-84.51(±0.24)
$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})				
0.00	-4.17(±0.62)	-4.34(±0.65)	-4.53(±0.67)	-4.68(±0.70)
0.01	-4.23(±0.64)	-4.42(±0.67)	-4.61(±0.69)	-4.74(±0.72)
0.03	-4.11(±0.60)	-4.28(±0.63)	-4.47(±0.64)	-4.59(±0.67)
0.05	-4.20(±0.65)	-4.38(±0.68)	-4.57(±0.70)	-4.70(±0.73)
Propylene glycol				
$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})				
0.00	-78.44(±0.21)	-80.78(±0.21)	-83.21(±0.21)	-85.71(±0.22)
0.01	-79.47(±0.00)	-81.86(±0.00)	-84.35(±0.01)	-86.85(±0.01)
0.03	-79.07(±0.00)	-81.45(±0.00)	-83.92(±0.01)	-86.39(±0.01)
0.05	-78.70(±0.00)	-81.07(±0.00)	-83.51(±0.00)	-85.91(±0.00)
$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})				
0.00	-4.18(±0.62)	-4.39(±0.64)	-4.53(±0.64)	-4.72(±0.67)
0.01	-1.88(±0.01)	-1.99(±0.01)	-2.05(±0.04)	-2.11(±0.04)
0.03	-1.85(±0.01)	-1.97(±0.02)	-2.02(±0.03)	-2.10(±0.04)
0.05	-1.83(±0.02)	-1.96(±0.01)	-2.01(±0.02)	-2.03(±0.02)
Hexylene glycol				
$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})				
0.00	-79.68(±0.00)	-82.08(±0.00)	-84.58(±0.00)	-87.16(±0.00)
0.01	-79.46(±0.00)	-81.86(±0.00)	-84.35(±0.01)	-86.88(±0.00)
0.03	-79.06(±0.00)	-81.45(±0.00)	-85.11(±1.15)	-86.41(±0.00)
0.05	-78.69(±0.00)	-81.08(±0.00)	-83.50(±0.01)	-85.93(±0.00)
$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})				
0.00	-1.86(±0.01)	-2.01(±0.01)	-1.99(±0.02)	-1.77(±0.01)
0.01	-1.87(±0.01)	-1.98(±0.01)	-1.99(±0.03)	-1.78(±0.01)
0.03	-1.85(±0.01)	-1.95(±0.01)	4.02(±3.49)	-1.76(±0.01)
0.05	-1.80(±0.00)	-1.88(±0.01)	-1.94(±0.02)	-1.73(±0.01)

$^{a}m_B$ states the molality of methanol solutions of methylparaben. Standard uncertainties u are u (T) = 0.01 K and u (p) = 0.01MPa, p = 0.1MPa states the experimental pressure.

The small size of S_k values suggests that the solute—solvent interactions are prevailing in the solution mixture and the solute—solute interactions are negligible at infinite dilution.

The temperature dependence of V_ϕ^0 can be written as follows

$$V_\phi^0 = a + bT + cT^2 \tag{4.6}$$

where T is the temperature, and a, b, and c are the empirical parameters (listed in **Table 4.6**). The deviations obtained from the experimental and calculated value of V_ϕ^0 are computed from these empirical parameters. These deviations ARD (σ) are evaluated from the succeeding equation as follows:

$$\sigma = (1/n)\,\Sigma[abs((Y_{exptl.} - Y_{calc.})/Y_{exptl.})] \tag{4.7}$$

where $Y_{exptl.}$ and $Y_{calc.}$ represents the experimental and calculated apparent molar volume at infinite dilution. The attained deviations are very small, and they fit in–to the general polynomial equation very finely.

Eq. (4.8) can be attained by differentiating Eq. (4.6) with respect to temperature to get limiting apparent molar expansibility E_ϕ^0 as follows:

$$E_\phi^0 = (\delta V^0{}_\varphi/\delta T)_p \ = b + 2cT \tag{4.8}$$

The limiting apparent molar expansibility is considered to be an essential parameter for determining the interactions between solute—solvent occurring in solution [27, 28]. The values of limiting apparent molar expansibility E_ϕ^0 for the ternary system are listed in **Table4.7**.

Table 4.7 The infinite dilution apparent molar expansion, E_{ϕ}^{0} of EG/PG/HG in MeOH solution of MePB at different temperatures and at atmospheric pressure.

${}^{a}m_B$ /(mol·kg^{-1})	$10^6 \cdot E_{\phi}^{0}$ / (m^3·mol^{-1}·K^{-1})			
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
Ethylene Glycol				
0.00	0.12	0.11	0.10	0.10
0.01	0.13	0.11	0.10	0.08
0.03	0.12	0.11	0.09	0.08
0.05	0.12	0.11	0.09	0.08
Propylene Glycol				
0.00	0.09	0.18	0.27	0.36
0.01	0.17	0.20	0.23	0.25
0.03	0.17	0.20	0.24	0.27
0.05	0.49	0.32	0.15	-0.02
Hexylene Glycol				
0.00	0.24	0.34	0.43	0.52
0.01	0.08	0.27	0.47	0.66
0.03	0.02	0.26	0.50	0.75
0.05	0.34	0.40	0.45	0.50

${}^{a}m_B$ is the molality of methanol solutions of methylparaben. Standard uncertainties u are u (T) = 0.01 K and u (p) = 0.01MPa, p = 0.1MPa states the experimental pressure.

The values of E_{ϕ}^{0} are positive, and they suggests the occurrence of the solute—solvent interactions in the system studied, supporting the data of apparent molar volume except for PG in 0.05 mol ·kg $^{-1}$ MePB—MeOH at 308.15 K, which is showing negative value of apparent molar expansibility. The positive values of E_{ϕ}^{0} may prevail due to phenomenon of packing or caging effect [29], which further recommends the existence of solute—solvent interaction. The E_{ϕ}^{0} values are nearly the same in the whole temperature range studied for EG in (0.00, 0.01, 0.03, and 0.05) mol·kg^{-1} MePB—MeOH systems; whereas, the E_{ϕ}^{0} values increase with temperature for PG and HG in (0.00, 0.01, 0.03, and 0.05) mol·kg^{-1} of MePB—MeOH systems because with escalation in temperature, thermal agitation increases resulting in the release of solute molecules from the solvent, thereby increasing the solution volume to a larger extent than that for the pure solvent.

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Part II

In previous part, we have reported the densities, ρ and speed of sound of ethylene glycol (EG), propylene glycol (PG), and hexylene glycol (HG) in (0.00, 0.01, 0.03, 0.05) mol·kg^{-1} methanol solutions of methylparaben at temperatures T = (293.15, 298.15, 303.15, 308.15) K. In continuation of our work on glycols, in this part we have reported the densities and speed of sound for EG and PG in (0.00, 0.01, 0.03, 0.05) mol·kg^{-1} aqueous solutions of sodium ethylparaben at temperatures T = (293.15, 298.15, 303.15, 308.15) K.

Density

The density and speed of sound experimental values for ethylene glycol and propylene glycol are in excellent agreement with the literatures values. The experimental density data has been compared with literature data [1-8]. It is depicted from **Figure 1 and 2** that present experimental density data for (EG + water) are in coherence with literature data [1-3] at several temperatures however, at 298.15 K for (PG + water) mixture the present density value are in good agreement with literature values [6, 7] and moreover, systematic deviations are also observed from the values reported in the literature [4, 5, 8].

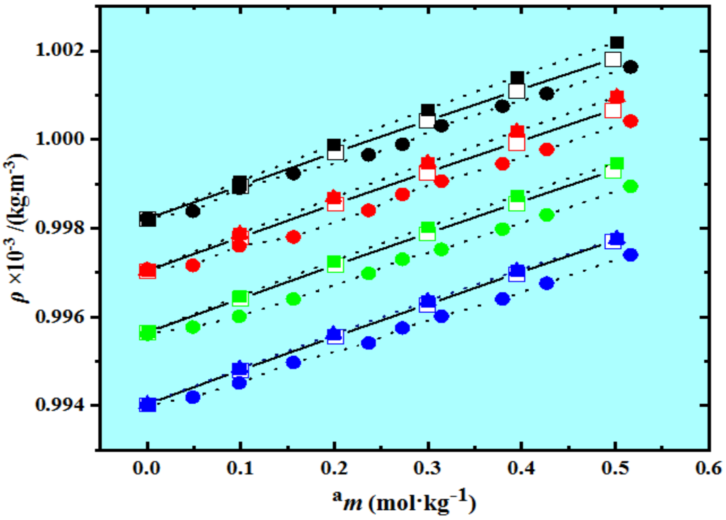


Figure 1: Graph of experimental (*empty square*) and literature data (*filled triangle* [1]; *filled circle* [2]; *filled square* [3]) of densities for mixtures of (EG + water) at various temperatures [*black*, 293.15 K; *red*, 298.15 K; *green*, 303.15 K; *blue*, 308.15 K]. (Solid lines, experimental data; dotted lines, literature data)

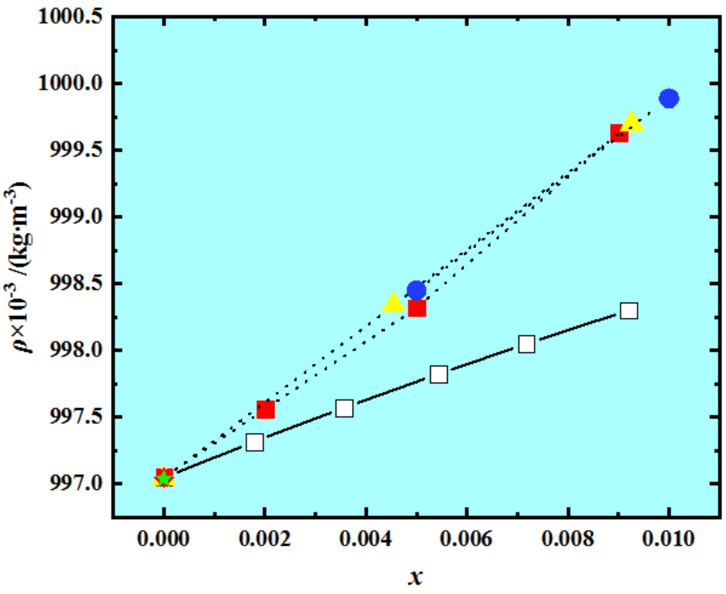


Figure 2: Graph of experimental (*empty square*) and literature values (*filled square* [4]; *filled triangle* [5]; *filled star* [6]; *filled diamond* [7]; *filled circle* [8]) of densities for mixtures of (PG + water) at 298.15K temperature. [Solid lines, experimental data; dotted lines, literature data]

It is well known that deviations are related to the procedure of calibration, solution preparation as well as its purity, different measuring method used. The variation among present measured data and the data from literature could be due to different measuring could be due to partial degassing of investigated samples. The density value decreases in accordance to temperature i.e. due to temperature escalation, the values of density decreases. **Table 4.8** tabulates the comparison of experimental density and speed of sound values with accessible literature values.

Table 4.8

Comparison of density (ρ) and speed of sound (u) of pure compounds with literature at temperature from T= (293.15 to 308.15) K at pressure, p=0.1 MPa.

Compound	T/K	$\rho\times10^{-3}$ /(kg·m^{-3})		u/(m·s^{-1})	
		experimental	literature	experimental	literature
Water	293.15	0.998211	0.99821[3]	1481.14	1482.3[3]
			0.99822[39]		1482.98[40]
			0.998701[40]		
	298.15	0.997047	0.997047[1]	1495.85	1495.85[1]
			0.99704[43]		1497.16[40]
			0.9972[39]		1498.24[42]
			0.9973[41]		
			0.997537[40]		
	303.15	0.995656	0.99566[3]	1508.84	1508.5[3]
			0.99564[39]		1509.62[40]
			0.996131[40]		
	308.15	0.994039	0.994039[1]	1519.14	1519.14[1]
			0.99403[43]		1520.63[42]
			0.9942[39]		

Ethylene glycol	293.15	1.112856	1.11323[46]	1667.64	1669.5[43]
			1.11202[43]		
	298.15	1.109359	1.1003[41]	1655.94	1662[47]
			1.1097[44]		1660.7[49]
			0.99707[45]		1656.4[43]
	303.15	1.105854	1.105825[39]	1644.26	1645.2[43]
	308.15	1.102341	1.1025[39]	1632	1635[47]
					163[43]
Propylene glycol	293.15	1.036381	1.036214[88]	1524.95	1522.42[50]
					1509.3[43]
	298.15	1.03271	1.03275[47]	1511.23	1508.41[50]
			1.0325[44]		1500.6[43]
			1.03261[45]		
			1.032526[48]		
	303.15	1.028998	1.02902[47]	1497.31	1492[47]
			1.0289[45]		1494.33[88]
					1495.5[43]
	308.15	1.025253	1.02540[47]	1483.39	1454[47]

	1.02516[45]	1480.19[50]
		1480.19[50]

Standard uncertainties u are $u\ (T) = \pm 0.01\text{K}$, $u\ (\rho) = \pm 0.15\ \text{kg·m}^{-3}$, $u\ (u) = \pm 1.0\ \text{m·s}^{-1}$, $u\ (p) = \pm 0.01\text{MPa}$.

The densities (ρ) values were measured for EG and PG in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} SEP solutions in water and are tabulated in **Table 4.9** at T = (293.15, 298.15, 303.15 and 308.15) K temperatures. It has been professed from the data recorded in **Table 4.9** that at a particular SEP concentration, the density of solution mixture accelerates with surge in concentration of glycols (EG and PG) and slightly reduces with temperature increase.

Table 4.9

Densities, ρ and apparent molar volumes, V_ϕ of ternary system (glycols + SEP + water) at various temperatures and atmospheric pressure, p = 0.1 MPa

$^a m$ (mol·kg^{-1})	$\rho \times 10^{-3}$ /(kg·m^{-3})				$V_\phi \times 10^6$ /(m^3·mol^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
EG + 0.00 mol·kg^{-1} *SEP*								
0.00000	0.99821	0.99704	0.99565	0.99403				
0.09955	0.99895	0.99779	0.99641	0.99480	54.59	54.61	54.63	54.64
0.20101	0.99971	0.99855	0.99717	0.99556	54.61	54.64	54.66	54.68
0.29914	1.00042	0.99926	0.99788	0.99628	54.64	54.67	54.69	54.71
0.39376	1.00109	0.99993	0.99856	0.99697	54.67	54.71	54.72	54.74
0.49716	1.00181	1.00066	0.99929	0.99771	54.72	54.74	54.75	54.77
EG + 0.01 mol·kg^{-1} *SEP*								
0.00000	0.99882	0.99765	0.99613	0.99459				
0.11173	0.99964	0.99848	0.99696	0.99543	54.72	54.74	54.76	54.79

0.19951	1.00027	0.99912	0.99760	0.99607	54.74	54.76	54.78	54.81
0.29565	1.00096	0.99981	0.99829	0.99677	54.75	54.78	54.80	54.84
0.39718	1.00168	1.00052	0.99902	0.99749	54.77	54.80	54.82	54.86
0.49387	1.00235	1.00120	0.99969	0.99817	54.78	54.81	54.84	54.88
EG + 0.03 mol·kg^{-1} *SEP*								
0.00000	1.00011	0.99892	0.99749	0.99586				
0.10147	1.00085	0.99966	0.99824	0.99661	54.73	54.76	54.79	54.79
0.19962	1.00155	1.00037	0.99895	0.99733	54.75	54.76	54.79	54.82
0.29992	1.00226	1.00108	0.99967	0.99805	54.76	54.77	54.80	54.84
0.39779	1.00294	1.00177	1.00036	0.99874	54.78	54.79	54.81	54.86
0.49677	1.00362	1.00246	1.00105	0.99943	54.79	54.80	54.82	54.88
EG + 0.05 mol·kg^{-1} *SEP*								
0.00000	1.00110	0.99987	0.99836	0.99675				
0.09792	1.00180	1.00058	0.99907	0.99747	54.83	54.85	54.86	54.87

0.19953	1.00251	1.00130	0.99980	0.99820	54.84	54.86	54.87	54.89
0.30119	1.00322	1.00201	1.00052	0.99892	54.86	54.87	54.88	54.90
0.39819	1.00388	1.00268	1.00119	0.99960	54.87	54.88	54.90	54.92
0.50258	1.00459	1.00339	1.00190	1.00032	54.88	54.89	54.91	54.93
PG + 0.00 mol·kg^{-1} *SEP*								
0.00000	0.99821	0.99704	0.99565	0.99403				
0.09917	0.99847	0.99731	0.99593	0.99432	73.54	73.55	73.57	73.62
0.19801	0.99872	0.99757	0.99619	0.99459	73.59	73.61	73.63	73.66
0.30136	0.99896	0.99782	0.99645	0.99486	73.65	73.66	73.68	73.72
0.39826	0.99918	0.99805	0.99668	0.99510	73.69	73.71	73.73	73.77
0.51059	0.99942	0.99830	0.99694	0.99536	73.74	73.75	73.77	73.81
PG + 0.01 mol·kg^{-1} *SEP*								
0.00000	0.99882	0.99765	0.99613	0.99459				
0.10113	0.99908	0.99792	0.99640	0.99487	73.58	73.61	73.64	73.69

0.19975	0.99932	0.99817	0.99666	0.99513	73.63	73.65	73.68	73.73
0.30093	0.99955	0.99841	0.99691	0.99539	73.67	73.70	73.71	73.75
0.39774	0.99977	0.99863	0.99714	0.99563	73.72	73.73	73.74	73.79
0.49430	0.99997	0.99884	0.99736	0.99586	73.75	73.77	73.78	73.81
PG + 0.03 mol·kg^{-1} *SEP*								
0.00000	1.00011	0.99892	0.99749	0.99586				
0.10086	1.00035	0.99917	0.99775	0.99613	73.63	73.65	73.67	73.71
0.20236	1.00059	0.99941	0.99800	0.99639	73.67	73.69	73.73	73.75
0.29894	1.00080	0.99963	0.99822	0.99662	73.71	73.74	73.77	73.78
0.40149	1.00102	0.99985	0.99845	0.99686	73.74	73.78	73.81	73.81
0.49727	1.00122	1.00005	0.99866	0.99708	73.77	73.81	73.84	73.85
PG + 0.05 mol·kg^{-1} *SEP*								
0.00000	1.00110	0.99987	0.99836	0.99675				
0.10131	1.00133	1.00012	0.99861	0.99701	73.68	73.70	73.71	73.74

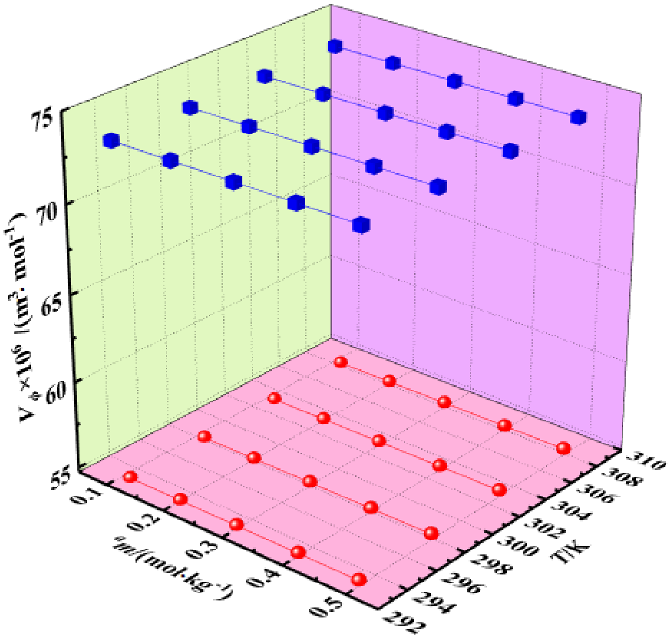
0.19956	1.00155	1.00034	0.99885	0.99725	73.71	73.74	73.76	73.79
0.31442	1.00179	1.00059	0.99910	0.99751	73.75	73.78	73.80	73.83
0.40016	1.00196	1.00076	0.99929	0.99770	73.78	73.81	73.83	73.87
0.50552	1.00217	1.00097	0.99951	0.99793	73.81	73.84	73.86	73.90

---

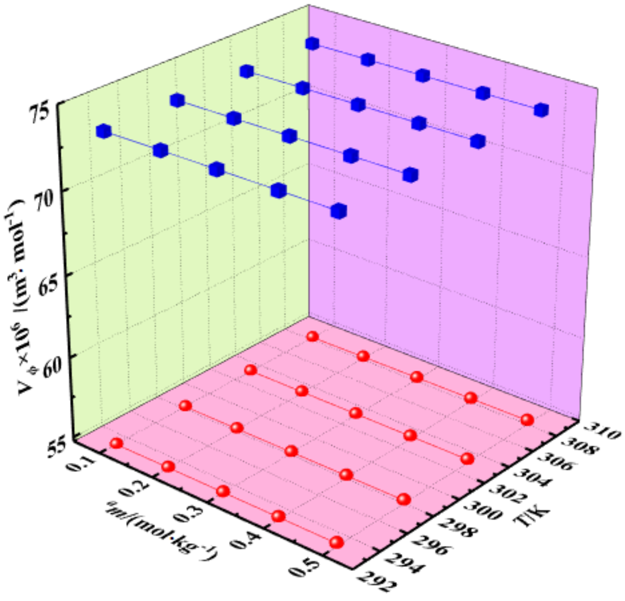
[a] m states the molalities of EG and PG in aqueous SEP solutions. Standard uncertainties u are $u_r(m)$ = 1%, u (V_ϕ) = ± (0.05–0.07) × 10^{-6} $\mathrm{m^3\cdot mol^{-1}}$, u (T) = 0.01 K, u (ρ) = 0.15 $\mathrm{kg\cdot\cdot m^{-3}}$ and u (p) = 0.01MPa

Apparent molar Volume

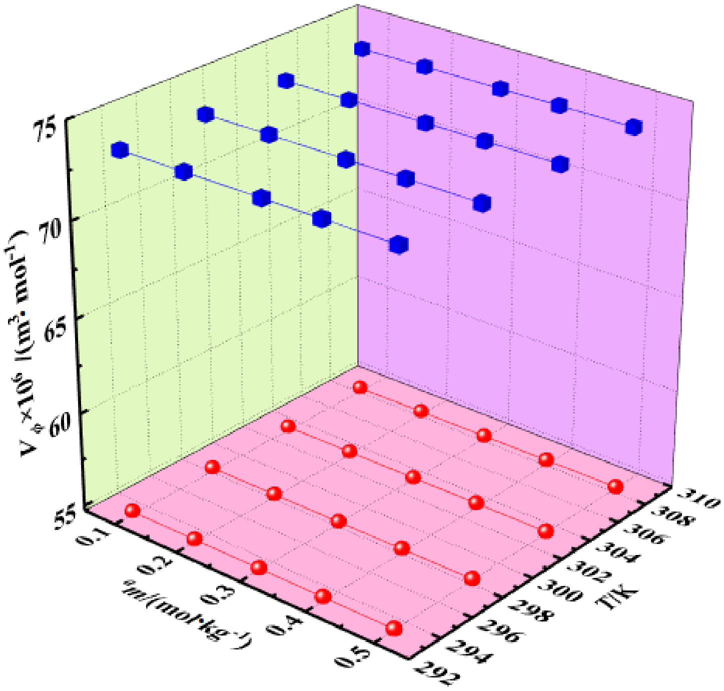
Using the **eq. 4.1**, the experimentally measured density (ρ) values are being employed for the computation of V_ϕ. The V_ϕ data are incorporated in **Table 4.9** and is presented in **Figure 3**.



(a)


75
70
65
60
55
V φ ×10⁶ /(m³· mol⁻¹)
0.1
0.2
0.3
0.4
0.5
ᵃm/(mol·kg⁻¹)
292
294
296
298
300
302
304
306
308
310
T/K

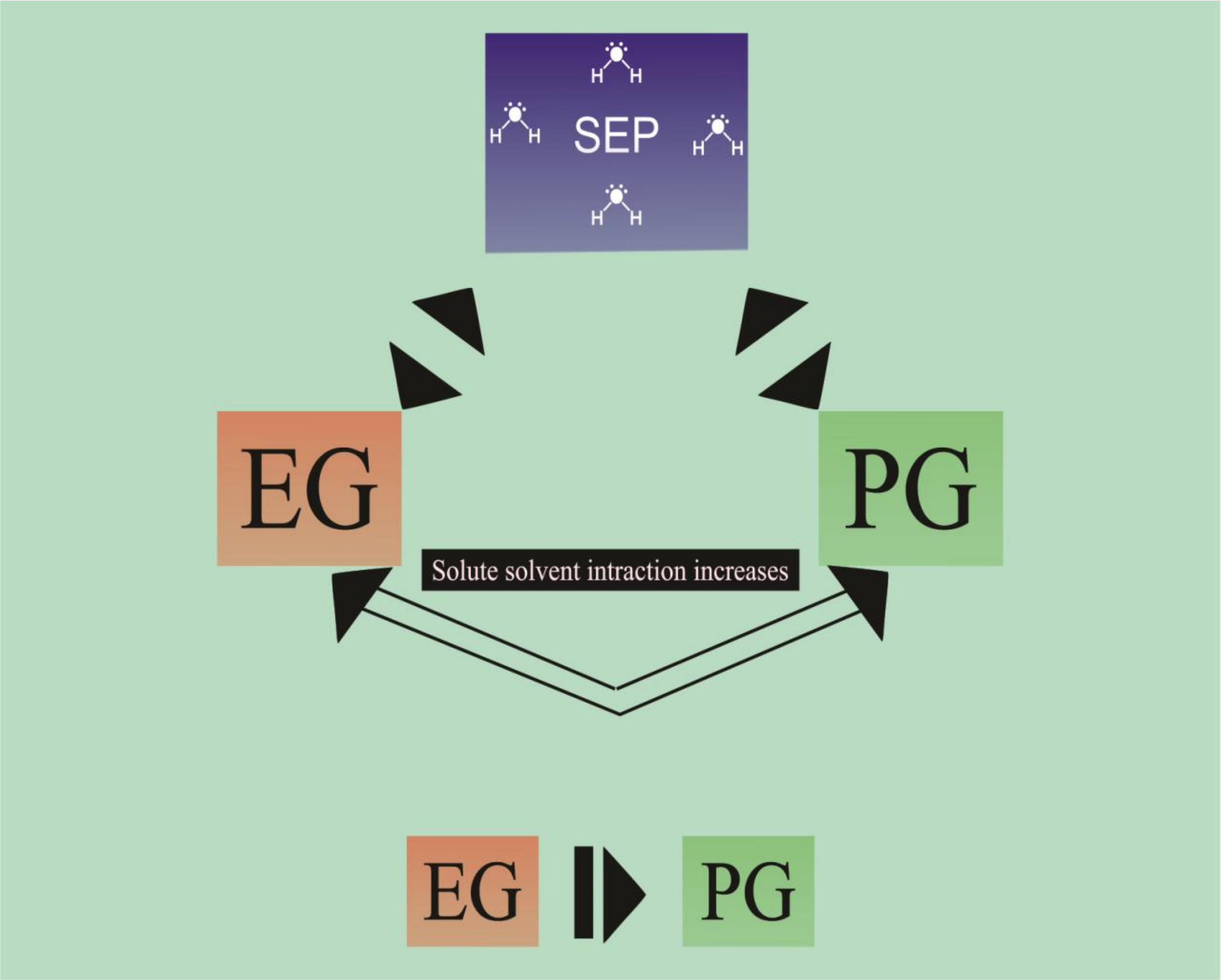
(b)


75
70
65
60
55
V φ ×10⁶ /(m³· mol⁻¹)
0.1
0.2
0.3
0.4
0.5
ᵃm/(mol·kg⁻¹)
292
294
296
298
300
302
304
306
308
310
T/K

(c)

Figure 3: Graph for V_ϕ, apparent molar volume versus ^{a}m, concentration of EG and PG in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1}aqueous SEP solution (Sphere EG and Cube PG) at various temperatures.

The estimated uncertainty for V_ϕ are ± (0.05–0.07) × 10^{6} $m^{3}\cdot mol^{-1}$. The data provided in Table 3 imply that at a certain SEP (sodium ethylparaben) concentration, V_ϕ surges with temperature escalation along with the glycols molality. An enhancement in V_ϕ data has also been noticed in **Table 4.9** with respect to ascent in SEP concentration, which infers the pronounced interactions within solute and solvent molecules. Different physical forces like dipole-induced - dipole, dipole-dipole interactions, hydrophilic effect and hydrophobic hydration in the water rich area can be accredited to this elevation in V_ϕ value [9]. Similarly, at whole SEP concentrations as well as temperatures, surge in data of V_ϕ is seen with upsurge in EG and PG molar mass, ensuing the extremum association midst solute and solvent for PG with regard to mixtures of EG as ascribed by **scheme 1**.



Scheme 1 Representation of Glycol-SEP interactions.

Partial molar volume

Partial molar volume at infinite dilution (V_{ϕ}^{0}), is achieved by technique of least square fitting of apparent molar volume by the **eq. 4.4**. The entire value ofV_{ϕ}^{0}, are coming out to be positive and thus rises with an rise in SEP concentration and temperature for all the glycols which can possibly arise as a result of strengthening of interaction amid solute and solvent as epitomized in **Figure 4**.

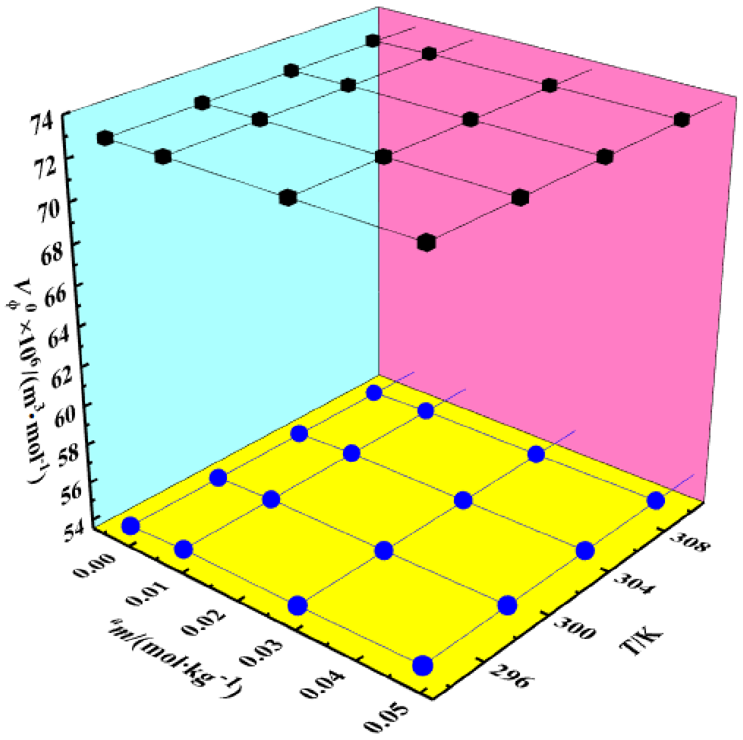


Figure 4: Graph of V_ϕ^0, partial molar volume at infinite dilution for EG and PG in various concentration of aqueous SEP solution at different temperatures (dot, EG; cube, PG).

Moreover, V_ϕ^0values escalates with a rise in molar mass [10] of glycols that is, from EG to PG at individual temperature resulting in greater V_ϕ^0 values for HG which implies the increased associations midst solute and solvent for PG with regard to EG. Table 7 represents the comparison of experimental V_ϕ^0 values with the data published in literature. The agreement of present limiting partial molar volume for (EG + water) with literature values is very satisfactory. The V_ϕ^0 value measures only ion—solvent interaction and is unaffected by ion-ion interactions [11-14]. As stated by the model of co-sphere overlap, [15, 16] groups of hydrophobic-hydrophobic and ion-hydrophobic overlap and cause bulk reduction whereas two ionic groups overlap with hydration cospheres cause volume enhancement. **Table 4.10** indexes the value of of V_ϕ^0 and S_v along with their standard errors computed by employing least square fitting technique for apparent molar volume.

Table 4.10

Partial molar volumes, (V_{ϕ}^{0}), experimental slopes, S_v of EG and PG in SEP solutions of water at various temperatures

^{a}m/ (mol·kg^{-1})	$V_{\phi}^{0}\times10^{6}$/(m^{3}· mol^{-1})				$S_v\times10^{6}$/(m^{3}·kg·mol^{-2})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
				EG				
0.00	54.55(±0.008)	54.58(±0.003)	54.60(±0.003)	54.61(±0.001)	0.32(±0.025)	0.33(±0.010)	0.31(±0.010)	0.31(±0.001)
0.01	54.71(±0.001)	54.73(±0.003)	54.74(±0.001)	54.76(±0.002)	0.14(±0.005)	0.17(±0.011)	0.21(±0.005)	0.24(±0.007)
0.03	54.72(±0.003)	54.75(±0.002)	54.78(±0.001)	54.78(±0.004)	0.15(±0.010)	0.10(±0.008)	0.09(±0.002)	0.20(±0.012)
0.05	54.82(±0.001)	54.84(±0.001)	54.85(±0.001)	54.86(±0.002)	0.13(±0.003)	0.11(±0.005)	0.13(±0.003)	0.13(±0.008)
				PG				
0.00	73.49(±0.005)	73.51(±0.010)	73.53(±0.008)	73.57(±0.005)	0.51(±0.014)	0.49(±0.030)	0.49(±0.025)	0.48(±0.016)
0.01	73.54(±0.004)	73.57(±0.005)	73.61(±0.003)	73.67(±0.002)	0.43(±0.011)	0.41(±0.014)	0.34(±0.008)	0.30(±0.007)
0.03	73.59(±0.007)	73.61(±0.005)	73.64(±0.010)	73.67(±0.003)	0.36(±0.021)	0.41(±0.016)	0.41(±0.031)	0.35(±0.010)
0.05	73.65(±0.002)	73.67(±0.005)	73.68(±0.006)	73.70(±0.008)	0.31(±0.007)	0.35(±0.014)	0.37(±0.017)	0.40(±0.024)

The positive value of V_ϕ^0 emanate owing to the fact that ion-hydrophilic associations are prominent with regard to ion – hydrophobic and hydrophobic-hydrophobic associations [17]. An acceleration in the values of V_ϕ^0 for glycols with increase in temperature and SEP concentration can be elucidated as the fragments of the solvent are removed from the solute in to the solution. It is inferred from the perceived larger V_ϕ^0 values that at superlative temperature, solution mixture expands due to discharge of fragment of solvent molecules from the solute secondary solvation layer. At infinite dilution, the apparent molar volume tends to increase with rise in glycol concentration due to the intensified associations midst solute and solvent fragments within hydroxyl groups of EG and SEP. Moreover, **Table 4.10** shows that at all the working temperatures and for all SEP concentrations magnitude of S_v has been perceived positive further suggesting the survival of associations midst solute and solute in the investigated solution mixture. As no regular trend is followed by S_v values, which demonstrates that some extra variables affect the association amid solute and solute interactions [18, 19]. The surplus values of V_ϕ^0 than S_v values recommend the manifestation of feeble association between solute and solute in comparison to solute-solvent associations.

Partial molar volume of transfer

The transfer volume of glycols from water to aqueous SEP solutions at infinite dilution was derived by using the following equation given below:

$$\Delta_{tr}V_\phi^0 = V_\phi^0 \text{ (in aqueous SEP) } - V_\phi^0\text{(water)} \tag{4.9}$$

The $\Delta_{tr}V_\phi^0$ are all positive and escalate with increased concentration of SEP concentration for each glycol that deduces enormous devitalisation effect on glycols. The values of $\Delta_{tr}V^0{}_\varphi$ do not show regular trend with temperature. The significant $\Delta_{tr}V_\phi^0$ values under inspection recommend robust ion-ion associations of SEP with all glycols. According to model of co sphere overlap, the perceived positive values ($\Delta_{tr}V_\phi^0$) values signify the solute structure building or sustaining property resulting from their solvophobic solvation and also the spatial connection of two cospheres [15, 16]. The data of $\Delta_{tr}V_\phi^0$ is mentioned in **Table 4.11**.

Table 4.11

Limiting partial molar volume of transfer, $\Delta_{tr}V_{\phi}^{0}$ of glycols in aqueous SEP solutions at different temperatures.

^{a}m/(mol·kg^{-1})	$\Delta_{tr}V_{\phi}^{0} \times 10^{6}$/(m^{3}·mol^{-1})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
	EG			
0.01	0.16(±0.007)	0.15(±0.001)	0.14(±0.002)	0.15(±0.002)
0.03	0.17(±0.005)	0.17(±0.001)	0.18(±0.003)	0.16(±0.004)
0.05	0.27(±0.007)	0.26(±0.002)	0.25(±0.003)	0.25(±0.002)
	PG			
0.01	0.05(±0.001)	0.06(±0.005)	0.08(±0.005)	0.09(±0.003)
0.03	0.11(±0.002)	0.11(±0.005)	0.11(±0.002)	0.10(±0.002)
0.05	0.16(±0.003)	0.16(±0.005)	0.15(±0.002)	0.13(±0.003)

^{a}m is the molality of aqueous solutions of SEP. Standard uncertainties u are $u_r(m)$ = 1%, $u(T)$ = 0.01 K.

The variety of possible interactions that subsist within the molecules of glycols and SEP might be hydrophilic-hydrophilic, hydrophobic- hydrophobic, ion-hydrophilic and ion-hydrophobic interactions. The model of co-sphere overlap affirmed that the positive response towards $\Delta_{tr}V_{\phi}^{0}$ brings into existence by hydrophilic-hydrophilic and ion-hydrophilic interactions moreover, hydrophobic-hydrophobic and ion-hydrophobic interactions make negative contribution to $\Delta_{tr}V_{\phi}^{0}$. In the recent investigation, the observed $\Delta_{tr}V_{\phi}^{0}$ values are found to be positive for all glycols which promote the supremacy of hydrophilic-hydrophilic and ion-hydrophilic interactions in comparison to hydrophobic-hydrophobic and ion-hydrophobic interactions.

Temperature dependent partial molar volume

The general polynomial equation (**eq. 4.6**) is employed in order to evaluate the temperature along with the apparent molar volume deviation. The values of these constants in aqueous SEP for EG and PG are provided in **Table 4.12**. In the aqueous SEP solutions, the negative value of scarcely statistically significant coefficient (c) has been discovered for EG and positive for PG. The ARD (σ) values are computed from the supporting data equation (**eq. 4.7**). The deviation values are establish to be very small and very magnificently fit in with the polynomial equation. At infinite dilution, the equation (**eq. 4.8**) represents the association for partial molar volume which dependent on temperature in accordance with absolute temperature (T). The similar equation (**eq. 4.8**) of the supporting information has been employed to measure limiting apparent molar expansion. The limiting apparent molar expansion, $E_{\phi}^{0} = (\partial V_{\phi}^{0}/\partial T)_{P}$ is believed to be most reliable measure for solute-solvent interactions arising in the combination of mixture [21, 22]. The values of constants, ARD in aqueous SEP for EG and PG are provided in **Table 4.12**. whereas the value of E_{ϕ}^{0}, $(\partial E_{\phi}^{0}/\partial T)_{P}$ and α are indexed in **Table 4.13**

Table 4.12

Values of **e**mpirical parameters of eq (3) for EG and PG in aqueous SEP solutions at different concentrations.

^{a}m/(mol·kg^{-1})	$a\times10^{6}$/(m^{3}.mol^{-1})	$b\times10^{6}$/(m^{3}.mol^{-1}.K^{-1})	$c\times10^{6}$/(m^{3}.mol^{-1}.K^{-2})	*ARD/(σ)*
EG				
0.00	54.67	0.019	-0.000612	0.0020
0.01	54.70	0.019	-0.000558	0.0012
0.03	54.72	0.019	-0.000720	0.0010
0.05	54.73	0.018	-0.000653	0.0017
PG				
0.00	73.51	0.004	0.000210	0.00004
0.01	73.57	0.007	0.000331	0.00003
0.03	73.61	0.004	0.000187	0.00004
0.05	73.67	0.003	0.000078	0.00007

^{a}m is the molality of aqueous solutions of SEP. Standard uncertainties u are $u_r(m)$ = 1%.

Table 4.13

Apparent molar expansion at infinite dilution, E_{ϕ}^{0} of EG and PG in aqueous solutions of SEP at different temperatures, T/K= (293.15 to 308.15), Hepler constant $(\partial E_{\phi}^{0}/\partial T)_P = 2c$ and α , thermal expansion coefficient at T = 298.15 K

^{a}m/ $(\mathrm{mol \cdot kg^{-1}})$	E_{ϕ}^{0}/ $(\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}})$				$(\partial E_{\phi}^{0}/\partial T)_P$/ $(\mathrm{m^3.mol^{-1}.K^{-2}})$	$\alpha \times 10^3$/ $(\mathrm{K^{-1}})$
	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15 K	T=298.15 K	T=298.15 K
			EG			
0.00	0.0251	0.0190	0.0129	0.0068	-0.0012	0.348
0.01	0.0246	0.0190	0.0134	0.0078	-0.0011	0.347
0.03	0.0262	0.0190	0.0118	0.0046	-0.0014	0.347
0.05	0.0245	0.0180	0.0115	0.0049	-0.0013	0.328
			PG			
0.00	0.0019	0.0040	0.0061	0.0082	0.00042	0.544
0.01	0.0037	0.0070	0.0103	0.0136	0.00066	0.951
0.03	0.0021	0.0040	0.0059	0.0077	0.00037	0.543
0.05	0.0022	0.0030	0.0038	0.0046	0.00016	0.407

Hepler [23, 24] proposed a thermodynamic expression to ascertain the structure constructing and structure splitting solute potential existing in the solution mixture employing equation as follows:

$$(\partial E_{\phi}^{0}/\partial T)_{P} = (\partial^{2} V_{\phi}^{0}/\partial T)_{P} = 2c \quad (4.10)$$

Hepler declared that if $(\partial E_{\phi}^{0}/\partial T)_{P}$ is positive, the structure manufacturer of solute exists however if it is negative then the solute is a structure breaker. The arriving positive E_{ϕ}^{0} values at entire SEP concentration and entire temperature range infer the persistence of association midst solute and solvent in the current examined systems, as earlier depicted by statistics of apparent molar volume. The occurrence of Packing effect or caging [25, 26] causes the positive value of E_{ϕ}^{0} which further tells the interaction between glycols and SEP molecules. No regular trend of E_{ϕ}^{0} values has been noted with regard to surge in SEP concentration along with temperature. The tiny negative and positive $(\partial E_{\phi}^{0}/\partial T)_{P}$ values specify the glycol structure construction in SEP solutions of water.

Thermal expansion coefficient

Coefficient of thermal expansion, α is acquired by the **eq. 4.11** as follows:

$$\alpha = 1/V_{\phi}^{0}(\partial V_{\phi}^{0}/\partial T) \quad (4.11)$$

Thermal expansion coefficient (α) (mentioned in **Table 4.13**) offers data on the subsistence of interactions within solute and solvent in the combination of solution [27, 28]. For EG and PG no expected trend has been noticed with respect to the concentration of SEP.

Speed of sound

Sound velocity (u) data has been experimentally ascertained for glycols (EG and PG) in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} SEP solutions in water at various temperatures T= (293.15 to 308.15) K. The literature values have been employed to compare the experimentally computed sound velocity values for (EG + water) [1, 3] and (PG + water) [44, 67, 68] mixtures. **Figure 5 and 6** shows the experimental and literature comparison of speed of sound values.

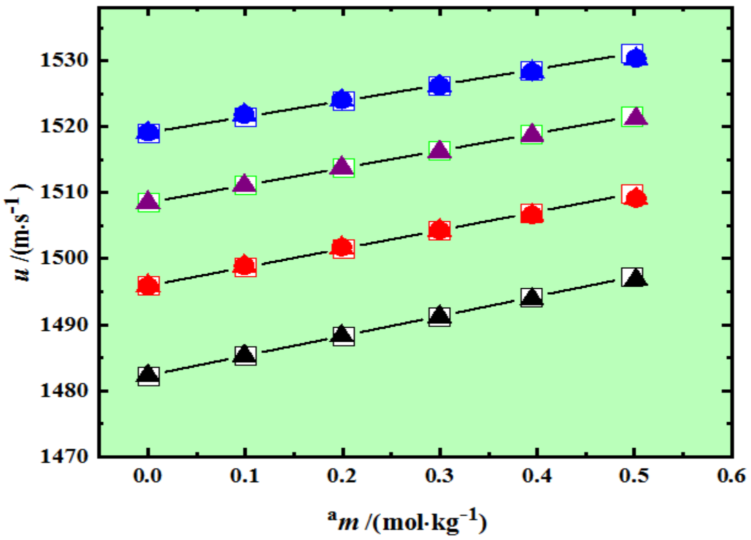


Figure 5: Graph of experimental (*empty square*) and literature values (*filled circle* [1]; *filled triangle* [3]) of speed of sound for mixtures of (EG + water) at various temperatures. [*black*, 293.15 K; *red*, 298.15 K; *green*, 303.15 K; *blue*, 308.15 K]. [Solid lines, experimental data; dotted lines, literature data]

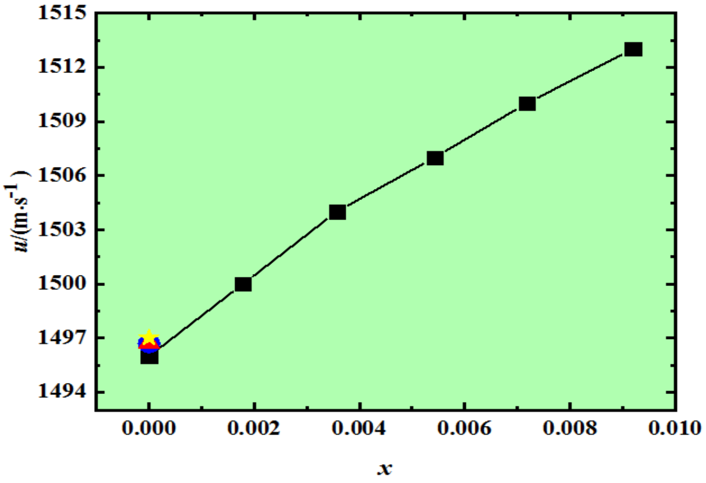


Figure 6: Graph of experimental (*filled square*) and literature values (*filled circle* [4]; *filled triangle* [5] *filled star* [6]) of speed of sound for mixtures of (PG + water) at 298.15K temperature.

The sound speed values at all working temperatures are indexed in **Table 4.14.**

Table 4.14

Speed of sound, *u* and apparent molar isentropic compression, ($K_{\phi,s}$) of ternary system (glycol + SEP + water) at various temperatures and atmospheric atmosphere, p = 0.1MPa.

^{a}m/ (mol·kg^{-1})	u/(m·s^{-1})				$K_{\phi,s}\times10^{6}$/(m^{3}· mol^{-1}·GPa^{-1})			
	T=293.15K	T=298.15K	T=303.15K	T=308.15K	T=293.15K	T=298.15K	T=303.15 K	T=308.15 K
EG + 0.00 mol·kg^{-1} *SEP*								
0.00000	1482	1496	1509	1519				
0.09955	1485	1499	1511	1521	-45.16	-44.27	-43.51	-42.92
0.20101	1488	1502	1514	1524	-45.42	-44.54	-43.77	-43.18
0.29914	1491	1504	1516	1526	-45.53	-44.64	-43.88	-43.28
0.39376	1494	1507	1519	1529	-45.60	-44.71	-43.94	-43.35
0.49716	1497	1510	1522	1531	-45.66	-44.76	-44.00	-43.40
EG + 0.01 mol·kg^{-1} *SEP*								
0.00000	1486	1499	1510	1520				
0.11173	1489	1501	1512	1523	-44.91	-44.12	-43.47	-42.88
0.19951	1491	1503	1514	1525	-45.11	-44.33	-43.67	-43.08
0.29565	1494	1505	1517	1527	-45.22	-44.43	-43.77	-43.18
0.39718	1496	1508	1519	1529	-45.29	-44.50	-43.84	-43.25
0.49387	1499	1510	1521	1531	-45.34	-44.55	-43.89	-43.30
EG + 0.03 mol·kg^{-1} *SEP*								
0.00000	1486	1500	1512	1522				

0.10147	1489	1503	1514	1524	-44.82	-43.99	-43.93	-42.72
0.19962	1492	1505	1517	1526	-45.07	-44.24	-44.18	-42.96
0.29992	1495	1508	1519	1528	-45.18	-44.35	-44.28	-43.07
0.39779	1497	1510	1521	1530	-45.25	-44.41	-44.35	-43.13
0.49677	1500	1513	1524	1532	-45.30	-44.47	-44.40	-43.19
EG + 0.05 mol·kg^{-1} *SEP*								
0.00000	1489	1502	1514	1524				
0.09792	1491	1505	1516	1527	-44.67	-43.85	-43.17	-42.59
0.19953	1494	1508	1519	1529	-44.94	-44.11	-43.42	-42.85
0.30119	1497	1510	1521	1531	-45.04	-44.22	-43.53	-42.95
0.39819	1501	1513	1524	1534	-45.11	-44.28	-43.59	-43.02
0.50258	1504	1516	1527	1536	-45.17	-44.34	-43.65	-43.07
PG+ 0.00 mol·kg^{-1} *SEP*								
0.00000	1482	1496	1509	1519				
0.09917	1486	1500	1513	1523	-42.62	-44.25	-43.49	-42.90
0.19801	1490	1504	1516	1526	-42.86	-44.49	-43.72	-43.13
0.30136	1493	1507	1520	1529	-42.95	-44.58	-43.81	-43.22
0.39826	1496	1510	1522	1532	-42.99	-44.62	-43.86	-43.27
0.51059	1499	1513	1525	1534	-43.03	-44.66	-43.89	-43.30
PG + 0.01 mol·kg^{-1} *SEP*								

0.00000	1486	1499	1510	1520				
0.10113	1489	1503	1514	1524	-44.84	-44.05	-43.40	-42.82
0.19975	1493	1507	1518	1528	-45.07	-44.28	-43.63	-43.04
0.30093	1498	1511	1522	1531	-45.16	-44.37	-43.71	-43.13
0.39774	1502	1515	1527	1535	-45.20	-44.42	-43.76	-43.17
0.49430	1507	1520	1530	1539	-45.24	-44.45	-43.79	-43.20
PG + *0.03* mol·kg^{-1} *SEP*								
0.00000	1486	1500	1512	1522				
0.10086	1491	1504	1516	1526	-44.80	-43.97	-43.27	-42.70
0.20236	1495	1509	1520	1530	-45.03	-44.20	-43.50	-42.93
0.29894	1500	1513	1524	1533	-45.11	-44.28	-43.58	-43.01
0.40149	1504	1516	1527	1536	-45.16	-44.33	-43.62	-43.05
0.49727	1509	1521	1532	1540	-45.19	-44.36	-43.65	-43.08
PG + *0.05* mol·kg^{-1} *SEP*								
0.00000	1489	1502	1514	1524				
0.10131	1494	1507	1519	1529	-44.66	-43.84	-43.16	-43.09
0.19956	1499	1512	1523	1533	-44.89	-44.07	-43.38	-43.32
0.31442	1504	1517	1528	1538	-44.99	-44.16	-43.47	-43.41
0.40016	1508	1521	1531	1541	-45.03	-44.20	-43.51	-43.44
0.50552	1513	1524	1535	1545	-45.06	-44.23	-43.54	-43.48

[a] m represents the molality of EG and PG in SEP solutions of water. Standard uncertainties u are $u_r(m)$ = 1%, $u(T)$ = 0.01 K, $u(u)$ = 1.0 $\mathrm{m \cdot s^{-1}}$, $u(K_{\phi,s}) = \pm 0.25 \times 10^{-6}\ \mathrm{m^3 \cdot mol^{-1} \cdot GPa^{-1}}$, $u(p)$ = 0.01MPa.

the sound speed escalates as the temperature rises. This elevation in temperature related sound speed is a feature of water and is involved in the building of water with three sided constructions of H-bonds [31]. It is also noticed from **Table 4.14** that the ultrasonic speed elevates with glycols molality at a determined SEP concentration.

Apparent molar isentropic compression

For all glycols in aqueous SEP solution, the apparent molar property of isentropic compression ($K_{\phi,s}$) has been evaluated by using **eq. 4.2.**

Laplace – Newton equation [32] explained isentropic compressibility with the help of **eq. 4.3.**

Table 4.14 provides the data of calculated values of $K_{\phi,s}$ for glycols in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} aqueous SEP solutions at various temperatures. It has been reviewed from the computed data of $K_{\phi,s}$ that the values are negative for whole concentration of SEP and at entire working temperatures. The negative $K_{\phi,s}$ values reduced with increase concentration of SEP and accelerate with temperature rise. It is estimated from the negative value of $K_{\phi,s}$ that the hydrogen bonded network [33] around solute molecules become less compressible in comparison to water fragments in augmented solution, ensuing in contraction of water fragments throughout the solute as a result of hydrophobic interaction of non polar group. Consequently, solution compressibility is by the virtue of stress on fragments of water. According to the acquired negative $K_{\phi,s}$ values, water molecules around the solute are less compressible as compared to water in bulk solution which also promotes robust solute-solvent connections midst the glycols and SEP fragments.

Partial molar isentropic compression

The variation of molality (m) with partial molar isentropic compression ($K^0_{\phi,s}$) is epitomized by using **eq 4.5.**

The $K^0_{\phi,s}$ and S_k both values along with their standard errors which are obtained from least square fitting technique are collected in **Table 4.15**.

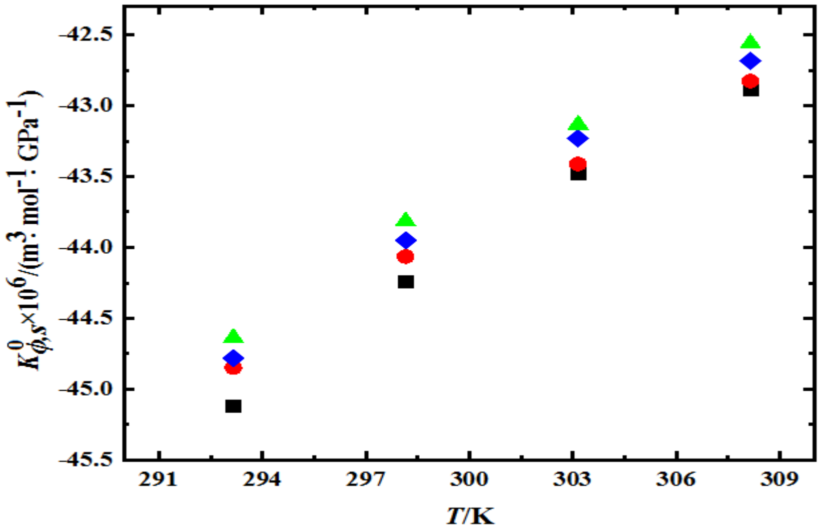
Table 4.15

Limiting apparent molar isentropic compression, ($K^0_{\phi,s}$) and experimental slope, S_k of EG and PG in aqueous solution of SEP at different temperatures.

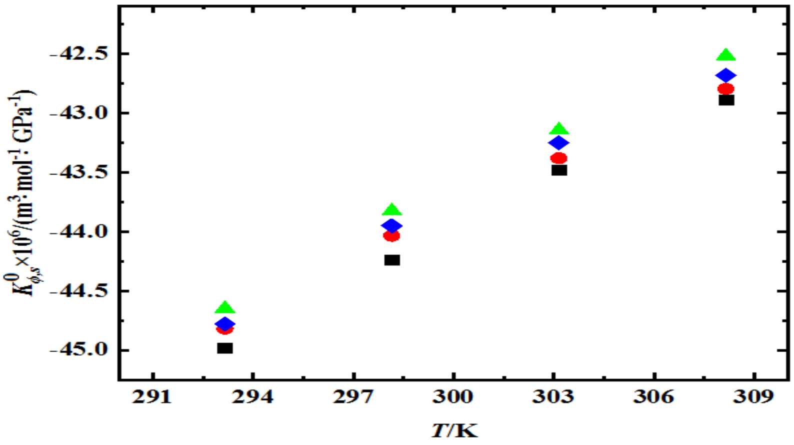
[a] *m*/ (mol·kg^{-1})	$K^0_{\phi,s}\times10^6$/(m^3·mol^{-1}·GPa^{-1})				$S_k\times10^6$/(kg·m^3·mol^{-2}·GPa^{-1})			
	T=293.15 K	*T*=298.15K	*T*=303.15K	*T*=308.15K	*T*=293.15 K	*T*=298.15K	*T*=303.15K	*T*=308.15K
				EG				
0.00	-45.12(±0.08)	-44.24(±0.08)	-43.48(±0.08)	-42.89(±0.08)	-1.18(±0.24)	-1.16(±0.24)	-1.15(±0.23)	-1.14(±0.23)
0.01	-44.85(±0.06)	-44.07(±0.06)	-43.41(±0.06)	-42.83(±0.06)	-1.08(±0.20)	-1.07(±0.19)	-1.06(±0.19)	-1.05(±0.19)
0.03	-44.78(±0.08)	-43.95(±0.07)	-43.23(±0.07)	-42.68(±0.07)	-1.15(±0.23)	-1.13(±0.22)	-1.12(±0.22)	-1.11(±0.22)
0.05	-44.64(±0.08)	-43.82(±0.08)	-43.13(±0.08)	-42.56(±0.08)	-1.16(±0.24)	-1.14(±0.24)	-1.13(±0.23)	-1.12(±0.23)
				PG				
0.00	-44.98(±0.08)	-44.24(±0.08)	-43.48(±0.08)	-42.89(±0.08)	-0.93(±0.23)	-0.93(±0.22)	-0.92(±0.22)	-0.91(±0.23)
0.01	-44.82(±0.08)	-44.04(±0.07)	-43.38(±0.07)	-42.80(±0.07)	-0.95(±0.23)	-0.93(±0.23)	-0.93((±0.22)	-0.92(±0.22)
0.03	-44.78(±0.07)	-43.95(±0.08)	-43.25(±0.07)	-42.68(±0.07)	-0.93(±0.23)	-0.92(±0.23)	-0.91(±0.22)	-0.91(±0.22)
0.05	-44.65((±0.07)	-43.83(±0.07)	-43.14(±0.07)	-42.52(±0.07)	-0.91(±0.22)	-0.90(±0.22)	-0.89(±0.212)	-0.89(±0.21)

[a] *m* is the molality of SEP solutions in water. Standard uncertainties *u* are $u_r(m)$ = 1%, *u* (*T*) = 0.01 K, *u* ($K^0_{\phi,s}$) = ±0.01×10^{-6} m^3·mol^{-1}·GPa^{-1} and *u* (S_k) = ±0.24×10^{-6} kg·m^3·mol^{-2}·GPa^{-1}

The interaction among the solute – solute molecules at infinite dilution become insignificant as a result of relatively small size of S_k values, which implies that the solute-solvent interactions [34, 55] prevail in the liquid mixture. Due to surge in temperature, negative $K^0_{\phi,s}$ values become less which indicates that the few molecules of water are released to the bulk. Also, these $K^0_{\phi,s}$ values turn out to be less negative with rise in SEP concentration. At low temperature, the greater negative values of $K^0_{\phi,s}$ for glycols point towards the strong attractive interaction within the molecules of glycol and water [35]. The presence of robust appealing associations midst SEP and water molecules causes glycols to be desiccated as a consequence of which the water molecules across the glycols are more compressible at greater SEP concentration than those at lower SEP concentrations. The $K^0_{\phi,s}$values are graphically shown in **Figure 7.**



(a)



(b)

Figure 7: Graph.of $K^0_{\phi,s}$, partial molar isentropic compression for (a) EG (b) PG in (0.00, 0.01, 0.03 and 0.05) mol·kg^{-1} SEP solutions of water at various temperatures.

At low temperature, the greater negative values of $K^0_{\phi,s}$ for glycols point towards the strong attractive interaction within the molecules of glycol and water [35]. The presence of robust appealing associations midst SEP and water molecules causes glycols to be desiccated as a consequence of which the water molecules across the glycols are more compressible at greater SEP concentration than those at lower SEP concentrations.

The comparison of assessed data and published limiting partial molar isentropic compression data for (EG + water) is recorded in **Table 4.16**. The acquired experimental values of $K^0_{\phi,s}$ are in excellent agreement with literature values and obey the similar trend as reported studied values.

Table 4.16
Comparison of partial molar volume and partial molar isentropic compression obtained in this work with the literature data.

T/K	$V_{\phi}^{0}\times10^{6}/(\mathrm{m^{3}.\ mol^{-1}})$		dev$^{\#}$/m^{3}. mol^{-1}	$K_{\phi,s}^{0}\times10^{6}/(\mathrm{m^{3}.mol^{-1}.GPa^{-1}})$		dev$^{\#}$/m^{3}. mol^{-1}.GPa^{-1}
	Experimental	Literature		Experimental	Literature	
Ethylene glycol +Water						
293.15	54.55	54.37[51]	0.18	-45.12	-45.13[3]	0.01
		54.43[52]	0.12			
298.15	54.58	53.66[76]	0.92	-44.24	-44.23[3]	-0.01
		53.67[1]	0.91		-44.34[1]	0.1
		54.59[51]	-0.01			
		54.59[53]	-0.01			
303.15	54.6	53.88[38]	0.72	-43.48	-43.48[3]	0
		54.13[1]	0.47			
		54.77[51]	-0.17			
		54.8[81]	-0.2			
308.15	54.61	54.08[38]	0.53	-42.89	-42.88[3]	-0.01
		54.54[1]	0.07		-42.99[1]	0.1
		54.97[51]	-0.36			
		54.89[54]	-0.28			

$^{\#}$Deviation between present work and the literature data

Partial molar isentropic compression of transfer

The apparent molar isentropic compression of transfer ($\Delta_{tr}K^0_{\phi,s}$) of each glycol from water to aqueous solution of SEP at infinite dilution is calculated from succeeding equation:

$$\Delta_{tr}K^0_{\phi,s} = K^0_{\phi,s}\ (in\ aqueous\ SEP) - K^0_{\phi,s}\ (in\ water) \qquad (4.12)$$

Where $K^0_{\phi,s}$ is the partial molar isentropic compression and the values of $\Delta_{tr}K^0_{\phi,s}$ is indexed in **Table 4.17** and are investigated to be positive at entire concentration of SEP and whole range of temperature with the exception of EG in 0.03 mol·kg^{-1} aqueous SEP solution at 303.15 K and PG in (0.01, 0.03, and 0.05) mol·kg^{-1} aqueous SEP solutions at 293.15 K. Therefore, intimate the preponderance of interactions among both glycols and SEP that further insinuates the tendency of solute to build structure.

Pair and triplet interaction coefficients

The volumetric and isentropic compressibility pair and triplet interaction coefficients were computed by McMillan and Mayer [36] that let the partition of effects caused as a result of interaction midst two or more solute fragments and those induced by their interaction between the solute pair. This theory of McMillan and Mayer was discussed further by Friedman and Krishnan [37, 56].

Transfer properties of partial molar volume and partial molar isentropic compression can be articulated through following equation

$$\Delta_{tr}V^0_{\phi}\ \text{(water to aqueous solution of SEP)} = 2V_{AB}\,m_B + 3V_{ABB}\,m^2{}_B \qquad (4.13)$$

$$\Delta_{tr}K^0_{\phi,s}\ \text{(water to aqueous solution of SEP)} = 2K_{AB}\,m_B + 3K_{ABB}\,m^2{}_B \qquad (4.14)$$

where m_B specifies the molality of SEP solutions in water, A denotes glycol and B denotes SEP; The pair interaction coefficients of volume and isentropic compression are represented as V_{AB} and K_{AB} on the other hand, the triplet interaction coefficients of volume and isentropic compression are stated as V_{ABB} and K_{ABB} respectively. **Table 4.17** provides the values of these parameters. The values are positive for pair interaction coefficient, V_{AB} for all the glycols whereas for triplet interaction coefficient, V_{ABB} the values are negative. For the isentropic compression, coefficient of pair interaction, K_{AB} is positive at all the temperatures apart from EG and PG at 303.15 K and 293.15 K whereas K_{ABB} is negative throughout all the temperatures excluding EG at 303.15 K and PG at 293.15 K. Overall large positive values of V_{AB} suggests the superiority of pair-wise interactions over triplet interactions in glycols-SEP-water ternary systems. As per this model, molecules of water are released from hydration co-spheres as a consequence of their association when non-bonding interaction occurs. The volume shift is positive if the bulk is more organized than water and would be negative if water is more organized than bulk, i.e. owing to different structural arrangement of water molecules in these two domains, water is removed from the co-sphere. The pair wise interaction among the aqueous solution of glycols and SEP is estimated by the V_{AB} positive values.

Table 4.17

Pair (V_{AB} and K_{AB}) and triplet (V_{ABB} and K_{ABB}) interaction coefficients for EG and PG in aqueous solutions of SEP at T = (293.15 K to 303.15) K.

From Volume		From Compression	
$V_{AB} \times 10^6$/($m^3 \cdot mol^{-1}$)	$V_{ABB} \times 10^6$/($m^3 \cdot mol^{-1}$)	$K_{AB} \times 10^6$/($m^3 \cdot mol^{-1} \cdot GPa^{-1}$)	$K_{ABB} \times 10^6$/($m^3 \cdot mol^{-1} \cdot GPa^{-1}$)
		EG	
5.12	-34.38	9.86	-69.68
4.91	-32.46	6.91	-37.25
5.22	-37.80	-14.01	225.03
4.97	-34.77	3.39	-1.55
		PG	
2.29	-8.88	-84.16	871.15
2.40	-10.55	7.80	-50.40
2.98	-20.84	4.79	-19.23
3.41	-28.86	9.80	-154.15

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Part III

In previous parts, we have reported the densities and ultrasonic speeds of (EG, PG and HG) with methyl paraben and two glycols (EG and PG)) with sodium ethylparaben. In continuation to our work on parabens with glycols, in the present part we have studied EG and PG in methanol solutions of propyl paraben.

Density and speed of sound

The experimental data and literature data of densities for EG + methanol [1, 2] and PG + methanol [3] are plotted from **Figure 1 to 3**. It is found that the experimental values follow the same trend as literature values.

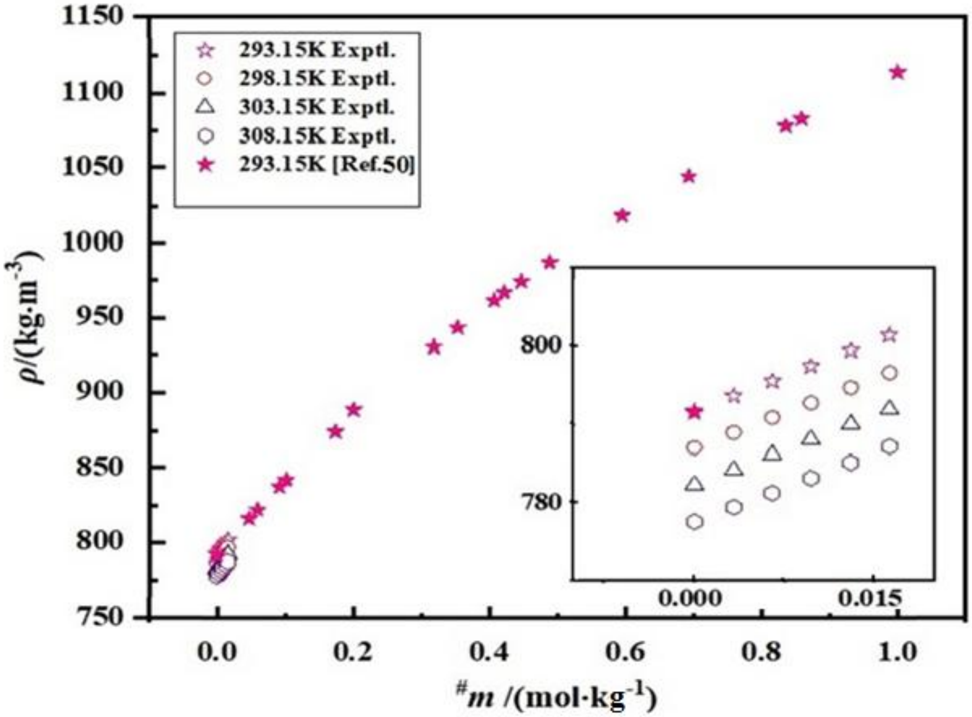

Figure 1: Plot of experimental and literature values [1] of density for EG+methanol mixtures at T=293.15K.

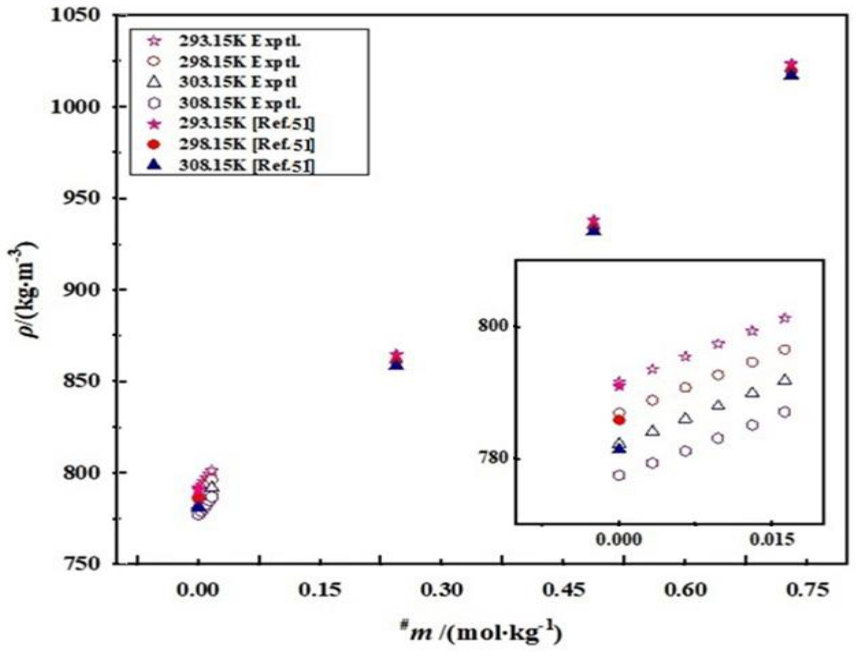

Figure 2: Plot of experimental and literature values [2] of density for EG+methanol mixtures at different temperatures**.**

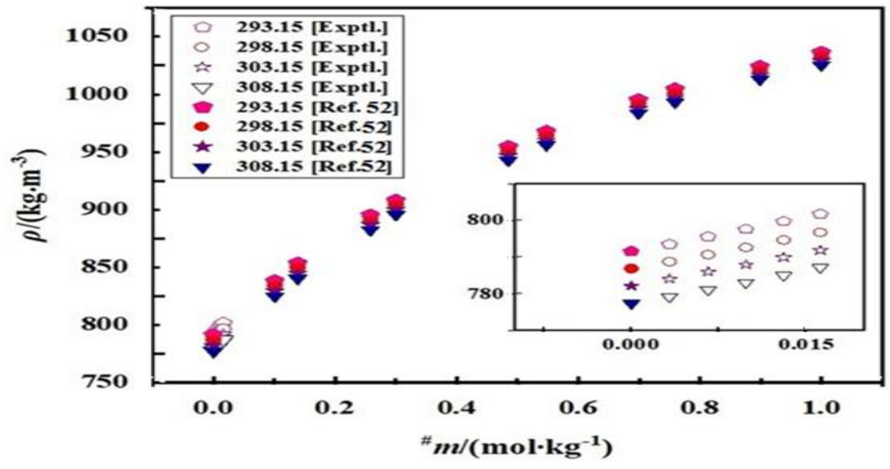

Figure 3: Plot of experimental and literature values [3] of density for PG+methanol at different temperatures.

The experimental and literature comparison of density and speed of sound values are listed in **Table 4.18**

Table 1 Comparison of experimental and literature density and speed of sound values.

Component	**T/K**	**$\rho\times10^{-3}$/(kg·m^{-3})**		
		experimental	literature	experimental
Methanol	293.15	0.791666	0.79145[a]	1120.07
			0.791786[j]	
			0.790004[c]	
			791.28[l]	
	298.15	0.786968	0.78654[b]	1103.59
			0.786548[j]	
			0.7866[m]	
			0.78657[n]	
			0.78664[r]	
			786.794[o]	
	303.15	0.782246	0.782374[c]	1087.2
			0.7782286[j]	
			0.782374[c]	

			781.84[l]		
			0.78185[n]		
	308.15	0.777507	777.3[d]	1071.06	
			0.777067[j]		
			0.7771[n]		
			0.77728[r]		
Ethylene glycol	293.15	1.112856	1.11323[a]	1667.64	
			1.11202[q]		
	298.15	1.109359	1.1003[f]	1655.94	
			1.1097[m]		
			0.99707[n]		
	303.15	1.105854	1.105825[e]	1644.26	
	308.15	1.102341	1.1025[e]	1632	
Propylene	293.15	1.036381	1.03275[g]	1524.95	1522.42[s]

glycol					1509.3[q]
	298.15	1.03271	1.03275[g]	1511.23	1508.41[s]
			1.0325[m]		1500.6[q]
			1.03261[n]		
			1032.526[o]		
	303.15	1.028998	1.02902[g]	1497.31	1492[g]
			1.0289[n]		1494.33[s]
					1495.5[q]
	308.15	1.025253	1.02540[g]	1483.39	1454[g]
			1.02516[n]		1480.19[s]
					1489.2[q]

a, [1]; b, [12]; c, [13]; d, [8]; e, [14]; f, [15]; g, [16;] h, [17]; j, [19]; s, [20]; l, [21]; m, [22]; n, [23] ;o, [52]; r, [18]; q, [24] The experimental values are in good agreement with literature values. The experimentally calculated data of densities and speed of sound for EG and PG in (0.00, 0.01, 0.03 and 0.05) mol.kg^{-1} methanol solutions of propylparaben at temperature T = (293.15, 298.15, 303.15 and 308.15) K is reported in **Table 4.19**.

Table 4.19 Densities (ρ), and speed of sound (u) for ethylene glycol/propylene glycol in methanol solutions of propylparaben ternary systems at different temperatures and experimental pressure p = 0.1 MPa

^{a}m /(mol·kg^{-1})	ρ ×10^{-3}/ (kg·m^{-3})				u /(m·s^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
EG + 0.00 mol·kg^{-1} propylparaben								
0.00000	0.791666	0.786968	0.782246	0.777507	1120.07	1103.59	1087.2	1071.06
0.10174	0.793584	0.788891	0.784122	0.779365	1123.78	1107.47	1090.89	1075.64
0.20228	0.795511	0.790820	0.786069	0.781201	1127.62	1111.24	1094.82	1079.82
0.30187	0.797400	0.792720	0.787985	0.783106	1131.47	1114.94	1098.59	1083.79
0.40599	0.799359	0.794682	0.789959	0.785122	1135.18	1118.96	1102.54	1087.87
0.50547	0.801317	0.796566	0.791858	0.787120	1138.86	1122.65	1106.15	1091.47
EG + 0.01 mol·kg^{-1} propylparaben								
0.00000	0.792535	0.787825	0.783106	0.778368	1121.98	1105.41	1088.97	1072.94
0.10026	0.794319	0.789715	0.784998	0.780154	1126.12	1109.56	1093.25	1077.82
0.19870	0.796209	0.791606	0.786920	0.781922	1130.14	1113.45	1097.22	1082.24
0.30086	0.798143	0.793550	0.788909	0.783866	1134.01	1117.41	1101.09	1086.62

0.40163	0.800037	0.795449	0.790812	0.785805	1137.88	1121.41	1104.97	1090.62
0.49648	0.801900	0.797245	0.792620	0.787734	1141.31	1125.26	1108.65	1094.29
EG + 0.03 mol·kg^{-1} propylparaben								
0.00000	0.794234	0.789463	0.784805	0.780019	1125.19	1108.53	1092.31	1075.62
0.10021	0.796105	0.791190	0.786553	0.781868	1129.46	1112.25	1096.75	1080.52
0.20138	0.798049	0.793074	0.788508	0.783752	1133.45	1116.26	1100.82	1085.02
0.29971	0.799912	0.794977	0.790339	0.785643	1137.23	1120.13	1104.83	1089.18
0.39919	0.801778	0.796843	0.792284	0.787525	1140.92	1124.07	1108.77	1093.28
0.49662	0.803681	0.798712	0.794149	0.789439	1144.53	1128.05	1112.85	1097.28
EG + 0.05 mol·kg^{-1} propylparaben								
0.00000	0.795953	0.791117	0.786598	0.781745	1128.28	1111.08	1095.28	1078.46
0.10046	0.797810	0.792997	0.788392	0.783509	1131.99	1114.82	1099.58	1083.13
0.20158	0.799751	0.794932	0.790324	0.785350	1135.8	1118.72	1103.68	1087.65
0.30199	0.801628	0.796813	0.792192	0.787289	1139.53	1122.38	1107.96	1091.87
0.39479	0.803399	0.798605	0.793947	0.789087	1143.01	1126.12	1111.72	1095.7
0.49729	0.805309	0.800505	0.795866	0.790922	1146.77	1130.28	1116.02	1099.95
PG+ 0.00 mol·kg^{-1} propylparaben								
0.00000	0.791666	0.786968	0.782246	0.777507	1120.07	1103.59	1087.2	1071.06
0.10172	0.793520	0.788759	0.784020	0.779218	1123.8	1107.17	1090.99	1075.54

0.20520	0.795550	0.790665	0.785950	0.781103	1127.52	1110.84	1094.79	1079.92
0.30599	0.797590	0.792647	0.787891	0.783051	1131.14	1114.54	1098.49	1083.88
0.40680	0.799712	0.794626	0.789890	0.785030	1134.89	1118.06	1102.14	1087.87
0.50507	0.801709	0.796697	0.791826	0.787190	1138.56	1121.49	1105.75	1090.47
PG + 0.01 mol·kg^{-1} propylparaben								
0.00000	0.792535	0.787825	0.783106	0.778368	1121.98	1105.41	1088.97	1072.94
0.10508	0.794341	0.789618	0.784926	0.780060	1126.22	1109.78	1093.47	1078.07
0.20280	0.796267	0.791439	0.786712	0.781833	1130.05	1113.68	1097.49	1082.45
0.29990	0.798212	0.793288	0.788555	0.783701	1133.9	1117.22	1101.34	1086.49
0.39654	0.800235	0.795238	0.790419	0.785613	1137.57	1120.89	1105.11	1090.52
0.50195	0.802338	0.797485	0.792596	0.787803	1141.73	1124.48	1108.97	1094.58
PG + 0.03 mol·kg^{-1} propylparaben								
0.00000	0.794234	0.789463	0.784805	0.780019	1125.19	1108.53	1092.31	1075.62
0.10205	0.795981	0.791059	0.786496	0.781805	1129.21	1112.56	1096.68	1080.68
0.19825	0.797829	0.792846	0.788231	0.783549	1132.93	1116.18	1100.61	1085.11
0.30546	0.799878	0.794866	0.790222	0.785589	1136.93	1120.42	1104.8	1089.71
0.40342	0.801832	0.796841	0.792192	0.787518	1140.56	1124.08	1108.64	1093.9
0.50400	0.803984	0.798919	0.794214	0.789758	1144.33	1127.8	1111.48	1097.77
PG + 0.05 mol·kg^{-1} propylparaben								

0.00000	0.795953	0.791117	0.786598	0.781745	1128.28	1111.08	1095.28	1078.46
0.10248	0.797704	0.792926	0.788339	0.783510	1131.92	1115.41	1099.77	1083.35
0.19863	0.799505	0.794704	0.790056	0.785249	1135.43	1119.38	1103.78	1087.72
0.30432	0.801531	0.796681	0.791974	0.787251	1139.42	1123.44	1108.08	1092.31
0.40183	0.803493	0.798656	0.793912	0.789157	1143.12	1127.24	1111.98	1096.47
0.50420	0.805641	0.800717	0.796004	0.791276	1146.92	1131.24	1116.00	1100.63

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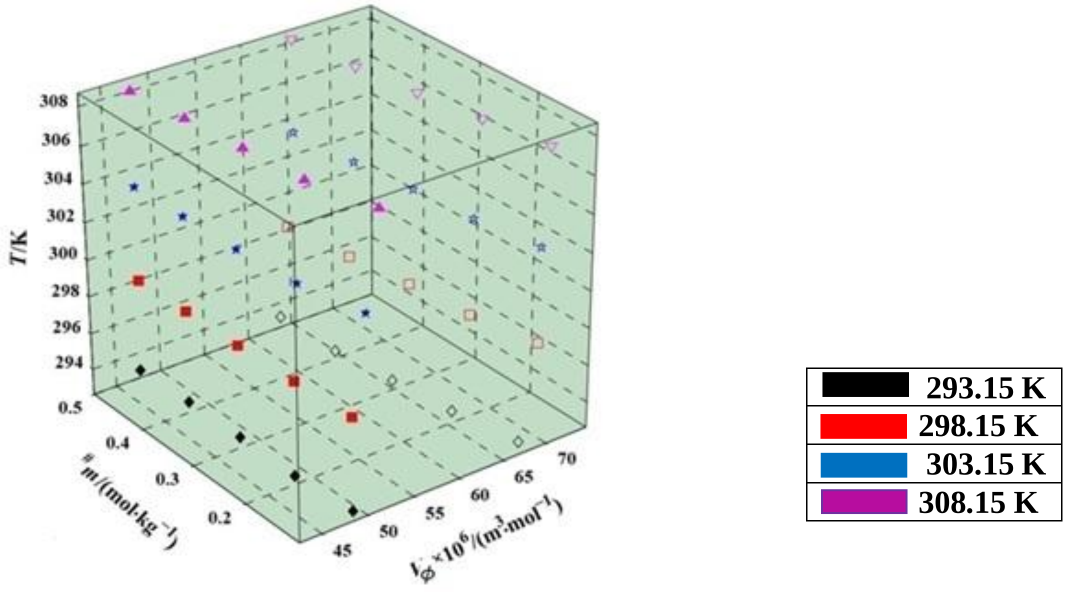
[a] *m* is the molalities of ethylene glycol and propylene glycol in methanol solution of propylparaben. Standard uncertainties u are u (*m*) = 5 ×10^{-5} mol.kg^{-1}, *u* (*T*) = 0.01 K, u (ρ) = 0.8 kg.m^{-3}, u (*u*) = 1.1 m.s^{-1} and u (*p*) = 0.01MPa

From the data reported in **Table 4.19** it has been observed that at a particular propylparaben concentration, density of the solution mixture decreases with rise in temperature and increases with increase in the concentration of glycol for each ternary system.

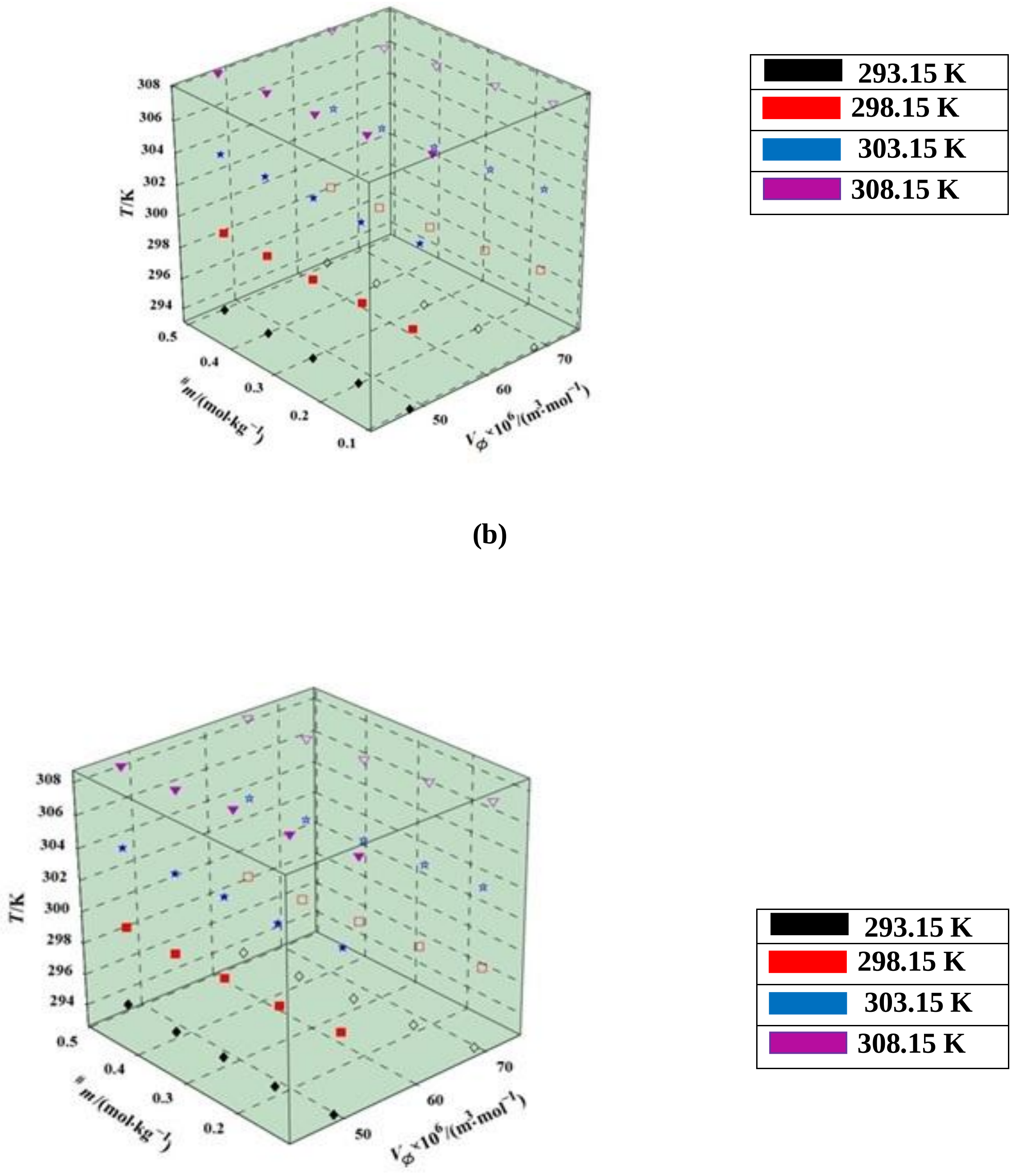
Apparent molar volume and apparent molar isentropic compression

The evaluation of apparent molar isentropic compression ($K_{\phi,s}$) and apparent molar volume (V_{ϕ}) by using **eq. 4.1 and 4.2**.

Figure 4 [(a), (b), (c)] shows the comparison of V_{ϕ} values with concentration for EG and PG in (0.01, 0.03 and 0.05) mol·kg^{-1} methanol solutions of propylparaben at different temperatures.



(a)



(b)

Figure 4: 3D-Plot for comparison of apparent molar volume V_ϕ against concentration m of EG (filled symbols) and PG (hollow symbols) in (a) 0.01 mol·kg^{-1} ; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1} methanol solutions of propylparaben at different temperatures [diamond, 293.15 K; square, 298.15 K; star, 303.15 K; triangle, 308.15 K].

The data of apparent molar volume and apparent molar isentropic compression is listed in **Table 4.20.**

Table 4.20 Apparent molar volume (V_ϕ) and apparent molar isentropic compression ($K_{\phi,s}$) of ethylene glycol/propylene glycol in methanol solution of propylparaben at different temperatures

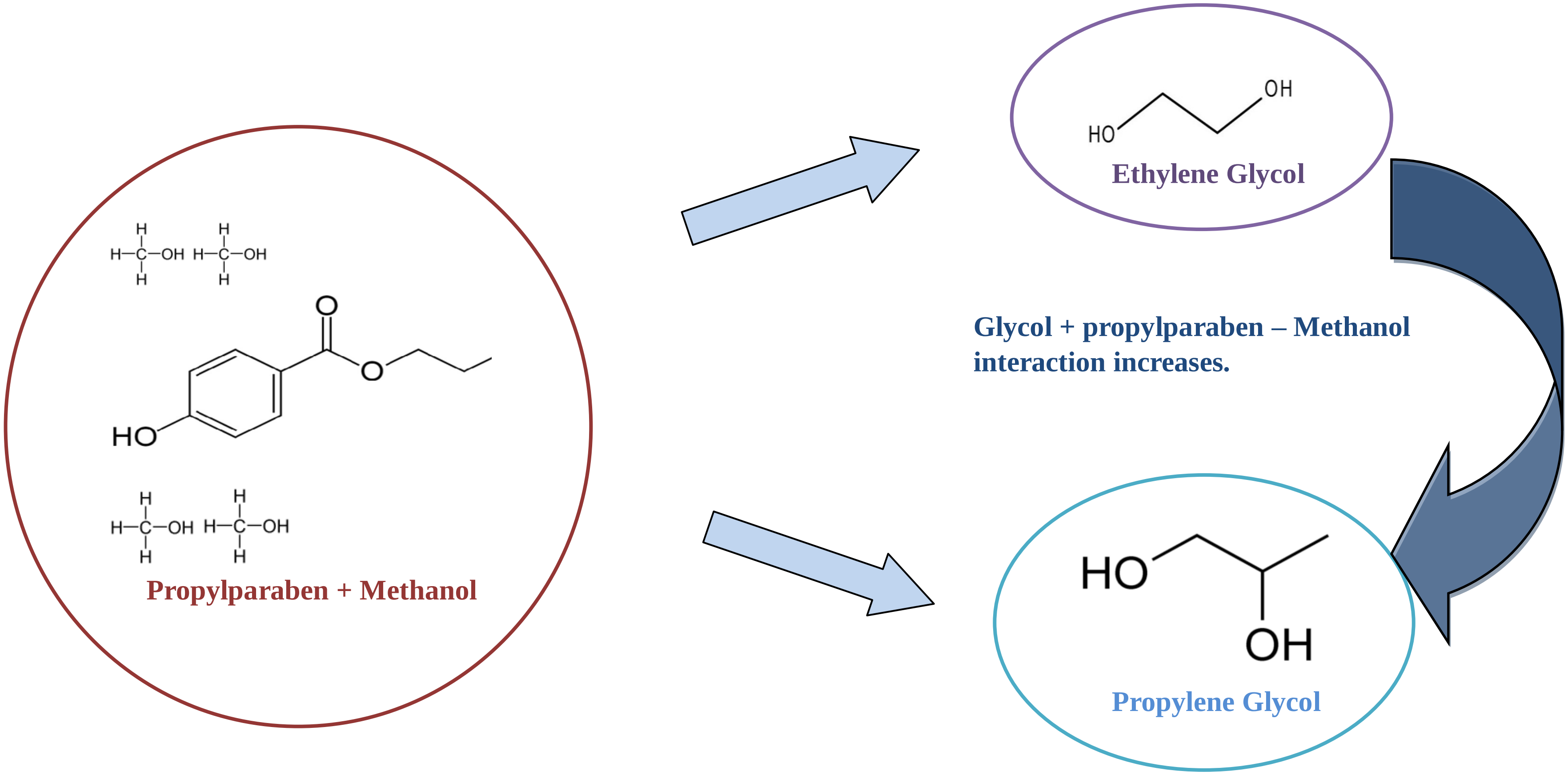
$^a m$	$V_\phi \times 10^6$ /(m^3·mol^{-1})				$K_{\phi,s} \times 10^6$ /(m^3·mol^{-1}·GPa^{-1})			
/(mol·kg^{-1})	T =293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T =293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
EG + 0.00 mol·kg^{-1} propylparaben								
0.10174	48.21	48.24	49.10	49.50	-78.66	-81.01	-83.45	-85.97
0.20228	47.84	47.89	48.23	49.39	-79.48	-81.86	-84.34	-86.88
0.30187	47.75	47.76	47.93	48.80	-79.88	-82.27	-84.77	-87.33
0.40599	47.71	47.72	47.83	48.33	-80.18	-82.59	-85.10	-87.68
0.50547	47.36	47.63	47.69	47.78	-80.44	-82.85	-85.37	-87.98
EG + 0.01 mol·kg^{-1} propylparaben								
0.10026	48.29	48.30	49.83	51.21	-78.38	-80.73	-83.16	-85.67
0.19870	47.85	47.90	48.46	49.41	-79.19	-81.58	-84.04	-86.59
0.30086	47.77	47.78	47.94	48.84	-79.60	-82.00	-84.49	-87.05
0.40163	47.73	47.74	47.87	48.42	-79.90	-82.31	-84.81	-87.39
0.49648	47.40	47.65	47.73	47.79	-80.14	-82.56	-85.07	-87.67
EG + 0.03 mol·kg^{-1} propylparaben								
0.10021	48.44	48.78	49.84	51.68	-77.82	-80.28	-82.65	-85.22
0.20137	47.89	48.59	48.60	49.56	-78.64	-81.12	-83.55	-86.15
0.29971	47.78	48.07	48.49	48.90	-79.03	-81.53	-83.96	-86.59
0.39919	47.74	47.98	48.00	48.59	-79.32	-81.83	-84.28	-86.91
0.496619	47.43	47.76	47.80	47.93	-79.57	-82.09	-84.55	-87.20
EG + 0.05 mol·kg^{-1} propylparaben								
0.10046	48.69	49.71	49.93	52.00	-77.51	-79.93	-82.21	-84.77
0.20158	48.01	48.62	48.80	50.34	-78.32	-80.77	-83.09	-85.68
0.30199	47.98	48.40	48.62	50.00	-78.71	-81.18	-83.51	-86.10
0.39479	47.76	48.02	48.37	48.80	-78.98	-81.46	-83.80	-86.43

0.49729	47.72	47.99	48.22	48.39	-79.23	-81.73	-84.08	-86.69
PG + 0.00 mol·kg^{-1} propylparaben								
0.10172	66.94	68.10	68.61	69.89	-83.57	-82.28	-84.78	-87.35
0.20520	65.62	67.28	67.45	68.56	-84.42	-82.48	-84.99	-87.57
0.30599	64.76	66.24	66.64	67.41	-84.85	-82.69	-85.20	-87.78
0.40680	63.92	65.65	65.92	66.63	-85.17	-82.89	-85.42	-88.01
0.50507	63.59	64.78	65.47	65.34	-85.45	-83.11	-85.63	-88.25
PG + 0.01 mol·kg^{-1} propylparaben								
0.10508	67.04	69.01	69.14	69.95	-79.62	-82.01	-84.50	-87.08
0.20280	65.66	67.60	67.97	68.70	-79.82	-82.20	-84.70	-87.28
0.2999	64.90	66.80	67.31	67.56	-80.01	-82.40	-84.89	-87.49
0.39654	64.09	65.86	66.44	66.69	-80.21	-82.60	-85.10	-87.70
0.50195	63.82	64.80	65.68	65.71	-80.43	-82.83	-85.33	-87.95
PG + 0.03 mol·kg^{-1} propylparaben								
0.10205	68.45	69.05	69.18	70.09	-79.12	-81.55	-83.99	-86.61
0.19825	66.72	67.63	68.23	68.73	-79.31	-81.73	-84.17	-86.81
0.30546	66.02	66.84	67.45	67.59	-79.51	-81.94	-84.39	-87.03
0.40342	65.31	65.89	66.42	66.73	-79.70	-82.14	-84.60	-87.25
0.50400	64.33	65.07	65.71	65.74	-79.92	-82.36	-84.81	-87.49
PG + 0.05 mol·kg^{-1} propylparaben								
0.10248	68.48	69.12	69.15	70.15	-78.71	-81.18	-83.53	-86.15
0.198632	67.07	67.69	68.31	68.78	-78.89	-81.36	-83.71	-86.34
0.30432	66.20	66.94	67.73	67.66	-79.09	-81.56	-83.92	-86.56
0.40183	65.36	65.91	66.70	66.83	-79.29	-81.76	-84.12	-86.77
0.50420	64.48	65.23	65.80	65.85	-79.50	-81.98	-84.34	-87.01

[a] *m* is the molalities of ethylene glycol and propylene glycol in methanol solution of propylparaben

The positive values of V_{ϕ} also shows the existence of stronger solute-solvent interactions which in turn increases from EG to PG as presented in **scheme 1**

Scheme1. Representation of Glycol+ propylparaben-methanol interactions.



The V_ϕ values reported in **Table 4.20** imply that apparent molar volume for ethylene glycol (EG) and propylene glycol (PG) increases with propylparaben-methanol concentration as well as with increase in temperature. The positive V_ϕ values describes the electrostriction interaction are prevailing in the solution mixture [4].

Limiting apparent molar volume and limiting apparent molar isentropic compression

The limiting apparent molar volume V_ϕ^0 and limiting apparent molar isentropic compression $K_{\phi,s}^0$ can be computed by using **eq. 4.4 and 4.5**

The increase of V_ϕ^0 values with increase in temperature and concentration of propylparaben-methanol which is due to enhanced solute-solvent effect. Further V_ϕ^0 values also increases with molar mass of glycols (EG and PG) at each temperature indicating the predominance of solute–solvent interaction in PG as compared to EG with small V_ϕ^0 values. This increase from EG to PG is due to the hydrophobic behaviour of side chain of glycols from EG to PG which lead to larger electrostriction interaction at terminal charged groups hence V_ϕ^0 value increases. Similar behaviour of V_ϕ^0 values with temperature increase was also noticed in (methanol+ methyl acetate) [8] system. The S_v values are smaller than those V_ϕ^0 values and are coming out to be negative at all the working temperatures which show the predominance of solute+ solvent interactions over solute+ solute interactions. The calculated V_ϕ^0 and $K_{\phi,s}^0$ values with S_v and S_k parameters along with their standard errors are attributed in **Table4.21.**

Table 4.21 Limiting apparent molar volumes, (V_ϕ^0), experimental slopes, S_v, limiting apparent molar isentropic compression ($K_{\phi,s}^0$) and experimental slope S_k of ethylene glycol/ propylene glycol in methanol solution of propylparaben at different temperatures

T/K	$V_\phi^0 \times 10^6$ /(m^3· mol^{-1})	$S_V \times 10^6$ /(m^3·kg·mol^{-2})	$K_{\phi,s}^0 \times 10^6$ /(m^3·mol^{-1}·GPa^{-1})	$S_k \times 10^6$ /(kg·m^3·mol^{-2}·GPa^{-1})
EG + 0.00 mol·kg^{-1} propylparaben				
293.15	48.19(±0.13)	-1.18(±0.38)	-78.45(±0.21)	-4.21(±0.63)
298.15	49.14(±0.23)	-7.05(±0.68)	-80.79(±0.22)	-4.36(±0.66)
303.15	50.14(±0.42)	-9.10(±1.26)	-83.22(±0.23)	-4.56(±0.69)
308.15	52.22(±0.34)	-9.33(±1.01)	-85.73(±0.23)	-4.74(±0.69)
EG + 0.01 mol·kg^{-1} propylparaben				
293.15	48.32(±0.11)	-1.80(±0.34)	-78.16(±0.21)	-4.26(±0.63)
298.15	48.26(±0.11)	-1.36(±0.33)	-80.51(±0.22)	-4.42(±0.67)
303.15	49.12(±0.29)	-3.18(±0.88)	-82.93(±0.23)	-4.62(±0.70)
308.15	50.11(±0.15)	-4.45(±0.45)	-85.42(±0.23)	-4.82(±0.72)
EG + 0.03 mol·kg^{-1} propylparaben				
293.15	48.38(±0.13)	-1.90(±0.40)	-77.61(±0.21)	-4.21(±0.64)
298.15	48.31(±0.13)	-1.48(±0.38)	-80.05(±0.22)	-4.39(±0.67)
303.15	49.81(±0.50)	-4.82(±1.50)	-82.42(±0.23)	-4.57(±0.70)
308.15	51.49(±0.49)	-7.87(±1.49)	-84.98(±0.24)	-4.78(±0.72)
EG + 0.05 mol·kg^{-1} propylparaben				
293.15	48.70(±0.22)	-2.22(±0.66)	-77.30(±0.21)	-4.17(±0.63)
298.15	49.78(±0.36)	-4.11(±1.08)	-79.71(±0.22)	-4.34(±0.66)
303.15	49.96(±0.36)	-3.91(±1.09)	-81.99(±0.23)	-4.50(±0.69)
308.15	52.56(±0.40)	-7.87(±1.21)	-84.54(±0.24)	-4.65(±0.72)
PG+ 0.00 mol·kg^{-1} propylparaben				
293.15	67.51(±0.32)	-8.34(±0.94)	-83.31(±0.21)	-4.59(±0.64)
298.15	68.91(±0.11)	-8.20(±0.34)	-82.06(±0.008)	-2.10(±0.02)
303.15	69.19(±0.24)	-7.77(±0.70)	-84.56(±0.008)	-2.14(±0.02)

308.15	70.90(±0.16)	-10.94(±0.49)	-87.11(±0.01)	-2.26(±0.03)
PG + 0.01 mol·kg^{-1} propylparaben				
293.15	67.54(±0.39)	-8.09(±1.17)	-79.40(±0.003)	-2.02(±0.01)
298.15	69.92(±0.18)	-10.30(±0.54)	-81.78(±0.01)	-2.05(±0.03)
303.15	69.88(±0.16)	-8.55(±0.48)	-84.27(±0.008)	-2.07(±0.02)
308.15	70.92(±0.16)	-10.61(±0.50)	-86.84(±0.01)	-2.18(±0.03)
PG + 0.03 mol·kg^{-1} propylparaben				
293.15	69.06(±0.36)	-9.56(±1.09)	-78.91(±0.008)	-1.97(±0.026)
298.15	69.80(±0.22)	-9.60(±0.66)	-81.33(±0.009)	-2.01(±0.002)
303.15	70.02(±0.10)	-8.67(±0.30)	-83.76(±0.009)	-2.05(±0.02)
308.15	70.99(±0.18)	-10.62(±0.55)	-86.37(±0.001)	-2.18(±0.04)
PG + 0.05 mol·kg^{-1} propylparaben				
293.15	69.23(±0.22)	-9.62(±0.67)	-78.50(±0.008)	-1.95(±0.02)
298.15	69.84(±0.26)	-9.48(±0.76)	-80.96(±0.008)	-1.99(±0.02)
303.15	70.03(±0.14)	-8.25(±0.43)	-83.31(±0.01)	-2.02(±0.03)
308.15	71.02(±0.20)	-10.47(±0.60)	-85.92(±0.01)	-2.12(±0.03)

With the help of general polynomial equation **eq. 4.6**, the relation of temperature with V_{ϕ}^{0} can be expressed. The values of these empirical parameters a, b, c are calculated by method of least square fitting. These deviations ARD (σ) are computed from the **eq. 4.7.**

The values of limiting molar expansivity are computed from **eq. 4.8.** It can be noticed that the values of E_{ϕ}^{0} are coming positive for all the system investigated at all working temperatures and concentrations of propylparaben except for EG in 0.01 and 0.03 mol·kg^{-1} propylparaben-methanol system at T=298.15 K. The positive E_{ϕ}^{0} values specify the occurrence of solute-solvent interaction in the system. E_{ϕ}^{0} values show irregular trend with all the concentration of propylparaben and with temperature. Similarly positive values of apparent molar expansibility has been reported for (BMIMBr + water) and ([MOA] + [Tf$_2$N]$^{-}$ + methanol) [8] systems. Due to the interaction between solute and solvent $K_{\phi,s}^{0}$values are discussed in terms of compressibility of solvent [9]. The apparent molar isentropic compression at infinite dilution results due to positive effect or solvent intrinsic effect because of intermolecular free space making the medium or solution more compressible and negative effect also known as solute intrinsic effect that occurs because of interaction between solute and solvent molecule into the intra-ionic free space due to that medium become less compressible because of electrostriction [10]. The solute intrinsic compressibility penetration effect is greater than intrinsic compressibility of the solvent which lead to negative value of limiting apparent molar isentropic compressibilities for EG and PG in (0.00, 0.01, 0.03, 0.05) mol·kg^{-1} propylparaben-methanol ternary system. The small size of S_k values suggests the negligible solute-solute interactions which further shows the predominance of solute – solvent interaction in the present system studied. The values of constants and apparent molar expansibility are represented in **Table 4.22** and **4.23.**

Table 4.22 Empirical parameters of eq (4.6) for ethylene glycol and propylene glycol in methanol solution of propylparaben at different concentrations

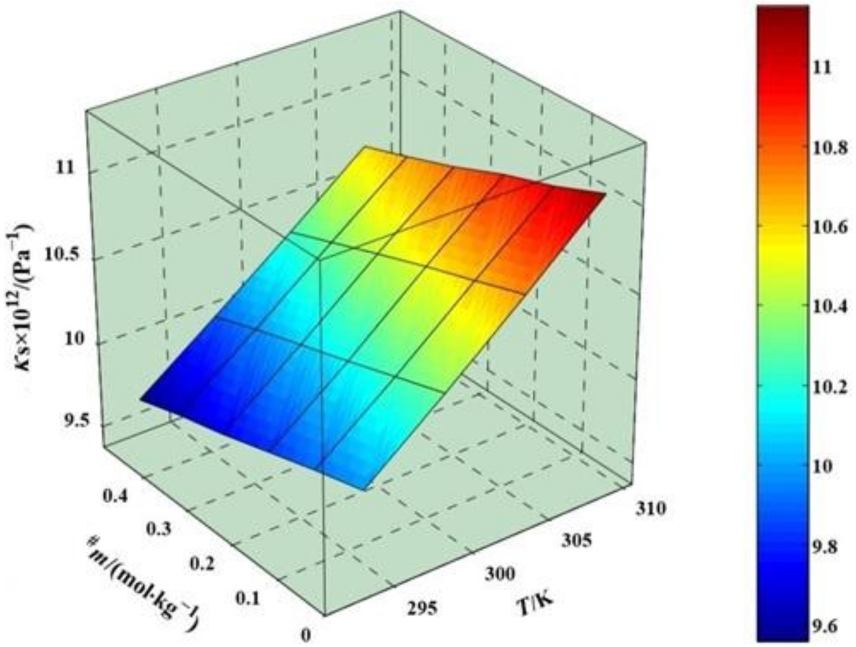
[a]m /(mol·kg^{-1})	$a\times10^6$ /(m^3·mol^{-1})	$b\times10^6$ /(m^3·mol^{-1}·K^{-1})	$c\times10^6$ /(m^3·mol^{-1}·K^{-2})	$ARD(\sigma)$
Ethylene Glycol				
0.00	48.99	0.20	0.01130	0.002097
0.01	48.38	0.07	0.01057	0.001611
0.03	48.52	0.13	0.01745	0.002792
0.05	49.28	0.16	0.01520	0.006627
Propylene Glycol				
0.00	68.53	0.19	0.00308	0.003711
0.01	69.39	0.27	-0.01340	0.004987
0.03	69.61	0.11	0.00225	0.001815
0.05	69.66	0.09	0.00368	0.001745

Table 4.23 Limiting molar expansivity, E_{ϕ}^{0} of ethylene glycol/propylene glycol in methanol solution of propylparaben at different temperatures.

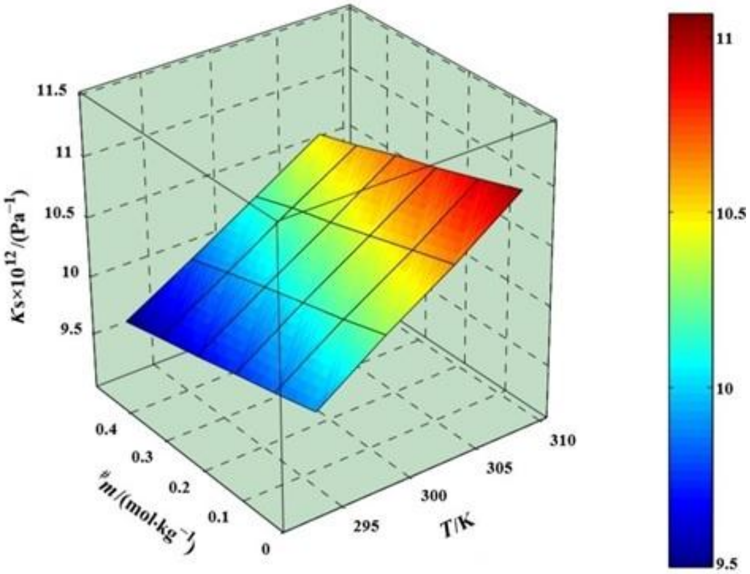
^{a}m/(mol·kg^{-1})	E_{ϕ}^{0} /(m^{3}·mol^{-1}·K^{-1})			
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
Ethylene Glycol				
0.00	0.09	0.20	0.32	0.43
0.01	-0.03	0.07	0.18	0.28
0.03	-0.05	0.13	0.30	0.48
0.05	0.01	0.16	0.31	0.46
Propylene Glycol				
0.00	0.16	0.19	0.22	0.26
0.01	0.40	0.27	0.14	0.00
0.03	0.09	0.11	0.13	0.15
0.05	0.09	0.11	0.13	0.15

[#] m is the molality of ethylene glycol and propylene glycol in methanol solution of propylparaben

An isentropic compressibility [11] has been computed from **eq. 4.3**. The values of isentropic compressibility against molality for EG in (0.01, 0.03 and 0.05) mol·kg^{-1} propylparaben-methanol at different concentration and temperatures are plotted in **Figure 5** whereas, plots for PG are shown in **Figure 6**.



(a)



(b)

(c)

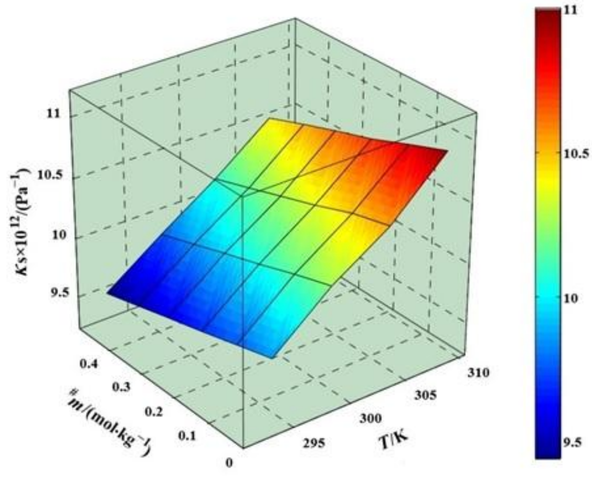
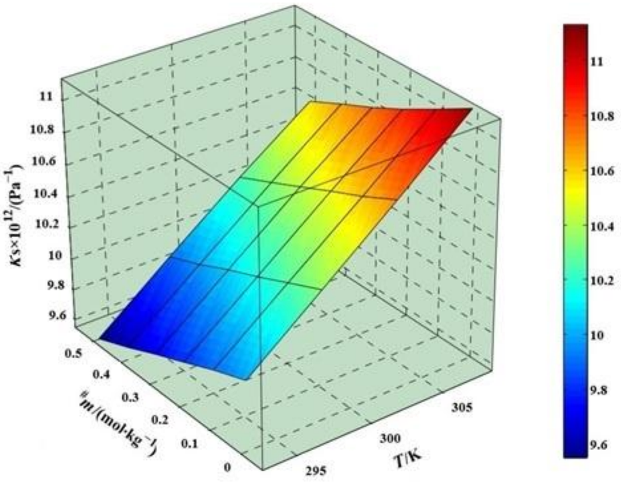
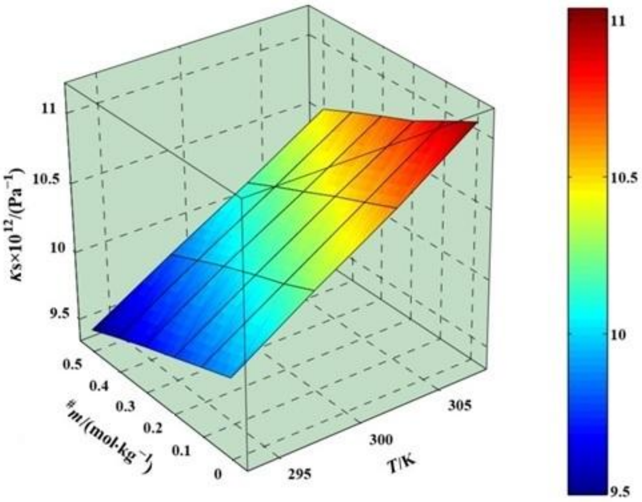


Figure 5: 3D - plots of isentropic compressibilityk_s against molality m of EG in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1} methanol solution of propylparaben at different temperatures.



(a)



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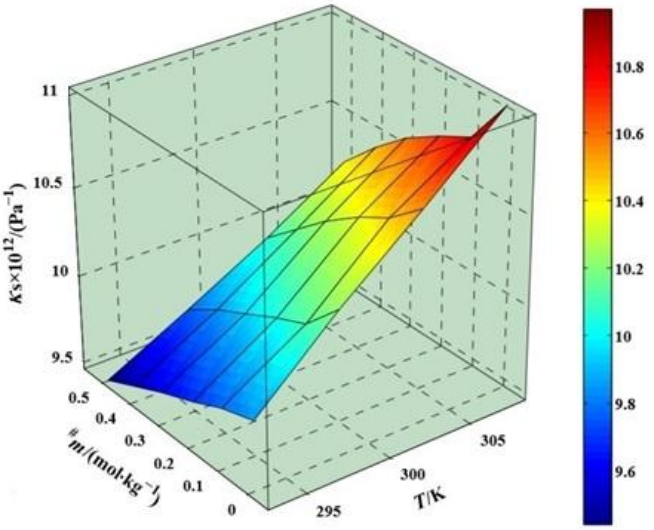

(c)

Figure 6: 3D - plots of isentropic compressibility k_s against molality m of PG in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1} ; (c) 0.05 mol·kg^{-1} methanol solution of propylparaben at different temperatures.

The isentropic compressibility comprises of two terms one is k_s solvent intrinsic compressibility caused by compression of (methanol) solvent and other is k_s solute intrinsic isentropic compressibility caused by compression of hydration shell of solute (glycols). For the investigated systems the isentropic compressibility, shows decreasing trend with concentration increase of solute due to disruption of solvents structure (propylparaben-methanol) and solvation of solute because k_s (solvent intrinsic) effect is dominated by k_s (solute intrinsic) effect.

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Part IV

In continuation to our earlier parts with parabens, in the present part we have studied two PEGs, polyethylene glycol-200 and polyethylene glycol-600 in aqueous solutions of sodium methylparaben at different concentrations and temperatures.

Density and speeds of sound examination

The values of density at a particular concentration of SMP are decreasing w.r.t. temperature. The present computed densities for (PEG-200 and PEG-400) mixture at various temperatures have been correlated with the data recorded in the literature [1-4] and are plotted in **Figure 1 and 2**.

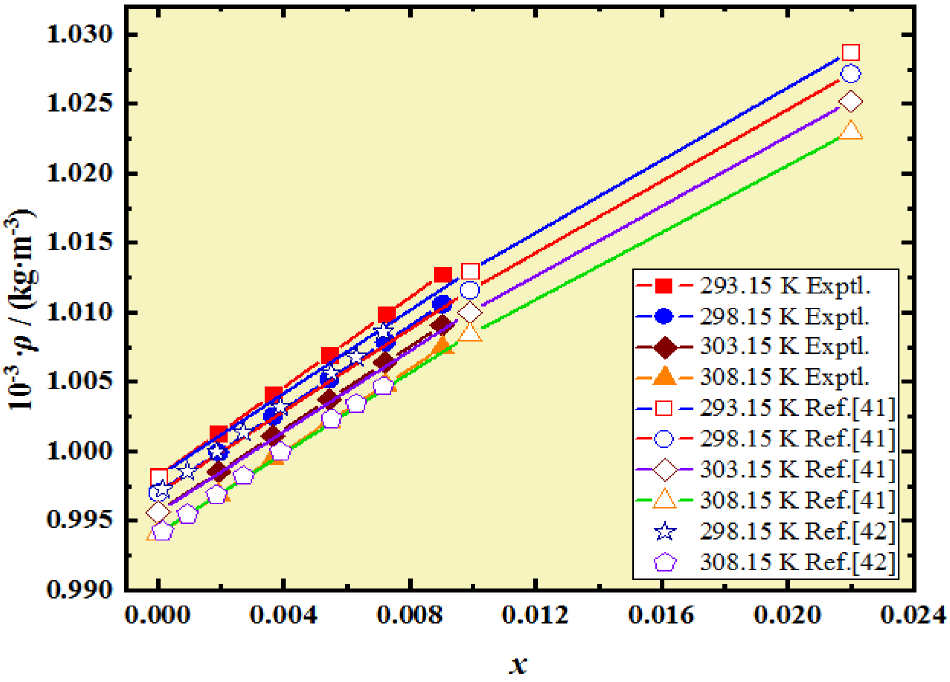

Figure 1: Representation of measured and values reported in literature [1, 2] of densities for (PEG-200+water) at various temperatures.

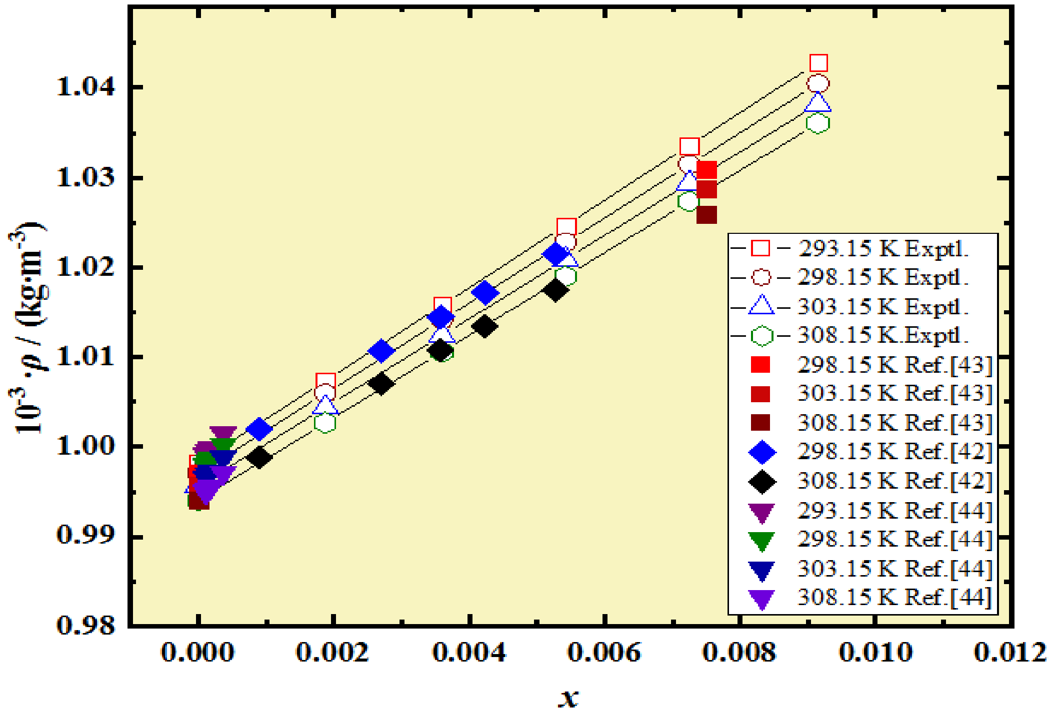

Figure 2: Representation of measured and values reported in the literature [2-4] of densities for (PEG-600+water) at various temperatures

It is depicted from the **Figure 1 and 2** that the present computed density data shows consistency with the author's data in literature. The elevation in *u* w.r.t. temperature is the property of water and is related to three- geometrical grid of hydrogen bonds in water structure [5, 6]. The greater connection is accredited to the intermolecular hydrogen bonding amidst the solute and solvent fragments as well as intermolecular hydrogen bonding amidst molecules of solute itself [7]. The densities, ρ and speed of sound, *u* for PEG-200 and PEG-600 in (0.00, 0.01, 0.03, 0.05) mol·kg^{-1} SMP solutions in water at four temperatures, have been indexed in **Table 4.24**. The values of density at a particular concentration of SMP are decreasing w.r.t. temperature.

Table 4.24 Values of experimental densities, ρ and speeds of sound, u of PEGs in aqueous solutions of sodium methylparaben at several temperatures and experimental pressure p = 0.1 MPa.

^{a}m / (mol·kg^{-1})	$10^{-3}\cdot\rho$ / (kg·m^{-3})				u/(m·s^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
PEG-200 + 0.00 mol·kg^{-1} SMP								
0.00000	0.998211	0.997047	0.995656	0.994039	1481.14	1495.85	1508.84	1519.84
0.10649	1.001086	0.999925	0.998514	0.996894	1491.35	1506.28	1519.04	1529.71
0.20264	1.003682	1.002521	1.001091	0.999471	1500.57	1515.70	1528.25	1538.62
0.30183	1.006360	1.005199	1.003749	1.002129	1510.08	1525.42	1537.75	1547.81
0.40099	1.009038	1.007877	1.006407	1.004787	1519.58	1535.13	1547.25	1557.00
0.50154	1.011753	1.010592	1.009101	1.007481	1529.22	1544.99	1556.88	1566.32
PEG-200 + 0.01 mol·kg^{-1} SMP								
0.00000	0.998697	0.997537	0.996187	0.994523	1482.58	1497.33	1510.32	1521.32
0.09955	1.001365	1.000212	0.998845	0.997181	1492.11	1507.04	1519.93	1530.73

0.19835	1.004013	1.002857	1.001488	0.999820	1501.64	1516.68	1529.47	1540.08
0.30477	1.006865	1.005697	1.004326	1.002652	1511.91	1527.05	1539.75	1550.14
0.40446	1.009536	1.008341	1.006973	1.005309	1521.52	1536.78	1549.38	1559.57
0.50868	1.012330	1.011103	1.009741	1.008071	1531.58	1546.94	1559.44	1569.42
PEG-200 + 0.03 mol·kg^{-1} SMP								
0.00000	0.999671	0.998510	0.997160	0.995491	1485.46	1500.30	1513.29	1524.29
0.10516	1.002468	1.001297	0.999947	0.998277	1495.57	1510.50	1523.48	1534.38
0.20372	1.005090	1.003909	1.002562	1.000891	1504.93	1520.05	1533.04	1543.84
0.31148	1.007956	1.006764	1.005422	1.003738	1515.16	1530.50	1543.48	1554.18
0.40480	1.010439	1.009237	1.007889	1.006214	1524.02	1539.55	1552.53	1563.14
0.49826	1.012925	1.011714	1.010382	1.008701	1532.89	1548.62	1561.58	1572.11
PEG-200 + 0.05 mol·kg^{-1} SMP								
0.00000	1.000645	0.999490	0.998140	0.996459	1488.34	1503.26	1516.25	1527.26
0.10757	1.003474	1.002319	1.000958	0.999289	1498.77	1513.58	1526.46	1537.58

0.20277	1.005978	1.004823	1.003453	1.001798	1507.80	1522.72	1535.50	1546.71
0.30701	1.008719	1.007564	1.006184	1.004546	1517.70	1532.72	1545.39	1556.71
0.40486	1.011293	1.010138	1.008747	1.007122	1526.99	1542.11	1554.68	1566.10
0.51913	1.014298	1.013130	1.011741	1.010101	1537.83	1553.08	1565.53	1577.06
PEG-600 + 0.00 mol·kg^{-1} SMP								
0.00000	0.998211	0.997047	0.995656	0.994039	1481.14	1495.85	1508.84	1519.84
0.10411	1.007362	1.005952	1.004385	1.002661	1510.65	1525.11	1536.98	1547.04
0.19978	1.015771	1.014132	1.012402	1.010582	1537.77	1551.99	1562.84	1572.04
0.30099	1.024667	1.022784	1.020883	1.018962	1566.45	1580.42	1590.19	1598.48
0.40249	1.033589	1.031463	1.029388	1.027366	1595.22	1608.94	1617.62	1625.00
0.50775	1.042841	1.040463	1.038210	1.036082	1625.06	1638.52	1646.07	1652.50
PEG-600 + 0.01 mol·kg^{-1} SMP								
0.00000	0.998697	0.997537	0.996187	0.994490	1482.50	1497.33	1510.32	1521.32
0.10134	1.007564	1.006151	1.004649	1.002850	1511.69	1526.21	1538.19	1548.17

0.20015	1.016210	1.014550	1.012899	1.011002	1540.14	1554.37	1565.36	1574.36
0.29810	1.024781	1.022876	1.021079	1.019083	1568.35	1582.29	1592.30	1600.32
0.40197	1.033870	1.031705	1.029752	1.027653	1598.27	1611.89	1620.86	1627.84
0.50975	1.043300	1.040866	1.038751	1.036544	1629.31	1642.61	1650.50	1656.40
PEG-600 + 0.03 mol$\cdot$kg^{-1} SMP								
0.00000	0.999671	0.998510	0.997160	0.995470	1485.46	1500.30	1513.29	1524.29
0.10121	1.008426	1.007032	1.005530	1.003769	1516.05	1530.78	1542.50	1552.44
0.20232	1.017172	1.015545	1.013892	1.012060	1543.73	1558.37	1568.93	1577.90
0.29791	1.025441	1.023594	1.021797	1.019899	1571.26	1585.80	1595.22	1603.24
0.40211	1.034454	1.032368	1.030414	1.028443	1601.27	1615.71	1623.87	1630.85
0.50998	1.043784	1.041450	1.039335	1.037288	1632.33	1646.66	1653.53	1659.43
PEG-600 + 0.05 mol$\cdot$kg^{-1} SMP								
0.00000	1.000645	0.999490	0.998140	0.996450	1488.34	1503.26	1516.25	1527.26
0.09938	1.009192	1.007808	1.006289	1.004530	1516.96	1532.08	1543.58	1553.50

0.20237	1.018049	1.016428	1.014734	1.012903	1546.62	1561.95	1571.90	1580.69
0.30044	1.026483	1.024637	1.022776	1.020876	1574.87	1590.39	1598.87	1606.58
0.40145	1.035170	1.033091	1.031059	1.029088	1603.96	1619.68	1626.65	1633.24
0.50234	1.043846	1.041536	1.039332	1.037290	1633.01	1648.94	1654.39	1659.88

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[a] m represents the molality of PEGs in aqueous SMP solutions; Standard uncertainties u are $u_r(m)$ = 1%, $u(T)$ = 0.01 K, $u(\rho)$ = 0.15 kg·m^{-3}, $u(u)$ = 1.2 m·s^{-1} and $u(p)$ = 0.01MPa.

The present evaluated *u* data for PEGs in water mixtures has been correlated with the data declared by the authors in the literature [2, 4] and are epitomized in **Figure 3 and 4**.

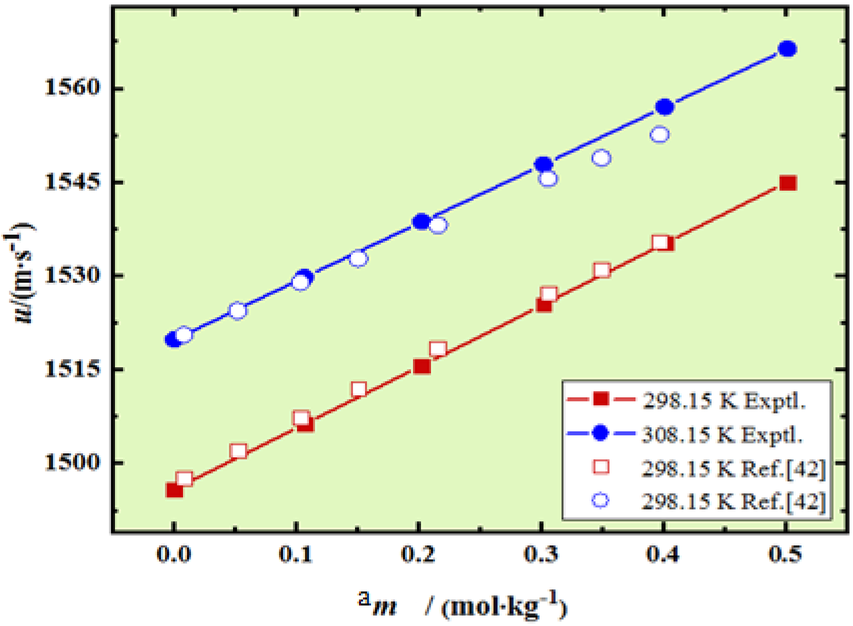


Figure 3: Representation of measured and values reported in the literature [2] of speed of sound for (PEG- 200+water) at various temperatures.

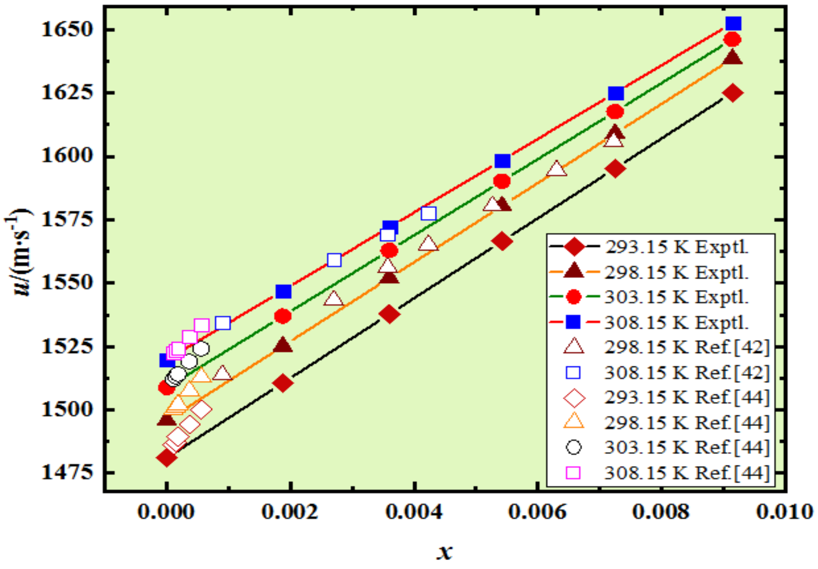


Figure 4: Representation of measured and values reported in the literature [2, 4] of speed of sound for (PEG-600+water) at various temperatures.

It is clear from the Figure 3 and 4 that the agreement of present measured speed of sound data with the data found in literature is satisfactory with one exception [4] in which values for aqueous PEG-600 mixture are systematically higher than the present experimental speed of sound values but the deviations are close to or within the estimated experimental uncertainties. These deviations could be caused by the partial degassing of the measured samples.

Apparent molar volume and apparent molar isentropic compression

The apparent molar volumes, [8] V_{ϕ} and apparent molar isentropic compressions, $K_{\phi,s}$ can be evaluated by applying the **eqs. 4.1 and 4.2.** The isentropic compression coefficient is estimated by exploiting the density and speed of sound data by employing Newton-Laplace's equation i.e. **eq. 4.3**

The attained V_{ϕ} develop positive values, whereas all $K_{\phi,s}$ develop negative values. The positive value of V_{ϕ} signifies the strong solute-solvent interactions [9], which surges from PEG-200 to PEG-600 at whole temperatures as represented in **Scheme 1.**

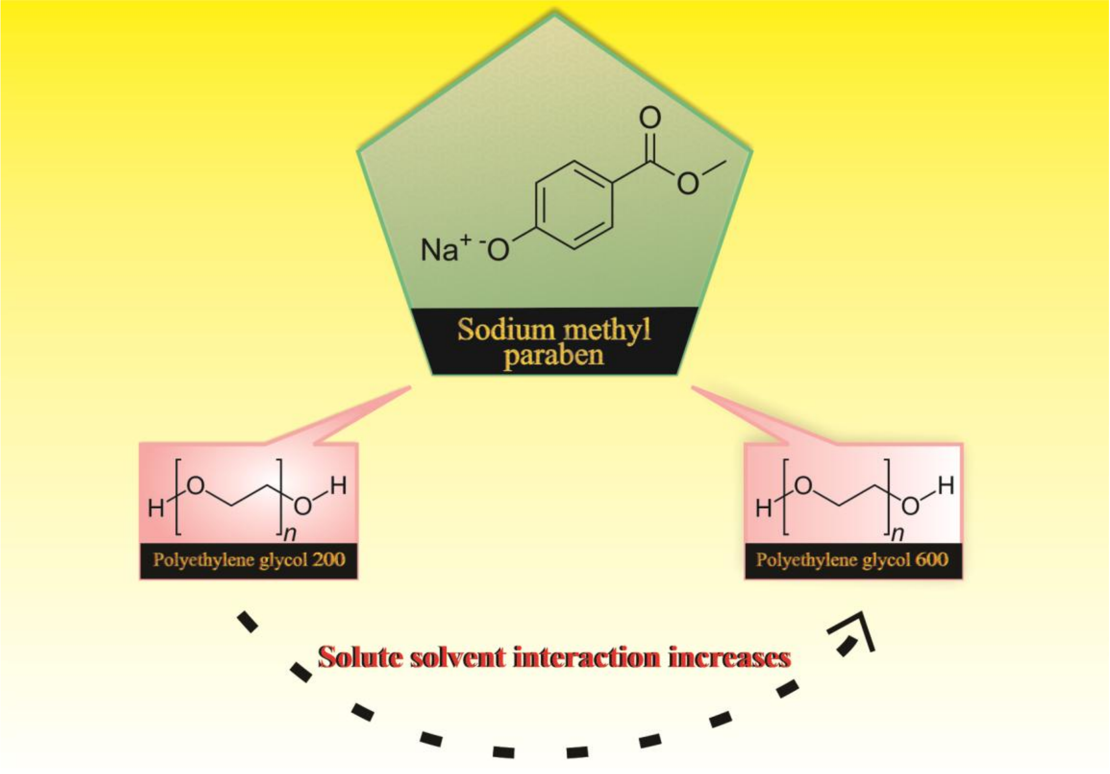


Table 4.25 constitutes the V_{ϕ} and $K_{\phi,s}$ data

Table 4.25 Values of apparent molar volume, V_ϕ and apparent molar isentropic compression, $K_{\phi,s}$ of PEGs in aqueous solutions of SMP at several temperatures and experimental pressure, p = 0.1 MPa.

^{a}m /(mol·kg^{-1})	$10^6 \cdot V_\phi$ / (m^3·mol^{-1})				$10^6 \cdot K_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
PEG-200 + 0.00 mol·kg^{-1} SMP								
0.10649	172.76	172.90	173.30	173.57	-45.28	-44.40	-43.63	-43.57
0.20264	172.32	172.47	172.87	173.13	-45.61	-44.71	-43.95	-43.88
0.30183	171.86	172.02	172.42	172.67	-45.80	-44.91	-44.13	-44.06
0.40099	171.40	171.56	171.97	172.21	-45.96	-45.06	-44.29	-44.22
0.50154	170.94	171.10	171.51	171.75	-46.11	-45.21	-44.43	-44.36
PEG-200 + 0.01 mol·kg^{-1} SMP								
0.09955	172.93	173.02	173.40	173.65	-45.16	-44.27	-43.51	-42.88
0.19835	172.47	172.62	172.92	173.18	-45.51	-44.61	-43.85	-43.22
0.30477	171.98	172.18	172.45	172.72	-45.72	-44.82	-44.05	-43.42

0.40446	171.53	171.79	172.03	172.27	-45.88	-44.97	-44.20	-43.57
0.50868	171.06	171.36	171.58	171.83	-46.03	-45.12	-44.35	-43.71
PEG-200 + 0.03 mol·kg^{-1} SMP								
0.10516	172.96	173.24	173.43	173.69	-45.01	-44.13	-43.37	-42.75
0.20372	172.51	172.79	172.97	173.22	-45.34	-44.45	-43.69	-43.06
0.31148	172.02	172.30	172.47	172.76	-45.55	-44.65	-43.89	-43.26
0.40480	171.60	171.87	172.06	172.32	-45.69	-44.79	-44.03	-43.39
0.49826	171.18	171.45	171.61	171.87	-45.83	-44.92	-44.16	-43.52
PEG-200 + 0.05 mol·kg^{-1} SMP								
0.10757	173.12	173.28	173.58	173.72	-44.85	-43.96	-43.21	-42.59
0.20277	172.68	172.85	173.15	173.27	-45.16	-44.27	-43.51	-42.89
0.30701	172.22	172.38	172.68	172.78	-45.36	-44.46	-43.70	-43.08
0.40486	171.78	171.94	172.24	172.34	-45.51	-44.61	-43.85	-43.22
0.51913	171.27	171.46	171.73	171.89	-45.67	-44.77	-44.00	-43.38
PEG-600+ 0.00 mol·kg^{-1} SMP								

0.10411	508.21	511.20	513.54	515.33	-45.56	-44.66	-43.88	-43.24
0.19978	504.00	507.08	509.50	511.29	-46.16	-45.23	-44.44	-43.79
0.30099	499.62	502.79	505.27	507.09	-46.64	-45.69	-44.89	-44.23
0.40249	495.31	498.56	501.10	502.94	-47.09	-46.12	-45.30	-44.63
0.50775	490.91	494.25	496.84	498.71	-47.53	-46.55	-45.71	-45.03
PEG-600 + 0.01 mol·kg^{-1} SMP								
0.10134	508.54	511.64	513.79	515.57	-45.45	-44.54	-43.77	-43.14
0.20015	504.21	507.41	509.61	511.42	-46.07	-45.14	-44.35	-43.70
0.29810	500.00	503.28	505.52	507.36	-46.54	-45.59	-44.78	-44.13
0.40197	495.60	498.97	501.27	503.13	-46.99	-46.02	-45.21	-44.54
0.50975	491.12	494.58	496.92	498.81	-47.44	-46.45	-45.63	-44.95
PEG-600 + 0.03 mol·kg^{-1} SMP								
0.10121	509.10	512.07	514.22	515.68	-45.27	-44.36	-43.60	-42.97
0.20232	504.72	507.78	509.98	511.46	-45.89	-44.96	-44.18	-43.54

0.29791	500.65	503.79	506.03	507.53	-46.33	-45.39	-44.60	-43.95
0.40211	496.29	499.51	501.80	503.31	-46.78	-45.82	-45.01	-44.36
0.50998	491.85	495.15	497.50	499.02	-47.23	-46.25	-45.43	-44.76
PEG-600 + 0.05 mol·kg^{-1} SMP								
0.09938	509.37	512.26	514.61	516.07	-45.07	-44.17	-43.41	-42.78
0.20237	504.94	507.91	510.33	511.81	-45.71	-44.78	-44.00	-43.36
0.30044	500.79	503.84	506.32	507.81	-46.16	-45.22	-44.42	-43.78
0.40145	496.59	499.72	502.25	503.76	-46.59	-45.63	-44.82	-44.17
0.50234	492.46	495.67	498.25	499.77	-47.00	-46.03	-45.20	-44.54

---

[a] *m* is the molality of PEGs in aqueous SMP solutions

The escalation in apparent molar volume with rise in temperature cause larger attraction for solvent which in turn intensifies the stronger interaction among solute and solvent [10]. The values of V_ϕ are larger for PEG-600 in contrast to PEG-200 which further describes that when the molecules of SMP interact with PEG-600 molecules, it shows strong interaction in comparison to PEG-200. The computed $K_{\phi,s}$ develop negative values at all the temperature and whole range of SMP concentration. The attained values of $K_{\phi,s}$ are less negative w.r.t. temperature rise as a result of augmentation of system at larger temperatures [11]. The negative $K_{\phi,s}$ values infers that the fragments of water in aggregate mixture are more compact than the water fragments in the vicinity of solute due to which water fragments tighten throughout the solute fragments owing to the hydrophobic interaction of nonpolar group [12].

Partial molar volume and partial molar isentropic compression

The partial molar volume, V_ϕ^0 and partial molar isentropic compression, $K_{\phi,s}^0$ is calculated by **eqs. 4.4 and 4.5**. The rise in the V_ϕ^0 values is due to the robust hydrogen bond interaction amid hydrogen atoms of water and oxygen atoms of PEGs. The V_ϕ^0 values supply the knowledge concerning solute-solvent interactions alone despite of solute-solute association at infinite dilution [13]. The difference in V_ϕ^0 of PEG-200 and PEG-600 is very large which further specifies that the association between unlike molecule is extremely affected by the body of hydrocarbon chain [14]. In agreement with co-sphere overlap model [15], hydrogen co-sphere ionic species overlay can boost the volume; on the other hand overlap of hydrophobic-hydrophobic group as well as ion-hydrophobic group cause reduction in volume. The supremacy of ion-hydrophilic upon ion-hydrophobic and hydrophobic-hydrophobic interactions is estimated by the positive V_ϕ^0 data. The value of Sv is negative and is less than V_ϕ^0 in the current investigation, which describes the predominance of solute-solvent interaction upon solute-solute interaction. The S_v values show no consistency in the drift which infers that the solute-solute interactions are simulated by numerous features [16]. The V_ϕ^0, S_v, $K_{\phi,s}^0$ and S_k data accompanying their standard errors are registered in **Table 4.26 and 4.27** individually.

Table 4.26 Limiting apparent molar volumes, V_{ϕ}^{0} and experimental slopes, S_v of PEGs in aqueous solution of SMP at several temperatures and experimental pressure, p = 0.1 MPa.

$^{a}m_B$/ (mol·kg^{-1})	$10^6 \cdot V_{\phi}^{0}$ / (m^3·mol^{-1})				$10^6 \cdot Sv$ / (m^3·kg·mol^{-2})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
PEG-200								
0.00	173.25(±0.003)	173.39(±0.002)	173.79(±0.004)	174.06(±0.001)	-4.61(±0.008)	-4.57(±0.007)	-4.53(±0.011)	-4.60(±0.004)
0.01	173.38(±0.003)	173.43(±0.008)	173.81(±0.024)	174.07(±0.017)	-4.58(±0.008)	-4.06(±0.022)	-4.42(±0.072)	-4.43(±0.050)
0.03	173.44(±0.003)	173.71(±0.003)	173.91(±0.015)	174.17(±0.017)	-4.54(±0.008)	-4.54(±0.008)	-4.61(±0.043)	-4.59(±0.052)
0.05	173.60(±0.003)	173.75(±0.013)	174.07(±0.003)	174.18(±0.034)	-4.49(±0.008)	-4.44(±0.037)	-4.50(±0.008)	-4.47(±0.100)
PEG-600								
0.00	512.60(±0.086)	515.51(±0.081)	517.79(±0.072)	519.55(±0.077)	-42.85(±0.257)	-42.01(±0.241)	-41.38(±0.216)	-41.18(±0.230)
0.01	512.78(±0.085)	515.80(±0.081)	517.91(±0.079)	519.66(±0.078)	-42.65(±0.255)	-41.78(±0.243)	-41.30(±0.237)	-41.03(±0.233)
0.03	513.29(±0.084)	516.19(±0.080)	518.29(±0.078)	519.74(±0.077)	-42.18(±0.251)	-41.40(±0.240)	-40.91(±0.233)	-40.76(±0.231)
0.05	513.47(±0.081)	516.28(±0.078)	518.58(±0.075)	520.03(±0.074)	-41.96(±0.243)	-41.16(±0.233)	-40.60(±0.225)	-40.45(±0.223)

$^{a}m_B$ states the molality of aqueous solutions of SMP.

Table 4.27 Limiting apparent molar isentropic compression, $K_{\phi,s}^{0}$ and experimental slope, S_k of PEGs in aqueous solution of SMP at different temperatures and experimental pressure, p = 0.1 MPa.

$^{a}m_B$/ (mol·kg^{-1})	$10^6 \cdot K_{\phi,s}^{0}$ / ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{GPa}^{-1}$)				$10^6 \cdot S_k$ / ($\text{kg}\cdot\text{m}^3\cdot\text{mol}^{-2}\cdot\text{GPa}^{-1}$)			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
PEG-200								
0.00	-45.14(±0.07)	-44.25(±0.07)	-43.50(±0.07)	-43.91(±0.07)	-2.03(±0.21)	-1.99(±0.21)	-1.95(±0.21)	-1.94(±0.20)
0.01	-45.03(±0.23)	-44.15(±0.23)	-43.39(±0.23)	-42.77(±0.22)	-2.05(±0.23)	-2.01(±0.23)	-1.98(±0.23)	-1.95(±0.22)
0.03	-44.87(±0.07)	-43.99(±0.07)	-43.23(±0.07)	-42.61(±0.07)	-2.01(±0.21)	-1.97(±0.21)	-1.94(±0.20)	-1.92(±0.20)
0.05	-44.71(±0.07)	-43.83(±0.07)	-43.08(±0.07)	-42.46(±0.07)	-1.93(±0.20)	-1.90(±0.20)	-1.87(±0.20)	-1.85(±0.20)
PEG-600								
0.00	-45.13(±0.07)	-44.25(±0.07)	-43.49(±0.07)	-42.86(±0.07)	-4.82(±0.22)	-4.62(±0.21)	-4.48(±0.21)	-4.38(±0.21)
0.01	-45.03(±0.08)	-44.14(±0.08)	-43.38(±0.07)	-42.76(±0.07)	-4.85(±0.23)	-4.64(±0.23)	-4.51((±0.22)	-4.41(±0.22)
0.03	-44.87(±0.08)	-43.98(±0.08)	-43.23(±0.07)	-42.60(±0.07)	-4.73(±0.23)	-4.55(±0.22)	-4.41(±0.22)	-4.32(±0.22)
0.05	-44.68((±0.08)	-43.80(±0.08)	-43.05(±0.08)	-42.43(±0.07)	-4.72(±0.23)	-4.53(±0.23)	-4.39(±0.23)	-4.30(±0.22)

$^{a}m_B$ is the molality of aqueous solutions of SMP.

It has been ascertained from **Table 4.26** that the complete values of V_{ϕ}^{0} are positive and enhance with ascent in temperature and SMP concentration for PEG-200 and PEG-600 as ascribed in **Figure 5**.

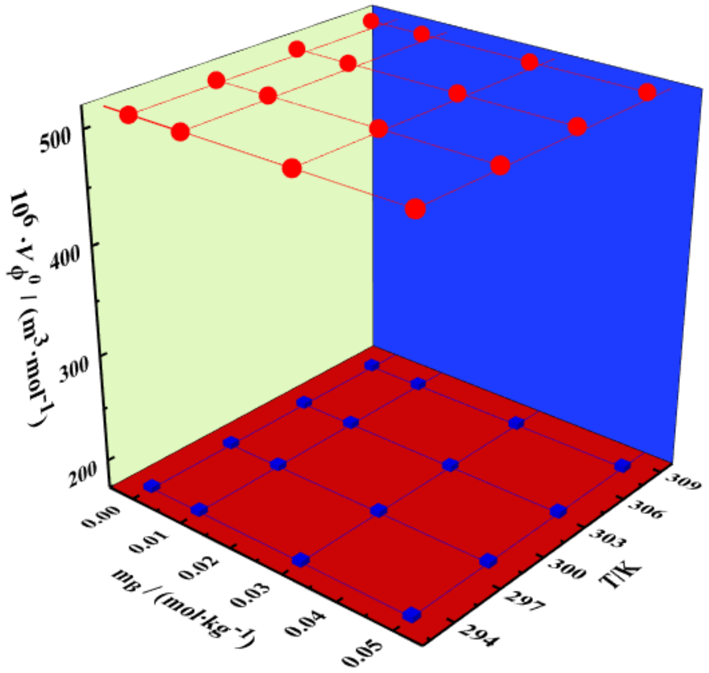
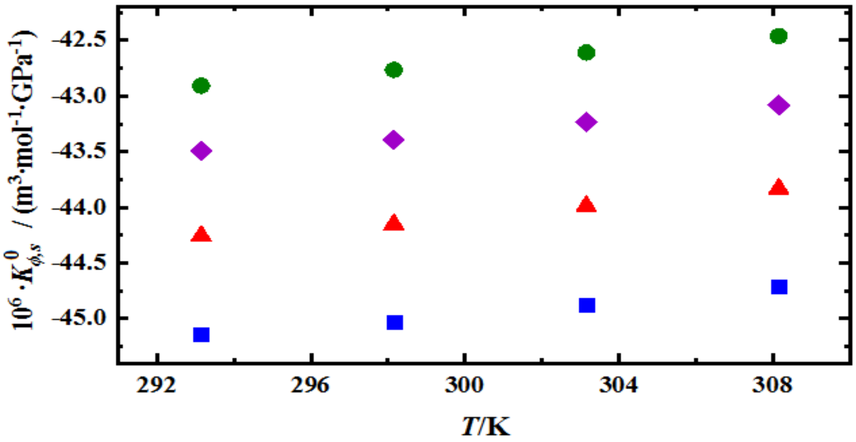
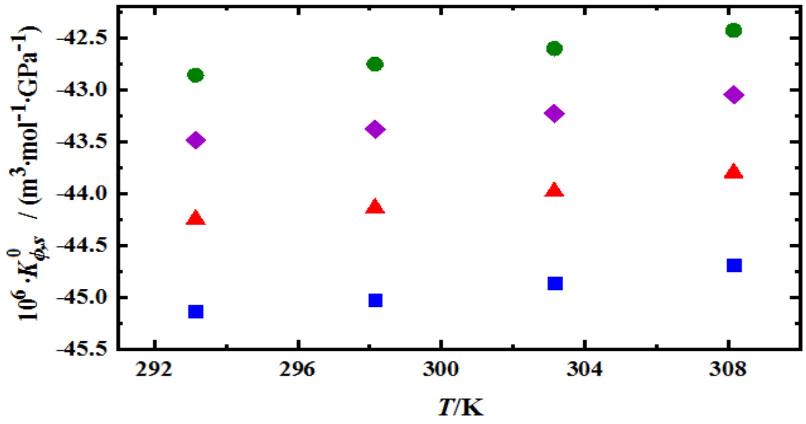


Figure 5: Graph of partial molar volume V_{ϕ}^{0} for PEG-200 (cube) and PEG-600 (dot) in various concentration of SMP solutions in water at different temperatures.

Table 4.27 contains the values of $K_{\phi,s}^{0}$ and their standard error, S_k. The negative $K_{\phi,s}^{0}$value reduces w.r.t. aggravation in temperature and SMP concentration as illustrated in **Figure 6**.



(a)



(b)

Figure 6: Graphs of partial molar isentropic compression $K^0_{\phi,s}$ for (a) PEG-200 (b) PEG-600 against temperature in various concentrations of SMP solutions in water. [cube, 0.00 mol·kg^{-1}; triangle, 0.01 mol·kg^{-1}; diamond, 0.03 mol·kg^{-1}; circle, 0.05 mol·kg^{-1}

Partial molar volume of transfer and partial molar isentropic compression of transfer

At infinite dilution, the partial molar volume of transfer, ΔV^0_ϕ and partial molar isentropic compression of transfer, $\Delta K^0_{\phi,s}$ for both PEGs from water to aqueous SMP solutions has been evaluated from the **eqs. 4.9 and 4.12**. The positive ΔV^0_ϕ values specify the strong interaction among water and PEGs in comparison to the molecular interaction of SMP and PEGs. Relating to pure arrangement of water, the occurrence of structural organization of water together with the comparatively bulky unoccupied region that may be ruptured via various fragments is suspected through the Pauling's model [18]. The structure creating/building capability is encouraged by the positive values ΔV^0_ϕ as structure moiety of SMP and PEG constitute polar group. As per co-sphere overlap model [19], ion-hydrophilic and hydrophilic-hydrophilic interaction built positive augmentation, while negative augmentation is built by ion-hydrophobic and hydrophobic-hydrophobic interactions. The computed ΔV^0_ϕ and $\Delta K^0_{\phi,s}$ data is recorded in **Table 4.28.**

Table 4.28 Partial molar volume of transfer, ΔV_{ϕ}^{0} and partial molar isentropic compression of transfer, $\Delta K_{\phi,s}^{0}$ of PEGs in aqueous solution of SMP at different temperatures and experimental pressure, p = 0.1 MPa.

$^{a}m_{B}$/ (mol·kg^{-1})	10^{6}. ΔV_{ϕ}^{0} /(m^{3}·mol^{-1})				10^{6}. $\Delta K_{\phi,s}^{0}$ /(m^{3}·mol^{-1}·GPa^{-1})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
PEG-200								
0.01	0.13	0.03	0.02	0.01	0.11	0.10	0.10	0.66
0.03	0.19	0.32	0.12	0.11	0.27	0.27	0.26	0.82
0.05	0.34	0.36	0.28	0.12	0.42	0.42	0.41	0.97
PEG-600								
0.01	0.19	0.30	0.12	0.11	0.11	0.11	0.11	0.10
0.03	0.69	0.68	0.50	0.19	0.27	0.27	0.26	0.25
0.05	0.88	0.77	0.79	0.47	0.45	0.45	0.44	0.43

$^{a}m_{B}$ is the molality of aqueous solutions of SMP.

Therefore, for present ternary mixture of PEGs in aqueous SMP, the hydrophilic-hydrophilic and ion-hydrophilic interactions are preeminent upon another interaction. The positive $\Delta K_{\phi,s}^0$ infers the structure designing/creating ability of solute along with the supremacy of interaction between SMP and PEGs. The structure manufacturing tendency of solute rises by the virtue of increase in the SMP concentration due to which solution become less compressible as compared to pure solvent

.

Temperature dependence of partial molar volume

The variability of V_ϕ^0 w.r.t. temperature can be expressed by utilizing **eq. 4.6**. **Table 4.29** accommodates the value of empirical constant a, b, and c. For PEGs the value of barely coefficient c is positive as well as negative. For the calculation of these deviations *ARD (□□)* the **eq. 4.7** is utilized. Since minute values of deviations are attained in the recent investigation, therefore it is estimated that these deviations fits very magnificently into the polynomial equation. The disparity of partial molar volume, V_ϕ^0 w.r.t. temperature in regard to absolute temperature, T might be determined by succeeding **eq. 4.7**. The values of limiting apparent molar expansibilities can be estimated with the help of **eq. 4.8**. The correlation amidst solute and solvent particles in the solution mixture may be inspected by examining the limiting apparent molar expansibilities, $E_\phi^0 = (\partial V_\phi^0/\partial T)_P$ [20]. The established thermodynamic formula (**eq. 4.15**), originated by Hepler [21] with the purpose to conclude the structure building or making tendency of solute in solvent. The sign of $(\partial V_\phi^0/\partial T)_P$ decides the structure building/making capability of solute [22]. The negative value of $(\partial E_\phi^0/\partial T)_P$ describes the structure breaking behaviour of solute whereas, positive and minute negative values signify the structure making/building property of solute. The theoretical V_ϕ^0 values were computed by making use of these empirical constants (entered in **Table 4.29**) and E_ϕ^0 values are entered in **Table 4.30.**

Table 4.29 Values of **e**mpirical parameters of eq (8) for PEGs in aqueous SMP solutions at experimental pressure, p = 0.1 MPa.

$^{a}m_B$/(mol·kg^{-1})	10^6. a /(m^3□mol^{-1})	10^6. b /(m^3□mol^{-1}□K^{-1})	10^6. c /(m^3□mol^{-1}□K^{-2})	*ARD/(□)*
PEG-200				
0.00	173.45	0.050	0.0013	0.00022
0.01	173.50	0.038	0.0021	0.00027
0.03	173.69	0.048	-0.0001	0.00008
0.05	173.81	0.043	-0.0005	0.00020
PEG-600				
0.00	515.49	0.520	-0.0115	0.00002
0.01	515.72	0.518	-0.0126	0.00011
0.03	516.17	0.502	-0.0145	0.00003
0.05	516.33	0.507	-0.0136	0.00007

$^{a}m_B$ is the molality of aqueous solutions of SMP.

Table 4.30 Limiting apparent molar expansibilities, E_{ϕ}^{0} for PEGs in aqueous solutions of SMP at different temperatures and experimental pressure, p = 0.1 MPa.

${}^{a}m_B$/ (mol·kg^{-1})	$10^6 \cdot E_{\phi}^{0}$/ (m^3·mol^{-1}·K^{-1})				$(\partial E_{\phi}^{0}/\partial T)_P$/ (m^3.mol^{-1}.K^{-2})
	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15 K	T=298.15 K
PEG-200					
0.00	0.0371	0.0499	0.0626	0.0754	0.0026
0.01	0.0170	0.0384	0.0599	0.0813	0.0043
0.03	0.0495	0.0483	0.0483	0.0483	-0.0002
0.05	0.0482	0.0435	0.0435	0.0435	-0.0009
PEG-600					
0.00	0.6353	0.5205	0.4056	0.2907	-0.0230
0.01	0.6443	0.5179	0.3915	0.2651	-0.0253
0.03	0.6470	0.5017	0.3563	0.2109	-0.0291
0.05	0.6433	0.5073	0.3713	0.2352	-0.0272

The entire limiting apparent molar expansibilities values are positive for both PEGs at complete range of SMP concentration and the working temperatures which moreover, suggest the correlation midst solute and solvent fragments in the present examined ternary liquid mixtures, thereby assisting the earlier data of apparent molar volume. The minute negative and positive $(\partial E_{\phi}^{0}/\partial T)_P$ for both PEGs mixtures attribute to the structure building potential of PEGs in entire SMP solutions in water.

The pair and triplet interaction coefficients

McMillan and Mayer [23] hypothesis of mixtures has been applied to compute the pair and triplet interaction coefficients and further explained by Friedman and Krishnan [24] to expedite co-solute-solute associations in the solvation sphere. The ΔV_{ϕ}^{0} and $\Delta K_{\phi,s}^{0}$ has been employed to adjudicate the coefficients of pair and triplet interaction parameters by utilizing **eqs. 4.13 and 4.14.** The data of V_{AB} and K_{AB} are positive for the entire range of temperature and SMP concentration. The V_{AB} are larger than V_{ABB} (except for PEG-200 at 303.15 K and PEG-600 at 308.15 K) which cause interactions owing to the overlay of hydration sphere [25] co-solute-solute fragments. The immense positive V_{AB} values indicate that the pair wise interactions among solute and solvent are dominant over triplet interactions. Likewise, the K_{AB} are positive for both PEGs whilst, K_{ABB} are negative for both PEGs at complete range of temperature and concentrations which once again speculate the pair wise interactions among PEGs along with SMP molecules. The data of these parameters (listed in **Table 4.31**) are attained via fitting of ΔV_{ϕ}^{0} and $\Delta K_{\phi,s}^{0}$ to above equations.

Table 4.31 Pair (V_{AB} and K_{AB}) and triplet (V_{ABB} and K_{ABB}) interaction coefficients for PEGs in aqueous solutions of SMP at different temperatures and experimental pressure, p = 0.1 MPa.

T/K	From Volume		From Compression	
	$10^6 . V_{AB}$ / ($m^3 \cdot mol^{-1}$)	$10^6 . V_{ABB}$ / ($m^3 \cdot mol^{-1}$)	$10^6 . K_{AB}$ / ($m^3 \cdot mol^{-1} \cdot GPa^{-1}$)	$10^6 . K_{ABB}$ / ($m^3 \cdot mol^{-1} \cdot GPa^{-1}$)
PEG-200				
293.15	4.18	-11.21	5.04	-10.76
298.15	5.57	-24.21	4.98	-10.06
303.15	0.85	25.53	4.91	-10.43
308.15	2.08	-11.09	26.01	-223.43
PEG-600				
293.15	13.70	-64.15	4.73	-3.43
298.15	16.83	-121.18	4.82	-4.82
303.15	7.79	2.36	4.70	-4.65
308.15	2.32	30.84	4.59	-4.38

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Part V

In this part, we have computed the densities and ultrasonic velocity of glycols (PEG-200 and PEG-600) in methanol solution of butyl paraben at different concentrations ad temperatures.

Measurements of density and sound velocity

The present density data reduces with surge in temperature whereas, accumulates with escalate in methanol-BuPB concentration which estimates the survival of strong molecular interactions amidst solute and solvent fragments. The data of *u* deliver the efficacious information concerning ion-ion, solute-solvent and ion-solvent association [1]. The experimental *u* values of polyethylene glycols in methanol-BuPB mixture increases with escalation in methanol-BuPB concentration as well as with molality of polyethylene glycols; on the other hand decline with levitate in temperature. The increment or declination in speed of sound is dependent on properties and arrangement of water [2]. The density and sound velocity for polyethylene glycol 200 and polyethylene glycol 600 in methanol and in (0.00, 0.01, 0.03 and 0.05) $mol{\cdot}kg^{-1}$ methanol-BuPB solutions as a function of polyethylene glycols concentration and temperature are recorded in **Table 4.32**.

Table 4.32 The values of densities, ρ and sound velocity, u of (polyethylene glycols +methanol +BuPB) ternary solutions at different temperatures and experimental pressure p = 0.1 MPa.

^{a}m / (mol·kg^{-1})	$10^{-3}\cdot\rho$ / (kg·m^{-3})				u/(m·s^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Polyethylene glycol-200 + methanol								
0.00000	0.791666	0.786540	0.782246	0.777507	1120.07	1103.59	1087.20	1071.06
0.10579	0.797484	0.792358	0.788064	0.783325	1127.77	1111.29	1094.90	1078.76
0.20844	0.803130	0.798004	0.793710	0.788971	1135.25	1118.77	1102.38	1086.24
0.30665	0.808532	0.803406	0.799112	0.794373	1142.40	1125.92	1109.53	1093.39
0.40475	0.813927	0.808801	0.804507	0.799768	1149.54	1133.06	1116.67	1100.53
0.50477	0.819429	0.814303	0.810009	0.805270	1156.82	1140.34	1123.95	1107.81
Polyethylene glycol-200 + 0.01 mol·kg^{-1} BuPB								
0.00000	0.793090	0.787964	0.783670	0.778931	1121.87	1105.39	1089.00	1072.86
0.10914	0.799071	0.793945	0.789651	0.784912	1129.73	1113.25	1096.97	1080.83
0.20143	0.804128	0.799002	0.794708	0.789969	1136.37	1119.89	1103.70	1087.56
0.30549	0.809831	0.804705	0.800411	0.795672	1143.87	1127.39	1111.30	1095.16
0.40025	0.815024	0.809898	0.805604	0.800865	1150.69	1134.21	1118.22	1102.08

0.51468	0.821294	0.816168	0.811874	0.807135	1158.93	1142.45	1126.57	1110.43
Polyethylene glycol-200 + 0.03 $\mathrm{mol{\cdot}kg^{-1}}$ BuPB								
0.00000	0.795938	0.790812	0.786518	0.781779	1125.46	1108.98	1092.59	1076.40
0.10684	0.801761	0.796635	0.792341	0.787602	1132.98	1116.67	1100.19	1084.00
0.20323	0.807014	0.801888	0.797594	0.792855	1139.76	1123.62	1107.05	1090.86
0.30784	0.812715	0.807589	0.803295	0.798556	1147.13	1131.15	1114.49	1098.30
0.41760	0.818697	0.813571	0.809277	0.804538	1154.86	1139.06	1122.30	1106.12
0.49068	0.822680	0.817554	0.813260	0.808521	1160.00	1144.33	1127.50	1111.31
Polyethylene glycol-200 + 0.05 $\mathrm{mol{\cdot}kg^{-1}}$ BuPB								
0.00000	0.798786	0.793660	0.789366	0.784627	1129.05	1112.57	1096.18	1080.04
0.10793	0.804614	0.799488	0.795194	0.790455	1136.70	1120.22	1103.84	1087.70
0.20532	0.809873	0.804747	0.800453	0.795714	1143.60	1127.12	1110.76	1094.62
0.31062	0.815559	0.810433	0.806139	0.801400	1151.07	1134.59	1118.23	1102.09
0.40750	0.820791	0.815665	0.811371	0.806632	1157.94	1141.46	1125.11	1108.97
0.51449	0.826568	0.821442	0.817148	0.812409	1165.52	1149.04	1132.71	1116.57
Polyethylene glycol-600 + methanol								
0.00000	0.791666	0.786540	0.782246	0.777507	1120.07	1103.59	1087.20	1071.06
0.09995	0.806159	0.801033	0.796739	0.792000	1139.06	1122.58	1106.19	1090.05

0.19958	0.820606	0.815480	0.811186	0.806447	1157.99	1141.51	1125.12	1108.98
0.30044	0.835230	0.830104	0.825810	0.821071	1177.15	1160.67	1144.28	1128.14
0.39955	0.849601	0.844475	0.840181	0.835442	1195.98	1179.50	1163.11	1146.97
0.50417	0.864770	0.859644	0.855350	0.850611	1215.86	1199.38	1182.99	1166.85

Polyethylene glycol-600 + 0.01 mol$\cdot$kg^{-1} BuPB

0.00000	0.793090	0.787964	0.783670	0.778931	1121.87	1105.39	1089.00	1072.86
0.10063	0.807630	0.802504	0.798210	0.793471	1141.13	1124.65	1108.26	1092.12
0.20324	0.822458	0.817332	0.813038	0.808299	1160.78	1144.30	1127.91	1111.77
0.30314	0.836894	0.831768	0.827474	0.822735	1179.91	1163.43	1147.04	1130.90
0.39928	0.850786	0.845660	0.841366	0.836627	1198.31	1181.83	1165.44	1149.30
0.49583	0.864738	0.859612	0.855318	0.850579	1216.80	1200.32	1183.93	1167.79

Polyethylene glycol-600 + 0.03 mol$\cdot$kg^{-1} BuPB

0.00000	0.795938	0.790812	0.786518	0.781779	1125.46	1108.98	1092.59	1076.40
0.10271	0.810666	0.805663	0.801267	0.796528	1144.90	1128.42	1112.03	1095.84
0.20151	0.824835	0.819951	0.815455	0.810716	1163.60	1147.12	1130.73	1114.54
0.30287	0.839369	0.834607	0.830010	0.825271	1182.78	1166.30	1149.91	1133.72
0.39954	0.853232	0.848586	0.843892	0.839153	1201.07	1184.59	1168.20	1152.02

0.49629	0.867107	0.862576	0.857786	0.853047	1219.39	1202.91	1186.52	1170.33
Polyethylene glycol-600 + 0.05 mol·kg^{-1} BuPB								
0.00000	0.798786	0.793660	0.789366	0.784627	1129.05	1112.57	1096.18	1080.04
0.10286	0.813413	0.808287	0.804024	0.799254	1148.39	1131.91	1115.52	1099.38
0.20213	0.827529	0.822403	0.818170	0.813370	1167.05	1150.57	1134.18	1118.04
0.30305	0.841880	0.836754	0.832551	0.827721	1186.02	1169.54	1153.15	1137.01
0.40123	0.855841	0.850715	0.846541	0.841682	1204.48	1188.00	1171.61	1155.47
0.49945	0.869808	0.864682	0.860538	0.855649	1222.95	1206.47	1190.08	1173.94

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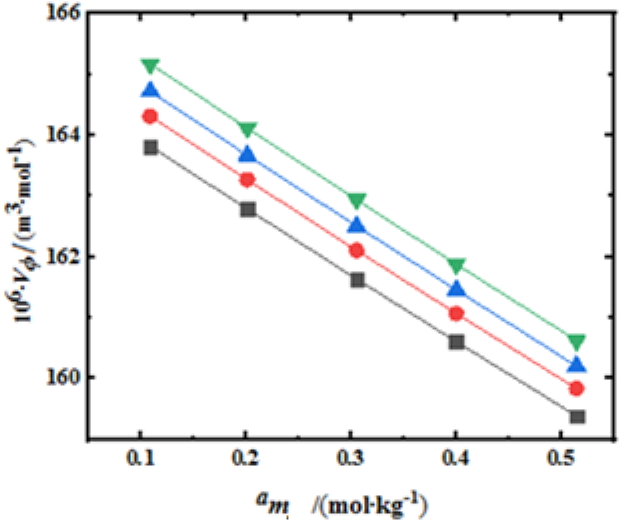
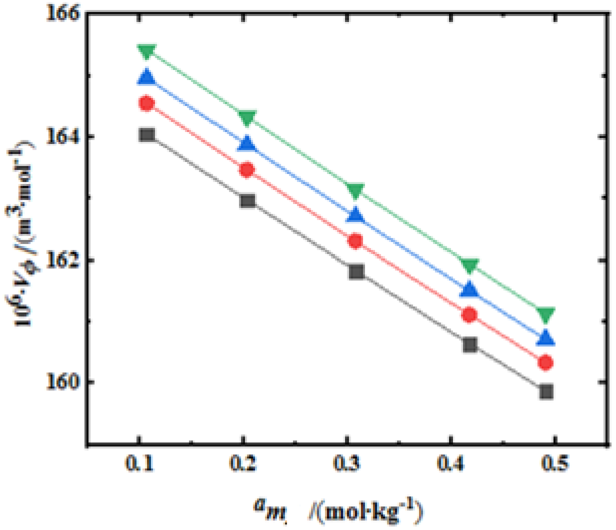
[a] m represents the number of moles of PEG-200 and PEG-600 per one kg of mixed solvent (methanol+BuPB) with the composition (0.00, 0.01, 0.03 and 0.05) mol BuPB per one kg of methanol; Standard uncertainties u are $u_r(m)$ = 1%, $u(T)$ = 0.01 K, $u(\rho)$ = 0.005 kg·m^{-3}, $u(u)$ = 0.05 m·s^{-1} and $u(p)$ = 0.01MPa.

Calculation of apparent molar properties

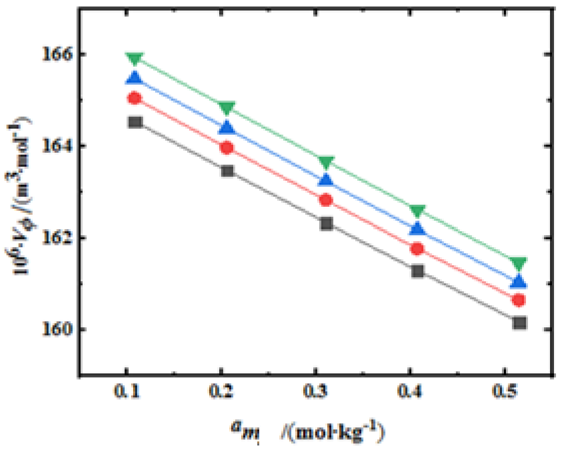
The apparent molar volume, V_ϕ and apparent molar isentropic compression, $K_{\phi,s}$ can be computed via succeeding **eqs. 4.1 and 4.2**. The attained positive data of V_ϕ [3] reveal the strong association midst solute and solvent fragments for polyethylene glycols in methanol-BuPB mixture. The ascertained data of V_ϕ are graphed in **Figure 1 and 2**.



(a)

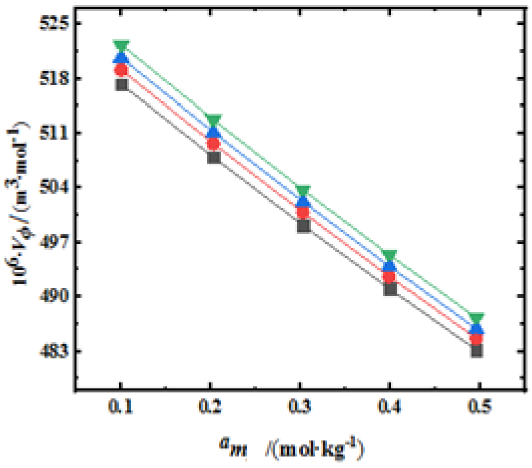


(b)

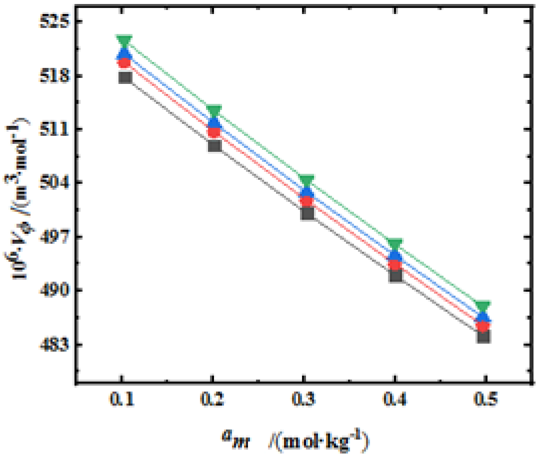


(c)

Figure 1: Graph of V_ϕ versus m_A for polyethylene glycol 200 in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1}; (c) 0.05 mol·kg^{-1} methanol-BuPB solution at several temperatures. (black, 293.15K; red, 298.15K; blue, 303.15K; green, 308.15K)


525
518
511
504
497
490
483
$10^6 \cdot V_\phi$ /($m^3 \cdot mol^{-1}$)
0.1
0.2
0.3
0.4
0.5
a_m /(mol·kg^{-1})

(a)


525
518
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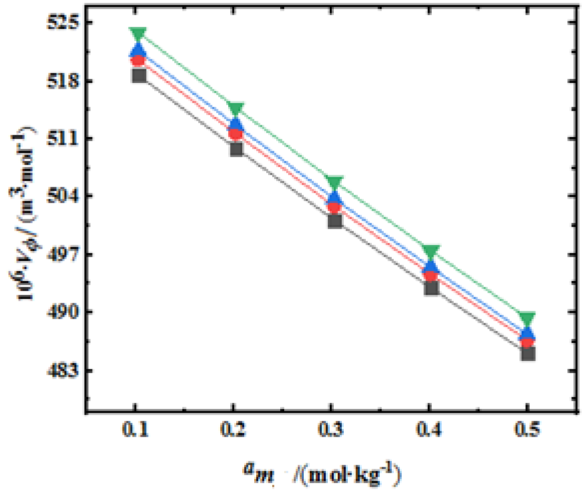
483
$10^6 \cdot V_\phi$ /($m^3 \cdot mol^{-1}$)
0.1
0.2
0.3
0.4
0.5
a_m /(mol·kg^{-1})

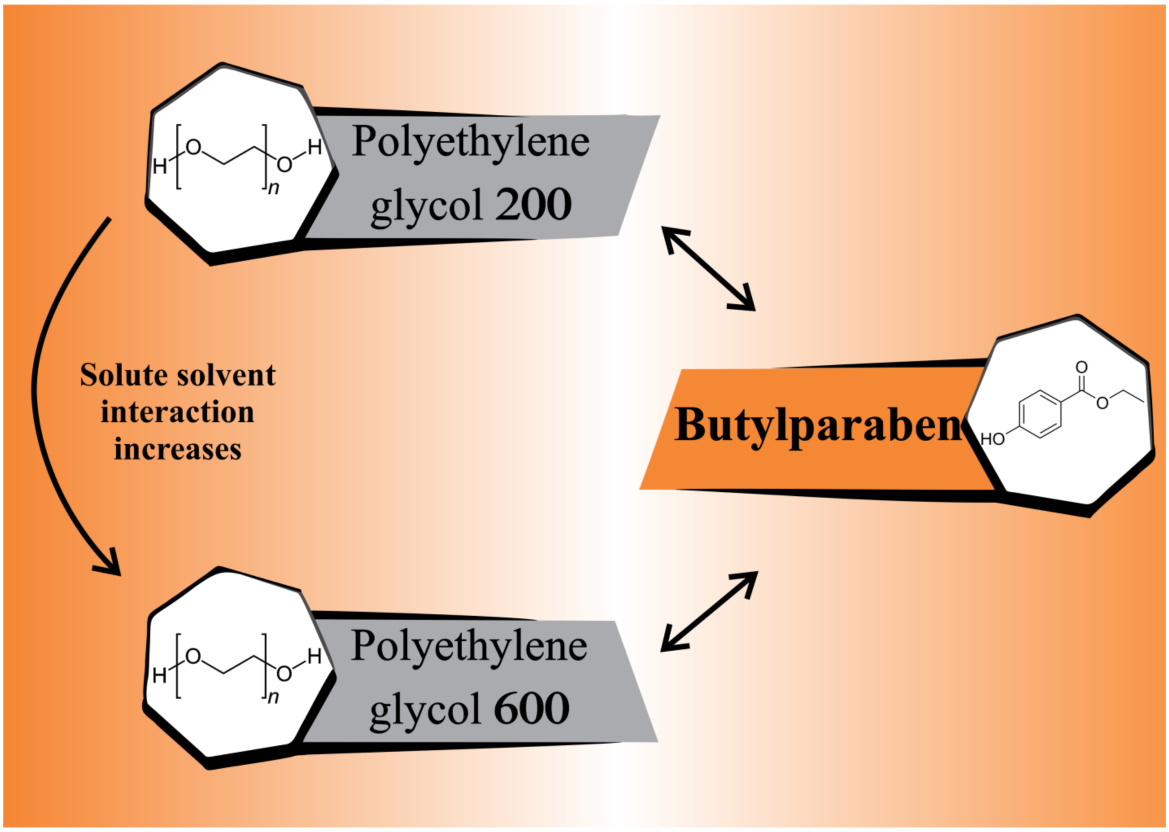
(b)



(c)

Figure 2: Graph of V_ϕ versus m_A for polyethylene glycol 600 in (a) 0.01 mol·kg^{-1}; (b) 0.03 mol·kg^{-1}; (c) 0.05 mol·kg^{-1} methanol-BuPB solution at several temperatures. (black, 293.15K; red, 298.15K; blue, 303.15K; green, 308.15K)

The V_ϕ data escalates from polyethylene glycol 200 to polyethylene glycol 600 at entire range of methanol-BuPB concentration and temperature; urge the enhancement of solute-solvent interactions from polyethylene glycol 200 to 600 as figured in **scheme 1**.



The data of V_ϕ and $K_{\phi,s}$ are entered in **Table 4.33**

Table 4.33 The values of apparent molar volume, V_{ϕ} and apparent molar isentropic compression, $K_{\phi,s}$ of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p = 0.1 MPa.

^{a}m /(mol·kg^{-1})	$10^6 \cdot V_{\phi}$ / (m^3·mol^{-1})				$10^6 \cdot K_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})			
	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Polyethylene glycol-200 + methanol								
0.10579	163.67	164.16	164.57	165.02	-88.84	-96.37	-104.19	-112.71
0.20844	162.52	163.00	163.40	163.84	-89.82	-97.38	-105.16	-113.68
0.30665	161.44	161.90	162.29	162.72	-90.71	-98.26	-106.02	-114.53
0.40475	160.37	160.82	161.20	161.62	-91.53	-99.07	-106.82	-115.30
0.50477	159.29	159.74	160.11	160.52	-92.32	-99.84	-107.56	-116.02
Polyethylene glycol-200 + 0.01 mol·kg^{-1} BuPB								
0.10914	163.82	164.31	164.72	165.17	-85.29	-92.56	-102.67	-111.08
0.20143	162.79	163.27	163.67	164.12	-86.21	-93.51	-103.54	-111.95
0.30549	161.64	162.11	162.51	162.94	-87.18	-94.50	-104.46	-112.85

0.40025	160.61	161.07	161.46	161.88	-88.01	-95.32	-105.23	-113.61
0.51468	159.39	159.84	160.21	160.63	-88.95	-96.25	-106.09	-114.44
Polyethylene glycol-200 + 0.03 mol·kg^{-1} BuPB								
0.10684	164.05	164.55	164.96	165.42	-78.55	-89.27	-94.38	-102.37
0.20323	162.98	163.47	163.88	164.33	-79.58	-90.25	-95.41	-103.36
0.30784	161.84	162.31	162.71	163.15	-80.63	-91.25	-96.43	-104.36
0.41760	160.65	161.12	161.51	161.94	-81.65	-92.21	-97.42	-105.33
0.49068	159.88	160.34	160.72	161.14	-82.30	-92.81	-98.03	-105.93
Polyethylene glycol-200 + 0.05 mol·kg^{-1} BuPB								
0.10793	164.55	165.06	165.48	165.95	-75.96	-82.76	-89.91	-97.47
0.20532	163.48	163.98	164.40	164.86	-77.01	-83.78	-90.94	-98.52
0.31062	162.34	162.83	163.24	163.69	-78.07	-84.83	-91.98	-99.57
0.40750	161.30	161.78	162.18	162.62	-78.99	-85.74	-92.88	-100.46
0.51449	160.18	160.65	161.04	161.47	-79.94	-86.68	-93.81	-101.37
Polyethylene glycol-600 + methanol								

0.09995	517.07	518.89	520.42	522.18	-147.63	-163.61	-180.16	-198.38
0.19958	507.97	509.70	511.15	512.82	-159.16	-175.38	-192.09	-210.51
0.30044	499.07	500.72	502.10	503.69	-169.30	-185.67	-202.50	-221.02
0.39955	490.63	492.20	493.51	495.03	-177.93	-194.38	-211.26	-229.83
0.50417	482.03	483.51	484.76	486.20	-185.76	-202.25	-219.13	-237.68

Polyethylene glycol-600 + 0.01 mol·kg^{-1} BuPB

0.10063	517.32	519.14	520.68	522.37	-146.87	-162.71	-180.16	-197.30
0.20324	507.99	509.73	511.18	512.79	-158.63	-174.72	-192.09	-209.65
0.30314	499.23	500.88	502.26	503.79	-168.56	-184.80	-202.50	-219.93
0.39928	491.08	492.65	493.97	495.43	-176.85	-193.18	-211.26	-228.39
0.49583	483.15	484.66	485.91	487.30	-184.07	-200.43	-219.13	-235.64

Polyethylene glycol-600 + 0.03 mol·kg^{-1} BuPB

0.10271	517.89	519.85	520.95	522.66	-134.16	-153.06	-165.39	-182.68
0.20151	508.99	510.79	511.89	513.52	-145.67	-164.68	-177.33	-194.80
0.30287	500.18	501.82	502.91	504.46	-155.96	-175.01	-187.91	-205.50

0.39954	492.05	493.56	494.64	496.11	-164.51	-183.55	-196.63	-214.27
0.49629	484.18	485.55	486.63	488.03	-171.97	-190.95	-204.15	-221.81
Polyethylene glycol-600 + 0.05 $\mathrm{mol \cdot kg^{-1}}$ BuPB								
0.10286	518.78	520.64	521.72	523.95	-123.30	-137.70	-153.45	-168.76
0.20213	509.93	511.71	512.70	514.85	-134.96	-149.58	-165.54	-181.13
0.30305	501.24	502.93	503.84	505.93	-145.34	-160.13	-176.22	-192.00
0.40123	493.06	494.68	495.52	497.54	-154.16	-169.07	-185.23	-201.13
0.49945	485.14	486.69	487.46	489.42	-161.87	-176.85	-193.03	-209.00

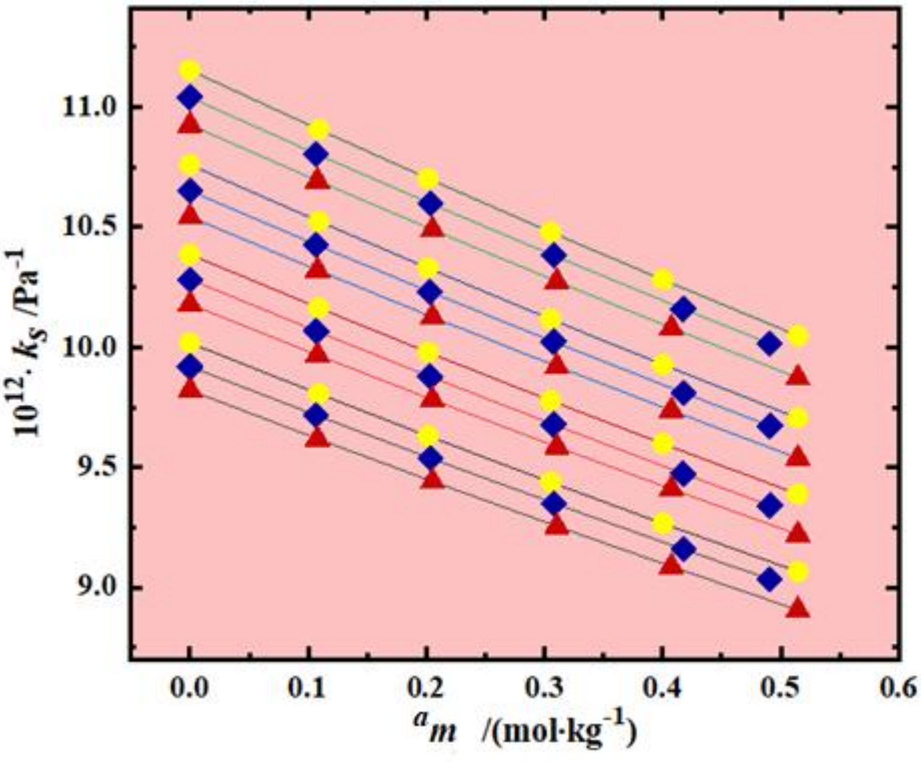
---

[a] *m* represents the number of moles of PEG-200 and PEG-600 per one kg of mixed solvent (methanol+BuPB) with the composition (0.00, 0.01, 0.03 and 0.05) mol BuPB per one kg of methanol.

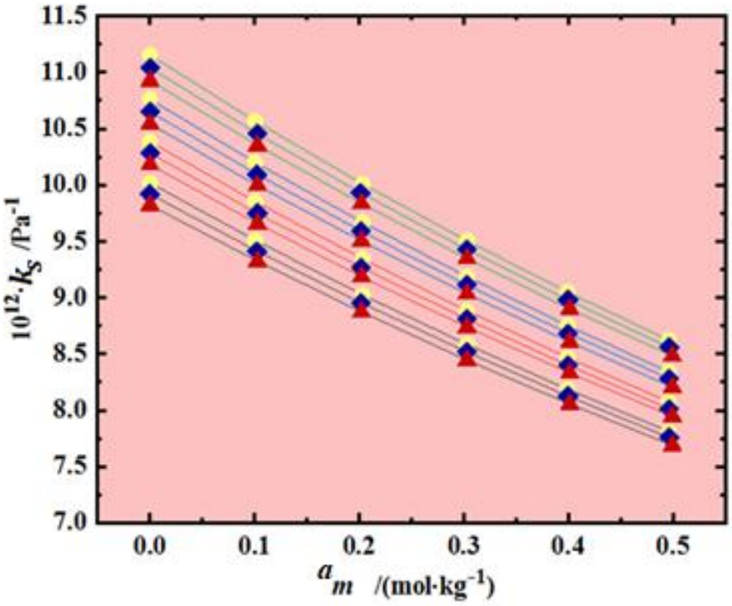
The $K_{\phi,s}$ which stipulates the evidence of sturdy attractive association amid solute and solvent fragments by the virtue of solute solvation. The $K_{\phi,s}$ escalate with the intensification of methanol-BuPB concentration and declines with the elevation in temperature. The association between solute and solvent fragments in case of (polyethylene glycol 600 + methanol+ BuPB) system is greater than (polyethylene glycol 200 + methanol+ BuPB) system.

The k_s, isentropic compressibility [4] assessed from Laplace-Newton i.e. **eq. 4.3**

The graph of k_s for (polyethylene glycol 200 + methanol+ BuPB) and (polyethylene glycol 600 + methanol+ BuPB) systems has been designed in **Figure 3.**



(a)



(b)

Figure 3: Graph of ks versus ${}^{a}m$ for (a) polyethylene glycol 200 and (b) polyethylene glycol 600 at several temperatures. (dot, 0.01 mol·kg^{-1}; diamond, 0.03 mol·kg^{-1}; triangle, 0.05 mol·kg^{-1})

The k_s is explicated from two terms one is solute intrinsic and another is solvent intrinsic compressibility. The constriction of solvent (methanol-BuPB) is imputable to solvent intrinsic effect however; solute intrinsic effect is attributable to constriction of hydrating infrastructure of solute. **Figure 3** manifest that k_s data accumulate with ameliorate in temperature for present ternary system by virtue of enhancement in thermal disturbance; which in turn increase the volume of mixture causing mixture much compressible by cause of release of solvent fragments from the solute. The solute congenital effect is overriding the solvent congenital effect as derangement of solvent complex and united consequence of hydrating fragments of methanol and BuPB leads in declination of k_s with escalation in concentration.

Estimation of apparent molar properties at infinite dilution

The interrelationship midst V_ϕ and $K_{\phi,s}$ can be elucidated via ensuing **eqs. 4.4 and 4.5**

The determined data of V_ϕ^0, $K_{\phi,s}^0$, S_v and S_k are tabulated in **Table 4.34** and **4.35**.

Table 4.34 The values of limiting apparent molar volumes, V_ϕ^0 and experimental slopes, S_v of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p =0.1MPa.

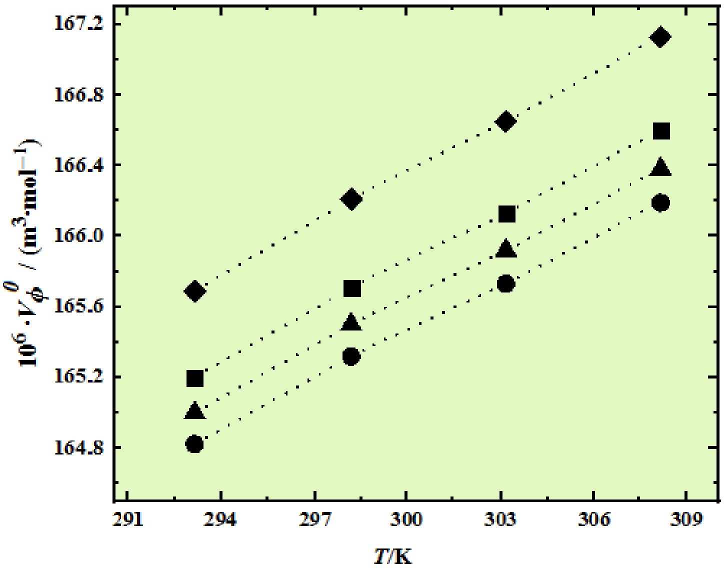
$^a m_B$/ (mol·kg^{-1})	$10^6 \cdot V_\phi^0$ / (m^3·mol^{-1})				$10^6 \cdot Sv$ / (m^3·kg·mol^{-2})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
Polyethylene glycol-200								
0.00	164.82(±0.01)	165.32(±0.01)	165.73(±0.01)	166.19(±0.01)	-10.99(±0.05)	-11.09(±0.05)	-11.17(±0.05)	-11.27(±0.05)
0.01	165.00(±0.01)	165.50(±0.01)	165.92(±0.01)	166.38(±0.01)	-10.93(±0.05)	-11.03(±0.05)	-11.12(±0.05)	-11.21(±0.05)
0.03	165.20(±0.01)	165.71(±0.01)	166.13(±0.01)	166.60(±0.01)	-10.87(±0.04)	-10.97(±0.04)	-11.05(±0.04)	-11.15(±0.04)
0.05	165.69(±0.01)	166.21(±0.01)	166.65(±0.01)	167.13(±0.01)	-10.75(±0.04)	-10.85(±0.05)	-10.94(±0.05)	-11.03(±0.05)
Polyethylene glycol-600								
0.00	525.42(±0.34)	527.32(±0.35)	528.91(±0.35)	530.75(±0.36)	-86.69(±1.04)	-87.51(±1.06)	-88.21(±1.07)	-89.00(±1.09)
0.01	525.72(±0.33)	527.63(±0.34)	529.23(±0.34)	531.00(±0.35)	-86.44(±1.01)	-87.26(±1.02)	-87.96(±1.04)	-88.73(±1.05)
0.03	526.40(±0.32)	528.51(±0.33)	529.62(±0.33)	531.40(±0.34)	-85.64(±0.98)	-87.14(±1.01)	-87.20(±1.01)	-87.98(±1.02)
0.05	527.22(±0.32)	529.16(±0.32)	530.31(±0.33)	532.61(±0.33)	-84.80(±0.96)	-85.61(±0.98)	-86.38(±1.00)	-87.06(±1.01)

$^a m_A$ represents the molality of polyethylene glycols in methanol-BuPB solutions.

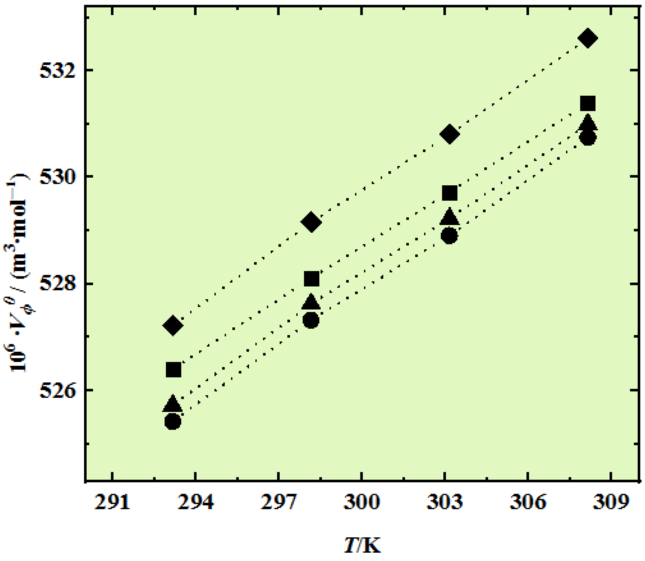
Table 4.35 The values of limiting apparent molar isentropic compression, $K^0_{\phi,s}$ and experimental slope, S_k of (polyethylene glycols+methanol+BuPB) ternary solutions at various temperatures and experimental pressure, p = 0.1 MPa.

$^a m_B$/ (mol·kg^{-1})	$10^6 \cdot K^0_{\phi,s}$ / (m^3·mol^{-1}·GPa^{-1})				$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
				Polyethylene glycol-200				
0.00	-87.98(±0.07)	-95.52(±0.08)	-103.36(±0.08)	-111.91(±0.09)	-8.72(±0.20)	-8.69(±0.24)	-8.45(±0.23)	-8.30(±0.26)
0.01	-84.37(±0.07)	-91.65(±0.09)	-101.81(±0.08)	-110.25(±0.08)	-9.02(±0.21)	-9.08(±0.25)	-8.45(±0.22)	-8.29(±0.25)
0.03	-77.56(±0.07)	-88.34(±0.07)	-93.44(±0.08)	-101.44(±0.07)	-9.76(±0.20)	-9.22(±0.20)	-9.48(±0.23)	-9.26(±0.22)
0.05	-74.97(±0.08)	-81.78(±0.07)	-88.94(±0.07)	-96.51(±0.09)	-9.78(±0.22)	-9.65(±0.20)	-9.58(±0.22)	-9.59(±0.25)
				Polyethylene glycol-600				
0.00	-139.64(±1.56)	-155.56(±1.64)	-172.08(±1.70)	-190.29(±1.78)	-94.17(±4.69)	-95.42(±4.93)	-96.25(±5.11)	-97.06(±5.35)
0.01	-138.76(±1.51)	-154.53(±1.59)	-171.42(±1.35)	-189.08(±1.72)	-93.99(±4.56)	-95.31(±4.81)	-98.55(±4.06)	-96.85(±5.20)
0.03	-125.61(±1.48)	-144.56(±1.54)	-156.72(±1.62)	-173.98(±1.68)	-95.95(±4.46)	-96.12(±4.66)	-98.34(±4.87)	-99.25(±5.26)
0.05	-114.62((±1.47)	-128.93(±1.53)	-144.62(±1.60)	-159.84(±1.68)	-97.14(±4.43)	-98.57(±4.60)	-99.65(±4.80)	-101.29(±5.04)

The V_ϕ^0 develop the positive value suggesting the pre-eminence of solute-solvent association in the current inspected system. The plot of V_ϕ^0 against temperature for polyethylene glycol 200 and 600 at different concentration of methanol-BuPB is ascribed in **Figure 4**.



(a)



(b)

Figure 4: Graph of V_{ϕ}^{0} versus temperature for (a) polyethylene glycol 200 (b) polyethylene glycol 600 in different methanol-BuPB concentration. (circle, 0.00 mol·kg^{-1}; triangle, 0.01 mol·kg^{-1}; square, 0.03 mol·kg^{-1}; diamond, 0.05 mol·kg^{-1}

The essential associations prevailing midst the polyethylene glycol and methanol-BuPB in accordance with co-sphere overlap model [6] are categorized as: hydrophilic-hydrophilic association amid fragments of hydrogen and polyethylene glycols via hydrogen bonding; hydrophobic-hydrophobic association amidst fragments of non-polar groups of BuPB and polyethylene glycols and hydrophilic-hydrophilic association midst fragment of methanol and polyethylene glycols via hydrogen-bonding. The V_{ϕ}^{0} of polyethylene glycols intensify with aggravation in concentration of BuPB owing to the hydrophobic-hydrophobic association among methanol and polyethylene glycols thereby, diminishes the association of polyethylene glycols in methanol-BuPB mixtures. The experimental slope, S_v possess lesser value than V_{ϕ}^{0} which again suggests the supremacy of connection amid solute and solvent contrary to connection midst solute and solute [7]. The data of $K_{\phi,s}^{0}$ is recorded displays the negative value of this computed parameter. The $K_{\phi,s}^{0}$ is the contribution of two impacts; positive impact (solvent congenital contractility) ascribed to intermolecular void hence, making the mixture much comprehensible and negative impact (solute congenital contractility) owing to solvent fragments compressibility in to inter-ionic void. The negative impact is a kind of electrostriction which decline the volume of mixture and therefore, tend to make the system less contractible and denser [8]. The negative $K_{\phi,s}^{0}$ for all the present examined ternary mixture owing to the pre-eminence of solute congenital contractility upon positive impact. The solvent around the solute (polyethylene glycols) provide the greater obstruction to constriction than the aggregate solvent by the virtue of negative impact. The data of V_{ϕ}^{0} and $K_{\phi,s}^{0}$ is recorded in **Table 4.34** and **Table 4.35.**

Table 4.34 The values of limiting apparent molar volumes, V_{ϕ}^{0} and experimental slopes, S_v of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p =0.1MPa.

$^{a}m_B$/ (mol·kg^{-1})	$10^6 \cdot V_{\phi}^{0}$ / (m^3·mol^{-1})				$10^6 \cdot Sv$ / (m^3·kg·mol^{-2})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
				Polyethylene glycol-200				
0.00	164.82(±0.01)	165.32(±0.01)	165.73(±0.01)	166.19(±0.01)	-10.99(±0.05)	-11.09(±0.05)	-11.17(±0.05)	-11.27(±0.05)
0.01	165.00(±0.01)	165.50(±0.01)	165.92(±0.01)	166.38(±0.01)	-10.93(±0.05)	-11.03(±0.05)	-11.12(±0.05)	-11.21(±0.05)
0.03	165.20(±0.01)	165.71(±0.01)	166.13(±0.01)	166.60(±0.01)	-10.87(±0.04)	-10.97(±0.04)	-11.05(±0.04)	-11.15(±0.04)
0.05	165.69(±0.01)	166.21(±0.01)	166.65(±0.01)	167.13(±0.01)	-10.75(±0.04)	-10.85(±0.05)	-10.94(±0.05)	-11.03(±0.05)
				Polyethylene glycol-600				
0.00	525.42(±0.34)	527.32(±0.35)	528.91(±0.35)	530.75(±0.36)	-86.69(±1.04)	-87.51(±1.06)	-88.21(±1.07)	-89.00(±1.09)
0.01	525.72(±0.33)	527.63(±0.34)	529.23(±0.34)	531.00(±0.35)	-86.44(±1.01)	-87.26(±1.02)	-87.96(±1.04)	-88.73(±1.05)
0.03	526.40(±0.32)	528.51(±0.33)	529.62(±0.33)	531.40(±0.34)	-85.64(±0.98)	-87.14(±1.01)	-87.20(±1.01)	-87.98(±1.02)
0.05	527.22(±0.32)	529.16(±0.32)	530.31(±0.33)	532.61(±0.33)	-84.80(±0.96)	-85.61(±0.98)	-86.38(±1.00)	-87.06(±1.01)

$^{a}m_A$ represents the molality of polyethylene glycols in methanol-BuPB solutions.

Table 4.35 The values of limiting apparent molar isentropic compression, $K_{\phi,s}^{0}$ and experimental slope, S_k of (polyethylene glycols+methanol+BuPB) ternary solutions at various temperatures and experimental pressure, p = 0.1 MPa.

$^{a}m_B$/ (mol·kg^{-1})	$10^6 \cdot K_{\phi,s}^{0}$ / (m^3·mol^{-1}·GPa^{-1})				$10^6 \cdot S_k$ / (kg·m^3·mol^{-2}·GPa^{-1})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
				Polyethylene glycol-200				
0.00	-87.98(±0.07)	-95.52(±0.08)	-103.36(±0.08)	-111.91(±0.09)	-8.72(±0.20)	-8.69(±0.24)	-8.45(±0.23)	-8.30(±0.26)
0.01	-84.37(±0.07)	-91.65(±0.09)	-101.81(±0.08)	-110.25(±0.08)	-9.02(±0.21)	-9.08(±0.25)	-8.45(±0.22)	-8.29(±0.25)
0.03	-77.56(±0.07)	-88.34(±0.07)	-93.44(±0.08)	-101.44(±0.07)	-9.76(±0.20)	-9.22(±0.20)	-9.48(±0.23)	-9.26(±0.22)
0.05	-74.97(±0.08)	-81.78(±0.07)	-88.94(±0.07)	-96.51(±0.09)	-9.78(±0.22)	-9.65(±0.20)	-9.58(±0.22)	-9.59(±0.25)
				Polyethylene glycol-600				
0.00	-139.64(±1.56)	-155.56(±1.64)	-172.08(±1.70)	-190.29(±1.78)	-94.17(±4.69)	-95.42(±4.93)	-96.25(±5.11)	-97.06(±5.35)
0.01	-138.76(±1.51)	-154.53(±1.59)	-171.42(±1.35)	-189.08(±1.72)	-93.99(±4.56)	-95.31(±4.81)	-98.55(±4.06)	-96.85(±5.20)
0.03	-125.61(±1.48)	-144.56(±1.54)	-156.72(±1.62)	-173.98(±1.68)	-95.95(±4.46)	-96.12(±4.66)	-98.34(±4.87)	-99.25(±5.26)
0.05	-114.62((±1.47)	-128.93(±1.53)	-144.62(±1.60)	-159.84(±1.68)	-97.14(±4.43)	-98.57(±4.60)	-99.65(±4.80)	-101.29(±5.04)

Estimation of limiting apparent molar expansivities

The correlation of temperature with V_{ϕ}^{0} may be conveyed with the help of **eq. 4.6**. The parameter c, which is barely statistically significant, possess negative values for both PEGs except for PEG-600 in 0.05 mol·kg^{-1} methanol-BuPB solution. The theoretical V_{ϕ}^{0} have been estimated by these empirical parameters. The differences resulting from theoretical and experimental V_{ϕ}^{0} data that are assessed from these parameters are also presented here. These deviations ARD *(□□)* are estimated by using succeeding **eq. 4.7.** The value of constants are entered in **Table 4.36** and the data of temperature dependence limiting apparent molar volume $V_{\phi}^{0}(T)$ along with its standard error is indexed in **Table 4.37**.

The E_{ϕ}^{0}, limiting apparent molar expansion [9] is established by differentiating **eq. 4.7** w.r.t. temperature which further gives **eq. 4.8.** The E_{ϕ}^{0} is considered to be an essential measure to determine the association midst solute and solvent molecules prevailing in the mixture [10]. The positive values of E_{ϕ}^{0} attribute to overriding of associations midst solute and solvent upon solute-solute association which supports the earlier data of V_{ϕ}. The E_{ϕ}^{0} data accelerates with rise in temperature for (polyethylene glycol 200 + methanol-BuPB) solution because discharge of solute fragments from solvent led to enhancement in thermal disturbance which accelerates the system volume to bigger range as compared to pure solvent by virtue of surge in temperature; on the other hand, inconsistent trend has been discovered for E_{ϕ}^{0} in case of (polyethylene glycol 600 + methanol-BuPB) solution w.r.t. temperature. The E_{ϕ}^{0} data is tabulated in **Table 4.38** which displays the positive value for all the concentration of polyethylene glycol 200 and 600 and temperatures.

Table 4.36 Values of **e**mpirical parameters of equation (6) for (polyethylene glycols +methanol +BuPB) ternary solutions at several temperatures and experimental pressure p = 0.1 MPa.

$^{a}m_B$/(mol·kg^{-1})	10^6. a /(m^3□mol^{-1})	10^6. b /(m^3□mol^{-1}□K^{-1})	10^6. c /(m^3□mol^{-1}□K^{-2})	*ARD/(□)*
Polyethylene glycol-200				
0.00	165.30	0.093	-0.0004	0.00007
0.01	165.48	0.093	-0.0004	0.00007
0.03	165.69	0.095	-0.0004	0.00007
0.05	166.19	0.097	-0.0004	0.00007
Polyethylene glycol-600				
0.00	527.24	0.354	-0.0006	0.00010
0.01	527.56	0.355	-0.0014	0.00008
0.03	528.26	0.338	-0.0032	0.00031
0.05	528.87	0.329	0.0035	0.00036

$^{a}m_B$ states the molality of methanol-BuPB solutions.

Table 4.37 The values of temperature dependent limiting apparent molar volumes, $V_{\phi}^{0}(T)$ of (polyethylene glycols+ methanol +BuPB) ternary solutions at different temperatures and experimental pressure, p =0.1MPa.

$^{a}m_B$/ (mol·kg^{-1})	$10^6 \cdot V_{\phi}^{0}(T)$ / (m^3·mol^{-1})			
	T=293.15 K	T=298.15K	T=303.15K	T=308.15K
	Polyethylene glycol-200			
0.00	164.83(±0.01)	165.01(±0.01)	165.21(±0.01)	165.70(±0.01)
0.01	165.30(±0.01)	165.48(±0.01)	165.69(±0.01)	166.19(±0.01)
0.03	165.76(±0.01)	165.94(±0.01)	166.16(±0.01)	166.67(±0.01)
0.05	165.19(±0.01)	166.37(±0.01)	166.60(±0.01)	167.12(±0.01)
	Polyethylene glycol-600			
0.00	525.46(±0.34)	525.74(±0.35)	526.48(±0.35)	527.31(±0.36)
0.01	527.24(±0.33)	527.56(±0.34)	528.26(±0.34)	528.87(±0.35)
0.03	529.00(±0.32)	529.30(±0.33)	529.87(±0.33)	530.60(±0.34)
0.05	530.72(±0.32)	530.97(±0.32)	531.32(±0.33)	532.51(±0.33)

$^{a}m_B$ states the molality of methanol-BuPB solutions.

Table 4.38 The values of limiting apparent molar expansion, E_ϕ^0 for (polyethylene glycols +methanol +BuPB) at various temperatures and experimental pressure p = 0.1 MPa.

$^a m_B$/ (mol·kg^{-1})	$10^6 . E_\phi^0$/ (m^3·mol^{-1}·K^{-1})			
	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15 K
	Polyethylene glycol-200			
0.00	0.0966	0.0975	0.0987	0.1007
0.01	0.0927	0.0935	0.0948	0.0967
0.03	0.0887	0.0895	0.0908	0.0927
0.05	0.0848	0.0856	0.0868	0.0887
	Polyethylene glycol-600			
0.00	0.3603	0.3689	0.3704	0.2943
0.01	0.3543	0.3553	0.3384	0.3291
0.03	0.3482	0.3417	0.3063	0.3639
0.05	0.3422	0.3282	0.2742	0.3987

$^a m_B$ states the molality of methanol-BuPB solutions.

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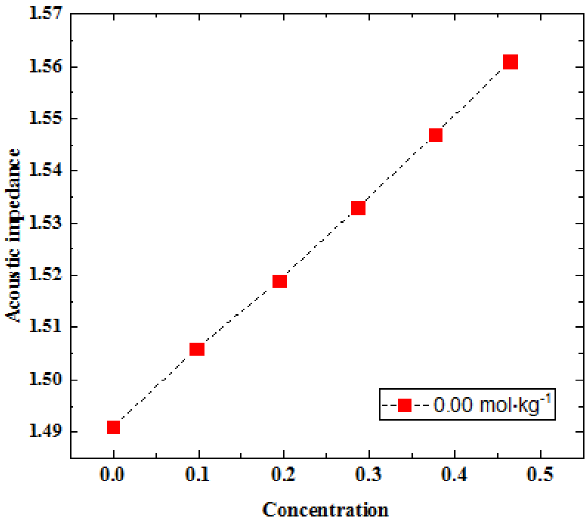
Part VI

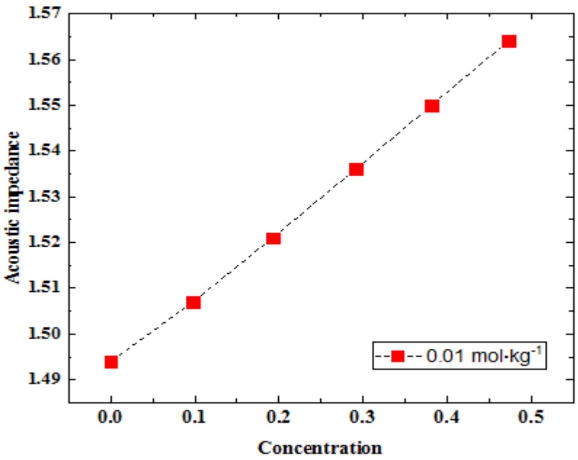
In this section, we have reported the viscometric and acoustical properties of ternary system (PEGs+ water+ sodium methylparaben) at 25^0 C and (glycols+ methanol+ methylparaben) at different temperatures.

ACOUSTIC IMPEDANCE (Z), ADIABATIC COMPRESSIBILITY (β), INTERMOLECULAR FREE LENGTH (L_f)

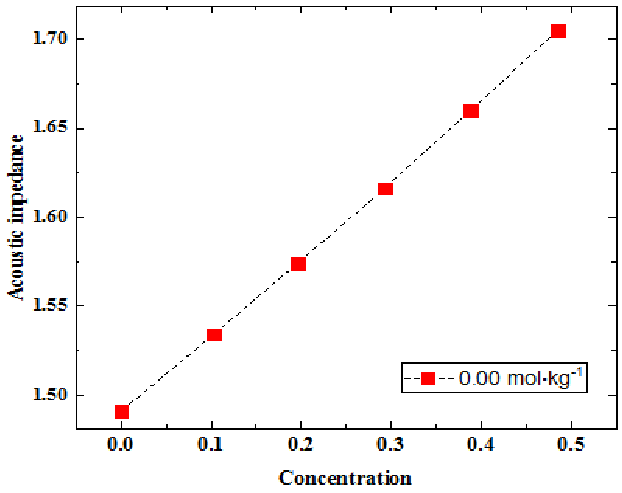
The plots for variation of acoustic impedance, adiabatic compressibility and intermolecular free length are shown in **Figures (sample)**.



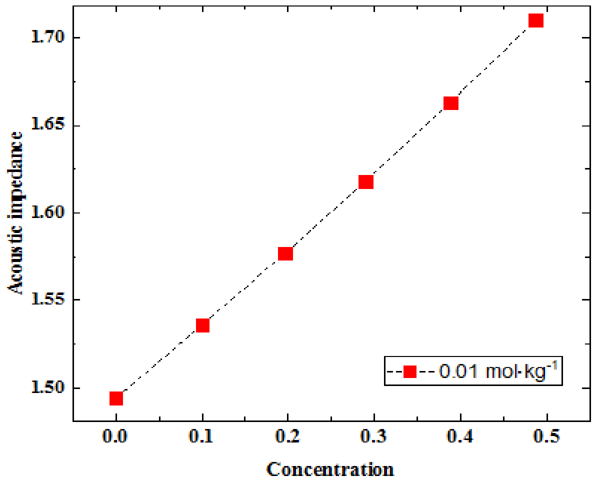
(a)**PEG-200**



(b)**PEG-200**

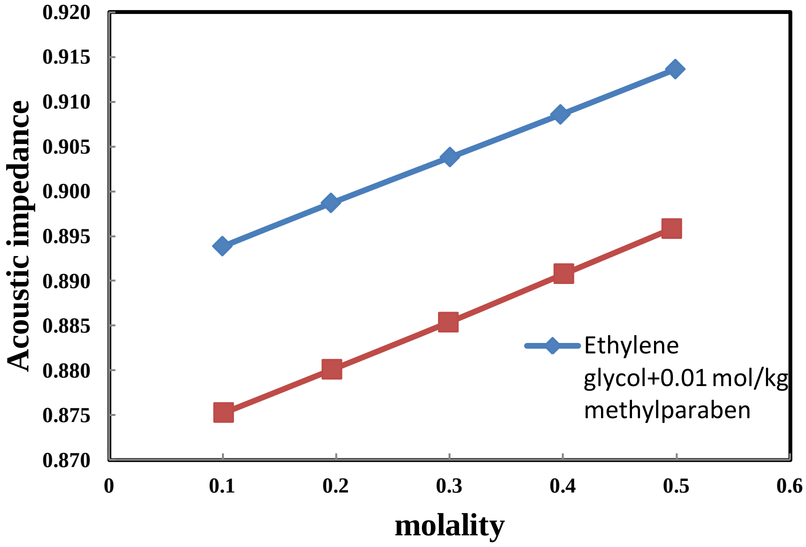


(c)**PEG-600**

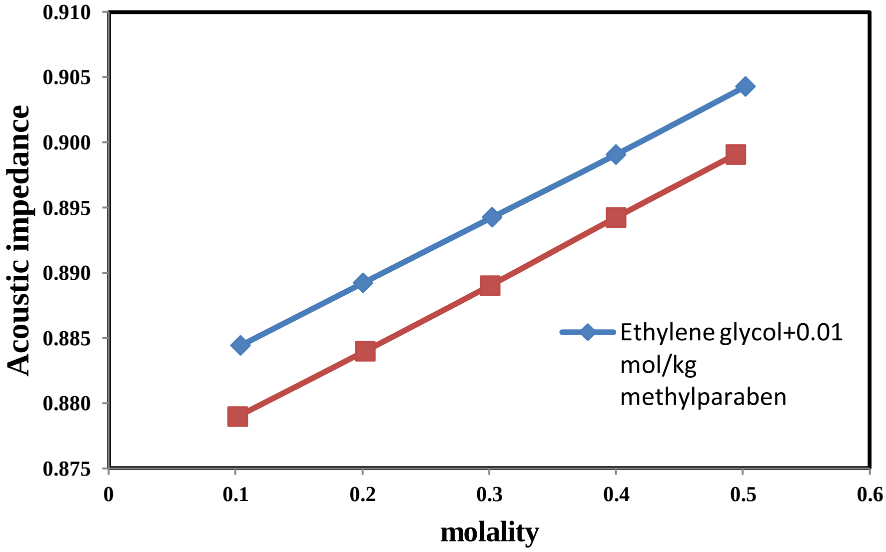


(d) **PEG-600**

Figure 1: Plots of acoustic impedance versus concentration for (PEGs+ water+ sodium methylparaben) at 25^{0}C

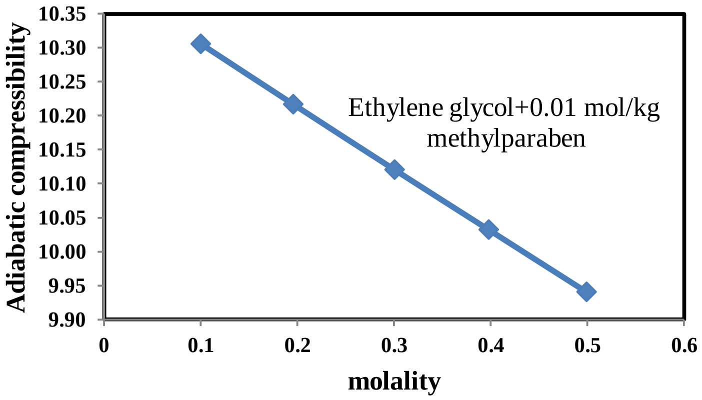


(a)

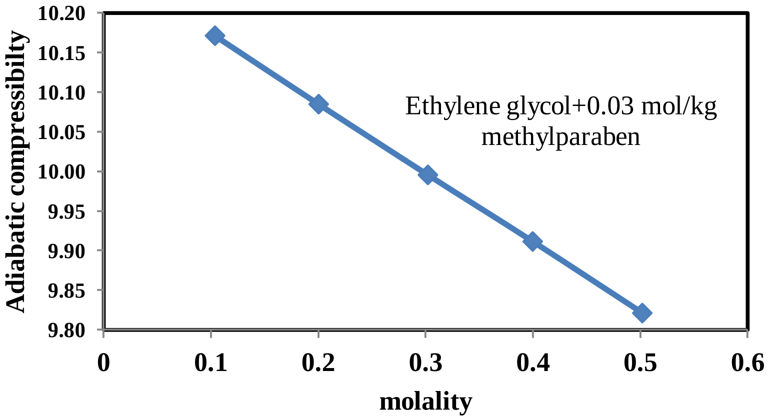


(b)

Figure 2. Variation of acoustic impedance with molal concentration of (glycols+ methanol+ methylparaben) at 25^{0}C.


Adiabatic compressibility
10.35
10.30
10.25
10.20
10.15
10.10
10.05
10.00
9.95
9.90
0
0.1
0.2
0.3
0.4
0.5
0.6
molality
Ethylene glycol+0.01 mol/kg methylparaben

(a)


Adiabatic compressibilty
10.20
10.15
10.10
10.05
10.00
9.95
9.90
9.85
9.80
0
0.1
0.2
0.3
0.4
0.5
0.6
molality
Ethylene glycol+0.03 mol/kg methylparaben

(c)

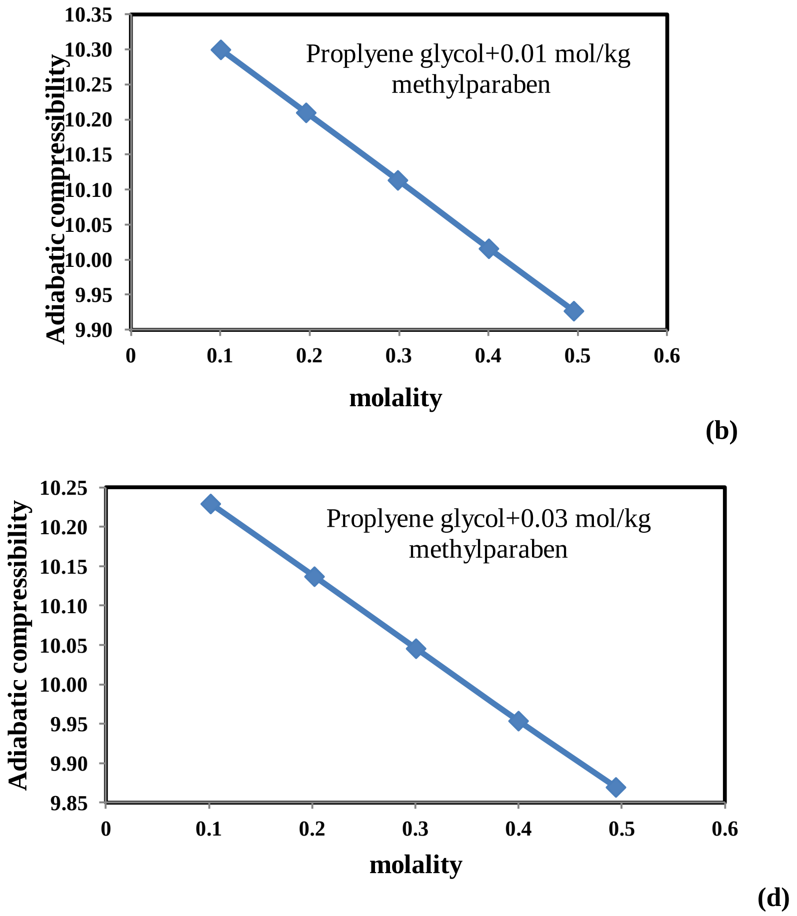
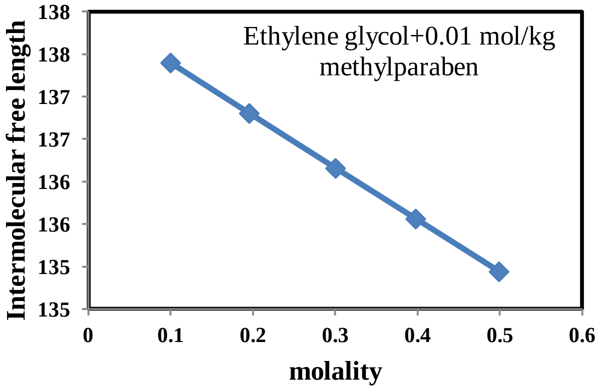
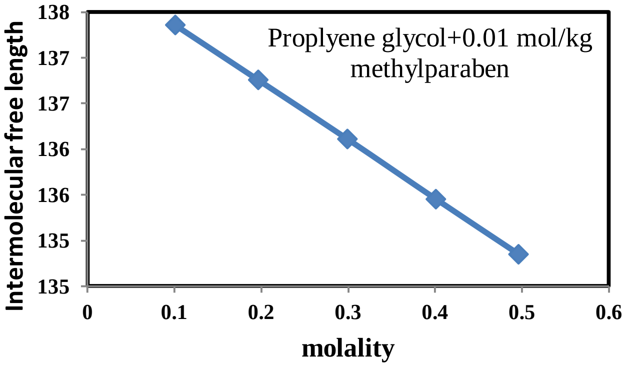


Figure 3: Variation of adiabatic compressibility against molality of (glycols+ methanol+ methylparaben) at 25^0 C.


Ethylene glycol+0.01 mol/kg methylparaben
Intermolecular free length
138
138
137
137
136
136
135
135
0
0.1
0.2
0.3
0.4
0.5
0.6
molality

(a)


Proplyene glycol+0.01 mol/kg methylparaben
Intermolecular free length
138
137
137
136
136
135
135
0
0.1
0.2
0.3
0.4
0.5
0.6
molality

(c

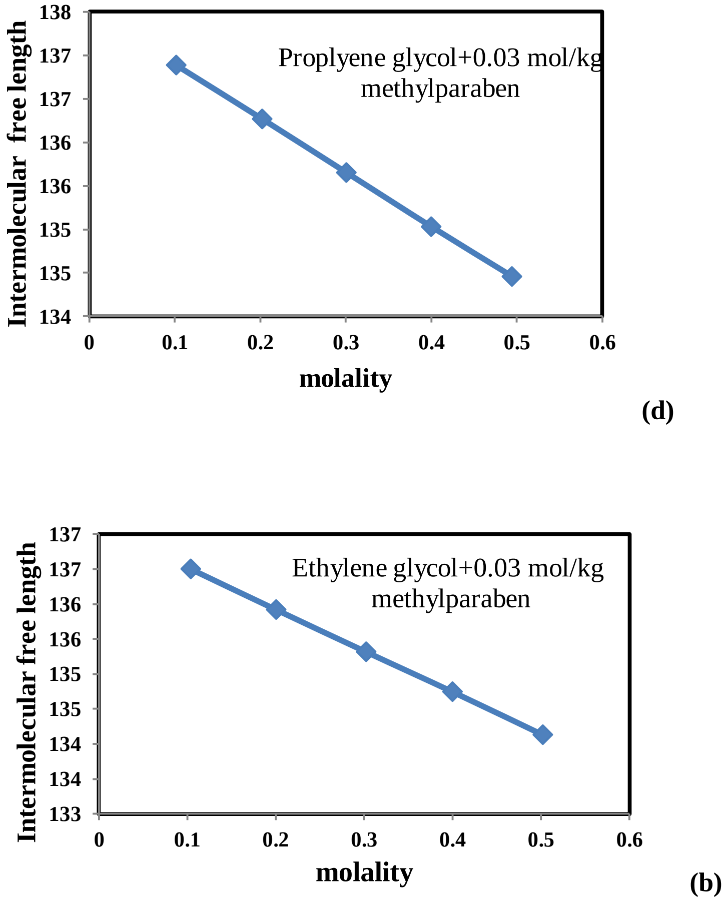


Figure 4: Variation of intermolecular free length versus molality of (glycols+ methanol+ methylparaben) at 25^0C .

From the figures, it can be noticed that acoustic impedance for the ternary systems (PEG 200, PEG 600+ water + sodium methylparaben) and (EG, PG+ methanol+ methylparaben) is increasing with increase in concentration of glycols and paraben. The reduction in values of *Z* has also been observed with respect to temperature.

That is, the adiabatic compressibilities and intermolecular free lengths are decreasing with surge in mole fraction of glycols as well as increases with surge in temperature. The trend for β and L_f for (EG, PG +methanol+ methylparaben) at 25^0C is shown in **Figures.** Both adiabatic compressibility and intermolecular free length possess same behaviour as depicted by their mathematical expression which is in agreement with experimental results. Such decrement in β and L_f values and increment in Z values supports the existence of strong interactions in the present systems.

ULTRASONIC ATTENUATION COEFFICIENT (α), RELAXATION TIME (τ)

The acoustical parameters ultrasonic attenuation and relaxation time are related to each other. Loss of the sound wave is termed as time delay between passing of ultrasonic wave and getting back of molecule to its equilibrium position. Hence, with rising in the molality concentration of glycols and paraben, ultrasonic attenuation increases and decreases with respect to temperature. The high value of relaxation time and viscosity along with the structural relaxation process is responsible for increase in the value of ultrasonic attenuation with concentration. In studying the structural and molecular properties of molecular components the structural relaxation process plays very vital role. .

GIBB'S FREE ENERGY (ΔG), RELATIVE ASSOCIATION (R_A)

It can be found from the data of (PEGs+ water+ sodium methylparaben) that the value of Gibb's free energy is inconsistent with the concentration of solute. On the other hand, for system (glycols+ methanol+ methylparaben), it can be found from the data that the values of Gibb's free energy increases with rise in the concentration of solute and temperature indicate increase in energy change. The relative association data increases with rise in the concentration. The values of impedance, adiabatic compressibility, intermolecular free length, Gibb's free energy, relative association, viscosity, relaxation time and ultrasonic attenuation are computed and are presented in **Table 4.39** and **Table 4.40.**

Table 4.39: Computed values of acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), Gibb's free energy (ΔG) and relative association (R_A) for ternary liquid mixture at 25^0C

(*m*) PEG	Concentration (*C*)	Impedance (Z) kg m^{-2} s^{-1} × 10^5	Adiabatic compressibility (β) N/m^2 × 10^{-7}	Intermolecular free length (L_f) Å x 10^{-10}	Gibb's free energy (ΔG) KJ mol^{-1} × 10^{-20}	relative association (R_A)
(0.00) PEG-200	0.0000	1.491	4.482	90.6145	1.2632	1.0070
	0.0982	1.506	4.407	89.8575	1.2630	1.0162
	0.1937	1.519	4.341	89.1833	1.2630	1.0254
	0.2865	1.533	4.275	88.4969	1.2629	1.0346
	0.3768	1.547	4.210	87.8202	1.2629	1.0441
	0.4648	1.561	4.145	87.1425	1.2628	1.0531
(0.01) PEG-200	0.0000	1.494	4.471	90.5027	1.2632	1.0080
	0.0978	1.507	4.402	89.7993	1.2631	1.0171
	0.1922	1.521	4.335	89.1108	1.2635	1.0268
	0.2910	1.536	4.264	88.3806	1.2629	1.0363
	0.3810	1.550	4.199	87.7058	1.2628	1.0459
	0.4724	1.564	4.133	87.0107	1.2629	1.0575
(0.00) PEG-600	0.0000	1.491	4.482	90.6145	1.2634	1.0196
	0.1028	1.534	4.274	88.4818	1.2630	1.0468
	0.1957	1.574	4.094	86.5979	1.2626	1.0746
	0.2925	1.616	3.914	84.6797	1.2623	1.1034
	0.3879	1.660	3.745	82.8280	1.2620	1.1332
	0.4853	1.705	3.580	80.9802	1.2615	1.1576
(0.01) PEG-600	0.0000	1.494	4.471	90.5027	1.2635	1.0208
	0.1002	1.536	4.267	88.4093	1.2631	1.0486
	0.1962	1.577	4.080	86.4475	1.2627	1.0764
	0.2899	1.618	3.905	84.5758	1.2623	1.1055
	0.3876	1.663	3.731	82.6667	1.2619	1.1363
	0.4873	1.710	3.561	80.7629	1.2617	1.1598

Table 4.40: Computed values of viscosity (η), relaxation time (τ) and ultrasonic attenuation (α/f^2) for ternary liquid mixture at 25^{0}C

(m) PEG	Concentration (C)	Viscosity (η)	Relaxationtime (τ) s x 10^{-5}	Ultrasonic Attenuation (α/f^2) $s^2\ m^{-1} \times 10^{-12}$
(0.00) PEG-200	0.0000	0.8942	5.3442	7.045
	0.0982	0.8987	5.2819	6.914
	0.1937	0.9128	5.2842	6.874
	0.2865	0.9191	5.2394	6.773
	0.3768	0.9324	5.2340	6.723
	0.4648	0.9405	5.1982	6.634
(0.01) PEG-200	0.0000	0.8959	5.3414	7.034
	0.0978	0.9048	5.3109	6.949
	0.1922	0.9469	5.4731	7.116
	0.2910	0.9180	5.2190	6.739
	0.3810	0.9243	5.1751	6.640
	0.4724	0.9482	5.2249	6.660
(0.00) PEG-600	0.0000	0.9110	5.4448	7.178
	0.1028	0.9247	5.2695	6.813
	0.1957	0.9382	5.1209	6.507
	0.2925	0.9526	4.9721	6.204
	0.3879	0.9716	4.8517	5.946
	0.4853	0.9833	4.6935	5.648
(0.01) PEG-600	0.0000	0.9173	5.4688	7.202
	0.1002	0.9306	5.2944	6.841
	0.1962	0.9430	5.1294	6.507
	0.2899	0.9592	4.9941	6.224
	0.3876	0.9745	4.8473	5.930
	0.4873	0.9987	4.7415	5.692

VISCOSITY (η), RELATIVE VISCOSITY ($\eta_0 / \eta - 1$), A and B coefficients

The value of viscosity increases with increase in the concentration of glycols and decreases with respect to temperature. The increment in the values of viscosity shows that as interaction among the molecules becomes strong with increase in the concentration of glycols and paraben. The value of relative viscosity increases with increase in the concentration of glycols at 25^0C. The values of A and B coefficients has been computed by utilizing Jone-Dole's equation for (PEGs+ water+ sodium methylparaben) at 25^0C and hence by plotting the graph of variation of $\eta_0 / \eta - 1$ versus C and $(\eta_0 / \eta - 1)/\sqrt{C}$ versus √C. The data of coefficient B is positive which indicate the existence of strong solute-solvent associations. The values of B signify that these polyethylene glycols act as a structure builder. The order of the structure builder solutes follows trend: PEG 600 >PEG 200. The coefficient A is considered to be positive for electrolytes, on the other hand it is considered as zero for non-electrolyte.

The values of $\eta_0 / \eta - 1$, $\eta_0 / \eta - 1$ versus C and $(\eta_0 / \eta - 1)/\sqrt{C}$ versus √C are indexed in **Table 4.41** and **4.42**

Table 4.41: Computed values of η_0 / η and concentration for ternary liquid mixture at 25^0C

(m) PEG	Concentration (C)	$\sqrt{C}$ $mol^{1/2}dm^{-3/2}$	$\eta_0 / \eta - 1$	$(\eta_0 / \eta - 1)/\sqrt{C}$
(0.00) PEG-200	0.0982	0.3135	0.0269	0.1033
	0.1937	0.4402	0.0323	0.1104
	0.2865	0.5353	0.0376	0.1157
	0.3768	0.6139	0.0428	0.1201
	0.4648	0.6818	0.0478	0.1239
(0.01) PEG-200	0.0978	0.3128	0.0433	0.1608
	0.1922	0.4385	0.0559	0.1699
	0.2910	0.5395	0.0582	0.1772
	0.3810	0.6173	0.0624	0.1828
	0.4724	0.6874	0.0751	0.1878

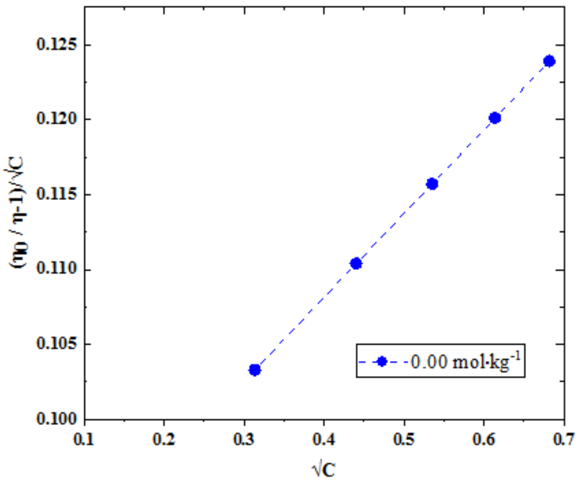
(0.00) PEG-600	0.1028	0.3207	0.1216	0.4062
	0.1957	0.4425	0.1223	0.4164
	0.2925	0.5408	0.1301	0.4247
	0.3879	0.6229	0.1472	0.4316
	0.4853	0.6967	0.1505	0.4378
(0.01) PEG-600	0.1002	0.3165	0.3165	0.4839
	0.1962	0.4430	0.4429	0.4953
	0.2899	0.5384	0.5383	0.5039
	0.3876	0.6226	0.6225	0.5115
	0.4873	0.6981	0.6980	0.5183

Table 4.42: Calculated parameters of Jone-Dole's equation for ternary liquid mixture at 25^{0}C

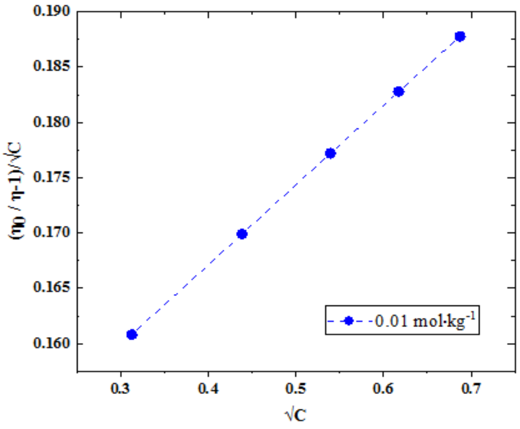
PEGs	$\eta_0 / \eta - 1$ versus C B/kn (dm^{3}mol^{-1})	$(\eta_0 / \eta - 1)/\sqrt{C}$ versus $\sqrt{C}$ B/kn (dm^{3}mol^{-1})
(0.00) PEG-200	0.056	0.056
(0.01) PEG-200	0.074	0.072
(0.00) PEG-600	0.086	0.084
(0.01) PEG-600	0.097	0.090

The values of A and B coefficients has been computed by utilizing Jon-Dole's equation for (PEGs+ water+ sodium methylparaben) at 25^{0}C and hence by plotting the graph of variation of $\eta_0 / \eta - 1$ versus C and $(\eta_0 / \eta - 1)/\sqrt{C}$ versus $\sqrt{C}$.

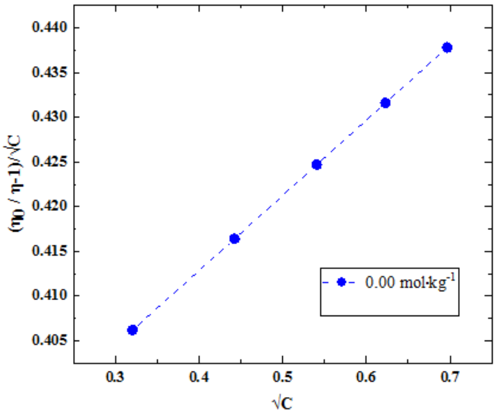
From the **Figures**, it is found that the value of B coefficient increases with rising in the molecular mass of polyethylene glycols i.e. from PEG 200 to PEG-600.



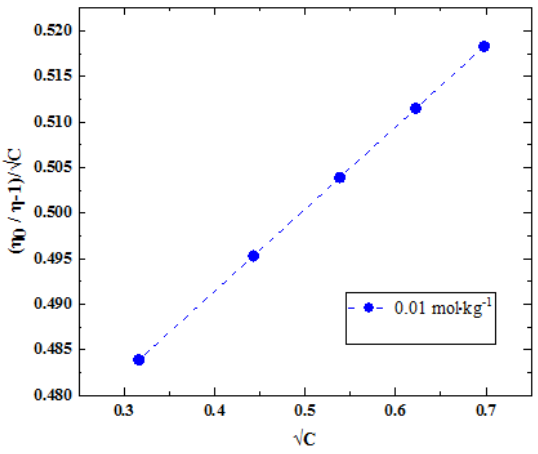
(a)**PEG-200**



(b) **PEG-200**



(c) **PEG-600**



(d) **PEG-600**

Figure 6: Variation of $\sqrt{C}$ and $(\eta_0 / \eta-1)/\sqrt{C}$ for (PEGs+ water+ sodium methylparaben) at 25^0C

On the other hand, the various acoustical parameters for (glycols+ methanol+ methylparaben) system at different temperatures (20^0C to 35^0C) and concentrations (0.01 and 0.03) are computed. The data of acoustic impedance at different concentration and different temperatures is indexed in **Table 4.43.**

Table 4.43: Computed Values of Acoustic impedance (Z) for ternary liquid mixture at different temperatures.

m (mol·kg^{-1})	Impedance (Z) kg m^{-2} s^{-1} × 10^5			
	20^0C	25^0C	30^0C	35^0C
Ethylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.09986	0.894	0.875	0.853	0.840
0.19552	0.899	0.880	0.855	0.845
0.30041	0.904	0.885	0.857	0.850
0.39780	0.909	0.890	0.859	0.855
0.49906	0.914	0.895	0.861	0.861
Ethylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10375	0.897	0.884	0.861	0.844
0.20032	0.902	0.889	0.865	0.849
0.30210	0.907	0.894	0.871	0.854
0.39976	0.912	0.899	0.875	0.859
0.50190	0.917	0.904	0.880	0.864
Propylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.10096	0.894	0.875	0.858	0.840
0.19642	0.899	0.880	0.862	0.845
0.29903	0.904	0.885	0.868	0.850
0.40085	0.909	0.891	0.873	0.856
0.49594	0.914	0.896	0.878	0.861
Propylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10151	0.897	0.879	0.861	0.842
0.20210	0.902	0.884	0.866	0.847
0.30056	0.907	0.889	0.871	0.852
0.39985	0.912	0.894	0.875	0.859
0.49429	0.917	0.899	0.881	0.865

The value of adiabatic compressibility for (glycols+ methanol+ methylparaben) system is listed in **Table 4.44.**

Table 4.44. Computed Values of Adiabatic compressibility (β) for ternary liquid mixture at different temperatures.

m (mol·kg^{-1})	Adiabatic compressibility (β) N/m^2 × 10^{-7}			
	20^{0}C	25^{0}C	30^{0}C	35^{0}C
	Ethylene glycol + 0.01 mol·kg^{-1} methylparaben			
0.09986	9.940	10.305	10.781	11.056
0.19552	9.856	10.217	10.757	10.955
0.30041	9.769	10.120	10.730	10.841
0.39780	9.689	10.032	10.704	10.739
0.49906	9.605	9.940	10.678	10.628
	Ethylene glycol + 0.03 mol·kg^{-1} methylparaben			
0.10375	9.880	10.171	10.611	10.972
0.20032	9.798	10.085	10.518	10.867
0.30210	9.714	9.996	10.422	10.762
0.39976	9.635	9.911	10.331	10.663
0.50190	9.555	9.821	10.240	10.559
	Propylene glycol + 0.01 mol·kg^{-1} methylparaben			
0.10096	9.939	10.299	10.666	11.049
0.19642	9.850	10.209	10.571	10.945
0.29903	9.760	10.113	10.470	10.832
0.40085	9.676	10.016	10.374	10.720
0.49594	9.592	9.926	10.286	10.615
	Propylene glycol + 0.03 mol·kg^{-1} methylparaben			
0.10151	9.878	10.229	10.608	10.994
0.20210	9.789	10.137	10.507	10.883
0.30056	9.707	10.045	10.416	10.780
0.39985	9.625	9.954	10.325	10.649
0.49429	9.540	9.869	10.230	10.546

The value of intermolecular free length for glycols+ methanol+ methylparaben) system is listed in **Table 4.45.**

Table 4.45. Computed Values of Intermolecular free length (L_f) for ternary liquid mixture

at different temperatures**.**

m (mol·kg^{-1})	Intermolecular free length (L_f) Å x 10^{-10}			
	20^0C	25^0C	30^0C	35^0C
Ethylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.09986	134.9404	137.3970	140.5333	142.3102
0.19552	134.3681	136.8032	140.3756	141.6603
0.30041	133.7730	136.1566	140.1975	140.9245
0.39780	133.2236	135.5615	140.0301	140.2556
0.49906	132.6461	134.9407	139.8576	139.5308
Ethylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10375	134.5331	136.4996	139.4176	141.7734
0.20032	133.9722	135.9185	138.8047	141.0913
0.30210	133.3958	135.3155	138.1699	140.4085
0.39976	132.8511	134.7452	137.5675	139.7606
0.50190	132.2970	134.1299	136.9595	139.0768
Propylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.10096	134.9308	137.3564	139.7783	142.2687
0.19642	134.3233	136.7557	139.1556	141.5953
0.29903	133.7083	136.1086	138.4890	140.8618
0.40085	133.1371	135.4504	137.8558	140.1365
0.49594	132.5589	134.8470	137.2666	139.4461
Propylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10151	134.5188	136.8884	139.3989	141.9113
0.20210	133.9112	136.2691	138.7374	141.1976
0.30056	133.3472	135.6529	138.1334	140.5270
0.39985	132.7802	135.0306	137.5303	139.6706
0.49429	132.1974	134.4582	136.8913	138.9922

The value of viscosity for (glycols+ methanol+ methylparaben) system is indexed in **Table 4.46.**

Table 4.46: Computed Values of viscosity (η) for ternary liquid mixture at different temperatures

m (mol·kg^{-1})	viscosity (η)			
	20^0C	25^0C	30^0C	35^0C
Ethylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.09986	0.615	0.567	0.536	0.510
0.19552	0.656	0.539	0.562	0.524
0.30041	0.661	0.626	0.589	0.555
0.39780	0.681	0.639	0.616	0.581
0.49906	0.692	0.665	0.643	0.599
Ethylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10375	0.646	0.587	0.569	0.530
0.20032	0.663	0.626	0.577	0.562
0.30210	0.688	0.653	0.614	0.582
0.39976	0.695	0.659	0.626	0.610
0.50190	0.718	0.679	0.648	0.623
Propylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.10096	0.681	0.614	0.577	0.553
0.19642	0.690	0.639	0.600	0.581
0.29903	0.724	0.667	0.630	0.601
0.40085	0.742	0.694	0.657	0.620
0.49594	0.782	0.721	0.670	0.647
Propylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10151	0.695	0.643	0.606	0.581
0.20210	0.713	0.661	0.628	0.596
0.30056	0.739	0.696	0.661	0.614
0.39985	0.788	0.719	0.686	0.647
0.49429	0.803	0.733	0.709	0.676

The value of ultrasonic attenuation and relaxation time for (glycols+ methanol+ methylparaben) system is enlisted in **Table 4.47** and **4.48**.

Table 4.47: Computed Values of Relaxation time (τ) for ternary liquid mixture at different temperatures.

m (mol·kg^{-1})	Relaxation time (τ) s x 10^{-5}			
	20^0C	25^0C	30^0C	35^0C
	Ethylene glycol + 0.01 mol·kg^{-1} methylparaben			
0.09986	8.1509	7.7955	7.7060	7.5141
0.19552	8.6163	7.3384	8.0646	7.6603
0.30041	8.6157	8.4513	8.4266	8.0254
0.39780	8.7971	8.5507	8.7918	8.3225
0.49906	8.8655	8.8087	9.1504	8.4856
	Ethylene glycol + 0.03 mol·kg^{-1} methylparaben			
0.10375	8.5100	7.9601	8.0508	7.7506
0.20032	8.6640	8.4177	8.0950	8.1428
0.30210	8.9102	8.6981	8.5337	8.3472
0.39976	8.9243	8.7068	8.6291	8.6680
0.50190	9.1459	8.8957	8.8492	8.7679
	Propylene glycol + 0.01 mol·kg^{-1} methylparaben			
0.10096	9.0253	8.4374	8.2055	8.1464
0.19642	9.0603	8.7006	8.4501	8.4820
0.29903	9.4151	8.9903	8.8006	8.6826
0.40085	9.5768	9.2677	9.0895	8.8654
0.49594	9.9988	9.5434	9.1899	9.1510
	Propylene glycol + 0.03 mol·kg^{-1} methylparaben			
0.10151	9.1529	8.7753	8.5759	8.5097
0.20210	9.3126	8.9377	8.7934	8.6461
0.30056	9.5644	9.3235	9.1753	8.8206
0.39985	10.1133	9.5426	9.4508	9.1814
0.49429	10.2116	9.6449	9.6766	9.5056

Table 4.48. Computed Values of Ultrasonic Attenuation (α/f^2) for (glycols+ methanol+ methylparaben) system at different temperatures.

m (mol·kg^{-1})	Ultrasonic Attenuation (α/f^2) s^2 m^{-1} × 10^{-12} 20^{0}C	 25^{0}C	 30^{0}C	 35^{0}C
Ethylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.09986	14.281	13.862	13.977	13.760
0.19552	15.049	13.008	14.627	13.979
0.30041	15.000	14.929	15.284	14.587
0.39780	15.270	15.055	15.946	15.073
0.49906	15.341	15.458	16.597	15.307
Ethylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10375	14.878	14.120	14.498	14.151
0.20032	15.101	14.885	14.530	14.812
0.30210	15.482	15.331	15.266	15.128
0.39976	15.461	15.299	15.388	15.656
0.50190	15.798	15.579	15.730	15.778
Propylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.10096	15.811	14.999	14.802	14.912
0.19642	15.819	15.416	15.191	15.469
0.29903	16.382	15.873	15.765	15.772
0.40085	16.612	16.304	16.228	16.042
0.49594	17.289	16.734	16.358	16.497
Propylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10151	15.999	15.558	15.441	15.533
0.20210	16.223	15.793	15.774	15.720
0.30056	16.610	16.418	16.407	15.979
0.39985	17.509	16.748	16.846	16.571
0.49429	17.622	16.875	17.189	17.093

The value of Gibb’s free energy for (glycols+ methanol+ methylparaben) system is reported in **Table 4.49**

Table 4.49. Computed Values of Gibb's free energy (ΔG) for ternary liquid mixture at different temperatures.

m (mol·kg^{-1})	Gibb's free energy (ΔG) KJ mol^{-1} × 10^{-20}			
	20^{0}C	25^{0}C	30^{0}C	35^{0}C
Ethylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.09986	1.2471	1.2680	1.2893	1.3105
0.19552	1.2478	1.2672	1.2899	1.3108
0.30041	1.2478	1.2690	1.2905	1.3114
0.39780	1.2480	1.2692	1.2911	1.3119
0.49906	1.2481	1.2696	1.2916	1.3121
Ethylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10375	1.2476	1.2683	1.2899	1.3109
0.20032	1.2478	1.2690	1.2900	1.3116
0.30210	1.2482	1.2694	1.2907	1.3119
0.39976	1.2482	1.2694	1.2908	1.3124
0.50190	1.2485	1.2697	1.2911	1.3125
Propylene glycol + 0.01 mol·kg^{-1} methylparaben				
0.10096	1.2484	1.2690	1.2902	1.3116
0.19642	1.2484	1.2694	1.2905	1.3121
0.29903	1.2489	1.2698	1.2911	1.3124
0.40085	1.2491	1.2702	1.2915	1.3127
0.49594	1.2496	1.2706	1.2916	1.3131
Propylene glycol + 0.03 mol·kg^{-1} methylparaben				
0.10151	1.2485	1.2695	1.2907	1.3121
0.20210	1.2488	1.2698	1.2911	1.3124
0.30056	1.2491	1.2703	1.2916	1.3126
0.39985	1.2498	1.2706	1.2920	1.3132
0.49429	1.2499	1.2707	1.2923	1.3136

The relative viscosity data has been indexed in **Table 4.50.**

Table 4.50: Computed Values of relative viscosity (η_0 / η) and concentration for (glycols+ methanol+ methylparaben) system at 25^0C.

Concentration (C)	$\sqrt{C}$ $mol^{1/2}dm^{-3/2}$	η_0 / η
	Ethylene glycol + 0.01 mol·kg^{-1} methylparaben	
0.0777	0.2788	1.0099
0.1535	0.3918	1.0638
0.2275	0.4770	1.1181
0.2996	0.5474	1.1725
0.3702	0.6084	1.2273
	Ethylene glycol + 0.03 mol·kg^{-1} methylparaben	
0.0778	0.2790	1.0957
0.1537	0.3921	1.1355
0.2278	0.4773	1.1756
0.3001	0.5478	1.2156
0.3707	0.6089	1.2561
	Propylene glycol + 0.01 mol·kg^{-1} methylparaben	
0.0777	0.2788	1.1315
0.1534	0.3918	1.1771
0.2274	0.4769	1.2279
0.2996	0.5474	1.2781
0.3701	0.6084	1.3279
	Propylene glycol + 0.03 mol·kg^{-1} methylparaben	
0.0778	0.2790	1.1847
0.1537	0.3921	1.2280
0.2277	0.4773	1.2714
0.3000	0.5478	1.3153
0.3706	0.6088	1.3592

SUMMARY AND CONCLUSION

5. Summary and Conclusion

The thesis entitled “**THERMO-ACOUSTICAL STUDY OF TERNARY LIQUID MIXTURES OF N-ALKYL PARABENS WITH DIFFERENT ORGANIC SOLVENTS**” tells about the acoustical and thermodynamic properties of the liquid mixtures comprising of glycols. To study the thermodynamic properties of liquid mixtures the density, speed of sound and viscosity of the mixtures have been measured at different temperatures with the help of Anton Paar DSA 5000 M density and velocity meter and Ostwald’s viscometer. With the help of these parameters, volumetric properties such as apparent molar volume and apparent molar isentropic compression, partial molar volume, partial molar isentropic compression and partial molar expansibilities, partial molar volume of transfer and partial molar isentropic compression of transfer, the pair and triplet interaction coefficients are computed.

The density and speed of sound measurements for EG, PG, and HG in methanol solutions of (MePB) at various concentrations and temperatures are described. The limiting partial molar volume for all the investigated system increases with upsurge in the temperature indicating that the strong intermolecular interaction increases from EG to PG to HG at all working temperatures. The negative $K_{\phi,s}^{0}$ value signifies the dominance of the negative effect (solute intrinsic compressibility) over the positive effect (solvent intrinsic effect). The positive values of E_{ϕ}^{0}, the apparent molar expansibility at infinite dilution imply the presence of solute−solvent interaction for all the ternary system studied. The isentropic compressibility values, β_s increases with increase in temperature for all the ternary system investigated.

The volumetric and compressibility studies of EG and PG have been examined at different concentrations of SEP solutions in water have been examined. Apparent molar properties and partial molar properties derived from experimental data of density and sound speed data supplies the subsistence of sturdy solute-solvent interactions among (glycols molecules and SEP). The degree of interactions heightens with the concentration of SEP solutions along with the molar mass of glycols which means that interactions amidst solute and solvent rises from EG to PG. At lessen temperatures, more negative $K_{\phi,s}^{0}$ values describes the intense and interesting connections with both the glycols and water molecules as water molecules are rigidly restricted to the solution. The $(\partial^2 V_\phi^0/\partial T)_P$, second derivative of temperature reveals the structure building property of glycols in the solutions of SEP. Further, rendering data concluded that ion-hydrophilic and hydrophilic-hydrophilic interactions predominated over ion-hydrophobic and hydrophobic- hydrophobic interactions. The information about experimental data on density and speed of the sound of EG and PG in methanol solutions of propylparaben have been reported at four different temperatures i.e. (293.15, 298.15, 303.15 and 308.15) and 0.1MPa. The data for (V_ϕ) apparent molar volumes and $(K_{\phi,s})$ apparent molar isentropic compressibilities have been computed from the experimentally obtained data of density and speed of the sound. For all the investigated system V_ϕ^0 values show pronounced increase with increase in temperature which indicates that at all working temperatures intermolecular interactions for PG in methanol solutions of propylparaben are stronger than EG in methanol solutions of propylparaben. The calculated positive E_ϕ^0, limiting apparent molar expansibility values show the existence of solute- solvent interactions in the solution mixture studied. The negative value of limiting apparent molar isentropic compressibilities $K_{\phi,s}^0$ belongs to the domination of penetration effect (solute intrinsic effect) over the solvent intrinsic compressibility. The acoustic and volumetric properties of PEG-200 along with PEG-600 have been scrutinized in aqueous sodium methylparaben are documented in temperature range from 293.15-308.15K. The positive ΔV_ϕ^0 values suggest the predominance of hydrophilic-hydrophilic and ion-hydrophilic interactions upon hydrophobic-hydrophobic and ion-hydrophobic interactions in the solution mixture. At lower temperature, more negative values of $K_{\phi,s}^0$ surmise the sturdy attractive interactions amidst the polyethylene glycols and water fragments as water throughout the solute fragment is strongly constrained to the solute. The minute negative and positive values of second order derivative of temperature, $(\partial^2 V_\phi^0/\partial T)_P$ narrate the complex building behaviour of PEGs in SMP. Moreover, pair wise interaction is assessed by V_{AB} and K_{AB} values among PEGs and SMP molecules. The thermo-physical, ultrasonic and volumetric properties of polyethylene glycols viz. polyethylene glycol 200 and polyethylene glycol 600 with BuPB in methanol medium are reported in the temperature range from 293.15 to 308.15 K and 0.1 MPa . sThe supremacy of negative impact upon positive impact is suggested by the negative $K_{\phi,s}^{0}$ data in the current inspected system. The increment in k_s values w.r.t. to temperature elevation intensify the volume of mixture and make the mixture more compressible as a result of thermal disturbance in the ternary mixture. Various derived parameters such as acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, ultrasonic attenuation, viscosity, Gibb's free energy are computed. Jone- Doles equation has been utilized to study the various interaction parameters.

Most of the acoustical parameters are varying linearly with respect to concentration suggesting the non-existence of complex formation in the system.

6. LIST OF PUBLICATIONS AND CONFERENCES ATTENDED

1. **Ashima Thakur**, K.C. Juglan, Harsh Kumar, "Intermolecular investigation of polyethylene glycols with butyl paraben in methanol medium attributing volumetric, ultrasonic and thermo-physical properties" submitted to *Journal of Molecular liquids*, doi.org/10.1016/j.molliq.2019.112000.

2. **Ashima Thakur**, K.C. Juglan, Harsh Kumar, Kirandeep Kaur, "Apparent molar properties of Glycols in methanol solutions of Propyl 4-Hydroxybenzoate (Propylparaben) at T= (293.15 to 308.15) K: An acoustic and volumetric approach" published in *Physics and Chemistry of Liquids*, doi.org/10.1080/00319104.2019.1660980.

3. **Ashima Thakur**, K.C. Juglan, Harsh Kumar, "Volumetric and ultrasonic investigation of polyethythene glycols (PEG-200 and PEG-600) in aqueous solutions of sodium methylparaben at various temperatures" published in *Journal of Chemical theromodynamics*, doi.org/10.1016/j.jct.2019.105916.

4. **Ashima Thakur**, K.C. Juglan, Harsh Kumar, Kirandeep Kaur," Investigation on molecular interaction of glycols in methanol solutions of methylparaben (methyl 4 –hydroxybenzoate) at different temperatures through thermo-acoustical analysis" *Journal of Molecular Liquids* 288 (2019) 111014.

Workshop / Seminars / Conferences / Certifications

- "Recent Advances in Fundamental and Applied Sciences (RAFAS)" at LPU in 5-6 November, 2019.

- "Innovations and Future Perspectives in Chemical Sciences and Technology", Dr B R Ambedkar National Institute of Technology, 16-20 April, 2019.
- "Innovations in Applied Science and Engineering (NCIASE)", Dr B R Ambedkar National Institute of Technology, 16-20 April, 2019.
- "The Indian Science Congress Association", Lovely Professional University, 3-7 January, 2019.
- "Recent Advances in Experimental and Theoretical Physics (RAETP)", Central University of Jammu, 17-18 April, 2019.
- "46th National Symposium on Acoustics", Aligarh Muslim University, 28-30 October, 2017.
- "Recent Advances in Fundamental and Applied Sciences (RAFAS)" at LPU in 25-26 November, 2016.

Papers presented in conferences

1. **Ashima**, K.C. Juglan, Harsh Kumar; "Acoustical and viscometric studies of ternary liquid mixtures of aqueous sodium methyl p-hydroxybenzoate with polyethylene glycols at 25^0C", *Recent Advances in Fundamental and Applied Sciences,* Lovely Professional University Phagwara, 2019.
2. **Ashima**, K.C. Juglan, Harsh Kumar; "Molecular interactions in ternary system of ethane-1,2-diol with methanol and methyl 4-hydroxybenzoate at 298 K: an acoustic approach", *Innovations in Applied Science and Engineering,* Dr. B R Ambedkar National Institute of Technology Jalandhar, 2019.
3. **Ashima**, K.C. Juglan, Harsh Kumar; "Ultrasonic studies of methylparaben at 298K", *The Indian Science Congress Association,* Lovely Professional University Phagwara, 2019.
4. **Ashima**, K.C. Juglan, Harsh Kumar; "Ultrasonic investigation study of molecular interaction in ternary mixtures of paraben in glycols and methanol", *Recent Advances in Experimental and Theoretical Physics (RAETP),* Central University of Jammu, 2018.
5. **Ashima**, K.C. Juglan, Harsh Kumar; "Thermo-acoustical molecular interaction study in mixtures of glycol, alcohol and paraben", *46th National Symposium on*

acoustics NSA, Aligarh Muslim University, 2017.

Papers communicated

1. **Ashima Thakur**, K. C. Juglan, Harsh Kumar “Ultrasonic and volumetric behaviour of glycols with sodium ethylparaben in aqueous medium from T = (293.15 to 308.15) K at atmospheric pressure”, *Results in Chemistry*.
2. **Ashima Thakur**, K. C. Juglan, Harsh Kumar “Acoustic and viscometric studies of ternary liquid mixtures of aqueous sodium methyl p-hydroxybenzoate with polyethylene glycols at 298K”, *Plant Archieve*.
3. **Ashima Thakur**, K. C. Juglan, Harsh Kumar “Ultrasonic and viscometric investigation of ternary liquid mixtures of glycols in methanol solution of methylparaben at different temperatures”, *Plant Archieve*.