STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME WATER SOLUBLE VITAMINS IN BINARY AQUEOUS MIXTURES OF SUGARS

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By

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DECLARATION

I declare that the thesis entitled "**STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME WATER SOLUBLE VITAMINS IN BINARY AQUEOUS MIXTURES OF SUGARS**" has been prepared by me under the guidance of **Dr. R.C. Thakur**, Professor and Associate Dean, Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Punjab. It is further certified that the results incorporated in this thesis have not been submitted, in part or full, to any other university or institution for the award of any degree or diploma.

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CERTIFICATE

It is hereby certified that thesis entitled, "**STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME WATER SOLUBLE VITAMINS IN BINARY AQUEOUS MIXTURES OF SUGARS**", being submitted by **Mr. Ravi Sharma, in department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Punjab,** for the award degree of **Doctor of Philosophy** in chemistry is a record of bonafied research work carried out by him. **Mr. Ravi Sharma** has worked under my supervision and guidance and has fulfilled all the requirements for the submission of the thesis. It is further certified that the results incorporated in this thesis have not been submitted, in part or full, to any other university or institution for the award of any degree or diploma.

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“I dedicate this thesis to
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And my loving brother (Kamaljit)
for their constant support and unconditional love.”

PREFACE

The study of solute - solvent interactions existing in various solutions is the current area of interest. The knowledge of the interactions is generally obtained from thermodynamic, acoustic and transport properties like partial molar volume, partial molar isentropic compressibility, viscosity and conductance studies. As the partial molar volume, partial molar isentropic compressibility and viscosity methods are the best parameters to derive information regarding solute - solute, solute - solvent as well as solvent - solvent interactions, therefore studies on partial molar volume, partial molar isentropic compressibility and viscosity parameters do a great help in characterizing the structure and properties of the solutions. Volumetric, acoustic and viscometric investigations play an important role in understanding type and extent of the pattern of molecular interactions that exist in different mixtures and their sensitivities of variations in compositions, temperature, pressure and chemical nature.

The transport properties are also fascinating studies in themselves because their industrial and practical values lie in the way they control important reaction rates. These transport properties are very useful for the study of solvation behavior of various biomolecules in different solvent systems. These properties can give information on the effective size of a moving particle in solution.

The present work has been carried out with some water soluble vitamins in aqueous and binary aqueous mixture of sugars. The water soluble vitamins which are used in the present work are vitamin C (L-ascorbic acid), Vitamin B_1 (Thiamine hydrochloride), vitamin B_3 (Nicotinic acid) and vitamin B_6 (Pyridoxine hydrochloride) and on the other hand carbohydrates used are D--Glucose, D-Fructose and D-Lactose respectively. To study the effect of compositions of solvent systems the partial molar volumes and partial molar isentropic compressibilities of above mentioned vitamins have been determined at single temperature i.e. at 303.15 K with the help of density and speed of sound measurements. The effect of temperature on the partial molar volumes and partial molar isentropic compressibilities of above mentioned vitamins was also analysed in lowest compositions of solvent systems at four equidistant temperatures (298.15, 303.15, 308.15 and 313.15)K. The density and speed of sound were obtained by using the Anton Paar DSA 5000 and results have been analysed by Masson's equation. The experimental values of slopes and partial molar volumes of these water soluble vitamins have been interpreted in terms of solute -solute and solute – solvent interactions. The partial molar volumes vary with temperature as a power series of temperature. Hepler's criterion was used to deduce the structure making or breaking capacities of vitamins.

Viscosity measurements were made with the help of the suspended level type viscometer and data has been analyzed using Jones – Dole equation. The obtained parameters i.e. A-coefficient and B-coefficient have been interpreted in terms of solute - solute and solute - solvent interactions. The viscosity data has also been analyzed on the basis of transition state treatment of relative viscosity as proposed by Feakins and from this hypothesis activation parameters are also determined which explains the mechanism of viscous flow.

All the obtained parameters i.e. partial molar volumes, partial molar expansibilities, partial molar isentropic compressibilities, B-coefficient viscosity parameters and the activation parameters of transition state theory for water soluble vitamins in aqueous and binary aqueous mixtures D-Glucose, D-Fructose and D-Lactose prove that except vitamin B_3 (Nicotinic acid) all other vitamins i.e. vitamin C(L-ascorbic acid), Vitamin B_1(Thiamine hydrochloride) and vitamin B_6 (Pyridoxine hydrochloride) behave as structure breakers in different solvent systems.

LIST OF ABBREVATIONS

A, B, D - Viscosity Coefficients of John-Dole's Equation

C - Molar Concentration

$\lambda_1, \lambda_2, \lambda_3$ - Assumed to be average volume per molecule

d - Derivative

J - Joule

K - Kelvin(Temperature in absolute)

M, M_1 - Molecular Weight

$\bar{X}_2$ - Partial molar quantity

$\bar{X}_1$ - Partial molar quantity

m_a - Molal concentration of solute

N - Avagadro's Number (constant)

n_1 - Number of moles of solvent

n_2 - Number of moles of solute

h - Planck's constant

P - Pressure

R - Gas constant

S_V^*, S_K^* - Experimental slopes

°C - Degree Celsius

θ - Temperature in degree celsius

T - Temperature in Kelvin

V - Volume

ϕ_V - Apparent Molar Volume

ϕ_V^0 ,V_2° - Limiting partial molar volume

ϕ_E° - Partial molar expasibility

∂ - Partial derivative

η - Dynamic viscosity of mixture

η_0 - Viscosity of pure component

η_r - Relative viscosity

ρ - Density of mixture

$\rho_\circ$ - Density of pure component

AR - Analytical reagent

N_A - Avogadro’s number

$\Delta\mu_1^{0*}$ - Free energy of activation of solvent

$\Delta\mu_2^{0*}$ - Free energy of activation of solute

ΔS_2^{0*} - Activation entropy

$\Delta G_1^{\neq}$ - Gibbs free energy of activation for viscous flow of solvent

$\Delta G_2^{\neq}$ - Gibbs free energy of activation for viscous flow of solute

$\Delta G_{1,2}^{\neq}$ - Average activation energy

ϕ_{Ks} - Apparent molar adiabatic compressibility

ϕ_{KS}^{0} - Limiting partial molar adiabatic compressibilty

$K_{S,b}^{\circ}$ - Compressibility of bulk water

$K_{\phi,S}^{\circ}(\text{elect})$ - Electrosriction partial molar compressibilty

$K_{\phi,S}^{\circ}(\text{int})$ - Intrinsic partial molar compressibility

β_S - Isothermal compressibility of mixture

Adiabatic compressibility of mixture

$\beta_{S,0}$ - Isothermal compressibility of pure component

Adiabatic compressibility of pure component

α_2 - Thermal expansion coefficient

s - Second

t - Time

S - Siemen

c - Speed of sound

x_i - Mole fraction

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Study of solution chemistry is one of the most interesting area in physical chemistry and it has been expanded in different directions during the last few decades. Due to availability of large range of solvents as reaction media the study has gained even more importance. There are different types of molecular interactions which exist in the solution. Among these solute-solute and solute – solvent interactions are of much importance. The thermodynamics of solute-solvent interactions is the current area of interest to understand the rates and reactions equilibria involved in solutions. The study of thermodynamic and transport properties of the electrolytic and non-electrolytic solutions provide an opportunity for extending the range of properties from which the structure of electrolytes and non-electrolytes can be inferred.

It is found that in mixed solvents, the extent of understanding of solvation behavior is easier than that of studying in pure solvents, because the values of dielectric constant and viscosity of the medium can be varied to a desired value in mixed solvents. The solute-solute and solute-solvent interactions play an important role in the solution chemistry [1-2]. Water has been used widely as a component in mixed solvents, for the study of solute-solvent interactions because of its easy availability and high dielectric constant.

It is found that the mixed binary aqueous solvent systems behave in an unexpected manner as compared to the non-aqueous systems [3-4]. These observations have given a new impetus to the detailed study of binary aqueous mixtures. The information drawn from thermodynamic and -transport studies has been related to structural aspect of the solvent in terms of the solute-solvent, solvent-solvent interactions and structure making/breaking capacity of various electrolytes. All living organisms are made up of different kind of biological molecules or biomolecules. A biomolecule is involved in the metabolic processes and maintenance of living organisms. Biomolecules are produced in the body by biological means and manage the growth of body. These are the organic compounds which actually form root of life, i.e. they develop the living system and lead to their growth and maintenance. The bio-molecules are related to living organisms in a sequence:

Bio-molecules → Organelles → Cells → Tissues → Organs → Living organism

The macromolecules exist in many forms like carbohydrates, lipids, proteins, vitamins, nucleic acids etc. and play important role in the growth of human body.

The thermodynamic properties are of course interesting in themselves, but their ultimate importance lies in what they can tell us about chemical equilibrium. Likewise, the transport properties are fascinating studies and their industrial and practical values lie in the way they control important reaction rates, including the most important reaction of all the human thought processes.

During the past few decades, the knowledge of solvation behavior has increased immensely. Different types of interactions exist in solutions, but in all the streams of chemistry the solute-solute and solute-solvent interactions are of great concern. From these interactions, the behavior of the solute and solvent can be interpreted easily and also help us to understand whether the solute makes or breaks the structure of solvent. If we look around, we are surrounded by biomolecules and their solution systems. These solution systems play a major role in environment and other systems. Properties of these solutions like mobility, reactivity, state which further depend on certain other properties like thermodynamic and transport properties of these solutions[5-6]. The nature of solute-solute and solute-solvent interactions has been deduced mainly from; thermodynamic, acoustic and transport properties like partial molar volume, free energy of transfer, adiabatic expansibility, adiabatic compressibility and viscosity.

Thermodynamic and acoustic properties play an important role in the design and operation of chemical plants, metal refining and in high density batteries. Various industries require accurate thermodynamic data for different substances covering a wide range of temperature, pressure and composition. Most processes in the chemical industries demand for the data on vapour-liquid, liquid-liquid, solid-liquid equilibria and different transport properties. Many pharmaceutical industries require the thermodynamic data for formulations of various kinds of drugs and syrups.

1.2 THERMODYNAMICS PROPERTIES

1.2.1 Apparent molar volume: The Apparent molar volume (ϕ_v) of a solute may be visualised by considering a large reservoir of solution so that the addition of one mole of solute will not alter the concentration of the solution. The change in volume of the solution on the addition of one mole of the solute to large reservoir of volume V is the partial molar volume of the solute at the indicated concentration at constant temperature, pressure and the moles of other constituents, if present.

Mathematically, the partial molar volume of a solute is represented as follows

$$V_1 = \phi_v^0 = \left(\frac{dV}{dn_1}\right)_{T,P,n_i} \qquad (1.1)$$

Here, n_i refers the number of moles of all other constituents except ith constituents. For a solution composed of two constituents equation (1.1) becomes

$$V_2 = \phi_v^0 = \left(\frac{dV}{dn_2}\right)_{T,P,n_i} \qquad (1.2)$$

In equation (1.2 and 1.3), subscript 2 denote solute and 1 denote solvent. The total volume in terms of partial contributions can be expressed as [7]

$$V_1 = n_1V_1 + n_2V_2(\text{ at constant T and P}) \qquad (1.3)$$

where, V= partial molar volume of solvent

n_1=number of moles of constituent 1

n_2= number of moles of constituent 2

However, in this form it is practically impossible to determine partial molar volumes. Generally, the partial molar volume is determined from the measurement of apparent molar volumes $\phi_v$which in turn may be evaluated from density measurements and is defined by the relation

$$\phi_v = \frac{V - n_1 V_1^0}{n_2} \quad \text{(at constant T and P)} \qquad (1.4)$$

$$V = n_2 \phi_v + n_1 V_1^0 \qquad (1.5)$$

Where n_1 and n_2 are the number of moles of solvent and solute respectively, V_1^0 is the molar volume of pure solvent and V is the total volume of the solution at given temperature and pressure.

By differentiating equation (1.5) with respect to n_2 keeping T, P and n_1 constant, we obtain

$$\left(\frac{dV}{dn_2}\right)_{T,P,n_i} = V_2 = \phi_v + n_2\left(\frac{dV}{dn_2}\right)_{T,P,n_i} \qquad (1.6)$$

Thus $V_2 = (V_{\Phi}^0)$ and ϕ_v are related to each other by equation (1.6)

From equations (1.3), (1.5) and (1.6), we obtain

$$V_1 = (V - n_2V_2)/n_1 = 1/n_1[n_1V_1^0 - n_2\left(\frac{\delta V_\Phi}{\delta n_2}\right)_{T,P,n_1}] \qquad (1.7)$$

In terms experimentally measured values of densities i.e. ρ and the molecular weights of solvent and solute i.e. M_1 and M_2, the apparent molar volume is given by:

$$\phi_v = \frac{1}{n_2}[(n_1M_1 + n_2M_2)/\rho - V_1^0] \qquad (1.8)$$

When the concentration is in moles per unit volume, then n_2=m i.e. the molality of the solution and n_1 is equal to the number of moles of water in 1000g, so that equation (1.8) becomes

$$\phi_v = \frac{M_2}{\rho} + [1000(\rho_0 - \rho)/m\rho\rho_0] \qquad (1.9)$$

Where ρ and ρ_0 are the densities of pure solvent, m is the solute molality and M is the solute molar mass. The factor 1000 appears when densities are given in gcm^{-3}which is generally the case, instead of kg m^{-3}.

When molar concentration is used, then $m\rho = C$ i.e. the molarity of the solution, then equation (1.9) becomes

Or
$$\phi_v = \frac{M_2}{\rho} + [1000(\rho_0 - \rho)/C\rho_0] \qquad (1.10)$$

1.2.2. Apparent molar volume at infinite dilution

The functional relation between apparent molar volume and molality reflects solute-solute and solute –solvent interactions. Thus, it is not surprising when experiments show distinct differences between ionic and non-ionic solutes experiment. Considering non-ionic solutes, literature has shown that a linear functional relationship between apparent molar volume and molality holds to quite high concentrations given by Masson in the form of following relation:

$$\phi_v = \phi_v^0 + S_v^*m \qquad (1.11)$$

where, ϕ_v^0 is the partial molar volume and S_v^* is the experimental slope. The slope S_v^* of equation (1.11) is usually very small in case of non electrolytes, the plot of ϕ_v against m are linear and ϕ_v^0 values are obtained by least squares fitting of the data to equation (1.11).

In case of ionic solutes , apparent molar volumes were fitted to equation

$$\phi_v = \phi_v^0 + S_v^* C^{1/2} \quad (1.12)$$

Like the S_v^* coefficient for non- ionic solutes, S_v^* is an empirical slope and it varies with the charge of the ions and type of the ions.

Based on the applications of Debye-Huckel limiting law, Redlich and Rosenfeld[8]predicted that a constant limiting slope should be obtained for a given ionic charge. On the basis, Redlich and Meyer[8]suggested the following extrapolation function

$$\phi_v = \phi_v^0 + S_v^* C^{1/2} + b_v C \quad (1.13)$$

where, S_v^* is the theoretical limiting slope calculated from Debye –Huckel limiting law and b_v is an empirical constant determined from the experimental results.

1.2.3 Partial molar isentropic compression

The partial molar isentropic compression is given by the following relation:

$$\phi_{KS}^0 = \left(\frac{\delta\phi_v^0}{\delta P}\right)_T \quad (1.14)$$

where, ϕ_v^0 is the partial molar volume. However, it is not easy to measure the partial molar volume as a function of pressure, therefore it may be easier to calculate apparent molar isentropic compression according to the equation.

$$\phi_{KS} = -\left(\frac{\delta\phi_v}{\delta P}\right)_T = K_s\phi_v + \frac{1000(K_s - K_s^0)}{m\rho_0} \quad (1.15)$$

where, $\phi_v$is the apparent molar volume, ρ_0 is the density of pure solvent and K_s, K_s^0 are the isentropic compressibilites of the solution and the pure solvent, respectively and is generally represented by the equation

$$K = -1/V\left(\frac{\delta V}{\delta P}\right)_T \quad (1.16)$$

In equation (1.15), the factor 1000 appears when densities and compressibilities are given in gcm^{-3} instead of $kg\ m^{-3}$.

The speeds of sound is related to the isentropic compressibility also called as coefficient of adiabatic compressibility K_s, according to the Laplace equation

$$K_s = \frac{1}{U^2\rho} \tag{1.17}$$

where U is the speed of the sound and ρ is the density of the solution. On the basis, it is possible to obtain apparent molar adiabatic compressibility according to the equation

$$\phi_{Ks} = \frac{MK_s}{\rho} + \frac{1000(K_s\rho_0 - K_s^0\ \rho)}{m\rho\rho_0} \tag{1.18}$$

where, m is the molality of the solution, M is the relative molar mass of the solute and $\rho_0, \rho,\ K_s^0$ and K_s are the densities and coefficients of adiabatic compressibilities of pure solvent and solution, respectively.

The relationship between apparent molar adiabatic compressibility and concentration depends upon the nature of the solute. If it is a non-electrolyte a linear function has proved to be adequate

$$\phi_{KS} = \phi_{KS}^0 + S_K^*\ m \tag{1.19}$$

where, ϕ_{KS} is the partial molar adiabatic compressibility at infinite dilution and S_K^* is an adjustable parameter.

Electrolyte behave differently and by differentiation the Redlich –Meyer[9] equation with respect to pressure, the following expression is obtained

$$\phi_{KS} = \phi_{KS}^0 + S_K^* C^{1/2} + S_K C \tag{1.20}$$

Here, $S_K^*$is the theoretical limiting slope and is determined by Debye-Huckel limiting law.

1.3 TRANSPORT PROPERTIES

The movement of solvent molecules in solutions is reflected in transport properties such as relaxation of dielectric polarization, conductance, viscosity and self-diffusion etc. In general the rates of movements of solvent molecules decrease if there is an increase in the structure due to increase in rigidity and vice-versa.

The transport phenomenon arises because any system in non-equilibrium state will always try to approach equilibrium if the intensive state variables are constant at all times and have the same magnitude at all positions in a system. At equilibrium the gradients of the parameters are absent, spontaneous processes do not occur and there is no net exchange of matter between the system and its surrounding. If the system is in a state in which these conditions are not satisfied then the system is said to be in the non - equilibrium state.

Suppose an equilibrium is disturbed to a non-equilibrium state by some external or internal disturbance, one of the state parameter becomes a function of position. When this disturbance is removed, an irreversible decay process occurs simultaneously and the system advances through a series of non-equilibrium states until equilibrium is reached. This process is a transport process, because some quantity is transferred throughout the system as the system tries to make all parameters independent of position. Thus any process in which some physical quantity such as mass, energy, electrical charge etc. is transported form one region of a system to another is known as transport process. The amount of physical quantity transported per unit time is called flux and is proportional to the gradient of some other physical quantities like temperature, pressure, concentration and electrical potential. The agency causing the flux is known as force.

Mathematically a transport process can be represented as:

$$J = LX \tag{1.21}$$

here, J is the flux, X is the force and L is the proportionality constant and is called, "transport coefficient" or "phenomenological coefficient" , which is a measure of the rate at which the system approaches equilibrium state.

Many of the transport processes in living and in non-living systems are similar since they obey all the laws of physics. Living systems are the open systems constantly exchanging matter and energy with the environment. This exchange is not random, rather it is highly selective transport of substance and energy. In many biological systems of chemical reactions and flows, there is a resultant flow of certain substances, even against a gradient such a transport flow of substance is called active transport.

It is a phenomenological representation of several familiar laws involving systems which are in non-equilibrium because of the presence of gradient of temperature, density or macroscopic velocity. They are associated with most familiar examples of transport processes such as heat conduction, diffusion and viscosity etc. For these examples the empirical laws are defined as follows:

(i) Fourier's Law of Heat Conduction. According to this law

$$q = -\lambda \, \mathrm{grad} \, T \tag{1.22}$$

here, q is a heat flux resulting from the transfer of heat caused by molecular interactions (pure heat flow), λ is a coefficient of thermal conductivity and grad T is a gradient of temperature.

(ii) Fick's Law Diffusion: According to this law

$$J_i = -D \, \mathrm{grad} \; C_i \tag{1.23}$$

Where J_i flux of chemical species i, C_i is concentration of i and D is the diffusion coefficient and is a characteristic of fluid only.

(iii) Newton's Law of Viscosity: This can be represented as follows:

$$\pi_{yx} = \eta\pi.\frac{\partial U_x}{\partial U_y} \tag{1.24}$$

Here, π_{yx} is term which represents a momentum flux in the y direction caused by a fluid flowing in x direction with velocity component U_x and η is a coefficient of shear viscosity.

1.3.1 Viscosity studies

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness". For example, honey has a much higher viscosity than water. Viscosity is a property arising from collisions between neighboring particles in a fluid that are moving at different velocities. When the fluid is forced through a tube, the particles which compose the fluid generally move more quickly near the tube's axis and more slowly near its walls: therefore some stress, (such as a pressure difference between the two ends of the tube), is needed to overcome the friction between particle layers to keep the fluid moving. For the same velocity pattern, the stress required is proportional to the fluid's viscosity. Relative viscosity is the ratio of the viscosity of a solution (η) to the viscosity of the solvent (η_0) used and is represented by the following equation:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t\,\rho}{t_0\rho_0} \qquad (1.25)$$

Here, η, η_0, t and t_0 are viscosities and the efflux times of solution and solvent respectively whereas ρ and ρ_0 are densities of solution and solvent.

1.3.2 Jones – Dole equation

The pioneer work of poiseuille[10], Jones and Dole [11] reviewed the effect of the addition of salts on the viscosity of water. Arrhenius[12] gave the following relationship between the relative viscosity and molar concentration C for the moderately dilute solutions

$$\eta_{rel} = A^C \qquad (1.26)$$

where, A is the constant for the given salt and temperature.

Accurate work on dilute solutions showed that viscosity concentration curves instead of becoming straight at the dilute end, registered negative curvature and thus showed the invalidity of equation (1.26). Mainly, salts may be divided into two categories depending upon whether they increase or decrease the viscosity of water and relative viscosity and molar concentration which is given by the following equation:

$$\eta = 1 + AC + B(1 - i) + C_aC^2 \qquad (1.27)$$

where, i is the degree of dissociation which is dependent on concentration

Further Schneider[13] and Applebey[14]made measurements with many more salts showed that the negative curvature was more marked at low concentration and low temperatures. At low concentrations a special behavior concluded by Jones and Dole that there must be some effects which are having fairly greater importance and for dilute solvents where viscosity η is plotted against C. This effect will always tend to increase but the overall effect of the addition of the salt can increase or decrease the viscosity. The interionic forces resulted in the increase in viscosity (η). From the results of Debye and Huckel, who previously shown that the effect of interionic forces in resisting the motion of ions is proportional to the square root of concentration in very dilute solutions, Jones and Dole gave the equation

$$\eta_r = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \tag{1.28}$$

$\eta_r$is the relative viscosity , whereas η and η_0 are viscosities of solution and solvent respectively. A is known as theoretical accessible limiting slope of the Falkenhagen and Vernon theory and is also called Falkenhagen coefficient and explains the solute-solute interactions[15]. In above equation B is an empirical parameter and is dependent on solute-solvent interactions C(mol.L^{-1}) i.e. concentration in moles per unit volume (molarity). With density values the molality 'm' was converted into molarity 'C'. The values of A and B can be obtained by fitting the data with the method of least squares to equations (1.28).

The extended form of Jones –Dole equation is represented below as

$$\eta_r = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC + DC^2 \tag{1.29}$$

It is expected that A will have different values for strong electrolytes and non-electrolytes. For all strong electrolytes A will have negative value and for non-electrolytes it will become zero. The value of B should be positive for those salts, which increases the relative viscosity (for example, cesium nitrate and potassium iodide) and negative for those, which decrease the relative viscosity. Also, for most salts, D or high coefficients can be omitted although they are necessary at high concentration. So the equation (1.29) reduces to

$$\eta_r = \frac{\eta}{\eta_0} = 1 + BC \tag{1.30}$$

1.3.3 Transition state treatment of relative viscosity

Nightingale and Benck[16] explained the theory that could be usefully applied to the viscosities of electrolyte solutions and have pointed out applicability of transition state theory to ionic conductance. Glasstone, Laidler and Eyring[17] identified an equation for the viscosity of a pure liquid.

$$\eta_0 = (h\lambda_1/\lambda_2\lambda_3\lambda^2)\exp(\Delta G_1^*/RT) \tag{1.31}$$

In exponential term, ΔG_1^* is the Gibbs free energy of activation for viscous flow is root of the transition state treatment. In Eyring's model, K is taken as unity i.e. the characteristic transmission coefficient of the theory and tunneling is neglected. Here, λ_1 is the distance apart of adjacent layers of molecules, which are sliding over each other, within such layer the mean separations of molecules perpendicular and parallel are λ_2 and λ_3 respectively to the direction of flow. When the molecule shifts from one equilibrium position to the next in the direction of flow the distance is transversed. If the approximation $\lambda = \lambda_1$ is made and if $\lambda_1\lambda_2\lambda_3$is let to be average volume per molecule, then equation (1.31) changes to equation

$$\eta_0 = (hN_A/V_1)\exp(\Delta G_1^*/RT) \tag{1.32}$$

where, V_1 is the molar volume of the liquid.

According to Eyring treatment, the viscosity η of a single solute in a pure solvent is given by the equation

$$\eta = (hN_A/V_{1,2})\exp(\Delta G_{1,2}^*/RT) \tag{1.33}$$

Here, $V_{1,2}$ is represented as the average molal volume of the solution and $\Delta G_{1,2}^*$ is term used to define common or average activation energy for the components and can be represented as

$$\Delta G_{1,2}^* = x_1\Delta\mu_1^* + x_2\Delta\mu_2^* \tag{1.34}$$

For relative viscosity, we have equation

$$\eta_r = \eta/\eta_0 = (V/V_{1,2})\exp[(\Delta G_{1,2}^* - \Delta G_1^*/RT)] \tag{1.35}$$

which can be represented in different ways.

In Jones –Dole equation (1.28), B tells about solute -solvent interaction. These interactions exists at infinite dilution; this tends to be concealed by the fact that as $c \longrightarrow 0$ and BC disappears faster than $AC^{1/2}$. Keeping in mind that terms in higher power of C must sometimes to be added to the right hand side of equation (1.28) to fit the observed data and it is helpful to think of B in the form of equation.

$$BC = \ln(V/V_{1,2})_0 + (\Delta G^*_{1,2} - \Delta G^*_1)_0/RT \qquad (1.36)$$

Under these conditions

$$V_{1,2} = x_1 V^0_1 + x_2 V^0_2 = V^0_1 - x_2(V^0_1 - V^0_2) \qquad (1.37)$$

Where V^0_1 and V^0_2 the partial molar volumes as C → 0 and $V^0_1 = V_1 = M_1/\rho_1$ .M_1 is the molecular weight of the solvent and ρ is its density

As,

$$x_2 \rightarrow 0 \,, x_2 = M_1 C / 1000\rho_1 \qquad (1.38)$$

$$\ln(V/V_{1,2})_0 = x_2(V^0_1 - V^0_2)/ V^0_1 = C\,(V^0_1 - V^0_2)\,/1000$$

$$\Delta G^*_{1,2} = x_2 \Delta\mu^*_2 + (1 - x_2)\Delta\mu^*_1 \qquad (1.39)$$

Where $\Delta\mu^*_1 = \Delta G^*_1$, the free energy of activation per mole of the pure solvent and $\Delta\mu^*_2$ is the contribution per mole of the solute to the free energy of activation for viscous flow of the solution.

Therefore,

$$\left(\Delta G^*_{1,2} - \Delta G^*_1\right) = x_2(\Delta\mu^{0*}_2 \text{-} \Delta\mu^{0*}_1) \qquad (1.40)$$

$$B = (V^0_1 - V^0_2)\,/1000) + M_1/1000\rho_1[(\Delta\mu^{0*}_2 - \Delta\mu^{0*}_1)/ RT] \qquad (1.41)$$

It will be observed that $\Delta\mu^{0*}_1$and $\Delta\mu^{0*}_2$ doesn't depend on the concentration scale chosen for the standard states. Equation (1.41) may be written in various ways.

We Know that $M_1/\rho_1 = V^0_1$, So equation (1.41) becomes

$$B = (V^0_1 - V^0_2)\,/1000 + V^0_1/1000[(\Delta\mu^{0*}_2 - \Delta\mu^{0*}_1)/ RT] \qquad (1.42)$$

For the densities of many electrolytic solutions, Root gave a equation[18]

$$\rho_{1,2}/\rho_1 = 1 + aC + bC^{3/2} \qquad (1.43)$$

The coefficient b is normally small, and at low concentrations

$$\rho_{1,2}/\rho_1 = 1 + a\,C \qquad (1.44)$$

It is shown that

$$a = (M_2 - \rho_1 V_2^0)/\ 1000\ \rho_1 \tag{1.45}$$

Hence, $$(V_1^0 - V_2^0)\ /1000 = (M_1 - M_2)/1000\rho_1 + a \tag{1.46}$$

Therefore, using equation (1.42), equation (1.46) becomes

$$B = (M_1 - M_2)/1000\rho_1 + a + M_1/1000\rho_1[(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})/\ RT] \tag{1.47}$$

The values $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ is the change in activation energy per mole on substituting one mole of solvent by one mole of solute in an infinitely dilute solution

The ionic activation energy, $\Delta\mu_1^{0*}$ varies numerically from the parameters so named by Nightingale and Benck[16] basically because of the different concentration scales used, but has the same qualitative importance. From the exact values of partial molar volumes, the calculation of $\Delta\mu_2^{0*}$ can be done by using equation (1.47) when the B-values are known.

If B is known at various temperatures, we can calculate the ionic activation entropy by using equation

$$d(\Delta\mu_2^{0*})/dT = -\ \Delta S_2^{0*} \tag{1.48}$$

And ionic activation enthalpy can be calculated from equation

$$\Delta H_2^{0*} = \Delta\mu_2^{0*} + T\,\Delta S_2^{0*} \tag{1.49}$$

1.4. LITERATURE REVIEW

Behavior of biomolecules in the solutions is revealed by various thermodynamic and transport properties like partial molar volumes, partial molar expansibilities, partial molar compressibilities, viscosities, relative viscosities etc. These studies help in predicting the solute-solute and solute- solvent interactions. During the last three decades a lot of data have been reported for various electrolytes, non-electrolytes and biomolecules in aqueous and binary aqueous mixtures and the same has been summarized as below:

Agnita Kundu and Nand Kishore[19] used the micro differential scanning calorimetry in the molality range to determine the apparent molar heat capacities, the partial molar volume, partial molar heat capacity and specific heat capacities of aqueous nicotinamide in aqueous solution. The results have been provided the thermodynamic parameters as a function of temperature. The result has been analyzed in the form of structure making and breaking nature.

Zhao Changwei and MA Peisheng[20] studied the solute-solvent interactions in ternary system of water-glucose-L-ascorbic acid and water-sucrose-L-ascorbic acid. They determined the densities and viscosities and interpreted the partial molar volume and B-coefficient values at different temperatures (293.5K -313.15 K) and the result has been analyzed in the form of structure making and breaking nature.

Changwei Zhao, Peisheng Ma and Jiding Li[21] determined densities and viscosities of an amino acid arginine in binary aqueous mixtures of ascorbic acid, glucose and sucrose at 298.15K. The apparent molar volume, partial molar volume and Jones Dole coefficient (A and B) values of arginine are determined using density and viscosity data. Finally they predicted that due to presence of H-bonding these sugars and vitamin C act as a water structure maker.

P.Ramasamia and R. Kakkar[22]obtained the molecular behavior of dl-aminobutanoic acid, β-alanine, 4-aminobutanoic acid, dl-norvaline, 5-aminopentanoic acid, 6-aminohexanoic acid and glycylglycine in water and sodium sulphate + water at different temperatures by determining the partial molar volume and partial molar adiabatic compressibilities at infinite dilution. Kirkwood model was used for interpretation of the results. The results obtained from the study reveals that the sodium sulphate behave as water-structure maker.

Parmar*et.al*[23] determined the relative viscosities of manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate and zinc sulphate and magnesium sulphate in aqueous and in different compositions of binary aqueous mixtures of ethylene glycol mixtures at 303.15 and temperature variation was also analysed in case of only 5% (w/w) EG + water. The Jones-Dole equations have been used for analyzing the obtained parameters and results were interpreted in terms of different interactions such as ion-ion and ion-solvent interactions.

Saadoon A.Isa, Ahlam M. Farhan and Hala H Hummadi[24] studied the solute –solvent interactions of vitamin B_1 and B_3 in water at different temperatures. They determined the partial molar volumes and Vander Waal volumes and viscosities of the above vitamins in aqueous medium. The B-coefficient values were found to be negative and proved the structure breaking nature of vitamin B_1 and B_3.

M.L. Parmar and R.C. Thakur[25] obtained the partial molar volumes of some divalent transition metal sulphates and magnesium sulphate in water and different binary aqueous mixtures of ethylene glycol using the Ward and Millero method. The obtained data has been analysed using the Masson equation and interpreted in terms of molecular interactions such as ion–ion and ion–solvent interactions. It is concluded that the magnesium sulphate and all the divalent transition metal sulphates act as structure maker in both water as well as in ethylene glycol+ water mixtures.

Guler Ayranci, Melike Sahin, Erol Ayranci[26] obtained density data and sound velocity data for L-ascorbic acid and thiamine hydrochloride in aqueous and in binary aqueous solution of NaCl at different temperatures ranging from 10.15 ^{0}C to 40.15 ^{0}C. The parameters obtained explain about the apparent molar volumes and apparent molar isentropic compressiblities. The apparent molar isentropic compressiblities of ascorbic acid were positive in H_2O and NaCl solutions at low molalities where as that of thiamine hydrochloride found to be negative.

A.Mohmmed, F.Karimaand Fadhil Ali[27] studied the densities and viscosities of vitamin B-complex in water at different range of temperatures. These values were used to determine the partial molar volume and viscosity B- coefficients using Masson's and Jones-Dole equation in terms of concentration and temperature effects and concluded the structure making nature of vitamin B-complex.

B.Sinha *et al.*[28] determined the viscosity of B-coefficients and apparent molar volumes of nicotinamide in aqueous solution of tetra butyl ammonium bromide at different temperatures over the range from 25^0 to 45^0 C. The structure making / structure breaking nature of a nicotinamide have been discussed in terms of the sign of $[(\partial^2\phi_v^0/\partial T^2)_P]$. The results proved the structure breaking nature of nicotinamide in aqueous solution of tetra butyl ammonium bromide.

Anwar Ali, Rajan Patel, Shahjahan Khan[29] obtained viscosities, densities and refractive indices of glycine, diglycine and triglycine in 0.01 m aqueous tartrazine solution at different temperature from 288.15 K to 313.15 K. The density data was used to evaluate transfer volumes, apparent molar volumes and partial molar volumes by using Masson's equation. The viscosity data was also analyzed by using the Jones-Dole equation to determine the viscosity A and B-coefficients and activation parameters. The activation parameters highlight the mechanism of viscous flow and the results obtained were interpreted in terms of ion-ion and ion-solvent interactions and the effect of increasing hydrophobicity on these interactions was also investigated in presence of the dye tartrazine as we move from glycine to triglycine.

B.Sinha, P.K. Roy and M.N. Roy[30] determined the apparent molar volumes and viscosity B-coefficients for glycine in binary aqueous solution of silver sulphate at different temperatures ranging from (298.15 to 318.15) K. The standard partial molar volume and experimental slopes have also been analyzed by using Masson equation and interpreted in terms of solute-solute and solute-solvent interactions. The viscosity data was analyzed by using the Jones-Dole equation, in which the derived parameters A and B were interpreted in terms of solute-solute and solute-solvent interactions. The standard volumes of transfer and viscosity B-coefficients of transfer of glycine from water to aqueous silver sulphate were also determined. Finally, the behaviour of glycine in terms of structure making or breaking has been discussed.

Anil G. Shankarwar, Vinod. A. Shelke, Sunil. G. Shankarwar and Balasaheb. R. Arbad[31] determined thermodynamic and transport properties like apparent molar volume, partial molar volume and B-coefficient of glycine at different temperatures in an aqueous medium and reported the structure- breaking capacity of glycine in water by using the Hepler's criterion.

K. Rajagopal, S. Edwin Gladson[32] determined the densities and speed of sound for glycine, l-alanine, l-valine, and l-leucine in binary aqueous solutions of sodium fluoride at temperatures (308.15, 313.15, and 318.15) K. Apparent molar volumes, partial molar volumes, transfer volumes, hydration number, adiabatic compressibility and relative change in compressibility, partial molar compressibility, transfer compressibility are evaluated using density data and ultrasonic speed data. The analysis shows that the ion–ion interactions dominate over ion–hydrophobic interactions for entire concentration range of NaF. Finally it is found that sodium fluoride has a strong dehydration effect on amino acids.

Patil *et al.*[33] studied the binary mixtures of Ethanol, Propan-2-ol and 2-Methyl Propan-2-ol at 25.15 and 35.15 ^{0}C and determined their density and partial molar volume. It is observed that the excess molar volume increases with increase in chain length of alkanols. Also, the dissociation of alkanol is found to decrease due to breaking of Hydrogen bonds. This also shows about the strong interactions between -OH and $–NH_2$ groups.

Parvinder Khanuja[34] explained the structure making and structure breaking nature of amino acids in binary aqueous solution of sucrose and reduced solute-solvent and solute-solute interactions by using the transfer molar volume, partial molar volume expansibility, free energy of activation, viscosity B-coefficient. It has been concluded that glycine act as structure promoter in aqueous solution of sucrose. The behavior of alanine in aqueous solution of sucrose has been found as structure breaker of water at higher concentration and region of temperature whereas structure maker of water structure at lower concentration and at higher region of temperature. This shows that L-alanine act as both as structure maker and structure breaker.

Shashi Kant and Kamini Sharma[35] determined the density, viscosity and conductance of sodium chloride in different compositions of lactose at different temperatures. The interactions such as solute-solvent and solvent-solvent for sodium chloride in different compositions of lactose solutions have been inferred from partial molar volume and B- coefficient of Jones Dole equation. It has been concluded that sodium chloride acts as a structure-breaker in different compositions of lactose.

Parvinder *et.al*[36] found that selected carbohydrates act as structure promoter in aqueous solution. Apparent molar volume, partial molar volume and viscosity B-coefficients were determined by using the viscosities and densities data at different temperatures (200^0 to 400^0) C of the carbohydrates. The above data conclude that the hydration of carbohydrate depends on hydroxyl group and potential of hydrogen bonding and also depends on their relative orientation. The hydrogen bond network of water is promoted and enhanced by non-polar solute which is present in water.

Taghried A. Salman Khatab and A. Abd[37] determined the partial molar volumes and viscosity of B-coefficients of nicotinic acid in binary aqueous solution of NaCl by using density and viscosity data at various temperatures from 293.15 to 308.15 K. The density values were analysed by using Masson equation and the viscosity data has been analyzed by using Jones-Dole equation and all the obtained parameters were interpreted in terms of solute-solvent and solute- solute interactions. The result has been concluded as structure making nature of nicotinic acid.

Arti Gupta, RoliSrivastava and Archana Pandey[38] determined solute (saccharide)-co-solute (ascorbic acid) interactions by using Jones Dole equations, viscosity coefficients (A and B) acoustical parameters like (ϕ_V), (ϕ_K), (β), hydration number (nH) by using the density, viscosity, ultrasonic velocity and refractive index data of aqueous solutions of galactose, glucose in aqueous ascorbic acid at temperatures from 303.15 K to 323.15 K.

Abhijit Sarkar and Biswijit Sinha[39] investigated that vitamin B-complex behaves as structure maker and its structure making ability decreases to some extent with increase in concentrations of nicotinic acid in the studied solutions. They also concluded that the interactions like ion–hydrophilic and hydrophilic–hydrophilic are greater in aqueous solutions of nicotinic acid .They also proved that Bu_4NHSO_4 in the aqueous solution of nicotinic acid act as structure maker.

Sudhakar S. Dhondge, Dinesh W. Deshmukh and Lalitmohan J. Paliwal[40] studied the molecular interactions of vitamins (thiamine hydrochloride, pyridoxine hydrochloride) in aqueous medium using the molar volumes and hydration numbers. The relative viscosity values and densities were used to determine the viscosity coefficients and partial molar volumes using Jones Dole equation and Masson's equations. B-coefficient values for both systems were found to increase with temperature up to 288.15 K and then decreases with the increase in temperature so it was found that the dB/dT is positive at lower temperatures which explain the structure breaking behaviour and negative at higher temperature which explains structure making behaviour.

U.D Chapke, B.P.Meshram and P.S. Agrawal[41] studied the structure-making and structure-breaking effects of drug molecules (nicotinamide, metformin hydrochloride, isoniazid, frusemide, ambroxol hydrochloride, atenolol, trimethoprim, albendazole and methyldopa) in aqueous 70% DMF using adiabatic compressibility, relative association and acoustic impedance which was determined from ultrasonic velocity, density and viscosity data at 300.15K. The results were analyzed in terms of molecular interactions and structure breaking capacity.

Ruchi Tyagi[42] determined the density (ρ), viscosity (η) and molar volume in aqueous and mixed aqueous solutions of concentrations ranging from 0.025 to 0.402 for serine and 0.00006 to 0.00201 for cysteine at 301.15 K. These experimental values have been performed to evaluate apparent molar volume, limiting apparent molar volume, viscosity coefficients A and B of Jones-Dole equation, relative viscosity, and excess Gibbs free energy of activation. These parameters are used to find solute-solvent and solute-solute interactions in the given mixed solution. From the magnitude of partial molar volume and the values of B-coefficient it can be concluded that serine possesses greater molecular association than cysteine in aqueous DTE solution. The PMV values suggested the increase in hydrophilic and hydrophobic group interaction with increase of the bulk of side chain length of amino acid.

ArunB.Nikumbh, Ganesh K.Kulkarni and RavindraC.Bhujba[43] studied the drug aspirin in water at various temperature (25.15, 30.15, 35.15, 40.15 and 45.15)^{0}C respectively by using viscometer and bi-capillary pycknometer. The flow and molecular interaction parameters of aspirin in aqueous solutions has been explained by the density and viscosity data. The Jones-Dole equation and Masson equation have been verified at various temperatures. This drug interacts with different molecules and biological membranes which are present in the biological system.

Dudhe V.G. *et al.*[44] studied the interactions of aqueous ascorbic acid at 293.15 K and proved the structure breaking nature of ascorbic acid in water and found that free volume, free length and adiabatic compressibility decreases with rise in concentration. This concludes the presence of strong solute-solvent interaction in a system.

Dhiraj Brahman and Biswajit Sinha[45] determined the viscosity B-coefficient and solvation number that is denoted by Sn and discussed solute - solvent and solute-co-solute interactions. B-coefficients for $CuL(NO_3)_2$ in the tertiary solutions show the presence of strong interactions which is solute - solvent interactions; these interactions increase with higher concentration of vitamin B_1 but decrease with higher experimental temperatures. From the results, it is found that vitamin B_1 acts as a structure maker.

M.N. Roy and Palash Chakraborti[46] studied the interactions of nicotinic acid, ascorbic acid and folic acid in aqueous cysteine solutions at 25^0 C using the apparent molar volume, B-coefficient value, molal refraction and adiabatic compressibility which were determined from the density, viscosity, refractive index and sound velocity data. Masson equation is used to interpret the solute-solvent interactions and solute-solute interactions using the limiting apparent molar volumes and experimental slopes. The data supported that the solute –solvent interactions are much greater than the solute-solute interactions.

K. Rajagopal and S. Edwin Gladson[47] determined the ultrasonic sound velocities and density of amino acids such as (glycine, l-valine, l-alanine and l-leucine) in binary aqueous mixtures of NaF at different temperatures ranging from 308.15K to 318.15 K. The apparent molar volumes, adiabatic compressibility, relative change in compressibility, transfer compressibility, partial molar compressibility, apparent molar compressibility and hydration number are determined from density and ultrasonic speed data. These values are analyzed in terms of solute-solute interactions and solute-solvent interactions, which concludes that sodium fluoride shows strong dehydration effect on amino acids as the solute-solute interactions are stronger than ion–hydrophobic interactions.

Vickramjeet Singh, Gyanendra Sharma and Ramesh L. Gardas[48] studied ultrasonic and volumetric properties of the ascorbic acid(AA) in aqueous solutions and in the presence of protic ionic liquid i.e. 1,8-diazabicyclo[5.4.0] undec-7-en-8-ium trifluoroacetate. Apparent molar volume, isentropic compressibility and infinite dilution partial molar volume are determined by using the density data. The increase in concentration of [DBU][TFA] (only after 0.20 $\text{mol}\cdot\text{kg}^{-1}$) which is due to decrease in volume was found to be positive at all temperatures. The negative values obtained for AA in aqueous solution proved that AA behaves as structure breaker.

M.N. Roy, Milan Chandra Roy, Siti Barman, Pran Kumar Roy and Kamalesh Roy[49] studied the solute-solvent interactions of nicotinic acid and ascorbic acid in aqueous solution of 1-ethyl pyridinium tetrafluoroborate at different temperatures. The Lorentz-Lorenz equation has been employed to determine the molar refraction. The temperature dependence behavior of partial molar quantities has been determined for the vitamins. The role of the solvent (aqueous ionic liquid mixture), and the extent of solute-solute and solute-solvent interactions to the solution complexes have also been discussed through the obtained parameters.

Xiaohui Xu[50] determined the densities and viscosities of ternary solutions (sugar alcohols + vitamin B_6 + water) at different temperature (293.15, 303.15, 313.15, 323.15) K. The Guimaraes equation was used to determine the limiting partial molar volumes of transfer and the apparent molar volumes. The viscosities obtained were analyzed using Jones−Dole equation to obtain the viscosity B-coefficients. The partial molar volume values increase with rising temperature as well as the molality of vitamin B6 in the solvent mixture. Partial molar volume of four sugar alcohols increase in the order erythritol< xylitol < sorbitol <maltitol. The limiting partial molar volumes of transfer become larger with the increase of the molality of vitamin B_6, while it decreases with the increase of temperature.

Milan Chandra Roy and Mahendra Nath Roy[51] investigated the solute–solvent interactions of phenylalanine, histidine and aqueous solution of nicotinic acid. They also determined the apparent molar volume, viscosity B-coefficient and molal refraction (RM) of phenylalanine and histidine in 0.01, 0.03 and 0.05 $mol.dm^{-3}$ aqueous vitamin solutions at different temperatures. Using the density data, Masson equation has been employed to obtain the limiting apparent molar volumes and experimental slopes, which deduced the solute–solvent and solute–solute interactions, respectively. Using the Jones–Dole equation, the viscosity data were examined to determine the viscosity A and B coefficients. The Lorentz–Lorenz equation has been employed to determine the molar refractions (RM). The results conclude that the solute- solvent interactions were strong between phenylalanine, histidine and nicotinic acid.

E. Yu. Tyunina and V. G. Badelin[52] studied the interaction between nicotinic acid and l-phenylalanine in aqueous phosphate buffer solutions (pH 7.35). The apparent molar volumes in buffer solution and in buffer–amino acid solutions were obtained by using densities of l-phenylalanine–buffer, NA–buffer and l-phenylalanine–NA–buffer mixtures at different temperatures ranging from 288.15K to 313.15K. The results are concluded as positive and strong solute-solvent interactions.

G. Singh, P. Patyar, T.Kaur and G. Kaur[53] determined the molecular interactions of glycine in aqueous buffer solutions of sodium succinate and succinic acid at different temperatures. The thermodynamic properties such as partial molar volumes and partial molar expansibilities have determined using the obtained density data. The results have been concluded in terms of structure making nature of glycine in aqueous sodium succinate whereas structure breaking nature in aqueous succinic acid.

Zhenning Yan, Xiangli Wen, Yunxia Kang and Wenwen Chu[54] determined the interactions of three glycyl dipeptides and four α-amino acids with drug domiphen bromide(DB) as the function of temperature and molality of DB by combining the volumetric and UV– spectroscopy methods. From the density data the standard partial molar volume, Hepler's factor, hydration number, standard partial molar transfer volumes, partial molar expansibility were calculated and interpreted in terms of solute-solvent interactions. The dependence of these parameters upon temperature, concentration, and hydrocarbon chain length of the amino acids/dipeptides clearly suggest the role of amino acids/dipeptides and domiphen bromide in solute-solvent interactions.

Ioana Gheorghe, Cristina Stoicescu and Florinela Sirbu[55]determined the partial molar volumes, partial molar expansibilities, isentropic compressibility coefficients, isobaric thermal expansion coefficient and the Hepler's constant values of D-Glucose and N-Methyl glycine in water using the data of the densities, speeds of sound and refractive indices at different temperatures from (298.15 to 323.15) K. Lorentz–Lorenz equation was used to analyze the refractive indices data. The obtained Hepler's constant values concluded in terms of structure breaker due to hydrophilic hydration of the NMG and D -Glucose in water. The tendencies of structure-breaking for the both solutes were found to be similar.

Anil Kumar Nain, Renu Pal and Preeti Droliya[56] determined densities, ultrasonic speeds and relative viscosities of solutions of alanine, l-valine, glycine, l- l-isoleucine in water and aqueous-streptomycin sulfate and streptomycin sulfate at different temperatures. The limiting apparent molar volume, the apparent molar volume, apparent molar compressibility, transfer volume, transfer compressibility, limiting apparent molar expansibility, Jones–Dole A and B coefficient, hydration number and temperature derivative of B-coefficient dB/dT were calculated from the above obtained parameters. The obtained results are analyzed in terms of molecular interactionssuch as solute-solute and solute-solvent and structural behavior.

XiaofenRen, Chunying Zhu and Youguang Ma[57] determined densities and viscosities of glycine, l-alanine, l-valine, l-threonine and l-arginine in binary aqueous sorbitol solutions at different temperatures. The apparent molar volume, limiting partial molar volumes, limiting partial molar volumes of transfer, viscosity B-coefficient and the free energies of activation per mole of solvent are calculated using Masson's equation, Jones–Dole equation , transition state theory and on the basis of the co-sphere overlap model. The hydration number and structure making/ breaking nature of amino acids were computed using the obtained limiting partial molar volume and viscosity B-coefficients.

Harsh Kumar and Isha Behal[58] determined apparent molar volumes and apparent molar isentropic compressibilities of glycine, l-alanine, l-valine and l-leucine in water and aqueous solution of thiamine hydrochloride at different temperatures from 303.15 K to 315.15 K using the values of densities and speed of sounds. Structural behavior has been determined in terms of making/breaking nature of amino acids in aqueous thiamine-HCl solutions.

Yukinori Satoa and Osato Miyawakib[59] obtained the molecular interactions for various sugars and urea in aqueous solutions using the partial molar volume and the hydration parameter which were determined using the densities and viscosities at different temperatures. The parameters indicated a good correlation with the number of equatorial-OH groups (e-OH) for sugars, suggesting that the sugar molecules with the higher e-OH fit more to the water-structure. The temperature dependence of the parameter (dh/dT) and the negative dB/dT for sugars suggested their water-structure making effect while the positive dB/dT for urea corresponded to its structure breaking effect.

Abhijit Sarkar and Biswajit Sinha[60] determined the densities and viscosities of lactose monohydrate in aqueous ascorbic acid solutions at different temperatures (298.–319) K. Partial molar volume, standard isobaric partial molar expansibility, viscosity B-coefficient and solvation number (Sn) were determined using experimental data. Viscosity B-coefficients were employed to obtain the free energies of activation of viscous flow per mole of the solvents and of the solute and were analysed in terms of solute-solute and solute-solvent interactions. The results are concluded in terms of structure making and breaking nature of lactose monohydrate in aqueous ascorbic acid solutions.

Ana Rita R. *et al*[61] determined the solvation ability and molecular-level mechanisms which rule the dissolution process solubility of D-(+)-glucose, D-(−)-fructose, D-(+)-galactose, D-(+)-mannose, L-(+)-arabinose and D-(+)-xylose in four ionic liquids (ILs) at different temperatures from 288.2 to 348.2 K. It was observed that the solubility of all the monosaccharides depends on the IL and it is found that D-(−)-fructose is the least soluble monosaccharide and D-(+)-xylose is the most soluble as it is found that IL cation and the anion play a major role in the solubility of monosaccharides. From different thermodynamic properties such as apparent molar volume, apparent molar isentropic compression, apparent molar expansion it has been concluded that enthalpy contributions are dominating which justifies the solubility effects.

Rekha Gaba, Amalendu Pal, Harsh Kumar, Dinkar Sharma and Navjot[62] determined the thermodynamic properties such as apparent molar volume, apparent molar isentropic compression, apparent molar expansion, Hepler's constant values, hydration numbers and specific volume for l-threonine and l-valine in water and binary aqueous solution of 1-methyl-3-pentylimidazolium chloride at different temperatures. On the basis of various kinds of interactions present in such solutions structure nurturing as well as taste behavior has been concluded and found that both amino acids retain different taste with ionic liquid.

Gavin R. Hedwig and Harald Hoiland[63] determined the partial molar isentropic compressions, partial molar heat capacities, partial molar isobaric expansions at infinite dilution, and partial molar isothermal compressions at infinite dilution using the sound velocity of the nucleosides adenosine, cytidine, and uridine at different temperatures from 288 K to 313 K. The results were rationalized in terms of nucleoside hydration and its temperature dependence.

Dhondge, Sudhakar S. *et al*[64] determined densities and relative viscosities of pyridoxine hydrochloride, thiamine hydrochloride and sodium-L-ascorbate in aqueous solutions at three different temperatures. Properties like apparent molar volume, partial molar volume, apparent molar expansivity and coefficient of thermal expansion, Falkenhagen coefficient A, Jones-Dole viscosity B-coefficient, temperature derivative of B-coefficient and hydration number has been obtained using densities and relative viscosities. For viscous flow free energy of activation per mole of solvent, per mole of solute entropy of activation per mole of viscous flow of solution and enthalpy of activation have also been computed through B-coefficient. The results have been concluded in terms of structural behavior of pyridoxine hydrochloride, thiamine hydrochloride and sodium-L-ascorbate in aqueous solutions.

Harsh Kumar, Sheetal, Isha Behal and Sanjay Sharma[65] determined densities and sound velocities of d(−)-ribose and d(+)-xylose in (0.2, 0.4, 0.6) $\text{mol}\cdot\text{kg}^{-1}$ in aqueous solutions of trilithium citrate (TLC) at different temperatures. The experimental results were used to calculate apparent molar and partial molar quantities such as partial molar volumes, partial molar isentropic compression of transfer and partial molar expansibilities. The pair and triplet interaction coefficients are computed from transfer parameters. The results have been interpreted in terms of prevailing interactions and structure making/breaking tendency of the solutes in aqueous solution of TLC.

Sheng Fang, Hu-Jun Xie, Hong-Yun Chen, Lu Wang and Shi-Yi Tian[66] determined densities of L-phenylalanine in water and in aqueous1-butyl-2,3-dimethylimidazolium bromide solutions, at different temperatures from 283.15 K to 303.15 K. The apparent molar volumes, standard partial molar volumes, limiting apparent molar expansibilities and standard partial molar volumes of transfer have been calculated using density data. These volumetric parameters are interpreted in terms of various mixing effects between L-phenylalanine and [BMMIm]Br in aqueous solution. The 1H NMR measurements of binary mixtures of L-phenylalanine and [BMMIm]Br in D_2O solutions have been carried out to understand the possible interactions. The results show that the interactions between the hydrophobic-hydrophobic groups of [BMMIm]Br and L-phenylalanine may be dominant in the studied system. Furthermore, the density functional theory calculations provide stabilization energies and suggest possible interacting ways that support the volumetric and NMR measurements.

OBJECTIVE OF PRESENT STUDIES

The behavior of electrolytes and non-electrolytes in solution depends mainly on solute-solute and solute -solvent interactions. The former interactions in general are stronger than the latter. Solute-solute interactions in dilute solutions can be well understood theoretically but the solute - solvent interactions still remains complex process. The literature survey revealed that although a number of studies on thermodynamic and transport properties (already discussed in the literature) have been conducted both in single component as well as in mixed solvent systems but a little attention has been paid to the behavior of biomolecules especially vitamins and carbohydrates mentioned below.

Carbohydrate is a biological molecule consists of carbon, hydrogen and oxygen i.e. hydrates of carbon. They are one of the most abundant organic compounds in living organisms and have multidimensional biomedical, physical and industrial useful properties[67]. Carbohydrates can be broken down to provide energy to cells in our body. Carbohydrates are the part of cell structure.

They are also known as saccharides or sugars. They are most abundant molecules in our nature. Carbohydrates play an important role in energy metabolism. Carbohydrates are able to perform numerous of activities in living systems i.e. storage, transport of energy and participation in immune system. The different types of carbohydrates are glucose, fructose, lactose, sucrose, galactose, xylose, ribose, maltose etc. Glucose is the major component of our diet and is the source of energy in the entire living organism. Glucose is taken as a supplement as it is an instant source of energy. Glucose has an important role in the business of sweet manufacturing. Glucose syrup is extensive component of vitamin-based tonics, cough syrups and also a prime ingredient used in cough lozenges. Fructose is also major component that contributes in many useful physical and functional attributes towards food, beverages including sweetness, color and flavor development, flavor enhancement, freezing-point depression and osmotic stability. HFS is extensively used in carbonated beverages, canned fruits, jams, jellies, baked goods and dairy products. Crystalline Fructose can be used as sweetener in beverage such as in Alcoholic Beverages, Carbonated Soft Drinks, Sports & Energy Drinks, Hypertonic Beverages, Hypotonic Beverages, Isotonic Beverages. Crystalline Fructose can be used as nutritional supplement in Pharmaceutical. Fructose has advantages in therapy[68]. Lactose is a disaccharide sugar composed of galactose and glucose that is found in milk so it is the major part of diet basically for infants. Lactose is used to sweeten stout beer, called a milk stout or a cream stout. Lactose because of its physical properties, i.e., compressibility, and low price is also added to pills as a filler and also for dilution of heroin[69].

Vitamins also play vital role in our life and play many important functions. They are needed in very small amount in diet of humans and animals to support chemical reactions in human body and also help in cell growth, biochemical reactions and maintenance of life. Various types of vitamins present in our body are A, B, C, D, E and K. Vitamins are classified based upon their solubility various roles played in our body to keep our body healthy[70]. Fat soluble vitamins are A, D, E and K and water soluble vitamins are B-complex vitamins and vitamin C.

Vitamin C i.e. L-ascorbic acid act as an important source in synthesizing of peptide hormones, creratinine and neurotransmitters[71]. It also acts as enhancing source to the ability of eye and deficiency of this is major reason of the disease scurvy. Collagen which is found in body requires vitamin C for its formation. Vitamin C is a vital antioxidant that helps to protect cells from damage caused by free radicals resulted from exposure to air pollution, cigarette smoke and ultraviolet light from the sun. The medical community is split over the benefits of vitamin C on the heart.

Vitamin B_1 i.e. Thiamine hydrochloride is a water-soluble vitamin and is a part of enzyme that is needed for energy metabolism and is also important for nerve functioning[72]. Thiamine hydrochloride is found in all nutritious foods that are grains, breads, cereals, nuts and seeds etc. This vitamin allows our body to break down alcohol and metabolize amino acids and carbohydrates.

Vitamin B_3 i.e. nicotinic acid is used in pharmacological doses[73] and has a great role in DNA repairing and production of steroid hormones. Also, it is used as an additive in food, forage and cosmetics.

Vitamin B_6 i.e. Pyridoxine hydrochloride, also known as vitamin B_6 and pyridoxol is commonly used in the food and dietary supplement[74]. It is used to treat and prevent many diseases such as pyridoxine deficiency, pyridoxine-dependent epilepsy, sideroblastic anaemia, certain metabolic disorders, problems from mushroom poisoning and isoniazid.

The mixed solvent systems are used in a wide range of applications and understanding the effects of changes in solvent composition remains a central problem within physical chemistry. During recent years there has been an increasing interest in the study of the behavior of biomolecules in mixed solvents, because the use of mixed solvents enables to know about the nature of solute-solute and solute -solvent interactions under the varied conditions simply by changing the solvent composition. The study of thermodynamic and transport properties of these biomolecules provides an opportunity for extending the range of properties from which the structure of molecules in solution can be inferred.

Moreover, mixed binary aqueous solvent systems behave in unexpected systems. These observations have given a new impetus to the detailed study of structure of binary aqueous mixtures. The information drawn from the studies of thermodynamic and transport properties have been related to structural aspect of the solvent in terms of solute – solvent interactions and structure making/breaking capacity of various biomolecules.

Since the results in mixed aqueous organic systems highlight the importance of solvent – solvent interactions and also of interactions between co-ordinate ions and solvent molecules in H – bonding media, therefore the main objectives of the present study is to investigate the thermodynamic properties viz; partial molar volume, partial molar expansibilities, partial molar heat capacities etc. and transport processes such as viscosities ,relative viscosities, Jones dole B-coefficients etc. of the above mentioned water soluble vitamins in water and binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose.

The main objectives of the present investigations are:

1. To determine the density and sound velocity of vitamins such as L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride and nicotinic acid in water as well as in binary aqueous mixtures of sugars (D-Glucose, D- Fructose, D-Lactose) at different temperatures.
2. To determine the partial molar volumes of some water soluble vitamins such as L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride and nicotinic acid in water as well as in binary aqueous mixtures of sugars (D-Glucose, D- Fructose, D-Lactose) using the density.
3. To determine the partial molar adiabatic compressibilities of some water soluble vitamins such as L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride and nicotinic acid in water as well as in binary aqueous mixtures of sugars (D-Glucose, D- Fructose, D-Lactose) using the ultrasonic sound velocities.

4. To test the various theories used for describing the uncoupled transport properties viz; viscous flow of L-ascorbic acid, nicotinic acid, pyridoxine hydrochloride and thiamine hydrochloride in water as well as binary aqueous mixtures of sugars (D-Glucose, D-Fructose, D-Lactose) at various temperatures.

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CHAPTER 2

EXPERIMENTAL DETAILS

For the sake of convenience the experimental part has been described under following sections:

2.1. CHEMICALS AND THEIR SPECIFICATIONS

2.2. EXPERIMENTAL TECHNIQUES

2.2.1 Preparation of solutions

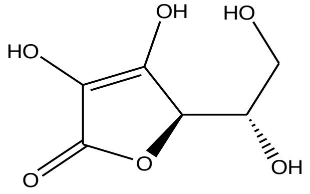
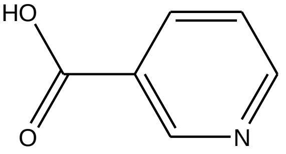
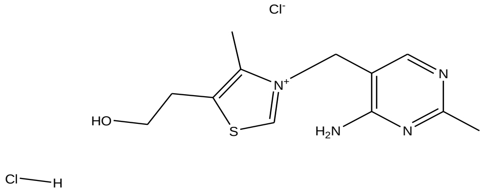
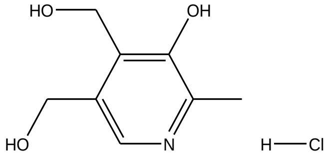
2.2.2 Experimental determination of density and speeds of sound

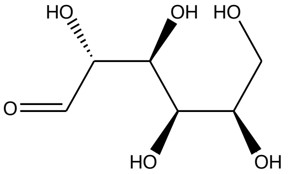
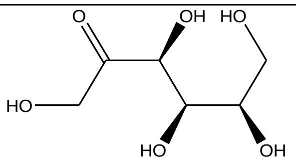
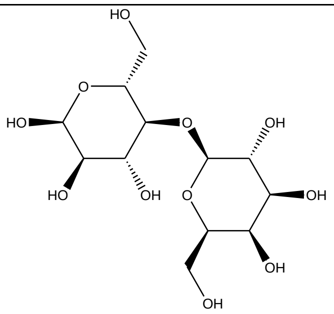
2.2.3 Experimental determination of viscosity

2.1 CHEMICALS AND THEIR SPECIFICATIONS

All the reagents L-ascorbic acid, nicotinic acid, thiamine hydrochloride, pyridoxine hydrochloride, D-Glucose, D-Fructose and D-Lactose taken in the present study were of A.R grade. The provenance and purity of the chemicals used in the study are given in table 2.1. All the chemicals were used without any further purification; however all the chemicals were dried over anhydrous calcium chloride in a vacuum desiccator for a period of more than 48 hours.

Table 2.1. Structure and specifications of chemicals used.

Chemical name	Provenance	Mass Fraction purity[#]	Structure
L- ascorbic acid	S.D Fine-Chem Limited	>0.99	
Nicotinic acid	S.D Fine-Chem Limited	>0.99	
Thiamine hydrochloride	S.D Fine-Chem Limited	>0.99	
Pyridoxine hydrochloride	S.D Fine-Chem Limited	>0.99	

D-Glucose	S.D Fine-Chem Limited	>0.99	
D-Fructose	LobaChemie	>0.99	
D-Lactose	LobaChemie	>0.99	

As stated by supplier

All chemicals where obtained in their highest priority as indicated in table 2.1. All the utilized carbohydrates and vitamins were having mass fraction purities greater than 0.99 and were used as such without further purification. However, before use these were dried under vacuum and kept over P_2O_5 in a vacuum desiccator for a minimum of 24 hours at room temperature.

2.2. EXPERIMENTAL TECHNIQUES

2.2.1 Preparation of solutions

Aqueous solutions and various other compositions were prepared by using the deionized triple distilled water having a pH of 7.1 and conductivity 1-2 μs-cm^{-1}. All the molal solutions were prepared using an analytical balance (FA2204B, Shanghai Jingke, China) at 298.15 K with an uncertainty of ± 0.0001 mol.kg^{-1}. All the samples were made fresh before use and were consumed same day to minimize decomposition due to a bacterial contamination.

All samples were kept tightly sealed in vacuum desiccator to minimize absorption of atmospheric moisture.

2.2.2 Experimental determination of density and speeds of sound

Densities (p) and speeds of sound (U) of pure liquids and mixtures were simultaneously and automatically measured, using an Anton Paar DSA 5000M shown in figures (2.1) and (2.2).

Fig. 2.1. DSA

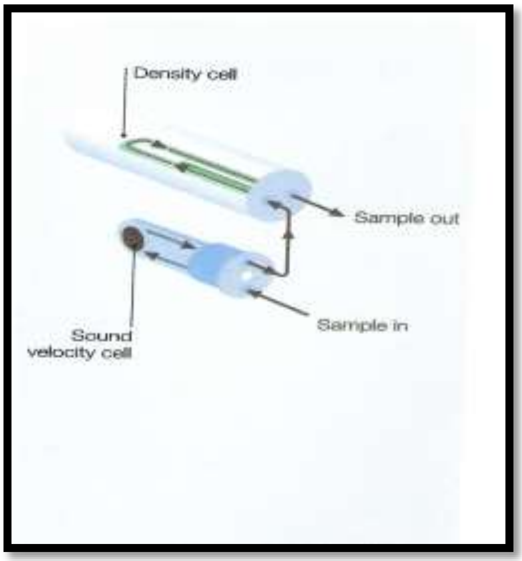


Fig. 2.2. Density cell and a pulse- echo speed of sound cell

All densities and speeds of sound values of the solutions were measured as a function of composition and temperature for the different solutes in aqueous solutions of different additives during this entire course of work with Anton Paar DSA 5000M.

The Anton Paar DSA 5000M simultaneously determines two physically independent properties within one sample. The two in one instrument is equipped with the density cell and a pulse-echo speed of sound cell is illustrated in fig. (2.2). A unique reference oscillator, in addition to the U-tube oscillator, provides extraordinary long-term stability and makes adjustments at the desired temperatures. DSA 5000M automatically corrects the errors related to viscosity in the density by measuring the damping of the U-tube's oscillation caused by the viscosity. Based on high – resolution electronics and additional measurements the cell is made up of stainless steel, so that speed of sound of the sample can be determined accurately.

Both measuring cells are temperature controlled using build-in solid state thermostat. Two integrated pt100 thermometers provided the highest accuracy in temperature control and are traceable to national standards. To perform a measurement, one out of a total 10 individual measuring methods were selected and the sample was filled into the measuring cells with the help of a syringe .Results were automatically converted into concentration, specific gravity or other density/velocity of sound related units using built-in conversion tables and functions. It can work in temperature range from 10^0C to 70^0C. Both the densities and speeds of sound are extremely sensitive to temperature, so it was controlled to 1×10^{-3} K by built-in solid state thermostat.

The measuring cells were cleaned with two liquids – water and alcohol. First of all the measuring cells are filled with water, using a 5ml capacity syringe with leer tip. The plunger of the syringe was moved in and out several times. This created gas bubble which improved the cleaning action of water and helped to remove residue, after this water was removed from cells. The measuring cells were filled with alcohol with the help of syringe. Alcohol was removed from the cells after some time and the air hose was attached to injection adapter. Then the air pump was turned using "pump" key and it was dried blew through the measuring cells for approximately 10 times when cells were dried, the air hose was removed from injection adapter.

A density check was done using the triple distilled, degassed water and with dry air at atmospheric pressure. The apparatus was calibrated with double distilled and degassed water at different temperatures before each series of measurements. The densities [1-3] and speeds of sound [4-5] were found to be in good agreement with literature values. The values are given below in table 2.2.

Table 2.2. Values of densities and sound velocities for water at different temperatures

T (K)	**Experimental Density $\rho \times 10^{-3}$ ($kg.m^{-3}$)**	**Literature Density $\rho \times 10^{-3}$ ($kg.m^{-3}$)**	**Experimental Speed of sound (ms^{-1})**	**Literature Speed of sound (ms^{-1})**

298.15	0.997047	0.997048	1497.12	1497.13
303.15	0.995650	0.995652	1509.29	1509.31
308.15	0.994034	0.994035	1519.92	1519.94
313.15	0.992218	0.992220	1528.82	1528.84

The reproducibility of density and speed of sound measurement was 1x10^{-6}kg.m^{-3} and 1x10^{-2} m-s^{-1}, respectively, and the uncertainties of these were assumed to be less than 3x10^{-6}kg.m^{-3}and 5x10^{-2} m-s^{-1}, respectively.

2.3.3. Experimental determination of viscosity

Apart from the thermodynamic parameters, viscosity is also very-very important parameter to study the molecular interactions present in different binary aqueous system solutions. This study was also used to support the conclusion drawn in the density and speeds of sound data. Here, viscosity was measured as a function of different additives during this entire course of work.

Measurement of viscosity

Viscosity measurements were made with the help of suspended level type viscometer (6-9). This has the time flow of 57 seconds for water at 303.15K. Runs were repeated until three successive determinations are obtained within ±0.1 second. The viscometer, shown in Fig. 3.3 consists of a U-tube with two bulbs D and E, along with a side arm F. The left hand limb is essentially a pipette with two definite marks A and B above and below the bulb D and a capillary about 10" long. Some volume of solution is introduced into the bulb E. Keeping the side arm, ‘F’, closed, the solution is forced through capillary tube C until the meniscus stood above the mark A. On opening the side arm, F, while -keeping the capillary limb closed, the solution below C will fall back and the column of the solution CA is held suspended. On opening the capillary limb the solution flows through the capillary and the time of flow of meniscus from A to B is noted. The column of liquid CA is the same in each case, independent of the volume of the solution in the viscometer.

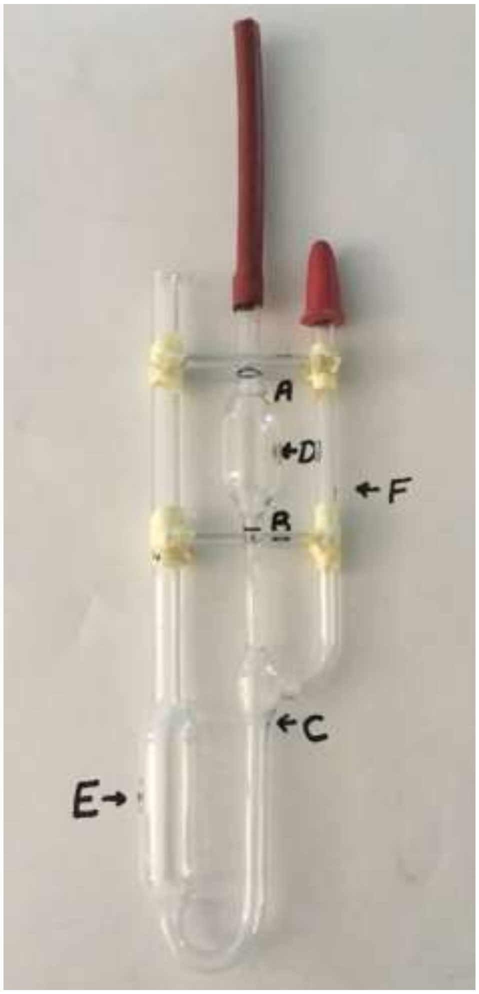


FIG. 2.3 Viscometer

The viscometer was cleaned by filling it with chromic acid, followed by washing with water and finally with acetone. It was then dried by applying vacuum. Flow time for volume of solution through the capillary, between the marks A and B was measured with the help of a stop watch capable of recording time up to 0.1 second. Viscosities of solutions were determined at different temperatures in water thermostat controlled up to ±0.01^{0}C by means of an electronic relay and contact thermometer. Time of flow (for solution in bulb) between marks A and B was determined by visual observation.

The relative viscosities of solutions are than obtained by using following equation:

$$\eta_r = \eta/\eta_o = \rho.t / \rho_o.t_o \tag{2.1}$$

where, η and η_o are the viscosities of sample solution and pure solvent respectively, η_r is the relative viscosity, ρ and ρ_o are the densities of sample solution and pure solvent respectively, t and t_o are their respective time of flow. The calibration of the viscometer was done with the help of conductivity water which was used as standard liquid.

Sources of error:

1. **Fluctuation of temperature:** Density, speed of sound and viscosity are function of temperature (temperature dependent), as these varies to a large extent by a small change in temperature than by other variables. So even a small change in the temperature in the instrument will cause a large error in these physical properties. In case of density and speed of sound this error was found to be negligible as the properties are obtained using DSA-5000. Since the viscosity of liquid decrease by 1 to 2 percent for each degree rise in the temperature so it has been minimized by suspending the viscometer in the water thermostat where the temperature fluctuation was controlled with in ± 0.01 ^{0}C.
2. **Solvent and Solute purity:** The error due to these impurities was minimized by using the AR grade chemicals and conductivity water for preparing the solutions.

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CHAPTER 3

RESULTS AND DISCUSSION

SECTION I

THERMODYNAMIC AND TRANSPORT PROPERTIES OF L-ASCORBIC ACID IN WATER ANDBINARY AQUEOUS MIXTURES OF D-FRUCTOSE AND D-GLUCOSE

The present section describes the thermodynamic and transport properties such as partial molar volumes, partial molar adiabatic compressibilities, partial molar expansibilities, viscosity A and

B coefficients of Jones Dole equation, activation energy parameters etc. of L-ascorbic acid in water and binary aqueous mixtures of D-Fructose and D-Glucose.

For the sake of convenience the section has been further divided into two parts.

A. THERMODYNAMIC PROPERTIES

B. TRANSPORT PROPERTIES

A. THERMODYNAMIC PROPERTIES:

The Thermodynamic properties such as partial molar volumes, partial molar adiabatic compressibilities and partial molar expansibilities were determined using the density and speed of sound data of L-ascorbic acid in water and binary aqueous mixtures of D-Fructose and D-Glucose. The effect of composition of D-Fructose and D-Glucose in water was also observed at one temperature i.e. 303.15 K only whereas the above mentioned properties have also been determined at different temperatures to analyze the effect of temperature. The densities (ρ), apparent molar volumes (ϕ_v), sound velocities (U) and apparent molar adiabatic compressibilities (ϕ_{ks}) of L-ascorbic acid in binary aqueous solutions of D-Glucose and D-Fructose (0.05, 0.15, 0.25 and 0.35) mol.kg^{-1} at 303.15K have been measured and are reported in tables 3.1and 3.2 respectively .

Table 3.1: Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes(ϕ_v^0) and experimental slopes (S_v^*) of L- ascorbic acid in different compositions of D-Fructose and D-Glucose in water at 303.15 K.

m^a (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x 10^{-3} (kg.m^{-3})	ϕ_v x 10^6 (m^3.mol^{-1})	ϕ_v^0 x 10^6 (m^3.mol^{-1})	S_v^* x 10^4 (m^3·L$^{1/2}$.mol$^{-3/2)}$
0.05 mol.kg^{-1} D-Fructose + water					
0.01024	10.11822	1.001592	105.13	104.08(±0.066)	0.096 (±0.002)
0.02970	17.21412	1.002950	105.71		
0.05023	22.36211	1.004356	106.25		
0.07032	26.43033	1.005709	106.71		
0.10032	31.51798	1.007711	107.13		
0.14964	38.39112	1.010909	107.90		
0.15 mol.kg^{-1} D-Fructose + water					
0.00979	9.926781	1.008283	105.21	104.18(±0.081)	0.095(±0.003)
0.02995	17.34398	1.009685	105.75		

0.05023	22.43671	1.011068	106.28		
0.07032	26.51829	1.012414	106.75		
0.10032	31.62249	1.014405	107.19		
0.14964	38.51781	1.017592	107.91		
0.25 mol.kg^{-1} D-Fructose + water					
0.01024	10.18542	1.01494	105.33	104.32(±0.091)	0.094(±0.003)
0.02970	17.32816	1.016282	105.99		
0.05023	22.50996	1.017681	106.34		
0.07032	26.60465	1.019019	106.83		
0.10032	31.72513	1.021001	107.24		
0.14964	38.64189	1.024159	108.04		
0.35 mol.kg^{-1} D-Fructose + water					
0.01025	10.21633	1.001588	105.59	104.85(±0.097)	0.086(±0.003)
0.02989	17.42742	1.002951	106.12		
0.05026	22.57347	1.004346	106.49		
0.07036	26.67853	1.005702	106.85		
0.10031	31.80266	1.007692	107.32		
0.14976	38.75291	1.010894	108.05		
0.05 mol.kg^{-1} D-Glucose + water					
0.01015	10.07362	1.001569	103.81	102.90(±0.066)	104.32(±0.091)
0.02990	17.27184	1.002968	104.58		
0.05018	22.35135	1.004381	105.09		
0.07009	26.38811	1.005748	105.50		
0.10023	31.50533	1.007791	105.98		
0.14979	38.41334	1.011092	106.54		
0.15 mol.kg^{-1} D-Glucose + water					
0.00979	9.926835	1.008294	104.10	103.12(±0.040)	0.094(±0.0015)
0.02995	17.34425	1.009716	104.73		
0.05023	22.43730	1.011122	105.22		
0.07032	26.51936	1.012496	105.60		
0.10032	31.62416	1.014512	106.13		
0.14964	38.52104	1.017763	106.78		
0.25 mol.kg^{-1} D-Glucose + water					
0.01025	10.18868	1.014724	104.26	103.40(±0.094)	0.091(±0.003)
0.02982	17.35993	1.016092	105.01		
0.05023	22.50808	1.017492	105.59		
0.07032	26.60270	1.018862	105.85		
0.10032	31.72370	1.020877	106.24		
0.14964	38.64131	1.024102	106.93		
0.35 mol.kg^{-1} D-Glucose + water					
0.01025	10.21418	1.001601	104.61	104.14(±0.034)	0.089(±0.001)
0.02989	17.42385	1.002981	105.22		
0.05026	22.56900	1.004388	105.71		
0.07036	26.67350	1.005758	106.09		

0.10031	31.79708	1.007772	106.55		
0.14976	38.74732	1.011039	107.10		

m^a molality of L-ascorbic acid in different solvent systems

Table 3.2: Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities (ϕ^0_{KS}) and experimental slopes (S^*_K) of L- ascorbic acid in different compositions of D-Fructose and D-Glucose in water at 303.15 K.

m^a (mol.kg^{-1})	**U (m.s^{-1})**	**K_S x 10^{10} (kg^{-1}.m.s^2)**	**ϕ_{KS} x 10^6 (m^3.mol^{-1}.G.Pa^{-1})**	**ϕ^0_{KS}x 10^6 (m^3.mol^{-1}.G.Pa^{-1})**	**S^*_K x 10^6 (kg.m^3.mol^{-2}.G.Pa^{-1})**
0.05 mol.kg^{-1} D-Fructose + water					
0.01024	1512.72	4.363	-39.52	-40.92(±0.818)	-24.87(±9.909)
0.02970	1513.47	4.352	-42.37		
0.05023	1514.17	4.342	-43.03		
0.07032	1514.93	4.332	-43.34		
0.10032	1515.86	4.318	-43.61		
0.14964	1517.72	4.294	-43.89		
0.15 mol.kg^{-1} D-Fructose + water					
0.00979	1518.76	4.299	-39.05	-40.52(±0.849)	-25.23(±10.290)
0.02995	1519.55	4.289	-42.04		
0.05023	1520.38	4.278	-42.68		
0.07032	1520.99	4.269	-42.98		
0.10032	1522.07	4.255	-43.25		
0.14964	1524.02	4.231	-43.52		
0.25 mol.kg^{-1} D-Fructose + water					
0.01024	1524.94	4.236	-38.99	-40.34(±0.784)	-23.84(±9.497)
0.0297	1525.71	4.227	-41.73		
0.05023	1526.86	4.214	-42.36		
0.07032	1527.14	4.207	-42.65		
0.10032	1528.42	4.192	-42.92		
0.14964	1530.37	4.169	-43.19		
0.35 mol.kg^{-1} D-Fructose + water					
0.01025	1530.89	4.260	-38.58	-39.95(±0.799)	-24.25(±9.670)
0.02989	1531.78	4.249	-41.37		
0.05026	1533.12	4.236	-42.00		
0.07036	1533.81	4.226	-42.30		
0.10031	1535.65	4.208	-42.57		
0.14976	1537.74	4.183	-42.85		

0.05 mol.kg^{-1} D-Glucose + water					
0.01015	1512.47	4.364	4.2934	-40.09 (±0.003)	-25.07(±10.039)
0.02990	1513.36	4.353	1.4517		
0.05018	1514.08	4.343	0.8617		
0.07009	1514.76	4.333	0.6147		
0.10023	1515.85	4.318	0.4275		
0.14979	1517.64	4.294	0.2835		
0.15 mol.kg^{-1} D-Glucose + water					
0.00979	1518.5	4.301	-39.07	-40.55(±0.850)	-25.29(±10.293)
0.02995	1519.35	4.290	-42.07		
0.05023	1520.11	4.280	-42.71		
0.07032	1520.88	4.269	-43.01		
0.10032	1522.12	4.254	-43.28		
0.14964	1524.00	4.230	-43.56		
0.25 mol.kg^{-1} D-Glucose + water					
0.01025	1525.06	4.237	-38.99	-40.34(±0.783)	-23.88(±9.493)
0.02982	1525.68	4.228	-41.73		
0.05023	1526.31	4.218	-42.36		
0.07032	1527.02	4.209	-42.66		
0.10032	1528.08	4.195	-42.92		
0.14964	1530.02	4.171	-43.2		
0.35 mol.kg^{-1} D-Glucose + water					
0.01025	1530.87	4.260	-38.58	-39.95(±0.799)	-24.28(±9.671)
0.02989	1531.75	4.249	-41.37		
0.05026	1533.09	4.236	-42.01		
0.07036	1533.84	4.226	-42.31		
0.10031	1535.61	4.208	-42.57		
0.14976	1537.76	4.182	-42.85		

m^a (mol.kg^{-1}) molality of L-ascorbic acid in different solvent systems

From the tables 3.1 and 3.2, it is clear that the density and sound velocity values increase with increase in concentration of L-ascorbic acid in different compositions of D-Glucose and D-Fructose in water. The respective density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities by using equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.1 and all the values are positive and increases in magnitude with increase in concentration of L-ascorbic acid in all compositions of D-Glucose + water and D-Fructose + water indicating the presence of great solute - solvent interaction[1-2]. Also, the values of adiabatic compressibilities (ϕ_{KS}) which are reported in table 3.3, are negative in all compositions of D- Glucose and D-Fructose in water which shows that water molecules around solute i.e. L-ascorbic acid are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of L-ascorbic acid and D- Glucose and D-Fructose molecules respectively.

Linear plots have been found in accordance with the Masson's equation (1.12) when the apparent molar volume values (ϕ_v) are plotted against root of molar concentrations ($C^{1/2}$) of L-ascorbic acid in different compositions of D- Glucose and D-Fructose in water. Sample plots for L-ascorbic acid in different compositions of D-Glucose and D-Fructose in water at 303.15K are shown in figs. (3.1) and (3.2) respectively.

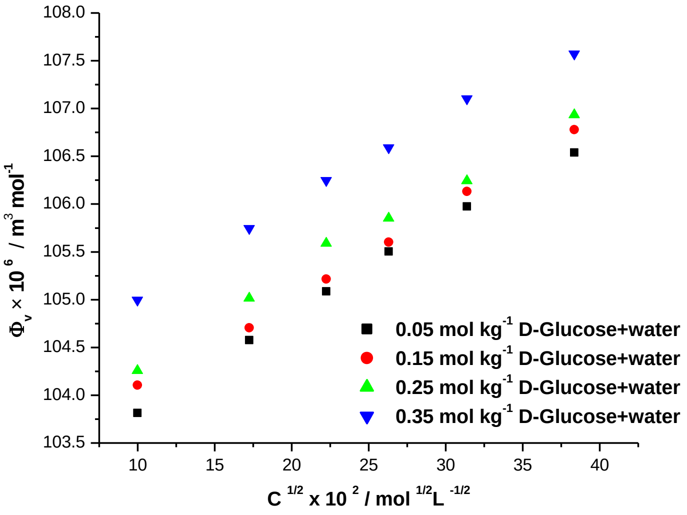

Fig. 3.1. Plot of ϕ_v vs $C^{1/2}$ for L-ascorbic acid in different compositions of D- Glucose in water at 303.15K.

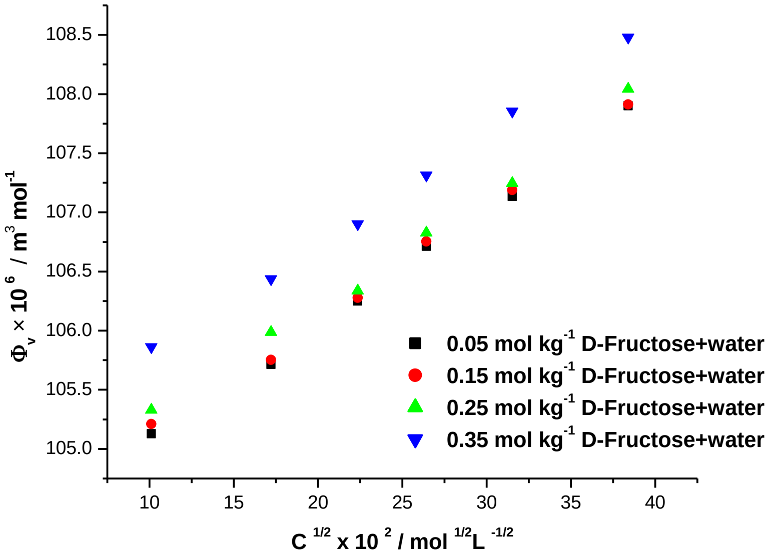

Fig. 3.2. Plot of ϕ_V vs $C^{1/2}$ for L-ascorbic acid in different compositions of D- Fructose in water at 303.15K

The values of partial molar volumes (ϕ_V^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^0) are determined by applying least square fitting to the plots of $\phi_V$vs square root of molar concentration and ϕ_{KS}vs molal concentration which are deduced by using equations (1.12) and (1.19) respectively. The values of these parameters for L-ascorbic acid in different compositions of binary aqueous solutions of D- glucose and D-Fructose at 303.15 K are reported in table 3.1 and 3.2 respectively.

It is clear, from table 3.1, that the values of slopes (S_V^*) are positive in different compositions of D-Glucose and D-Fructose in water at 303.15 K. The positive values of slopes indicate the presence of strong solute- solute interactions and magnitude of S_V^* values decreases with increase in compositions of D-Glucose and D-Fructose in water indicating that these interactions are further weakened which trait to the increase in solvation. On the other hand the values of ϕ_V^0 are positive and increase with increase in molalities of D-Glucose and D-Fructose in water thereby showing that solute - solvent interactions further increase on the addition of D- Glucose and D-Fructose in water. Also on comparing the magnitudes of ϕ_V^0 values with the values of S_V^* , ϕ_V^0values are more than S_V^* which proves that solute - solvent interactions dominate over the solute- solute interactions in mixtures of D-Glucose and D-Fructose in water. The magnitude of ϕ_{KS}^{0} values indicates solute-solvent interactions[4].It has been found in the present study that the values of ϕ_{KS}^{0} for L-ascorbic acid are negative which attribute to the strong attractive interactions between L- ascorbic acid and water. With increase in compositions of D-Glucose and D-Fructose in water values ofϕ_{KS}^{0}become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of L-ascorbic acid and therefore at high concentrations of D-Glucose and D-Fructose, water molecules around L-ascorbic acid are more compressible than those at lower concentrations.

Effect of temperature

As behavior of L-ascorbic acid was found to be similar for entire range of compositions of D-Glucose and D-Fructose in water at one temperature. So, the effect of temperature has been studied on the lowest composition of D-Glucose and D-Fructose in water. Densities (ρ), apparent molar volumes (ϕ_v), sound velocities (U), and apparent molar adiabatic compressibilities (ϕ_{ks}) of L-ascorbic acid in water, 0.05 molkg^{-1} D- Glucose + water and 0.05 molkg^{-1} D-Fructose + water at different temperatures have been measured and are reported in tables 3.3 and 3.4 respectively.

Table 3.3:Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes(ϕ_v^0) and experimental slopes (S_v^*) of L- ascorbic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

m^a (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x10^{-3} (kg.m^{-3})	ϕ_v x 10^6 (m^3.mol^{-1})	ϕ_v^0 x 10^6 (m^3.mol^{-1})	S_v^* x 10^4 (m^3.L$^{1/2}$.mol$^{-3/2}$)
Water **298.15 K**					
0.01001	9.98507	0.997778	103.12	102.38(±0.058)	0.068 (±0.002)
0.02998	17.26247	0.999221	103.48		
0.04997	22.26338	1.000642	103.91		
0.06994	26.31168	1.002049	104.19		
0.09993	31.40194	1.004141	104.50		
0.14997	38.36864	1.007561	105.02		
303.15 K					
0.01001	9.97807	0.996378	103.46		

0.02998	17.25030	0.997813	103.90	102.78(±0.032)	0.065 (±0.001)
0.04997	22.24769	0.999232	104.22		
0.06994	26.29310	1.000634	104.49		
0.09993	31.37970	1.002719	104.80		
0.14997	38.34134	1.006128	105.32		
308.15 K					
0.01001	9.96995	0.994758	103.92	103.26(±0.037)	0.064 (±0.001)
0.02998	17.23621	0.996184	104.39		
0.04997	22.22947	0.997596	104.67		
0.06994	26.27145	0.998987	105.00		
0.09993	31.35379	1.001064	105.25		
0.14997	38.30943	1.004454	105.76		
313.15 K					
0.01001	9.96084	0.992940	104.18	103.55(±0.009)	0.062 (±0.003)
0.02998	17.22044	0.994362	104.65		
0.04997	22.20910	0.995769	104.96		
0.06994	26.24743	0.997161	105.20		
0.09993	31.32499	0.999226	105.54		
0.14997	38.27440	1.002619	105.96		
0.05 mol.kg^{-1} D-Fructose +water **298.15 K**					
0.01024	10.12541	1.003017	104.40	103.27(±0.115)	0.105 (±0.004)
0.02970	17.22644	1.004386	105.06		
0.05023	22.37814	1.005797	105.74		
0.07032	26.44934	1.007156	106.25		
0.10032	31.54057	1.009156	106.81		
0.14964	38.41925	1.012391	107.41		
303.15 K					
0.01024	10.11822	1.001592	105.13	104.08(±0.066)	0.096 (±0.002)
0.02970	17.21412	1.002950	105.71		
0.05023	22.36211	1.004356	106.25		
0.07032	26.43033	1.005709	106.71		
0.10032	31.51798	1.007711	107.13		
0.14964	38.39112	1.010909	107.90		
308.15 K					
0.01024	10.10986	0.999938	106.07	105.28(±0.059)	0.090 (±0.002)
0.02970	17.19977	1.001278	106.68		
0.05023	22.34329	1.002666	107.21		
0.07032	26.40806	1.004015	107.47		
0.10032	31.49115	1.005996	107.90		
0.14964	38.35867	1.009201	108.39		
313.15 K					
0.01024	10.10051	0.998089	106.72		

0.02970	17.18380	0.999420	107.26	105.93(±0.083)	0.086 (±0.003)
0.05023	22.32252	1.000803	107.68		
0.07032	26.38341	1.002141	107.99		
0.10032	31.46164	1.004112	108.39		
0.14964	38.32237	1.007292	108.91		
0.05 mol.kg^{-1} D-Glucose +water **298.15 K**					
0.01015	10.08075	1.002987	103.38	102.39(±0.115)	0.105(±0.004)
0.02990	17.28409	1.004392	104.20		
0.05018	22.36715	1.005801	104.92		
0.07009	26.40686	1.007178	105.23		
0.10023	31.52777	1.009227	105.70		
0.14979	38.44047	1.012521	106.39		
303.15 K					
0.01015	10.07362	1.001569	103.81	102.89(±0.066)	0.096 (±0.002)
0.02990	17.27184	1.002968	104.58		
0.05018	22.35135	1.004381	105.09		
0.07009	26.38811	1.005748	105.50		
0.10023	31.50533	1.007791	105.98		
0.14979	38.41334	1.011092	106.54		
308.15 K					
0.01015	10.06539	0.999932	104.06	103.17(±0.059)	0.090(±0.002)
0.02990	17.25772	1.001329	104.77		
0.05018	22.33312	1.002743	105.20		
0.07009	26.36673	1.004119	105.48		
0.10023	31.47972	1.006153	106.06		
0.14979	38.38221	1.009454	106.62		
313.15 K					
0.01015	10.05613	0.998093	104.32	103.54(±0.083)	0.086(±0.003)
0.02990	17.24181	0.999484	105.10		
0.05018	22.31252	1.000894	105.51		
0.07009	26.34230	1.002259	105.87		
0.10023	31.45075	1.004302	106.27		
0.14979	38.34698	1.007602	106.79		

m^a (mol.kg^{-1}) molality of L-ascorbic acid in different solvent systems

Table 3.4: Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities (ϕ_{KS}^0) and experimental slopes (S_K^*) of L- ascorbic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

m^a ($mol.kg^{-1}$)	U ($m.s^{-1}$)	K_S x 10^{10} ($kg^{-1}.m.s^2$)	ϕ_{KS} x 10^6 ($m^3.mol^{-1}.G.Pa^{-1}$)	ϕ_{KS}^0x 10^6 ($m^3.mol^{-1}.G.Pa^{-1}$)	S_K^* x 10^6 ($kg.m^3.mol^{-2}.G.Pa^{-1}$)
Water **298.15 K**					
0.01001	1497.43	4.469	-40.17	-41.68 (±0.866)	-26.07(±10.510)
0.01001	1498.20	4.458	-40.26		
0.04997	1499.20	4.446	-43.89		
0.04997	1499.80	4.436	-43.95		
0.09993	1501.14	4.419	-44.49		
0.14997	1503.17	4.392	-44.80		
303.15 K					
0.01001	1509.45	4.404	-39.51	-41.00(±0.856)	-25.71(±10.371)
0.02998	1510.15	4.394	-42.53		
0.04997	1511.07	4.382	-43.18		
0.06994	1511.62	4.373	-43.49		
0.09993	1512.99	4.356	-43.78		
0.14997	1514.80	4.331	-44.07		
308.15 K					
0.01001	1520.21	4.349	-38.95	-40.42(±0.846)	-25.41(±10.260)
0.02998	1520.65	4.341	-41.93		
0.04997	1521.51	4.330	-42.57		
0.06994	1522.00	4.321	-42.88		
0.09993	1523.10	4.306	-43.16		
0.14997	1525.03	4.280	-43.46		
313.15 K					
0.01001	1529.07	4.307	-38.48	-39.94(±0.840)	-25.20(±10.179)
0.02998	1529.67	4.297	-41.44		
0.04997	1530.42	4.287	-42.08		
0.06994	1530.85	4.279	-42.38		
0.09993	1531.84	4.264	-42.66		
0.14997	1533.59	4.240	-42.95		

0.05 mol.kg^{-1}D-Fructose +water **298.15 K**					
0.01024	1500.73	4.426	-40.16	-41.58(±0.829)	-25.22(±10.039)
0.02970	1501.51	4.416	-43.05		
0.05023	1502.32	4.405	-43.72		
0.07032	1503.16	4.394	-44.03		
0.10032	1504.35	4.378	-44.31		
0.14964	1506.34	4.353	44.6		
303.15 K					
0.01024	1512.72	4.363	-39.52	-40.92(±0.818)	-24.87(±9.909)
0.02970	1513.47	4.352	-42.37		
0.05023	1514.17	4.342	-43.03		
0.07032	1514.93	4.332	-43.34		
0.10032	1515.86	4.318	-43.61		
0.14964	1517.72	4.294	-43.89		
308.15 K					
0.01024	1523.03	4.311	-38.94	-40.33(±0.809)	-24.59(±9.803)
0.02970	1523.82	4.301	-41.76		
0.05023	1524.27	4.292	-42.41		
0.07032	1524.88	4.283	-42.72		
0.10032	1525.97	4.268	-42.99		
0.14964	1527.70	4.245	-43.27		
313.15 K					
0.01024	1523.03	4.319	-38.44	-39.84(±0.812)	-24.63(±9.839)
0.02970	1523.82	4.309	-41.27		
0.05023	1524.27	4.300	-41.93		
0.07032	1524.88	4.291	-42.23		
0.10032	1525.97	4.276	-42.5		
0.14964	1527.70	4.253	-42.78		
0.05 mol.kg^{-1}D-Glucose +water **298.15 K**					
0.01015	1500.58	4.427	-40.12	-41.41(±0.829)	-25.07(±10.039)
0.02990	1501.72	4.414	-43.06		
0.05018	1502.38	4.404	-43.72		
0.07009	1503.08	4.394	-44.03		
0.10023	1504.23	4.379	-44.31		
0.14979	1506.22	4.353	-44.6		
303.15 K					

0.01015	1512.47	4.364	4.2934	-40.90(±0.829)	-25.07(±10.039)
0.02990	1513.36	4.353	1.4517		
0.05018	1514.08	4.343	0.8617		
0.07009	1514.76	4.333	0.6147		
0.10023	1515.85	4.318	0.4275		
0.14979	1517.64	4.294	0.2835		
308.15 K					
0.01015	1512.27	4.372	-38.86	-40.29(±0.832)	-25.11(±10.07)
0.02990	1513.36	4.360	-41.77		
0.05018	1514.02	4.350	-42.43		
0.07009	1514.96	4.339	-42.73		
0.10023	1515.85	4.325	-43.01		
0.14979	1517.64	4.301	-43.30		
313.15 K					
0.01015	1531.81	4.269	-38.49	-39.87(±0.802)	-24.45(±9.724)
0.02990	1532.58	4.259	-41.29		
0.05018	1533.06	4.251	-41.94		
0.07009	1533.75	4.241	-42.24		
0.10023	1534.75	4.227	-42.51		
0.14979	1536.21	4.205	-42.80		

m^a (mol.kg^{-1}) molality of L-ascorbic acid in different solvent systems

From the analysis of tables 3.3 and 3.4, it is clear that the density and sound velocity values increase with increase in temperature for L-ascorbic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water respectively. The density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities by using equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.3 and all the values are positive and increases in magnitude with increase in temperature for L-ascorbic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water indicating the presence of strong solute - solvent interaction. On the other hand, the values of adiabatic compressibilities(ϕ_{KS}) which are reported in table 3.4, are negative at all temperatures which shows that water molecules around solute i.e. L-ascorbic acid are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of L-ascorbic acid and D- Glucose and D-Fructose molecules. The plots of apparent molar volumes ϕ_v against the $C^{1/2}$ were found to be linear with the positive slopes in water and in 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures and are shown in figs. (3.3), (3.4) and (3.5) respectively

The values of partial molar volumes (ϕ_v^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^0) are determined by applying least square fitting to the plots of $\phi_v$vs the square root of molar concentration and ϕ_{KS}vs molal concentration which are deduced by using equations (1.12) and (1.19) respectively. The values of these parameters for L-ascorbic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water at different temperatures are reported in tables 3.3 and 3.4 respectively.

It is clear, from table 3.3, that the values of slopes (S_v^*) are positive in water, 0.05 molkg^{-1} D-Glucose + water and 0.05 molkg^{-1} D-Fructose + water for the entire temperature range . The positive values of slopes indicate the presence of strong solute- solute interactions and magnitude of S_v^*values decrease with increase in the temperature in water as well as in 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} Glucose + water indicating that these interactions are weakened which trait to the increase in solvation with increase in temperature. On the other hand values of partial molar volumes (ϕ_v^0) are found to increase with increase in temperature in water as well as in 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water indicating that solute-solvent interactions increase with increase in temperature.

It has also been found in the present study that the values of ϕ_{KS}^0 for L-ascorbic acid are negative which attribute to the strong attractive interactions between L- ascorbic acid and water. With increase in temperature values of ϕ_{KS}^0 become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of L-ascorbic acid and therefore at high temperature water molecules around L-ascorbic acid are more compressible than those at lower temperature.

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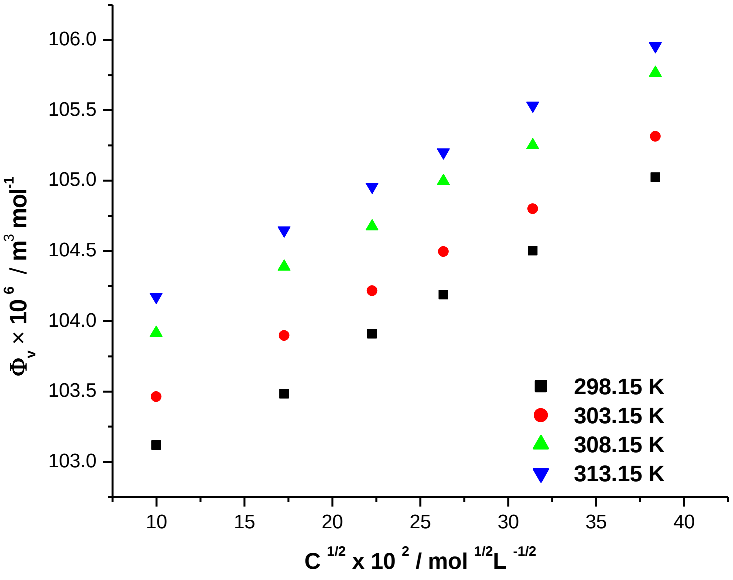

Fig. 3.3. Plot of ϕ_v vs $C^{1/2}$ for L-ascorbic acid in water at different temperatures.

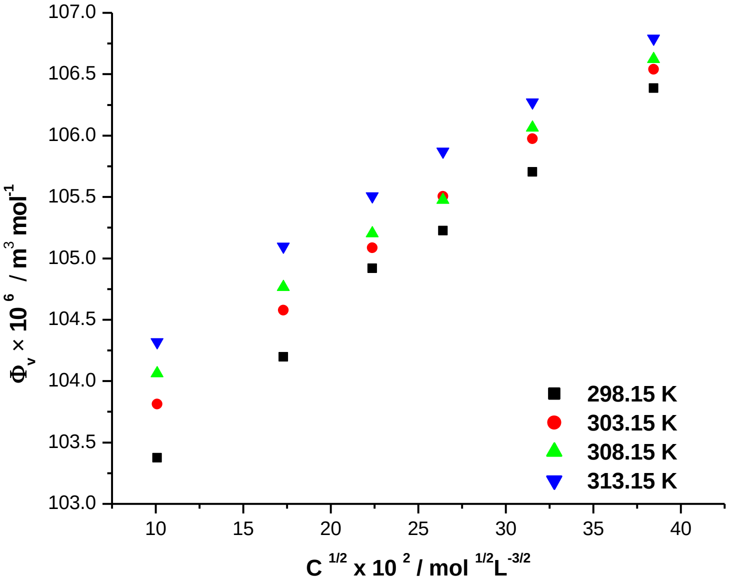

Fig. 3.4. Plot of ϕ_v vs $C^{1/2}$ for L-ascorbic acid in 0.05 mol.kg$^-$D-Glucose + water at different temperatures.

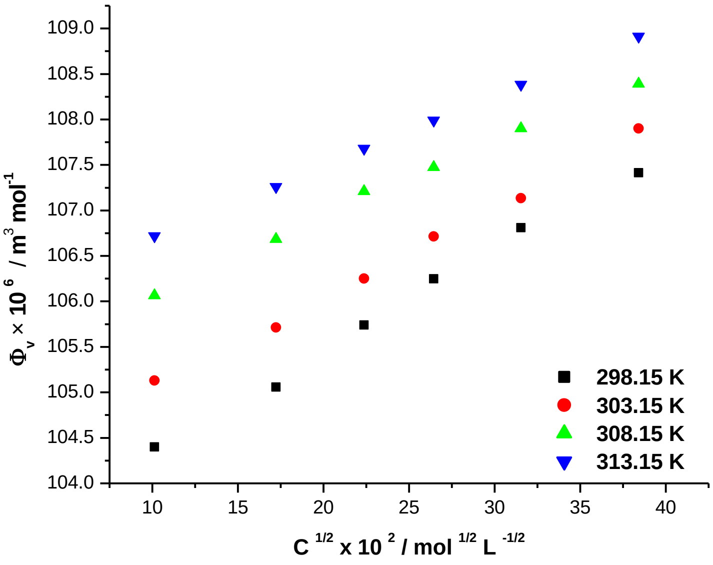

Fig. 3.5. Plot of ϕ_v vs $C^{1/2}$ for L-ascorbic acid in 0.05 mol.kg^{-1} D-Fructose + water at different temperatures.

Partial molar expansibilities(ϕ_E^0) is one of the parameter, which help in determining the structure making or breaking behavior of a solute in any of the solvent[6].

It is found that L-ascorbic acid shows similar behavior in all the compositions of D-Glucose and D-Fructose in water. So the partial molar expansibilities (ϕ_E^0), Isobaric thermal expansion coefficient (α_2), and the molar heat capacities are determined only for the lowest compositions of D-Glucose and D-Fructose in water. The temperature dependence of ϕ_v^0 at different temperatures were obtained by using the following relation:

$$\phi_v^0 = A + BT + CT^2 \tag{3.0}$$

The temperature dependence of ϕ_v^0 in water , 0.05 molkg^{-1} D-Glucose + water and 0.05 molkg^{-1} D-Fructose + water for L- ascorbic acid are as follow:

$$\phi_v^0 = -102.32 + 1.282T - 0.002T^2 \quad \text{in water} \tag{3.1}$$

$$\phi_v^0 = -017.79 + 0.701T - 0.001T^2 \quad \text{in 0.05 m D-Glucose + water} \tag{3.2}$$

$$\phi_v^0 = -034.88 + 0.761T - 0.001T^2 \quad \text{in 0.05 m D-Fructose + water} \tag{3.3}$$

Partial molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]$which is temperature dependent function of ϕ_v^0 is calculated for L-ascorbic acid in water , 0.05 molkg^{-1} D-Glucose + water and 0.05 molkg^{-1} D-Fructose + water by using relations (3.1) to (3.3) and are given in table 3.5.

Table. 3.5. Partial molar expansibilities (ϕ_E^0), for L-ascorbic acid in water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose +water mixture at different temperatures.

T (K)	**Water**	**0.05 molkg^{-1} D-Fructose + water**	**0.05 molkg^{-1} D-Glucose + water**
ϕ_E^0x 10^6(m^3 mol^{-1} K^{-1})			
298.15	0.089	0.105	0.165
303.15	0.069	0.095	0.155
308.15	0.049	0.085	0.145
313.15	0.029	0.075	0.135

From table 3.5, it is clear that the ϕ_E^0 values are positive at entire range of temperature but these values decrease with rise in temperature which shows that L-ascorbic acid is not behaving like symmetrical tetra alkyl ammonium salts[7] but behaving like common salts[8-9] because the molar volume expansibilities should decrease with the rise in temperature for a common salt. The decreasing ϕ_E^0 values indicates the absence of "packing effect"[6]. The variation of ϕ_E^0 with temperature for L-ascorbic acid in water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water is linear and as shown in fig. (3.6).

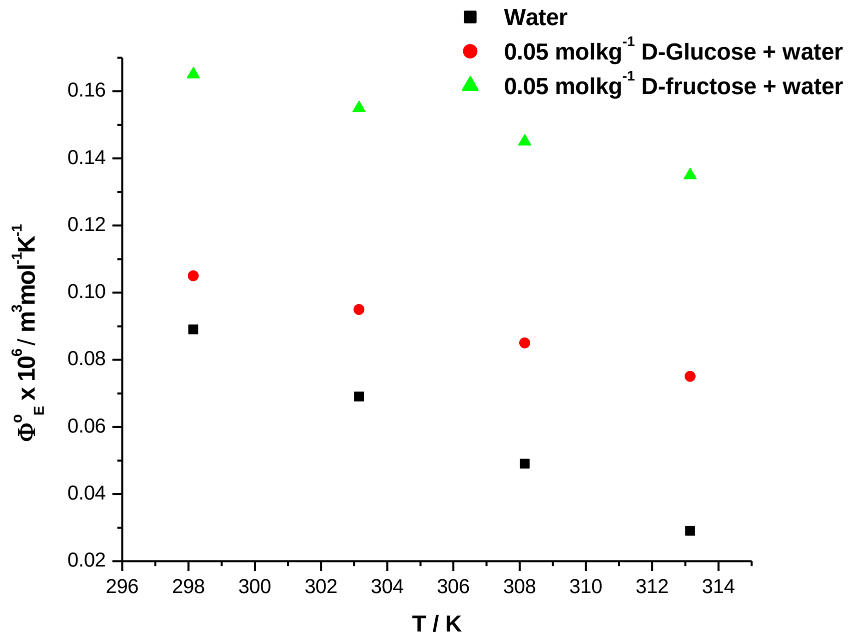

Fig.3.6. Plot of ϕ_E^0 vs temperature for L-ascorbic acid in water , 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water.

Partial molar heat capacities are determined by taking the second derivative of partial molar volume with respect to temperature at constant pressure using the general thermodynamic expression.[6]

$$(\partial C_p/\partial P)_T = -T\,(\partial^2\phi_v^0/\partial T^2)_P \qquad (3.4)$$

It is observed from relations (3.1 to 3.3) that sign of the values of $(\partial C_p/\partial P)_T$for the solutions of L-ascorbic acid is positive there by showing that L-ascorbic acid behaves as structure breaker in water as well as in binary aqueous mixtures of D-Glucose and D-Fructose. The values of $(\partial C_p/\partial P)_T$ are reported in table 3.7.The values of ϕ_v^0 andϕ_E^0 are further used to calculate the isobaric thermal expansion coefficient, α_2.[10]

$$\alpha_2 = \frac{\phi_E^0}{\phi_v^0} \qquad (3.5)$$

The calculated values of α_2 are presented in table 3.6.

Table 3.6: Partial molar heat capacities$(\partial C_p/\partial P)_T$, isobaric thermal expansion coefficient(α_2) for L-ascorbic acid in water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water mixture at different temperatures.

T (K)	**Water**		**0.05 molkg^{-1} D-Fructose + water**		**0.05 mol.kg^{-1} D-Glucose + water**	
	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	α_2 (K^{-1})
298.15	1.193	0.00087	0.596	0.00102	0.596	0.00160
303.15	1.213	0.00068	0.606	0.00092	0.606	0.00149
308.15	1.233	0.00048	0.616	0.00082	0.616	0.00137
313.15	1.253	0.00028	0.626	0.00072	0.626	0.00127

The α_2 value for L-ascorbic acid decreases with increase in temperature in water as well as in 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water mixtures suggesting that the expansibilities increase with increase in temperature for L-ascorbic acid in water as well as in 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water mixtures[10].

B. TRANSPORT PROPERTIES

In the present study, viscous flow of L-ascorbic acid has been determined in water and in binary aqueous mixtures of D-Glucose and D-Fructose at various concentrations of solute and at different temperatures. The relative viscosities of the L-ascorbic acid in water and binary aqueous mixtures of D-Glucose and D-Fructose at different temperatures were calculated by using the following equation:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t\,\rho}{t_0\rho_0} \tag{3.6}$$

Here, η, η_0, t, t_0, ρ and ρ_0 are the respective viscosities, efflux times and the densities of solution and solvent respectively.

The obtained relative viscosities were interpreted by Jones-Dole equation (1.28) where a straight line plot was obtained when $(\eta_r - 1)/C^{1/2}$ is plotted against $C^{1/2}$. The values of A and B parameters of Jones-Dole equation (1.28) were obtained using least square fit to the linear plots of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$. A parameter is the intercept which represents solute-solute interactions whereas B parameter is the slope which represents the solute- solvent interactions[11].

The viscosities, relative viscosities and values of A and B coefficients of the Jones – Dole equation for L-ascorbic acid were determined in different compositions of D-Fructose, D-Glucose in water (0.05, 0.15, 0.25, 0.35) mol.kg^{-1}at 303.15K and are reported in table 3.7.

TABLE 3.7: Viscosities(η), relative viscosities (η_r) and values of A and B coefficients of the Jones – Dole equation for L-ascorbic acid in different compositions of D-Fructose, D-Glucose in water at 303.15 K.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
0.05 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.83310	-	3.049(±0.355)	0.408(±0.013)
0.01024	10.11822	0.83893	1.00700		
0.02970	17.21412	0.84771	1.01754		
0.05023	22.36211	0.85584	1.0273		
0.07032	26.43033	0.86423	1.03737		
0.10032	31.51798	0.87562	1.05104		
0.14964	38.39112	0.89180	1.07047		
0.15 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.86720	-	2.583(±0.348)	0.415(±0.013)
0.00979	9.926781	0.87277	1.00643		
0.02995	17.34398	0.88197	1.01703		
0.05023	22.43671	0.89045	1.02681		
0.07032	26.51829	0.89935	1.03707		
0.10032	31.62249	0.91085	1.05033		
0.14964	38.51781	0.92807	1.07019		
0.25 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.90150	-	1.964(±0.391)	0.426(±0.014)
0.01024	10.18542	0.90701	1.00611		
0.02970	17.32816	0.91638	1.01651		
0.05023	22.50996	0.92496	1.02603		
0.07032	26.60465	0.93423	1.03631		
0.10032	31.72513	0.94656	1.04999		
0.14964	38.64189	0.96438	1.06975		
0.35 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.93490	-		
0.01025	10.21633	0.94030	1.00578		
0.02989	17.42742	0.94961	1.01573		
0.05026	22.57347	0.95853	1.02528		

0.07036	26.67853	0.96845	1.03588	1.450(±0.397)	0.433(±0.015)
0.10031	31.80266	0.98100	1.04931		
0.14976	38.75291	0.99955	1.06915		
0.05 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.81900	-	3.115(±0.346)	0.407(±0.013)
0.01015	10.07362	0.82474	1.00701		
0.02990	17.27184	0.83340	1.01759		
0.05018	22.35135	0.84154	1.02752		
0.07009	26.38811	0.84952	1.03727		
0.10023	31.50533	0.86075	1.05098		
0.14979	38.41334	0.87676	1.07052		
0.15 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.85300	-	2.630(±0.375)	0.414(±0.014)
0.00979	9.926835	0.85849	1.00644		
0.02995	17.34425	0.86755	1.01706		
0.05023	22.4373	0.87606	1.02703		
0.07032	26.51936	0.88455	1.03699		
0.10032	31.62416	0.89617	1.05061		
0.14964	38.52104	0.91274	1.07004		
0.25 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.88700	-	2.134(±0.397)	0.423(±0.015)
0.01025	10.18868	0.89257	1.00628		
0.02982	17.35993	0.90167	1.01654		
0.05023	22.50808	0.91055	1.02655		
0.07032	26.60270	0.91927	1.03638		
0.10032	31.72370	0.93172	1.05042		
0.14964	38.64131	0.94888	1.06977		
0.35 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.92010	-	1.444(±0.375)	0.434(±0.014)
0.01025	10.21418	0.92543	1.00579		
0.02989	17.42385	0.93460	1.01576		
0.05026	22.56900	0.94339	1.02531		
0.07036	26.67350	0.95302	1.03578		
0.10031	31.79708	0.96555	1.04939		
0.14976	38.74732	0.98386	1.06930		

m^a (mol.kg^{-1}) molality of L-ascorbic acid in different solvent systems

The relative viscosity data at different compositions has been analyzed with the help of Jones Dole equation (1.28). The values of coefficients A and B are obtained by plotting graphs between $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ where A is the intercept and B is the slope for the respective graph. The values of A and B parameters for L-ascorbic acid in different compositions of D-Fructose and D-Glucose in water at 303.15 K are recorded in table 3.7. Sample plots of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$for L-ascorbic acid in different compositions of D-Fructose and D-Glucose in water are shown in figures 3.7 and 3.8 respectively.

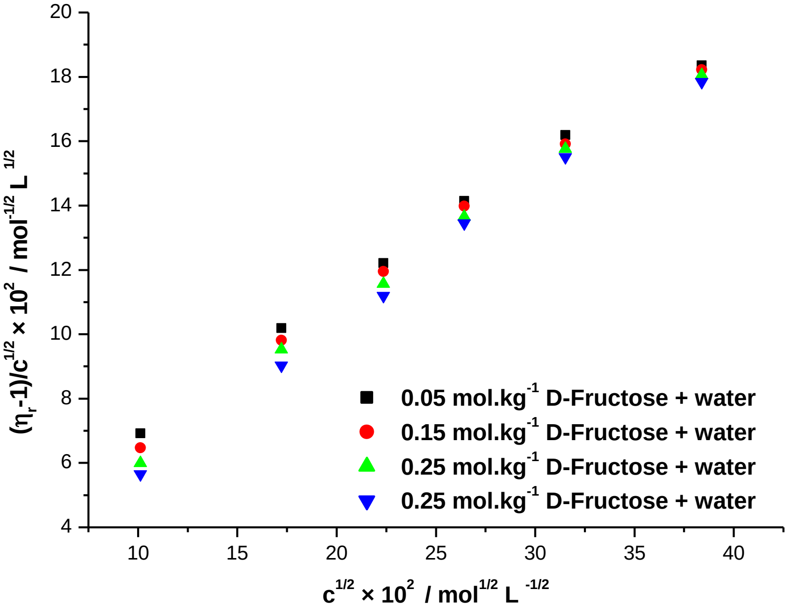

Fig. 3.7 . Plot of $(\eta_r\text{-}1)/ C^{1/2}$ vs $C^{1/2}$ for L-ascorbic acid in different compositions of D-Fructose in water at 303.15 K

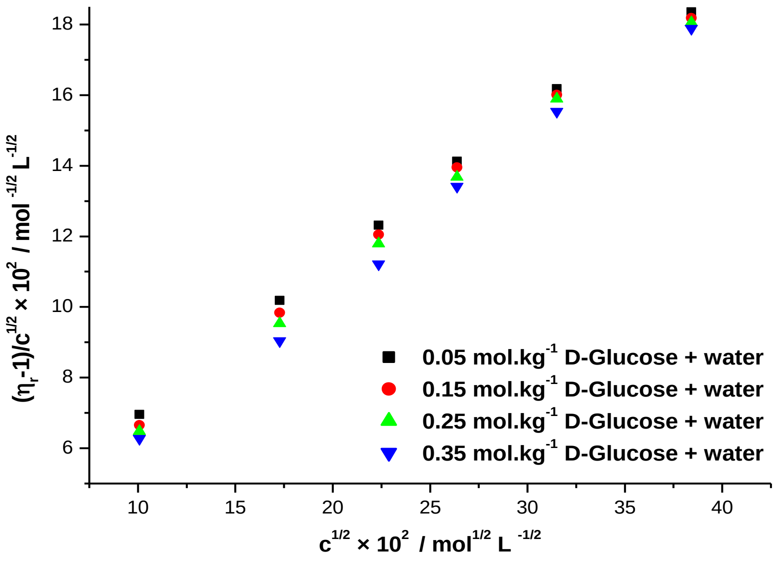

Fig. 3.8. Plot of $(\eta_{r}\text{-}1)/\ C^{1/2}$ vs $C^{1/2}$ for L-ascorbic acid in different compositions of D-Glucose in Water at 303.15 K.

The values of A-coefficient in table 3.7 are positive and decrease with the increase in the concentration of D-Fructose and D-Glucose in water indicating the weakening of solute-solute interactions with the increase of D-Fructose and D-Glucose content in water. Also, it is found that values of B-coefficient are positive indicating the presence of strong solute-solvent interactions. This may be attributed to the strong solvation of L-ascorbic acid in the binary aqueous mixtures of D-Fructose and D-Glucose in water. From the table 3.7, it is clear that B-coefficient values further increase with the increase of D-Fructose and D-Glucose content in water at 303.15 K, thereby showing that solute – solvent interactions are further strengthened with the increase of D-Fructose and D-Glucose content in water. So, it is clear that there is a great change in the solute - solvent interactions when we switch from lower to higher composition of the solvents[12-13]. In other words the solvation is enhanced as the composition of D-Fructose and D-Glucose in water increases.

The analysis of data was also done on the basis of transition state theory proposed by Feakins *et.al*[14]. The B-coefficient in terms of transition state theory is given by the relation.

$$B = \frac{\overline{V_1^0} - \overline{V_2^0}}{1000} + \frac{\overline{V_1^0}}{1000}\left[\frac{\Delta\mu_2^0 - \Delta\mu_1^0}{RT}\right] \qquad (3.7)$$

Where $\overline{V_1^0}$ is the mean volume of the solvent, $\overline{V_2^0}$ is the partial molar volume of the L-ascorbic acid, $\Delta\mu_1^{0^*}$ is the free energy of activation per mole of pure solvent and $\Delta\mu_2^{0^*}$ is the contribution of the solute to the free energy of activation for the viscous flow of solution respectively and all these parameters were determined by the following relations:

$$\Delta\mu_1^{0^*} = \mathrm{RTIn}\left(\eta_0\overline{V_1^0}/\mathrm{hN}\right) \tag{3.8}$$

$$\Delta\mu_2^{0^*} = \Delta\mu_1^{0^*} + \mathrm{RT}/\overline{V_1^0}\left[1000\mathrm{B} - \left(\overline{V_1^0} - \overline{V_2^0}\right)\right] \tag{3.9}$$

Where T is the absolute temperature, R is the universal gas constant, h is the Planck's constant, η_0 is the viscosity of the solvent and N is the Avogadro number.

The values of $\Delta\mu_1^{0^*}$ were determined using relation (3.8) and are reported in table 3.8 for mixed solvents, each solvent mixture was treated as pure and the molar volume is taken as a mean volume of the solvent and given as

$$\overline{V_1^0} = (x_1M_1 + x_2M_2)/\rho_1 \tag{3.10}$$

Where x_1, M_1 are mole fraction and molar mass of the water and x_2, M_2 are the mole fractions and molar mass of the D-Fructose and D-Glucose respectively where as ρ_1 is the density of solvent mixtures (D-Fructose + water and D-Glucose + water). The values of $\overline{V_2^0}$ for L-ascorbic acid were determined using the density data (discussed in previous section). The parameters, $\Delta\mu_2^{0^*}$ and $\overline{V_1^0}$ were determined by using relations (3.9) and (3.10) and are reported in table 3.8.

TABLE 3.8: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for L-ascorbic acid in different composition of D-Fructose + water and D-Glucose + water at 303.15 K.

m (mol.kg^{-1})	$\overline{V_1^0} \times 10^6$ (m^3.mol^{-1})	$\overline{V_2^0} \times 10^6$ (m^3.mol^{-1})	$\Delta\mu_1^{0^*}$ (kJ.mol^{-1})	$\Delta\mu_2^{0^*}$ (kJ.mol^{-1})
D-Fructose + water				
0.05	18.12	104.08	61.39	68.76
0.15	18.12	104.18	61.49	69.75
0.25	18.13	104.32	61.59	71.26
0.35	18.15	104.85	61.68	72.22
D-Glucose + water				
0.05	18.12	102.90	61.34	67.76
0.15	18.12	103.12	61.45	69.46
0.25	18.13	103.40	61.55	70.72
0.35	18.15	104.14	61.64	71.70

It is evident from the above table that values of $\Delta\mu_1^{0^*}$ do not change much with the change in composition of D-Fructose and D-Glucose in water at 303.15 K i.e. the values of$\Delta\mu_1^{0^*}$are practically held constant in the entire composition range of D-Fructose and D-Glucose in water at 303.15 K. It is clear that the values of $\Delta\mu_2^{0^*}$are positive and increase with solvent composition of D-Fructose and D-Glucose in water at 303.15 K suggesting that the transition state formation is less favored in the presence of L-ascorbic acid and is followed by breaking or distortions of the intermolecular bonds[14].

Effect of temperature

As the behavior of L-ascorbic acid is similar for different compositions of D-Fructose, D-Glucose in water at 303.15 K, so only lower composition i.e. 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose +water was taken for analyzing the effect of temperature. The viscosity and the relative viscosity data along with values of A and B coefficients of the Jones – Dole equation at different temperatures is given in table 3.9.

TABLE 3.9: Viscosities (η), relative viscosities (η_r) and the values of A and B coefficients of the Jones – Dole equation for L-ascorbic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
Water 298.15 K					
0.01001	9.98507	0.90021	1.00729	3.187(±0.399)	0.396(±0.015)
0.02998	17.26247	0.90893	1.01704		
0.04997	22.26338	0.91672	1.02575		
0.06994	26.31168	0.92637	1.03655		
0.09993	31.40194	0.93854	1.05018		
0.14997	38.36864	0.95607	1.06978		
303.15 K					
0.01001	9.97807	0.80607	1.00670	2.354(±0.343)	0.402(±0.132)
0.02998	17.25030	0.81314	1.01553		
0.04997	22.24769	0.82022	1.02437		
0.06994	26.29310	0.82814	1.03427		
0.09993	31.37970	0.83864	1.04738		
0.14997	38.34134	0.85554	1.06850		

308.15 K					
0.01001	9.969956	0.72690	1.00609	1.427(±0.647)	0.413(±0.024)
0.02998	17.23621	0.73234	1.01362		
0.04997	22.22947	0.73868	1.0224		
0.06994	26.27145	0.74672	1.03352		
0.09993	31.35379	0.75541	1.04556		
0.14997	38.30943	0.77036	1.06624		
313.15 K					
0.01001	9.960841	0.65952	1.00536	0.557(±0.735)	0.420(±0.028)
0.02998	17.22044	0.66424	1.01255		
0.04997	22.20910	0.66920	1.02012		
0.06994	26.24743	0.67648	1.03122		
0.09993	31.32499	0.68510	1.04436		
0.14997	38.27443	0.69786	1.06381		
0.05 mol.kg^{-1} D-Fructose + water **298.15 K**					
0.01024	10.12541	0.93659	1.00774	3.767(±0.248)	0.400(±0.009)
0.02970	17.22644	0.94656	1.01846		
0.05023	22.37814	0.95613	1.02876		
0.07032	26.44934	0.96474	1.03802		
0.10032	31.54057	0.97819	1.05250		
0.14964	38.41925	0.99682	1.07254		
303.15 K					
0.01024	10.11822	0.83893	1.00700	3.049(±0.355)	0.408(±0.013)
0.02970	17.21412	0.84771	1.01754		
0.05023	22.36211	0.85584	1.0273		
0.07032	26.43033	0.86423	1.03737		
0.10032	31.51798	0.87562	1.05104		
0.14964	38.39112	0.89180	1.07047		
308.15 K					
0.01024	10.10986	0.75715	1.00658	2.376(±0.368)	0.417(±0.014)
0.02970	17.19977	0.76453	1.0164		
0.05023	22.34329	0.77145	1.02559		
0.07032	26.40806	0.77953	1.03633		
0.10032	31.49115	0.78968	1.04983		
0.14964	38.35867	0.80425	1.06919		
313.15 K					
0.01024	10.10051	0.68746	1.00536	1.099(±0.275)	0.421(±0.010)
0.02970	17.1838	0.69364	1.01439		
0.05023	22.32252	0.69950	1.02297		
0.07032	26.38341	0.70657	1.03330		
0.10032	31.46164	0.71472	1.04522		
0.14964	38.32237	0.72870	1.06567		
0.05 mol.kg^{-1} D-Glucose + water					

298.15 K					
0.01015	10.08075	0.92097	1.00774	3.756(±0.321)	0.401(±0.012)
0.02990	17.28409	0.93066	1.01834		
0.05018	22.36715	0.94037	1.02897		
0.07009	26.40686	0.94855	1.03791		
0.10023	31.52777	0.96229	1.05295		
0.14979	38.44047	0.98020	1.07255		
303.15 K					
0.01015	10.07362	0.82474	1.00701	3.115(±0.346)	0.407(±0.013)
0.02990	17.27184	0.83340	1.01759		
0.05018	22.35135	0.84154	1.02752		
0.07009	26.38811	0.84952	1.03727		
0.10023	31.50533	0.86075	1.05098		
0.14979	38.41334	0.87676	1.07052		
308.15 K					
0.01015	10.06539	0.74408	1.00660	2.309(±0.340)	0.419(±0.013)
0.02990	17.25772	0.75125	1.01630		
0.05018	22.33312	0.75806	1.02552		
0.07009	26.36673	0.76589	1.03611		
0.10023	31.47972	0.77604	1.04984		
0.14979	38.38221	0.79069	1.06966		
313.15 K					
0.01015	10.05613	0.67521	1.00538	1.124(±0.233)	0.426(±0.008)
0.02990	17.24181	0.68120	1.01429		
0.05018	22.31252	0.68794	1.02433		
0.07009	26.3423	0.69382	1.03308		
0.10023	31.45075	0.70224	1.04562		
0.14979	38.34698	0.71630	1.06655		

m^a (mol.kg^{-1}) is the molality of L-ascorbic acid

The plots of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$ have been found to be linear at all the four different temperatures. Sample plots for L-ascorbic acid in water, 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water at different temperatures are shown in figures (3.9), (3.10) and (3.11) respectively. This is in accordance to the Jones – Doles equation.

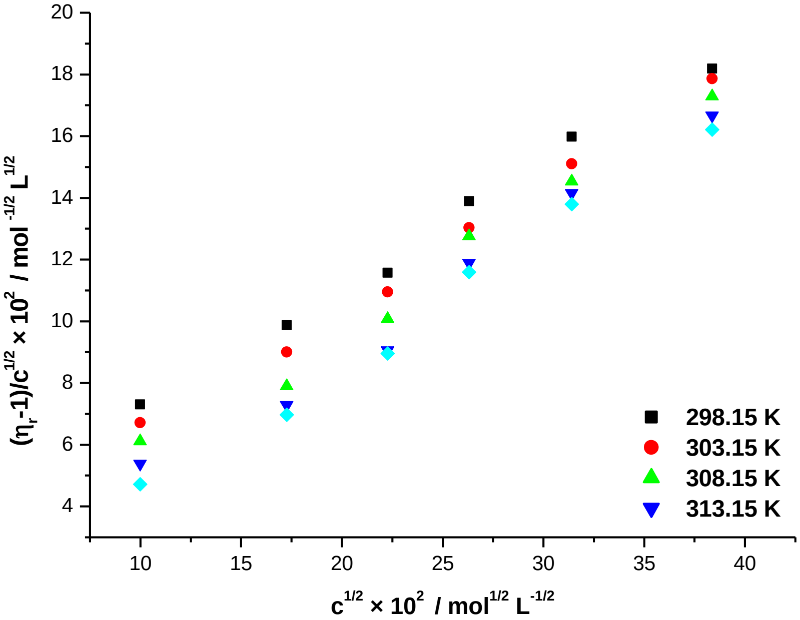

Fig. 3.9. Plot of$(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for L-ascorbic acid in water at different temperatures.

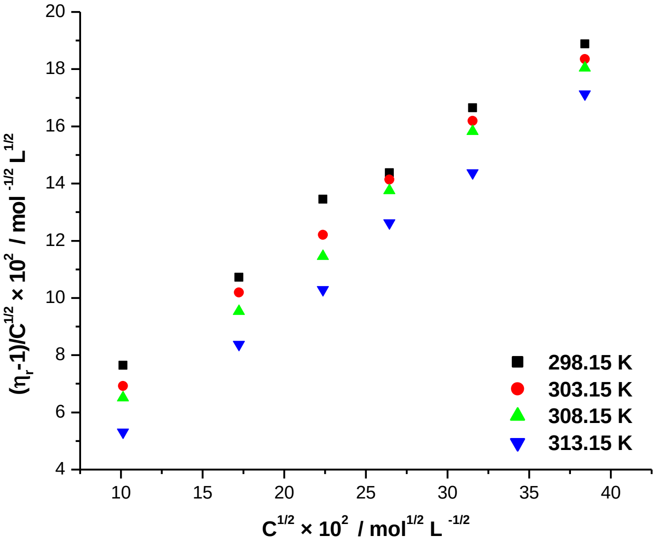

Fig. 3.10. Plot of$(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for L-ascorbic acid in 0.05 mol.kg^{-1}D-Fructose + water at different temperatures.

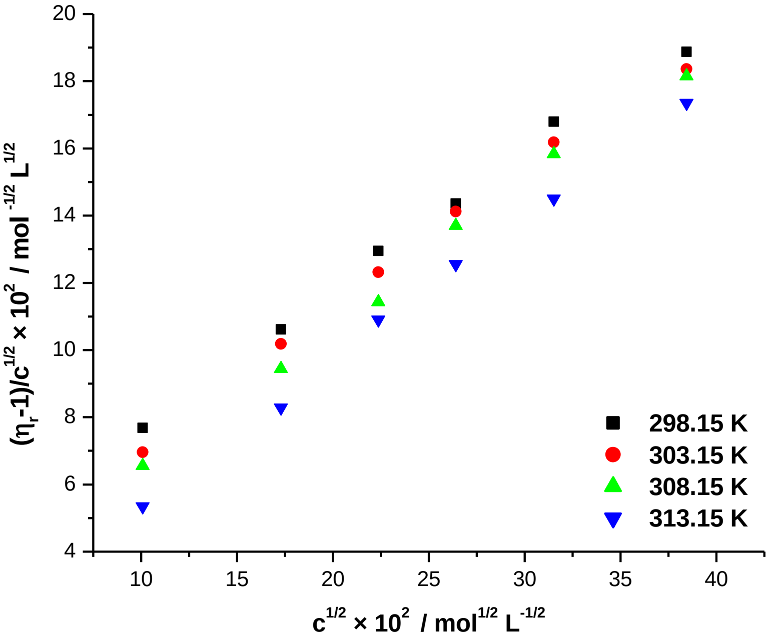

Fig. 3.11. Plot of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$for L-ascorbic acid in 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

The values of A-coefficient reported in table 3.9 are positive for the entire range of temperature indicating the presence of solute-solute interactions. Further the values of A-coefficient decrease with rise in temperature in water, 0.05 mol.kg^{-1} D-Fructose + water as well as in 0.05 mol.kg^{-1} D-Glucose + water indicating the weakening of solute-solute interactions with the rise in temperature. Also the values of B-coefficient are positive in water, 0.05 mol.kg^{-1} D-Fructose + water as well as in 0.05 mol.kg^{-1} D-Glucose + water at all temperatures thereby showing the presence of strong solute-solvent interactions. Further the values of B-coefficient increase with the rise in temperature which suggest that solute-solvent interactions are further strengthened with the rise in temperature[15]. The viscosity data has also been examined by applying the transition state theory at different temperatures from 298.15-318.15 K and the calculated values of$\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ have also been recorded in table 3.10.

TABLE 3.10: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$and $\Delta\mu_2^{0^*}$ for L-ascorbic acid in 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

T (K)	$\overline{V_1^0} \times 10^6$ **(m^3.mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3.mol^{-1})**	$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$\Delta\mu_2^{0^*}$ **(kJ.mol^{-1})**
0.05 mol.kg^{-1}D-Fructose + water				
298.15	18.12	103.27	60.65	66.43
303.15	18.15	104.08	61.39	68.67
308.15	18.17	105.28	62.15	71.12
313.15	18.21	105.93	62.91	72.80
0.05 mol.kg^{-1}D-Glucose + water				
298.15	18.12	102.39	60.60	65.90
303.15	18.15	102.89	61.35	67.67
308.15	18.18	103.17	62.10	69.84
313.15	18.21	103.54	62.86	71.74

According to Feakins model[14] increase in the values of $\Delta\mu_2^{0^*}$with temperature leads to the structure breaking ability of the solute and simultaneously transition state formation is less favoured due to breaking or distortion of intermolecular bonds in the solvent mixture by the presence of solute. In the present study values of$\Delta\mu_2^{0^*}$increase with increase in temperature supporting the structure breaking ability of L-ascorbic acid and simultaneously transition state formation is less favoured in 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water mixtures respectively by the presence of L-ascorbic acid.

TABLE 3.11: Values of ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$),T$\Delta S_2^{0^*}$and $\Delta H_2^{0^*}$for L-ascorbic acid in 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

T (K)	$\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$T.\Delta S_2^{0^*}$ **(kJ.mol^{-1})**	$\Delta H_2^{0^*}$ **(kJ.mol^{-1})**
0.05 mol.kg^{-1}D-Fructose + water			
298.15	5.79	-133.57	-67.14
303.15	7.28	-135.81	-67.14
308.15	8.98	-138.05	-66.93
313.15	9.89	-140.29	-67.49
0.05 mol.kg^{-1} D-Glucose + water			
298.15	5.30	-125.82	-59.92
303.15	6.32	-127.93	-60.26

308.15	7.73	-130.04	-60.20
313.15	8.88	-132.15	-60.41

The quantity ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$), the change in the activation energy per mole of solute, on replacing the one mole of solvent by one mole of solute at infinite dilution, is given in table 3.11. Since the quantity ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$) is positive and increase for L-ascorbic acid in both 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water solvent systems at different temperatures, so it may be concluded that transitions state is accompanied by breaking/distortion of intermolecular bonds. In other word transition state is less favored in the presence of L-ascorbic acid in the entire temperature range studied here. The values of$\Delta\mu_2^{0^*}$at various temperatures are also used to calculate the entropy of activation $\Delta S_2^{0^*}$ for L-ascorbic acid from the following equations[16]

$$\frac{d\left(\Delta\mu_2^{0^*}\right)}{dT} = -\Delta S_2^{0^*} \qquad (3.11)$$

The $\Delta S_2^{0^*}$values have been determined from the slopes of linear plots of $\Delta\mu_2^{0^*}$ vs temperature. The values of enthalpy of activation i.e. $\Delta H_2^{0^*}$ has been determined by relation (3.12):

$$\Delta H_2^{0^*} = \Delta\mu_2^{0^*} + T.\Delta S_2^{0^*} \qquad (3.12)$$

The $T.\Delta S_2^{0^*}$ and $\Delta H_2^{0^*}$ values at different temperatures are recorded in table 3.11.As both the parameters enthalpy of activation and entropy of activation are found negative for L-ascorbic acid which indicates that the transition state is associated with bond formation between solute and solvent molecules[14].

SECTION II

THERMODYNAMIC AND TRANSPORT PROPERTIES OF THIAMINE HYDROCHLORIDE IN WATER ANDBINARY AQUEOUS MIXTURES OF D-GLUCOSE AND D-FRUCTOSE

The present section describes the thermodynamic and transport properties such as partial molar volumes, partial molar adiabatic compressibilities, partial molar expansibilities, viscosity A and B coefficients of Jones Dole equation, activation energy parameters etc. for thiamine hydrochloride in water and binary aqueous mixtures of D-Fructose and D-Glucose.

For the sake of convenience the section has been further divided into two parts.

A. THERMODYNAMIC PROPERTIES
B. TRANSPORT PROPERTIES

A. THERMODYNAMIC PROPERTIES

Thermodynamic properties such as partial molar volumes, partial molar adiabatic compressibilities and partial molar expansibilities were determined using density and speed of sound data of thiamine hydrochloride in water and binary aqueous mixtures of D-Fructose and D-Glucose. Present study includes the effect of composition of D-Fructose and D-Glucose in water at one temperature i.e. 303.15 K and above mentioned properties has also been determined at different temperatures to analyze the effect of temperature. The densities (ρ), apparent molar volumes (ϕ_v), sound velocities (U) and apparent molar adiabatic compressibilities (ϕ_{ks}) of thiamine hydrochloride in binary aqueous mixtures of D- glucose and D-Fructose (0.05, 0.15, 0.25 and 0.35) mol.Kg^{-1} at 303.15K have been measured and are reported in tables 3.12 and 3.13 respectively.

Table 3.12: Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes(ϕ_v^0) and experimental slopes (S_v^*) of thiamine hydrochlorideín different compositions of D-Fructose and D-Glucose in water at 303.15 K.

m^a (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x 10^{-3} (kg.m^{-3})	ϕ_v x 10^6 (m^3.mol^{-1})	ϕ_v^0 x 10^6 (m^3.mol^{-1})	S_v^* x 10^4 (m^3.L$^{1/2}$.mol$^{-3/2}$)
0.05 mol.kg^{-1} D-Fructose + water					
0.01011	10.04713	1.001869	237.70	236.83(±0.010)	0.085(±0.000)
0.02997	17.25777	1.003807	238.32		
0.05001	22.24011	1.005729	238.75		
0.07001	26.25186	1.007617	239.10		

0.10090	31.40096	1.010481	239.55		
0.14994	38.05925	1.014911	240.10		
0.15 mol.kg^{-1} D-Fructose + water					
0.00989	9.970691	1.008557	238.39	237.53(±0.019)	0.085(±0.000)
0.02997	17.31506	1.010483	239.03		
0.05013	22.33986	1.012382	239.47		
0.07022	26.37666	1.014248	239.78		
0.10012	31.38359	1.016968	240.25		
0.14984	38.16819	1.021378	240.81		
0.25 mol.kg^{-1} D-Fructose + water					
0.01014	10.12863	1.015188	239.60	238.72(±0.034)	0.083(±0.001)
0.02989	17.34819	1.017041	240.15		
0.05013	22.41173	1.018907	240.56		
0.07012	26.44225	1.020719	240.91		
0.10011	31.48096	1.023387	241.35		
0.14984	38.28596	1.027691	241.94		
0.35 mol.kg^{-1} D-Fructose + water					
0.01011	10.13936	1.020347	240.87	240.02(±0.015)	0.082(±0.000)
0.02997	17.41488	1.022168	241.45		
0.05006	22.45197	1.023975	241.90		
0.07008	26.49992	1.025748	242.23		
0.10011	31.55734	1.028359	242.64		
0.14997	38.39265	1.032574	243.20		
0.05 mol.kg^{-1} D-Glucose + water					
0.01009	10.03708	1.001841	237.31	236.43(±0.044)	0.091(±0.001)
0.02997	17.25759	1.003786	238.02		
0.05003	22.24431	1.005714	238.49		
0.07011	26.27011	1.007613	238.87		
0.10009	31.27753	1.010399	239.32		
0.14996	38.06179	1.014918	239.87		
0.15 mol.kg^{-1} D-Glucose + water					
0.00998	10.01573	1.008543	237.68	236.79(±0.023)	0.089(±0.000)
0.02997	17.31498	1.010474	238.34		
0.05005	22.32229	1.012379	238.79		
0.07008	26.35096	1.014248	239.17		
0.10003	31.37034	1.016994	239.61		
0.14998	38.1866	1.021455	240.18		
0.25 mol.kg^{-1} D-Glucose + water					
0.01001	10.06259	1.014961	238.34		

0.02998	17.37247	1.016859	238.96	237.47(±0.017)	0.086(±0.000)
0.05012	22.40768	1.018738	239.42		
0.07005	26.4274	1.020568	239.77		
0.10030	31.50849	1.023299	240.17		
0.14989	38.29124	1.027648	240.77		
0.35 mol.kg^{-1} D-Glucose + water					
0.01015	10.15725	1.019930	239.10	238.26(±0.032)	0.085(±0.001)
0.02999	17.41736	1.021784	239.77		
0.05013	22.46364	1.023632	240.21		
0.07014	26.50701	1.025439	240.55		
0.10011	31.55335	1.028099	240.95		
0.14996	38.38818	1.032399	241.52		

m^a (mol.kg^{-1}) molality of Thiamine hydrochloride in different solvent systems

Table 3.13: Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities (ϕ^0_{KS}) and experimental slopes (S^*_K) of thiamine hydrochloride in different compositions of D-Fructose and D-Glucose in Water at 303.15 K.

m^a (mol.kg^{-1})	U (m.s^{-1})	K_S x 10^{10} (kg^{-1}.m.s^2)	ϕ_{KS} x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	ϕ^0_{KS} x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	S^*_K x 10^6 (kg.m^3.mol^{-2}.G.Pa^{-1})
0.05 mol.kg^{-1} D-Fructose + water					
0.01011	1501.21	4.422	-40.12	-40.91(±0.832)	-26.15(±10.065)
0.02997	1501.99	4.409	-43.10		
0.05001	1502.87	4.396	-43.78		
0.07001	1503.63	4.383	-44.11		
0.10090	1504.94	4.363	-44.43		
0.14994	1507.14	4.331	-44.77		
0.15 mol.kg^{-1} D-Fructose + water					
0.00989	1519.09	4.296	-39.10	-40.55(±0.842)	-26.24(±10.204)
0.02997	1519.94	4.283	-42.08		
0.05013	1520.85	4.270	-42.73		
0.07022	1521.41	4.259	-43.06		
0.10012	1522.72	4.240	-43.35		
0.14984	1524.63	4.211	-43.69		
0.25 mol.kg^{-1} D-Fructose + water					
0.01014	1525.44	4.233	-38.967	-40.33(±0.795)	-24.95(±9.635)

0.02989	1526.27	4.220	-41.769		
0.05013	1527.39	4.206	-42.413		
0.07012	1527.87	4.196	-42.728		
0.10011	1528.99	4.179	-43.019		
0.14984	1531.28	4.149	-43.34		
0.35 mol.kg^{-1} D-Fructose + water					
0.01011	1531.41	4.178	-38.68	-40.033(±0.785)	-24.46(±9.514)
0.02997	1532.28	4.166	-41.45		
0.05006	1533.76	4.151	-42.08		
0.07008	1533.58	4.145	-42.38		
0.10011	1536.04	4.121	-42.67		
0.14997	1538.19	4.093	-42.98		
0.05 mol.kg^{-1} D-Glucose + water					
0.01009	1501.19	4.422	-40.11	-40.90(±0.835)	-26.22(±10.115)
0.02997	1502.17	4.408	-43.10		
0.05003	1502.84	4.396	-43.78		
0.07011	1503.66	4.383	-44.12		
0.10009	1504.79	4.364	-44.43		
0.14996	1506.71	4.334	-44.78		
0.15 mol.kg^{-1} D-Glucose + water					
0.00998	1518.97	4.297	-39.17	-40.60(±0.830)	-25.87(±10.058)
0.02997	1519.81	4.284	-42.11		
0.05005	1520.63	4.271	-42.76		
0.07008	1521.48	4.259	-43.09		
0.10003	1522.61	4.241	-43.39		
0.14998	1524.75	4.210	-43.72		
0.25 mol.kg^{-1} D-Glucose + water					
0.01001	1525.58	4.233	-38.91	-40.30(±0.808)	-25.29(±9.787)
0.02998	1526.19	4.222	-41.77		
0.05012	1526.92	4.210	-42.41		
0.07005	1527.63	4.198	-42.73		
0.10030	1528.58	4.182	-43.03		
0.14989	1530.81	4.152	-43.35		
0.35 mol.kg^{-1} D-Glucose + water					
0.01015	1531.28	4.181	-38.70	-40.04(±0.780)	-24.48(±9.452)
0.02999	1532.26	4.168	-41.45		
0.05013	1533.59	4.153	-42.08		
0.07014	1534.32	4.142	-42.39		
0.10011	1536.15	4.121	-42.68		

0.14996	1538.36	4.092	-42.99		

m^a (mol.kg^{-1}) molality of Thiamine hydrochloride in different solvent systems

It is clear from the tables 3.12 and 3.13 that the density and sound velocity values increase with increase in concentration of thiamine hydrochloride in different compositions of D-Glucose and D-Fructose in water. The density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities by using the equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.12 and all the values are positive and increases in magnitude with increase in concentration of thiamine hydrochloride in all compositions of D-Glucose and D-Fructose in water indicating the presence of great solute - solvent interaction[1-2]. Also, the values of adiabatic compressibilities (ϕ_{KS}) which are reported in table 3.13, are negative in all compositions of D- Glucose and D-Fructose in water which shows that water molecules around solute i.e. thiamine hydrochloride are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of thiamine hydrochloride and D- Glucose and D-Fructose molecules.

Linear plots have been found in accordance with Masson’s equation (1.12) when the apparent molar volume values are plotted against root of molar concentrations of thiamine hydrochloride in different compositions of D- Glucose and D-Fructose in water. Sample plots for thiamine hydrochloride in different compositions of D- Glucose and D-Fructose in water at 303.15K are shown in fig. (3.12) and (3.13) respectively.

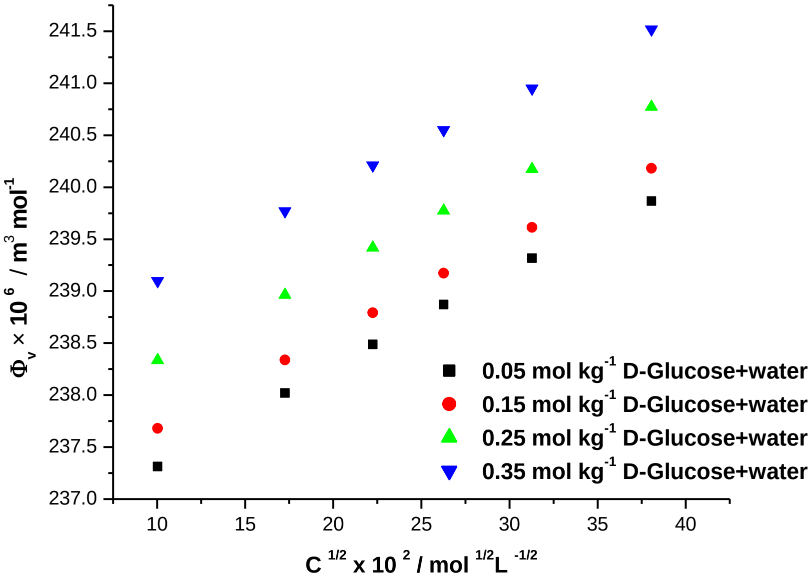

Fig. 3.12. Plot of ϕ_V vs $C^{1/2}$ for thiamine hydrochloride in different compositions of D- Glucose in water at 303.15K.

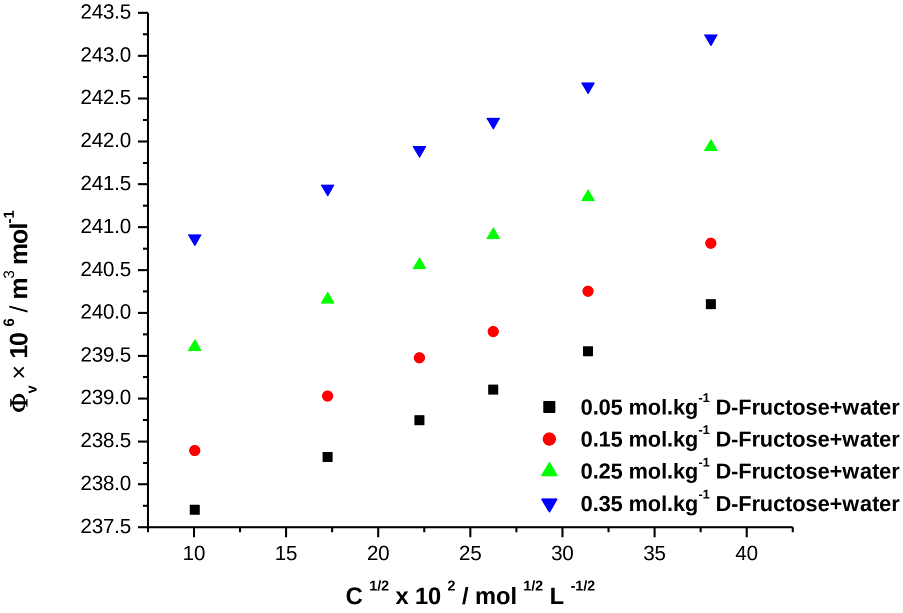

Fig. 3.13. Plot of ϕ_V vs $C^{1/2}$ for thiamine hydrochloride in different compositions of D- Fructose in water at 303.15K

Values of partial molar volumes (ϕ_v^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^0)are determined by applying least square fitting to the plots of $\phi_v$vs square root of molar concentration and ϕ_{KS}vs molal concentration which are determined by using equations (1.12) and (1.19) respectively. The values of these parameters for thiamine hydrochloride in different compositions of D- Glucose and D-Fructose in water at 303.15 K are reported in tables 3.12 and 3.13 respectively.

It is clear, from table 3.12, that the values of slopes (S_v^*) are positive in different compositions of D-Glucose and D-Fructose in water at 303.15 K indicating the presence of strong solute- solute interactions and magnitude of S_v^*values further decrease with increase in compositions of D-Glucose and D-Fructose in water, indicating that these interactions are weakened which trait to the increase in solvation. On the other hand values of ϕ_v^0 are positive and increase with increase in compositions of D-Glucose and D-Fructose in water showing that solute - solvent interactions further increase on the addition of D-Glucose and D-Fructose in water. On comparing the magnitudes of ϕ_v^0 values with the values of S_v^*, ϕ_v^0values are more thanS_v^* which proves that solute - solvent interactions dominate over the solute- solute interactions in mixtures of D-Glucose and D-Fructose in water. The magnitude of ϕ_{KS}^0 values indicates solute-solvent interactions[4].It has been found in the present study that the values of ϕ_{KS}^0 for thiamine hydrochloride are negative which attribute to the strong interactions between thiamine hydrochloride and water. With increase in compositions of D-Glucose and D-Fructose in water values ofϕ_{KS}^0 become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of thiamine hydrochloride and therefore at high concentrations of D-Glucose and D-Fructose, water molecules around thiamine hydrochloride are more compressible than those at lower concentrations.

Effect of temperature

As the behavior of thiamine hydrochloride was found similar for entire range of compositions of D-Glucose and D-Fructose in water at one temperature. So, effect of temperature has been studied on the lowest composition of D- Glucose in water and D-Fructose in water. Densities (ρ), apparent molar volumes (ϕ_v), sound velocities (U), and apparent molar adiabatic compressibilities (ϕ_{ks}) of thiamine hydrochloride in water, 0.05 mol.kg^{-1} D- Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water at different temperatures have been measured and are reported in tables 3.14 and 3.15 respectively.

Table 3.14: Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes(ϕ_v^0) and experimental slopes (S_v^*) of thiamine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

m^a (mol.kg^{-1})	**$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)**	**ρ x 10^{-3} (kg.m^{-3})**	**ϕ_v x 10^6 (m^3.mol^{-1})**	**ϕ_v^0 x 10^6 (m^3.mol^{-1})**	**S_v^* x 10^4 (m^3.L$^{1/2}$.mol$^{-3/2}$)**
Water 298.15 K					
0.00999	9.968524	0.998061	235.93	234.94(±0.045)	0.103(±0.001)
0.02997	17.22545	1.000051	236.73		
0.04998	22.19237	1.002007	237.26		
0.06995	26.19279	1.003928	237.67		
0.09998	31.20462	1.006764	238.18		
0.14984	37.98039	1.011352	238.81		
303.15 K					
0.00999	9.961495	0.996654	237.12	236.20(±0.022)	0.092(±0.000)
0.02997	17.21319	0.998628	237.80		
0.04998	22.17647	1.000572	238.22		
0.06995	26.17386	1.002478	238.64		
0.09998	31.18191	1.005299	239.07		
0.14984	37.95226	1.009854	239.70		
308.15 K					
0.00999	9.953346	0.995024	238.76	237.86(±0.025)	0.090(±0.000)
0.02997	17.19890	0.996971	239.41		
0.04998	22.15777	0.998885	239.90		
0.06995	26.15153	1.000768	240.24		
0.09998	31.15471	1.003546	240.71		
0.14984	37.91819	1.008042	241.28		
313.15 K					
0.00999	9.944214	0.993199	239.93	239.03(±0.058)	0.089(±0.002)
0.02997	17.18300	0.995128	240.58		
0.04998	22.13718	0.997030	240.95		
0.06995	26.12696	0.998888	241.44		
0.09998	31.12516	1.001643	241.86		
0.14984	37.88167	1.006101	242.41		

0.05 mol.kg^{-1}D-Fructose + water **298.15 K**					
0.01011	10.05425	1.003291	237.11	236.10(±0.019)	0.101(±0.000)
0.02997	17.27002	1.005233	237.85		
0.05001	22.25587	1.007155	238.39		
0.07001	26.27044	1.009044	238.77		
0.10090	31.4231	1.011906	239.28		
0.14994	38.08567	1.016321	239.95		
303.15 K					
0.01011	10.04713	1.001869	237.70	236.83(±0.010)	0.085(±0.000)
0.02997	17.25777	1.003807	238.32		
0.05001	22.24011	1.005729	238.75		
0.07001	26.25186	1.007617	239.10		
0.10090	31.40096	1.010481	239.55		
0.14994	38.05925	1.014911	240.10		
308.15 K					
0.01011	10.03882	1.000214	238.92	238.10(±0.018)	0.083(±0.000)
0.02997	17.24336	1.002132	239.55		
0.05001	22.22137	1.004035	239.97		
0.07001	26.22955	1.005905	240.30		
0.10090	31.37393	1.008742	240.73		
0.14994	38.02586	1.013131	241.26		
313.15 K					
0.01011	10.02955	0.998367	239.58	238.71(±0.021)	0.084(±0.000)
0.02997	17.22741	1.000279	240.15		
0.05001	22.20078	1.002175	240.57		
0.07001	26.20521	1.004039	240.90		
0.10090	31.34471	1.006864	241.35		
0.14994	37.99015	1.011229	241.93		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01009	10.04419	1.003261	236.53	235.39(±0.033)	0.114(±0.001)
0.02997	17.26985	1.005213	237.39		
0.05003	22.26013	1.007145	237.95		
0.07011	26.28878	1.009045	238.41		
0.10009	31.29955	1.011822	239.03		
0.14996	38.08811	1.016322	239.73		
303.15 K					
0.01009	10.03708	1.001841	237.31	236.43(±0.044)	0.091(±0.001)
0.02997	17.25759	1.003786	238.02		
0.05003	22.24431	1.005714	238.49		
0.07011	26.27011	1.007613	238.87		
0.10009	31.27753	1.010399	239.32		

0.14996	38.06179	1.014918	239.87		
308.15 K					
0.01009	10.02883	1.000195	238.63	237.75(±0.025)	0.090(±0.000)
0.02997	17.24325	1.002119	239.32		
0.05003	22.22565	1.004027	239.77		
0.07011	26.24785	1.005906	240.14		
0.10009	31.25067	1.008664	240.57		
0.14996	38.02821	1.013128	241.16		
313.15 K					
0.01009	10.01959	0.998353	239.39	238.54(±0.028)	0.086(±0.001)
0.02997	17.22732	1.000268	240.05		
0.05003	22.20507	1.002169	240.45		
0.07011	26.22351	1.004041	240.81		
0.10009	31.22155	1.006785	241.26		
0.14996	37.99273	1.011238	241.79		

m^a (mol.kg^{-1}) molality of thiamine hydrochloride in different solvent systems

Table 3.15: Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities(ϕ^0_{KS}) andexperimental slopes (S^*_K) of thiamine hydrochloridein water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

m^a (mol.kg^{-1})	U (m.s^{-1})	K_S x 10^{10} (kg^{-1}.m.s^2)	ϕ_{KS} x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	ϕ^0_{KS}x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	S^*_K x 10^6 (kg.m^3.mol^{-2}.G.Pa^{-1})
Water **298.15 K**					
0.00999	1497.98	4.465	-40.18	-41.68(±0.869)	-27.30(±10.543)
0.02997	1498.68	4.452	-43.26		
0.04998	1499.45	4.438	-43.95		
0.06995	1499.99	4.427	-44.29		
0.09998	1505.67	4.381	-44.62		
0.14984	1508.36	4.345	-44.97		
303.15 K					
0.00999	1509.96	4.400	-39.52	-41.00(±0.859)	-26.85(±10.412)
0.02997	1511.05	4.385	-42.56		
0.04998	1511.56	4.374	-43.24		
0.06995	1512.41	4.361	-43.58		
0.09998	1513.47	4.342	-43.89		
0.14984	1515.12	4.313	-44.24		
308.15 K					

0.00999	1520.64	4.346	-38.96	-40.42(±0.849)	-26.50(±10.297)
0.02997	1521.19	4.334	-41.96		
0.04998	1522.04	4.321	-42.63		
0.06995	1522.74	4.309	-42.96		
0.09998	1523.61	4.292	-43.27		
0.14984	1525.59	4.262	-43.61		
313.15 K					
0.00999	1529.46	4.304	-38.49	-39.94(±0.842)	-26.24(±10.216)
0.02997	1530.11	4.292	-41.47		
0.04998	1530.99	4.279	-42.13		
0.06995	1531.43	4.268	-42.46		
0.09998	1532.51	4.250	-42.77		
0.14984	1534.22	4.222	-43.10		
0.05 mol.kg^{-1} D-Fructose + water **298.15 K**					
0.01011	1501.21	4.422	-40.12	-41.57(±0.843)	-26.47(±10.200)
0.02997	1501.99	4.409	-43.10		
0.05001	1502.87	4.396	-43.78		
0.07001	1503.63	4.383	-44.11		
0.10090	1504.94	4.363	-44.43		
0.14994	1507.14	4.331	-44.77		
303.15 K					
0.01011	1513.19	4.359	-39.48	-40.91(±0.832)	-26.15(±10.065)
0.02997	1514.09	4.345	-42.42		
0.05001	1514.88	4.332	-43.09		
0.07001	1515.56	4.320	-43.42		
0.10090	1516.53	4.302	-43.74		
0.14994	1518.03	4.275	-44.07		
308.15 K					
0.01011	1523.63	4.306	-38.90	-40.31(±0.824)	-25.85(±9.960)
0.02997	1524.36	4.294	-41.81		
0.05001	1525.49	4.279	-42.47		
0.07001	1526.18	4.268	-42.80		
0.10090	1527.05	4.251	-43.11		
0.14994	1528.28	4.225	-43.44		
313.15 K					
0.01011	1531.92	4.268	-38.45	-39.86(±0.818)	-25.62(±9.893)
0.02997	1532.74	4.255	-41.34		
0.05001	1533.18	4.244	-42.00		

0.07001	1533.99	4.232	-42.32		
0.10090	1534.81	4.216	-42.63		
0.14994	1536.16	4.190	-42.95		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01009	1501.19	4.422	-40.11	-41.56(±0.846)	-26.62(±10.252)
0.02997	1502.17	4.408	-43.10		
0.05003	1502.84	4.396	-43.78		
0.07011	1503.66	4.383	-44.12		
0.10009	1504.79	4.364	-44.43		
0.14996	1506.71	4.334	-44.78		
303.15 K					
0.01009	1512.91	4.360	-39.47	-40.90(±0.835)	-26.22(±10.115)
0.02997	1513.88	4.346	-42.42		
0.05003	1514.69	4.333	-43.09		
0.07011	1515.29	4.322	-43.42		
0.10009	1516.75	4.302	-43.73		
0.14996	1518.24	4.274	-44.07		
308.15 K					
0.01009	1522.99	4.310	-38.91	-40.33(±0.826)	-25.92(±10.009)
0.02997	1523.44	4.299	-41.83		
0.05003	1523.94	4.288	-42.49		
0.07011	1524.24	4.278	-42.82		
0.10009	1525.54	4.259	-43.12		
0.14996	1525.88	4.239	-43.46		
313.15 K					
0.01009	1532.21	4.266	-38.44	-39.85(±0.822)	-25.67(±9.957)
0.02997	1533.08	4.253	-41.34		
0.05003	1533.82	4.241	-42.00		
0.07011	1534.25	4.231	-42.32		
0.10009	1535.45	4.213	-42.62		
0.14996	1536.74	4.187	-42.95		

m^a (mol.kg^{-1}) molality of thiamine hydrochloride in different solvent systems

From the analysis of table 3.14 and 3.15 it is found that the density and sound velocity values increase with increase in temperature for thiamine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water. The density and sound velocity data is used to determine the apparent molar volumes (ϕ_v) and apparent molar adiabatic compressibilities (ϕ_{KS}) by using equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.14 and all the values are found positive and these values further increases in magnitude with increase in temperature for thiamine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water indicating the presence of strong solute - solvent interaction. On the other hand values of adiabatic compressibilities (ϕ_{KS})which are reported in table 3.15, are negative at all temperatures which shows that water molecules around solute i.e. thiamine hydrochloride are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of thiamine hydrochloride and D- Glucose and D-Fructose molecules.

The values of partial molar volumes(ϕ_v^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^0)are determined by applying least square fitting to the plots of $\phi_v$vs the square root of molar concentration and ϕ_{KS} vs molal concentration which are determined by using equations (1.12) and (1.19) respectively. The values of these parameters for thiamine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures are recorded in tables 3.14 and 3.15 respectively.

It is clear, from table 3.14, that the values of slopes (S_v^*) are positive in water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 molkg^{-1} D-Fructose + water in the entire temperature range . The positive values of slopes indicate the presence of strong solute- solute interactions and magnitude of S_v^*values decrease with increase in temperature in water as well as in 0.05 molkg^{-1} D- Glucose + water and 0.05 molkg^{-1} D-Fructose + water, indicating that these interactions are weaken which trait to the increase in solvation with increase in temperature. The values of partial molar volume(ϕ_v^0) are found to increase with increase in temperature in water as well as in 0.05 mol.kg^{-1} D- Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water indicating the increase in solute-solvent interaction with the rise in temperature. The plots of apparent molar volumes ϕ_v against C$^{1/2}$ were found to be linear with the positive slopes in water and in aqueous solutions of D- Glucose and D-Fructose are shown in figs. (3.14), (3.15) and (3.16) respectively.

It has also been found in the present study that the values of ϕ_{KS}^0 for thiamine hydrochloride are negative which attribute to the strong attractive interactions between thiamine hydrochloride and water. With increase in temperature, values ofϕ_{KS}^0 become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of thiamine hydrochloride and therefore at high temperature water molecules around thiamine hydrochloride are more compressible than those at lower temperature.

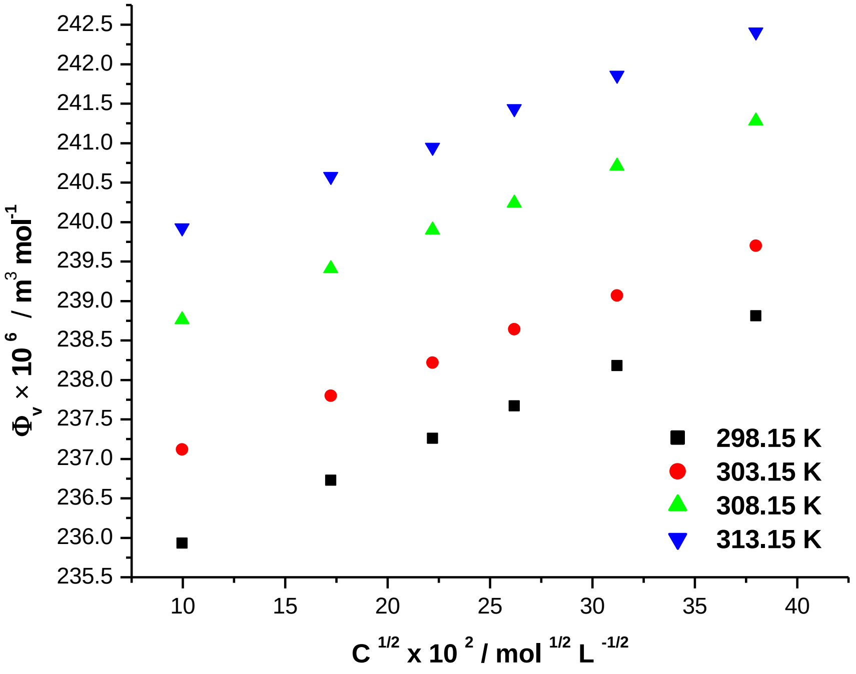

Fig. 3.14. Plot of ϕ_v vs $C^{1/2}$ for thiamine hydrochloride in water at different temperatures.

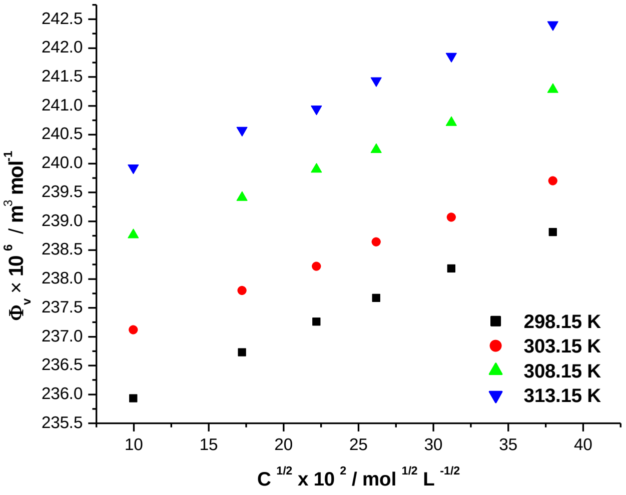

Fig. 3.15. Plot of ϕ_v vs $C^{1/2}$ for thiamine hydrochloride in 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

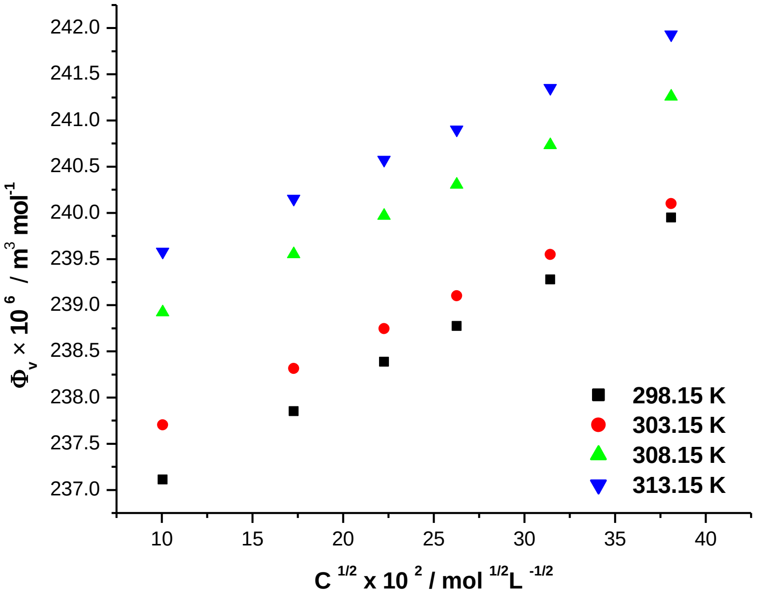

Fig. 3.16. Plot of ϕ_v vs $C^{1/2}$ for thiamine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water at different temperatures.

Partial molar expansibilities (ϕ_E^0) is one of the another parameter, which helps in determining the structure making or breaking behavior of a solute in any of the solvent^6.

It is found that thiamine hydrochloride shows similar kind of behavior in all the compositions of D-Glucose and D-Fructose in water. So the partial molar expansibilities(ϕ_E^0), Isobaric thermal expansion coefficient (α_2) and the molar heat capacities are determined only for the lower compositions of D-Glucose and D-Fructose in water.

The temperature dependence of ϕ_v^0 in water , 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water for thiamine hydrochloride are given as follow:

ϕ_v^0= -135.61 + 0.915T - 0.001T ^{2} in water (3.12)

ϕ_v^0= -43.51 + 1.651T - 0.002T ^{2}in 0.05 m D-Glucose + water (3.13)

ϕ_v^0 = -84.27 + 0.867T - 0.001T ^{2} in 0.05 m D-Fructose + water (3.14)

Partial molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]$ which is temperature dependent function of ϕ_v^0 is calculated for thiamine hydrochloride in water , D-Glucose + water and D-Fructose + water by using relations (3.12), (3.13) and (3.14) and are given in table 3.16.

Table. 3.16. Partial molar expansibilities(ϕ_E^0) for thiamine hydrochloride in water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose +water mixture at different temperatures.

T(K)	**Water**	**0.05 mol.kg^{-1} D-Fructose + water**	**0.05 mol.kg^{-1} D-Glucose + water**
ϕ_E^0 x 10^6(m^3 mol^{-1} K^{-1})			
298.15	0.259	0.151	0.220
303.15	0.248	0.139	0.196
308.15	0.237	0.127	0.172
313.15	0.226	0.115	0.148

From table 3.16, It is clear that the ϕ_E^0 values are positive at entire range of temperature but the values decrease in magnitude with rise in temperature which shows that thiamine hydrochloride is not behaving like symmetrical tetra alkyl ammonium salts[7] but behaving like common salts[8-9] because the molar volume expansibilities should decrease with the rise in temperature for a common salt. The decreasing ϕ_E^0 values indicates the absence of "packing effect"[6]. The variation of $\phi_E^0$with temperature for thiamine hydrochloride in aqueous and binary aqueous mixtures of D-Glucose and D-Fructose is linear and as shown in fig. 3.17.

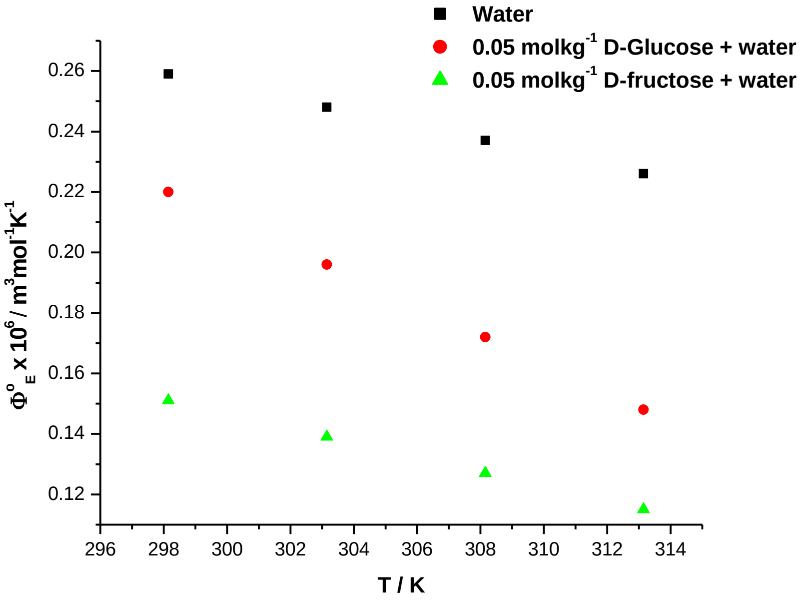

Fig.3.17. Plot of ϕ_E^0 vs temperature for thiamine hydrochloride in water , 0.05 molKg^{-1} D-Glucose + water and 0.05 molKg^{-1} D-Fructose + water.

Partial molar heat capacities are determined by taking the second derivative of partial molar volume with respect to temperature at constant pressure using the general thermodynamic expression[6] (3.4).

It is observed from relations (3.12 to 3.14) that sign of the values of $(\partial C_p/\partial P)_T$ for the solutions of thiamine hydrochloride are positive showing thereby that thiamine hydrochloride behaves as structure breakers in water as well as in binary aqueous mixtures of D-Glucose and D-Fructose. The values of $(\partial C_p/\partial P)_T$ are reported in table 3.17.The values of ϕ_v^0 and ϕ_E^0 are further used to calculate the isobaric thermal expansion coefficient[10], α_2 using equation (3.5). The calculated values of α_2 are included in table 3.17.

Table 3.17: Partial molar heat capacities, $(\partial C_p/\partial P)_T$, isobaric thermal expansion coefficient, α_2 for thiamine hydrochloride in water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water mixtures at different temperatures.

T (K)	Water		0.05 mol.kg^{-1} D-Fructose + water		0.05 mol.kg^{-1} D-Glucose + water	
	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	α_2 (K^{-1})
298.15	0.656	0.00110	0.716	0.00064	1.431	0.00093
303.15	0.667	0.00105	0.728	0.00059	1.455	0.00083
308.15	0.678	0.00100	0.740	0.00054	1.479	0.00072
313.15	0.689	0.00095	0.752	0.00048	1.503	0.00062

The α_2 value for thiamine hydrochloride decreases with increase in temperature in water as well as in 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water mixtures suggesting that the expansibility increase with increase in temperature for thiamine hydrochloride in water as well as in 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water mixtures

TRANSPORT PROPERTIES

In the present study, viscous flow of thiamine hydrochloride has been determined in water and in binary aqueous mixtures of D-Glucose and D-Fructose at various concentrations of solute and at different temperatures. The relative viscosities of the thiamine hydrochloride in water and binary aqueous mixtures of D-Glucose and D-Fructose at different temperatures were calculated by using equation (3.6).

The obtained relative viscosities were represented by Jones-Dole equation (1.28) where a straight line plot was obtained when $(\eta_r - 1)/C^{1/2}$ is plotted against $C^{1/2}$. The values of A and B parameters of Jones-Dole equation (1.28) were obtained using least square fit to the plots of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$. A parameter represents solute-solute interactions whereas B parameter represents the solute- solvents interactions[11].

The viscosities and relative viscosities along with A and B coefficients of the Jones – Dole equation for thiamine hydrochloride were determined in different compositions of D-Fructose, D-Glucose in water (0.05, 0.15, 0.25, 0.35) mol.kg^{-1} at 303.15K and are reported in table 3.18.

TABLE 3.18: Viscosities(η), relative viscosities (η_r) and values of A and B coefficients of the Jones – Dole equation for thiamine hydrochloride in different compositions of D-Fructose + water and D-Glucose + water at 303.15 K.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
0.05 mol.kg^{-1}D-Fructose + water					
0.00000	0.00000	0.83310	-	3.624(±0.202)	0.456(±0.007)
0.01011	10.04713	0.84001	1.00830		
0.02997	17.25777	0.84943	1.01960		
0.05001	22.24011	0.85886	1.03092		
0.07001	26.25186	0.86701	1.04070		
0.10090	31.40096	0.88073	1.05718		
0.14994	38.05925	0.89934	1.07952		
0.15 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.86720	-	3.595(±0.182)	0.468(±0.007)
0.00989	9.970691	0.87443	1.00834		
0.02997	17.31506	0.88452	1.01997		
0.05013	22.33986	0.89446	1.03144		
0.07022	26.37666	0.90355	1.04192		
0.10012	31.38359	0.91760	1.05812		
0.14984	38.16819	0.93801	1.08165		
0.25 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.90150	-		
0.01014	10.12863	0.90923	1.00858		
0.02989	17.34819	0.91993	1.02045		

0.05013	22.41173	0.93025	1.03189	3.583(±0.179)	0.476(±0.006)
0.07012	26.44225	0.93982	1.04251		
0.10011	31.48096	0.95499	1.05933		
0.14984	38.28596	0.97655	1.08325		
0.35 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.93490	-	3.567(±0.150)	0.483(±0.005)
0.01011	10.13936	0.94296	1.00862		
0.02997	17.41488	0.95445	1.02091		
0.05006	22.45197	0.96495	1.03215		
0.07008	26.49992	0.97516	1.04307		
0.10011	31.55734	0.99099	1.06000		
0.14997	38.39265	1.01414	1.08476		
0.05 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.81900	-	2.534(0.374)	0.391(0.014)
0.01009	10.03708	0.82413	1.00626		
0.02997	17.25759	0.83199	1.01587		
0.05003	22.24431	0.83987	1.02548		
0.07011	26.27011	0.84761	1.03493		
0.10009	31.27753	0.85640	1.04566		
0.14996	38.06179	0.87261	1.06546		
0.15 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.85300	-	2.513(±0.276)	0.416(±0.010)
0.00998	10.01573	0.85859	1.00655		
0.02997	17.31498	0.86739	1.01686		
0.05005	22.32229	0.87591	1.02685		
0.07008	26.35096	0.88372	1.03601		
0.10003	31.37034	0.89373	1.04775		
0.14998	38.1866	0.91310	1.07046		

0.25 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.88700	-	2.503(±0.228)	0.450(±0.008)
0.01001	10.06259	0.89334	1.00715		
0.02998	17.37247	0.90250	1.01747		
0.05012	22.40768	0.91209	1.02828		
0.07005	26.4274	0.92138	1.03876		
0.10030	31.50849	0.93365	1.05259		
0.14989	38.29124	0.95374	1.07524		
0.35 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.92010	-	2.430(±0.188)	0.481(±0.007)
0.01015	10.15725	0.92706	1.00757		
0.02999	17.41736	0.93712	1.01850		
0.05013	22.46364	0.94735	1.02962		
0.07014	26.50701	0.95757	1.04073		
0.10011	31.55335	0.97091	1.05522		
0.14996	38.38818	0.99419	1.08052		

m^a (mol.kg^{-1}) is the molality of thiamine hydrochloride in different solvent systems

The values of coefficients A and B are obtained by plotting graphs between $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$ where A is the intercept and B is the slope for the respective graph. The values of A and B parameters for thiamine hydrochloride in different compositions of binary aqueous solution of D-Fructose and D-Glucose at 303.15 K are recorded in table 3.18 respectively. Sample plots of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$for thiamine hydrochloride in different compositions of D-Fructose and D-Glucose in water are shown in figures (3.18) and (3.19).

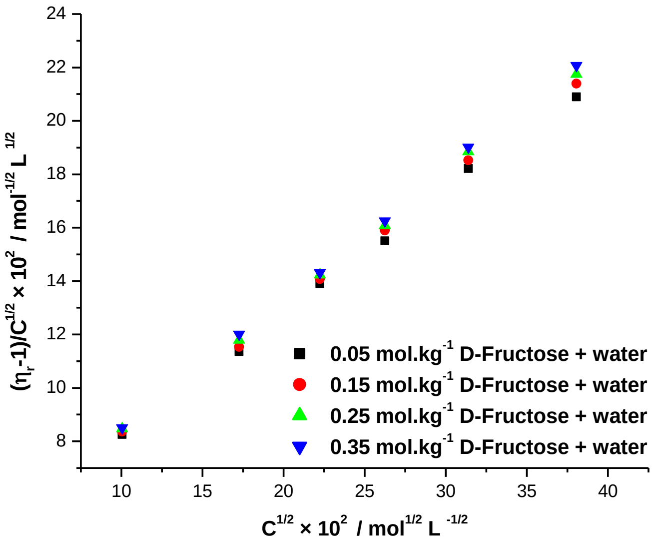

Fig. 3.18 . Plot of (η_{r}-1)/ $C^{1/2}$ vs $C^{1/2}$ for thiamine hydrochloride in different compositions of D-Fructose in water at 303.15 K.

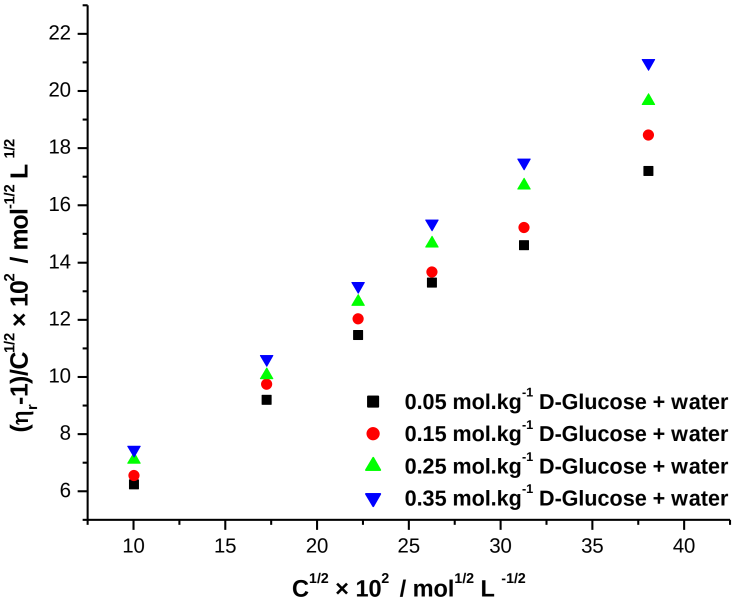

Fig. 3.19. Plot of (η_{r}-1)/ $C^{1/2}$ vs $C^{1/2}$ for thiamine hydrochloride in different compositions of D-Glucose in water at 303.15 K.

The values of A-coefficient in table 3.18 are positive and decrease with the increase in the concentration of D-Fructose and D-Glucose in water indicating the weakening of solute-solute interactions with the increase of D-Fructose and D-Glucose content in water. Also it is found that values of B-coefficient are positive indicating the presence of strong solute-solvent interactions which may be attributed to the strong solvation of thiamine hydrochloride in the binary mixtures of D-Fructose + water and D-Glucose +water. From the table 3.18, it is clear that B-coefficient values increase with the increase of D-Fructose and D-Glucose content in water at 303.15 K, thereby showing that solute – solvent interactions are further strengthened with the increase of D-Fructose and D-Glucose content in water. So, it is clear that there is a great change in the solute - solvent interactions when we switch from lower to higher composition of the solvents[12-13]. In other words the solvation is enhanced as the composition of D-Fructose and D-Glucose in water increases.

The analysis of data was also done on the basis of transition state theory proposed by Feakins *et al*[14]. The B-coefficient in terms of transition state theory is given by the relation (3.7) whereas all other parameters such as $\Delta\mu_1^{0^*}$, $\Delta\mu_2^{0^*}$ and $\overline{V_1^0}$, were determined by using relations (3.8), (3.9) and(3.10) respectively and are reported in table 3.19.

TABLE 3.19: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for thiamine hydrochloride in different composition of D-Fructose + water and D-Glucose + water at 303.15 K.

m (mol.kg^{-1})	$\overline{V_1^0} \times 10^6$ **(m^3.mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3.mol^{-1})**	$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$\Delta\mu_2^{0^*}$ **(kJ.mol^{-1})**
D-Fructose + water				
0.05	17.98	236.83	26.65	94.60
0.15	17.83	237.53	26.69	97.23
0.25	17.68	238.72	26.72	99.37
0.35	17.56	240.02	26.75	101.27
D-Glucose + water				
0.05	17.98	236.43	26.63	85.43
0.15	17.83	236.73	26.67	89.77
0.25	17.69	237.47	26.70	95.47
0.35	17.57	238.26	26.74	100.69

It is evident from the above table that values of $\Delta\mu_1^{0^*}$ do not change much with the change in composition of D-Fructose and D-Glucose in water at 303.15 K, i.e. the values of $\Delta\mu_1^{0^*}$ are practically held constant in the entire composition range of D-Fructose and D-Glucose in water at 303.15 K. It is clear that the values of $\Delta\mu_2^{0^*}$ are positive and increase with solvent composition of D-Fructose and D-Glucose in water at 303.15 K suggesting that the transition state formation is less favored in the presence of thiamine hydrochloride and is followed by breaking or distortions of the intermolecular bonds[14].

Effect of temperature

As the behavior of thiamine hydrochloride is similar for different compositions of D-Fructose and D-Glucose in water at 303.15 K, so only lowest composition i.e. 0.05 mol.kg^{-1} D-Fructose +water and 0.05 mol.kg^{-1} D-Glucose +water was taken for analyzing the effect of temperature. The viscosity and the relative viscosity data along with A and B coefficients of the Jones – Dole equation at different temperatures is given in table 3.20.

TABLE 3.20: Viscosities (η), relative viscosities(η_r) and the values of A and B coefficients of the Jones – Dole equation for thiamine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
Water					
298.15 K					
0.00999	9.968524	0.89862	1.00550	2.524(±0.086)	0.300(±0.003)
0.02997	17.22545	0.90551	1.01322		
0.04998	22.19237	0.91193	1.02040		
0.06995	26.19279	0.91833	1.02756		
0.09998	31.20462	0.92668	1.03690		
0.14984	37.98039	0.94106	1.05300		
303.15 K					
0.00999	9.961495	0.80530	1.00575		

0.02997	17.21319	0.81183	1.01390	2.485(±0.182)	0.325(±0.007)
0.04998	22.17647	0.81765	1.02116		
0.06995	26.17386	0.82373	1.02876		
0.09998	31.18191	0.83286	1.04016		
0.14984	37.95226	0.84546	1.05590		
308.15 K					
0.00999	9.953346	0.72684	1.00600	2.456(±0.323)	0.352(±0.012)
0.02997	17.19890	0.73318	1.01478		
0.04998	22.15777	0.73873	1.02247		
0.06995	26.15153	0.74389	1.02961		
0.09998	31.15471	0.75364	1.0431		
0.14984	37.91819	0.76565	1.05973		
313.15 K					
0.00999	9.944214	0.66018	1.00636	2.416(±0.260)	0.386(±0.010)
0.02997	17.18300	0.66633	1.01575		
0.04998	22.13718	0.67163	1.02383		
0.06995	26.12696	0.67692	1.03189		
0.09998	31.12516	0.68565	1.04521		
0.14984	37.88167	0.69881	1.06525		
0.05 mol.kg^{-1} D-Fructose + water **298.15 K**					
0.01011	10.05425	0.93685	1.00801	3.636(±0.274)	0.439(±0.010)
0.02997	17.27002	0.94720	1.01916		
0.05001	22.25587	0.95758	1.03032		
0.07001	26.27044	0.96639	1.0398		
0.10090	31.42310	0.98117	1.05571		
0.14994	38.08567	1.00053	1.07654		
303.15 K					

0.01011	10.04713	0.84001	1.00830	3.624(±0.202)	0.456(±0.007)
0.02997	17.25777	0.84943	1.01960		
0.05001	22.24011	0.85886	1.03092		
0.07001	26.25186	0.86701	1.04070		
0.10090	31.40096	0.88073	1.05718		
0.14994	38.05925	0.89934	1.07952		
308.15 K					
0.01011	10.03882	0.75866	1.00859	3.606(±0.279)	0.476(±0.010)
0.02997	17.24336	0.76727	1.02003		
0.05001	22.22137	0.77589	1.03150		
0.07001	26.22955	0.78360	1.04175		
0.10090	31.37393	0.79681	1.05931		
0.14994	38.02586	0.81409	1.08227		
313.15 K					
0.01011	10.02955	0.68986	1.00886	3.580(±0.374)	0.497(±0.014)
0.02997	17.22741	0.69804	1.02082		
0.05001	22.20078	0.70574	1.03208		
0.07001	26.20521	0.71283	1.04245		
0.10090	31.34471	0.72568	1.06125		
0.14994	37.99015	0.74245	1.08576		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01009	10.04419	0.91924	1.00585	2.624(±0.223)	0.337(±0.008)
0.02997	17.26985	0.92730	1.01466		
0.05003	22.26013	0.93489	1.02297		
0.07011	26.28878	0.94202	1.03077		
0.10009	31.29955	0.95123	1.04085		
0.14996	38.08811	0.96735	1.05849		

303.15 K					
0.01009	10.03708	0.82413	1.00626	2.534(±0.374)	0.391(±0.014)
0.02997	17.25759	0.83199	1.01587		
0.05003	22.24431	0.83987	1.02548		
0.07011	26.27011	0.84761	1.03493		
0.10009	31.27753	0.85640	1.04566		
0.14996	38.06179	0.87261	1.06546		
308.15 K					
0.01009	10.02883	0.74440	1.00704	2.463(±0.386)	0.447(±0.014)
0.02997	17.24325	0.75197	1.01727		
0.05003	22.22565	0.75903	1.02683		
0.07011	26.24785	0.76751	1.03830		
0.10009	31.25067	0.77785	1.05229		
0.14996	38.02821	0.79318	1.07303		
313.15 K					
0.01009	10.01959	0.67671	1.00761	2.408(±0.493)	0.478(±0.019)
0.02997	17.22732	0.68390	1.01831		
0.05003	22.20507	0.69026	1.02778		
0.07011	26.22351	0.69795	1.03923		
0.10009	31.22155	0.70736	1.05325		
0.14996	37.99273	0.72533	1.08000		

m^a (mol.kg^{-1}) is the molality of thiamine hydrochloride

The plots of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$ have been found linear at all four different temperatures. Sample plots for thiamine hydrochloride in water, 0.05mol.kg^{-1}D-Fructose +water and 0.05mol.kg^{-1}D-Glucose + water at different temperatures are shown in figs. (3.20), (3.21) and (3.22) respectively. This is in accordance to the Jones – Doles equation.

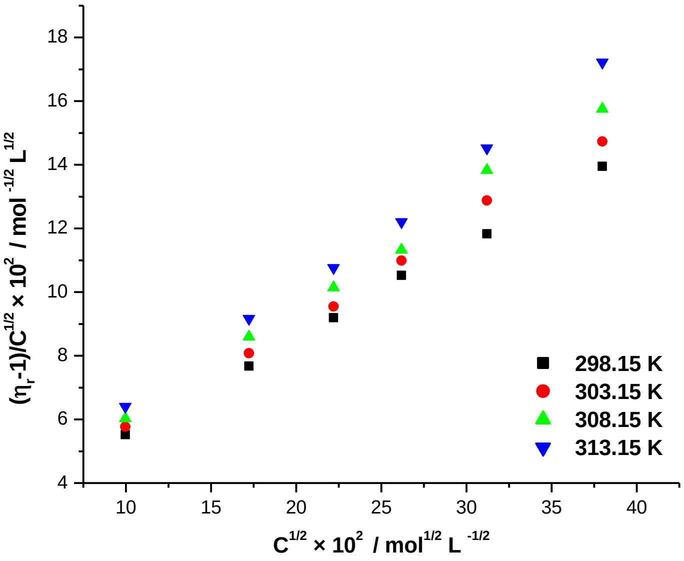

Fig.3.20. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for thiamine hydrochloride in water at different temperatures.

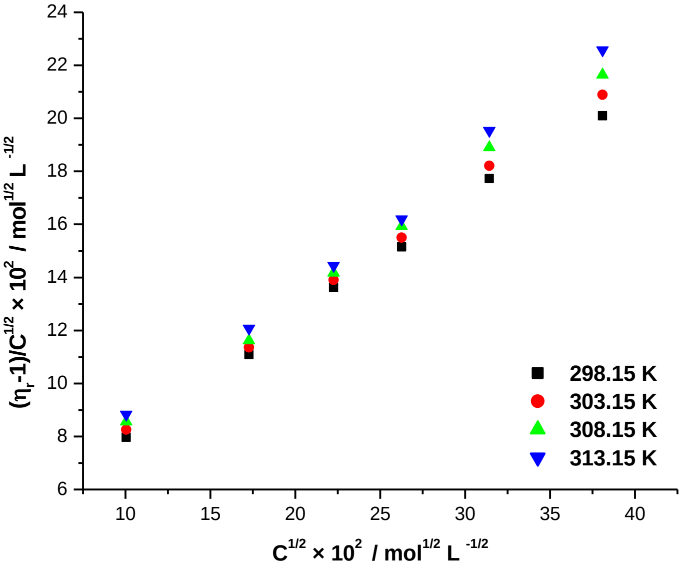

Fig. 3.21. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for thiamine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water at different temperatures.

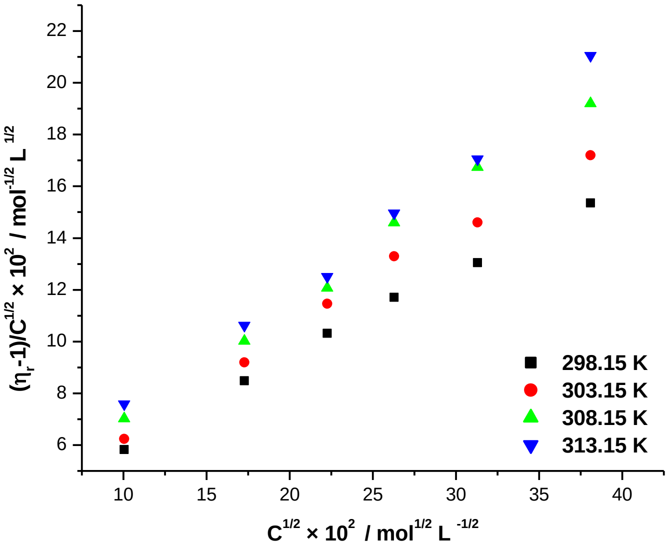

Fig. 3.22. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for thiamine hydrochloride in 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

The values of A-coefficient reported in table 3.20 are positive for the entire range of temperature indicating the presence of solute-solute interactions. Further values of A-coefficient decrease with rise in temperature in water, 0.05 mol.kg^{-1} D-Fructose + water as well as in 0.05 mol.kg^{-1} D-Glucose + water indicating the weakening of solute-solute interactions with the rise in temperature. Also the values of B-coefficient are positive in water, 0.05 mol.kg^{-1} D-Fructose + water as well as in 0.05 mol.kg^{-1} D-Glucose + water at all temperatures thereby showing the presence of strong solute-solvent interactions and these values further increase with the rise in temperature which suggest that solute-solvent interaction are further strengthened with the rise in temperature[15]. Viscosity data has also been examined by applying the transition state theory at different temperatures and calculated values of $\overline{V_1^0}$, $\overline{V_2^0}$,$\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ have also been recorded in table 3.21.

TABLE 3.21: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for thiamine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

T (K)	$\overline{V_1^0} \times 10^6$ **(m^3·mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3·mol^{-1})**	$\Delta\mu_1^{0^*}$ **kJ.mol^{-1}**	$\Delta\mu_2^{0^*}$ **kJ.mol^{-1}**
0.05 mol.kg^{-1}D-Fructose + water				
298.15	17.96	236.10	26.33	90.74
303.15	17.98	236.83	26.65	94.61
308.15	18.01	238.10	26.98	99.03
313.15	18.05	238.71	27.31	103.57
0.05 mol.kg^{-1} D-Glucose + water				
298.15	17.96	235.39	26.31	76.56
303.15	17.98	236.43	26.63	85.44
308.15	18.01	237.75	26.96	94.85
313.15	18.05	238.54	27.29	100.80

According to Feakins model[14] increase in the values of $\Delta\mu_2^{0^*}$with temperature leads to the structure breaking ability of the solute and simultaneously transition state formation is less favoured due to breaking and distortion of intermolecular bonds in the solvent mixture by the presence of solute. In the present study, values of $\Delta\mu_2^{0^*}$increase with increase in temperature supporting the structure breaking ability of thiamine hydrochloride and simultaneously transition state formation is less favoured in 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water mixtures respectively by the presence of thiamine hydrochloride.

TABLE 3.22: Values of ($\Delta\mu_2^{0*}$-$\Delta\mu_1^{0*}$),T$\Delta S_2^{0*}$and $\Delta H_2^{0*}$for thiamine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

T / K	**$\Delta\mu_2^{0*}$-$\Delta\mu_1^{0*}$ / (kJ mol^{-1})**	**T. ΔS_2^{0*} / (kJ mol^{-1})**	**ΔH_2^{0*} / (kJ mol^{-1})**
0.05 mol.kg^{-1}D-Fructose + water			
298.15	64.41	-255.84	-165.11
303.15	67.96	-260.13	-165.52
308.15	72.05	-264.42	-165.39
313.15	76.25	-268.71	-165.15
0.05 mol.kg^{-1}D-Glucose + water			
298.15	50.24	-489.86	-413.31
303.15	58.81	-498.08	-412.64
308.15	67.89	-506.29	-411.44
313.15	73.51	-514.51	-413.71

The values of change in activation energy per mole solute ($\Delta\mu_2^{0*}$-$\Delta\mu_1^{0*}$) on replacing one mole of solvent by one mole of solute at infinite dilution are recorded in table 3.22. Since the values are positive and increase in both 0.05 mol.kg^{-1}D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water solvent systems at different temperatures. So, it may be concluded that transitions state is accompanied by breaking/distortion of bonds. In other word transition state is less favored in the presence of thiamine hydrochloride in the entire temperature range studied here. The entropy of activation ΔS_2^{0*}[16]and values of enthalpy of activation i.e.ΔH_2^{0*} for thiamine hydrochloride has been determined from the equations (3.17) and (3.18)

The T. ΔS_2^{0*} and ΔH_2^{0*} values at different temperatures are recorded in table 3.22. As both the parameters enthalpy of activation and entropy of activation are found negative for thiamine hydrochloride which indicates that the transition state is associated bond formation between solute and solvent molecules[14].

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SECTION III

THERMODYNAMIC AND TRANSPORT PROPERTIES OF NICOTINIC ACID IN WATER AND BINARY AQUEOUS MIXTURES OF D-GLUCOSE, D-FRUCTOSE AND D-LACTOSE

The Present section describes the thermodynamic and transport properties such as partial molar volumes, partial molar adiabatic compressibilities, partial molar expansibilities, viscosity A and B coefficients of Jones Dole equation, activation energy parameters etc. for nicotinic acid in water and binary aqueous mixtures of D-Fructose, D-Glucose and D-Lactose.

For the sake of convenience the section has been further divided into two parts.

A. THERMODYNAMIC PROPERTIES
B. TRANSPORT PROPERTIES

A. THERMODYNAMIC PROPERTIES

Thermodynamic properties such as partial molar volumes, partial molar adiabatic compressibilities and partial molar expansibilities were determined using density and speed of sound data for nicotinic acid in water and binary aqueous mixtures of D-Fructose, D-Glucose and D-Lactose. The effect of compositions of D-Fructose, D-Glucose and D-Lactose in water has also been determined at one temperature i.e. 303.15 K whereas the above mentioned properties are also determined at different temperatures to analyze the effect of temperature. The densities (ρ), apparent molar volumes (ϕ_v), sound velocities (U) and apparent molar adiabatic compressibilities (ϕ_{ks}) of nicotinic acid in binary aqueous mixtures of D-Fructose, D- Glucose and D-lactose (0.05, 0.15, 0.25 and 0.35) mol.kg^{-1} at 303.15K have been measured and are reported in tables 3.23 and 3.24 respectively.

Table 3.23: Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes(ϕ_v^0) and experimental slopes (S_v^*) of nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K.

m^a (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x10^{-3} (kg.m^{-3})	ϕ_v x 10^6 (m^3.mol^{-1})	ϕ_v^0 x 10^6 (m^3.mol^{-1})	S_v^* x 10^4 (m^3·L$^{1/2}$.mol$^{-3/2)}$
0.05 mol.kg^{-1} D-Fructose + water					
0.01021	10.10460	1.001285	82.00	81.41(±0.020)	0.059(±0.000)
0.02998	17.30084	1.002081	82.45		
0.05003	22.33087	1.002877	82.71		
0.07012	26.41483	1.003660	82.99		
0.10012	31.52418	1.004817	83.28		

0.14984	38.48521	1.006696	83.68		
0.15 mol.kg^{-1} D-Fructose + water					
0.00989	9.978426	1.007990	82.51	81.94(±0.014)	0.056(±0.000)
0.02997	17.35572	1.008784	82.91		
0.05013	22.42749	1.009568	83.19		
0.07022	26.52128	1.010337	83.45		
0.10012	31.62834	1.011468	83.73		
0.14984	38.61147	1.013312	84.10		
0.25 mol.kg^{-1} D-Fructose + water					
0.01014	10.13679	1.014623	82.81	82.18(±0.016)	0.055(±0.000)
0.02989	17.38930	1.015391	83.23		
0.05013	22.50064	1.016165	83.52		
0.07012	26.58869	1.016916	83.80		
0.10011	31.72914	1.018026	84.12		
0.14984	38.73541	1.019828	84.54		
0.35 mol.kg^{-1} D-Fructose + water					
0.01015	10.16762	1.019799	83.29	82.61(±0.020)	0.052(±0.000)
0.02987	17.42761	1.020551	83.72		
0.05016	22.56423	1.021309	84.06		
0.07015	26.66132	1.022045	84.32		
0.10021	31.82433	1.023134	84.64		
0.14996	38.84661	1.024886	85.13		
0.05 mol.kg-1 D-Glucose + water					
0.01011	10.05490	1.001254	81.70	81.00(±0.013)	0.069 (±0.000)
0.02996	17.29488	1.002057	82.22		
0.05002	22.32839	1.002853	82.58		
0.07014	26.41831	1.003641	82.85		
0.10011	31.52226	1.004794	83.21		
0.14994	38.49728	1.006668	83.69		
0.15 mol.kg^{-1} D-Glucose + water					
0.00998	10.02356	1.007968	82.08	81.42(±0.024)	0.067(±0.009)
0.02997	17.35554	1.008763	82.61		
0.05013	22.42731	1.009552	82.92		
0.07012	26.50235	1.010322	83.19		
0.10002	31.61246	1.011451	83.56		
0.14994	38.62392	1.013302	84.00		
0.25 mol.kg^{-1} D-Glucose + water					
0.01025	10.18983	1.014403	82.47		
0.02982	17.36572	1.015171	82.89		
0.05023	22.52084	1.015957	83.22		

0.07032	26.62374	1.016716	83.53	81.76(±0.041)	0.060(±0.001)
0.10032	31.75941	1.017828	83.92		
0.14964	38.70672	1.019628	84.32		
0.35 mol.kg^{-1} D-Glucose + water					
0.01015	10.16545	1.019365	82.74	82.04(±0.025)	0.060(±0.000)
0.02999	17.45886	1.020131	83.25		
0.05013	22.55295	1.020895	83.56		
0.07014	26.65411	1.021637	83.89		
0.10011	31.80242	1.022734	84.24		
0.14996	38.83964	1.024518	84.69		
0.05 mol.kg^{-1} D-Lactose + water					
0.01011	10.06435	1.003137	82.41	81.63(±0.015)	0.075(±0.006)
0.02997	17.31388	1.003925	82.92		
0.05001	22.34675	1.004703	83.31		
0.07008	26.43114	1.005469	83.63		
0.10011	31.55050	1.006595	84.02		
0.14994	38.53075	1.008419	84.54		
0.15 mol.kg^{-1} D-Lactose + water					
0.01011	10.12685	1.015635	82.65	81.97(±0.022)	0.068(±0.008)
0.02997	17.42117	1.016406	83.19		
0.05001	22.48498	1.017171	83.51		
0.07008	26.59436	1.017925	83.77		
0.10011	31.74481	1.019032	84.13		
0.14994	38.76700	1.020823	84.63		
0.25 mol.kg^{-1} D-Lactose + water					
0.01011	10.18181	1.026689	82.92	82.26(±0.018)	0.066(±0.006)
0.02997	17.51552	1.027445	83.43		
0.05001	22.60648	1.028193	83.77		
0.07008	26.73772	1.028929	84.06		
0.10011	31.91541	1.030014	84.38		
0.14994	38.97433	1.031771	84.83		
0.35 mol.kg^{-1} D-Lactose + water					
0.01001	10.18926	1.038451	83.24	82.59(±0.001)	0.065(±0.001)
0.02998	17.61829	1.039192	83.77		
0.05007	22.74863	1.039924	84.08		
0.07001	26.87610	1.040638	84.35		
0.10009	32.09276	1.041699	84.65		
0.14997	39.19724	1.043402	85.16		

m^a (mol.kg^{-1}) molality of nicotinic acid in different solvent systems

Table 3.24: Sound velocities (U), coefficient of adiabatic compressibilities (K_s), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities(ϕ_{KS}^0) andexperimental slopes (S_K^*) of nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K.

m^a (mol.kg^{-1})	U (m.s^{-1})	K_s x 10^{10} (kg^{-1}.m.s^2)	ϕ_{KS} x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	ϕ_{KS}^0x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	S_K^* x 10^6 (kg.m^3.mol^{-2}.G.Pa^{-1})
0.05 mol.kg^{-1} D-Fructose + water					
0.01021	1512.91	4.363	-39.49	-41.00(±0.855)	-24.37(±10.371)
0.02998	1513.69	4.355	-42.34		
0.05003	1514.38	4.347	-42.96		
0.07012	1515.26	4.339	-43.24		
0.10012	1516.11	4.329	-43.48		
0.14984	1517.93	4.311	-43.71		
0.15 mol.kg^{-1} D-Fructose + water					
0.00989	1518.99	4.299	-39.08	-40.54(±0.838)	-23.75(±10.148)
0.02997	1519.78	4.291	-42.00		
0.05013	1520.64	4.283	-42.61		
0.07022	1521.29	4.276	-42.89		
0.10012	1522.37	4.265	-43.12		
0.14984	1524.38	4.246	-43.34		
0.25 mol.kg^{-1} D-Fructose + water					
0.01014	1525.23	4.236	-38.94	-40.32(±0.794)	-22.75(±9.620)
0.02989	1525.96	4.229	-41.69		
0.05013	1527.06	4.220	-42.29		
0.07012	1527.41	4.215	-42.56		
0.10011	1528.71	4.203	-42.79		
0.14984	1530.67	4.185	-43.00		
0.35 mol.kg^{-1} D-Fructose + water					
0.01015	1531.09	4.182	-38.67	-40.03(±0.779)	-22.28(±9.431)
0.02987	1532.02	4.174	-41.37		
0.05016	1533.38	4.164	-41.96		
0.07015	1533.18	4.162	-42.23		
0.10021	1535.89	4.143	-42.45		
0.14996	1537.98	4.124	-42.66		
0.05 mol.kg^{-1} D-Glucose + water					

0.01011	1512.68	4.364	-39.44	-40.90(±0.832)	-23.82(±10.084)
0.02996	1513.73	4.355	-42.34		
0.05002	1514.39	4.347	-42.96		
0.07014	1514.99	4.341	-43.24		
0.10011	1516.25	4.328	-43.48		
0.14994	1517.93	4.311	-43.71		
0.15 mol.kg^{-1} D-Glucose + water					
0.00998	1518.83	4.300	-39.14	-40.59(±0.828)	-23.56(±10.037)
0.02997	1519.63	4.292	-42.03		
0.05013	1520.43	4.284	-42.64		
0.07012	1521.28	4.276	-42.91		
0.10002	1522.42	4.265	-43.14		
0.14994	1524.35	4.247	-43.37		
0.25 mol.kg^{-1} D-Glucose + water					
0.01025	1525.28	4.237	-38.98	-40.33(±0.783)	-22.61(±9.486)
0.02982	1525.99	4.230	-41.69		
0.05023	1526.72	4.222	-42.29		
0.07032	1527.43	4.215	-42.56		
0.10032	1528.31	4.206	-42.79		
0.14964	1530.41	4.187	-43.00		
0.35 mol.kg^{-1} D-Glucose + water					
0.01015	1531.08	4.184	-38.67	-40.03(±0.780)	-22.32(±9.451)
0.02999	1531.96	4.176	-41.38		
0.05013	1533.39	4.165	-41.96		
0.07014	1534.14	4.158	-42.23		
0.10011	1535.98	4.144	-42.45		
0.14996	1538.06	4.126	-42.66		
0.05 mol.kg^{-1} D-Lactose + water					
0.01011	1514.71	4.344	-39.35	-40.79(±0.827)	-23.622(±10.019)
0.02997	1515.16	4.338	-42.22		
0.05001	1515.68	4.332	-42.84		
0.07008	1516.02	4.327	-43.12		
0.10011	1516.59	4.319	-43.35		
0.14994	1516.99	4.309	-43.58		
0.15 mol.kg^{-1} D-Lactose + water					
0.01011	1524.78	4.234	-38.94	-40.33 (±0.796)	-22.730 (±9.645)
0.02997	1525.31	4.228	-41.71		
0.05001	1525.98	4.221	-42.30		

0.07008	1526.48	4.216	-42.57		
0.10011	1526.09	4.213	-42.80		
0.14994	1526.62	4.203	-43.01		
0.25 mol.kg^{-1} D-Lactose + water					
0.01011	1533.87	4.139	-38.56	-39.91(±0.770)	-21.968(±9.326)
0.02997	1534.42	4.133	-41.24		
0.05001	1534.99	4.127	-41.81		
0.07008	1535.46	4.122	-42.07		
0.10011	1536.02	4.114	-42.29		
0.14994	1536.63	4.104	-42.50		
0.35 mol.kg^{-1} D-Lactose + water					
0.01001	1543.83	4.040	-38.12	-39.43(±0.752)	-21.347(±9.116)
0.02998	1544.39	4.034	-40.74		
0.05007	1544.98	4.028	-41.29		
0.07001	1545.37	4.023	-41.54		
0.10009	1545.91	4.016	-41.75		
0.14997	1546.46	4.007	-41.95		

m^a (mol.kg^{-1}) molality of nicotinic acid in different solvent systems

From the table 3.23 and 3.24 it is found that the density and sound velocity values increase with increase in concentration of nicotinic acid in different compositions of D-Glucose, D-Fructose and D-Lactose in water. The respective density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities by using equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.23 and are positive and increases in magnitude with increase in concentration of nicotinic acid in all compositions of D-Fructose, D-Glucose and D-Lactose in water indicating the presence of great solute - solvent interactions[1-2]. Also, the values of adiabatic compressibilities (ϕ_{KS}) which are reported in table 3.24, are negative in all compositions of D- Glucose, D-Fructose and D-Lactose in water which shows that water molecules around solute i.e. nicotinic acid are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of nicotinic acid and D- Glucose, D-Fructose and D-Lactose molecules.

Linear plots have been found in accordance with Masson's equation (1.12) when the apparent molar volume values (ϕ_V) are plotted against root of molar concentrations ($C^{1/2}$) of nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water. Sample plots for nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15K are shown in fig. (3.23), (3.24) and (3.25) respectively.

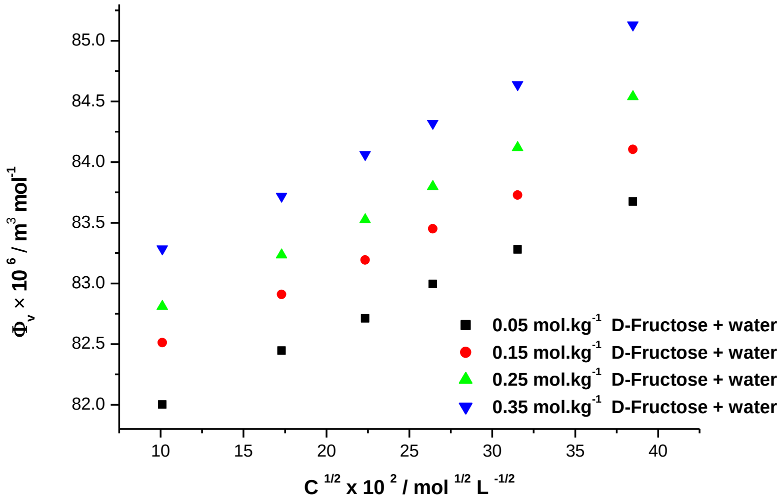

Fig. 3.23. Plot of ϕ_V vs $C^{1/2}$ for nicotinic acid in different compositions of D-Fructose in water at 303.15K

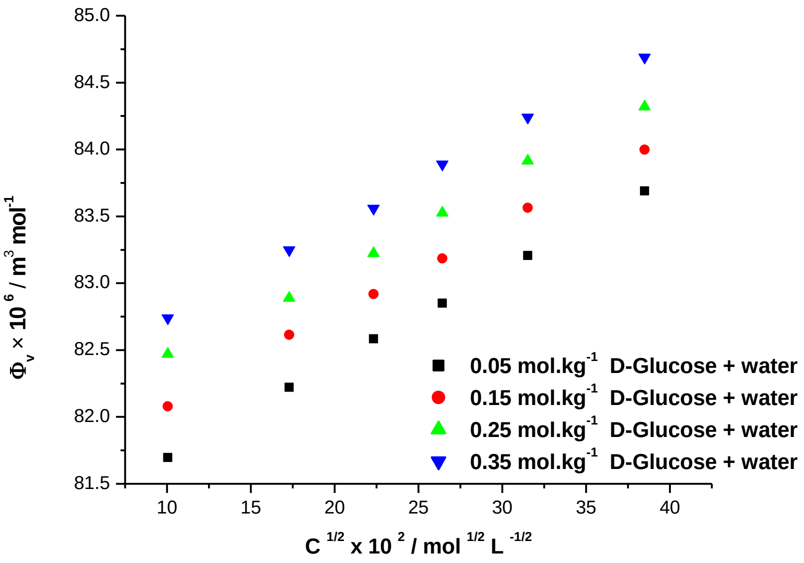

Fig. 3.24. Plot of ϕ_V vs $C^{1/2}$ for nicotinic acid in different compositions of D- Glucose in water at 303.15K.

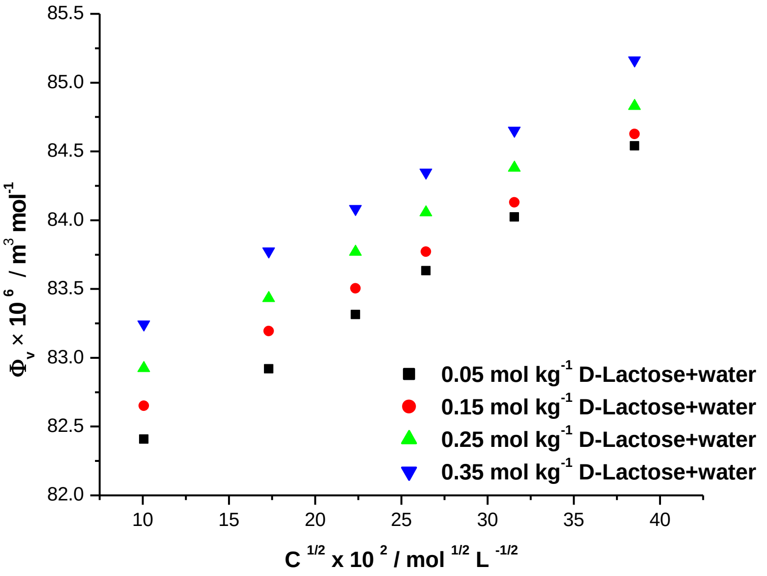

Fig. 3.25. Plot of ϕ_V vs $C^{1/2}$ for nicotinic acid in different compositions of D- lactose in water at 303.15K.

Values of partial molar volumes (ϕ_v^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^0) are determined by applying the least square fitting to the plots of $\phi_v$vs square root of molar concentration and ϕ_{KS} vs molal concentration which are deduced by using equations (1.12) and (1.19) respectively. The values of these parameters for nicotinic acid in different compositions of binary aqueous solutions of D- Glucose, D-Fructose and D-Lactose at 303.15 K are reported in table 3.23 and 3.24.

It is clear from table 3.23, that the values of slopes (S_v^*) are positive in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K indicating the presence of strong solute- solute interactions and magnitude of S_v^* values decreases with increase in compositions of D-Fructose, D-Glucose and D-Lactose in water, indicating that these interactions are weakened which trait to the increase in solvation. On the other hand values of ϕ_v^0 are positive and increase with increase in molalities of D-Fructose, D-Glucose and D-Lactose in water showing that solute - solvent interactions further increase on the addition of D- Glucose, D-Fructose and D-Lactose in water. Also on comparing the magnitudes of ϕ_v^0 values with the values of S_v^*, ϕ_v^0values are more than that of S_v^* which prove that solute - solvent interactions dominate over solute- solute interactions in mixtures of D-Fructose, D-Glucose and D-Lactose in water. It has been found in the present study that the values of ϕ_{KS}^0 for nicotinic acid are negative which attribute to the strong attractive interactions between nicotinic acid and water. With increase in compositions of D-Glucose, D-Fructose and D-Lactose in water values ofϕ_{KS}^0 become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of nicotinic acid and therefore at high concentrations of D-Glucose, D-Fructose and D-Lactose water molecules around nicotinic acid are more compressible than those at lower concentrations.

Effect of temperature

As the behavior of nicotinic acid was found similar in entire range of composition of D-Fructose, D-Glucose and D-Lactose in water at one temperature. So, the effect of temperature has been studied on the lowest composition of D-Fructose, D-Glucose and D-Lactose in water respectively. Densities (ρ), apparent molar volumes (ϕ_v), sound velocities (U) and apparent molar adiabatic compressibilities (ϕ_{ks}) of nicotinic acid in water, 0.05 mol.kg^{-1} D- Glucose, 0.05 mol.kg^{-1} D-Fructose and 0.05 mol.kg^{-1} D-Lactose at different temperatures have been measured and are reported in tables 3.25 and 3.26 respectively.

Table 3.25:Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes (ϕ_v^0) and experimental slopes (S_v^*) of nicotinic acid in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

m^a (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x10^{-3} (kg.m^{-3})	ϕ_v x 10^6 (m^3.mol^{-1})	ϕ_v^0 x 10^6 (m^3.mol^{-1})	S_v^* x 10^4 (m^3.L$^{1/2}$.mol$^{-3/2}$)
Water 298.15 K					
0.01001	9.986193	0.997472	80.73	80.08 (±0.011)	0.064 (±0.000)
0.02998	17.26820	0.998304	81.20		
0.04997	22.27574	0.999122	81.53		
0.06994	26.33209	0.999928	81.80		
0.09993	31.43663	1.001121	82.13		
0.14997	38.43223	1.003072	82.56		
303.15 K					
0.01001	9.97916	0.996068	81.49	80.84 (±0.030)	0.063 (±0.000)
0.02998	17.25594	0.996887	81.92		
0.04997	22.25980	0.997693	82.24		
0.06994	26.31309	0.998485	82.52		
0.09993	31.41375	0.999664	82.79		
0.14997	38.40354	1.001575	83.30		
308.15 K					
0.01001	9.97103	0.994447	82.06	81.48 (±0.010)	0.057 (±0.000)
0.02998	17.24183	0.995257	82.46		
0.04997	22.24151	0.996054	82.77		
0.06994	26.29142	0.996841	83.00		
0.09993	31.38767	0.998005	83.30		
0.14997	38.37165	0.999912	83.69		
313.15 K					
0.01001	9.96189	0.992623	82.95	82.47 (±0.009)	0.048 (±0.000)
0.02998	17.22589	0.993418	83.32		
0.04997	22.22083	0.994203	83.56		
0.06994	26.26684	0.994978	83.76		
0.09993	31.35814	0.996128	84.00		
0.14997	38.33525	0.998016	84.31		
0.05 mol.kg^{-1} D-Fructose + water 298.15 K					
0.01021	10.11179	1.002712	81.07		

0.02998	17.31331	1.003526	81.49	80.45(± 0.022)	0.060 (±0.000)
0.05003	22.34713	1.004338	81.79		
0.07012	26.43431	1.005141	82.04		
0.10012	31.54771	1.006318	82.39		
0.14984	38.51473	1.008241	82.76		
303.15 K					
0.01021	10.10460	1.001285	82.00	81.41(± 0.020)	0.059 (±0.000)
0.02998	17.30084	1.002081	82.45		
0.05003	22.33087	1.002877	82.71		
0.07012	26.41483	1.003660	82.99		
0.10012	31.52418	1.004817	83.28		
0.14984	38.48521	1.006696	83.68		
308.15 K					
0.01021	10.09628	0.999638	82.27	81.76(± 0.010)	0.050 (±0.000)
0.02998	17.2866	1.000432	82.65		
0.05003	22.31249	1.001226	82.90		
0.07012	26.39315	1.002013	83.09		
0.10012	31.49836	1.003172	83.35		
0.14984	38.45389	1.005058	83.70		
313.15 K					
0.01021	10.08691	0.997783	83.52	83.03(±0.012)	0.048 (±0.000)
0.02998	17.27038	0.998555	83.87		
0.05003	22.29133	0.999328	84.09		
0.07012	26.36782	1.000091	84.31		
0.10012	31.46769	1.001219	84.54		
0.14984	38.41549	1.003052	84.88		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01011	10.06203	1.002676	80.85	80.13(±0.014)	0.070 (±0.000)
0.02996	17.30729	1.003495	81.36		
0.05002	22.34458	1.004308	81.71		
0.07014	26.43765	1.005111	81.99		
0.10011	31.54567	1.006287	82.36		
0.14994	38.52645	1.008194	82.88		
303.15 K					
0.01011	10.0549	1.001254	81.70	81.00(±0.0134)	0.069 (±0.000)
0.02996	17.29488	1.002057	82.22		
0.05002	22.32839	1.002853	82.58		
0.07014	26.41831	1.003641	82.85		
0.10011	31.52226	1.004794	83.21		
0.14994	38.49728	1.006668	83.69		
308.15 K					
0.01011	10.04666	0.999615	82.16		
0.02996	17.28070	1.000414	82.56		

0.05002	22.31006	1.001207	82.87	81.57(±0.016)	0.058 (±0.000)
0.07014	26.3966	1.001992	83.12		
0.10011	31.49640	1.003146	83.41		
0.14994	38.46591	1.005028	83.80		
313.15 K					
0.01011	10.03737	0.997766	83.43	82.86(±0.011)	0.056 (±0.000)
0.02996	17.26452	0.998541	83.84		
0.05002	22.28895	0.999313	84.10		
0.07014	26.37134	1.000075	84.35		
0.10011	31.46576	1.001195	84.64		
0.14994	38.42750	1.003022	85.02		
0.05 mol.kg^{-1} D-Lactose + water **298.15 K**					
0.01011	10.07153	1.004569	82.15	81.38 (±0.039)	0.077 (±0.001)
0.02997	17.32623	1.005358	82.76		
0.05001	22.36274	1.006141	83.09		
0.07008	26.45001	1.006905	83.48		
0.10011	31.57306	1.008035	83.86		
0.14994	38.55838	1.009866	84.36		
303.15 K					
0.01011	10.06435	1.003137	82.41	81.63 (±0.015)	0.075 (±0.002)
0.02997	17.31388	1.003925	82.92		
0.05001	22.34675	1.004703	83.31		
0.07008	26.43114	1.005469	83.63		
0.10011	31.55050	1.006595	84.02		
0.14994	38.53075	1.008419	84.54		
308.15 K					
0.01011	10.05606	1.001485	83.07	82.35 (±0.025)	0.072 (±0.009)
0.02997	17.29950	1.002259	83.66		
0.05001	22.32811	1.003027	83.99		
0.07008	26.40898	1.003783	84.28		
0.10011	31.52383	1.004894	84.65		
0.14994	38.49772	1.006691	85.17		
313.15 K					
0.01011	10.04676	0.999635	83.45	82.80 (±0.024)	0.065 (±0.009)
0.02997	17.28350	1.000406	83.94		
0.05001	22.30742	1.001169	84.29		
0.07008	26.38448	1.001922	84.56		
0.10011	31.49459	1.003031	84.90		
0.14994	38.46222	1.004835	85.31		

m^a(mol kg^{-1}) molality of nicotinic acid in in different solvent systems

Table 3.26: Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities(ϕ^0_{KS}) and experimental slopes (S^*_K) of nicotinic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

m^a (mol.kg^{-1})	U (m.s^{-1})	K_S x 10^{10} (kg^{-1}.m.s^2)	ϕ_{KS} x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	ϕ^0_{KS}x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	S^*_K x 10^6 (kg.m^3.mol^{-2}.G.Pa^{-1})
Water 298.15 K					
0.01001	1497.58	4.470	-40.16	-41.67 (±0.867)	-24.73(±10.509)
0.02998	1498.68	4.460	-43.18		
0.04997	1499.45	4.452	-43.82		
0.06994	1499.99	4.445	-44.11		
0.09993	1501.34	4.432	-44.35		
0.14997	1503.27	4.412	-44.59		
303.15 K					
0.01001	1509.65	4.405	-39.5	-41.00 (±0.855)	-24.37(±10.371)
0.02998	1510.85	4.394	-42.48		
0.04997	1511.47	4.387	-43.11		
0.06994	1511.93	4.381	-43.40		
0.09993	1513.32	4.368	-43.64		
0.14997	1514.99	4.350	-43.87		
308.15 K					
0.01001	1520.44	4.349	-38.94	-40.42 (±0.846)	-24.09(±10.253)
0.02998	1520.89	4.343	-41.88		
0.04997	1521.74	4.335	-42.50		
0.06994	1522.32	4.328	-42.79		
0.09993	1523.31	4.318	-43.03		
0.14997	1525.28	4.298	-43.26		
313.15 K					
0.01001	1529.27	4.307	-38.47	-39.94(±0.839)	-23.87 (±10.171)
0.02998	1529.91	4.300	-41.39		
0.04997	1530.74	4.292	-42.01		
0.06994	1530.91	4.288	-42.29		
0.09993	1531.98	4.277	-42.52		
0.14997	1533.82	4.259	-42.75		
0.05 mol.kg^{-1} D-Fructose + water 298.15 K					
0.01021	1500.91	4.427	-40.13	-41.57(±0.832)	-23.99(±10.088)
0.02998	1501.83	4.418	-43.02		
0.05003	1502.55	4.410	-43.65		

0.07012	1503.46	4.401	-43.94		
0.10012	1504.53	4.389	-44.18		
0.14984	1506.64	4.369	-44.41		
303.15 K					
0.01021	1512.91	4.363	-39.49	-40.92(±0.822)	-23.64(±9.956)
0.02998	1513.69	4.355	-42.34		
0.05003	1514.38	4.347	-42.96		
0.07012	1515.26	4.339	-43.24		
0.10012	1516.11	4.329	-43.48		
0.14984	1517.93	4.311	-43.71		
308.15 K					
0.01021	1523.23	4.311	-38.91	-40.32(±0.813)	-23.39(±9.853)
0.02998	1524.16	4.302	-41.73		
0.05003	1524.49	4.297	-42.35		
0.07012	1525.08	4.290	-42.63		
0.10012	1526.25	4.279	-42.86		
0.14984	1527.98	4.261	-43.09		
313.15 K					
0.01021	1523.23	4.319	-38.42	-39.83(±0.816)	-23.41(±9.889)
0.02998	1524.08	4.311	-41.25		
0.05003	1524.58	4.305	-41.86		
0.07012	1525.25	4.298	-42.14		
0.10012	1526.31	4.287	-42.37		
0.14984	1528.28	4.268	-42.60		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01011	1500.79	4.427	-40.09	-41.56(±0.843)	-24.17(±10.217)
0.02996	1501.99	4.417	-43.02		
0.05002	1502.59	4.410	-43.65		
0.07014	1503.28	4.402	-43.94		
0.10011	1504.41	4.390	-44.18		
0.14994	1506.53	4.370	-44.41		
303.15 K					
0.01011	1500.79	4.427	-40.09	-40.90(±0.832)	-23.82(±10.084)
0.02996	1501.99	4.417	-43.02		
0.05002	1502.59	4.410	-43.65		
0.07014	1503.28	4.402	-43.94		
0.10011	1504.41	4.390	-44.18		
0.14994	1506.53	4.370	-44.41		
308.15 K					
0.01011	1512.43	4.373	-38.83	-40.29(±0.835)	-23.88(±10.120)
0.02996	1513.71	4.362	-41.74		
0.05002	1514.39	4.355	-42.36		
0.07014	1515.32	4.346	-42.64		

0.10011	1516.21	4.336	-42.88		
0.14994	1517.99	4.318	-43.10		
313.15 K					
0.01011	1532.08	4.269	-38.42	-39.85(±0.817)	-23.33(±9.896)
0.02996	1532.88	4.262	-41.26		
0.05002	1533.42	4.255	-41.87		
0.07014	1533.92	4.249	-42.15		
0.10011	1535.05	4.238	-42.38		
0.14994	1536.44	4.223	-42.60		
0.05 mol.kg^{-1} D-Lactose + water **298.15 K**					
0.01011	1502.65	4.408	-40.00	-41.46 (±0.838)	-23.94(±10.152)
0.02997	1503.22	4.401	-42.91		
0.05001	1503.76	4.395	-43.53		
0.07008	1504.18	4.389	-43.82		
0.10011	1504.63	4.381	-44.06		
0.14994	1505.02	4.371	-44.28		
303.15 K					
0.01011	1514.71	4.344	-39.35	-40.79 (±0.827)	-23.62 (±10.01)
0.02997	1515.16	4.338	-42.22		
0.05001	1515.68	4.332	-42.84		
0.07008	1516.02	4.327	-43.12		
0.10011	1516.59	4.319	-43.35		
0.14994	1516.99	4.309	-43.58		
308.15 K					
0.01011	1525.09	4.293	-38.81	-40.23(±0.818)	-23.35 (±9.916)
0.02997	1525.66	4.286	-41.65		
0.05001	1526.18	4.280	-42.26		
0.07008	1526.87	4.273	-42.54		
0.10011	1527.25	4.266	-42.77		
0.14994	1527.89	4.255	-42.99		
313.15 K					
0.01011	1533.97	4.251	-38.34	-39.75 (±0.812)	-23.16 (±9.836)
0.02997	1534.58	4.244	-41.16		
0.05001	1535.06	4.238	-41.76		
0.07008	1535.75	4.231	-42.04		
0.10011	1536.34	4.223	-42.27		
0.14994	1537.01	4.212	-42.48		

m^a(mol.kg^{-1}) molality of nicotinic acid in in different solvent systems

From the analysis of table 3.25 and 3.26, it is found that the values of density and sound velocity increase with increase in temperature for nicotinic acid in water, 0.05 mol.kg^{-1} D-Fructose +

water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 molkg^{-1} D-Lactose + water. The density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities by using equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_V) are reported in table 3.25 and all the values are positive and increase in magnitude with increase in temperature for nicotinic acid in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water indicating the presence of strong solute - solvent interactions. On the other hand, the values of adiabatic compressibilities(ϕ_{KS}) which are reported in table 3.26, are negative at all temperatures which shows that water molecules around solute i.e. nicotinic acid are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of nicotinic acid and D-Fructose, D-Glucose and D-Lactose molecules.

The values of partial molar volumes (ϕ_V^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^0) are determined by applying the least square fitting to the plots of $\phi_V$vs square root of molar concentration and ϕ_{KS} vs molal concentration which are deduced by using equations (1.12 and 1.19) respectively. The values of these parameters for nicotinic acid in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures are reported in table 3.25 and 3.26 respectively.

It is clear, from table 3.25, that the values of slopes (S_V^*) are positive in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 molkg^{-1} D-Lactose + water in the entire temperature range indicating the presence of strong solute- solute interactions and magnitude of, S_V^* values decreases with increase in the temperature in water as well as in 0.05 mol.kg^{-1} D- Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 molkg^{-1} D-Lactose + water, indicating that these interactions are weakened which trait to the increase in solvation with increase in temperature. The values of partial molar volume (ϕ_V^0) are found to increase with increase in temperature in water as well as 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water indicating the increase in solute-solvent interactions with the rise in temperature. The plots of apparent molar volumes ϕ_V against the C$^{1/2}$ were found linear with the positive slopes in water , 0.05 mol.kg^{-1} D-Glucose + water, 0.05

mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures and are shown in figs. (3.27), (3.28) and (3.29) respectively. It has been found in the present study that the values of ϕ_{KS}^{0} for nicotinic acid are negative which attribute to the strong attractive interactions between nicotinic acid and water. With increase in temperature values ofϕ_{KS}^{0} become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of nicotinic acid and therefore at high temperature water molecules around nicotinic acid are more compressible than those at lower temperature.

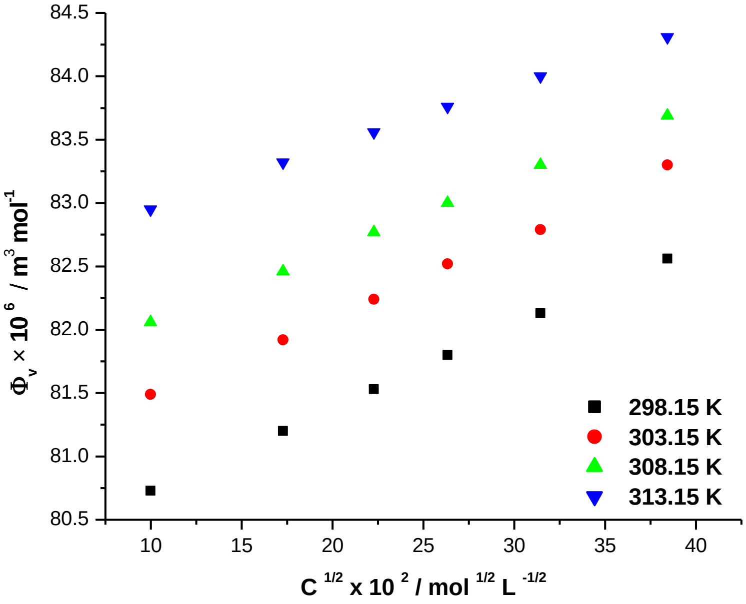

Fig.3.26. Plot of $\phi_v$vs C$^{1/2}$ for nicotinic acid in water at different temperatures.

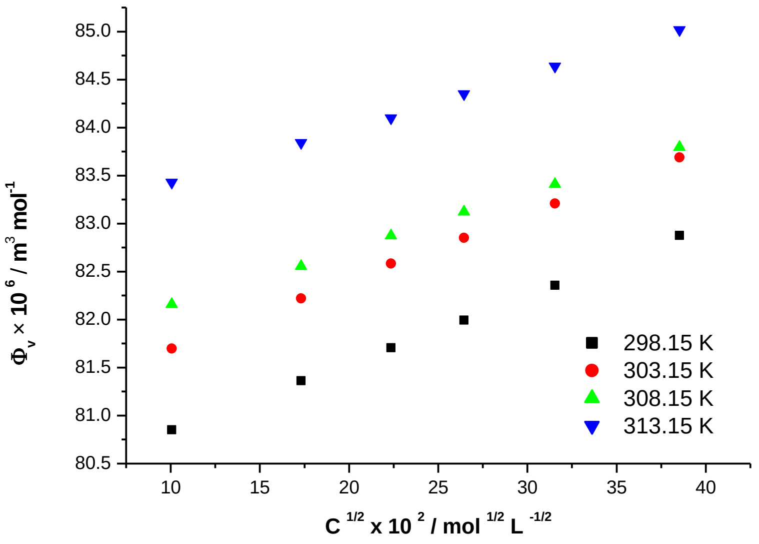

Fig.3.27. Plot of $\phi_v$vs $C^{1/2}$ for nicotinic acid in 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

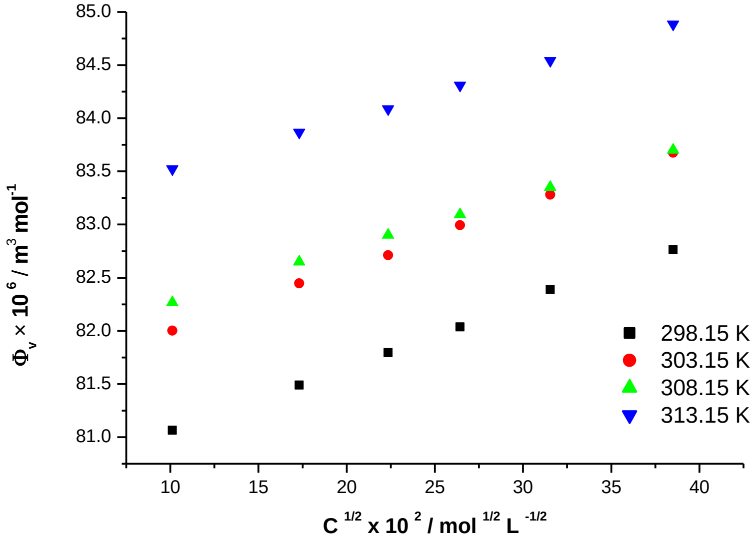

Fig.3.28. Plot of ϕ_v vs $C^{1/2}$ for nicotinic acid in 0.05 mol.kg^{-1} D-Fructose + water at different temperatures.

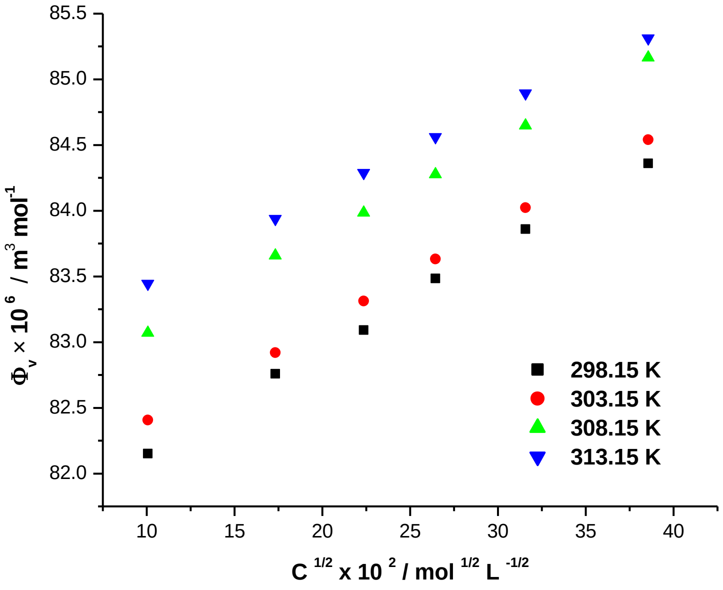

Fig. 3.29. Plot of ϕ_V vs $C^{1/2}$ for nicotinic acid in 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

Partial molar expansibilities (ϕ_E^0) is another parameter, which help in determining the structure making or breaking behavior of a solute in any of the solvent[6].

It is found that nicotinic acid shows similar behavior in all the compositions of D-Glucose, D-Fructose and D-Lactose in water, hence partial molar expansibilities (ϕ_E^0), Isobaric thermal expansion coefficient (α_2), and the molar heat capacities are determined only for the lower compositions i.e 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water. The temperature dependence of ϕ_V^0 in water , 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water for nicotinic acid are as follows:

$\phi_V^0 = 212.65 - 1.042\ T + 0.002\ T^2$ in water (3.15)

$\phi_V^0 = 389.43 - 2.230\ T + 0.004\ T^2$ in 0.05 mol.kg^{-1} D-Glucose + water (3.16)

$\phi_V^0 = 294.38 - 1.612\ T + 0.003T^2$ in 0.05 mol.kg^{-1} D-Fructose+ water (3.17)

$\phi_V^0 = 151.64 - 0.533\ T + 0.001T^2$ in 0.05 mol.kg^{-1} D-Lactose + water (3.18)

Partial molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_V^0}{\partial T}\right]_P$, which are temperature dependent function of ϕ_V^0 are calculated for nicotinic acid in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water by using relations (3.15) to (3.18) and are given in table 3.27.

Table. 3.27. Partial molar expansibilities, (ϕ_E^0) for nicotinic acid in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

T (K)	Water	0.05 mol.kg^{-1} D-Fructose +water	0.05 mol.kg^{-1} D-Glucose + water	0.05 mol.kg^{-1} D-Lactose +water
ϕ_E^0 x 10^6(m^3 mol^{-1} K^{-1})				
298.15	0.150	0.176	0.155	0.063
303.15	0.170	0.206	0.195	0.073
308.15	0.190	0.236	0.235	0.083
313.15	0.210	0.266	0.275	0.093

From table 3.27 it is clear that the values ofϕ_E^0, are positive at entire range of temperature but the values increases in magnitude with rise in temperature which show that nicotinic acid is behaving like symmetrical tetra alkyl ammonium salts[7] but not like common salts[8,9] because the molar volume expansibilities should decrease with the rise in temperature for a common salt. The increasing ϕ_E^0 values indicates the presence of "packing effect"[6]. The variation of ϕ_E^0 with temperature for nicotinic acid in water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water is linear and as shown in fig. (3.30).

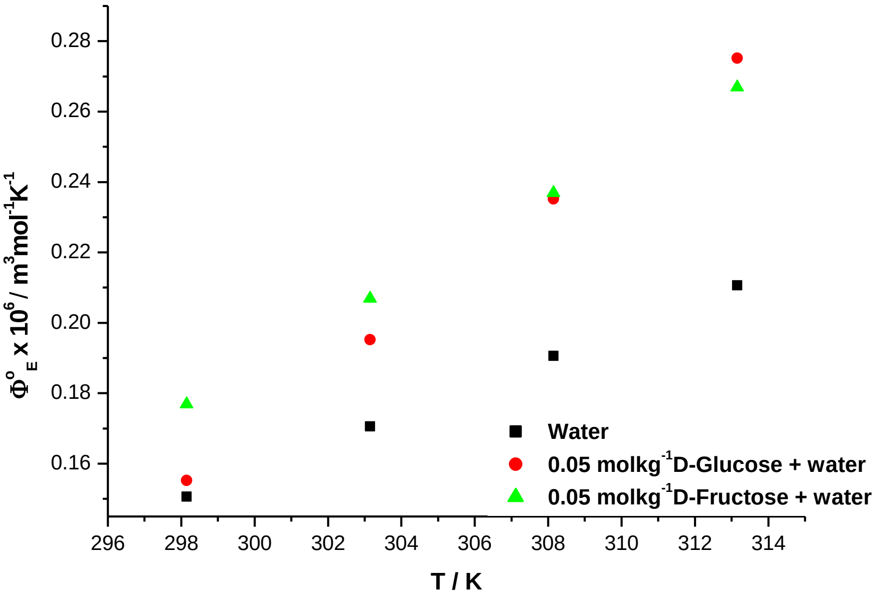

Fig.3.30. Plot of ϕ^0_E vs temperature for nicotinic acid in water ,0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Fructose + water.

Partial molar heat capacities are determined by taking the second derivative of partial molar volume with respect to temperature at constant pressure using the general thermodynamic expression (3.4)[6].

It is observed from relations (3.15) to (3.18) that sign of the values of $(\partial C_p/\partial P)_T$for the solutions of nicotinic acid are negative thereby showing that nicotinic acid behave as structure maker in aqueous and binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose[10]. The values of $(\partial C_p/\partial P)_T$ are reported in table 3.28.The values of ϕ^0_V andϕ^0_E are further used to calculate the isobaric thermal expansion coefficient[10]using equation (3.5). The calculated values of α_2 are included in table 3.28.

Table 3.28: Partial molar heat capacities,$(\partial C_p/\partial P)_T$, isobaric thermal expansion coefficient, (α_2) for nicotinic acid in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water mixture at different temperatures (K).

T (K)	**Water**		**0.05 mol.kg^{-1} D-Fructose + water**		**0.05 mol.kg^{-1} D-Glucose + water**		**0.05 mol.kg^{-1} D-Lactose + water**	
	$(\partial C_p/\partial P)_T$ **(m^{3}mol^{-1} K^{-1})**	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ **(m^{3}mol^{-1} K^{-1})**	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ **(m^{3}mol^{-1} K^{-1})**	α_2 (K^{-1})	$(\partial C_p/\partial P)_T$ **(m^{3}mol^{-1} K^{-1})**	α_2 (K^{-1})
298.15	-1.193	0.00188	-1.789	0.00220	-2.385	0.00194	-0.596	0.00078
303.15	-1.213	0.00211	-1.819	0.00254	-2.425	0.00241	-0.606	0.00090
308.15	-1.233	0.00234	-1.849	0.00290	-2.465	0.00288	-0.616	0.00101
313.15	-1.253	0.00255	-1.879	0.00321	-2.505	0.00332	-0.626	0.00113

The α_2 values for nicotinic acid increase with increase in temperature in water as well as in 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water mixtures suggesting that the expansibility decreases[10] with increase in temperature for nicotinic acid in water as well as in 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water mixtures.

B. TRANSPORT PROPERTIES

In the present study, viscous flow of nicotinic acid has been determined in water and in binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose at various concentrations of solute and at different temperatures. The relative viscosities of the nicotinic acid in water and binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose at different temperatures were calculated by using equation (3.6).

The obtained relative viscosities were interpreted by Jones-Dole equation (1.28) where a straight line plot was obtained when $(\eta_r - 1)/C^{1/2}$ is plotted against $C^{1/2}$. The values of A and B parameters of Jones-Dole equation (1.28) were obtained using least square fit to the plots of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$. A parameter represents solute-solute interactions whereas the B parameter represents solute- solvents interactions[11].

The Viscosities and relative viscosities along with A and B coefficients of the Jones – Dole equation for nicotinic acid were determined in water and in different compositions of D-Fructose, D-Glucose and D-Lactose in water (0.05, 0.15, 0.25, 0.35) mol.kg^{-1}at 303.15K and are reported in table 3.29.

TABLE 3.29: Viscosities(η) , relative viscosities (η_r) and values of A and B coefficients of the Jones – Dole equation for nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K.

m^a (mol·kg^{-1})	**C$^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)**	**η (mPa·s)**	**η_r**	**A (L$^{1/2}$.mol$^{-1/2}$)**	**B (L.mol^{-1})**
0.05 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.83310	-	4.243 (±0.309)	0.382 (±0.011)
0.01021	10.10460	0.83966	1.00788		
0.02998	17.30084	0.84896	1.01903		
0.05003	22.33087	0.85727	1.02901		
0.07012	26.41483	0.8653	1.03865		
0.10012	31.52418	0.8758	1.05125		
0.14984	38.48521	0.8932	1.07214		
0.15 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.86720	-	4.212(±0.191)	0.390(±0.007)
0.00989	9.978426	0.87408	1.00794		
0.02997	17.35572	0.88374	1.01907		
0.05013	22.42749	0.89269	1.02939		
0.07022	26.52128	0.90121	1.03922		
0.10012	31.62834	0.91249	1.05223		
0.14984	38.61147	0.93131	1.07393		
0.25 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.90150	-	4.148(±0.214)	0.399(±0.008)
0.01014	10.13679	0.90887	1.00818		

0.02989	17.38930	0.91887	1.01927		
0.05013	22.50064	0.92832	1.02975		
0.07012	26.58869	0.93761	1.04006		
0.10011	31.72914	0.94926	1.05298		
0.14984	38.73541	0.96965	1.0756		
0.35 mol.kg^{-1} D-Fructose + water					
0.00000	0.00000	0.93490	-	4.116(±0.171)	0.407(±0.006)
0.01015	10.16762	0.94274	1.00839		
0.02987	17.42761	0.95309	1.01945		
0.05016	22.56423	0.96316	1.03023		
0.07015	26.66132	0.97265	1.04038		
0.10021	31.82433	0.98509	1.05369		
0.14996	38.84661	1.0076	1.07776		
0.05 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.81900	-	4.348(±0.150)	0.266(±0.005)
0.01011	10.0549	0.82490	1.00720		
0.02996	17.29488	0.83140	1.01514		
0.05002	22.32839	0.83790	1.02307		
0.07014	26.41831	0.84371	1.03017		
0.10011	31.52226	0.85178	1.04003		
0.14994	38.49728	0.86524	1.05646		
0.15 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.85300	-	4.307(±0.232)	0.274(±0.008)
0.00998	10.02356	0.85922	1.00729		
0.02997	17.35554	0.86606	1.01531		
0.05013	22.42731	0.87318	1.02366		
0.07012	26.50235	0.87903	1.03052		
0.10002	31.61246	0.88774	1.04072		

0.14994	38.62392	0.90272	1.05829		
0.25 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.88700	-	4.245(±0.339)	0.287(±0.012)
0.01025	10.18983	0.8937	1.00755		
0.02982	17.36572	0.90086	1.01562		
0.05023	22.52084	0.90875	1.02452		
0.07032	26.62374	0.91451	1.03102		
0.10032	31.75941	0.92399	1.0417		
0.14964	38.70672	0.94077	1.06062		
0.35 mol.kg^{-1} D-Glucose + water					
0.00000	0.00000	0.92010	-	4.140(±0.274)	0.303(±0.010)
0.01015	10.16545	0.92712	1.00763		
0.02999	17.45886	0.93476	1.01593		
0.05013	22.55295	0.94298	1.02486		
0.07014	26.65411	0.94976	1.03224		
0.10011	31.80242	0.9603	1.04369		
0.14996	38.83964	0.97763	1.06253		
0.05 mol.kg^{-1} D-Lactose + water					
0.00000	0.00000	0.86300	-	4.349(±0.141)	0.384(±0.005)
0.01011	10.05108	0.87000	1.00812		
0.02997	17.29988	0.87961	1.01925		
0.05001	22.31279	0.88823	1.02924		
0.07008	26.35837	0.89614	1.03841		
0.10011	31.43371	0.90780	1.05191		
0.14994	38.35193	0.92652	1.0736		
0.15 mol.kg^{-1} D-Lactose + water					
0.00000	0.00000	0.90240	-		
0.01011	10.12345	0.90978	1.00818		

0.02997	17.40391	0.92008	1.01959	4.340(±0.072)	0.387 (±0.002)
0.05001	22.44794	0.92924	1.02974		
0.07008	26.53314	0.93754	1.03894		
0.10011	31.64098	0.95006	1.05281		
0.14994	38.57865	0.96988	1.07477		
0.25 mol.kg^{-1} D-Lactose + water					
0.00000	0.00000	0.94120	-	4.230(±0.162)	0.404(±0.007)
0.01011	10.16325	0.94909	1.00839		
0.02997	17.50079	0.95994	1.01991		
0.05001	22.56862	0.96992	1.03052		
0.07008	26.66955	0.97875	1.03989		
0.10011	31.80471	0.99344	1.0555		
0.14994	38.78449	1.01391	1.07726		
0.35 mol.kg^{-1} D-Lactose + water					
0.00000	0.00000	0.98130	-	4.181 (±0.367)	0.421(±0.013)
0.01001	10.18577	0.98972	1.00858		
0.02998	17.60325	1.00127	1.02036		
0.05007	22.70555	1.01210	1.03139		
0.07001	26.81636	1.02176	1.04123		
0.10009	31.98339	1.03867	1.05846		
0.14997	39.00315	1.05965	1.07985		

m^a (mol.kg^{-1}) is the molality of nicotinic acid in different solvent systems

The values of coefficients A and B are obtained by plotting graphs between $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ where A is the intercept and B is the slope for the respective graph. The values of A and B parameters for nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K are recorded in table 3.29 respectively. Sample plots of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in different compositions of D-Fructose, D-Glucose and D-Lactose in water are shown in figures (3.31), (3.32) and (3.33) respectively.

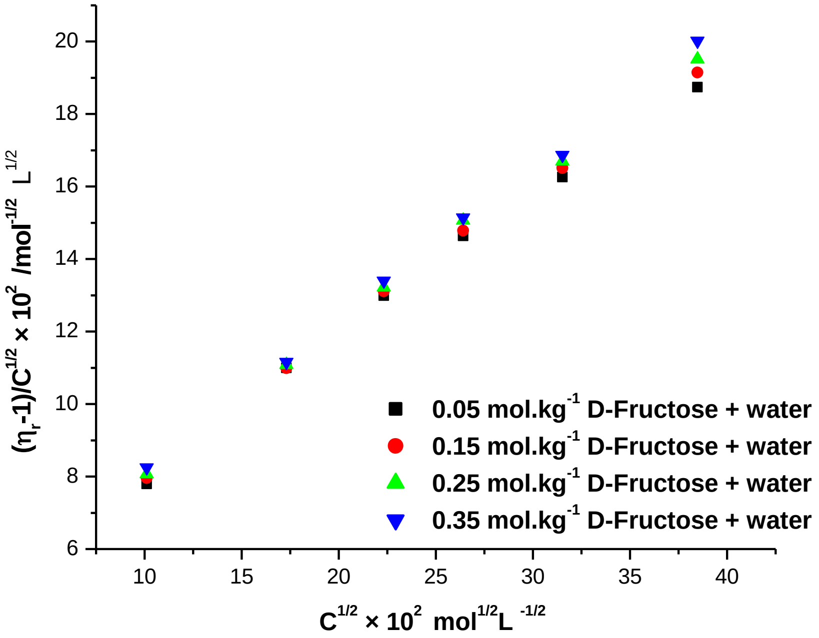

Fig. 3.31. Plot of $(\eta_{r\text{-}}\text{-}1)/\ C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in different compositions of D-Fructose in water at 303.15 K

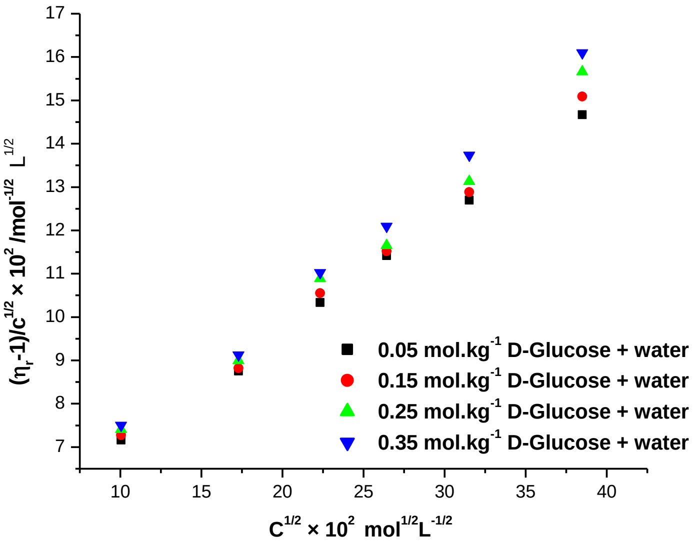

Fig. 3.32. Plot of $(\eta_{r\text{-}}\text{-}1)/\ C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in different compositions of D-Glucose in water at 303.15 K.

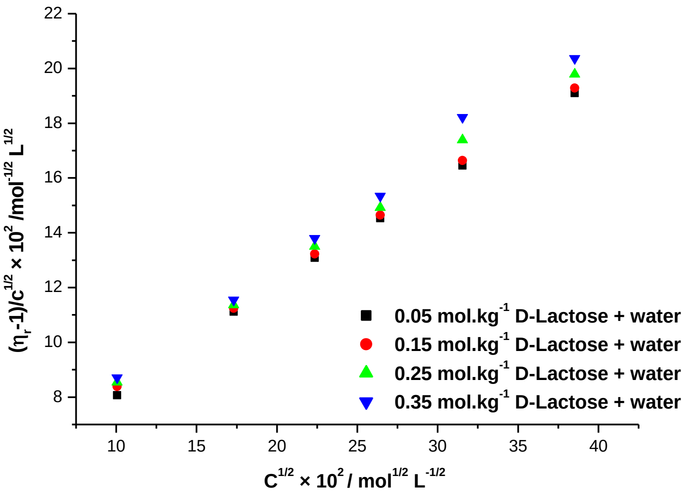

Fig. 3.33: Plot of $(\eta_{r}\text{-}1)/C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in different composition of D-Lactose in water at 303.15K.

The values of A-coefficient in table 3.29 are positive and decrease with the increase in the concentration of D-Fructose, D-Glucose and D-Lactose in water indicating the weakening of solute-solute interactions with the increase of D-Fructose, D-Glucose and D-Lactose content in water. Also, it is found that values of B-coefficient are positive indicating the presence of strong solute-solvent interactions. This may be attributed to the strong solvation of nicotinic acid in the binary aqueous mixtures of D-Fructose, D-Glucose and D-Lactose in water. From the table 3.29, it is clear that B-coefficient values increase with the increase of D-Fructose, D-Glucose and D-Lactose content in water at 303.15 K, thereby showing that solute – solvent interactions are further strengthened with the increase of D-Fructose, D-Glucose and D-Lactose content in water. So, it is clear that there is a great change in the solute - solvent interactions when we switch from lower to higher composition of the solvents[12-13]. In other words the solvation is enhanced as the composition of D-Fructose, D-Glucose and D-Lactose in water increases.

The analysis of data was done on the basis of transition state theory proposed by Feakins *et al*[14]. The B-coefficient in terms of transition state theory is given by the relation (3.7) whereas all other parameter $(\Delta\mu_1^{0*}, \Delta\mu_2^{0*} \text{and} \overline{V_1^0},)$ were determined by the equations (3.8), (3.9) and

(3.10)respectively. The values of $\overline{V_2^0}$ for nicotinic acid were determined using the density data. All the parameters $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$and $\Delta\mu_2^{0^*}$are reported in table 3.30.

TABLE 3.30: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$and $\Delta\mu_2^{0^*}$ for nicotinic acid in different composition of D-Fructose + water, D-Glucose + water and D-Lactose + water at 303.15 K.

m (mol.kg^{-1})	$\overline{V_1^0} \times 10^6$ **(m^3.mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3.mol^{-1})**	$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$\Delta\mu_2^{0^*}$ **(kJ. mol$^{-1)}$**
D-Fructose + water				
0.05	18.15	81.41	26.66	63.87
0.15	18.31	81.94	26.72	63.13
0.25	18.48	82.18	26.77	62.89
0.35	18.67	82.61	26.82	62.45
D-Glucose + water				
0.05	18.15	81.00	26.64	48.46
0.15	18.31	81.42	26.70	47.79
0.25	18.48	81.76	26.75	46.42
0.35	18.68	82.04	26.80	45.70
D-Lactose + water				
0.05	18.86	81.63	26.74	62.86
0.15	20.69	81.97	26.89	61.84
0.25	23.02	82.26	27.06	60.87
0.35	26.00	82.59	27.23	60.43

It is evident from the above table that values of $\Delta\mu_1^{0^*}$ do not change much with the change in composition of D-Fructose and D-Glucose in water at 303.15 K i.e values of $\Delta\mu_1^{0^*}$are practically held constant in the entire composition range of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K. It is clear that the values of $\Delta\mu_2^{0^*}$decrease with solvent composition of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K suggesting that the transition state formation is more favored in the presence of nicotinic acid and is followed by making of the intermolecular bonds[14].

Effect of temperature

As the behavior of nicotinic acid was found similar for different compositions of D-Fructose + water, D-Glucose + water and D-Lactose + water at 303.15 K, so only lowest compositions i.e.

0.05 mol.kg^{-1}D-Fructose +water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water was taken for analyzing the effect of temperature. The viscosity and the relative viscosity data along with A and B coefficients of the Jones – Dole equation at different temperatures is given in table 3.31.

TABLE 3.31: Viscosities (η), relative viscosities (η_r) and the values of A and B coefficients of the Jones – Dole equation for nicotinic acid in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
Water **298.15 K**					
0.00000	0.00000	0.89370	-	3.601(±0.059)	0.088(±0.002)
0.01001	9.98619	0.89763	1.00439		
0.02998	17.26820	0.90162	1.00886		
0.04997	22.27574	0.90498	1.01262		
0.06994	26.33209	0.90787	1.01586		
0.09993	31.43663	0.91143	1.01984		
0.14997	38.43223	0.91755	1.02668		
303.15 K					
0.00000	0.00000	0.80070	-	3.575(±0.048)	0.105(±0.001)
0.01001	9.97916	0.80441	1.00463		
0.02998	17.25594	0.80816	1.00932		
0.04997	22.25980	0.81121	1.01313		
0.06994	26.31309	0.81397	1.01657		
0.09993	31.41375	0.81817	1.02182		
0.14997	38.43223	0.82412	1.02925		
308.15 K					
0.00000	0.00000	0.72250	-		

0.01001	9.97103	0.72603	1.00488	3.491(±0.157)	0.132(±0.006)
0.02998	17.24183	0.72946	1.00963		
0.04997	22.24151	0.73276	1.0142		
0.06994	26.29142	0.73606	1.01876		
0.09993	31.38767	0.73989	1.02407		
0.14997	38.37165	0.74611	1.03268		
313.15 K					
0.00000	0.00000	0.65600	-	3.353(±0.209)	0.169(±0.008)
0.01001	9.96189	0.65943	1.00522		
0.02998	17.22589	0.66275	1.01029		
0.04997	22.22083	0.66632	1.01573		
0.06994	26.26684	0.66952	1.02061		
0.09993	31.35814	0.67383	1.02718		
0.14997	38.33525	0.68085	1.03788		
0.05 mol.kg-1 D-Fructose +water **298.15 K**					
0.00000	0.00000	0.92940	-	4.261(±0.272)	0.359(±0.010)
0.01021	10.11179	0.93662	1.00776		
0.02998	17.31331	0.94653	1.01843		
0.05003	22.34713	0.95536	1.02794		
0.07012	26.43431	0.96281	1.03594		
0.10012	31.54771	0.97575	1.04988		
0.14984	38.51473	0.99351	1.06898		
303.15 K					
0.00000	0.00000	0.83310	-		
0.01021	10.10460	0.83966	1.00788		
0.02998	17.30084	0.84896	1.01903		
0.05003	22.33087	0.85727	1.02901		

0.07012	26.41483	0.86530	1.03865	4.218(±0.216)	0.403(±0.008)
0.10012	31.52418	0.87580	1.05125		
0.14984	38.48521	0.89320	1.07214		
308.15 K					
0.00000	0.00000	0.75220	-	4.243(±0.309)	0.382(±0.011)
0.01021	10.09628	0.75835	1.00818		
0.02998	17.28660	0.76714	1.01986		
0.05003	22.31249	0.77424	1.0293		
0.07012	26.39315	0.78187	1.03945		
0.10012	31.49836	0.79215	1.05311		
0.14984	38.45389	0.80916	1.07573		
313.15 K					
0.00000	0.00000	0.68380	-	4.192(±0.275)	0.427(±0.010)
0.01021	10.08691	0.6897	1.00862		
0.02998	17.27038	0.69769	1.02031		
0.05003	22.29133	0.70459	1.0304		
0.07012	26.36782	0.71125	1.04014		
0.10012	31.46769	0.72125	1.05476		
0.14984	38.41549	0.73865	1.08022		
0.05 mol.kg-1 D-Glucose + water **298.15 K**					
0.00000	0.00000	0.91390	-	4.360(±0.184)	0.222(±0.007)
0.01011	10.06203	0.92008	1.00676		
0.02996	17.30729	0.92647	1.01376		
0.05002	22.34458	0.93302	1.02093		
0.07014	26.43765	0.93896	1.02742		
0.10011	31.54567	0.94679	1.03599		
0.14994	38.52645	0.95931	1.04969		

303.15 K					
0.00000	0.00000	0.81900	-	4.348(±0.150)	0.266(±0.005)
0.01011	10.05490	0.8249	1.0072		
0.02996	17.29488	0.8314	1.01514		
0.05002	22.32839	0.8379	1.02307		
0.07014	26.41831	0.84371	1.03017		
0.10011	31.52226	0.85178	1.04003		
0.14994	38.49728	0.86524	1.05646		
308.15 K					
0.00000	0.00000	0.73920	-	4.233(±0.338)	0.328(±0.013)
0.01011	10.04666	0.74486	1.00766		
0.02996	17.28070	0.75196	1.01727		
0.05002	22.31006	0.75818	1.02568		
0.07014	26.39660	0.7635	1.03288		
0.10011	31.49640	0.77398	1.04705		
0.14994	38.46591	0.78722	1.06497		
313.15 K					
0.00000	0.00000	0.67160	-	4.224(±0.392)	0.346(±0.015)
0.01011	10.03737	0.67703	1.00808		
0.02996	17.26452	0.68332	1.01745		
0.05002	22.28895	0.68901	1.02593		
0.07014	26.37134	0.69459	1.03423		
0.10011	31.46576	0.70404	1.0483		
0.14994	38.42750	0.71738	1.06817		
0.05 mol.kg-1 D-Lactose + water **298.15 K**					
0.00000	0.00000	0.97770	-	4.444(±0.209)	0.369(±0.008)
0.01011	10.07153	0.98555	1.00803		

0.02997	17.32623	0.99627	1.019		
0.05001	22.36274	1.00576	1.0287		
0.07008	26.45001	1.01430	1.03743		
0.10011	31.57306	1.02790	1.05135		
0.14994	38.55838	1.04740	1.07129		
303.15 K					
0.00000	0.00000	0.86300	-	4.349(±0.141)	0.384(±0.005)
0.01011	10.06435	0.87000	1.00812		
0.02997	17.31388	0.87961	1.01925		
0.05001	22.34675	0.88823	1.02924		
0.07008	26.43114	0.89614	1.03841		
0.10011	31.5505	0.90780	1.05191		
0.14994	38.53075	0.92652	1.07360		
308.15 K					
0.00000	0.00000	0.76660	-	4.249(±0.121)	0.401(±0.004)
0.01011	10.05606	0.77289	1.00820		
0.02997	17.29950	0.78155	1.01950		
0.05001	22.32811	0.78944	1.02979		
0.07008	26.40898	0.79668	1.03924		
0.10011	31.52383	0.80734	1.05315		
0.14994	38.49772	0.82460	1.07566		
313.15 K					
0.00000	0.00000	0.70960	-	4.188(±0.094)	0.412(±0.003)
0.01011	10.04676	0.71551	1.00834		
0.02997	17.28350	0.72354	1.01964		
0.05001	22.30742	0.73095	1.03009		
0.07008	26.38448	0.73776	1.03969		
0.10011	31.49459	0.74779	1.05382		

0.14994	38.46222	0.76451	1.07738		

m^a (mol.kg^{-1}) is the molality of nicotinic acid in different solvent systems

The plots of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$ have been found linear at all the four temperatures and sample plots for nicotinic acid in 0.05 mol.kg^{-1}D-Fructose +water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1}D-Lactose + water at different temperatures are shown in figures (3.34), (3.35), (3.36) and (3.37) respectively. This is in accordance to the Jones – Doles equation.

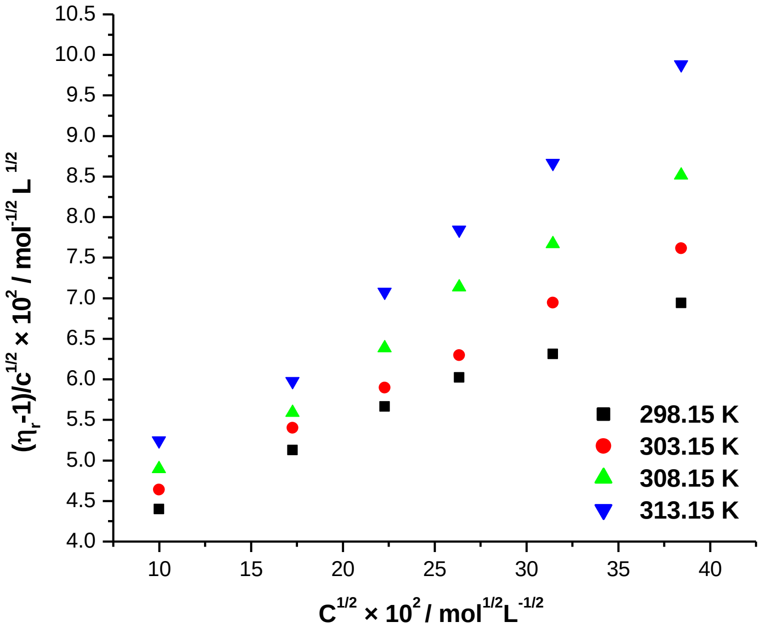

Fig. 3.34. Plot of$(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in water at different temperatures.

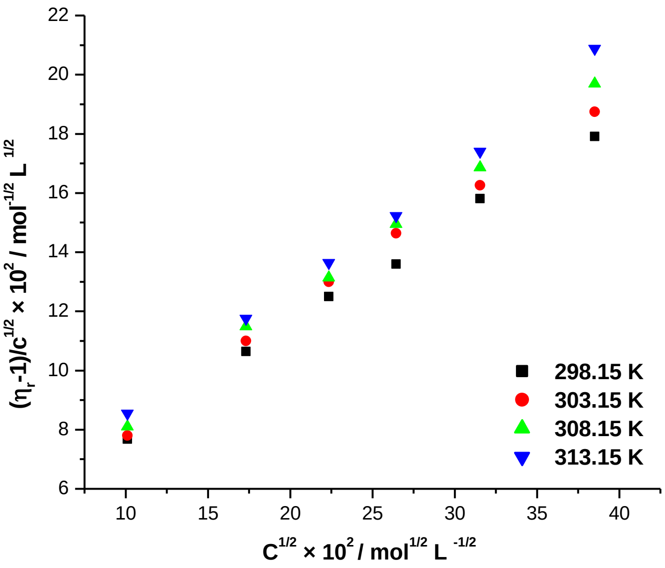

Fig. 3.35. Plot of$(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in 0.05 mol.kg^{-1}D-Fructose + water at different temperatures.

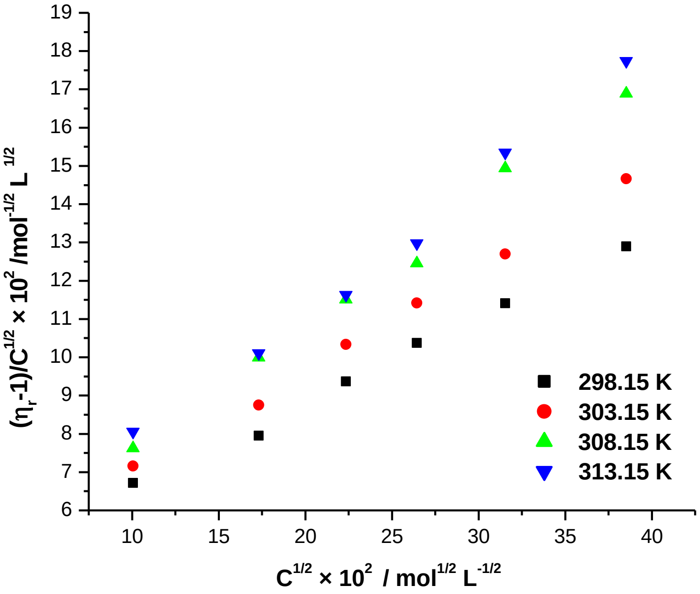

Fig. 3.36. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$for nicotinic acid in 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

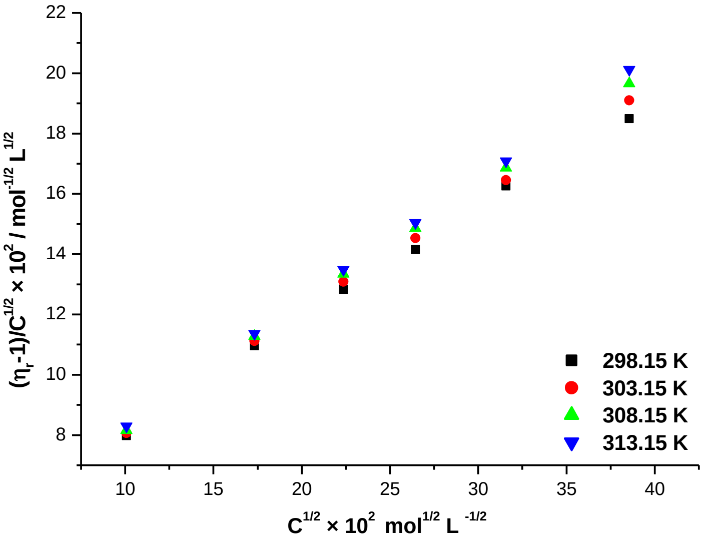

Fig. 3.37. Plot of $(\eta_{r}-1)/C^{1/2}$ vs $C^{1/2}$ for nicotinic acid in 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

The values of A-coefficient reported in table 3.31 are positive for the entire range of temperature indicating the presence of solute-solute interactions. Further the values of A-coefficient decrease with rise in temperature in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 05 mol.kg^{-1} D-Lactose + water indicating the weakening of solute-solute interactions with the rise in temperature. Also the values of B-coefficient are positive in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at all temperatures thereby showing the presence of strong solute-solvent interactions. Further the values of B-coefficient increase with the rise in temperature which suggest that solute-solvent interaction are strengthened with the rise in temperature[15]. The viscosity data has also been examined by applying the transition state theory at different temperatures from 298.15-318.15 K and the calculated values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ have also been recorded in table 3.32.

TABLE 3.32: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for nicotinic acid in 0.05 mol.kg^{-1}D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

T (K)	$\overline{V_1^0} \times 10^6$ **(m^3.mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3.mol^{-1})**	$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$\Delta\mu_2^{0^*}$ **(kJ.mol^{-1})**
0.05 mol.kg^{-1} D-Fructose + water				
298.15	18.12	80.45	26.34	62.25
303.15	18.15	81.41	26.66	60.11
308.15	18.18	81.76	26.99	58.46
313.15	18.21	83.03	27.32	55.24
0.05 mol.kg^{-1} D-Glucose + water				
298.15	18.12	80.13	26.32	58.52
303.15	18.15	81.00	26.64	56.02
308.15	18.18	81.57	26.97	54.15
313.15	18.21	82.86	27.30	51.98
0.05 mol.kg^{-1} D-Lactose + water				
298.15	18.25	81.38	26.40	64.47
303.15	18.27	81.63	26.71	62.11
308.15	18.30	82.36	27.02	60.42
313.15	18.34	82.80	27.37	57.33

According to Feakins model[14] decreases in the values of $\Delta\mu_2^{0^*}$with temperature leads structure making ability of the solute and simultaneously transition state formation is more favoured due to making of intermolecular bonds in the solvent mixture by the presence of solute. In the present study values of $\Delta\mu_2^{0^*}$decrease with increase in temperature supporting structure making ability of nicotinic acid and simultaneously transition state formation is more favoured in 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water mixtures respectively by presence of nicotinic acid.

TABLE 3.33: Values of ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$),T$\Delta S_2^{0^*}$and $\Delta H_2^{0^*}$for nicotinic acid in 0.05 mol.kg^{-1}D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

T (K)	$\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$ (kJ.mol^{-1}	T. $\Delta S_2^{0^*}$ (kJ.mol^{-1})	$\Delta H_2^{0^*}$ (kJ.mol^{-1})
0.05 mol.kg^{-1} D-Fructose + water			
298.15	35.91	134.17	134.17
303.15	33.45	136.42	136.42
308.15	31.47	138.67	138.67
313.15	27.92	140.92	140.92
0.05 mol.kg^{-1} D-Glucose + water			
298.15	32.20	125.22	164.10
303.15	29.38	127.32	173.03
308.15	27.18	129.42	184.62
313.15	24.68	131.52	190.27
0.05 mol.kg^{-1} D-Lactose + water			
298.15	38.07	137.15	195.88
303.15	35.40	139.45	201.18
308.15	33.40	141.75	206.87
313.15	29.96	144.05	211.73

The values of change in activation energy per mole of solute ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$) on replacing one mole of solvent by one mole of solute at infinite dilution are recorded in table 3.33. Since the values are positive and decreases for nicotinic acid in 0.05 mol.kg^{-1}D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1}D-Lactose + water solvent systems at different temperatures, so it may be concluded that transitions state is accompanied by making of intermolecular bonds. In other word transition state is more favored in the presence of nicotinic acid in the entire temperature range studied here. The entropy of activation $\Delta S_2^{0^*}$[16] and values of enthalpy of activation i.e $\Delta H_2^{0^*}$ for nicotinic acid has been determined from the following equations 3.11 and 3.12.

The T. $\Delta S_2^{0^*}$ and $\Delta H_2^{0^*}$ values at different temperatures are recorded in table 3.33. As both the parameters enthalpy of activation and entropy of activation are positive for nicotinic acid this indicate that the transition state is associated with bond breaking between solute and solvent molecules[14].

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SECTION IV

THERMODYNAMIC AND TRANSPORT PROPERTIES OF PYRIDOXINE HYDROCHLORIDE IN WATER AND BINARY AQUEOUS MIXTURES OF D-FRUCTOSE, D-GLUCOSE AND D-LACTOSE

The present section describes the thermodynamic and transport properties such as partial molar volumes, partial molar adiabatic compressibilities, partial molar expansibilities, viscosity A and B coefficients of Jones Dole equation, activation energy parameters etc. of pyridoxine hydrochloride in water and binary aqueous mixtures of D-Fructose, D-Glucose and D-Lactose.

For the sake of convenience this section has been further divided into two parts.

A. THERMODYNAMIC PROPERTIES
B. TRANSPORT PROPERTIES

A. THERMODYNAMIC PROPERTIES

Thermodynamic properties such as partial molar volumes, partial molar adiabatic compressibilities and partial molar expansibilities were determined using the density and speed of sound data of pyridoxine hydrochloride in water and binary aqueous mixtures of D-Fructose, D-Glucose and D-Lactose. The effect of composition of D-Fructose, D-Glucose and D-Lactose in water was determined at one temperature i.e. 303.15K whereas the above mentioned properties have been determined at different temperatures to analyze the effect of temperature. The densities (ρ), apparent molar volumes(ϕ_v), sound velocities (U) and apparent molar adiabatic compressibilities (ϕ_{ks}) of pyridoxine hydrochloride in binary aqueous mixtures of D-Glucose and D-Fructose and D-Lactose (0.05, 0.15, 0.25 and 0.35) mol.kg^{-1} at 303.15K have been measured and are reported in tables 3.34 and 3.35 respectively.

Table 3.34: Densities (ρ), apparent molar volumes (ϕ_v), partial molar volumes(ϕ_v^0) and experimental slopes (S_v^*) of pyridoxine hydrochloride in different compositions of D-Fructose + water, D-Glucose + water and D-Lactose + water at 303.15 K.

m^a (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x 10^{-3} (kg.m^{-3})	ϕ_v x 10^6 (m^3.mol^{-1})	ϕ_v^0 x 10^6 (m^3.mol^{-1})	S_v^* x 10^4 (m^3.L$^{1/2}$.mol$^{-3/2)}$
0.05 mol.kg^{-1} D-Fructose + water					
0.01011	10.05173	1.001457	147.02	146.53(±0.012)	0.047(±0.000)
0.02997	17.28119	1.002603	147.35		
0.05001	22.29042	1.003744	147.59		
0.07001	26.33483	1.004868	147.81		
0.10090	31.54360	1.006585	148.03		

0.14994	38.31467	1.009256	148.36		
0.15 mol.kg^{-1} D-Fructose + water					
0.00989	9.975197	1.008159	147.54	147.07(±0.013)	0.044(±0.000)
0.02997	17.33878	1.009296	147.84		
0.05013	22.39098	1.010422	148.07		
0.07022	26.46103	1.011531	148.26		
0.10012	31.52639	1.013161	148.48		
0.14984	38.42659	1.015818	148.80		
0.25 mol.kg^{-1} D-Fructose + water					
0.01014	10.13339	1.014790	148.12	147.67(±0.010)	0.043(±0.000)
0.02989	17.37218	1.015884	148.43		
0.05013	22.46363	1.016989	148.67		
0.07012	26.52777	1.018069	148.84		
0.10011	31.62591	1.019667	149.07		
0.14984	38.54840	1.022268	149.36		
0.35 mol.kg^{-1} D-Fructose + water					
0.01015	10.16416	1.019959	149.03	148.60(±0.022)	0.042(±0.000)
0.02987	17.41027	1.021022	149.36		
0.05016	22.52670	1.022102	149.57		
0.07015	26.59951	1.023151	149.78		
0.10021	31.71959	1.024714	149.95		
0.14996	38.65707	1.027242	150.27		
0.05 mol.kg^{-1} D-Glucose + water					
0.01009	10.04166	1.001428	146.81	146.31(±0.020)	0.050(±0.000)
0.02997	17.28097	1.002577	147.22		
0.05003	22.29458	1.003722	147.45		
0.07011	26.35320	1.004855	147.65		
0.10009	31.41835	1.006524	147.89		
0.14996	38.31689	1.009242	148.26		
0.15 mol.kg^{-1} D-Glucose + water					
0.00999	10.02529	1.008138	147.22	146.72(±0.010)	0.049(±0.000)
0.02998	17.34146	1.009274	147.60		
0.05009	22.38191	1.010401	147.85		
0.07011	26.44033	1.011511	148.03		
0.10002	31.51070	1.013144	148.30		
0.14995	38.44029	1.015819	148.64		
0.25 mol.kg^{-1} D-Glucose + water					
0.01001	10.06720	1.014557	147.92	147.44(±0.022)	0.048(±0.000)
0.02998	17.39628	1.015665	148.32		
0.05012	22.45896	1.016767	148.57		

0.07005	26.51182	1.017847	148.73		
0.10030	31.65205	1.019458	149.01		
0.14989	38.55056	1.022052	149.32		
0.35 mol.kg^{-1} D-Glucose + water					
0.01015	10.16201	1.019527	148.31	147.83(±0.022)	0.047(±0.000)
0.02999	17.44148	1.020611	148.68		
0.05013	22.51554	1.021695	148.94		
0.07014	26.59257	1.022761	149.12		
0.10011	31.69825	1.024337	149.33		
0.14996	38.65060	1.026898	149.69		
0.05 mol.kg^{-1} D-Lactose + water					
0.01009	10.05108	1.003309	147.63	147.02(±0.015)	0.058(±0.000)
0.02998	17.29988	1.004439	148.03		
0.05002	22.31279	1.005561	148.31		
0.07001	26.35837	1.006665	148.55		
0.10001	31.43371	1.008298	148.85		
0.14998	38.35193	1.010958	149.27		
0.15 mol.kg-1 D-Lactose + water					
0.01011	10.12345	1.015799	148.16	147.58(±0.010)	0.056(±0.000)
0.02997	17.40391	1.016893	148.57		
0.05001	22.44794	1.017981	148.84		
0.07008	26.53314	1.019054	149.09		
0.10011	31.64098	1.020639	149.37		
0.14994	38.57865	1.023211	149.75		
0.25 mol.kg^{-1} D-Lactose + water					
0.01008	10.16325	1.026842	148.77	148.23(±0.028)	0.053(±0.001)
0.02998	17.50079	1.027905	149.15		
0.05001	22.56862	1.028956	149.47		
0.07005	26.66955	1.029994	149.70		
0.10008	31.80471	1.031532	149.93		
0.14996	38.78449	1.034025	150.30		
0.35 mol.kg^{-1} D-Lactose + water					
0.01001	10.18577	1.038597	149.17	148.71(±0.041)	0.047(±0.001)
0.02999	17.60325	1.039631	149.57		
0.05005	22.70555	1.040656	149.78		
0.07003	26.81636	1.041658	150.03		
0.10008	31.98339	1.043155	150.21		
0.14998	39.00315	1.045582	150.53		

m^a (mol.kg^{-1}) molality of pyridoxine hydrochloride in different solvent systems.

Table 3.35: Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities(ϕ_{KS}^{0}) and experimental slopes (S_K^*) of pyridoxine hydrochloride in different compositions of D-Fructose + Water, D-Glucose + Water and D-Lactose + water at 303.15 K.

m^a ($mol.kg^{-1}$)	U ($m.s^{-1}$)	$K_S \times 10^{10}$ ($kg^{-1}.m.s^2$)	$\phi_{KS} \times 10^6$ ($m^3.mol^{-1}.G.Pa^{-1}$)	$\phi_{KS}^{0} \times 10^6$ ($m^3.mol^{-1}.G.Pa^{-1}$)	$S_K^* \times 10^6$ ($kg.m^3.mol^{-2}.G.Pa^{-1}$)
0.05 $mol.kg^{-1}$ D-Fructose + water					
0.01011	1513.51	4.359	-39.46	-40.90(±0.831)	-24.51(±10.052)
0.02997	1514.39	4.349	-42.37		
0.05001	1515.18	4.339	-43.00		
0.07001	1516.06	4.329	-43.30		
0.10090	1517.61	4.313	-43.56		
0.14994	1518.53	4.296	-43.82		
0.15 $mol.kg^{-1}$ D-Fructose + water					
0.00989	1519.44	4.296	-39.09	-40.55(±0.837)	-24.46(±10.146)
0.02997	1520.38	4.286	-42.03		
0.05013	1521.24	4.276	-42.65		
0.07022	1522.09	4.267	-42.94		
0.10012	1523.47	4.252	-43.19		
0.14984	1525.08	4.232	-43.45		
0.25 $mol.kg^{-1}$ D-Fructose + water					
0.01014	1526.03	4.224	-38.95	-40.32(± 0.794)	-22.75(±9.620)
0.02989	1526.56	4.211	-41.72		
0.05013	1527.96	4.204	-42.33		
0.07012	1528.42	4.193	-42.61		
0.10011	1529.33	4.170	-42.86		
0.14984	1531.57	4.231	-43.11		
0.35 $mol.kg^{-1}$ D-Fructose + water					
0.01015	1531.89	4.177	-38.68	-40.03(± 0.779)	-22.28(±9.431)
0.02987	1532.62	4.169	-41.40		
0.05016	1534.28	4.156	-42.00		
0.07015	1534.08	4.153	-42.27		
0.10021	1536.39	4.134	-42.51		
0.14996	1538.22	4.114	-42.76		
0.05 $mol.kg^{-1}$ D-Glucose + water					
0.01009	1513.28	4.360	-39.45	-40.90(±0.834)	-24.59(±10.104)
0.02997	1514.03	4.351	-42.37		

0.05003	1514.99	4.340	-43.00		
0.07011	1515.43	4.333	-43.30		
0.10009	1517.18	4.316	-43.56		
0.14996	1518.43	4.297	-43.82		
0.15 mol.kg^{-1} D-Glucose + water					
0.00999	1519.13	4.298	-39.16	-40.59(±0.827)	-24.25(±10.024)
0.02998	1520.24	4.287	-42.06		
0.05009	1520.99	4.278	-42.68		
0.07011	1522.02	4.267	-42.97		
0.10002	1522.99	4.255	-43.22		
0.14995	1525.11	4.232	-43.48		
0.25 mol.kg^{-1} D-Glucose + water					
0.01001	1526.02	4.232	-38.89	-40.30(±0.807)	-23.65(±9.774)
0.02998	1526.34	4.226	-41.72		
0.05012	1527.07	4.217	-42.33		
0.07005	1527.99	4.208	-42.61		
0.10030	1529.01	4.195	-42.86		
0.14989	1531.12	4.173	-43.11		
0.35 mol.kg^{-1} D-Glucose + water					
0.01015	1531.88	4.179	-38.68	-40.03(±0.779)	-22.96(±9.441)
0.02999	1532.56	4.171	-41.40		
0.05013	1533.98	4.159	-42.00		
0.07014	1534.89	4.150	-42.28		
0.10011	1536.48	4.135	-42.52		
0.14996	1539.02	4.111	-42.76		
0.05 mol.kg^{-1} D-Lactose + water					
0.01009	1515.31	4.340	-39.35	-40.79(±0.829)	-24.37(±10.045)
0.02998	1516.16	4.330	-42.25		
0.05002	1516.99	4.321	-42.88		
0.07001	1517.72	4.312	-43.17		
0.10001	1518.19	4.302	-43.43		
0.14998	1518.99	4.287	-43.69		
0.15 mol.kg^{-1} D-Lactose + water					
0.01011	1525.28	4.231	-38.95	-40.33(±0.796)	-23.39(±9.641)
0.02997	1525.92	4.223	-41.73		
0.05001	1526.36	4.216	-42.34		
0.07008	1527.18	4.207	-42.62		
0.10011	1527.89	4.197	-42.87		
0.14994	1528.11	4.185	-43.11		
0.25 mol.kg^{-1} D-Lactose + water					
0.01008	1534.07	4.138	-38.56	-39.90(±0.773)	-22.63(±9.364)

0.02998	1534.92	4.129	-41.26		
0.05001	1535.49	4.122	-41.85		
0.07005	1536.03	4.114	-42.12		
0.10008	1536.88	4.104	-42.36		
0.14996	1537.12	4.093	-42.59		
0.35 mol.kg^{-1} D-Lactose + water					
0.01001	1544.33	4.037	-38.12	-39.43(±0.752)	-21.91(±9.112)
0.02999	1545.09	4.029	-40.76		
0.05005	1545.98	4.020	-41.32		
0.07003	1546.17	4.015	-41.58		
0.10008	1546.98	4.005	-41.81		
0.14998	1547.39	3.994	-42.04		

m^a (mol.kg^{-1}) molality of pyridoxine hydrochloride in different solvent systems

From the table 3.34 and 3.35 it is found that the density and sound velocity values increase with increase in concentration of pyridoxine hydrochloride in different compositions of D-Glucose, D-Fructose and D-Lactose in water. The density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities by using equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.34 and all the values are positive and increases in magnitude with increase in concentration of pyridoxine hydrochloride in all compositions of D- Glucose, D-Fructose and D-Lactose in water indicating the presence of great solute - solvent interaction[1-2]. Also, the values of adiabatic compressibilities (ϕ_{KS}) which are reported in table 3.35, are negative in all compositions of D- Glucose, D-Fructose and D-Lactose in water which shows that water molecules around solute i.e. pyridoxine hydrochloride are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of pyridoxine hydrochloride and D- Glucose, D-Fructose and D-Lactose molecules respectively.

Linear plots have been found in accordance with the Masson's equation(1.12) when the apparent molar volume values(ϕ_v) are plotted against root of molar concentrations ($C^{1/2}$) of pyridoxine hydrochloride in different compositions of D-Fructose, D-Glucose and D-Lactose in water. Sample plots for pyridoxine hydrochloride in different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15K are shown in figs. (3.38), (3.39) and (3.40) respectively.

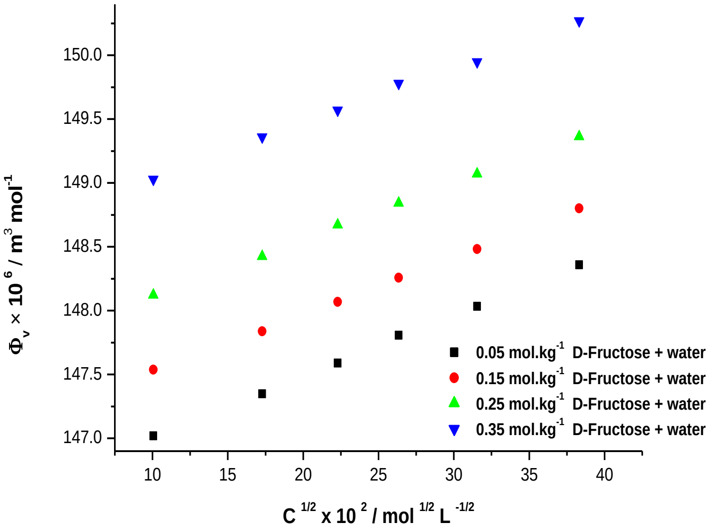

Fig. 3.38. Plot of ϕ_v vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Fructose in water at 303.15K.

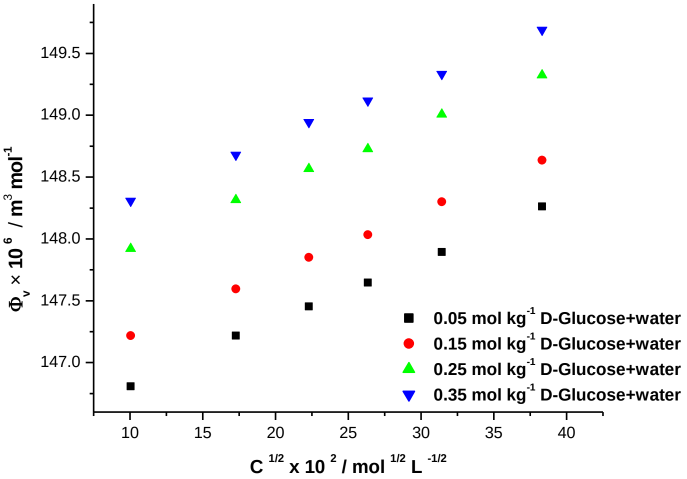

Fig. 3.39. Plot of ϕ_v vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Glucose in water at 303.15K.

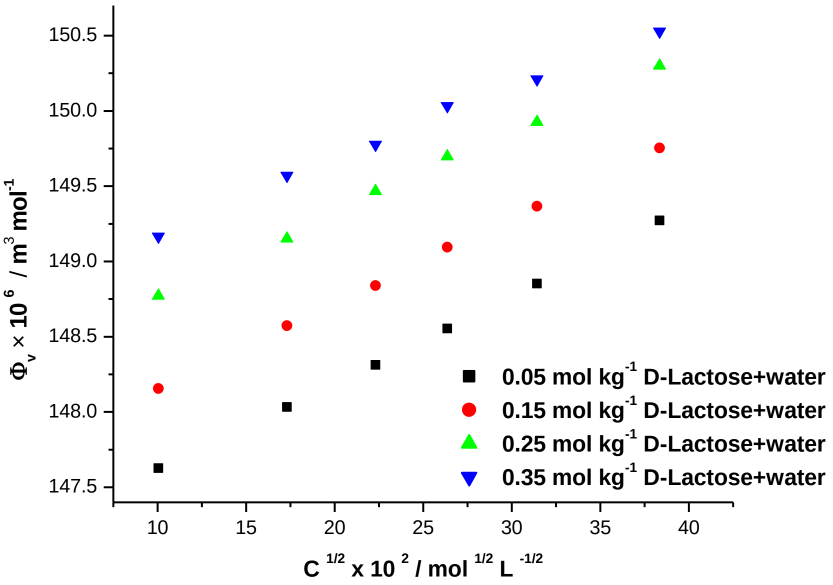

Fig. 3.40. Plot of ϕ_V vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Lactose in water at 303.15K.

The values of partial molar volumes(ϕ_V^0) and the partial molar adiabatic compressibilities(ϕ_{KS}^0) are determined by applying the least square fitting to the plots of $\phi_V$vs square root of molar concentration and ϕ_{KS}vs molal concentration which are deduced by using equations (1.12) and (1.19) respectively. The values of these parameters for pyridoxine hydrochloride in different compositions of binary aqueous solutions of D- glucose, D-Fructose and D-Lactose at 303.15 K are reported in table 3.34 and 3.35 respectively.

It is clear, from table 3.34, that the values of slopes (S_V^*) are positive in different compositions of D-Glucose + water, D-Fructose + water and D-Lactose + water at 303.15 K. The positive values of slopes indicate the presence of strong solute- solute interactions and magnitude of S_V^* values decrease with increase in compositions of D-Glucose, D-Fructose and D-Lactose in water, indicating that these interactions are further weakened which trait to the increase in solvation. On the other hand, the values of ϕ_V^0 are positive and increase with increase in compositions of D-Glucose, D-Fructose and D-Lactose in water thereby showing that solute - solvent interactions further increases on the addition of D- glucose, D-Fructose and D-Lactose in water.

The magnitude of ϕ_{KS}^{0} values indicates solute-solvent interactions[4] and it has been found in the present study that values of ϕ_{KS}^{0} for pyridoxine hydrochloride are negative which attribute to the strong attractive interactions between pyridoxine hydrochloride and water. With increase in compositions of D-Glucose, D-Fructose and D-Lactose in water values of ϕ_{KS}^{0} become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of pyridoxine hydrochloride and therefore at high concentrations of D-Glucose, D-Fructose and D-Lactose, water molecules around pyridoxine hydrochloride are more compressible than those at lower concentrations.

Effect of temperature

As the behavior of pyridoxine hydrochloride was found similar for entire range of compositions of D-Glucose, D-Fructose and D-Lactose in water at one temperature i.e. 303.15 K, so the effect of temperature has been studied on the lowest composition of D- Glucose, D-Fructose and D-Lactose in water. Densities (ρ), apparent molar volumes (ϕ_V), sound velocities (U) and apparent molar adiabatic compressibilities (ϕ_{ks}) of pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Glucose, 0.05 mol.kg^{-1} D-Fructose and 0.05 mol.kg^{-1} D-Lactose at different temperatures have been measured and are reported in tables 3.36 and 3.37.

Table 3.36: Densities (ρ), apparent molar volumes (ϕ_V), partial molar volumes(ϕ_V^0) and experimental slopes (S_V^*) of pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

m (mol.kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	ρ x 10^{-3} (kg.m^{-3})	ϕ_V x 10^6 (m^3.mol^{-1})	ϕ_V^0 x 10^6 (m^3.mol^{-1})	S_V^* x 10^4 (m^3.L$^{1/2}$.mol$^{-3/2}$)
Water **298.15 K**					
0.00998	9.96800	0.997646	145.79	145.26(±0.018)	0.054(±0.0007)
0.02998	17.25150	0.998829	146.20		
0.04997	22.23993	0.999994	146.49		
0.06994	26.27305	1.001145	146.71		
0.09993	31.3364	1.002851	146.97		
0.14997	38.24972	1.005642	147.33		
303.15 K					

0.00998	9.96098	0.996240	146.82	146.24(±0.039)	0.053(±0.0015)
0.02998	17.23922	0.997408	147.13		
0.04997	22.22395	0.998558	147.40		
0.06994	26.25396	0.999691	147.66		
0.09993	31.31328	1.001372	147.93		
0.14997	38.22077	1.004120	148.30		
308.15 K					
0.00998	9.95288	0.994621	147.26	146.75(±0.009)	0.051(±0.0003)
0.02998	17.22515	0.995781	147.64		
0.04997	22.20578	0.996925	147.89		
0.06994	26.23248	0.998056	148.08		
0.09993	31.28758	0.999729	148.35		
0.14997	38.18928	1.002466	148.71		
313.15 K					
0.00998	9.94376	0.992799	148.03	147.52(±0.017)	0.050(±0.0006)
0.02998	17.20929	0.993948	148.38		
0.04997	22.18521	0.995079	148.67		
0.06994	26.20805	0.996198	148.85		
0.09993	31.25823	0.997854	149.12		
0.14997	38.15307	1.000566	149.45		
0.05 mol.kg^{-1} D-Fructose + water **298.15 K**					
0.01011	10.05886	1.002879	146.50	145.98(±0.005)	0.050(±0.0002)
0.02997	17.29350	1.004032	146.86		
0.05001	22.30634	1.005179	147.12		
0.07001	26.35374	1.006311	147.32		
0.10090	31.56632	1.008035	147.59		
0.14994	38.34243	1.010719	147.93		
303.15 K					
0.01011	10.05173	1.001457	147.02	146.53(±0.012)	0.047(±0.0004)
0.02997	17.28119	1.002603	147.35		
0.05001	22.29042	1.003744	147.59		
0.07001	26.33483	1.004868	147.81		
0.10090	31.54360	1.006585	148.03		
0.14994	38.31467	1.009256	148.36		
308.15 K					
0.01011	10.04343	0.999804	147.96	147.49(±0.021)	0.046(±0.0008)
0.02997	17.26680	1.000934	148.30		
0.05001	22.27170	1.002059	148.54		
0.07001	26.31254	1.003167	148.76		
0.10090	31.51658	1.004861	148.98		
0.14994	38.28129	1.007498	149.28		
313.15 K					

0.01011	10.03415	0.997958	148.42	148.00(±0.008)	0.041(±0.0003)
0.02997	17.25083	0.999083	148.74		
0.05001	22.25107	1.000204	148.95		
0.07001	26.28818	1.001311	149.12		
0.10090	31.48737	1.002999	149.34		
0.14994	38.24580	1.005631	149.61		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01009	10.04878	1.002850	145.89	145.26(±0.012)	0.062(±0.0004)
0.02997	17.29334	1.004013	146.36		
0.05003	22.31064	1.005168	146.69		
0.07011	26.37228	1.006311	146.92		
0.10009	31.44120	1.007989	147.25		
0.14996	38.34501	1.010724	147.67		
303.15 K					
0.01009	10.04166	1.001428	146.81	146.31(±0.020	0.050(±0.0007)
0.02997	17.28097	1.002577	147.22		
0.05003	22.29458	1.003722	147.45		
0.07011	26.35320	1.004855	147.65		
0.10009	31.41835	1.006524	147.89		
0.14996	38.31689	1.009242	148.26		
308.15 K					
0.01009	10.03343	0.999787	147.55	147.06(±0.013)	0.047(±0.0005)
0.02997	17.26674	1.000927	147.87		
0.05003	22.27613	1.002061	148.12		
0.07011	26.33126	1.003183	148.33		
0.10009	31.39204	1.004839	148.55		
0.14996	38.28453	1.007538	148.88		
313.15 K					
0.01009	10.02418	0.997946	148.11	147.71(±0.009)	0.040(±0.0003)
0.02997	17.25079	0.999079	148.40		
0.05003	22.25552	1.000208	148.61		
0.07011	26.30688	1.001326	148.78		
0.10009	31.36294	1.002977	148.97		
0.14996	38.24906	1.005672	149.25		
0.05 mol.kg^{-1} D-Lactose + water **298.15 K**					
0.01009	10.05827	1.004745	146.91	146.11(±0.019)	0.077(±0.0007)
0.02998	17.31231	1.005883	147.44		
0.05002	22.32885	1.007009	147.82		
0.07001	26.37735	1.008115	148.14		
0.10001	31.45624	1.009744	148.56		
0.14998	38.37921	1.012397	149.08		
303.15 K					

0.01009	10.05108	1.003309	147.63	147.02(±0.015)	0.058(±0.0005)
0.02998	17.29988	1.004439	148.03		
0.05002	22.31279	1.005561	148.31		
0.07001	26.35837	1.006665	148.55		
0.10001	31.43371	1.008298	148.85		
0.14998	38.35193	1.010958	149.27		
308.15 K					
0.01009	10.04281	1.001658	148.27	147.78(±0.027)	0.046(±0.0010)
0.02998	17.28559	1.002781	148.58		
0.05002	22.29433	1.003898	148.80		
0.07001	26.33658	1.005001	148.96		
0.10001	31.40767	1.006628	149.25		
0.14998	38.32030	1.009291	149.57		
313.15 K					
0.01009	10.03352	0.999805	149.03	148.58(±0.010)	0.045(±0.0003)
0.02998	17.26951	1.000916	149.36		
0.05002	22.27348	1.002021	149.58		
0.07001	26.31178	1.003109	149.78		
0.10001	31.37795	1.004724	149.99		
0.14998	38.28364	1.007361	150.30		

m^a(mol. kg^{-1}) molality of pyridoxine hydrochloride in different solvent systems.

Table 3.37:Sound velocities (U), coefficient of adiabatic compressibilities (K_S), apparent molar adiabatic compressibilities (ϕ_{KS}), partial molar adiabatic compressibilities (ϕ^0_{KS}) andexperimental slopes (S^*_K) of pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose +water at different temperatures.

m^a (mol.kg^{-1})	U (m.s^{-1})	K_S x 10^{10} (kg^{-1}.m.s^2)	ϕ_{KS} x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	ϕ^0_{KS}x 10^6 (m^3.mol^{-1} .G.Pa^{-1})	S^*_K x 10^6 (kg.m^3.mol^{-2}.G.Pa^{-1})
Water **298.15 K**					
0.00998	1498.98	4.461	-40.16	-41.68(±0.869)	-25.53(±10.531)
0.02998	1499.91	4.450	-43.21		
0.04997	1500.45	4.441	-43.86		
0.06994	1502.99	4.421	-44.17		
0.09993	1506.44	4.394	-44.44		
0.14997	1510.57	4.357	-44.71		
303.15 K					
0.00998	1510.35	4.400	-39.50	-40.99 (±0.858)	-25.16(±10.403)

0.02998	1511.22	4.390	-42.51		
0.04997	1511.99	4.380	-43.15		
0.06994	1512.73	4.371	-43.45		
0.09993	1513.92	4.357	-43.72		
0.14997	1515.39	4.336	-43.98		
308.15 K					
0.00998	1520.94	4.346	-38.93	-40.41(±0.849)	-24.88(±10.289)
0.02998	1521.49	4.338	-41.91		
0.04997	1522.14	4.329	-42.54		
0.06994	1523.12	4.318	-42.84		
0.09993	1524.31	4.304	-43.10		
0.14997	1526.13	4.282	-43.37		
313.15 K					
0.00998	1529.97	4.303	-38.47	-39.93(±0.840)	-24.68(±10.188)
0.02998	1523.72	4.333	-41.40		
0.04997	1531.44	4.284	-42.05		
0.06994	1532.31	4.275	-42.34		
0.09993	1533.08	4.263	-42.60		
0.14997	1534.62	4.243	-42.86		
0.05 mol.kg^{-1} D-Fructose + water **298.15 K**					
0.01011	1501.41	4.423	-40.10	-41.56(±0.842)	-24.85(±10.186)
0.02997	1502.43	4.412	-43.05		
0.05001	1503.15	4.403	-43.69		
0.07001	1503.99	4.393	-43.99		
0.1009	1505.33	4.377	-44.26		
0.14994	1507.44	4.354	-44.52		
303.15 K					
0.01011	1513.51	4.359	-39.46	-40.90(±0.831)	-24.51(±10.052)
0.02997	1514.39	4.349	-42.37		
0.05001	1515.18	4.339	-43.00		
0.07001	1516.06	4.329	-43.30		
0.1009	1517.61	4.313	-43.56		
0.14994	1518.53	4.296	-43.82		
308.15 K					
0.01011	1524.13	4.305	-38.88	-40.31(±0.822)	-24.21(±9.946)
0.02997	1525.36	4.293	-41.76		
0.05001	1526.09	4.284	-42.38		
0.07001	1526.68	4.276	-42.68		
0.1009	1527.75	4.263	-42.94		
0.14994	1528.58	4.247	-43.19		
313.15 K					
0.01011	1532.03	4.269	-38.43	-39.85(±0.817)	-24.039(±9.878)

0.02997	1532.98	4.259	-41.29		
0.05001	1533.58	4.251	-41.91		
0.07001	1534.22	4.242	-42.20		
0.1009	1535.13	4.230	-42.46		
0.14994	1536.58	4.211	-42.71		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.01009	1501.32	4.424	-40.09	-41.56(±0.845)	-24.93(±10.239)
0.02997	1502.39	4.412	-43.05		
0.05003	1503.03	4.403	-43.69		
0.07011	1503.98	4.393	-43.99		
0.10009	1505.01	4.379	-44.26		
0.14996	1507.03	4.356	-44.52		
303.15 K					
0.01009	1513.28	4.360	-39.45	-40.90(±0.834)	-24.59(±10.104)
0.02997	1514.03	4.351	-42.37		
0.05003	1514.99	4.340	-43.00		
0.07011	1515.43	4.333	-43.30		
0.10009	1517.18	4.316	-43.56		
0.14996	1518.43	4.297	-43.82		
308.15 K					
0.01009	1523.43	4.309	-38.89	-40.32(±0.825)	-24.31(±10.000)
0.02997	1524.22	4.300	-41.78		
0.05003	1524.03	4.296	-42.40		
0.07011	1524.89	4.286	-42.70		
0.10009	1525.63	4.275	-42.96		
0.14996	1526.18	4.261	-43.22		
313.15 K					
0.01009	1532.88	4.264	-38.43	-39.85(±0.818)	-24.09(±9.914)
0.02997	1533.58	4.255	-41.29		
0.05003	1534.22	4.247	-41.91		
0.07011	1535.02	4.238	-42.20		
0.10009	1535.98	4.226	-42.46		
0.14996	1537.14	4.208	-42.71		
0.05 mol.kg^{-1} D-Lactose + water **298.15 K**					
0.01009	1503.35	4.403	-40.00	-41.46(±0.840)	-24.69(±10.176)
0.02998	1503.92	4.395	-42.94		
0.05002	1504.46	4.387	-43.58		
0.07001	1505.18	4.378	-43.87		
0.10001	1505.33	4.370	-44.13		
0.14998	1506.12	4.354	-44.40		
303.15 K					
0.01009	1515.31	4.340	-39.35		

0.02998	1516.16	4.330	-42.25	-40.79(±0.829)	-24.37(±10.045)
0.05002	1516.99	4.321	-42.88		
0.07001	1517.72	4.312	-43.17		
0.10001	1518.19	4.302	-43.43		
0.14998	1518.99	4.287	-43.69		
308.15 K					
0.01009	1525.89	4.287	-38.81	-40.23(±0.820	-24.11(±9.934)
0.02998	1526.22	4.281	-41.68		
0.05002	1526.96	4.272	-42.30		
0.07001	1527.47	4.264	-42.59		
0.10001	1528.33	4.253	-42.85		
0.14998	1529.24	4.236	-43.10		
313.15 K					
0.01009	1534.17	4.249	-38.34	-39.75(±0.814)	-23.90(±9.867)
0.02998	1535.38	4.238	-41.18		
0.05002	1535.99	4.230	-41.80		
0.07001	1536.55	4.222	-42.09		
0.10001	1537.24	4.211	-42.34		
0.14998	1537.99	4.196	-42.59		

m^a(mol kg^{-1}) molality of pyridoxine hydrochloride in different solvent systems

From the analysis of table 3.36 and 3.37, it is clear that the density and sound velocity values increase with increase in temperature for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water respectively. The density and sound velocity values are used to determine the apparent molar volumes and apparent molar adiabatic compressibilities using the equations (1.10) and (1.18) respectively.

The values of apparent molar volumes (ϕ_v) are reported in table 3.36 and all the values are positive and increases in magnitude with increase in temperature for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water indicating the presence of greater solute - solvent interactions. On the other hand, values of adiabatic compressibilities (ϕ_{KS}) which are reported in table 3.37, are negative at all temperatures which shows that water molecules around solute i.e. pyridoxine hydrochloride are less compressible than water molecules in the bulk which is attributed to strong solute–solvent interactions[3] between molecules of pyridoxine hydrochloride and D- Glucose, D-Fructose and D-Lactose molecules. The values of partial molar volumes(ϕ_v^0) and the partial molar adiabatic compressibilities (ϕ_{KS}^{0}) are determined by applying least square fitting to the plots of $\phi_v$vs the square root of molar concentration and ϕ_{KS} vs molal concentration which are deduced by using equations (1.12) and (1.19) respectively. The values of these parameters for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures are reported in tables 3.36 and 3.37 respectively.

It is clear, from table 3.36, that the values of slopes (S_v^*) are positive in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water for the entire temperature range. The positive values of slopes indicate the presence of strong solute-solute interactions and magnitude of S_v^* values decrease with increase in the temperature in water as well as in 0.05 mol.kg^{-1} D- Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water indicating that these interactions are further weakened which trait to the increase in solvation with increase in temperature. The values of partial molar volumes (ϕ_v^0) increase with increase in temperature in water as well as in 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water, indicating that solute-solvent interactions increase with increase in temperature. The plots of apparent molar volumes ϕ_v against C$^{1/2}$ were found linear and are shown in figs. (3.41), (3.42), (3.43) and (3.44) respectively. It has been found in the present study that the values of ϕ_{KS}^{0} for pyridoxine hydrochloride are negative which attribute to the strong attractive interactions between pyridoxine hydrochloride and water. With increase in temperature values ofϕ_{KS}^{0} become less negative which means that electrostriction is reduced and some water molecules are released to the bulk[4]. Furthermore the attractive interactions between the molecules of sugars and water molecules induce the dehydration of pyridoxine hydrochloride and therefore at high temperature water molecules around pyridoxine hydrochloride are more compressible than those at lower temperature.

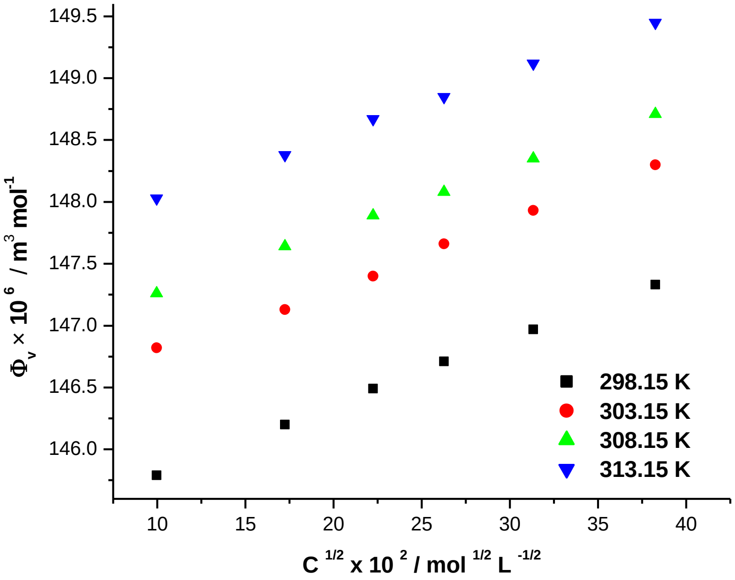

Fig. 3.41. Plot of $\phi_v$vs $C^{1/2}$ for pyridoxine hydrochloride in water at different temperatures.

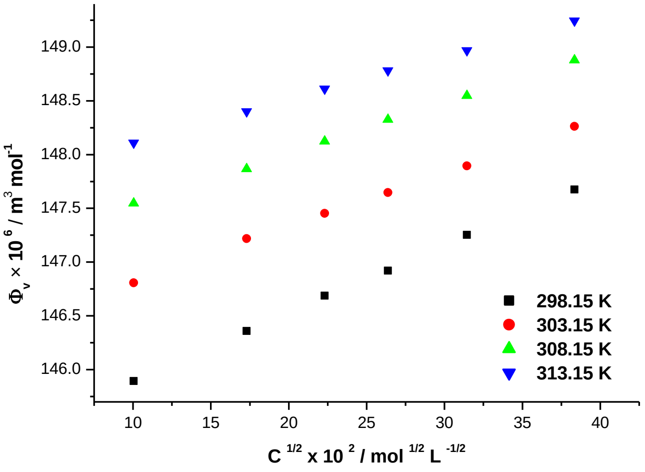

Fig. 3.42. Plot of ϕ_v vs $C^{1/2}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1} D-Glucose + water at different temperatures.

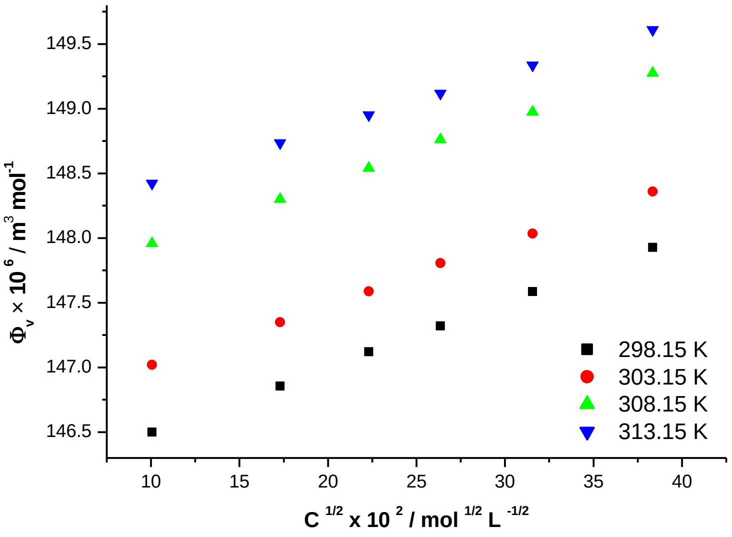

Fig. 3.43. Plot of ϕ_V vs $C^{1/2}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water at different temperatures.

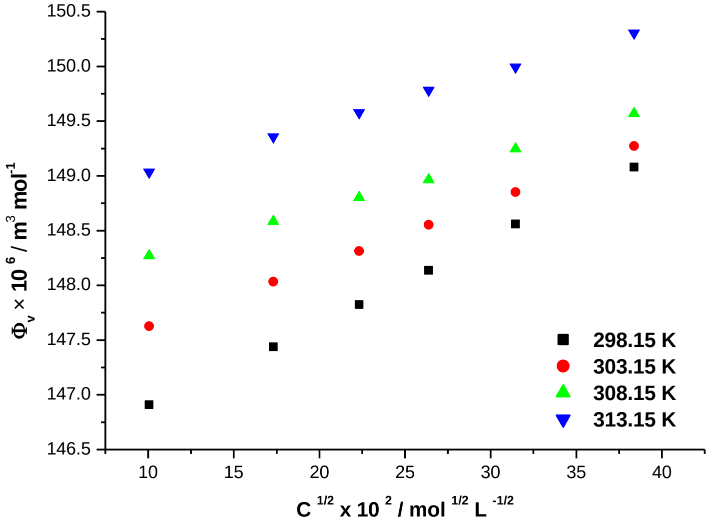

Fig. 3.44. Plot of ϕ_V vs $C^{1/2}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

Partial molar expansibilities, (ϕ_E^0) is one of the parameter, which help in determining the structure making or breaking behavior of a solute in any of the solvent[6].

It is found that pyridoxine hydrochloride shows similar kind of behavior in all the compositions of D-Glucose, D-Fructose and D-Lactose in water. So the partial molar expansibilities (ϕ_E^0), Isobaric thermal expansion coefficient (α_2) and the molar heat capacities are determined only for the lower compositions of D-Glucose, D-Fructose and D-Lactose in water.

The temperature dependence of ϕ_V^0 in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water for pyridoxine hydrochloride are as follow:

ϕ_V^0= -94.13 + 1.398 T - 0.002 T ^{2} in water (3.19)

ϕ_V^0= -231.51 + 2.314 T -0.003 T ^{2} in 0.05 mol.kg^{-1} D-Glucose + water (3.20)

ϕ_V^0 = -157.09 + 1.911 T - 0.003T ^{2} in 0.05 mol.kg^{-1} D-Fructose + water (3.21)

ϕ_V^0 = -01.56 + 0.783 T - 0.001T ^{2} in 0.05 mol.kg^{-1} D-Lactose + water (3.22)

Partial molar expansibilities $\phi_E^0= \left[\frac{\partial \phi_V^0}{\partial T}\right]_P$,which is temperature dependent function of ϕ_V^0 are calculated for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1}D-Fructose +water, 0.05 mol.kg^{-1}D-Glucose + water, and 0.05 mol.kg^{-1} D-Lactose +water by using relations (3.19), (3.20),(3.21) and (3.22) and are given in table 3.38.

Table.3.38. Partial molar expansibilities, (ϕ_E^0) for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1}D-Fructose +water, 0.05 mol.kg^{-1}D-Glucose + water, and 0.05 mol.Kg^{-1} D-Lactose +water mixtures at different temperatures.

T (K)	**Water**	**0.05 mol.kg^{-1} D-Fructose +water**	**0.05 mol.kg^{-1} D-Glucose + water**	**0.05 mol.kg^{-1} D-Lactose +water**
		ϕ_E^0 x 10^6(m^3 mol^{-1} K^{-1})		
298.15	0.2054	0.1221	0.1594	0.1867
303.15	0.1854	0.0921	0.1394	0.1767
308.15	0.1654	0.0621	0.1194	0.1667
313.15	0.1454	0.0321	0.0994	0.1567

From table 3.38, it is clear that the ϕ_E^0 values are positive in entire range of temperature but the value decrease in magnitude with rise in temperature which shows that pyridoxine hydrochloride is not behaving like symmetrical tetra alkyl ammonium salts[7] but behaving like common salts[8-9] because the molar volume expansibilities should decrease with the rise in temperature for a common salt. The decreasing ϕ_E^0, values indicates the absence of "packing effect"[6]. The variation of ϕ_E^0 with temperature for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water is linear and as shown in fig. (3.45).

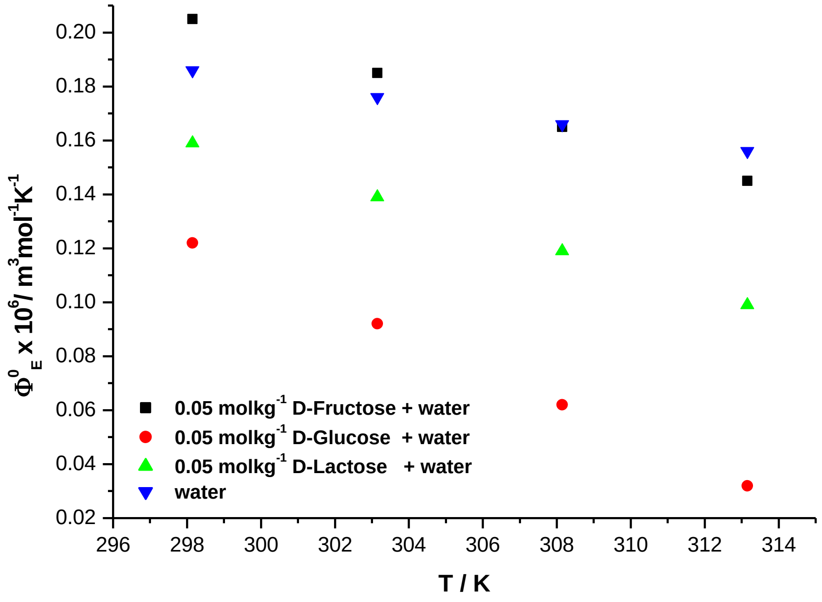

Fig. 3.45. Plot of ϕ_E^0 vs temperature for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water.

Partial molar heat capacities are determined by taking the second derivative of partial molar volume with respect to temperature at constant pressure using the general thermodynamic expression[6](3.4).

It is observed from relations (3.19 to 3.22) that sign of the values of $(\partial C_p/\partial P)_T$ for the solutions of pyridoxine hydrochloride are positive thereby showing that pyridoxine hydrochloride behaves as structure breakers in water as well as in binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose. The values of $(\partial C_p/\partial P)_T$ are reported in table 3.39.The values of ϕ_V^0 and ϕ_E^0 are further used to calculate the isobaric thermal expansion coefficient using equation[10] (3.5). The calculated values of α_2 are included in table 3.39.

Table 3.39: Partial molar heat capacities,$(\partial C_p/\partial P)_T$, isobaric thermal expansion coefficient, (α_2)for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water mixture at different temperatures.

T (K)	**Water**		**0.05 mol.kg^{-1} D-Fructose + water**		**0.05 mol.kg^{-1} D-Glucose + water**		**0.05 mol.kg^{-1} D-Lactose + water**	
	$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})	**α_2 (K^{-1})**	**$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})**	**α_2 (K^{-1})**	**$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})**	**α_2 (K^{-1})**	**$(\partial C_p/\partial P)_T$ (m^{3}mol^{-1} K^{-1})**	**α_2 (K^{-1})**
298.15	1.1926	0.00141	1.7889	0.00084	1.1926	0.00110	0.00037	0.00128
303.15	1.2126	0.00127	1.8189	0.00063	1.2126	0.00095	0.00035	0.00120
308.15	1.2326	0.00113	1.8489	0.00042	1.2326	0.00081	0.00033	0.00113
313.15	1.2526	0.00099	1.8789	0.00022	1.2526	0.00067	0.00031	0.00105

The α_2 value for pyridoxine hydrochloride decreases with increase in temperature in water as well as in 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water mixtures suggesting that the expansibility[10] increases with increase in temperature for pyridoxine hydrochloride in water as well as in 0.05 mol.kg^{-1} D-Glucose + water, 0.05 mol.kg^{-1} D-Fructose + water and 0.05 mol.kg^{-1} D-Lactose + water mixtures.

B. TRANSPORT PROPERTIES

In the present study, viscous flow of pyridoxine hydrochloride has been determined in water and in binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose at various concentrations of solute and at different temperatures. The relative viscosities of the pyridoxine hydrochloride in water and binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose at different temperatures were calculated by using equation (3.6)

The obtained relative viscosities were interpreted by Jones-Dole equation (1.28) where a straight line plot was obtained when $(\eta_r - 1)/C^{1/2}$ is plotted against $C^{1/2}$. The values of A and B parameters of Jones-Dole equation (1.28) were obtained using least square fit to the linear plots of $(\eta_r - 1)/C^{1/2}$vs $C^{1/2}$. A parameter represents solute-solute interactions whereas the B parameter represents solute- solvents interactions[11].

The viscosities and relative viscosities along with A and B coefficients of the Jones – Dole equation for pyridoxine hydrochloride were determined in different compositions of D-Fructose, D-Glucose and D-Lactose in water (0.05, 0.15, 0.25, 0.35) mol.kg^{-1} at 303.15K and are reported in table 3.40.

TABLE 3.40: Viscosities(η), relative viscosities (η_r) and values of A and B coefficients of the Jones – Dole equation for pyridoxine hydrochloride in different compositions of D-Fructose , D-Glucose and D-Lactose in water at 303.15 K.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
0.05 mol.kg^{-1} D-Fructose + water					
0.00000	0.000000	0.83310	-	3.413(±0.233)	0.385(±0.008)
0.01011	10.05173	0.83910	1.00720		
0.02997	17.28119	0.84756	1.01736		
0.05001	22.29042	0.85546	1.02684		
0.07001	26.33483	0.86337	1.03633		
0.10090	31.54360	0.8745	1.04969		
0.14994	38.31467	0.89035	1.06871		
0.15 mol.kg^{-1} D-Fructose + water					
0.00000	0.000000	0.86720	-	2.987(±0.328)	0.390 (±0.012)
0.00989	9.975197	0.87309	1.00680		
0.02997	17.33878	0.88163	1.01663		
0.05013	22.39098	0.89002	1.02632		
0.07022	26.46103	0.89842	1.03600		
0.10012	31.52639	0.90987	1.04921		
0.14984	38.42659	0.92602	1.06783		

0.25 mol.kg^{-1} D-Fructose + water					
0.00000	0.000000	0.90150	-	2.524(±0.328)	0.398(±0.012)
0.01014	10.13339	0.90745	1.00660		
0.02989	17.37218	0.91602	1.01611		
0.05013	22.46363	0.92477	1.02581		
0.07012	26.52777	0.93336	1.03534		
0.10011	31.62591	0.94562	1.04894		
0.14984	38.54840	0.96245	1.06761		
0.35 mol.kg^{-1} D-Fructose + water					
0.00000	0.000000	0.93490	-	1.998(±0.360)	0.402(±0.013)
0.01015	10.16416	0.94073	1.00624		
0.02987	17.41027	0.94921	1.01530		
0.05016	22.52670	0.95785	1.02455		
0.07015	26.59951	0.96735	1.03471		
0.10021	31.71959	0.97967	1.04789		
0.14996	38.65707	0.99731	1.06675		
0.05 mol.kg^{-1} D-Glucose + water					
0.00000	0.000000	0.81900	-	3.692(±0.237)	0.377(±0.009)
0.01009	10.04166	0.82518	1.00754		
0.02997	17.28097	0.83322	1.01736		
0.05003	22.29458	0.84099	1.02685		
0.07011	26.35320	0.84877	1.03635		
0.10009	31.41835	0.85967	1.04966		
0.14996	38.31689	0.87529	1.06873		
0.15 mol.kg^{-1} D-Glucose + water					
0.00000	0.000000	0.85300	-		
0.00999	10.02529	0.85894	1.00697		
0.02998	17.34146	0.86720	1.01664		

0.05009	22.38191	0.87546	1.02633	3.093(±0.335)	0.387(±0.012)
0.07011	26.44033	0.88372	1.03601		
0.10002	31.51070	0.89499	1.04922		
0.14995	38.44029	0.91088	1.06786		
0.25 mol.kg^{-1} D-Glucose + water					
0.00000	0.000000	0.88700	-	2.575(±0.326)	0.396(±0.012)
0.01001	10.06720	0.89285	1.00659		
0.02998	17.39628	0.90130	1.01612		
0.05012	22.45896	0.90990	1.02581		
0.07005	26.51182	0.91835	1.03535		
0.10030	31.65205	0.93042	1.04896		
0.14989	38.55056	0.94698	1.06762		
0.35 mol.kg^{-1} D-Glucose + water					
0.00000	0.000000	0.92010	-	2.115(±0.382)	0.399(±0.014)
0.01015	10.16201	0.92599	1.00640		
0.02999	17.44148	0.93421	1.01533		
0.05013	22.51554	0.94272	1.02458		
0.07014	26.59257	0.95209	1.03476		
0.10011	31.69825	0.96423	1.04796		
0.14996	38.65060	0.98162	1.06686		
0.05 mol.kg^{-1} D-Lactose + water					
0.00000	0.000000	0.86300	-	3.381(±0.236)	0.410(±0.009)
0.01009	10.05108	0.86959	1.00763		
0.02998	17.29988	0.87879	1.01829		
0.05002	22.31279	0.88715	1.02798		
0.07001	26.35837	0.89451	1.03651		
0.10001	31.43371	0.90734	1.05138		
0.14998	38.35193	0.92685	1.07399		

0.15 mol.kg^{-1} D-Lactose + water					
0.00000	0.000000	0.90240	-	2.726(±0.089)	0.413(±0.003)
0.01011	10.12345	0.90878	1.00707		
0.02997	17.40391	0.91794	1.01722		
0.05001	22.44794	0.92667	1.0269		
0.07008	26.53314	0.93498	1.03611		
0.10011	31.64098	0.94781	1.05033		
0.14994	38.57865	0.96753	1.07217		
0.25 mol.kg^{-1} D-Lactose + water					
0.00000	0.000000	0.94120	-	2.008(±0.162)	0.416(±0.006)
0.01008	10.16325	0.94706	1.00623		
0.02998	17.50079	0.95689	1.01667		
0.05001	22.56862	0.96527	1.02558		
0.07005	26.66955	0.97395	1.03479		
0.10008	31.80471	0.98704	1.04871		
0.14996	38.78449	1.00737	1.07031		
0.35 mol.kg^{-1} D-Lactose + water					
0.00000	0.000000	0.98130	-	1.679 (±0.150)	0.420(±0.005)
0.01001	10.18577	0.98722	1.00603		
0.02999	17.60325	0.99730	1.01630		
0.05005	22.70555	1.00592	1.02508		
0.07003	26.81636	1.01541	1.03476		
0.10008	31.98339	1.02894	1.04854		
0.14998	39.00315	1.05051	1.07053		

m^a (mol.kg^{-1}) is the molality of pyridoxine hydrochloride

The values of coefficients A and B are obtained by plotting graphs between $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ where A is the intercept and B is the slope for the respective graph. The values of A and B parameters for pyridoxine hydrochloride in different compositions of binary aqueous solutions of D-Fructose, D-Glucose and D-Lactose at 303.15 K are recorded in table 3.40 respectively.

Sample plots of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Fructose, D-Glucose and D-Lactose in water are shown in figs. (3.46), (3.47) and (3.48) respectively.

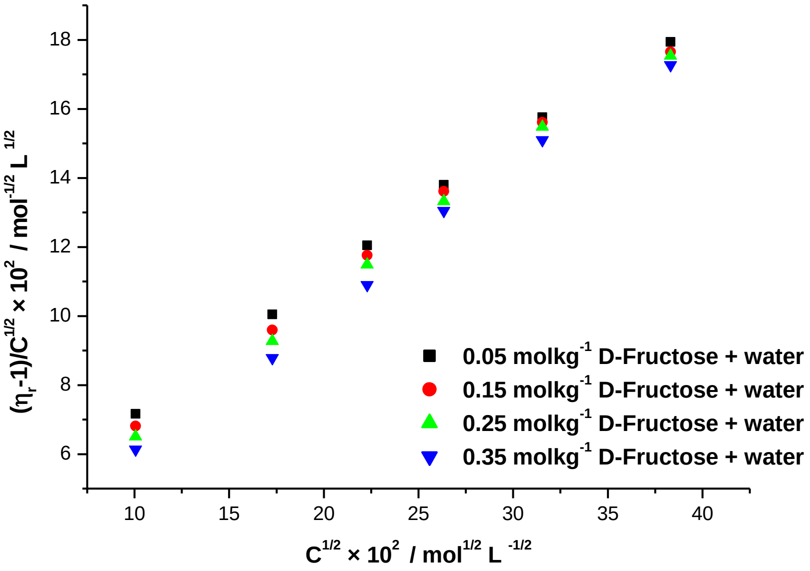

Fig. 3.46. Plot of $(\eta_r\text{-}1)/ C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Fructose in water at 303.15 K

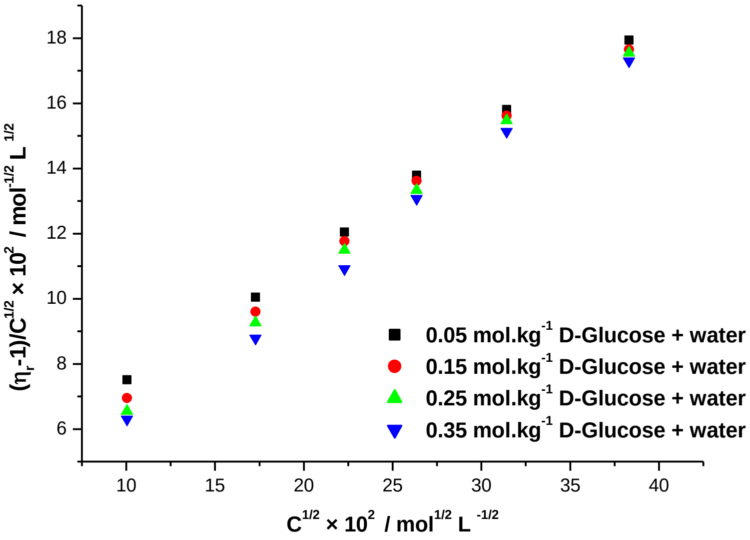

Fig. 3.47. Plot of $(\eta_r\text{-}1)/ C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Glucose in water at 303.15 K

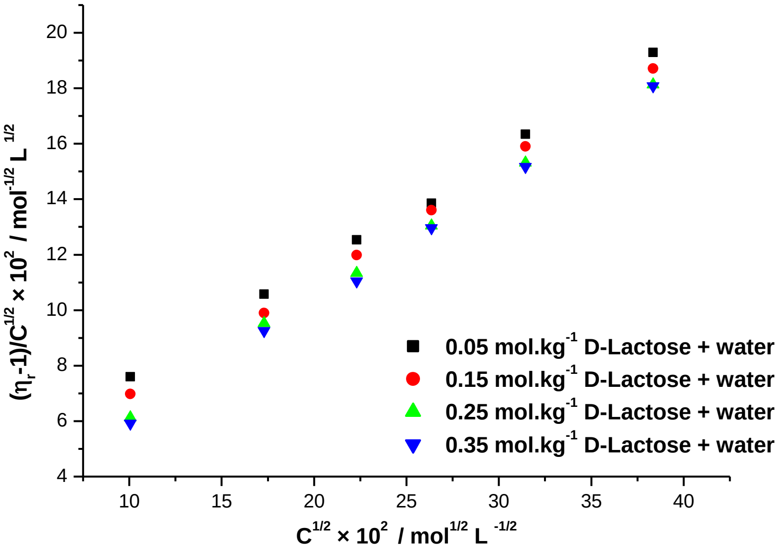

Fig. 3.48. Plot of $(\eta_r\text{-}1)/ C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in different compositions of D-Lactose in water at 303.15 K

The values of A-coefficient in table 3.40 are positive and decrease with the increase in the concentration of D-Fructose, D-Glucose and D-Lactose in water indicating the weakening of solute-solute interactions with the increase of D-Fructose, D-Glucose and D-Lactose content in water. Also, it is found that values of B-coefficient are positive indicating the presence of strong solute-solvent interactions. This may be attributed to the strong solvation of pyridoxine hydrochloride in the binary mixtures of D-Fructose, D-Glucose and D-Lactose in water. From the table 3.40, it is clear that B-coefficient values further increase with the increase of D-Fructose, D-Glucose and D-Lactose content in water at 303.15 K, thereby showing that solute – solvent interactions are further strengthened with the increase of D-Fructose, D-Glucose and D-Lactose content in water. So, it is clear that there is a great change in the solute - solvent interactions when we switch from lower to higher composition of the solvents[12-13]. In other words the solvation is enhanced as the composition of D-Fructose, D-Glucose and D-Lactose in water increases.

The analysis of data was also done on the basis of transition state theory proposed by Feakins *et al*[14]. The B-coefficient in terms of transition state theory is given by the relation (3.7) whereas as all other parameters such as $\Delta\mu_1^{0^*}$,$\Delta\mu_2^{0^*}$and $\overline{V_1^0}$ were determined by the equation (3.8), (3.9) and (3.10) and are reported in table 3.41.

TABLE 3.41: Values of $\overline{V_1^0}, \overline{V_2^0}, \Delta\mu_1^{0^*}$and $\Delta\mu_2^{0^*}$ for pyridoxine hydrochloride in different composition of D-Fructose + water, D-Glucose + water and D-Lactose + water at 303.15 K.

M (mol.kg^{-1})	$\overline{V_1^0} \times 10^6$ **(m^3.mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3.mol^{-1})**	$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$\Delta\mu_2^{0^*}$ **(kJ. mol$^{-1)}$**
D-Fructose + water				
0.05	17.98	146.53	26.65	72.00
0.15	17.83	147.07	26.69	73.42
0.25	17.68	147.67	26.72	75.28
0.35	17.56	148.60	26.75	76.52
D-Glucose + water				
0.05	17.98	146.31	26.63	70.84
0.15	17.83	146.72	26.67	72.94
0.25	17.69	147.44	26.70	74.94
0.35	17.57	147.83	26.74	75.95
D-Lactose + water				

0.05	17.95	147.02	26.69	75.71
0.15	17.70	147.58	26.72	77.34
0.25	17.47	148.23	26.75	78.88
0.35	17.25	148.71	26.79	80.62

It is evident from the above table that values of $\Delta\mu_1^{0*}$ do not change much with the change in composition of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K i.e. the values of $\Delta\mu_1^{0*}$ are practically held constant in the entire composition range of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K. It is clear that the values of $\Delta\mu_2^{0*}$ are positive and increase with solvent composition of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K suggesting that the transition state formation is less favored in the presence of pyridoxine hydrochloride and is followed by breaking or distortions of the intermolecular bonds[14].

Effect of temperature

As the behavior of pyridoxine hydrochloride was similar for different compositions of D-Fructose, D-Glucose and D-Lactose in water at 303.15 K, so only lowest composition i.e. 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water was taken for analyzing the effect of temperature. The viscosity and the relative viscosity data along with A and B coefficients of the Jones – Dole equation at different temperatures is given in table 3.42.

TABLE 3.42: Viscosities (η), relative viscosities (η_r) and the values of A and B coefficients of the Jones – Dole equation for pyridoxine hydrochloride in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

m^a (mol·kg^{-1})	$C^{1/2}$ x10^2 (mol$^{1/2}$.L$^{-1/2}$)	η (mPa·s)	η_r	A (L$^{1/2}$.mol$^{-1/2}$)	B (L.mol^{-1})
Water **298.15 K**					
0.00000	0.00000	0.89370	-		
0.00998	0.89871	1.0056	1.00560		

0.02998	0.90379	1.01129	1.01129	4.644(±0.061)	0.106(±0.005)
0.04997	0.90778	1.01575	1.01575		
0.06994	0.91114	1.01952	1.01952		
0.09993	0.91611	1.02507	1.02507		
0.14997	0.92332	1.03314	1.03314		
303.15 K					
0.00000	0.00000	0.80070	-	4.087 (±0.057)	0.117(±0.003)
0.00998	9.96098	0.80497	1.00533		
0.02998	17.23922	0.80901	1.01038		
0.04997	22.22395	0.81262	1.01489		
0.06994	26.25396	0.81552	1.01850		
0.09993	31.31328	0.82028	1.02445		
0.14997	38.22077	0.82706	1.03292		
308.15 K					
0.00000	0.00000	0.72250	-	3.977(±0.308)	0.118(±0.010)
0.00998	9.952883	0.72628	1.00524		
0.02998	17.22515	0.72984	1.01017		
0.04997	22.20578	0.73327	1.01491		
0.06994	26.23248	0.73553	1.01803		
0.09993	31.28758	0.73987	1.02405		
0.14997	38.18928	0.74619	1.03279		
313.15 K					
0.00000	0.00000	0.65600	-	3.799 (±0.216)	0.121 (±0.004)
0.00998	9.943763	0.6593	1.00503		
0.02998	17.20929	0.66262	1.01009		
0.04997	22.18521	0.66545	1.0144		
0.06994	26.20805	0.66802	1.01833		
0.09993	31.25823	0.67145	1.02356		

0.14997	38.15307	0.67732	1.0325		
0.05 mol.kg^{-1} D-Fructose + water **298.15 K**					
0.00000	0.00000	0.92940	-	3.977(±0.170)	0.118(±0.006)
0.01024	10.05886	0.93708	1.00826		
0.02970	17.2935	0.94623	1.01811		
0.05023	22.30634	0.9557	1.02829		
0.07032	26.35374	0.96377	1.03698		
0.10032	31.56632	0.97742	1.05167		
0.14964	38.34243	0.99517	1.07077		
303.15 K					
0.00000	0.00000	0.83310	-	3.798(±0.067)	0.121(±0.002)
0.01011	10.05173	0.8391	1.0072		
0.02997	17.28119	0.84756	1.01736		
0.05001	22.29042	0.85546	1.02684		
0.07001	26.33483	0.86337	1.03633		
0.10090	31.5436	0.8745	1.04969		
0.14994	38.31467	0.89035	1.06871		
308.15 K					
0.00000	0.00000	0.75220	-	2.418(±0.318)	0.403(±0.012)
0.01011	10.04343	0.75718	1.00662		
0.02997	17.2668	0.76414	1.01588		
0.05001	22.2717	0.77085	1.0248		
0.07001	26.31254	0.77861	1.03511		
0.10090	31.51658	0.78866	1.04847		
0.14994	38.28129	0.80315	1.06774		
313.15 K					
0.00000	0.00000	0.68380	-		

0.01011	10.03415	0.68737	1.00523	1.088(±0.246)	0.415(±0.009)
0.02997	17.25083	0.69329	1.01387		
0.05001	22.25107	0.69994	1.02361		
0.07001	26.28818	0.70574	1.03209		
0.10090	31.48737	0.71405	1.04425		
0.14994	38.2458	0.72799	1.06463		
0.05 mol.kg^{-1} D-Glucose + water **298.15 K**					
0.00000	0.00000	0.91390	-	4.521(±0.170)	0.368(±0.006)
0.01009	10.04878	0.92146	1.00827		
0.02997	17.29334	0.93092	1.01862		
0.05003	22.31064	0.94009	1.02865		
0.07011	26.37228	0.94804	1.03735		
0.10009	31.4412	0.96111	1.05165		
0.14996	38.34501	0.97861	1.07081		
303.15 K					
0.00000	0.00000	0.81900	-	3.692(±0.237)	0.377(±0.009)
0.01009	10.04166	0.82518	1.00754		
0.02997	17.28097	0.83322	1.01736		
0.05003	22.29458	0.84099	1.02685		
0.07011	26.3532	0.84877	1.03635		
0.10009	31.41835	0.85967	1.04966		
0.14996	38.31689	0.87529	1.06873		
308.15 K					
0.00000	0.00000	0.73920	-	2.701(±0.405)	0.395(±0.015)
0.01009	10.03343	0.74435	1.00697		
0.02997	17.26674	0.75095	1.01589		
0.05003	22.27613	0.75755	1.02482		

0.07011	26.33126	0.76518	1.03514		
0.10009	31.39204	0.77503	1.04847		
0.14996	38.28453	0.78932	1.06780		
313.15 K					
0.00000	0.00000	0.67160	-	1.378(±0.249)	0.406(±0.009)
0.01009	10.02418	0.67535	1.00559		
0.02997	17.25079	0.68092	1.01388		
0.05003	22.25552	0.68747	1.02362		
0.07011	26.30688	0.69317	1.03212		
0.10009	31.36294	0.70131	1.04424		
0.14996	38.24906	0.71504	1.06469		
0.05 mol.kg^{-1} D-Lactose + water **298.15 K**					
0.00000	0.00000	0.97770	-	4.152(±0.195)	0.401(±0.007)
0.01009	10.05827	0.98557	1.00805		
0.02998	17.31231	0.99679	1.01953		
0.05002	22.32885	1.00662	1.02958		
0.07001	26.37735	1.01552	1.03868		
0.10001	31.45624	1.02964	1.05313		
0.14998	38.37921	1.05066	1.07462		
303.15 K					
0.00000	0.00000	0.86300	-	3.381(±0.236)	0.410(±0.009)
0.01009	10.05108	0.86959	1.00763		
0.02998	17.29988	0.87879	1.01829		
0.05002	22.31279	0.88715	1.02798		
0.07001	26.35837	0.89451	1.03651		
0.10001	31.43371	0.90734	1.05138		
0.14998	38.35193	0.92685	1.07399		

308.15 K					
0.00000	0.00000	0.76660	-	2.339(±0.123)	0.434(±0.004)
0.01009	10.04281	0.77172	1.00668		
0.02998	17.28559	0.77975	1.01715		
0.05002	22.29433	0.78726	1.02695		
0.07001	26.33658	0.79412	1.03590		
0.10001	31.40767	0.80534	1.05053		
0.14998	38.3203	0.82227	1.07262		
313.15 K					
0.00000	0.00000	0.70960	-	1.072(±0.251)	0.466(±0.009)
0.01009	10.03352	0.71356	1.00557		
0.02998	17.26951	0.72084	1.01585		
0.05002	22.27348	0.72777	1.02561		
0.07001	26.31178	0.73495	1.03573		
0.10001	31.37795	0.74487	1.04970		
0.14998	38.28364	0.76027	1.07140		

m^a (mol.kg^{-1}) is the molality of pyridoxine hydrochloride

The plots of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ have been found linear at all the temperatures and sample plots for pyridoxine hydrochloride in 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures are shown in figs. (3.49), (3.50), (3.51) and (3.52) respectively. This is in accordance with Jones-Dole equation.

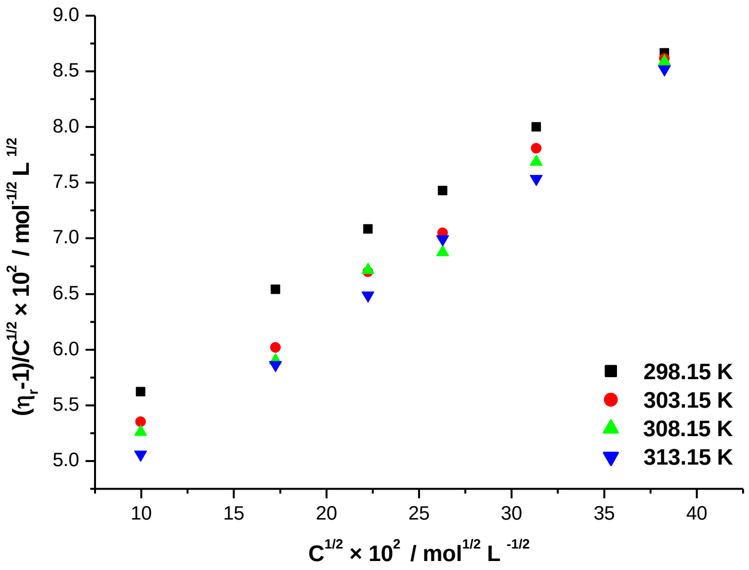

Fig.3.49. Plot of$(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in water at different temperatures.

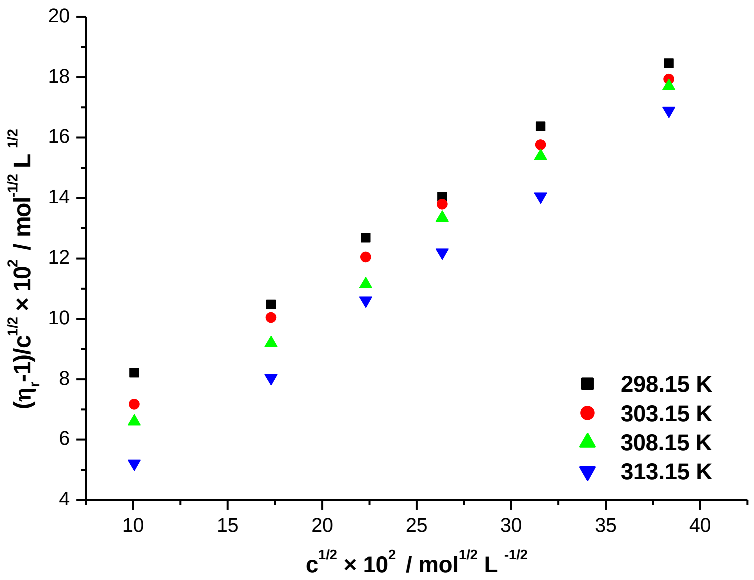

Fig. 3.50. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1} D-Fructose + water at different temperatures.

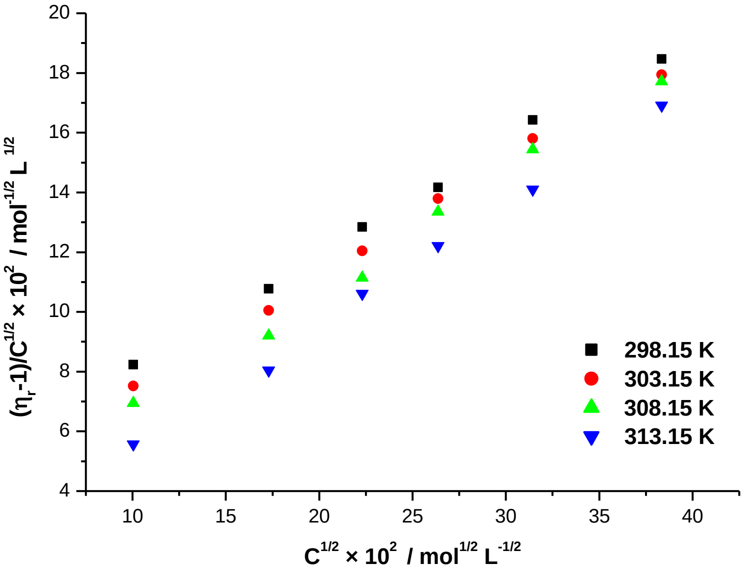

Fig. 3.51. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$for pyridoxine hydrochloride in 0.05 mol.kg^{-1}D-Glucose + water at different temperatures.

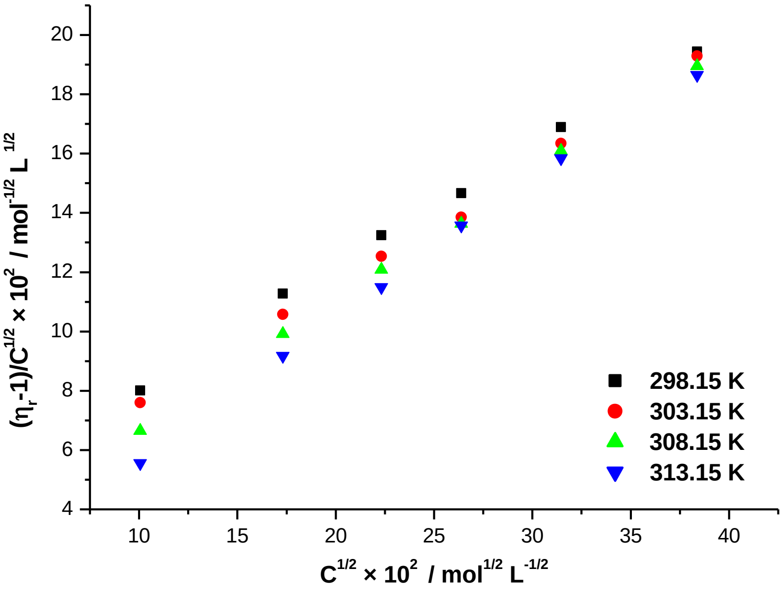

Fig. 3.52. Plot of $(\eta_r - 1)/C^{1/2}$ vs $C^{1/2}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1}D-Lactose + water at different temperatures.

The values of A-coefficient reported in table 3.42 are positive for the entire range of temperature indicating the presence of solute-solute interactions. Further the values of A-coefficient decrease with rise in temperature in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1}D-Lactose + water indicating the weakening of solute-solute interactions with the rise in temperature. Also the values of B-coefficient are positive in water, 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1}D-Lactose + water at all temperatures thereby showing the presence of strong solute-solvent interactions. Further the values of B-coefficient increase with the rise in temperature which suggest that solute-solvent interactions are further strengthened with the rise in temperature[15]. The viscosity data has also been examined by applying the transition state theory at different temperatures from 298.15-318.15 K and the calculated values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$have been recorded in table 3.43.

TABLE 3.43: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water at different temperatures.

T (K)	$\overline{V_1^0} \times 10^6$ **(m^3.mol^{-1})**	$\overline{V_2^0} \times 10^6$ **(m^3.mol^{-1})**	$\Delta\mu_1^{0^*}$ **(kJ.mol^{-1})**	$\Delta\mu_2^{0^*}$ **(kJ.mol^{-1})**
0.05 mol.kg^{-1} D-Fructose + water				
298.15	17.96	145.98	26.33	68.91
303.15	17.98	146.53	26.65	72.00
308.15	18.01	147.49	26.98	75.76
313.15	18.05	148.00	27.31	78.65
0.05 mol.kg^{-1} D-Glucose + water				
298.15	17.96	145.26	26.31	68.39
303.15	17.98	146.31	26.63	70.85
308.15	18.01	147.06	26.96	74.56
313.15	18.05	147.71	27.29	77.45
0.05 mol.kg^{-1} D-Lactose + water				
298.15	17.92	146.11	26.38	73.21
303.15	17.95	147.02	26.69	75.72
308.15	17.98	147.78	27.00	80.37
313.15	18.01	148.58	27.35	86.25

According to Feakins model[14] increase in the values of $\Delta\mu_2^{0^*}$ with temperature leads to structure breaking ability of the solute and simultaneously transition state formation is less favoured due to breaking or distortion of intermolecular bonds in the solvent mixture by the presence of solute. In the present study values of $\Delta\mu_2^{0^*}$ increase with increase in temperature supporting the structure breaking ability of pyridoxine hydrochloride and simultaneously transition state formation is less favoured in 0.05 mol.kg^{-1} D-Fructose + water, 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg^{-1} D-Lactose + water mixtures respectively by the presence of pyridoxine hydrochloride.

TABLE 3.44: Values of ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$),$T\Delta S_2^{0^*}$ and $\Delta H_2^{0^*}$ for pyridoxine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water , 0.05 mol.kg^{-1} D-Glucose + water and 0.05 mol.kg-1 D-Lactose + water at different temperatures.

T (K)	**$\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$ (kJ.mol^{-1})**	**$T.\Delta S_2^{0^*}$ (kJ.mol^{-1})**	**$\Delta H_2^{0^*}$ (kJ.mol^{-1})**
0.05 mol.kg^{-1} D-Fructose + water			
298.15	42.58	-196.63	-127.72
303.15	45.35	-199.93	-127.93
308.15	48.78	-203.22	-127.46
313.15	51.34	-206.52	-127.87
0.05 mol.kg^{-1} D-Glucose + water			
298.15	42.08	-183.96	-115.57
303.15	44.21	-187.04	-116.20
308.15	47.60	-190.13	-115.57
313.15	50.16	-193.21	-115.76
0.05 mol.kg^{-1} D-Lactose + water			
298.15	46.83	-260.88	-187.67
303.15	49.03	-265.26	-189.54
308.15	53.37	-269.63	-189.27
313.15	58.90	-274.01	-187.75

The values of change in activation energy per mole of solute ($\Delta\mu_2^{0^*}$-$\Delta\mu_1^{0^*}$) on replacing one mole of solvent by one mole of solute at infinite dilution are recorded in table 3.44. Since the values are positive and increase for pyridoxine hydrochloride in 0.05 mol.kg^{-1}D-Fructose + water, 0.05 mol.kg^{-1}D-Glucose + water and 0.05 mol.kg^{-1}D-Lactose + water solvent systems at different temperatures, so it may be concluded that transitions state is accompanied by breaking/distortion of bonds. In other words transition state is less favored in the presence of pyridoxine hydrochloride in the entire temperature range studied here. The entropy of activation $\Delta S_2^{0^*}$[16] and values of enthalpy of activation i.e.$\Delta \mathrm{H}_2^{0^*}$ for pyridoxine hydrochloride has been determined from the equations (3.17) and (3.18).

The $\mathrm{T}.\Delta S_2^{0^*}$ and $\Delta \mathrm{H}_2^{0^*}$ values at different temperatures are recorded in table 3.44. As both the parameters enthalpy of activation and entropy of activation are found negative for pyridoxine hydrochloride which indicates that the transition state is associated with bond formation between solute and solvent molecules[14].

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CONCLUSION:

The present study has been done to determine the molecular interactions present between the biomolecules using thermodynamic and transport properties. During the initial stage of the research a vast literature has been conducted and it has been found that a number of studies have been conducted on various electrolytes, non-electrolytes and biomolecules but studies on thermodynamic and transport parameters for some of the water soluble vitamins and carbohydrates were less available in literature. Hence the thermodynamic and transport parameters of some water soluble vitamins viz; L-ascorbic acid, thiamine hydrochloride, pyridoxine hydrochloride and nicotinic acid have been studied in water as well as in binary aqueous mixtures of D-Glucose, D- Fructose, D- Lactose using density, ultrasonic sound velocity and relative viscosity data. The densities and the ultrasonic sound velocities have been obtained by using the density and sound velocity analyzer i.e. Anton Paar DSA-5000 whereas the viscosities has been obtained using the traditional suspended level type viscometer. From the results it has been found that the densities, viscosities and ultrasonic sound velocities of all the vitamins mentioned above increases with increase in compositions and with increase in temperature in water as well as in different compositions of binary aqueous mixtures of sugars D-Glucose, D- Fructose and D-Lactose. The density and speed of sound has been analyzed by using the Masson's equation and Hepler's criterion to obtain the values of partial molar volume, partial molar adiabatic compressibilities, partial molar expansibilities etc. whereas the relative viscosities has been analyzed using the Jones Dole equations in order to obtain the A and B parameters of Jones Dole equation. All vitamins viz; L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride are analysed in different compositions of D-Glucose, D- Fructose and D- Lactose at single temperature i.e. 303.15 K and it is found that the solute – solvent interactions increase with increase in the compositions of D-Glucose, D- Fructose and D-Lactose in water at 303.15 K. As the behavior of all the vitamins has been found similar in different compositions of D-Glucose, D- Fructose and D- Lactose hence effect of temperature has been studied only in the lowest compositions i.e. 0.05 molkg^{-1} D-Glucose + water, 0.05 molkg^{-1} D- Fructose + water and 0.05 molkg^{-1} D- Lactose + water. From the results it has been concluded that the solute –solute interactions decrease whereas solute – solvent interactions increase with increase in temperature. The obtained data has also been used to obtain partial molar expansibilities as it is one of important parameter, which help in determining the structure making or breaking behavior of a solute in any of the solvent as per Hepler's criterion. It is found that L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride and nicotinic acid show similar kind of behavior in all the compositions of D-Glucose, D- Fructose and D- Lactose in water at 303.15K. So the partial molar expansibilities, isobaric thermal expansion coefficient and the molar heat capacities are determined only for the lower compositions of D-Glucose, D-Fructose and D-Lactose in water at different temperatures. The values of partial molar expansibilities are found positive at entire range of temperature for all the vitamins and decrease in magnitude with rise in temperature for L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride whereas these values increase for nicotinic acid which shows that the three vitamins viz; L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride are not behaving just like symmetrical tetra alkyl ammonium salts but are behaving like common salts because the molar volume expansibilities should decrease with the rise in temperature for a common salt. But in case of nicotinic acid values of partial molar expansibilities increase in magnitude with rise in temperature which shows that nicotinic acid does not behave like common salt but behaves like symmetrical tetra alkyl ammonium salts. Above observation reveals the presence of "packing effect" in case of nicotinic acid and absence of "packing effect" in case of L-ascorbic acid, pyridoxine hydrochloride and thiamine hydrochloride.

In the present study values of partial molar heat capacities $(\partial C_p/\partial P)_T$ for the solutions of L-ascorbic acid, pyridoxine hydrochloride, thiamine hydrochloride respectively are positive showing thereby that all these behave as structure breaker in water and binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose whereas that sign of the values of $(\partial C_p/\partial P)_T$ for the solutions nicotinic acid are negative showing thereby that nicotinic acid behave as structure maker in water and binary aqueous mixtures of D-Glucose, D-Fructose and D-Lactose.

The viscosity data has also been analyzed by using Jones Dole equation so as to obtain the A and B- coefficients. The obtained data for A and B- coefficient of Jones Dole equation for L-ascorbic acid, thiamine hydrochloride, pyridoxine hydrochloride and nicotinic acid supports the results obtained from thermodynamic studies i.e. the solute –solute interactions decrease and solute-solvent interactions increase with increase in compositions of D-Glucose, D- Fructose and D-Lactose in water as well as with increase in temperature. The viscosity data has also been analyzed using the transition state theory and various activation energy parameters have been obtained using the respective equations and finally analyzed in terms of structure making and breaking behavior of above mentioned vitamins. Transport studies reveal the same results as obtained from the thermodynamic studies in terms of structure making and breaking behavior of all the vitamins in water as well as in binary aqueous mixtures of sugars viz; D-Glucose, D-Fructose and D- Lactose.