STUDIES ON INTERMOLECULAR INTERACTIONS IN BIOCHEMICAL SYSTEMS

THESIS
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BY
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To
My Brother
For His
Immense Sacrifices

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Certificate

This is to certify that the work presented in this thesis entitled "***Studies on intermolecular interactions in biochemical systems***", is original, carried out by Mr. Mushtaq Ahmad Malik under my supervison and is suitable for submission for the award of Ph.D. degree in Chemistry of this university.

(Prof. Nurul Islam)
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CONTENTS

Abstract

Measurements of density (ρ), viscosity (η) and ultrasonic velocity (u) have been made using the mixtures of aminoacids and alkali chlorides in their aqueous media. The aminoacids used were glycine, l-leucine and l-threonine while the alkali chlorides were those of sodium and potassium. These measurements were made for several compositions at different temperatures.

The ultrasonic velocity has been found to increase with increases in temperature and salt concentration. Such an increase in the ultrasonic velocity values with increase in salt concentration may be attributed to an increase in the intermolecular interaction. Nomoto relation, Van Dael and Vangeel's ideal mixing relation and the Schaaffs' collision factor theory have been found to almost reproduce the experimental ultrasonic velocity values for the systems under investigation. Such a close agreement between the experimental and the computed values has been ascribed to the extremely dilute nature of these systems as well as to the close ultrasonic velocity values of the pure components.

Using the ultrasonic velocity and the density data, the adiabatic compressibility (β_S) has been calculated. The adiabatic compressibility has been found to decrease with increases in the salt concentration and the temperature. Such a decrease in the β_S values with increase in temperature may be attributed to the thermal rupture of the associated solvent molecules while the decrease with an increase in concentration of the salt may be due to an increase in the ion-ion interaction. Furthermore, an increase in the number of incompressible ions has also been suggested as one of the reasons for the decrease in the compressibility values. Similarly, changes in the compressibility ($\Delta\beta_S$) and the relative compressibility ($\Delta\beta_S/\beta_{S0}$) have also been computed in order to see the trend and the magnitude of such changes which may suggest the presence of weak interactions due to an extremely dilute nature of the systems under investigation. In addition, the molar sound velocity (R) and specific acoustic impedance (Z) have been computed and are found to vary linearly with composition. These values have been found to increase with an increase in temperature.

The isothermal compressibility (β_T) of these systems have been computed by using the Mc Gowan's as well as Pandey's relations. A good agreement has been found between the isothermal compressibility values obtained by using the above two relations. The β_T values have been found to decrease with increases in salt concentration as well as in temperature. The nature of variation of β_T with an increase in salt concentration has been found to be similar to that of β_S. The internal pressure (P_i), the solubility parameter (δ) and the Pseudo Grüneisen parameter (Γ) have also been computed. On one hand, an increase in the internal pressure with an increase in temperature may apparently be associated with a possible decrease in the repulsive forces among the components of the mixtures under investigation. While an increase in the values of Γ with an increase in temperature may be attributed to an increase in the kinetic energy in the systems.

The density and the adiabatic compressibility values have been employed to compute the apparent molal volume ($\phi_{V,1}$) and the apparent molal compressibility ($\phi_{K,1}$) of component 1 i.e; aqueous salt solutions, in the systems under investigation. The values of $\phi_{V,1}$ have been found to increase with increase in temperature which may be attributed to the positive values of molal expansibilities due to volume expansion. The $\phi_{V,1}$ at infinite dilution was obtained from the Redlich's equation and the increase in $\phi^0_{V,1}$ values with increase in temperature may be attributed to a corresponding decrease in the hydration number of solute(s) at higher temperatures. The apparent molal compressibility of component 1($\phi_{K,1}$) has been found to decrease with increase in temperature which seems to have been due to a change in the solvation of the molecules. The variation in the $\phi_{K,1}$ values with salt concentration has been ascribed to the presence of ion-ion interaction, the electrostriction effect as well as to an increase in the number of cations. The apparent molal compressibility at infinite dilution ($\phi^0_{K,1}$) has been obtained and is found to decrease with an increase in temperature. This may be due to the presence of structural repulsion between the individual components of the systems. Similarly, the low magnitude of slopes S_V and S_K also point to the presence of possible weak interactions.

The viscosity (η) values have been found to decrease with increases in salt concentration as well as in temperature. The decrease in the values of viscosity with increase in salt concentration may be attributed to a change in the solvation of aminoacids. The excess viscosity (η^E) values have been obtained and have been fitted to the Redlich and Kister's equation. Rheochor [R] and excess rheochor [R^E] have also been computed. The said excess properties reinforce the presence of weak interactions in the systems under investigation. In addition, the additivity of rheochor values was checked by computing the η values from them and comparing the same with those of the experimental values of viscosities which turned out to be very close to those of the computed values.

Thus, the systems under investigations turn out to be an almost ideal ones in respect of their said behaviour.

General Introduction

Ultrasonics provide fruitful information regarding the nature of intermolecular/ interionic interactions. The measurements of sound velocity and its derived parameters viz., adiabatic compressibility, change/relative change in compressibility with respect to solvent, molar ultrasonic velocity, specific acoustic impedance, Wada's constant and other parameters help in exploring the nature of different interactions and physical nature of aggregates occuring in liquid phase [1]. A departure from linearity of sound velocity versus composition plot is taken as an indication of the existence of interaction between different species [2,3].

Evaluation of ultrasonic velocity in liquid mixtures at different concentrations based on the theoretical molecular models has been the interest of many workers [4-10]. Nomoto [4] relation meant for the molecular liquids and Van Dael and Vangeel's [5] ideal mixing relation have been utilized to compute the ultrasonic velocity in various binary and ternary [11-13] liquid mixtures. Schaaffs' [6] collision factor theory and the free-length theory of Jacobson [7,8] have also been successfully employed to evaluate the ultrasonic velocity in various binary liquid mixtures [14-19]. In addition, the Flory-Patterson theory [9,10] has ben found to give satisfactory results of ultrasonic velocity of liquid systems [20]. Although these theories have been proposed for the molecular liquids, they turned out to be equally good for the molten electrolytes and their mixtures [21-23] as well as for the ionic salt solutions [24]. A comparison of the experimental data with those of the computed values has been found to be good.

A number of fluid equations of state based on the hard-sphere model have been proposed by various workers [25-35] to evaluate the various equilibrium thermodynamic properties of a number of liquids, liquid mixtures as well as of electrolytes' solutions [36-38]. Some of these equations [30,33,34] have been used to calculate the isothermal compressibility of various systems [39,40]. Isothermal compressibility can be deduced from the density and the ultrasonic velocity if the thermal expansion coefficient and the specific heat ratio for a particular system are known.

Mc Gowan, in 1966 gave an empirical relation [41] which directly relates the isothermal compressibility with the density and ultrasonic velocity. Such a relation has been used for a variety of liquids. An alternative expression has been proposed by Pandey [42] for the evaluation of isothermal compressibility of various liquid systems by replacing the arbitrary constant in Mc Gowan's relation by a temperature term.

Another derived parameter, the internal pressure has been found to be extremely useful in explaining the behaviour of liquids [43]. The thermodynamic and the ultrasonic measurements help in determining the internal pressure of liquids. It may also be obtained by using a relation proposed by Buchler *et al.* [44] which has been extensively used for the determination of internal pressure of molten salts [45] and liquid metals [46].

Volumetric and compressibility studies have been useful in understanding the structural interactions in solutions [47-49]. Since the early investigations by Traube [50], a remarkable work has been done on apparent molal volumes of solutes in solutions [51-54]. Such studies have been the focus of investigations in liquid systems [55,56], electrolytes [57-58] and many other compounds of biological importance [59-69]. Till now many theories [70,71] have been developed to study the apparent molal volumes for exploring the nature of different types of interactions in solutions. The partial molal volumes of electrolytes can also be used to calculate the effect of pressure on ionic equilibria in engineering and oceanography. Similarly, the partial molal properties at infinite dilution can also be utilised to gain information about the intermolecular/interionic interactions as well as the solvation processes [72].

The intermolecular interactions influence the structural arrangement and the shape of the molecules. The measurements of viscosity and some thermodynamic functions associated with it, are important to understand the transport properties of a system. The temperature and concentration dependences of viscosity have been used to characterise the strength and the nature of interaciton of different species in solutions [73]. Theoretical evaluation of viscosity in binary liquid mixtures has become an important subject to estimate the strength of molecular interactions. Several empirical relations [74-78] have been used to represent the concentration dependence of viscosity of binary liquid mixtures. Theories explaining the solution behaviour [79,80] have been employed in the determination of viscosity, its related thermodynamic quantities and their excess functions in binary [81-84] and ternary [85] liquid mixtures. Some workers [86,87] have introduced empirical coefficients (B and D) whose negative or positive values can offer some clue for the assessment of the type of interaction occurring in solutions. The non thermodynamic parameters e.g., reochor and its excess function may also be used to understand the intermolecular interactions [88]. The positive deviation of reochor values and those of the excess function, from the linear dependence on mole fraction and the presence of maximum in such plots may be attributed to the presence of strong interactions leading to complex formation while the negative deviations of these properties may be attributed to the presence of dispersion forces [89,90].

Studies of organisation and thermal stability of proteins have been the focus of investigations in biochemistry for decades [91,92]. Structural details revealed by high-resolution X-ray crystallography, neutron diffraction, spectroscopy and thermodynamic methods have contributed a great deal to the understanding of proteins' behaviour. However, the limitations of the experimental techniques to studying the fast in vivo processes which are believed to take place instantaneously during the ribosomal synthesis, turn out to be a major impediment to obtaining such direct information. The focus of study thus shifts to consideration of indirect methods of investigations which include the determination of aminoacid sequence and its correlation with structure [93], the study of refolding experiments using denaturants [94], theoretical modeling using computer simulation [95] and thermodynamic analysis of conformations involved in folding processes [96] have been useful in explaining the behaviour of such biomolecules.

There has been an increased interest in the state of water in living cells. Since most of the biological macromolecules are physiologically active in aqueous solutions, a knowledge of the protein-water interaction is necessary to understand the role of water solvated to soluble organics in living cells. A better understanding of this type of interaction may be obtained by studying the physico-chemical properties and quantitative characterisation of aminoacids which are the basic constituents of proteins. Since aminoacids are zwitterions in their aqueous solutions [97-99], their thermodynamic properties may reflect structural interactions with water molecules. Moreover, aminoacids are the fundamental structural untis of certain types of hormones, enzymes, antibodies and many compounds of biological relevance[100]. It is generally recognised that in the absence of experimental thermodynamic data for these macromolecules, aminoacids can serve as useful models in estimating their properties [101,102]. Even in situations where experimental data are available, the properties of these smaller units are still found applicable in exploring the various aspects of structural organization in the larger biomolecules [103].

Alkali metal chlorides particularly NaCl and KCl are also physiologically important. Na^+ and K^+ ions maintain the osmotic pressure of body fluid and protect our body from excessive fluid loss and regulate the potential across the cell membrane. In addition to it, K^+ ions are important in transmission of nerve impulses. Both Na^+ and K^+ ions when associated with chlorine maintain the acid-base balance in the body.

The thermodynamic properties of electrolytes , their mixtures [104-106] as well as of non-electrolytes [107] have been extensively studied. Salt solutions have large effects on the structure and properties of proteins including their solubility and denaturation [108]. A number of workers have successfully investigated the thermodyamic properties of aminoacids in aqueous solutions [109-115] and mixed solvents [116,117]. The volumetric and compressibility properties of all the aminoacids, over a wide range of temperature (288.15-343.15 K) have been studied by Kharkoz [118]. Yasuda *et al.* [119] have studied the thermodynamic properties of aminoacids in high salt concentrations.

However, less efforts have been made to investigate the behaviour of electrolyte-non electrolyte systems in aqueous solutions. Therefore, investigations have been made to study the effects of $NaCl_{(aq)}/KCl_{(aq)}$ on aqueous solutions of aminoacids (glycine, leucine and threonine), by measuring their density, viscosity and ultrasosnic velocity as functions of temperature and composition in order to understand the type of interactions, thereby gaining information about the ideal or non-ideal behaviour of such systems.

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Experimental

MATERIALS AND SAMPLE PREPARATION

Aminoacids (Extrapure) were purchased from SRL Bombay (India) and used without further purification. NaCl and KCl (AR Grade) were obtained from Glaxo Laboratories (India). All the aminoacids and the salts used were dried at 110 and 50°C respectively and then kept in a desiccator over P_2O_5 for several hours before weighing. Aqueous solutions of aminoacids (Glycine 0.2 M, Threonine 0.2 M, Leucine 0.1 M) and Salts (NaCl and KCl, 0.25 M) were prepared in triply distilled water. Threonine and Leucine used were in l-stereoisomeric form.

Mixtures of different composition were prepared and following systems were studied as functions of temperature and composition :

System	Composition
1.	x $NaCl_{(aq)}$ +(1-x) $Glycine_{(aq)}$
2.	x $NaCl_{(aq)}$ +(1-x) $Leucine_{(aq)}$
3.	x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$
4.	x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$
5.	x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$
6.	x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$

All the systems were considered to be binary and different combinations were studied as

Compositions	Mole fraction(x) of Salt ($NaCl_{(aq)}$/$KCl_{(aq)}$) in Systems (1) (2) (4) and (5)	Mole fraction (x) of Salt ($NaCl_{(aq)}$/$KCl_{(aq)}$) in Systems (3) and (6)	V Salt/ V Amino acids
A	0.000	0.000	0/100%
B	0.101	0.103	10/90%

C	0.201	0.203	20/80%
D	0.301	0.303	30/70%
E	0.401	0.403	40/60%
F	0.501	0.503	50/50%
G	0.601	0.603	60/40%
H	0.701	0.703	70/30%
I	0.801	0.803	80/20%
J	0.901	0.903	90/10%
K	1.000	1.000	100/0%

Molecular weights of each of the components were calculated by using the relation,

$$M = M_1 x + M_2 (1-x)$$

where the subscript 1 and 2 refer to the pure components.

TEMPERATURE CONTROL

A thermostated paraffin bath was used to maintain a constant temperature during the measurements of density and viscosity. The paraffin bath having 5 litres' capacity consisted of an immersion heater (1.5 KW), a stirrer (Remi make), a check and a contact thermometer (GDR) and a relay (Jumo Type GKU 10, 220 V ~ 10 A Germany). Thermal stability was found to be within ± 0.1°.

DENSITY MEASUREMENTS

A pyknometer consisting of a small bulb with flat bottom (~ 5 ml capacity) and graduated stem was used for the density measurements. Each mark on the stem of the pyknometer was calibrated using triply distilled water as a reference liquid. The pyknometer was dried, weighed and filled with water and weighed again. The weight of water was determined by the difference in the two weights. The pyknometer was immersed in a paraffin bath maintained at the required temperature and the volume changes were recorded as a function of temperature and thus each mark on the stem was caliberated. The density of water at different temperatures required for caliberation was obtained from the relation,

$$\rho = 1.000525 - 2 \times 10^{-5}\, t - 4.72 \times 10^{-6}\, t^2 \qquad (t/^{0}C)$$

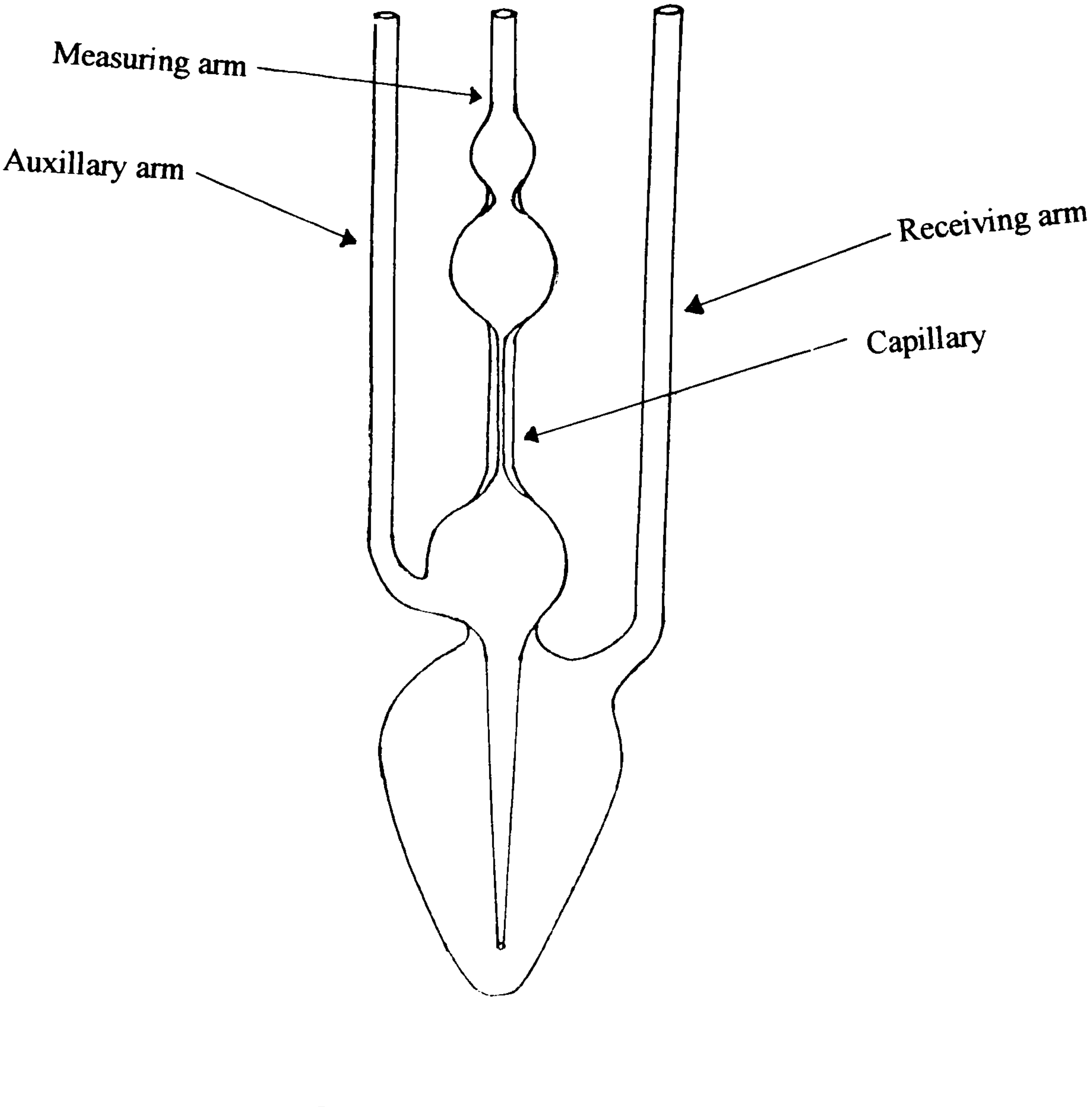
where t is the temperature in ^{0}C. The ratio of the amount of water to the above calculated densities at different temperatures gave the volume of the pyknometer at the corresponding mark on the stem. Reproducibility was checked by repeating the procedure with different weights of water using the known volume of caliberated pyknometer at each mark and mass of water, the densities at the required temperature were determined. The accuracy of the density measurements was within $\pm$ 0.01%.

The test solution was taken in the pyknometer before immersing it into the paraffin bath. By recording the volume changes as a function of temperature, the densities at the required temperatures were determined.

VISCOSITY MEASUREMENTS

Cannon-Fenske viscometer was used for the viscosity measurements of aqueous aminoacid and salt mixtures. The viscometer consists of three parallel arms with a common base as shown in the diagram.

The viscometer was filled with the triply distilled water and was clamped in the thermostated paraffin bath keeping the measuring arm perfectly



Cannon-Fenske Viscometer

vertical. The open ends of the viscometer were attached to the tubes containing anhydrous calcium chloride to prevent the absorption of moisture. Water was sucked into the measuring bulb and was allowed to stand for few minutes before recording the time of fall of the liquid from the upper to the lower end of the bulb. Mean values of almost identical readings were taken at several temperatures. Viscosity was calculated using Poisuilles equation,

$$\eta = \pi \, h \, \rho \, g \, r^4 t/8lv$$

where h is the height of the column of the viscometer, ρ is the density of the liquid, g is the acceleration due to gravity, r is the radius of the capillary of the viscometer, l is the length and t is the time of fall of the test liquid of volume v to fall through the capillary. Equation (a) may be written as,

$$\eta = \rho \, \beta \, t$$

where $\beta = \pi \, h \, g \, r^4/8lv$ and is constant for a given viscometer. It has been calculated by making use of the reported values [33] of viscosities of water at different temperatures. The reproducibility of viscosity measurements was found to be within $\pm$ 0.006 x 10^3 kg $m^{-1}s^{-1}$. The viscosities of the test solution was determined by noting the time of fall at different temperatures using the relation,

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

where η, ρ and t are the viscosity, the density and the time of fall respectively. The subscripts 1 and 2 refer to the two components, i.e., water and the test solution, respectively.

MEASUREMENT OF ULTRASONIC VELOCITY (INSTRUMENTATION)

(a) Working principle :

An ultrasonic interferometer (Mittals M77, India) was used to determine the ultrasonic velocity in the test solutions at a frequency of 4 M Hz. Water from an ultrathermostat (Type U-10, Germany) was circulated through the brass jacket surrounding the cell and the quartz crystal. The jacket is well insulated and the temperature of the liquids under investigation was maintained to an accuracy of ± 0.1°.

Its principle of working is based on the accurate determination of wavelength, λ, in the medium. The ultrasonic waves of frequency, ν, are produced by a quartz crystal fixed at the bottom of the cell and are reflected by a movable metallic plate kept parallel to the quartz crystal. The standing waves are formed, if the separation between these two plates is exactly a whole multiple of the sound wave length. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum.

If the distance is now increased or decreased and the variation is exactly one-half wave length (λ/2) or multiple of it, the anode current is maximum. The ultrasonic velocity can thus be obtained from the relation,

$$u = \lambda \times \nu$$

(b) Description :

Ultrasonic interferometer consists of two parts. (i) High frequency generator and (ii) Measuring cell.

(i) High frequency generator : It is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the measuring cell. On the panel of the high frequency generator, a micrometer is provided to observe the change in current and two controls for the purpose of sensitivity and initial adjustment of micrometer.

(ii) Measuring cell : It is a double walled cell for maintaining a constant temperature of the liquid during experiment, and at its top, a fine micrometer screw has been provided which can lower or raise the reflector plate in the liquid (in the cell) through a known distance. It has a quartz crystal fixed at the bottom.

Adjustment of Ultrasonic Interferometer :

It is done in the following manner,

(1) The cell is inserted in the square base socket and clamped to it with the help of a screw provided on one of its sides.

(2) The curled cap of the cell is unscrewed and removed from the cell, then the experimental liquid is poured into it and curled cap is screwed on it.

(3) Water is circulated through the two tubes in the double walled cell in order to maintain the desired temperature.

(4) The cell wall is connected with a high frequency generator by a co-axial cable provided with the instrument.

For the initial adjustment two knobs are provided on the high frequency generator, one is marked with 'Adj' and the other with 'Gain'. With knob marked 'Adj' the position of needle on the ammeter is adjusted and the knob marked 'Gain' is used to increase the sensitivity of instrument for greater deflection. The ammeter is used to record the maximum deflection by adjusting the micrometer.

Measurements : The measuring cell was connected to the out-put terminal of high frequency generator through a co-axial cable. The cell was filled with the experimental liquid before switching on the generator. The ultrasonic waves of 3 MHz *frequency produced by a gold plated quartz crystal fixed at the bottom* of a cell are passed through the medium and are reflected by a movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal. Acoustic resonance due to these standing waves gives rise to an electrical reaction to the generator driving the quartz plate and the anode current of the generator becomes maximum. The micrometer screw was raised slowly to record the maximum anode current. The wavelength was determined with the help of the total distance moved by the micrometer for twenty maxima of the anode current. The total distance, d travelled by the micrometer gives the value of the wavelength with the help of the relation, $d = n \times \lambda/2$, where n is the number of maxima in anode current. Once, the wavelenth is known, the ultrasonic velocity can be calculated as described earlier. The accuracy in the ultrasonic velocity measurement was found to be within $\pm$ 0.16%.

Chapter - 1

Density, ultrasonic velocity and the derived parameters of ultrasonic velocity for the aqueous mixtures of aminoacids and alkali chlorides

INTRODUCTION

Ultrasonic velocity measurements of liquids, a physical characteristic have been the subject of great importance reflecting the intermolecular/interionic interactions and dynamic processes occuring in solutions. This technique has been employed to examine the intermolecular/interionic interactions which provide the basis for qualitative estimation of the mechanism of some intermolecular processes.

The ultrasound velocity measurements has been made in pure liquids [1-2] as well as in their binary [3], ternary [4-8] and quaternary [9] mixtures with a view to examining the different types of molecular interactions. Investigations have also been made in aqueous solutions of electrolytes [10], in molten salts as well as in their mixtures [11,12]. Many workers have investigated such behaviours in solutions containing aminoacids [13-17], disaccharides [18] and proteins [19].

Right from the development of this technique, different empirical relations have been proposed by some workers to calculate the ultrasonic velocity theoretically. For example, Nomoto's relation [20] meant for the molecular liquids. Van Dael and Vangeel's ideal mixing relation [21], Schaaffs' collision factor theory [22], the free-length theory of Jacobson [23,24] and other relations [25-28] have successfully been employed for evaluating the ultrasonic velocities in various liquid mixtures [29,30], molten electrolytes and their mixtures [12,31] as well as in aqueous biochmical systems [32].

Several theoretical and experimental investigations have revealed that a representation in terms of derived parameters from the ultrasonic velocity such as adiabatic compressibility (β_S), molar ultrasonic velocity (R), the specific acoustic impedance (Z), change in adiabatic compressibility ($\Delta\beta$) and the relative change in compressibility ($\Delta\beta/\beta_{S0}$) can provide a better insight into the understanding of the extent of intermolecular/interionic interactions, e.g., strong/weak, ion-ion, ion-solvent, solute-solute, solute-solvent interactions or no interaction at all as in the cases of ideal mixing.

The present studies have been carried out to study the intermolecular/ interionic interactions in aminoacids and electrolytes in their aqueous solutions by undertaking the measurements of ultrasonic velocity and density. Theoretical evaluation of ultrasound velocities using Nomoto relation, Van Dael and Vangeel's ideal mixing relation and Schaaffs' collision factor theory have been employed to the systems under investigation for the purpose of examining the feasibility of these models in explaining the experimental sound velocity results.

THEORETICAL

The experimental values of densities and ultrasonic velocities were used for the evaluation of various derived parameters by employing the following relations :

[1.1] $\beta_S = u^{-2}\rho^{-1}$

[1.2] $R = Mu^{1/3}/\rho = Vu^{1/3}$

[1.3] $Z = u.\rho$

[1.4] $\Delta\beta = \beta_S - \beta_{S0}$

[1.5] $\Delta\beta_{rel} = \Delta\beta/\beta_{S0}$

where u stands for the ultrasonic velocity, ρ the density, V the molar volume, Z the specific acoustic impedance and R the molar ultrasonic velocity while β_S and β_{S0} are the adiabatic compressibilities of solution and solvent, respectively. In the present studies β_{S0} was taken as the adiabatic compressibility of aminoacid (aqueous) and β_S, the compressibility of the binary mixtures of aminoacid and electrolyte.

The molar ultrasonic velocity, R, is expressed by Nomoto as

[1.6] $R = R_1 x + R_2 (1-x)$

where R_1 and R_2 are the molar ultrasonic velocities of the pure components. R is considered to be a linear function of the two components. x and (1-x) are the mole fractions of the electrolyte and the aminoacid, respectively.

R may also be expressed as,

[1.7] $$R = Vu^{1/3}.$$

The molar volume being additive in nature is expressed as

[1.8] $$V = V_1 x + V_2 (1-x).$$

Substituting the values of R and V in eq. [1.7], we get,

[1.9] $$u = \left\{ \frac{R_1 x + R_2 (1-x)}{V_1 x + V_2 (1-x)} \right\}^3.$$

The above equations are found to be quite satisfactory when applied to molecular liquids. Another equation for the theoretical evaluation of ultrasonic velocity of mixtures has been proposed by Van Dael and Vangeel using adiabatic compressibility,

[1.10] $$\beta_S (im) = \phi_1 \beta_{S1} + \phi_2 \beta_{S2}$$

where ϕ_1 and ϕ_2 refer to the volume fractions of the two pure components. This equation may also be expressed in terms of linear combinations of mole fractions asuming that V_1 and V_2 are equal

[1.11] $$\beta_S(im) = x \beta_{S1} + \beta_{S2}(1-x).$$

Therefore, the ultrasonic velocity may be expressed as

[1.12] $$\frac{1}{M_1 x + M_2(1-x)} \quad \frac{1}{u^2(im)} = \frac{x}{M_1 u_1^2} + \frac{(1-x)}{M_2 u_2^2}$$

in which M_1 and M_2 are the molecular weights of the two components. u(im) stands for the ultrasonic velocity for ideal mixing in solutions.

Based on the collision factor theory, Schaaffs developed the following expression for the ultrasonic velocities in pure liquids,

$$[1.13] \qquad u = u_{\infty} S \frac{B}{V}$$

where $u_{\infty} = 1600$ m/s, S is the collision factor, B the volume of molecules per mole and V is the molar volume of the pure liquid. Nutsch-Kuhnkies (33) extended equaition [1.13] to binary liquid mixtures by expressing $u_{(mix)}$ as,

$$[1.14] \qquad u_{(mix)} = u_{\infty} \{S_1 \; x + S_2 (1-x)\} \frac{\{B_1 \; x + B_2 (1-x)\}}{V} \; .$$

The actual volume of the pure component per mole is given by,

$$[1.15] \qquad B = \frac{4}{3} \pi r^3 N$$

where r is the molecular radius and N is the Avogadro's number,

$$[1.16] \qquad r = \left[\alpha \; \{1-\beta (1 + \frac{1}{3\beta})^{1/2} - 1\}\right]^{1/3};$$

$$\alpha = \left(\frac{3V}{16\pi N}\right)^{1/3}; \quad \beta = \left(\frac{RT}{Mu^2}\right);$$

while R is the gas constant.

RESULTS AND DISCUSSION

The experimental values of densities of all the six systems under investigation have been least-squares fitted to a polynomial equation,

$$[1.18] \qquad \rho_{(t)} = \sum_{i=0}^{2} \rho_i \, t^i$$

The parameters alongwith the standard deviation are listed in Table 1. The densities of

TABLE 1 **Best-fit parameters of equation $\rho = \sum_{i=0}^{2} \rho_i t^i$ for the following systems :**

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	ρ_0	$\rho_1 \times 10^5$	$-\rho_2 \times 10^6$	$\sigma_i\rho_i \times 10^5$
A	1.0047	−1.076	4.643	1.1
B	1.0051	4.429	5.000	2.2
C	1.0060	−1.873	4.714	2.2
D	1.0063	−2.756	4.429	2.6
E	1.0058	4.391	5.643	1.3
F	1.0064	2.652	5.357	2.0
G	1.0062	8.974	6.286	1.0
H	1.0081	−4.739	4.999	1.9
I	1.0079	3.878	5.643	1.5
J	1.0076	8.378	6.071	1.3
K	1.0099	1.270	5.286	2.2

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	ρ_0	$\rho_1 \times 10^5$	$-\rho_2 \times 10^6$	$\sigma_i\rho_i \times 10^5$
A	1.0047	−1.076	4.643	1.1
B	1.0049	−2.716	4.714	2.2
C	1.0039	8.483	5.999	1.9
D	1.0060	−4.315	3.714	1.5
E	1.0060	2.043	5.000	2.9
F	1.0067	9.600	5.000	2.9
G	1.0064	9.600	5.000	2.9
H	1.0096	−8.607	3.643	1.3
I	1.0097	-4.478	4.357	1.5
J	1.0102	−3.078	4.643	1.1
K	1.0094	6.965	5.643	1.3

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	ρ_0	ρ_1 x 10^5	$-\rho_2$ x 10^6	$\sigma_i\rho_i$ x 10^5
A	1.0014	1.529	5.000	1.9
B	1.0022	6.757	4.643	2.0
C	1.0046	–6.480	4.357	1.5
D	1.0030	6.087	6.000	1.9
E	1.0062	–8.484	3.715	3.0
F	1.0063	–7.207	3.929	2.0
G	1.0052	2.043	5.000	2.9
H	1.0051	5.564	5.357	1.1
I	1.0069	9.549	4.999	2.9
J	1.0088	–5.664	4.643	1.1
K	1.0099	1.270	5.286	2.2

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	ρ_0	ρ_1 x 10^5	$-\rho_2$ x 10^6	$\sigma_i\rho_i$ x 10^5
A	1.0014	1.529	5.000	1.9
B	1.0021	9.557	5.000	0.9
C	1.0046	2.679	4.643	3.6
D	1.0063	8.000	4.000	2.7
E	1.0089	14.037	3.643	1.3
F	1.0087	9.693	3.643	2.8
G	1.0069	8.972	6.286	3.3
H	1.0083	2.477	5.357	2.3
I	1.0080	7.008	6.072	7.8
J	1.0103	1.044	5.000	0.9
K	1.0094	6.965	5.643	1.3

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	ρ_0	ρ_1 x 10^5	$-\rho_2$ x 10^6	$\sigma_i\rho_i$ x 10^5
A	1.0083	−14.357	2.714	1.2
B	1.0074	−8.164	3.500	5.6
C	1.0059	4.078	5.357	1.1
D	1.0078	−4.601	4.286	1.5
E	1.0068	6.429	6.000	2.4
F	1.0086	−1.991	4.643	2.0
G	1.0094	−3.963	4.357	1.3
H	1.0084	5.155	5.671	1.4
I	1.0099	−1.928	4.714	3.7
J	1.0089	8.228	6.286	3.0
K	1.0099	1.270	5.286	2.2

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	ρ_0	ρ_1 x 10^5	$-\rho_2$ x 10^6	$\sigma_i\rho_i$ x 10^5
A	1.0826	−14.357	2.714	1.2
B	1.0111	−27.958	9.998	0.9
C	1.0126	−34.322	2.142	3.2
D	1.0085	−3.688	4.285	0.5
E	1.0082	9.575	5.000	0.9
F	1.0092	−2.567	4.642	1.1
G	1.0089	−2.482	4.929	2.2
H	1.0092	−1.649	4.643	2.0
I	1.0107	−9.123	3.643	1.5
J	1.0102	−4.479	4.357	1.5
K	1.0940	6.965	5.643	1.3

each of the systems have been found to increase with increase in the electrolyte concentration and decrease with increase in temperature. The experimental values of ultrasonic velocity of each of the systems have been least-squares fitted to a polynomial equation of the form given above.

$$[1.19] \qquad u = \sum_{i=0}^{2} u_i x^i .$$

The results alongwith the standard deviation are given in Table 2. The experimental as well as the computed values of ultrasonic velocities are listed in Table 3.

The ultrasonic velocity is found to increase with increase in concentration of the electrolyte as well as with temperature (Fig. 1) in all the systems under investigation. An increase in the values of ultrasonic velocity with increase in electrolyte concentration may be attributed to a corresponding increase in the intermolecular interaction between the aminoacid and the salt. A good agreement has been found between the experimental and the computed values of ultrasonic velocities obtained employing the said empirical equations. An examination of the computed ultrasonic velocities show insignificant deviations from those of the experimental values irrespective of the models employed. Such an outcome may be attributed to extremely dilute nature of these systems. In addition, close values of the ultrasonic velocities of the pure components may also be the reason for the said insignificant difference in the ultrasonic velocities in the computed and the experimental values as well as on variations in salt concentration. These results suggest an almost ideal nature of the said extremely dilute systems.

The adiabatic compressibility (Table 4) is found to increase with increase in the electrolyte concentration as well as in temperature (Fig. 2). A decrease in the compressibility values with increase in the electrolyte concentration may be attributed to an increase in the ion-ion interaction, viz., the electrolyte ions and the

TABLE 2 Least-Squares fitted parameters of equation $u = \sum_{i=0}^{2} u_i x^i$ for the following systems

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

T(K)	u_0	u_1	u_2	σu_i
293.15	1499.45	6.370	1.774	0.70
298.15	1511.84	3.289	2.390	0.51
303.15	1521.28	7.167	–0.240	0.41
308.15	1529.70	9.362	–3.839	0.20
313.15	1537.60	3.857	2.192	0.43
318.15	1544.76	3.640	2.248	0.32

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

T(K)	u_0	u_1	u_2	σu_i
293.15	1498.82	3.133	2.728	0.29
298.15	1511.27	0.900	4.822	0.41
303.15	1521.30	3.383	1.351	0.20
308.15	1529.26	8.403	3.300	0.27
313.15	1537.33	5.476	–0.884	0.16
318.15	1544.72	3.573	0.263	0.19

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	u_0	u_1	u_2	σu_i
293.15	1501.12	4.530	2.137	0.55
298.15	1511.28	7.514	–0.650	0.26
303.15	1520.31	10.174	–2.377	0.60
308.15	1528.23	10.836	–4.289	0.52
313.15	1536.91	5.627	1.060	0.54
318.15	1542.28	8.218	–1.188	0.60

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	u_0	u_1	u_2	σu_i
293.15	1501.12	4.711	1.937	0.56
298.15	1511.31	7.250	−0.443	0.30
303.15	1520.24	10.128	−2.246	0.50
308.15	1528.32	11.199	−4.831	0.27
313.15	1537.33	5.329	0.812	0.25
318.15	1542.82	9.161	9.161	0.29

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	u_0	u_1	u_2	σu_i
298.15	1509.29	10.315	−1.466	0.33
303.15	1521.68	6.546	0.125	0.28
308.15	1531.95	3.644	−0.261	0.10
313.15	1539.35	8.101	−3.082	0.10
318.15	1545.33	4.589	1.244	0.20

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	u_0	u_1	u_2	σu_i
298.15	1509.42	4.777	2.876	0.24
303.15	1521.73	2.812	1.464	0.21
308.15	1531.83	3.057	−0.528	0.10
313.15	1538.97	1.581	1.296	0.13
318.15	1545.30	1.926	1.315	0.14

TABLE 3 Experimental and computed values of ultrasonic velocity (u, m s^{-1}) as functions of temperature and composition for the following system :

(a) x NaCl$_{(aq)}$ + (1 - x) Glycine$_{(aq)}$

X	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1498.4	1511.2	1521.2	1529.6	1537.2	1544.4
B		1500.7^a	1512.5	1522.1	1530.7	1538.0	1545.3
		(1499.44)^b	(1511.93)	(1521.96)	(1530.16)	(1537.88)	(1545.08)
		{1499.43}^{c}	{1511.92}	{1521.95}	{1530.16}	{1537.87}	{1545.08}
		[1499.45]^d	[1511.94]	[1521.97]	[1530.17]	[1537.89]	[1545.09]
C		1501.6	1513.0	1522.4	1531.2	1538.8	1545.6
		(1500.48)	(1512.66)	(1522.72)	(1530.72)	(1538.56)	(1545.76)
		{1500.45}	{1512.64}	{1522.70}	{1530.71}	{1538.55}	{1545.75}
		[1500.49]	[1512.67]	[1522.73]	[1530.73]	[1538.57]	[1545.77]
D		1501.6	1513.3	1523.2	1532.6	1539.6	1546.7
		(1501.56	(1513.39)	(1523.48)	(1531.28)	(1539.24)	(1546.44)
		{1501.48}	{1513.36}	{1523.45}	{1525.26}	{1539.22}	{1546.42}
		[1501.53]	[1513.40]	[1523.49]	[1513.29]	[1539.25]	[1546.45]
E		1502.5	1513.7	1524.8	1532.9	1540.0	1546.9
		(1502.55)	(1514.11)	(1524.23)	(1531.84)	(1539.92)	(1547.12)
		{1502.51}	{1514.09}	{1524.21}	{1531.82}	{1539.89}	{1547.10}
		[1502.57]	[1514.13]	[1524.25]	[1531.85]	[1539.93]	[1547.13]
F		1503.2	1514.1	1525.2	1533.6	1540.0	1547.2
		(1503.59)	(1514.84)	(1524.99)	(1532.40)	(1540.60)	(1547.80)
		{1503.55}	{1514.82}	{1524.97}	{1532.38}	{1540.57}	{1547.78}
		[1503.61]	[1514.86]	[1525.01]	[1532.41]	[1540.61]	[1547.81]
G		1504.0	1514.7	1525.5	1533.6	1540.3	1547.7
		(1504.63)	(1515.57)	(1525.75)	(1532.96)	(1541.28)	(1548.48)
		{1504.59}	{1515.55}	{1525.73}	{1532.94}	{1541.25}	{1548.46}
		[1504.65]	[1515.59]	[1525.77]	[1532.97]	[1541.29]	[1548.49]
H		1504.3	1515.2	1525.9	1534.1	1540.8	1548.0
		(1505.67)	(1516.31)	(1526.52)	(1533.52)	(1541.96)	(1549.16)
		{1505.64}	{1516.28}	{1526.49}	{1533.50}	{1541.94}	{1549.14}
		[1505.69]	[1516.32]	[1526.53]	[1533.53]	[1541.97]	[1541.97]

I	1504.9 (1506.72) {1506.79} [1506.73]	1515.2 (1517.04) {1517.02} [1517.05]	1526.3 (1527.28) {1527.26} [1527.29]	1534.8 (1534.08) {1534.07} [1534.09]	1541.9 (1542.64) {1542.63} [1542.65]	1548.8 (1549.84) {1549.83} [1549.85]
J	1505.9 (1507.76) {1507.75] [1507.77]	1516.0 (1517.76) {1517.76} [1517.78]	1527.2 (1528.04) {1528.03} [1528.05]	1535.2 (1534.64) {1534.64} [1534.65]	1543.2 (1543.32) {1543.31} [1543.33]	1549.6 (1549.52) {1550.51} [1550.53]
K	1508.8	1518.5	1528.8	1535.2	1544.0	1551.2

a. Experimental values

b. Computed values using Nomoto relation.

c. Computed values using Van Dael and Vangeel's relation.

d. Computed values using Schaaffs' collision factor theory.

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

X	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1498.4	1511.2	1521.2	1529.6	1537.2	1544.4
B		1599.2[a]	1511.5	1521.7	1530.0	1537.9	1545.3
		(1499.06)[b]	(1511.77)	(1521.72)	(1530.08)	(1537.68)	(1544.84)
		{1499.08}[c]	{1511.76}	{1521.71}	{1530.07}	{1537.67}	{1544.83}
		[1499.06][d]	[1511.77]	[1521.72]	[1530.08]	[1537.68]	[1544.84]
C		1500.0	1511.6	1522.1	1530.4	1538.4	1545.6
		(1499.72)	(1512.34)	(1522.24)	(1530.56)	(1538.16)	(1545.28)
		{1499.70}	{1512.32}	{1522.22}	{1530.54}	{1538.14}	{1545.27}
		[1499.72)]	[1512.92]	[1522.24]	[1530.56]	[1538.16]	[1545.28]
D		1500.3	1512.0	1522.4	1531.3	1539.2	1545.9
		(1500.38)	(1512.91)	(1522.76)	(1531.04)	(1538.64)	(1545.72)
		{1500.36}	{1512.89}	{1522.74}	{1531.02}	{1538.62}	{1545.71}
		[1500.39]	[1512.92]	[1522.77]	[1531.05]	[1538.65]	[1545.72]
E		1500.7	1512.3	1522.9	1532.0	1539.5	1546.4
		(1501.04)	(1513.48)	(1523.28)	(1531.52)	(1539.12)	(1546.16)
		{1501.2}	{1513.46}	{1523.26}	{1531.50}	{1539.10}	{1546.14}
		[1501.05]	[1513.49]	[1523.29]	[1531.53]	[1539.13]	[1546.16]
F		1500.9	1512.9	1523.3	1533.1	1539.7	1546.4
		(1501.7)	(1514.05)	(1523.80)	(1532.00)	(1539.60)	(1546.60)
		{1501.68}	{1514.03}	{1523.78}	{1531.98}	{1539.58}	{1546.58}
		[1501.71]	[1514.06]	[1523.81]	[1532.01]	[1539.61]	[1546.61]
G		1501.6	1513.3	1524.0	1533.4	1540.0	1546.9
		(1502.36)	(1514.62)	(1524.32)	(1532.58)	(1540.08)	(1547.04)
		{1502.34}	{1514.60}	{1524.30}	{1532.46}	{1540.06}	{1547.02}
		[1502.37]	[1514.63]	[1524.33]	[1532.49]	[1540.09]	[1547.04]
H		1502.0	1514.5	1524.4	1533.6	1540.8	1547.2
		(1503.02)	(1515.19)	(1524.84)	(1532.96)	(1540.56)	(1547.48)
		{1503.00}	{1515.17}	{1524.82}	{1532.94}	{1540.55}	{1547.47}
		[1503.03]	[1515.20]	[1524.85]	[1532.97]	[1540.57]	[1547.49]

I	1502.8	1515.2	1524.7	1533.7	1541.2	1547.7
	(1503.68)	(1515.76)	(1525.36)	(1533.44)	(1541.04)	(1547.92)
	{1503.66}	{1515.74}	{1525.34}	{1533.43}	{1541.02}	{1547.91}
	[1503.68]	[1515.76]	[1525.36]	[1533.44]	[1541.04]	[1547.92]
J	1503.9	1516.0	1525.0	1534.0	1541.5	1548.0
	(1504.34)	(1516.33)	(1525.88)	(1533.92)	(1541.53)	(1548.36)
	{1504.33}	{1516.32}	{1525.87}	{1533.91}	{1541.51}	{1548.35}
	[1504.34]	[1516.33]	[1525.88]	[1533.92]	[1541.52]	[1548.36]
K	1505.0	1516.9	1526.4	1534.4	1542.0	1548.8

a. Experimental values

b. Computed values using Nomoto relation.

c. Computed values using Van Dael and Vangeel's relation.

d. Computed values using Schaaffs' collision factor theory.

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

X	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1500.8	1511.2	1519.2	1527.2	1536.8	1541.6
B		1501.6[a] (1501.60)[b] {1501.58}[c] [1501.61][d]	1512.0 (1511.93) {1511.92} [1511.94]	1522.4 (1520.16) {1520.14} [1520.17]	1530.0 (1528.0) {1527.99} [1528.01]	1537.2 (1537.52) {1537.50} [1537.53]	1544.0 (1542.56) {1544.54} [1547.57]
C		1502.0 (1502.40) {1502.37} [1502.42]	1512.8 (1512.66) {1512.64} [1512.68]	1522.8 (1521.12) {1521.09} [1521.14]	1531.0 (1528.80) {1528.78} [1528.82]	1539.2 (1538.24) {1538.22} [1538.25]	1545.6 (1543.52) {1543.49} [1543.54]
D		1503.2 (1503.18) {1503.15} [1503.22]	1513.4 (1513.37) {1513.34} [1513.40]	1523.0 (1522.06) {1522.02} [1522.10]	1531.9 (1529.58) {1529.55} [1529.62]	1539.6 (1538.94) {1538.91} [1538.98]	1546.0 (1544.46) {1544.42} [1544.50]
E		1504.0 (1503.99) {1503.95} [1504.02]	1514.4 (1514.15) {1514.08} [1514.13]	1524.1 (1523.03) {1522.98} [1523.06]	1532.0 (1530.40) {1530.36} [1530.42]	1540.0 (1539.68) {1539.64} [1539.70]	1546.0 (1545.43) {1545.39} [1545.42]
F		1504.0 (1504.79) {1504.75} [1504.82]	1515.2 (1514.85) {1514.81} [1514.87]	1524.7 (1523.99) {1523.94} [1524.02]	1532.2 (1532.19) {1531.15} [1531.22]	1540.2 (1540.39) {1540.36} [1540.42]	1546.4 (1546.39) {1546.34} [1546.38]
G		1504.8 (1505.59) {1505.55} [1505.62]	1515.7 (1515.58) {1515.54} [1515.60]	1525.6 (1524.95) {1524.90} [1524.98]	1532.8 (1531.99) {1531.96} [1532.02]	1540.4 (1541.16) {1541.08} [1541.14]	1546.9 (1547.35) {1547.31} [1547.34]
H		1505.0 (1506.40) {1506.36} [1506.42]	1516.0 (1516.31) {1516.28} [1516.33]	1526.0 (1525.92) {1525.87} [1525.94]	1533.6 (1532.80) {1532.76} [1532.82]	1540.8 (1541.84) {1541.81} [1541.85]	1547.8 (1548.31) {1548.28} [1548.34]

I	1505.2	1516.3	1526.4	1534.0	1541.6	1548.0
	(1507.20)	(1517.04)	(1526.88)	(1533.60)	(1542.56)	(1549.28)
	{1507.17}	{1517.02}	{1526.85}	{1533.58}	{1542.54}	{1549.25}
	[1507.22]	[1517.06]	[1526.90]	[1533.62]	[1542.57]	[1549.30]
J	1506.4	1517.5	1527.2	1534.4	1543.0	1548.4
	(1508.0)	(1517.78)	(1527.84)	(1534.41)	(1543.28)	(1550.24)
	{1507.98}	{1517.76}	{1527.82}	{1534.39}	{1543.27}	{1550.22}
	[1508.01]	[1517.78]	[1527.85]	[1534.41]	[1543.29]	[1550.25]
K	1508.8	1518.5	1528.8	1535.2	1544.0	1551.2

a. Experimental values

b. Computed values using Nomoto relation.

c. Computed values using Van Dael and Vangeel's relation.

d. Computed values using Schaaffs' collision factor theory.

I	1504.0	1515.8	1524.5	1532.7	1540.4	1547.7
	(1504.16)	(1515.74)	(1524.96)	(1532.96)	(1540.96)	(1547.36)
	{1504.14}	{1515.74}	{1524.93}	{1532.97}	{1540.94}	{1547.33}
	[1504.16]	[1515.77]	[1524.97]	[1532.97]	[1540.97]	[1547.37]
J	1504.2	1516.0	1524.8	1533.2	1540.8	1548.4
	(1504.58)	(1516.33)	(1525.68)	(1533.68)	(1541.48)	(1548.08)
	{1504.57}	{1516.31}	{1525.67}	{1533.69}	{1541.47}	{1548.07}
	[1504.58]	[1516.34]	[1525.69]	[1533.69]	[1541.49]	[1548.09]
K	1505.0	1516.9	1526.4	1534.4	1542.0	1548.8

a. Experimental values

b. Computed values using Nomoto relation.

c. Computed values using Van Dael and Vangeel's relation.

d. Computed values using Schaaffs' collision factor theory.

(e) x NaCl$_{(aq)}$ + (1 - x) Threonine$_{(aq)}$

X	T(K)	298.15	303.15	308.15	313.15	318.15
A		1509.4	1521.7	1532.0	1539.0	1545.2
B		1510.4[a]	1522.4	1532.2	1540.0	1546.0
		(1510.32)[b]	(1522.42)	(1532.32)	(1539.51)	(1545.81)
		{1510.31}[c]	{1522.40}	{1532.32}	{1539.50}	{1545.80}
		[1510.34][d]	[1522.43]	[1532.33]	[1539.52]	[1545.82]
C		1511.2	1522.7	1532.8	1540.5	1546.5
		(1511.22)	(1523.2)	(1532.64)	(1540.00)	(1546.40)
		{1511.12}	{1523.11}	{1532.63}	{1539.99}	{1546.39}
		[1511.25]	[1523.14]	[1532.65]	[1540.02]	[1546.42]
D		1512.0	1523.6	1533.0	1541.2	1546.9
		(1512.12)	(1523.82)	(1532.96)	(1540.49)	(1546.99)
		{1512.09}	{1523.80}	{1532.95}	{1540.48}	{1546.98}
		[1512.16]	[1523.85]	[1532.97]	[1540.52]	[1547.02]
E		1513.0	1524.7	1533.4	1541.7	1547.2
		(1513.02)	(1524.53)	(1533.28)	(1540.99)	(1546.59)
		{1513.00}	{1524.51}	{1533.27}	{1540.98}	{1547.58}
		[1513.07]	[1524.56]	[1533.29]	[1541.02]	[1547.62]
F		1514.2	1525.2	1533.7	1542.5	1547.8
		(1513.93)	(1525.24)	(1533.59)	(1541.49)	(1548.19)
		{1513.90}	{1525.21}	{1533.59}	{1541.48}	{1548.17}
		[1513.98]	[1525.27]	[1533.61]	[1541.52]	[1548.22]
G		1515.6	1525.6	1534.0	1542.8	1548.5
		(1514.84)	(1525.95)	(1533.91)	(1541.99)	(1548.79)
		{1514.81}	{1525.93}	{1533.91}	{1541.98}	{1548.78}
		[1514.89]	[1525.98]	[1533.93]	[1542.02]	[1548.82]
H		1516.0	1526.3	1534.3	1543.2	1549.5
		(1515.76)	(1526.66)	(1534.24)	(1542.49)	(1549.39)
		{1515.73}	{1526.64}	{1534.23}	{1542.48}	{1549.38}
		[1515.80]	[1526.69]	[1534.25]	[1542.52]	[1549.42]

I	1516.4	1526.8	1534.8	1543.5	1550.0
	(1516.68)	(1527.38)	(1534.56)	(1543.00)	(1550.0)
	{1516.66}	{1527.37}	{1534.55}	{1542.99}	{1549.99}
	[1516.71]	[1527.40]	[1534.57]	[1543.02]	[1550.02]
J	1516.8	1527.2	1535.2	1544.0	1550.4
	(1517.60)	(1528.01)	(1534.88)	(1543.51)	(1550.61)
	{1517.59}	{1528.09}	{1534.88}	{1543.50}	{1550.60}
	[1517.62]	[1528.11]	[1534.89]	[1543.52]	[1550.62]
K	1518.5	1528.8	1535.2	1544.0	1551.2

a. Experimental values

b. Computed values using Nomoto relation.

c. Computed values using Van Dael and Vangeel's relation.

d. Computed values using Schaaffs' collision factor theory.

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

X	T(K)	298.15	303.15	308.15	313.15	318.15
A		1509.4	1521.7	1532.0	1539.0	1545.2
B		1510.0[a] *(1510.16)*[b] {1510.15}[c] [1510.18][d]	1522.0 *(1522.12)* {1522.17} [1522.18]	1532.0 *(1532.24)* {1532.24} [1532.25]	1539.0 *(1539.30)* {1539.30} [1539.31]	1545.5 *(1545.57)* {1545.56} [1545.57]
C		1510.7 (1510.90) {1510.89} (1510.92)	1522.3 (1522.64) {1522.63} (1522.65]	1532.3 (1532.48) {1532.48} [1532.49]	1539.3 (1539.60) {1539.60} [1539.61]	1546.0 (1545.92) {1545.91} [1545.93]
D		(1511.0 (1511.65) {1511.63} [1511.67]	(1522.7 (1523.11) {1523.10} [1523.12]	(1532.7 (1532.72) {1532.71} [1532.73]	(1539.7 (1539.90) {1539.89} [1539.91]	(1546.0 (1546.28) {1546.27} [1546.29]
E		1511.7 (1512.39) {1512.37} [1512.42]	1523.4 (1523.57) {1523.56} [1523.59]	1533.0 (1532.96) {1532.95} [1532.97]	1540.0 (1540.20) {1540.19} [1540.21]	1546.4 (1546.64) {1546.63} [1546.65]
F		1512.2 (1513.14) {1513.12} [1513.18]	1523.7 (1524.04) {1524.03} [1524.06]	1533.3 (1523.20) {1533.19} [1533.21]	1540.0 (1540.50) {1540.49} [1540.51]	1546.6 (1547.00) {1546.99} [1547.01]
G		1513.2 (1513.89) {1513.87} [1513.92]	1523.7 (1524.52) {1524.50} [1524.53]	1533.5 (1533.44) {1533.43} [1533.45]	1540.5 (1540.80) {1540.79} [1540.81]	1547.0 (1547.36) {1547.35} [1547.37]
H		1514.7 (1514.65) {1514.63} [1514.67]	1524.3 (1524.99) {1524.98} [1525.00]	1533.8 (1533.68) {1533.67} [1533.69]	1540.7 (1541.10) {1541.09} [1541.11]	1547.3 (1547.72) {1547.71} [1547.73]

I	1515.4	1524.8	1534.0	1541.2	1547.5
	(1515.40)	(1525.46)	(1533.92)	(1541.40)	(1548.08)
	{1515.39}	{1525.45}	{1533.92}	{1541.39}	{1548.08}
	[1515.42]	[1525.47]	[1533.93]	[1541.41]	[1548.09]
J	1516.0	1525.1	1534.4	1541.4	1548.0
	(1516.16)	(1525.94)	(1534.16)	(1541.71)	(1548.45)
	{1516.15}	{1525.93}	{1534.16}	{1541.70}	{1548.44}
	[1516.17]	[1525.94]	[1534.17]	[1541.71]	[1548.45]
K	1516.9	1526.4	1535.2	1542.0	1548.8

a. Experimental values

b. Computed values using Nomoto relation.

c. Computed values using Van Dael and Vangeel's relation.

d. Computed values using Schaaffs' collision factor theory.

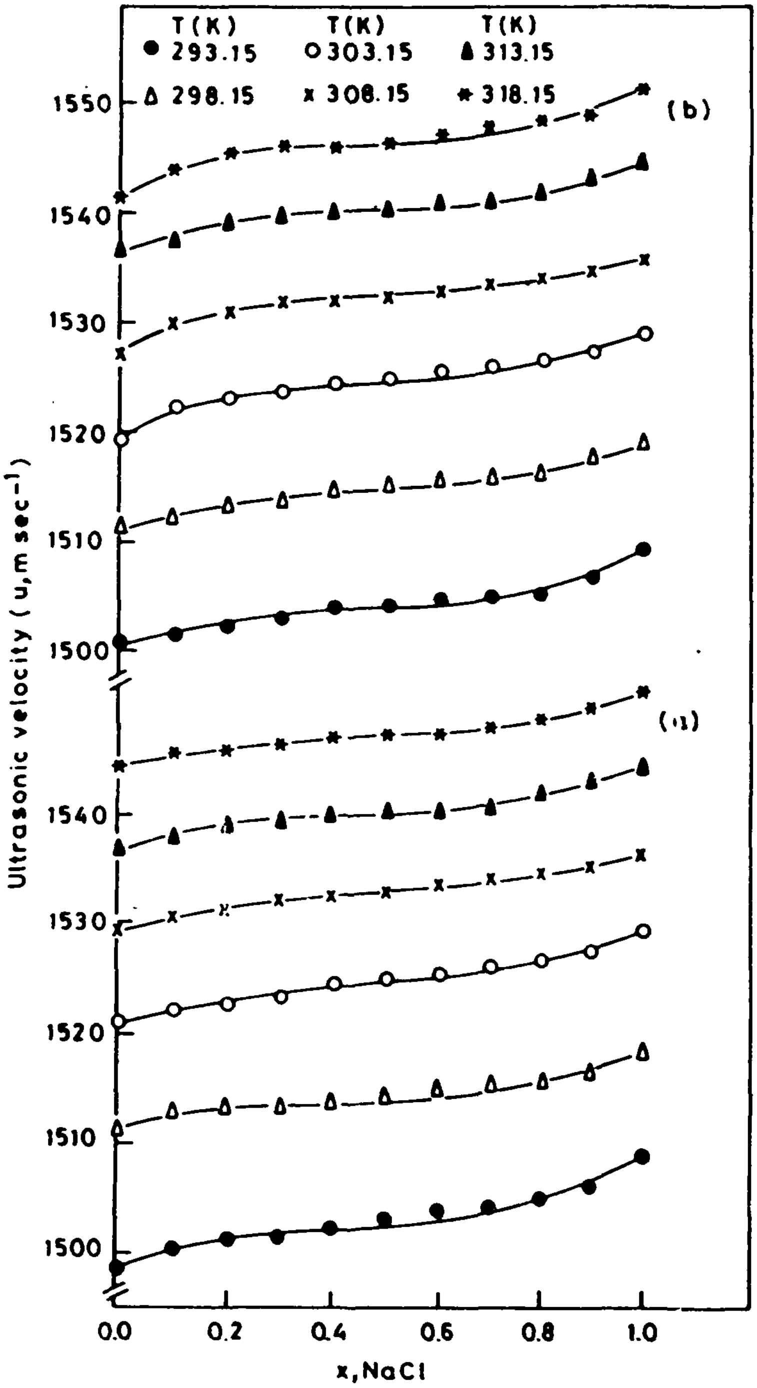
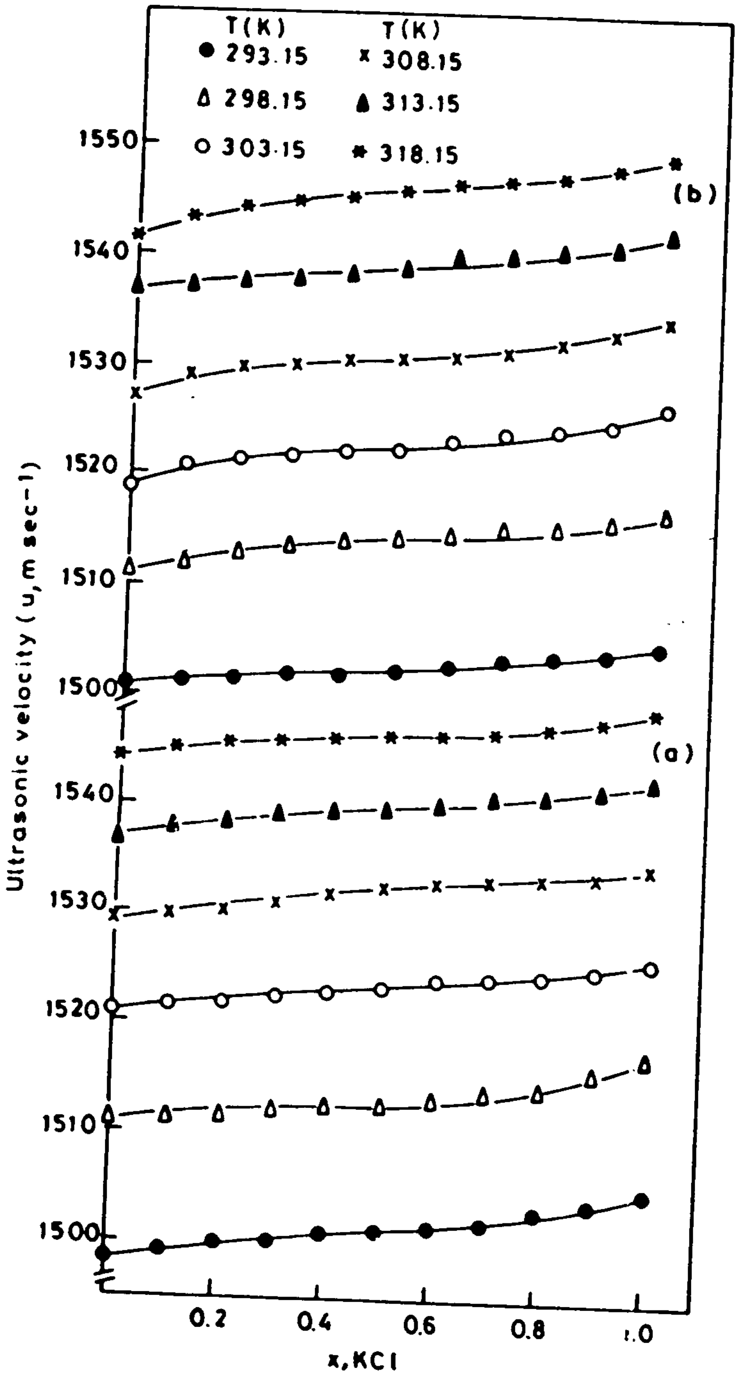
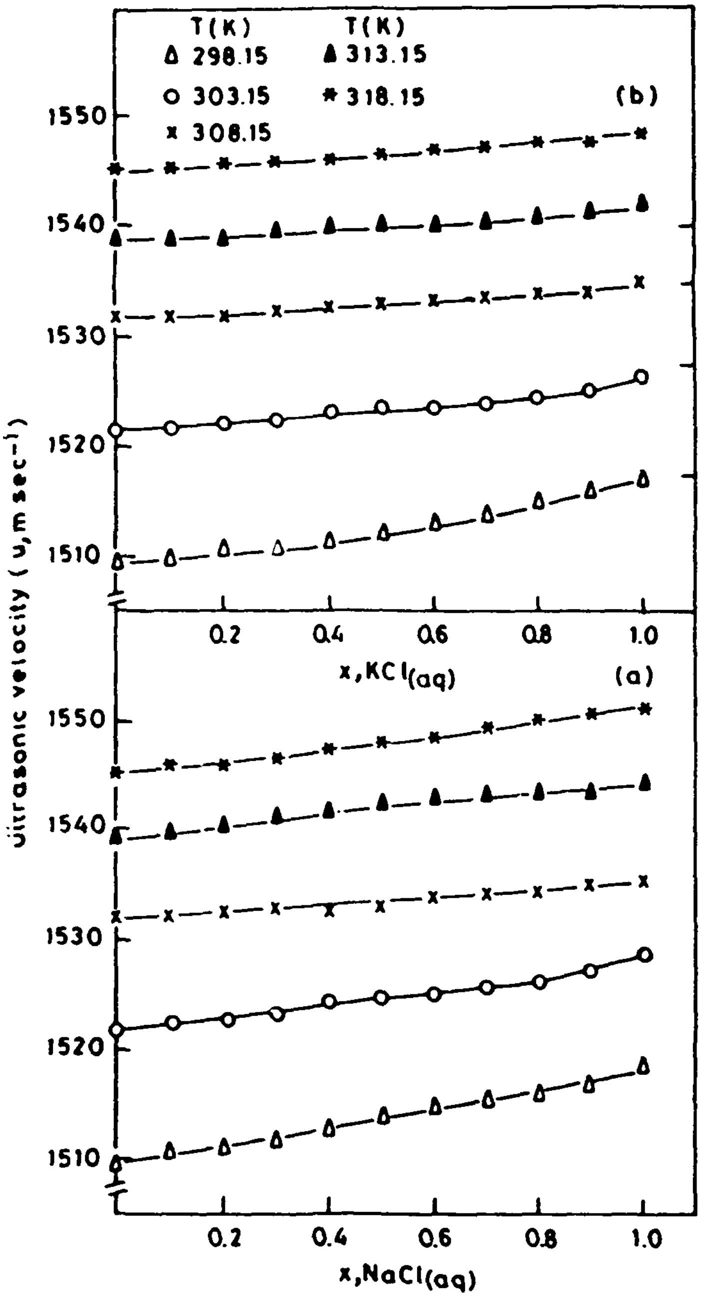


Fig. 1. (i) Plots of ultrasonic velocity vs mole fraction of NaCl of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$ and (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ systems at several temperatures.



(ii) Plots of ultrasonic velocity vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$ and (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ systems at several temperatures.



(iii) Plots of ultrasonic velocity vs mole fraction of NaCl/KCl of (a) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ and (b) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

TABLE 4 Adiabatic compressibility (β_s x 10^{11}, m^2N^{-1}) as functions of temperature and composition for the following systems:

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		44.42	43.72	43.21	42.80	42.46	42.14
B		44.26	43.62	43.13	42.72	42.39	42.08
C		44.19	43.57	43.09	42.67	42.33	42.05
D		44.17	43.54	43.04	42.58	42.26	41.98
E		44.10	43.50	42.92	42.50	42.23	41.95
F		44.04	43.46	42.88	42.44	42.21	41.91
G		43.97	43.40	42.83	42.45	42.17	41.85
H		43.93	43.35	42.80	42.41	42.13	41.82
I		43.87	43.33	42.75	42.35	42.04	41.76
J		43.80	43.25	42.68	42.30	41.94	41.68
K		43.57	43.07	42.55	42.26	41.86	41.57

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		44.42	43.72	43.21	42.80	42.46	42.14
B		44.36	43.69	43.16	42.76	42.40	42.08
C		44.30	43.66	43.12	42.72	42.35	42.05
D		44.27	43.63	43.09	42.66	42.28	41.99
E		44.21	43.58	43.03	42.58	42.24	41.95
F		44.17	43.52	42.99	42.51	42.22	41.94
G		44.12	43.49	42.94	42.48	42.20	41.91
H		44.04	43.38	42.87	42.43	42.11	41.89
I		43.97	43.30	42.82	42.39	42.06	41.79
J		43.88	43.23	42.78	42.35	42.02	41.76
K		43.78	43.13	42.65	42.27	41.93	41.64

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		44.41	43.84	43.44	43.06	42.60	42.42
B		44.34	43.77	43.23	42.87	42.52	42.25
C		44.26	43.68	43.18	42.79	42.42	42.16
D		44.18	43.63	43.14	42.73	42.37	42.11
E		44.08	43.53	43.04	42.67	42.30	42.05
F		44.06	43.47	42.99	42.64	42.28	42.02
G		44.00	43.42	42.91	42.54	42.23	41.96
H		43.97	43.37	42.85	42.50	42.17	41.88
I		43.91	43.32	42.80	42.44	42.11	41.85
J		43.77	43.18	42.69	42.35	41.96	41.72
K		43.57	43.07	42.55	42.26	41.86	41.57

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		44.41	43.85	43.44	43.06	42.60	42.42
B		44.34	43.78	43.33	42.94	42.54	42.31
C		44.25	43.65	43.20	42.83	42.47	42.20
D		44.18	43.57	43.16	42.78	42.44	42.10
E		44.12	43.47	43.09	42.72	42.36	42.04
F		44.07	43.44	43.03	42.62	42.26	41.96
G		43.99	43.36	42.93	42.64	42.17	41.87
H		43.93	43.30	42.87	42.56	42.13	41.83
I		43.90	43.27	42.81	42.50	42.10	41.79
J		43.86	43.21	42.78	42.38	42.04	41.72
K		43.78	43.13	42.65	42.27	41.93	41.64

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		43.77	43.12	42.61	42.30	42.04
B		43.68	43.07	42.59	42.23	41.99
C		43.62	43.03	42.55	42.20	41.95
D		43.53	42.92	42.47	42.09	41.85
E		43.45	42.84	42.43	42.09	41.80
F		43.37	42.80	42.40	42.00	41.76
G		43.29	42.78	42.38	41.97	41.75
H		43.26	42.73	42.36	41.94	41.69
I		43.22	42.68	42.32	41.92	41.66
J		43.19	42.65	42.29	41.88	41.63
K		43.07	42.55	42.26	41.86	41.57

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		43.77	43.12	42.61	42.30	42.04
B		43.72	43.09	42.60	42.28	42.01
C		43.66	43.05	42.56	42.25	41.97
D		43.63	43.02	42.53	42.21	41.96
E		43.56	42.95	42.48	42.17	41.92
F		43.50	42.91	42.44	42.15	41.87
G		43.42	42.89	42.41	42.10	41.84
H		43.32	42.83	42.37	42.08	41.80
I		43.27	42.80	42.35	42.05	41.78
J		43.21	42.75	42.32	42.00	41.74
K		43.14	42.65	42.27	41.93	41.64

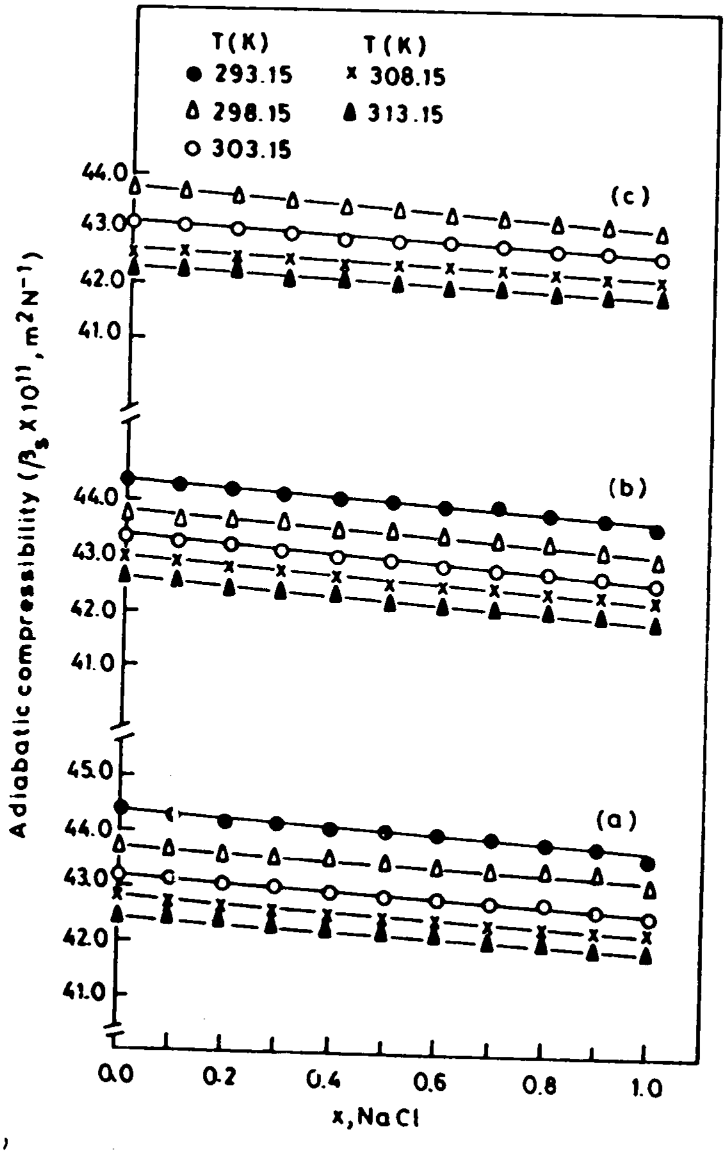
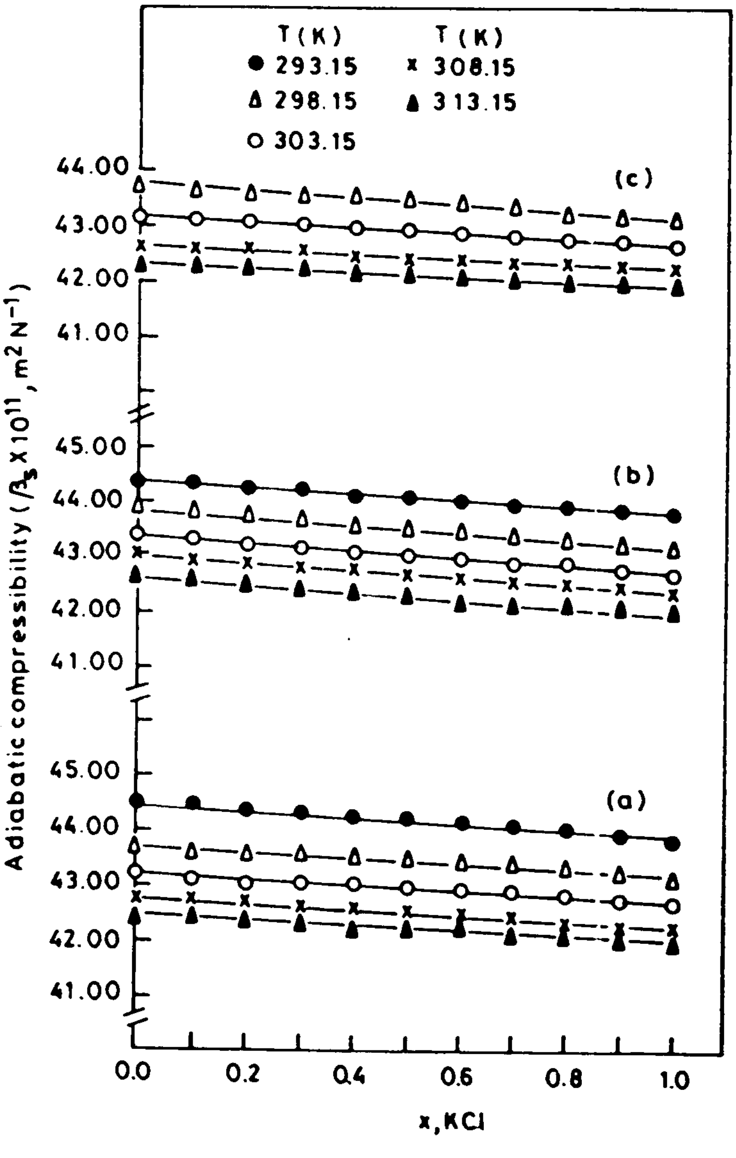


Fig. 2. (i) Plots of adiabatic compressibility vs mole fraction of NaCl of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of adiabatic compressibility vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

charged centres of the dipolar ions of the aminoacid. The decrease in the compressibility may also be caused by a corresponding increase in the number of incompressible ions with increase in salt concentration. Another reason for decrease in compressibility values may be viewed as due to a change in the structure of water around the ions. Similarly, a decrease in the compressibility values with increase in temperature may be attributed to the thermal rupture of the associated solvent molecules [34]. As the temperture increases, the cluster part of water decreases causing decrease in the compressibility values. Addition of NaCl solution has been found to lower the compressibility of the binary mixture slightly more than that by the KCl. Addition of NaCl solution to that of the aqueous aminoacid solution causes more decrease in compressibility, since NaCl is a week structure making salt than that of KCl which is considered to be a weak structure breaker. The latter, in turn, increases the thermal motion of water molecules around it [34]. The change in adiabatic compressibility ($\Delta\beta$) values have been given in Table 5. The relative change in adiabatic compressibility ($\Delta\beta/\beta_{S0}$) has been calculated by taking the adiabatic compressibility of aqueous aminoacid solution as β_{S0}. The values of $\Delta\beta_S/\beta_{S0}$ are listed in Table 6 and are found to increase with increase in salt concentration. Fig. 3 displays the characteristic plots for the relative increase in interaction.

Molar ultrasonic valocity and specific acoustic impedance vary linearly with composition, x as shown in Figs. 4 and 5. The apparent linearity may be attributed to an almost ideal behaviour caused by extremely dilute nature of the systems under investigation. An examination of Tables 7 and 8 show that the molar ultrasonic velocity as well as specific acoustic impedance increase with increase in temperature.

TABLE 5 **Change in adiabatic compressibility ($\Delta\beta_s$ x 10^{11}, m^2N^{-1}) as functions of temperature and composition for the following systems:**

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B	−0.16	−0.10	−0.08	−0.08	−0.07	−0.06
C	−0.23	−0.15	−0.12	−0.13	−0.13	−0.09
D	−0.25	−0.18	−0.17	−0.22	−0.20	−0.16
E	−0.32	−0.22	−0.29	−0.30	−0.23	−0.19
F	−0.38	−0.26	−0.33	−0.36	−0.25	−0.23
G	−0.45	−0.32	−0.38	−0.35	−0.29	−0.29
H	−0.49	−0.37	−0.41	−0.39	−0.33	−0.32
I	−0.55	−0.39	−0.46	−0.45	−0.42	−0.38
J	−0.62	−0.47	−0.53	−0.50	−0.52	−0.46

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B	−0.06	−0.03	−0.05	−0.04	−0.06	−0.06
C	−0.12	−0.06	−0.09	−0.08	−0.11	−0.09
D	−0.15	−0.09	−0.12	−0.14	−0.18	−0.15
E	−0.21	−0.14	−0.18	−0.22	−0.22	−0.19
F	−0.25	−0.20	−0.22	−0.29	−0.24	−0.20
G	−0.30	−0.23	−0.27	−0.32	−0.26	−0.23
H	−0.38	−0.34	−0.34	−0.37	−0.35	−0.25
I	−0.45	−0.42	−0.39	−0.41	−0.40	−0.35
J	−0.54	−0.49	−0.43	−0.45	−0.44	−0.38

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		–0.07	–0.07	–0.21	–0.19	–0.08	-0.17
C		–0.15	–0.16	–0.26	–0.27	–0.18	-0.26
D		–0.23	–0.21	–0.30	–0.33	–0.23	-0.31
E		–0.33	–0.31	–0.40	–0.39	–0.30	-0.37
F		–0.35	–0.37	–0.45	–0.42	–0.32	-0.40
G		–0.41	–0.42	–0.53	–0.52	–0.37	-0.46
H		–0.44	–0.47	–0.59	–0.56	–0.43	-0.54
I		–0.50	–0.52	–0.64	–0.62	–0.49	-0.57
J		–0.64	–0.66	–0.75	–0.71	–0.64	-0.70

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		–0.07	–0.07	–0.14	–0.12	–0.06	–0.11
C		–0.16	–0.20	–0.24	–0.23	–0.13	–0.22
D		–0.21	–0.28	–0.28	–0.28	–0.16	–0.32
E		–0.29	–0.38	–0.35	–0.34	–0.24	–0.38
F		–0.34	–0.41	–0.41	–0.42	–0.34	–0.46
G		–0.42	–0.49	–0.51	–0.44	–0.43	–0.55
H		–0.48	–0.55	–0.57	–0.50	–0.47	–0.59
I		–0.51	–0.58	–0.63	–0.56	–0.50	–0.63
J		–0.55	–0.64	–0.66	–0.68	–0.56	–0.70

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		−0.09	−0.05	−0.02	−0.07	−0.05
C		−0.15	−0.09	−0.06	−0.10	−0.09
D		−0.24	−0.20	−0.14	−0.21	−0.19
E		−0.37	−0.28	−0.18	−0.30	−0.24
F		−0.40	−0.32	−0.32	−0.21	−0.30
G		−0.48	−0.34	−0.23	−0.33	−0.29
H		−0.51	−0.39	−0.25	−0.36	−0.35
I		−0.55	−0.44	−0.29	−0.38	−0.38
J		−0.58	−0.47	−0.32	−0.42	−0.41

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		−0.05	−0.03	−0.01	−0.02	−0.06
C		−0.11	−0.07	−0.05	−0.05	−0.07
D		−0.14	−0.10	−0.08	−0.09	−0.08
E		−0.21	−0.17	−0.13	−0.13	−0.12
F		−0.27	−0.21	−0.17	−0.15	−0.17
G		−0.35	−0.23	−0.20	−0.20	−0.20
H		−0.45	−0.29	−0.24	−0.22	−0.24
I		−0.50	−0.32	−0.26	−0.25	−0.26
J		−0.56	−0.37	−0.29	−0.30	−0.30

TABLE 6 Relative change in adiabatic compressibility ($\Delta\beta/\beta_{so}$ x 10^2) as functions of temperature and composition for the following systems:

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		–0.36	–0.23	–0.19	–0.19	–0.16	–0.14
C		–0.52	–0.34	–0.28	–0.30	–0.31	–0.21
D		–0.56	–0.41	–0.39	–0.51	–0.47	–0.38
E		–0.72	–0.50	–0.67	–0.70	–0.54	–0.45
F		–0.86	–0.59	–0.76	–0.84	–0.59	–0.55
G		–1.01	–0.73	–0.88	–0.82	–0.68	–0.69
H		–1.10	–0.85	–0.95	–0.91	–0.78	–0.76
I		–1.24	–0.89	–1.06	–1.05	–0.99	–0.90
J		–1.40	–1.18	–1.23	–1.17	–1.22	–1.09

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		–0.14	–0.07	–0.12	–0.09	–0.14	–0.14
C		–0.27	–0.14	–0.21	–0.19	–0.26	–0.21
D		–0.34	–0.21	–0.28	–0.33	–0.42	–0.36
E		–0.47	–0.32	–0.42	–0.51	–0.52	–0.45
F		–0.56	–0.46	–0.51	–0.68	–0.57	–0.47
G		–0.68	–0.53	–0.62	–0.75	–0.61	–0.55
H		–0.86	–0.78	–0.79	–0.86	–0.82	–0.59
I		–1.01	–0.96	–0.90	–0.96	–0.94	–0.83
J		–1.22	–1.12	–1.00	–1.05	–1.04	–0.90

(c) x NaCl$_{(aq)}$ + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		−0.16	−0.16	−0.48	−0.44	−0.19	−0.40
C		−0.34	−0.36	−0.60	−0.63	−0.42	−0.61
D		−0.52	−0.48	−0.69	−0.77	−0.54	−0.73
E		−0.74	−0.71	−0.92	−0.91	−0.70	−0.87
F		−0.79	−0.84	−1.04	−0.98	−0.75	−0.94
G		−0.92	−0.96	−1.22	−1.21	−0.87	−1.08
H		−0.99	−1.07	−1.36	−1.30	−1.01	−1.27
I		−1.13	−1.19	−1.47	−1.44	−1.15	−1.34
J		−1.44	−1.51	−1.73	−1.65	−1.50	−1.50

(d) x KCl$_{(aq)}$ + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		−0.16	−0.16	−0.32	−0.28	−0.14	−0.26
C		−0.36	−0.46	−0.55	−0.53	−0.31	−0.52
D		−0.47	−0.64	−0.64	−0.65	−0.38	−0.75
E		−0.65	−0.87	−0.81	−0.79	−0.56	−0.90
F		−0.77	−0.94	−0.94	−0.98	−0.80	−1.08
G		−0.95	−1.12	−1.17	−1.02	−1.01	−1.30
H		−1.08	−1.25	−1.31	−1.16	−1.10	−1.39
I		−1.15	−1.32	−1.45	−1.30	−1.17	−1.49
J		−1.24	−1.46	−1.52	−1.58	−1.31	−1.65

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K) 298.15	303.15	308.15	313.15	318.15
B	−0.21	−0.12	−0.05	−0.17	−0.12
C	−0.34	−0.21	−0.14	−0.24	−0.21
D	−0.55	−0.46	−0.33	−0.55	−0.45
E	−0.73	−0.65	−0.42	−0.50	−0.57
F	−0.91	−0.74	−0.49	−0.71	−0.67
G	−1.10	−0.79	−0.54	−0.78	−0.69
H	−1.17	−0.90	−0.59	−0.85	−0.83
I	−1.26	−1.02	−0.68	−0.90	−0.90
J	−1.33	−1.09	−0.75	−0.99	−0.98

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K) 298.15	303.15	308.15	313.15	318.15
B	−0.11	−0.07	−0.02	−0.05	−0.14
C	−0.25	−0.16	−0.12	−0.12	−0.17
D	−0.32	−0.23	−0.19	−0.21	−0.19
E	−0.48	−0.39	−0.31	−0.31	−0.29
F	−0.62	−0.49	−0.40	−0.35	−0.40
G	−0.80	−0.53	−0.47	−0.47	−0.48
H	−1.03	−0.67	−0.56	−0.52	−0.57
I	−1.14	−0.74	−0.61	−0.59	−0.62
J	−1.28	−0.86	−0.68	−0.71	−0.71

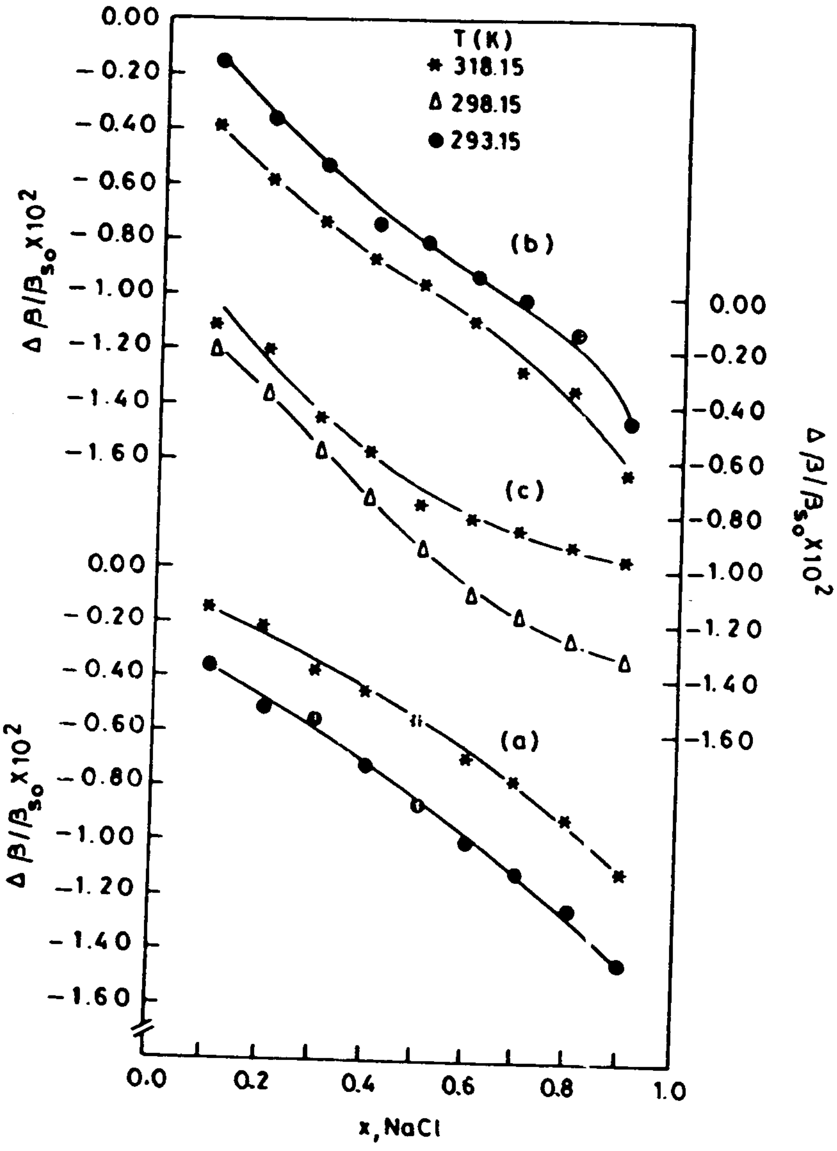
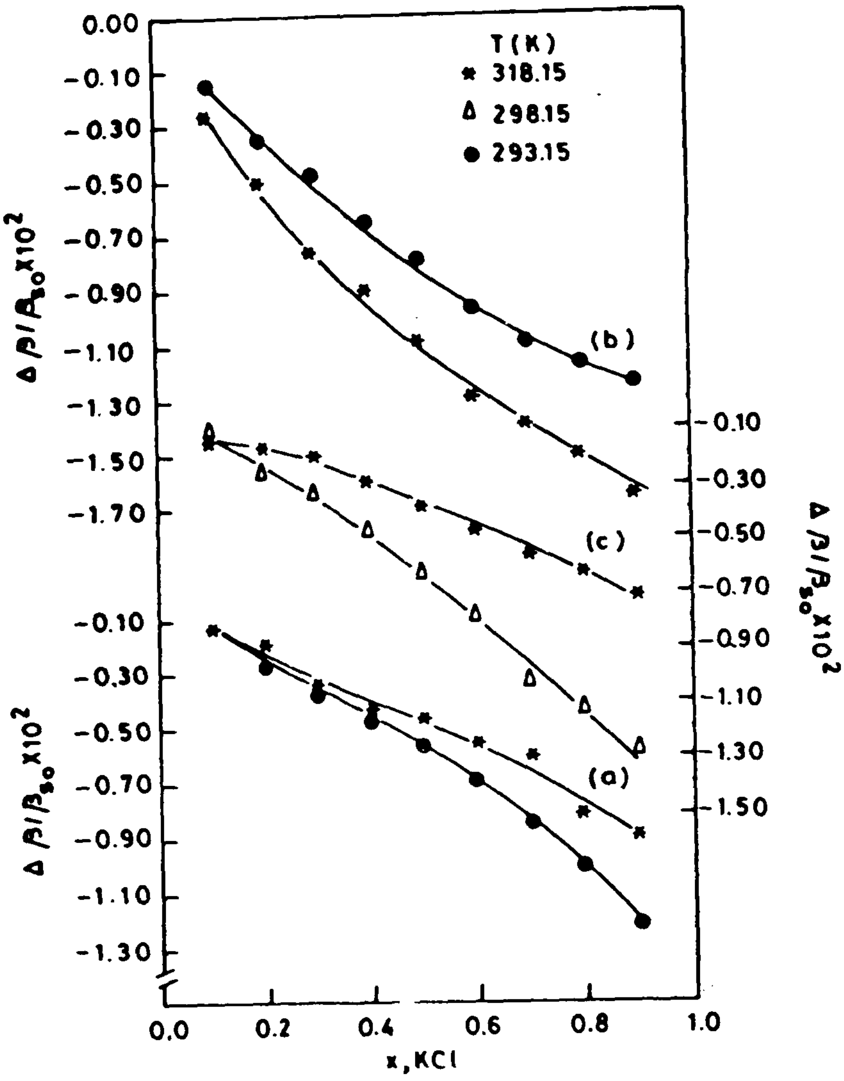


Fig. 3. (i) Plots of $\Delta\beta_s/\beta_{so}$ vs mole fraction of NaCl of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of $\Delta\beta_S/\beta_{S0}$ vs mole fraction of KCl of (a) x KCl$_{(aq)}$ + (1-x) Glycine$_{(aq)}$, (b) x KCl$_{(aq)}$ + (1-x) Leucine$_{(aq)}$ and (c) x KCl$_{(aq)}$ + (1-x) Threonine$_{(aq)}$ systems at several temperatures.

TABLE 7 Molar ultrasonic velocity (R$\times10^6$, m mol^{-1} s$^{-1/3}$) as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	207.61	208.42	209.15	209.87	210.60	211.35
B	207.58	208.35	209.06	209.81	210.52	211.30
C	207.51	208.26	208.98	209.74	210.46	211.22
D	207.43	208.20	208.94	209.71	210.39	211.14
E	207.38	208.12	208.90	209.61	210.33	211.11
F	207.32	208.03	208.83	209.54	210.23	211.01
G	207.22	207.90	208.67	209.38	210.09	210.87
H	207.11	207.83	208.61	209.34	210.04	210.81
I	207.05	207.74	208.52	209.26	209.98	210.75
J	206.99	207.62	208.42	209.10	209.86	210.59
K	206.85	207.54	208.28	208.92	209.72	210.05

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	207.61	208.42	209.15	209.87	210.60	211.35
B	207.65	208.43	209.19	209.88	210.62	211.38
C	207.70	208.43	209.15	209.87	210.61	211.39
D	207.70	208.37	209.20	209.90	210.60	211.28
E	207.63	208.39	209.13	209.86	210.58	211.32
F	207.61	208.41	209.14	209.92	210.64	211.35
G	207.67	208.34	209.18	209.94	210.54	211.40
H	207.50	208.28	209.08	209.84	210.49	211.26
I	207.46	208.27	209.00	209.77	210.47	211.22
J	207.43	208.15	208.96	209.73	210.23	211.21
K	207.42	208.15	208.83	209.51	210.20	210.96

(c) x NaCl$_{(aq)}$ + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		208.48	209.17	209.81	210.52	211.34	211.99
B		208.37	209.05	209.81	210.47	211.20	211.92
C		208.09	208.86	209.63	210.38	211.16	211.92
D		208.08	208.75	209.49	210.21	211.01	211.77
E		207.83	208.59	209.32	210.04	210.76	211.48
F		207.75	208.53	209.26	209.94	210.71	211.41
G		207.70	208.41	209.13	209.77	210.50	211.22
H		207.58	208.27	208.98	209.64	210.32	211.06
I		207.35	208.09	208.82	209.50	210.23	210.96
J		207.03	207.77	208.48	209.12	209.89	210.55
K		206.85	207.54	208.28	208.92	209.72	210.50

(d) x KCl$_{(aq)}$ + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		208.58	209.17	209.81	210.52	211.34	211.99
B		208.44	209.16	209.84	210.54	211.32	212.03
C		208.11	208.88	209.55	210.30	210.04	211.79
D		208.00	208.80	209.50	210.23	210.98	211.77
E		207.75	208.63	209.35	210.11	210.93	211.74
F		207.70	208.54	209.21	209.99	210.70	211.47
G		207.61	208.37	208.98	209.68	210.49	211.26
H		207.57	208.33	208.97	209.71	210.45	211.24
I		207.57	208.34	208.92	209.74	210.49	211.23
J		207.41	208.20	208.89	209.63	210.37	211.20
K		207.42	208.15	208.83	209.51	210.23	210.96

(e) x NaCl$_{(aq)}$ + (1 - x) Threonine$_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		211.07	211.94	212.76	213.44	214.14
B		210.67	211.59	212.40	213.14	213.81
C		210.31	211.20	212.05	212.81	213.44
D		209.83	210.64	211.41	212.16	212.84
E		209.48	210.29	211.03	211.79	212.48
F		209.16	209.95	210.68	211.49	212.17
G		208.89	209.62	210.34	211.14	211.85
H		208.56	209.30	210.02	210.80	211.53
I		208.22	208.93	209.71	210.48	211.20
J		207.87	208.57	209.35	210.12	210.85
K		207.54	208.28	208.92	209.72	210.50

(f) x KCl$_{(aq)}$ + (1 - x) Threonine$_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		211.07	211.94	212.76	213.44	214.14
B		210.80	211.65	212.46	213.10	213.85
C		210.52	211.33	212.11	212.82	213.57
D		210.22	211.06	211.85	212.52	213.30
E		209.90	210.71	211.49	212.22	213.00
F		209.57	210.39	211.17	211.88	212.60
G		209.28	210.06	210.84	211.54	212.29
H		209.04	209.75	210.52	211.53	211.98
I		208.78	209.50	210.26	210.95	211.72
J		208.46	209.12	209.88	210.62	211.40
K		208.17	208.83	209.51	210.23	210.96

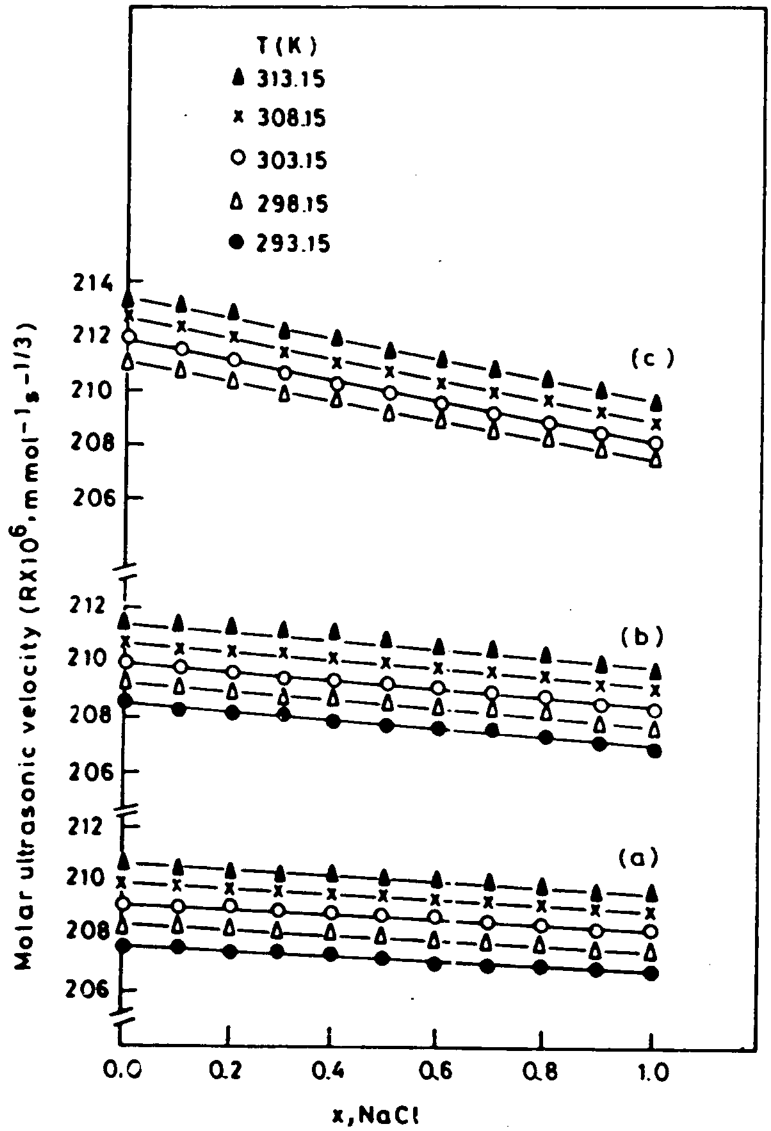
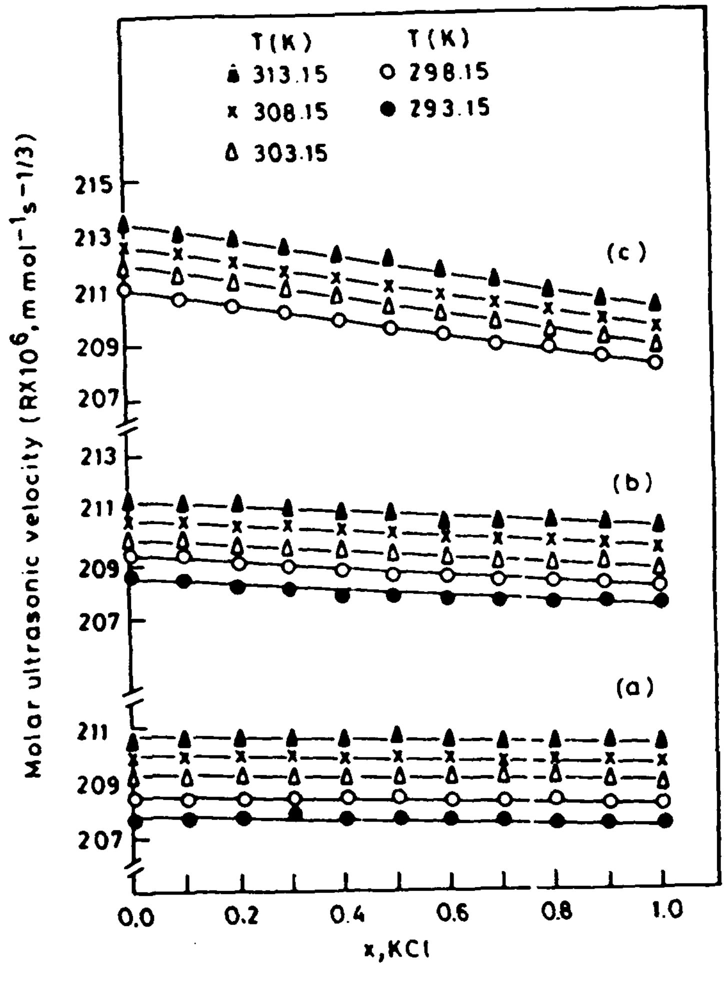


Fig. 4. (i) Plots of molar ultrasonic velocity vs mole fraction of NaCl of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of molar ultrasonic velocity vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

TABLE 8 Specific acoustic impedance ($Z \times 10^{-3}$, kg m^{-2} s^{-1}) as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	1502.3	1513.5	1521.5	1527.5	1532.3	1536.4
B	1505.5	1515.7	1523.3	1529.3	1533.9	1537.9
C	1507.2	1516.1	1524.2	1530.4	1535.3	1538.8
D	1507.6	1516.7	1525.5	1532.5	1536.9	1540.4
E	1509.2	1518.7	1527.9	1533.5	1537.7	1541.2
F	1510.4	1519.8	1528.9	1534.0	1538.3	1542.3
G	1512.1	1521.5	1530.4	1536.3	1539.7	1543.8
H	1513.3	1522.6	1531.2	1536.9	1540.7	1544.5
I	1514.5	1523.2	1532.4	1538.3	1542.5	1546.1
J	1516.1	1525.1	1534.2	1540.0	1545.1	1548.2
K	1521.0	1528.9	1537.4	1541.2	1547.1	1548.9

(b) x $KCl_{(aq)}$ + (1 - x) Glycine(aq)

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	1502.3	1513.5	1521.5	1527.5	1532.3	1536.4
B	1503.6	1514.4	1522.5	1528.5	1533.6	1537.9
C	1504.8	1515.2	1523.8	1529.6	1534.9	1538.8
D	1505.7	1515.9	1524.4	1531.2	1536.6	1540.5
E	1507.3	1517.4	1526.1	1532.9	1537.7	1541.5
F	1508.3	1518.7	1527.1	1534.5	1538.3	1541.8
G	1509.3	1519.5	1528.3	1535.2	1538.3	1542.6
H	1511.6	1522.2	1530.0	1536.8	1541.3	1544.6
I	1513.5	1524.1	1531.6	1538.0	1542.7	1546.0
J	1514.5	1525.9	1532.8	1539.2	1543.8	1547.1
K	1517.8	1528.4	1536.2	1541.9	1546.8	1550.5

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1500.4	1509.2	1515.3	1520.8	1527.6	1529.3
B		1502.1	1510.9	1519.4	1524.7	1529.5	1533.5
C		1504.4	1513.3	1521.0	1526.4	1531.7	1534.6
D		1505.9	1514.6	1522.1	1528.0	1533.1	1536.1
E		1508.5	1517.0	1524.6	1529.8	1535.2	1538.1
F		1509.0	1518.2	1525.6	1530.7	1535.7	1538.8
G		1510.2	1519.6	1527.6	1532.5	1537.3	1540.7
H		1511.2	1520.6	1529.2	1534.4	1539.0	1542.9
I		1512.9	1522.4	1530.5	1535.7	1540.5	1543.7
J		1518.6	1526.2	1533.9	1538.9	1544.7	1547.0
K		1521.0	1529.0	1537.4	1541.2	1547.1	1550.9

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1500.4	1509.2	1515.3	1520.8	1527.6	1529.3
B		1502.1	1510.8	1517.6	1523.1	1528.9	1531.5
C		1504.9	1514.3	1521.1	1526.5	1531.4	1534.8
D		1506.6	1516.3	1522.4	1527.9	1532.5	1537.0
E		1508.9	1519.1	1524.5	1529.6	1534.5	1538.6
F		1510.2	1520.2	1526.4	1531.8	1537.5	1541.4
G		1512.4	1523.6	1529.2	1534.7	1540.2	1544.1
H		1514.8	1524.0	1530.6	1536.0	1541.2	1545.0
I		1514.5	1524.7	1532.1	1537.2	1541.9	1546.2
J		1516.4	1526.5	1533.2	1539.0	1543.7	1548.3
K		1517.8	1528.4	1536.2	1541.9	1546.8	1550.5

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		1513.8	1524.0	1531.9	1536.2	1539.5
B		1515.7	1525.1	1532.4	1537.4	1540.6
C		1517.1	1526.1	1533.4	1538.2	1541.6
D		1519.4	1529.1	1536.1	1541.5	1543.9
E		1521.0	1530.8	1537.1	1542.6	1544.9
F		1522.7	1531.6	1537.7	1543.6	1545.6
G		1524.2	1532.3	1538.3	1544.2	1546.6
H		1525.0	1533.3	1538.8	1544.9	1548.0
I		1525.7	1534.4	1539.4	1545.4	1548.8
J		1526.5	1535.3	1540.3	1546.3	1549.3
K		1529.0	1537.4	1541.2	1547.1	1550.9

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		1513.8	1524.0	1531.9	1536.2	1539.5
B		1514.8	1524.7	1532.3	1537.0	1540.3
C		1516.1	1525.8	1533.5	1537.8	1541.2
D		1517.0	1526.7	1534.2	1538.8	1541.5
E		1518.7	1528.4	1535.6	1539.7	1542.5
F		1520.6	1529.5	1536.6	1540.5	1544.0
G		1521.8	1530.3	1537.6	1541.9	1545.1
H		1523.9	1531.6	1538.7	1542.6	1546.1
I		1525.1	1532.4	1539.2	1543.4	1546.6
J		1526.6	1534.0	1540.3	1544.8	1547.9
K		1528.3	1536.2	1541.9	1546.8	1550.5

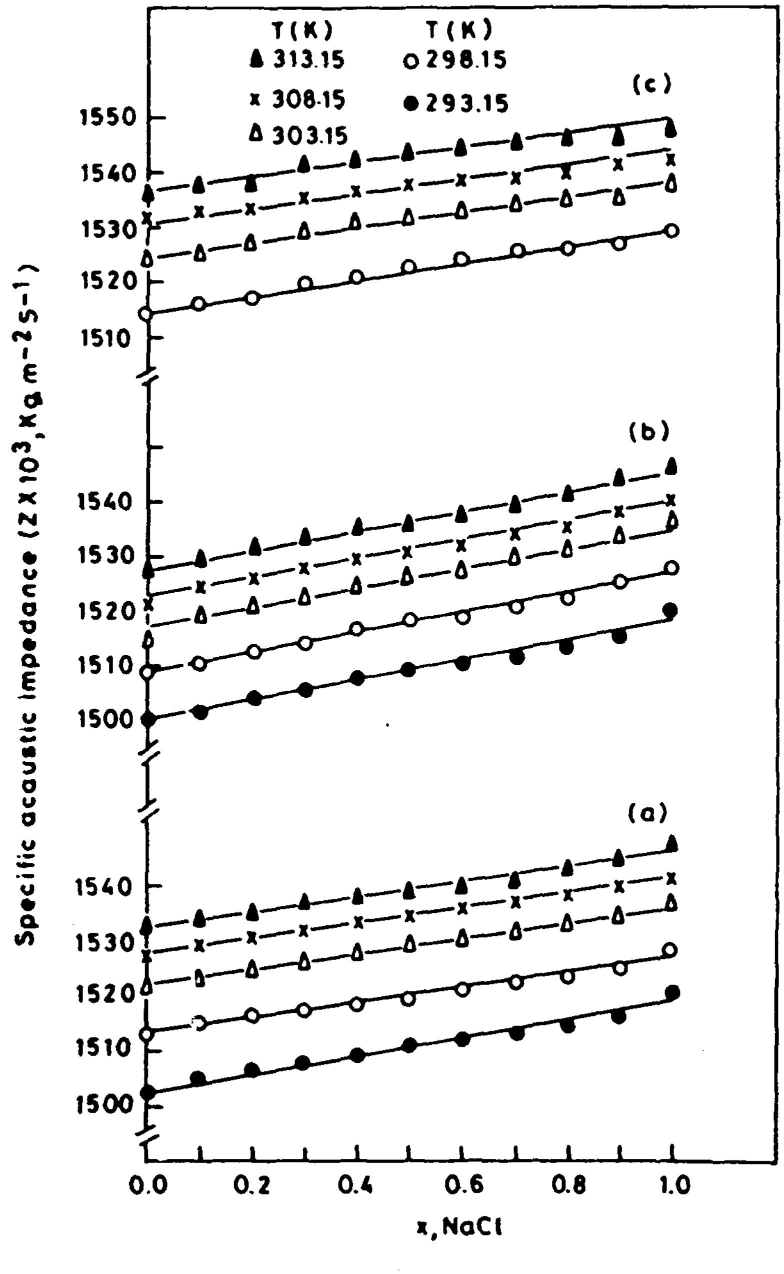
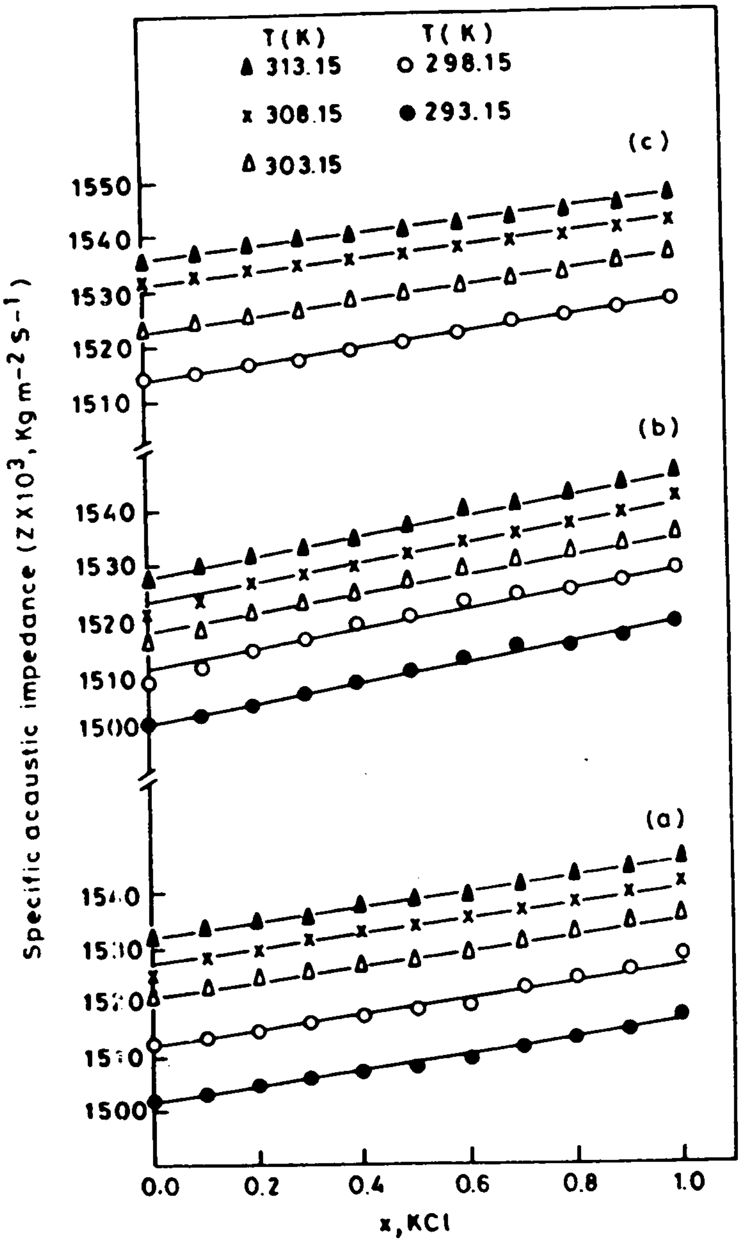


Fig. 5. (i) Plots of specific acoustic impedance vs mole fraction of NaCl of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of specific acoustic impedance vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

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Chapter - 2

Isothermal compressibility, internal pressure, solubility parameter and Pseudo-Grüneisen parameter of aqueous mixtures of aminoacids and alkali chlorides

INTRODUCTION

Many thermodynamic parameters derived from ultrasonic velocity measurements have been found to yield a fruitful information regarding the nature of molecular interaction in liquids. Isothermal compressibility (β_T). heat capacity ratio (γ) and internal pressure (P_i) are known to be the key thermodynamic parameters in molecular thermodynamics of liquid phase equilibria.

Internal pressure was first studied by Richards [1]. Later on, attempts were made by Hildebrand *et al.* [2], Barton [3], Cagle [4], Rosseinsky [5] and others [6,7] to show the significance of internal pressure as a fundamental property of liquid state and its correlation with other properties.

Isothermal compressibility which helps in the determination of certain thermodynamic functions, has been studied for various liquid systems [8] and electrolytes [9].

The Pseudo-Grüneisen parameter (Γ), a dimensionless constant. is another useful parameter and it which characterises the lattice behaviour of liquids [10].

Similarly, the solubility parameter is employed to assess the compressibilities of various substances and selection of proper solvents [11, 12] for polymeric substances and paints.

Consequently, in this chapter the isothermal compressibility, internal pressure, solubility parameter and Pseudo-Grüneisen parameter have been evaluated as functions of temperature and composition.

RESULTS AND DISCUSSION

Using the experimental values of ultrasonic velocity and density, the isothermal compressibilities of aqueous binary mixtures of electrolytes and aminoacids were calculated using the Mc Gowan relation [13],

$$[2.1] \qquad \beta_T = \frac{1.33 \times 10^{-8}}{6.4 \times 10^{-4}\, u^{3/2}\, \rho}$$

where the terms have their usual meaning.

Recently J.D. Pandey [14] has proposed an equation to calculate the isothermal compressibilities of various liquid systems by replacing the arbitrary constant in the denominator of equation [2.1] by a temperature term and the resulting equation is expressed as,

$$[2.2] \qquad \beta_T = \frac{17.1 \times 10^{-4}}{T^{4/9}\, u^2 \rho^{4/3}} .$$

A good agreement was found between the isothermal compressibility values calculated by using equations [2.1] and [2.2] as shown in Table 1. In each of the systems studied, the isothermal compressibility has been found to decrease with increase in mole fraction, x_2 and also with increase in temperature (Fig. 1). The decrease in isothermal compressibility values with increase in temperature may be attributed to the loss of water molecules around the ions. The nature of variation in isothermal compressibility with increase in salt composition is similar to that of β_S described earlier.

The internal pressure which is the resultant of attractive and repulsive forces has been evaluated by using the expression,

TABLE 1 Isothermal Compressibity (β_T x 10^{11}, m^2N^{-1}) as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		58.58[a]	57.56	56.82	56.26	55.79	55.37
		(60.78)[b]	(59.39)	(58.28)	(57.35)	(56.52)	(55.75)
B		58.32	57.40	56.70	56.13	55.68	55.26
		(60.54)	(59.24)	(58.17)	(57.23)	(56.42)	(55.65)
C		58.20	57.31	56.64	56.05	55.58	55.21
		(60.43)	(59.17)	(58.11)	(57.16)	(56.33)	(55.60)
D		58.17	57.26	56.55	55.90	55.47	55.10
		(60.41)	(59.12)	(58.03)	(57.03)	(56.23)	(55.51)
E		58.06	57.19	56.37	55.84	55.42	55.04
		(60.30)	(59.01)	(57.87)	(56.90)	(56.18)	(55.45)
F		57.97	57.12	56.30	55.76	55.38	54.98
		(60.22)	(58.99)	(57.81)	(56.97)	(56.15)	(55.40)
G		57.85	57.01	56.21	55.66	55.30	54.88
		(60.10)	(58.88)	(57.72)	(56.81)	(56.08)	(55.31)
H		57.77	56.93	56.15	55.62	55.24	54.83
		(60.03)	(58.81)	(57.67)	(56.77)	(56.02)	(55.26)
I		57.68	56.90	56.08	55.52	55.11	54.74
		(59.95)	(58.78)	(57.60)	(56.68)	(55.90)	(55.18)
J		57.56	56.77	55.95	55.42	54.94	54.60
		(59.84)	(58.67)	(57.48)	(56.59)	(55.74)	(55.01)
K		57.20	56.48	55.74	55.36	54.81	54.41
		(59.51)	(58.40)	(57.29)	(56.53)	(55.63)	(54.89)

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		58.58[a]	57.56	56.82	56.26	55.79	55.37
		(60.78)[b]	(59.39)	(58.28)	(57.35)	(56.52)	(55.75)
B		58.48	57.50	56.76	56.19	55.70	55.26
		(60.69)	(59.34)	(58.22)	(57.29)	(56.43)	(55.65)
C		58.38	57.45	56.67	56.12	55.61	55.21
		(60.60)	(59.29)	(58.14)	(57.22)	(56.36)	(55.60)
D		58.32	57.40	56.63	55.01	55.50	55.11
		(60.54)	(59.24)	(58.11)	(57.12)	(56.26)	(55.51)
E		58.22	57.30	56.52	55.89	55.43	55.04
		(60.45)	(59.16)	(58.01)	(56.02)	(56.20)	(55.45)
F		57.16	57.22	56.45	55.78	55.39	55.03
		(60.39)	(58.08)	(57.95)	(56.91)	(56.16)	(55.44)
G		57.08	57.16	56.37	55.73	55.35	54.97
		(60.32)	(59.02)	(57.87)	(56.87)	(56.12)	(55.39)
H		57.93	56.97	56.26	55.64	55.20	54.85
		(60.18)	(58.85)	(57.77)	(56.78)	(55.99)	(55.29)
I		57.80	56.84	56.17	55.57	55.11	54.77
		(60.06)	(58.74)	(57.69)	(56.73)	(55.91)	(55.21)
J		57.65	56.73	56.09	55.50	55.05	54.70
		(59.93)	(58.63)	(57.62)	(56.66)	(55.85)	(55.15)
K		57.49	56.56	55.87	55.34	54.88	54.50
		(59.78)	(58.47)	(57.41)	(56.52)	(55.69)	(54.97)

(c) x NaCl + (1 - x) Leucine$_{(aq)}$

x	T(K) 293.15	298.15	303.15	308.15	313.15	318.15
A	58.62[a] (60.82)[b]	57.80 (59.62)	57.23 (58.66)	56.70 (57.75)	56.05 (56.76)	55.83 (56.16)
B	58.50 (60.71)	57.68 (59.50)	56.91 (58.36)	56.40 (57.48)	55.93 (56.65)	55.57 (55.92)
C	58.35 (60.57)	57.53 (59.36)	56.81 (58.27)	56.28 (57.37)	55.77 (56.50)	55.43 (55.80)
D	58.23 (60.46)	57.43 (59.28)	56.74 (58.21)	56.18 (57.28)	55.67 (56.41)	55.34 (55.72)
E	58.05 (60.30)	57.27 (59.13)	56.57 (58.05)	56.07 (57.18)	55.55 (56.30)	55.24 (55.63)
F	58.03 (60.27)	57.18 (59.04)	56.50 (57.99)	56.01 (57.13)	55.52 (56.27)	55.18 (55.58)
G	57.93 (60.18)	57.08 (58.95)	56.36 (57.86)	55.89 (57.02)	55.43 (56.19)	55.07 (55.48)
H	57.87 (60.13)	57.01 (58.88)	56.26 (57.78)	55.77 (56.91)	55.33 (56.10)	54.93 (55.35)
I	57.77 (60.03)	56.91 (58.80)	56.18 (57.70)	55.69 (56.83)	55.22 (56.00)	54.88 (55.31)
J	57.52 (59.80)	56.67 (58.57)	55.97 (57.50)	55.51 (56.67)	54.96 (55.77)	54.69 (55.14)
K	57.20 (59.51)	56.48 (58.40)	55.74 (57.29)	55.36 (56.53)	54.81 (55.63)	54.41 (54.89)

(d) x KCl + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		58.62[a] (60.82)[b]	57.80 (59.62)	57.23 (58.66)	56.70 (57.75)	56.05 (56.76)	55.83 (56.16)
B		58.50 (60.71)	57.69 (59.52)	57.05 (58.49)	56.52 (57.59)	55.98 (56.68)	55.67 (56.01)
C		58.33 (60.55)	57.47 (59.31)	56.83 (58.29)	56.32 (57.40)	55.83 (56.55)	55.46 (55.83)
D		58.23 (60.46)	57.33 (59.18)	56.76 (58.22)	56.23 (57.32)	55.76 (56.49)	55.31 (55.70)
E		58.09 (60.33)	57.15 (59.02)	56.62 (58.10)	56.12 (57.22)	55.63 (56.37)	55.21 (55.60)
F		58.00 (60.25)	57.09 (58.96)	56.51 (58.00)	55.98 (57.10)	55.45 (56.21)	55.05 (55.46)
G		57.85 (60.11)	56.95 (58.83)	56.34 (57.83)	55.82 (56.95)	55.29 (56.07)	54.89 (55.31)
H		57.76 (60.02)	56.85 (58.74)	56.24 (57.75)	55.72 (56.87)	55.23 (56.01)	54.83 (55.26)
I		57.71 (59.98)	56.79 (58.69)	56.14 (57.66)	55.65 (56.79)	55.18 (55.97)	54.76 (55.20)
J		57.60 (59.87)	56.69 (58.60)	56.08 (57.60)	55.53 (56.69)	55.07 55.87)	54.64 (55.10)
K		57.49 (59.78)	56.56 (58.47)	55.87 (57.41)	55.34 (56.52)	54.88 (55.69)	54.50 (54.97)

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		57.60[a]	56.67	55.95	55.52	55.18
		(59.42)[b]	(58.14)	(57.07)	(56.28)	(55.58)
B		57.46	56.59	55.92	55.43	55.10
		(59.30	(58.07)	(57.04)	(56.20)	(55.50)
C		57.36	56.53	55.84	55.38	55.03
		(59.20)	(58.01)	(56.97)	(56.15)	(55.45)
D		57.20	56.34	55.69	55.18	54.90
		(59.06)	(57.84)	(56.84)	(56.00)	(55.33)
E		57.08	56.21	55.63	55.11	54.84
		(58.85)	(57.72)	(56.78)	(55.90)	55.27)
F		56.95	56.15	55.59	55.03	54.78
		(58.84)	(57.67)	(56.74)	(55.84)	(55.22)
G		56.83	56.10	55.55	54.99	54.71
		(58.72	57.63	56.70	55.80	55.16
H		56.78	56.03	55.51	54.94	54.61
		(58.67)	(57.56)	(56.67)	(55.76)	(55.07)
I		56.73	55.95	55.46	54.91	54.56
		(58.63)	(57.49)	(56.63)	(55.73)	(55.03)
J		56.67	55.89	55.41	54.85	54.53
		(58.57)	(57.44)	(56.58)	(55.67)	(54.99)
K		56.48	55.74	55.36	54.81	54.41
		(58.40)	(57.29)	56.53)	(55.63)	(54.89)

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		57.60^a	56.67	55.95	55.52	55.18
		(59.42)^b	(58.14)	(57.07)	(56.28)	(55.58)
B		57.52	56.62	55.93	55.48	55.13
		(59.35)	(58.10)	(57.05)	(56.24)	(55.53)
C		57.42	56.55	55.85	55.43	55.07
		(59.27)	(58.04)	(56.98)	(56.20)	(55.47)
D		57.36	56.49	55.80	55.37	55.05
		(59.21)	(57.98)	(56.94)	(54.14)	(55.46)
E		57.25	56.38	55.72	55.31	54.98
		(59.11)	(57.88)	(56.86)	(56.09)	(55.40)
F		57.16	56.31	55.66	55.27	54.90
		(59.02)	(57.82)	(56.81)	(56.05)	(55.32)
G		57.03	56.27	55.60	55.18	54.83
		(58.90)	(57.78)	(56.75)	(55.97)	(55.26)
H		56.87	56.14	55.53	55.14	55.77
		(58.76)	(57.66)	(56.69)	(55.93)	(55.21)
I		56.79	56.12	55.50	55.09	54.74
		(58.68)	(57.64)	(56.66)	(55.89)	(55.18)
J		56.68	56.03	55.44	55.00	54.66
		(58.59)	(57.56)	(56.61)	(55.80)	(55.11)
K		56.57	55.87	55.34	54.88	55.50
		(58.48)	(57.41)	(56.52)	(55.69)	(54.97)

a. Computed Values using Mc Gowan's relation

b. Computed Values using Pandey's relation

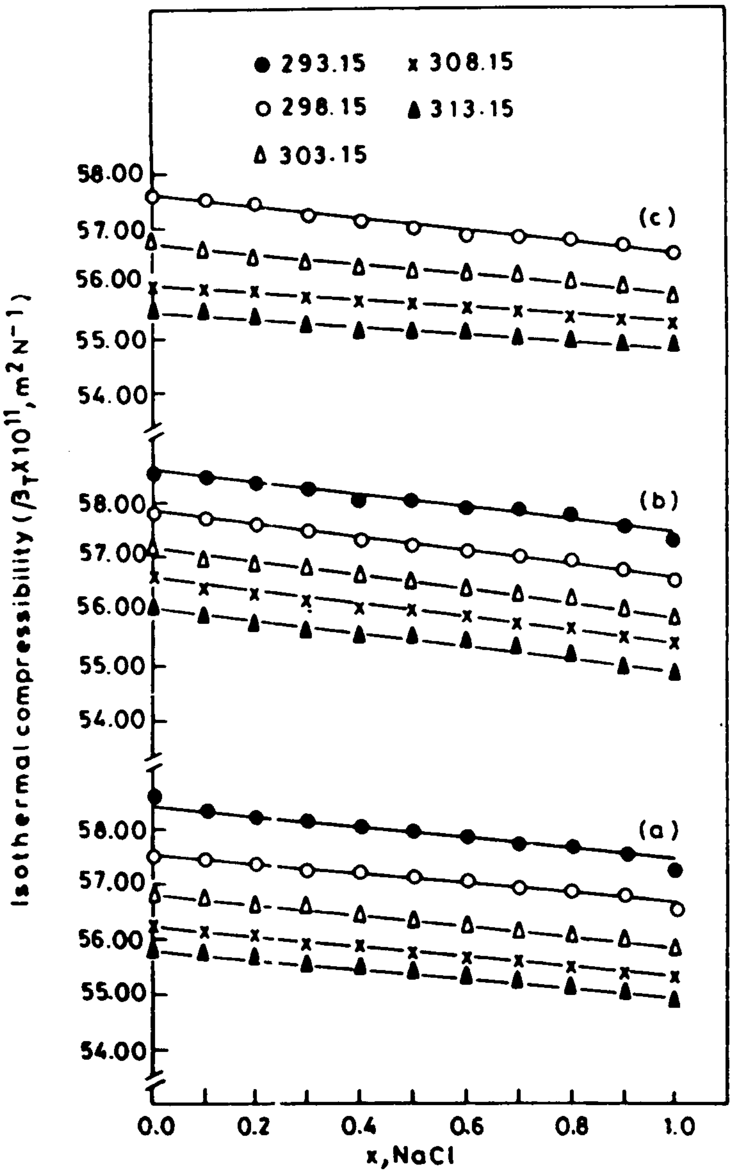
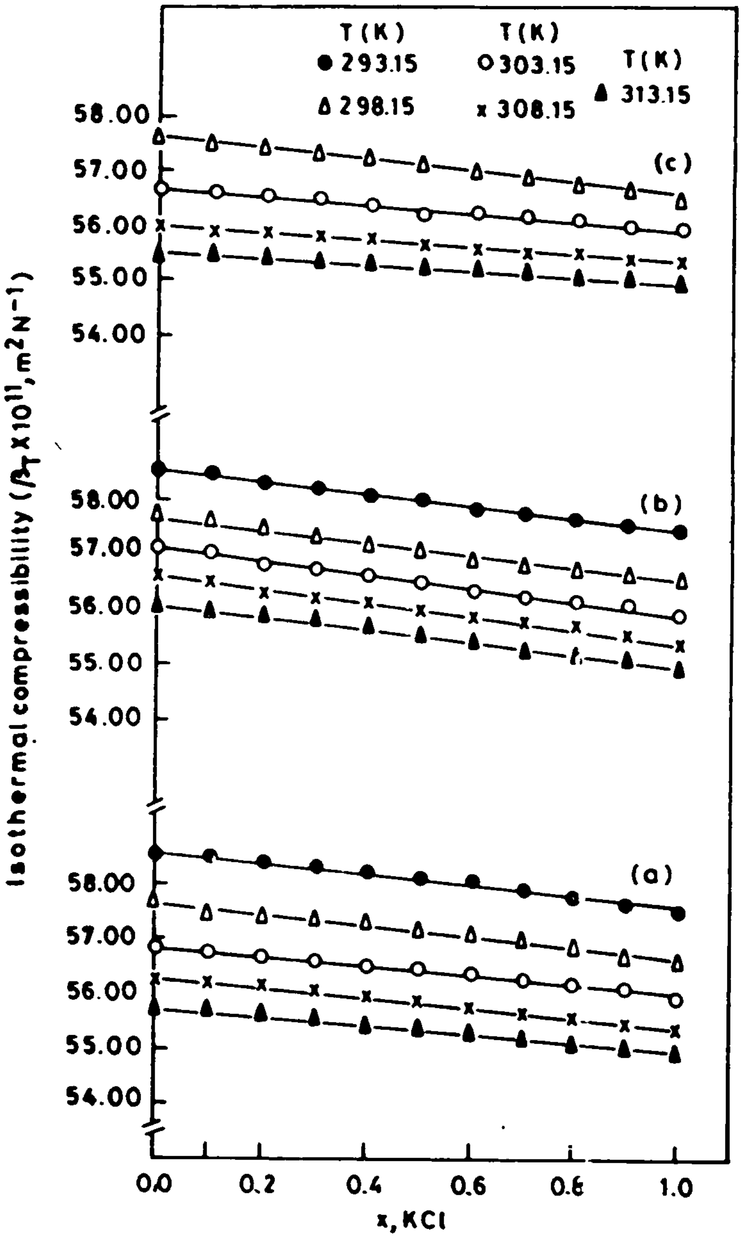


Fig. 1. (i) Plots of isothermal compressibility vs mole fraction of NaCl of (a) x NaCl$_{(aq)}$ + (1-x) Glycine$_{(aq)}$, (b) x NaCl$_{(aq)}$ + (1-x) Leucine$_{(aq)}$ and (c) x NaCl$_{(aq)}$ + (1-x) Threonine$_{(aq)}$ systems at several temperatures.



(ii) Plots of isothermal compressibility vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

[2.3] $P_i = \alpha T/\beta_T$.

β_T values otained by equaiton [2.1] have been used in the above relation. α, the thermal expansion coefficient is obtained using the relation.

[2.4] $\alpha = - 1/\rho\ (d\rho/dt)$.

The internal pressure has been found to increase with increase in temperature (Table 2) which may apparently be attributed to a decrease in the repulsive forces among the components of the system. The values of P_i also vary with composition.

The solubility parameter δ is obtained (Table 3) by taking the square root of the internal pressure.

[2.5] $\delta = (\alpha T/\beta_T)^{1/2}$.

It has been found to increase with increase in temperature. The Pseudo Grüneisen parameter, Γ, has been computed by using the relation.

[2.6] $\Gamma = (\gamma-1)/\alpha T$

in which γ is the usual specific heat ratio obtained from the relation.

[2.7] $\beta_T = \beta_S\gamma$

The values of Pseudo-Grüneisen parameter are listed in Table 4. The decrease in the values of Γ with increase in temperature may be attributed to an increase in the kinetic energy of the system.

TABLE 2 Internal pressure (P_i x 10^{-8}, Nm^{-2}) as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$+(1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		0.980	1.256	1.542	1.841	2.152	2.475
B		0.780	1.260	1.366	1.679	2.001	2.347
C		1.040	1.320	1.362	1.918	2.235	2.563
D		1.027	1.292	1.570	1.864	2.159	2.470
E		0.945	1.238	1.581	1.936	2.306	2.691
F		0.945	1.254	1.584	1.924	2.275	2.644
G		1.246	1.168	1.545	1.935	2.340	2.766
H		1.247	1.549	1.868	2.197	2.536	2.891
I		0.944	1.268	1.614	1.972	2.343	2.730
J		0.804	1.415	1.512	1.890	2.288	2.698
K		1.101	1.319	1.646	1.981	2.338	2.707

(b) x $KCl_{(aq)}$+ (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		0.980	1.256	1.542	1.841	2.152	2.475
B		1.078	1.360	1.655	1.960	2.279	2.611
C		0.776	1.113	1.469	1.841	2.229	2.633
D		0.960	1.185	1.421	1.667	1.922	2.186
E		0.900	1.190	1.496	1.812	2.146	2.490
F		0.522	0.799	1.092	1.402	1.720	2.052
G		0.883	1.229	1.549	1.907	2.274	2.659
H		1.165	1.396	1.635	1.884	2.140	2.415
I		1.103	1.369	1.645	1.934	2.233	2.540
J		1.092	1.373	1.663	1.968	2.284	2.610
K		0.788	1.111	1.449	1.802	2.171	2.555

(c) x $\mathrm{NaCl_{(aq)}}$ + (1 - x) $\mathrm{Leucine_{(aq)}}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	0.924	1.212	1.512	1.827	2.162	2.497
B	0.591	0.851	1.126	1.669	1.710	2.205
C	1.199	1.464	1.741	2.030	2.332	2.641
D	0.900	1.240	1.598	1.974	2.367	2.772
E	1.175	1.405	1.648	1.897	2.160	2.426
F	1.154	1.397	1.600	1.666	2.185	2.465
G	0.905	1.196	1.501	1.817	2.148	2.491
H	0.800	1.106	1.428	1.763	2.113	2.477
I	0.527	0.805	1.099	1.466	1.727	2.059
J	1.226	1.510	1.807	2.111	2.436	2.763
K	0.982	1.319	1.646	1.981	2.238	2.707

(d) x $\mathrm{KCl_{(aq)}}$ + (1 - x) $\mathrm{Leucine_{(aq)}}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	0.924	1.212	1.512	1.827	2.162	2.497
B	0.523	0.799	1.088	1.392	1.712	2.041
C	0.797	1.064	1.343	1.635	1.940	2.562
D	0.401	0.623	0.854	1.097	1.352	1.619
E	0.026	0.217	0.418	0.629	0.852	1.086
F	0.245	0.443	0.651	0.686	1.099	1.338
G	0.814	1.170	1.540	1.929	2.338	2.763
H	0.955	1.269	1.592	1.931	2.287	2.657
I	0.871	2.200	1.577	1.959	2.355	2.770
J	0.509	1.252	1.718	1.877	2.210	2.560
K	0.788	1.113	1.449	1.802	2.171	2.555

(e) x NaCl$_{(aq)}$ + (1 - x) Threonine$_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		1.441	1.636	1.837	2.037	2.244
B		1.327	1.559	1.799	2.046	2.297
C		1.175	1.501	1.843	2.195	2.559
D		1.350	1.625	1.911	2.205	2.506
E		1.224	1.588	1.965	2.362	2.764
F		1.311	1.604	1.907	2.225	2.546
G		1.342	1.619	1.906	2.208	2.513
H		1.211	1.554	1.912	2.289	2.675
I		1.331	1.628	1.934	2.258	2.588
J		1.213	1.590	1.982	2.397	2.822
K		1.317	1.646	1.981	2.338	2.700

(f) x KCl$_{(aq)}$ + (1 - x) Threonine$_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
A		1.441	1.609	1.837	2.037	2.244
B		1.435	4.622	5.395	6.100	6.829
C		2.329	2.481	2.718	2.909	2.106
D		1.299	1.564	1.858	2.148	2.449
E		0.799	1.076	1.403	1.723	2.054
F		1.337	1.603	1.936	2.248	2.574
G		1.409	1.690	2.044	2.376	2.721
H		1.295	1.558	1.889	2.199	2.524
I		1.425	1.637	1.916	2.171	2.437
J		1.371	1.620	1.935	2.234	2.543
K		1.111	1.425	1.802	2.171	2.555

TABLE 3 Solubility parameter, $\delta \times 10^{-4}$, $(Nm^{-2})^{1/2}$ as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	0.990	1.121	1.242	1.357	1.467	1.573
B	0.883	1.122	1.169	1.296	1.416	1.532
C	1.020	1.148	1.269	1.385	1.495	1.601
D	1.013	1.137	1.253	1.364	1.469	1.571
E	0.956	1.112	1.257	1.392	1.518	1.640
F	0.972	1.120	1.258	1.387	1.508	1.626
G	1.116	1.081	1.243	1.391	1.529	1.663
H	1.117	1.245	1.367	1.482	1.592	1.700
I	0.971	1.126	1.270	1.404	1.531	1.652
J	0.897	1.070	1.230	1.375	1.513	1.643
K	1.005	1.148	1.283	1.407	1.529	1.645

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	0.990	1.121	1.242	1.357	1.467	1.573
B	1.038	1.166	1.286	1.400	1.510	1.616
C	0.881	1.055	1.212	1.357	1.493	1.623
D	0.980	1.089	1.192	1.291	1.386	1.478
E	0.949	1.091	1.223	1.347	1.465	1.578
F	0.722	0.894	1.045	1.184	1.311	1.432
G	0.939	1.109	1.244	1.381	1.508	1.631
H	1.079	1.182	1.279	1.373	1.463	1.554
I	1.050	1.170	1.283	1.391	1.494	1.594
J	1.045	1.171	1.290	1.403	1.511	1.616
K	0.888	1.054	1.204	1.343	1.473	1.598

(c) x NaCl$_{(aq)}$ + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		0.961	1.101	1.229	1.351	1.470	1.580
B		0.769	0.992	1.061	1.292	1.308	1.485
C		1.095	1.210	1.320	1.425	1.527	1.625
D		0.948	1.114	1.264	1.405	1.538	1.665
E		1.084	1.186	1.284	1.377	1.470	1.558
F		1.074	1.182	1.265	1.291	1.478	1.570
G		0.951	1.093	1.225	1.348	1.466	1.578
H		0.894	1.052	1.195	1.328	1.453	1.574
I		0.726	0.898	1.048	1.186	1.314	1.435
J		1.107	1.229	1.344	1.453	1.567	1.662
K		1.005	1.148	1.283	1.407	1.529	1.645

(d) x KCl$_{(aq)}$ + (1 - x) Leucine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		0.961	1.102	1.230	1.352	1.470	1.580
B		0.723	0.894	1.043	1.180	1.308	1.428
C		0.893	1.032	1.159	1.128	1.393	1.502
D		0.633	0.789	0.924	1.047	1.163	1.272
E		0.162	0.466	0.646	0.793	0.923	1.042
F		0.495	0.666	0.807	0.932	1.049	1.157
G		0.902	1.082	1.241	1.389	1.529	1.662
H		0.978	1.126	1.262	1.389	1.512	1.630
I		0.933	1.104	1.256	1.400	1.535	1.664
J		0.713	1.190	1.317	1.370	1.487	1.600
K		0.888	1.055	1.204	1.343	1.473	1.598

TABLE 4 Pseudo-Grüneisen parameter ($\Gamma \times 10^{-2}$) as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15
A		555.8	438.4	359.3	303.2	261.2
B		698.9	516.5	406.8	333.1	281.2
C		523.9	416.4	344.0	292.1	252.4
D		530.6	425.7	353.8	301.0	261.4
E		597.4	445.0	351.2	290.4	244.9
F		577.1	438.3	351.1	292.7	247.6
G		670.4	471.4	359.4	288.7	240.4
H		437.2	354.9	297.5	354.5	220.0
I		678.6	433.8	344.7	284.1	240.8
J		678.4	480.9	367.6	296.8	246.6
K		514.7	417.6	337.8	282.7	244.1

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15
A		555.8	438.4	359.3	303.2	261.2
B		504.5	404.1	335.4	285.1	247.4
C		701.7	493.9	377.1	364.0	252.5
D		566.2	464.4	390.1	335.1	293.4
E		605.1	462.0	371.4	308.5	262.3
F		945.8	688.7	507.6	399.1	327.5
G		615.6	456.4	358.5	293.6	247.8
H		466.6	393.5	339.2	296.7	263.2
I		494.3	402.2	337.7	289.4	252.0
J		498.7	400.6	348.4	284.8	246.6
K		690.6	494.8	382.8	309.3	259.3

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15
A		591.0	453.9	366.4	306.1	260.7
B		922.2	648.0	493.1	397.0	329.4
C		454.6	376.4	319.3	275.7	242.2
D		607.0	443.6	347.3	284.1	238.3
E		464.7	391.3	336.7	295.2	260.9
F		473.4	394.4	347.3	336.5	258.0
G		604.8	461.6	369.9	309.3	262.9
H		682.7	495.5	389.5	317.3	266.9
I		988.5	685.2	506.6	398.5	326.0
J		445.2	364.6	307.4	265.3	231.6
K		557.0	417.6	337.8	282.7	244.1

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15
A		591.0	453.9	366.4	306.1	260.7
B		1043.3	690.3	510.6	401.7	329.8
C		684.4	518.6	414.1	342.1	290.8
D		1361.6	885.4	649.8	509.0	416.6
E		1548.2	1436.8	1327.9	889.2	660.6
F		1731.2	1241.9	851.2	643.7	511.7
G		668.6	470.1	359.6	287.0	240.5
H		570.9	434.5	348.5	287.2	246.2
I		626.6	450.9	350.7	283.4	239.2
J		1067.7	440.0	356.3	297.5	254.7
K		690.6	494.8	382.8	309.8	259.3

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15
A		380.8	372.2	304.6	276.7
B		413.2	355.9	311.1	276.0
C		467.3	370.1	303.1	256.6
D		406.6	341.9	292.3	255.5
E		449.3	349.5	284.5	239.1
F		419.1	346.7	293.4	252.4
G		410.2	342.4	293.7	255.3
H		455.2	357.1	292.1	246.5
I		414.4	341.4	289.0	250.0
J		454.0	348.8	282.2	235.8
K		417.6	337.8	282.7	241.1

(f) x $KCl_{(aq)}$ +(1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15
A		380.8	372.2	304.6	276.7
B		136.4	118.0	103.7	92.2
C		235.5	220.1	205.5	193.5
D		422.6	352.2	310.0	262.3
E		686.5	507.4	399.1	327.3
F		410.9	339.8	288.5	250.3
G		389.4	322.5	273.7	237.2
H		925.0	349.5	295.5	255.6
I		385.4	332.9	291.6	259.2
J		401.4	337.0	288.9	252.2
K		494.6	382.9	309.8	259.3

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Chapter - 3

Apparent molal volume and apparent molal compressibility of aqueous mixtures of aminoacids and alkali chlorides

INTRODUCTION

Apparent molal volume and apparent molal compressibility of electrolytes and non-electrolytes have been used to investigate the structural interactions in solutions [1,2]. The dependence of these properties upon the size and the configuration of solute and their sensitivity to interactions can prove to help a better insight into the solution behaviour [3]. The partial specific volumes of the macromolecules during some biochemical reactions depend on the intra and inter-molecular interactions as well as on the electrostriction of the solvent [4]. At infinite dilution where ion-ion or solute-solute interactions vanish, these properties are useful in understanding the solute-solvent, the ion-solvent and the solvent-solvent interactions [5-7]. The partial molal compressibility of infinite dilute solutions of non-electrolytes is a measure of resistance offered against the compression which the solute molecule imparts towards the solvent and gives useful information about the solute-solvent interactions [8] and can also be used to monitor the solute hydration in aqueous solutions [9,10]. Investigations have been made using electrolytes [11-13], carbohydrates [14,15], proteins [16] as well as aminoacids [17,24]. Consequently, the apparant molal volumes and the apparant molal compressibilities of binary mixtures of aminoacid$_{(aq)}$ and KCl/NaCl$_{(aq)}$ have been computed using the experimental density and the ultrasonic velocity data of solutions.

RESULTS AND DISCUSSION

Experimetnal values of density have been used to compute the apparent molal volume of component 1 i.e. NaCl$_{(aq)}$/KCl$_{(aq)}$ in the binary systems under investigation, by using the following relation [25].

$$[3.1] \qquad \phi_{V,1} = \frac{M_2(1-x)(\rho-\rho_2)}{x.\rho.\rho_2} + \frac{M_1}{\rho}$$

where M_2, ρ_2 and (1-x) stand for the molecular weight, the density and the mole fraction of component 2 i.e., aminoacid$_{(aq)}$, respectively. M_1 and x represent the molecular weight and the mole fraction of component 1 while ρ stands for the density of the solution.

In each of the systems studied, the values of $\phi_{V,1}$ have been found to increase with increase in temperature as apparent from Table 1. The increase of apparent molal volume with increase in temperature is attributed to the positive values of apparant molal expansibilities [26] due to volume expansion at higher temperatures .

However, the $\phi_{V,1}$ values are found to be weakly affected by increase in concentration (Fig. 1) which may be attributed to weak solute-solute interaction.

The apparent molal volume at infinite dilutions was obtained by extrapolating the plot of $\phi_{V,1}$ versus x of Redlich's equaiton [27] to zero concentration,

[3.2] $$\phi_{V,1} = \phi^0_{V,1} + S_V\, x$$

where $\phi^0_{V,1}$ is the apparent molal volume at infinite dilution and S_V is the experimental slope.

The $\phi^0_{V,1}$ and S_V values alongwith the standard deviation are given in Table 2. The $\phi^0_{V,1}$ values have been found to increase with increase in temperature, a behaviour similar to those of the electrolytic [28] and non-electrolytic [29] solutions. The increase of $\phi^0_{V,1}$ with increase in temperature is ascribed to the following effects :

1. Increase in volume due to decrease in hydration number of solute(s) at higher temperatures.

TABLE 1 Apparent molal volume (cm^3, mol^{-1}) as functions of temperature and composition for the following systems :

(a) x NaCl$_{(aq)}$ + (1 - x) Glycine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		18.026	18.046	18.069	18.116	18.149	18.203
C		18.045	18.060	18.087	18.125	18.157	18.203
D		18.050	18.070	18.099	18.128	18.154	18.197
E		18.053	18.073	18.096	18.125	18.163	18.203
F		18.055	18.071	18.098	18.127	18.163	18.203
G		18.050	18.064	18.087	18.116	18.154	18.194
H		18.046	18.066	18.092	18.123	18.159	18.198
I		18.048	18.068	18.091	18.123	18.157	18.198
J		18.050	18.064	18.089	18.116	18.150	18.189

(b) x KCl$_{(aq)}$ + (1 - x) Glycine$_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		18.153	18.154	18.196	18.207	18.240	18.276
C		18.152	18.154	18.169	18.198	18.230	18.276
D		18.146	18.160	18.183	18.200	18.221	18.245
E		18.125	18.140	18.164	18.188	18.220	18.257
F		18.123	18.143	18.167	18.195	18.228	18.268
G		18.131	18.148	18.171	18.200	18.236	18.276
H		18.108	18.133	18.159	18.188	18.221	18.257
I		18.105	18.127	18.152	18.184	18.216	18.255
J		18.104	18.126	18.151	18.182	18.217	18.255

(c) x $\text{NaCl}_{(aq)}$ + (1 - x) $\text{Leucine}_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		18.078	18.096	18.119	18.131	18.163	18.181
C		18.015	18.060	18.101	18.148	18.190	18.245
D		18.060	18.078	18.107	18.136	18.181	18.229
E		18.037	18.069	18.097	18.129	18.158	18.199
F		18.056	18.085	18.112	18.141	18.177	18.214
G		18.069	18.086	18.110	18.136	18.169	18.205
H		18.073	18.088	18.109	18.135	18.165	18.202
I		18.064	18.085	18.108	18.137	18.170	18.208
J		18.044	18.064	18.087	18.114	18.147	18.183

(d) x $\text{KCl}_{(aq)}$ + (1 - x) $\text{Leucine}_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		18.151	18.187	18.211	18.240	18.273	18.328
C		18.033	18.069	18.092	18.139	18.172	18.217
D		18.054	18.090	18.125	18.160	18.199	18.241
E		18.037	18.078	18.119	18.162	18.208	18.254
F		18.060	18.092	18.119	18.152	18.184	18.224
G		18.066	18.081	18.104	18.133	18.172	18.211
H		18.078	18.099	18.122	18.153	18.186	18.227
I		18.094	18.114	18.129	18.169	18.204	18.240
J		18.090	18.112	18.138	18.168	18.203	18.244

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x T(K)	298.15	303.15	308.15	313.15	318.15
B	18.022	18.100	18.147	18.196	18.212
C	18.038	18.091	18.138	18.187	18.203
D	18.008	18.027	18.056	18.092	18.133
E	18.020	18.041	18.069	18.104	18.148
F	18.031	18.056	18.085	18.123	18.164
G	18.044	18.066	18.095	18.132	18.172
H	18.051	18.074	18.105	18.138	18.178
I	18.056	18.075	18.113	18.146	18.182
J	18.059	18.078	18.114	18.147	18.186

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x T(K)	298.15	303.15	308.15	313.15	318.15
B	18.147	18.173	18.202	18.197	18.267
C	18.138	18.154	18.174	18.214	18.267
D	18.135	18.160	18.189	18.213	18.273
E	18.124	18.154	18.173	18.213	18.266
F	18.118	18.143	18.172	18.210	18.248
G	18.116	18.142	18.171	18.204	18.245
H	18.118	18.141	18.170	18.206	18.246
I	18.122	18.147	18.176	18.209	18.250
J	18.119	18.140	18.171	18.206	18.248

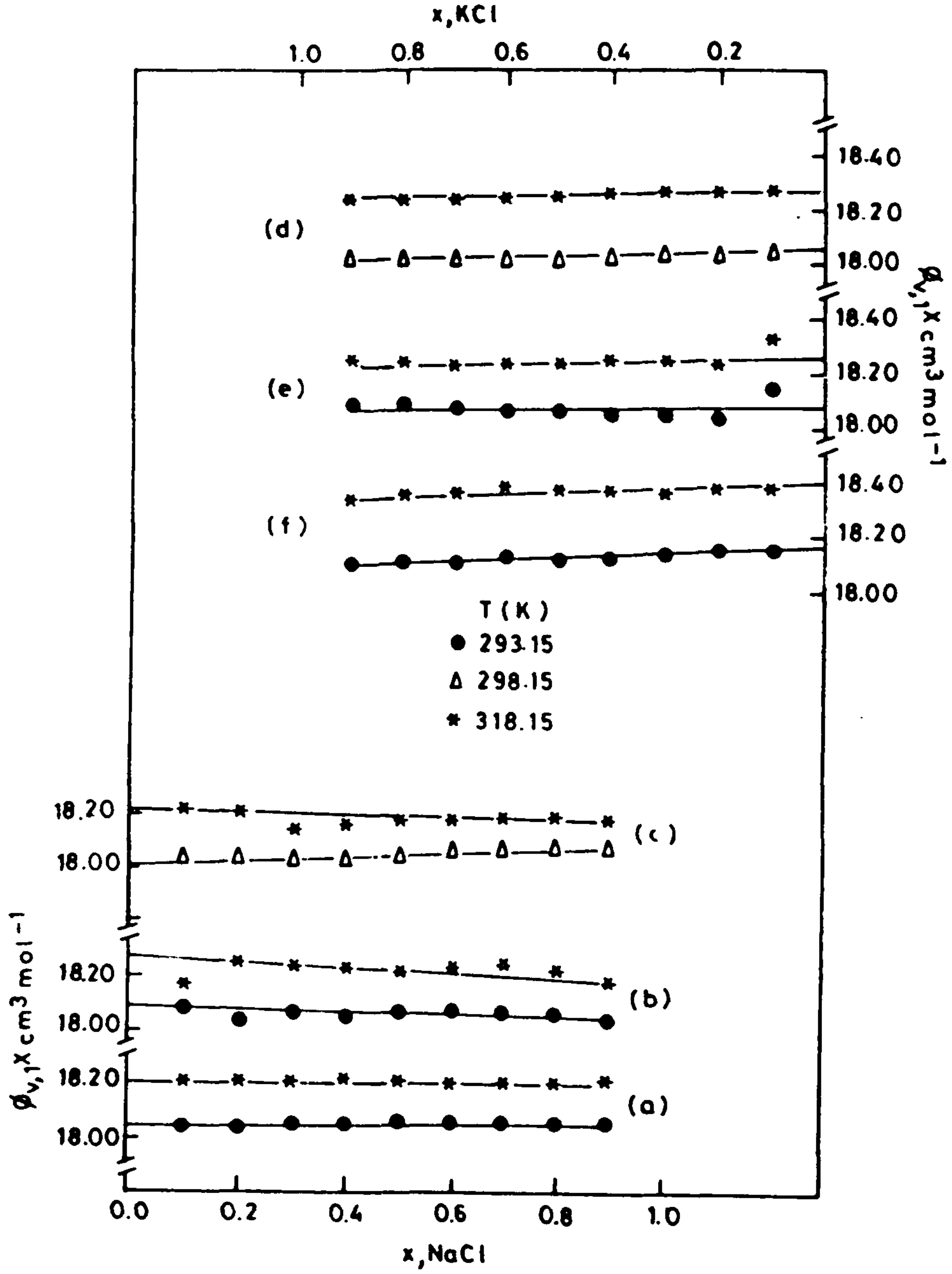

Fig. 1. Plots of apparent molal volume vs mole fraction, x of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$, (c) x $NaCl_{(aq)}$ + (1-x) Threonine (d) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (e) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (f) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

TABLE 2 Least-squares fitted parameters of equation, $\phi_{V,1} = \phi^{0}_{V,1} + S_V x$ for the following systems ;

(a) x NaCl$_{(aq)}$ + (1-x) Glycine$_{(aq)}$

T(K)	$\phi^{0}_{V,1}$(cm^3 mol^{-1})	$S_V \times 10^2$	S.D x 10^3
293.15	18.050	–0.01	2.45
298.15	18.068	–0.12	4.02
303.15	18.095	–0.58	4.26
308.15	18.129	–1.25	3.19
313.15	18.160	–0.19	3.81
318.15	18.207	–1.54	3.98

(b) x KCl$_{(aq)}$ + (1-x) Glycine$_{(aq)}$

T(K)	$\phi^{0}_{V,1}$(cm^3 mol^{-1})	$S_V \times 10^2$	S.D x 10^3
293.15	18.161	–6.78	6.21
298.15	18.163	–3.98	5.67
303.15	18.191	–4.53	7.32
308.15	18.206	–2.57	4.70
313.15	18.235	–1.97	6.60
318.15	18.272	–1.73	10.4

(c) x NaCl$_{(aq)}$ + (1-x) Leucine$_{(aq)}$

T(K)	$\phi^{0}_{V,1}$(cm^3 mol^{-1})	$S_V \times 10^2$	S.D x 10^3
293.15	18.049	1.15	1.28
298.15	18.080	–0.26	1.21
303.15	18.113	–1.50	0.84
308.15	18.142	–1.60	2.60
313.15	18.181	–2.41	1.09
318.15	18.220	–2.52	1.92

(d) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$

T(K)	$\phi^{0}_{V,1}$(cm^3 mol^{-1})	S_V x 10^2	S.D x 10^3
293.15	18.075	-0.08	3.49
298.15	18.115	-2.40	3.44
303.15	18.146	-3.36	3.23
308.15	18.184	-4.00	2.90
313.15	18.221	-4.10	2.84
318.15	18.271	-5.60	3.12

(e) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$

T(K)	$\phi^{0}_{V,1}$(cm^3 mol^{-1})	S_V x 10^2	S.D x 10^3
298.15	17.960	9.46	7.56
303.15	18.070	–0.28	2.32
308.15	18.110	–1.38	2.96
313.15	18.160	–3.32	3.30
318.15	18.180	–0.88	2.48

(f) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$

T(K)	$\phi^{0}_{V,1}$(cm^3 mol^{-1})	S_V x 10^2	S.D x 10^3
298.15	18.143	–3.37	0.59
303.15	18.168	–3.38	0.59
308.15	18.191	–2.63	0.81
313.15	18.208	–0.34	1.71
318.15	18.274	–3.36	0.64

2. Volume expansion, indicating the absence of solvent-solvent interactions.

The S_V values in all the cases are weakly negative suggesting the presence of weak solute-solute interactions.

The apparent molal adiabatic compressibility, $\phi_{K.1}$ of component 1 has been obtained by using the relation [25],

$$[3.3] \qquad \phi_{K.1} = \beta_S \, \phi_{V.1} + \frac{(1-x)\, M_2 \, (\beta_S - \beta_S^2)}{x.\rho_2}$$

The terms have their usual meanings.

The $\phi_{K.1}$ values have been listed in Table 3. These values have been found to decrease with increase in temperature which may be attributed to a change in the solvation of molecules, which apparently contributes to close packing of molecules and decrease in compressibility. The $\phi_{K.1}$ also varies with composition x as shown in Fig. 2. The variation in the values of $\phi_{K.1}$ with composition x, may be ascribed to the following :

1. Ion-ion interaction which lowers the compressibility.
2. Electrostriction effect due to hydration of aminoacids.
3. Decrease in compressibility due to an increase in the number of cations.

In all the systems under investigation, Na^+ ions are found to lower the compressibility more than those of K^+ ions. Na^+ ions are more dehydrated than K^+ ions thereby result an increase in its interaction with the zwitterions and corresponding decrease in compressibility [30]. The variation of $\phi_{K.1}$ with composition x, has been shown in Fig. 2. The plots indicate a little variation of $\phi_{K.1}$ values with increasing composition x, which may be ascribed to the hydrophobic or hydrophillic nature of aminoacids under investigation. Threonine

TABLE 3 Apparent molal compressibility (ϕ_K x 10^{11}, $m^2N^{-1}mol^{-1}$) as functions of temperature and composition for the following systems :

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
C		78.04	77.58	77.07	76.40	75.92	75.89
D		78.67	77.92	77.18	76.26	75.87	75.71
E		78.75	78.02	76.88	76.21	76.07	75.86
F		78.83	78.07	77.01	76.28	76.21	75.87
G		78.82	78.01	77.01	76.48	76.21	75.79
H		78.90	78.03	77.12	76.56	76.25	75.85
I		78.93	78.11	77.13	76.55	76.14	75.82
J		78.93	78.03	77.10	76.53	76.02	75.72

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		79.56	78.83	77.72	77.20	76.52	75.93
C		79.55	78.83	77.69	77.16	76.48	76.20
D		79.70	78.85	77.85	77.05	76.40	75.97
E		79.56	78.68	77.67	76.85	76.39	76.07
F		79.60	78.60	77.70	76.82	76.54	76.25
G		79.63	78.65	77.70	76.93	76.55	76.31
H		79.45	78.40	77.59	76.89	76.46	76.29
I		79.40	78.30	77.55	76.90	76.44	76.13
J		79.33	78.26	77.57	76.91	76.46	76.16

(c) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		79.03	78.07	74.92	74.63	75.93	74.04
C		78.65	77.73	76.27	75.49	75.85	75.02
D		78.82	77.98	76.84	76.09	76.05	75.44
E		78.61	77.81	76.80	76.30	75.99	75.51
F		78.92	77.94	77.05	76.59	76.27	75.80
G		79.01	78.02	77.07	76.52	76.28	75.83
H		79.12	78.08	77.14	76.64	76.27	78.81
I		78.09	78.11	77.21	76.69	76.29	75.94
J		78.85	77.87	77.06	76.57	76.01	75.72

(d) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		79.35	78.49	77.12	76.37	76.75	75.75
C		78.64	77.42	76.42	76.02	76.23	75.27
D		78.91	77.63	77.04	76.50	76.56	75.43
E		78.79	77.55	77.12	76.66	76.47	75.70
F		78.97	77.85	77.22	76.63	76.23	75.63
G		78.96	77.81	77.10	76.57	76.11	75.58
H		79.04	77.94	77.25	76.72	76.25	75.78
I		79.20	78.12	77.32	76.85	76.41	75.94
J		79.23	78.13	77.46	76.86	76.41	75.97

(e) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		77.02	77.16	76.97	75.71	75.67
C		77.60	77.19	76.74	76.02	75.71
D		77.37	76.52	76.09	75.26	75.26
E		77.42	76.42	76.18	75.63	75.34
F		77.47	76.70	76.30	75.57	75.49
G		77.53	76.87	76.41	75.71	75.52
H		77.69	76.93	76.50	75.79	75.51
I		77.79	76.94	76.52	75.89	75.58
J		77.88	77.01	76.54	75.92	75.65

(f) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		78.54	77.83	77.38	76.61	76.26
C		78.39	77.65	76.99	76.59	76.16
D		78.53	77.70	77.02	76.50	76.33
E		78.38	77.47	76.85	76.45	76.24
F		78.32	77.47	76.81	76.48	76.09
G		78.24	77.53	76.82	76.40	76.09
H		78.14	77.47	76.80	76.44	76.08
I		78.19	77.52	76.86	76.46	76.13
J		78.18	77.47	76.84	76.40	76.11

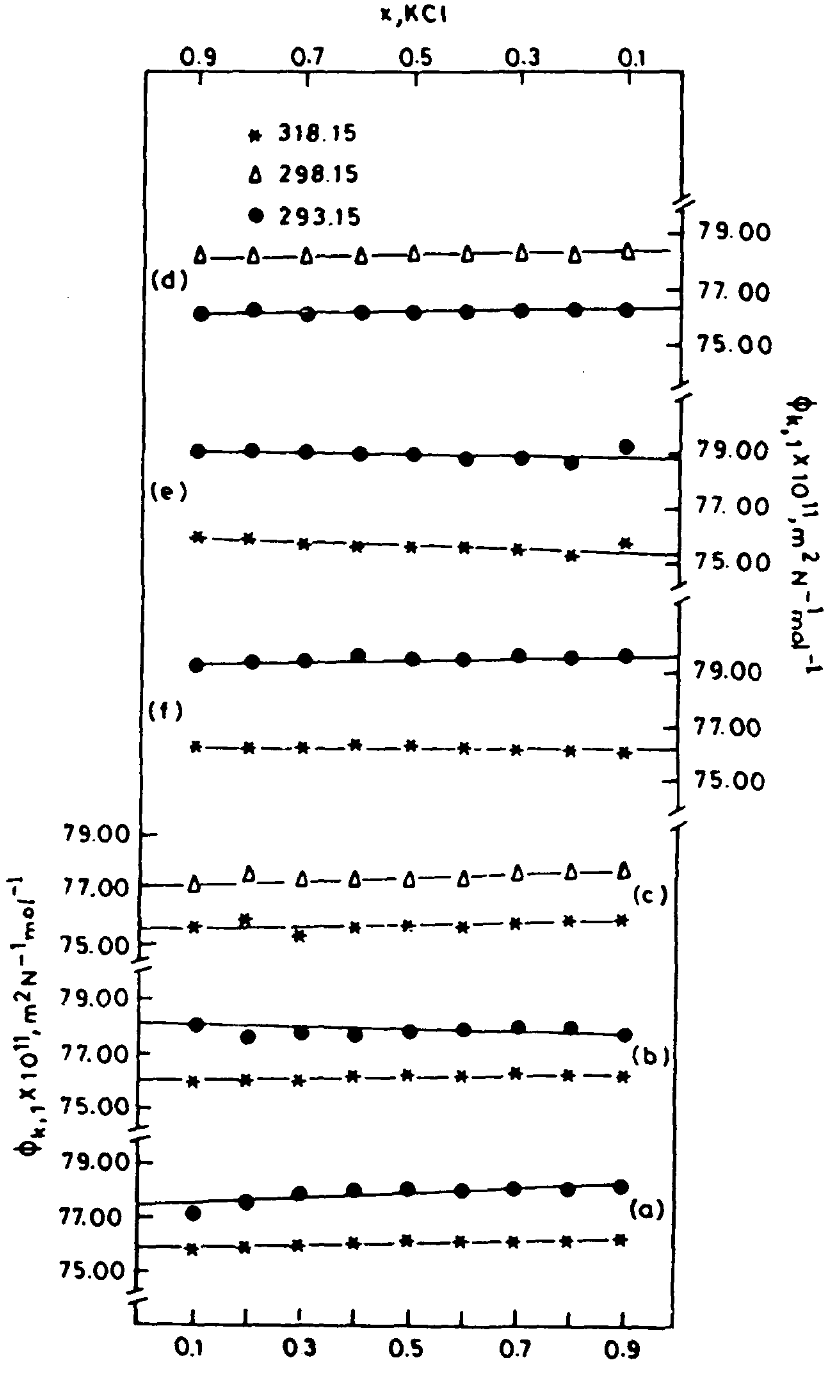

Fig. 2. Plots of apparent molal compressibility vs mole fraction, x of (a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ (c) x $NaCl_{(aq)}$ + (1-x) Threonine (d) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (e) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (f) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

having one -OH group is known to be influenced by the hydrogen bonding with water, thereby affecting its compressibility values [31].

The apparent molal compressibility at infinite dilution, $\phi^0_{K,1}$ has been obtained by extrapolating the $\phi_{K,1}$ values versus x plots to zero concentration, using the equation [27],

[3.4] $$\phi_{K,1} = \phi^0_{K,1} + S_K\,x$$

where $\phi^0_{K,1}$ is the apparent molal compressibility at infinite dilution. The values of $\phi^0_{K,1}$ (Table 4) have been found to decrease with increase in temperature which may be due to structural repulsion between the individual components. The slopes indicate a weak solute-solute interaction, which accounts for an almost ideal behaviour of the systems under investigation.

TABLE 4 Least-squares fitted parameters of equation, $\phi_{K,1} = \phi^{\circ}_{K,1} + S_K x$ for the following systems :

(a) x $NaCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$

T(K)	$\phi^{\circ}_{K,1}$(10^{11} m^2 N^{-1} mol^{-1})	S_K	S.D
293.15	77.718	1.687	0.31
298.15	77.414	0.920	0.19
303.15	76.846	0.338	0.12
308.15	76.298	0.240	0.11
313.15	75.851	0.406	0.11
318.15	75.759	0.067	0.08

(b) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$

T(K)	$\phi^{\circ}_{K,1}$(10^{11} m^2 N^{-1} mol^{-1})	S_K	S.D
293.15	79.681	–0.300	0.07
298.15	79.001	–0.800	0.06
303.15	77.800	–0.252	0.05
308.15	77.150	–0.363	0.08
313.15	76.478	–0.013	0.07
318.15	76.013	–0.103	0.10

(c) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$

T(K)	$\phi^{\circ}_{K,1}$(10^{11} m^2 N^{-1} mol^{-1})	S_K	S.D
293.15	78.766	0.267	0.15
298.15	77.894	0.125	0.11
303.15	75.684	2.042	0.41
308.15	75.182	2.013	0.34
313.15	75.901	0.395	0.12
318.15	75.576	1.757	0.32

(d) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$

T(K)	$\phi^{0}_{K,1}$(10^{11} m^2 N^{-1} mol^{-1})	S_K	S.D
293.15	78.874	0.272	0.19
298.15	77.754	0.257	0.29
303.15	76.744	0.743	0.19
308.15	76.530	0.800	0.13
313.15	76.175	0.147	0.09
318.15	75.383	0.578	0.14

(e) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$

T(K)	$\phi^{0}_{K,1}$(10^{11} m^2 N^{-1} mol^{-1})	S_K	S.D
298.15	77.211	0.095	0.97
303.15	76.886	−0.030	0.22
308.15	76.584	−0.222	0.24
313.15	75.589	0.263	0.19
318.15	75.508	0.035	0.13

(f) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$

T(K)	$\phi^{0}_{K,1}$(10^{11} m^2 N^{-1} mol^{-1})	S_K	S.D
298.15	78.572	−0.493	0.05
303.15	77.755	−0.372	0.07
308.15	77.183	−0.503	0.11
313.15	76.599	−0.233	0.03
318.15	76.278	−0.223	0.06

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Chapter - 4

Viscosity, rheochor and their excess functions of aqueous mixtures of aminoacids and alkali chlorides

INTRODUCTION

Viscometric studies enable one to investigate the intermolecular association and dissociation since such measurements provide valuable information about the size and the state of solvation of molecules in solution [1]. Several investigations have already been carried out to understand the nature and the extent of interaction that are present in aqueous [2,3] and non-aqueous [4,5] binary mixtures by evaluating some of the thermodynamic parameters such as association constants, free-energy change and enthalpy change. A number of workers have successfully utilised such thermodynamic/ interaction parameters in understanding the biological macromolecules such as aminoacids [6-9] in aqueous and non-aqueous solutions. Similarly, quantities such as rheochor and excess rheochor have also been used to gain information about the type and the extent of interaction between the unlike molecules [10]. Flory's statistical mechanical theory has also been applied for the evaluation of viscosity in binary liquid mixtures [11] and molten salts [12].

In this chapter viscosity measurements of binary mixtures of aminoacids and salts have been carried out at varying compositions and several temperatures. The rheochor and the excess rheochor values have also been obtained for such studies.

RESULTS AND DISCUSSION

The experimental values of viscosity of the binary systems under investigation are presented in Table 1. An examination of this table shows that η values decrease with increase in composition, x as well as with increase in temperature. The decrease in viscosity with increase in the mole fraction of salt (Fig. 1) may be attributed to a change in the solvation of aminoacids by the addition of salt.

TABLE 1 Experimental and Computed values of viscosity (η x 10^3 kg $m^{-1}s^1$) as function of temperature and compositon for the following systems :

(a) x $KCl_{(aq)}$ + (1 - x) Glycine

x T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A	1.071	0.940	0.840	0.752	0.674	0.629
B	1.067[a]	0.936	0.836	0.747	0.673	0.629
	(1.064)[b]	(0.938)	(0.838)	(0.751)	(0.671)	(0.629)
C	1.065	0.936	0.835	0.743	0.673	0.629
	(1.058)	(0.940)	(0.833)	(0.752)	(0.670)	0.625)
D	1.059	0.935	0.832	0.740	0.671	0.623
	(1.058)	(0.935)	(0.834)	(0.748)	(0.669)	(0.626)
E	1.057	0.933	0.827	0.738	0.670	0.622
	(1.054)	(0.929)	(0.829)	(0.743)	(0.670)	(0.622)
F	1.056	0.932	0.825	0.735	0.667	0.621
	(1.048)	(0.924)	(0.825)	(0.739)	(0.668)	(0.619)
G	1.048	0.923	0.820	0.732	0.665	0.620
	(1.042)	(0.925)	(0.822)	(0.741)	(0.668)	(0.615)
H	1.047	0.920	0.818	0.730	0.663	0.619
	(1.035)	(0.920)	(0.815)	(0.737)	(0.665)	(0.611)
I	1.039	0.917	0.816	0.730	0.663	0.612
	(1.037)	(0.914)	(0.514)	(0.732)	(0.665)	(0.613)
J	1.026	0.915	0.812	0.729	0.663	0.608
	(1.031)	(0.916)	(0.812)	(0.732)	(0.663)	(0.609)
K	1.022	0.908	0.809	0.729	0.662	0.606

(b) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1.089	0.964	0.855	0.767	0.693	0.636
B		1.087[a]	0.962	0.851	0.762	0.691	0.631
		(1.081)[b]	(0.953)	(0.845)	(0.757)	(0.690)	(0.634)
C		1.085	0.958	0.850	0.760	0.689	0.628
		(1.073)	(0.954)	(0.844)	(0.757)	(0.688)	(0.629)
D		1.076	0.957	0.847	0.756	0.687	0.628
		(1.072)	(0.946)	(0.838)	(0.751)	(0.687)	(0.628)
E		1.076	0.953	0.843	0.754	0.685	0.627
		(1.064)	(0.945)	(0.837)	(0.744)	(0.681)	(0.627)
F		1.071	0.945	0.840	0.753	0.684	0.626
		(1.056)	(0.938)	(0.830)	(0.738)	(0.681)	(0.622)
G		1.059	0.940	0.838	0.751	0.682	0.625
		(1.048)	(0.930)	(0.830)	(0.737)	(0.680)	(0.621)
H		1.051	0.938	0.835	0.748	0.680	0.624
		(1.039)	(0.930)	(0.832)	(0.731)	(0.675)	(0.621)
I		1.045	0.925	0.830	0.746	0.679	0.622
		(1.039)	(0.922)	(0.822)	(0.724)	(0.674)	(0.620)
J		1.030	0.920	0.825	0.738	0.673	0.616
		(1.031)	(0.900)	(0.815)	(0.724)	(0.667)	(0.614)
K		1.024	0.914	0.814	0.720	0.665	0.612

(c) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1.089	0.964	0.855	0.767	0.693	0.636
B		1.084[a]	0.956	0.850	0.765	0.685	0.623
		(1.086)[b]	(0.958)	(0.849)	(0.762)	(0.693)	(0.633)
C		1.082	0.953	0.848	0.763	0.681	0.622
		(1.075)	(0.948)	(0.840)	(0.759)	(0.691)	(0.631)
D		1.078	0.951	0.845	0.759	0.679	0.619
		(1.072)	(0.945)	(0.838)	(0.751)	(0.684)	(0.624)
E		1.075	0.950	0.842	0.760	0.678	0.614
		(1.061)	(0.942)	(0.835)	(0.749)	(0.682)	(0.622)
F		1.067	0.940	0.838	0.758	0.673	0.614
		(1.057)	(0.932)	(0.826)	(0.747)	(0.680)	(0.620)
G		1.061	0.937	0.835	0.755	0.671	0.612
		(1.054)	(0.929)	(0.824)	(0.745)	(0.678)	(0.618)
H		1.050	0.934	0.830	0.752	0.668	0.610
		(1.043)	(0.926)	(0.814)	(0.742)	(0.676)	(0.616)
I		1.038	0.926	0.826	0.750	0.666	0.609
		(1.039)	(0.924)	(0.812)	(0.734)	(0.669)	(0.609)
J		1.029	0.920	0.820	0.740	0.663	0.607
		(1.028)	(0.913)	(0.810)	(0.732)	(0.667)	(0.607)
K		1.022	0.909	0.809	0.729	0.662	0.606

(d) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1.096	0.964	0.855	0.767	0.693	0.636
B		1.091[a]	0.958	0.849	0.761	0.690	0.636
		(1.086)[b]	(0.956)	(0.848)	(0.761)	(0.692)	(0.633)
C		1.088	0.955	0.847	0.759	0.686	0.632
		(1.085)	(0.955)	(0.847)	(0.759)	(0.685)	(0.632)
D		1.085	0.950	0.843	0.754	0.683	0.630
		(1.076)	(0.948)	(0.840)	(0.753)	(0.684)	(0.630)
E		1.079	0.948	0.840	0.750	0.681	0.628
		(1.067)	(0.947)	(0.839)	(0.746)	(0.678)	(0.625)
F		1.071	0.944	0.838	0.747	0.679	0.626
		(1.059)	(0.939)	(0.832)	(0.739)	(0.677)	(0.624)
G		1.067	0.940	0.834	0.742	0.673	0.623
		(1.058)	(0.931)	(0.831)	(0.739)	(0.676)	(0.623)
H		1.056	0.934	0.829	0.740	0.670	0.620
		(1.049)	(0.931)	(0.824)	(0.732)	(0.675)	(0.622)
I		1.050	0.930	0.827	0.732	0.669	0.617
		(1.040)	(0.923)	(0.823)	(0.725)	(0.675)	(0.616)
J		1.040	0.920	0.823	0.730	0.667	0.614
		(1.032)	(0.922)	(0.816)	(0.724)	(0.668)	(0.614)
K		1.024	0.914	0.814	0.720	0.662	0.612

(e) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
A		1.096	0.964	0.855	0.767	0.693	0.636
B		1.094[a]	0.963	0.852	0.765	0.692	0.635
		(1.091)[b]	(0.961)	(0.852)	(0.764)	(0.691)	(0.632)
C		1.091	0.961	0.851	0.764	0.691	0.633
		(1.079)	(0.950)	(0.842)	(0.762)	(0.688)	(0.630)
D		1.087	0.956	0.846	0.758	0.688	0.630
		(1.075)	(0.947)	(0.840)	(0.753)	(0.686)	(0.627)
E		1.079	0.950	0.844	0.754	0.684	0.627
		(1.064)	(0.944)	(0.837)	(0.751)	(0.684)	(0.624)
F		1.073	0.946	0.840	0.748	0.680	0.625
		(1.060)	(0.934)	(0.828)	(0.748)	(0.676)	(0.617)
G		1.065	0.937	0.837	0.745	0.677	0.621
		(1.056)	(0.931)	(0.825)	(0.746)	(0.674)	(0.615)
H		1.059	0.933	0.831	0.739	0.672	0.617
		(1.044)	(0.928)	(0.822)	(0.743)	(0.672)	(0.613)
I		1.051	0.923	0.827	0.735	0.666	0.614
		(1.041)	(0.924)	(0.819)	(0.735)	(0.669)	(0.610)
J		1.042	0.920	0.821	0.730	0.663	0.610
		(1.029)	(0.914)	(0.810)	(0.732)	(0.663)	(0.608)
K		1.022	0.909	0.809	0.729	0.662	0.607

a. Experimental values

b. Computed values using equation [4.7]

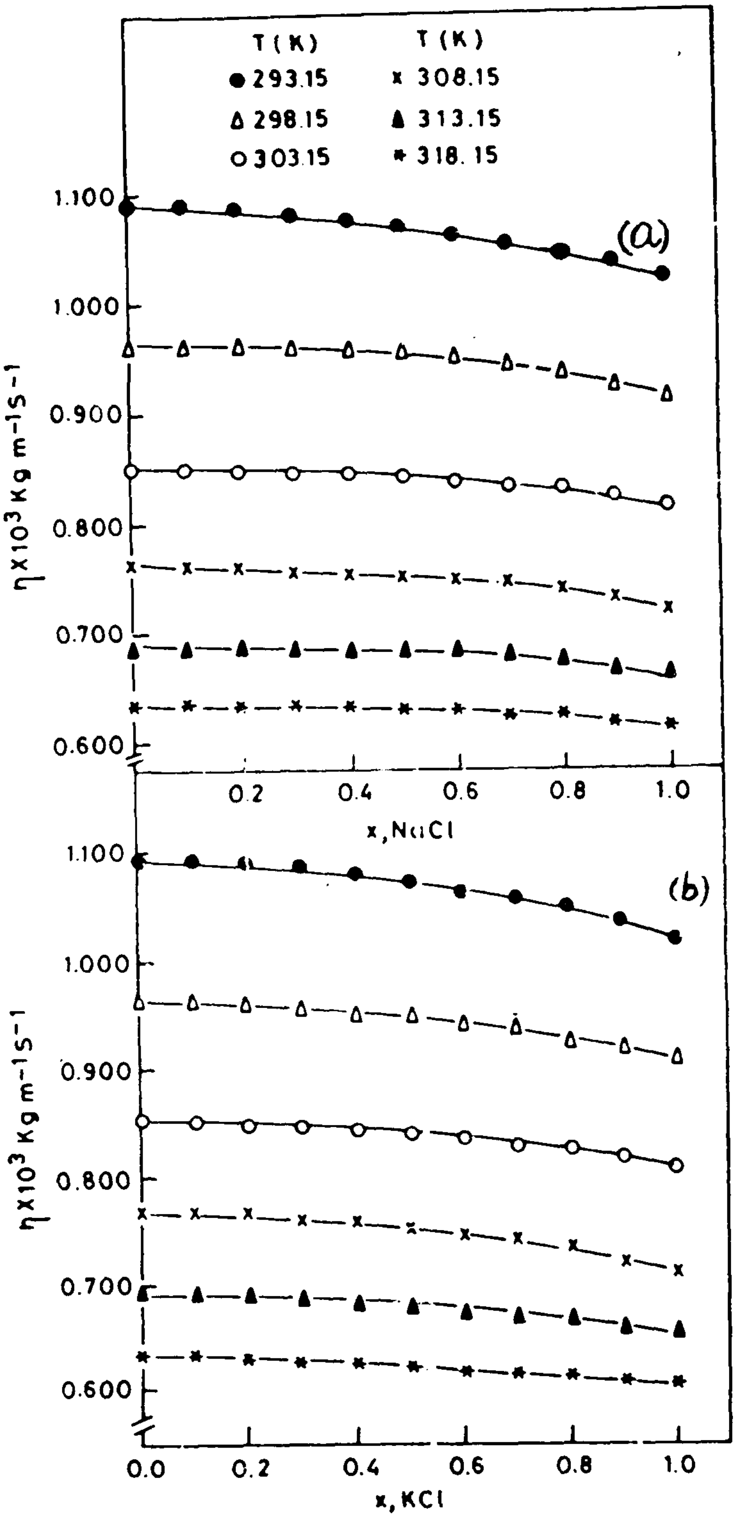
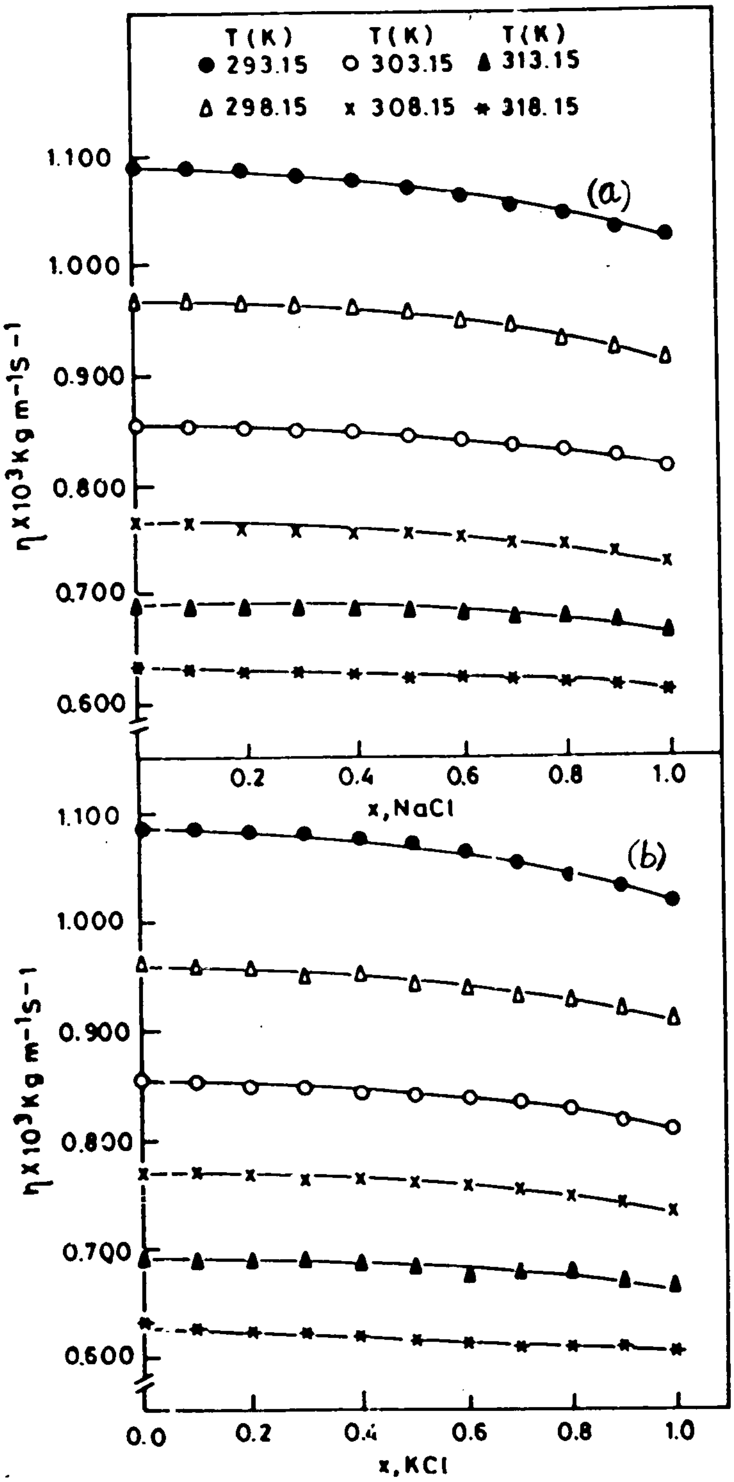
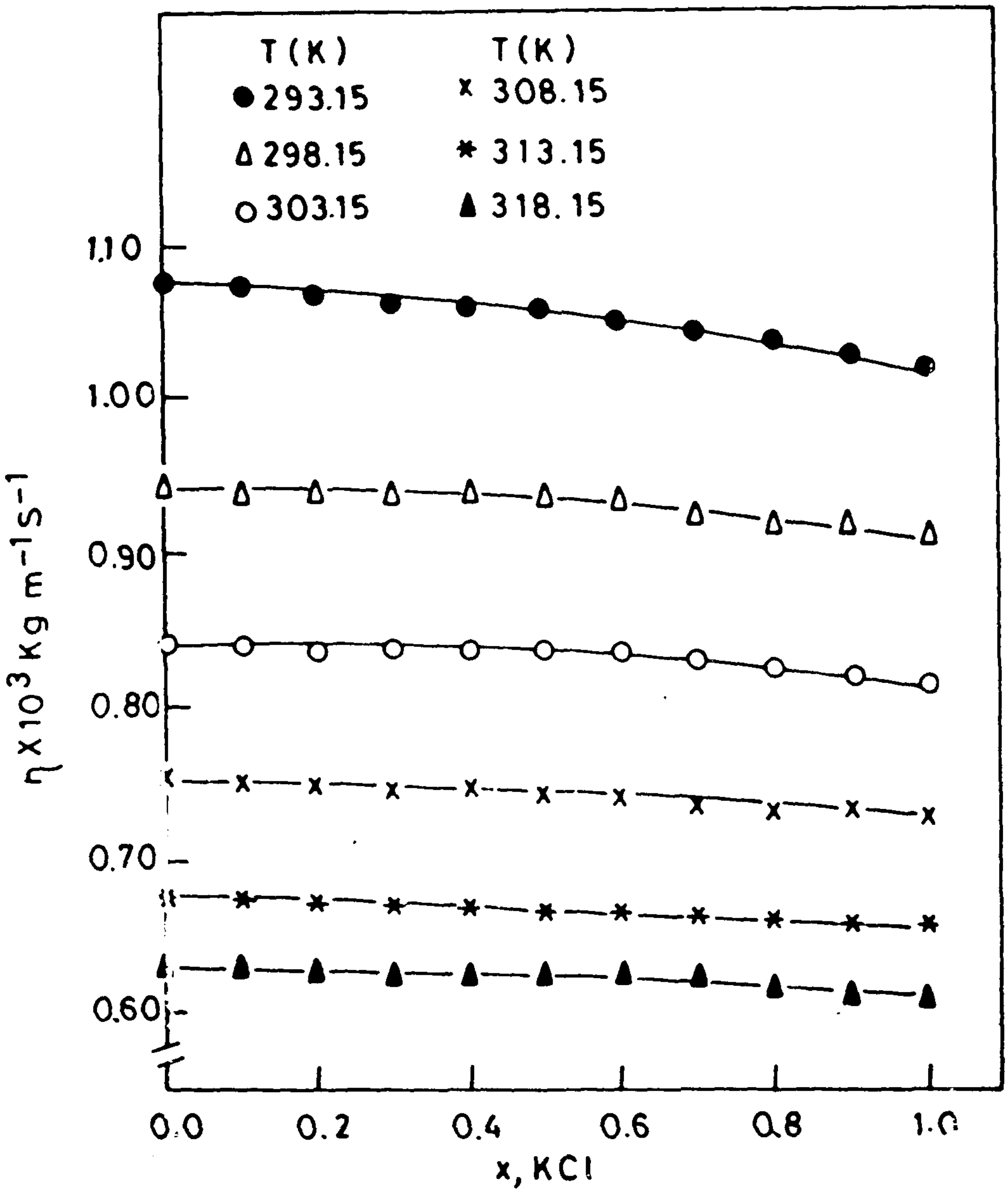


Fig. 1. (i) Plots of viscosity vs mole fraction of NaCl/KCl of (a) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ and (b) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of viscosity vs mole fraction of NaCl/KCl of (a) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ systems at several temperatures.



(iii) Plots of viscosity vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$ systems at several temperatures.

The concentration dependence of viscosity has been studied by using the polynomial equation,

$$[4.1] \qquad \eta = \sum_{i=o}^{2} \eta_i x^i$$

where the terms have their usual meanings.

The coefficients are listed in Table 2 alongwith the standard deviation. Such a small magnitude of deviation suggests the suitability of the said expression for explaining the concentration dependence of viscosity in the systems under investigation.

The excess viscosity is defined by the relation,

$$[4.2] \qquad \eta^1 = \eta - [\eta_1 x + \eta_2 (1-x)]$$

where η_1 and η_2 are the viscosities of the pure components. The low positive values of η^1 in most of the cases (Table 3) may be attributed to the formation of weak and unstable complexes due to weak interactions. The plots of η^1 versus mole fraction (Fig. 2) also suggest weak interactions. The maximum in each of the curves lies nearly at $x = 0.5$ and decreases with increase in salt concentration due to change in the solvation of aminoacids.

The η^1 values have been fitted to the Redlich Kister equation [13],

$$[4.3] \qquad \eta^1 = x(1-x) = \sum_{i=0}^{3} a_k \{x-(1-x)\}^k$$

in which a_k is an adjustable parameter. The coefficients alongwith the standard deviations are listed in Table 4.

In addition, rheochor [R] values have been obtained by using the following relation [14].

TABLE 2 Least-squares fitted parameters of equation $\eta = \sum_{i=0}^{2} \eta_i x^i$ as functions of temperature and compositon for the following systems

(a) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

T(K)	η_0	$\eta_1 \times 10^2$	$\eta_2 \times 10^2$	$\sigma\eta \times 10^3$
293.15	1.069	-1.305	-3.410	2.3
298.15	0.939	-0.978	-2.119	1.7
303.15	0.839	-2.787	-0.266	1.7
308.15	0.750	-4.170	2.022	1.3
313.15	0.675	-1.720	0.355	1.0
318.15	0.629	-0.790	-1.570	1.6

(b) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	η_0	$\eta_1 \times 10^2$	$\eta_2 \times 10^2$	$\sigma\eta \times 10^3$
293.15	1.089	-1.800	-4.920	2.2
298.15	0.964	-1.900	-3.260	1.8
303.15	0.853	-1.160	-2.450	1.7
308.15	0.763	-0.664	-3.495	3.9
313.15	0.692	-0.025	-2.550	2.9
318.15	0.632	-0.864	-1.026	1.9

(c) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	η_0	$\eta_1 \times 10^2$	$\eta_2 \times 10^2$	$\sigma\eta \times 10^3$
293.15	1.088	-1.730	-5.140	1.8
298.15	0.961	-2.400	-2.600	2.2
303.15	0.853	-1.570	-2.540	1.5
308.15	0.765	-0.530	-3.770	2.3
313.15	0.691	-4.190	1.310	1.3
318.15	0.632	-5.171	2.690	2.1

(d) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	η_0	$\eta_1 \times 10^2$	$\eta_2 \times 10^2$	$\sigma \eta \times 10^3$
293.15	1.095	−1.808	−4.975	1.7
298.15	0.962	−2.522	−2.171	1.5
303.15	0.853	−2.646	−1.014	1.5
308.15	0.766	−3.102	−1.221	1.5
313.15	0.693	−3.199	−0.181	1.0
318.15	0.637	−1.935	−0.590	1.9

(e) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	η_0	$\eta_1 \times 10^2$	$\eta_2 \times 10^2$	$\sigma \eta \times 10^3$
293.15	1.096	−1.618	−5.357	2.2
298.15	0.965	−2.488	−3.145	1.5
303.15	0.854	−1.037	−3.168	1.5
308.15	0.769	−3.708	−0.509	1.5
313.15	0.694	−2.188	−1.310	1.4
318.15	0.637	−1.904	−1.131	1.6

TABLE 3 Excess viscosity (η^E x 10^2) as functions of temperature and composition for the following systems :

(a) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		0.90	–0.07	–0.09	0.02	–0.80	0.23
C		0.38	0.24	0.12	0.14	–0.16	0.46
D		0.27	0.46	0.23	0.06	–0.24	0.09
E		0.56	0.58	0.04	0.08	–0.32	0.22
F		0.95	0.80	0.15	–0.10	–0.50	0.35
G		0.64	0.22	0.16	–0.18	–0.58	0.48
H		0.10	0.24	0.07	–0.26	–0.66	0.61
I		0.73	0.26	0.18	–0.14	–0.54	0.14
J		–0.08	0.38	0.09	–0.19	–0.42	–0.03

(b) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		0.46	0.31	0.01	–0.03	0.08	–0.26
C		0.91	0.41	0.32	0.24	0.16	–0.32
D		0.60	0.80	0.43	0.31	0.24	–0.78
E		1.31	0.91	0.44	0.58	0.32	0.06
F		1.45	0.61	0.55	0.95	0.50	0.20
G		0.91	0.61	0.76	0.12	0.58	0.34
H		0.76	0.91	0.87	0.14	0.66	0.48
I		0.81	0.10	0.78	0.16	0.84	0.52
J		–0.04	0.11	0.28	0.13	0.52	0.16

(c) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		0.18	−0.24	−0.35	0.18	−0.48	−0.09
C		0.45	0.00	0.22	0.36	−0.58	−0.79
D		0.92	0.36	0.38	0.34	−0.47	−0.79
E		0.13	0.81	0.54	0.82	−0.25	−0.99
F		0.12	0.36	0.60	1.00	−0.47	−0.69
G		0.12	0.61	0.76	1.08	−0.34	−0.59
H		0.79	0.86	0.72	1.16	−0.32	−0.49
I		0.27	0.61	0.49	1.34	−0.22	−0.29
J		0.04	0.51	0.29	0.72	−0.20	−0.19

(d) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		0.24	−0.09	−0.18	−0.12	0.02	0.25
C		0.66	0.12	0.03	0.15	−0.07	0.08
D		1.08	0.12	0.04	0.12	−0.06	0.13
E		1.20	0.42	0.15	0.19	0.05	0.16
F		1.12	0.52	0.36	0.36	0.16	0.21
G		1.44	0.62	0.37	0.33	−0.13	0.15
H		1.06	0.52	0.28	0.64	−0.12	0.09
I		1.18	0.62	0.49	0.27	0.09	0.03
J		0.90	0.11	0.51	0.24	0.17	0.03

(e) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	293.15	298.15	303.15	308.15	313.15	318.15
B		0.01	0.47	0.17	0.19	0.22	0.19
C		0.10	0.82	0.53	0.47	0.43	0.29
D		1.34	0.87	0.49	0.25	0.44	0.28
E		1.28	0.82	0.75	0.23	0.35	0.26
F		1.42	0.97	0.81	0.01	0.26	0.35
G		1.36	0.62	0.97	0.09	0.27	0.25
H		1.50	0.77	0.83	−0.13	0.08	0.14
I		1.44	0.32	0.89	−0.15	−0.21	0.12
J		1.28	0.57	0.70	−0.26	−0.20	0.02

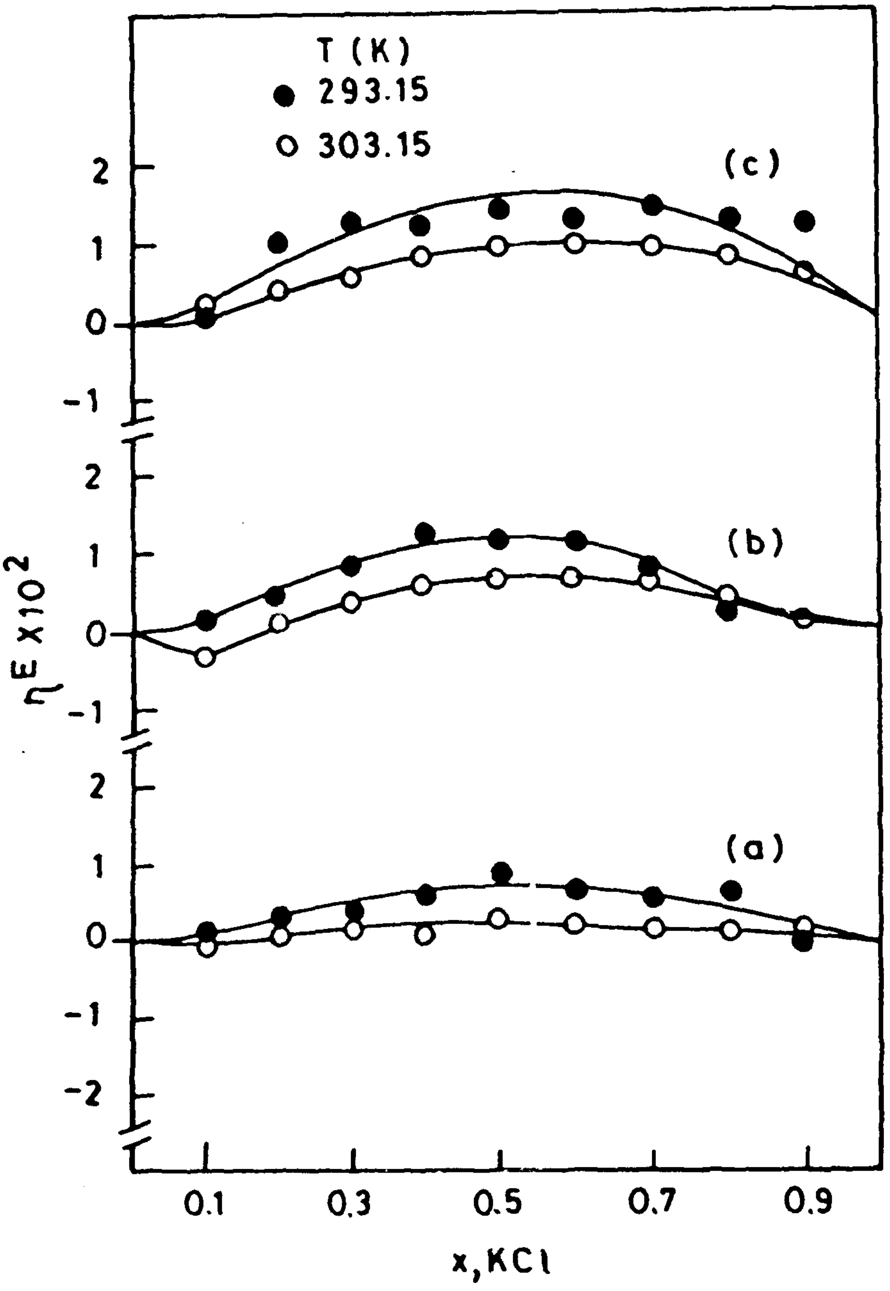
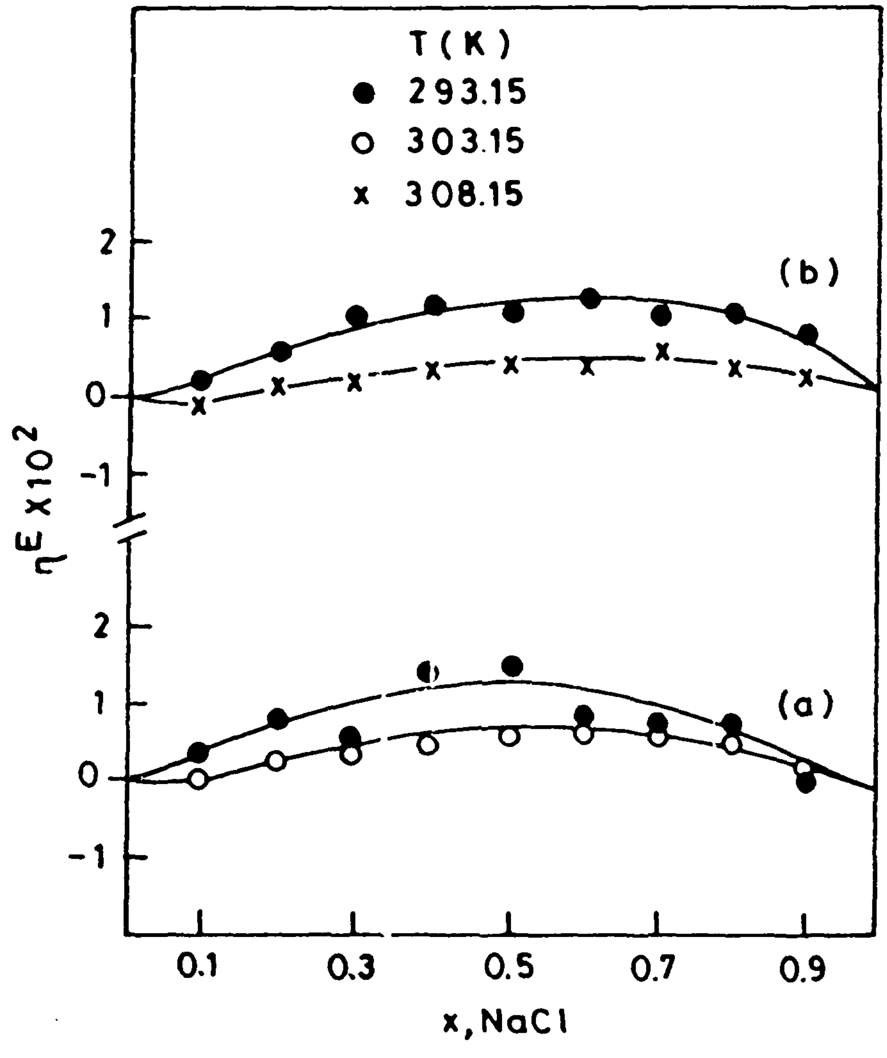


Fig. 2. (i) Plots of excess viscosity vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $KCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of excess viscosity vs mole fraction of NaCl of (a) x $NaCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (b) x $NaCl_{(aq)}$ + (1-x) $Threonine_{(aq)}$ systems at several temperatures.

TABLE 4 Correlation coefficients of equation, $\eta^E = x\,(1-x)\sum_{K=0}^{3} a_K\,(x-(1-x))^K$ for the following systems :

(a) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

T(K)	a_0	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	S.D.x10^2
293.15	0.028	1.546	−3.370	−3.739	1.4
298.15	0.021	−3.406	−0.821	1.273	0.5
303.15	0.007	−0.843	−0.628	3.229	0.4
308.15	0.002	−2.028	−0.849	0.985	0.3
313.15	0.016	2.447	−0.385	7.184	0.6
318.15	0.013	0.368	−0.432	3.132	0.4

(b) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	a_0	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	S.D.x10^2
293.15	0.049	0.453	−2.526	−4.718	1.2
298.15	0.032	−0.590	−1.920	−1.300	0.9
303.15	0.025	1.376	2.448	4.982	0.2
308.15	0.021	−2.146	−2.513	5.931	0.8
313.15	0.019	0.958	2.576	0.389	0.3
318.15	0.005	6.948	−1.386	−6.315	0.8

(c) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	a_0	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	S.D.x10^2
293.15	0.026	0.538	1.356	7.887	0.7
298.15	0.051	−0.538	−6.471	−0.474	0.4
303.15	0.028	−0.432	−0.619	1.202	1.6
308.15	0.038	5.224	2.349	−1.923	0.6
313.15	0.013	−4.233	−2.139	−0.031	0.3
318.15	0.033	−3.661	−1.168	−0.012	0.2

(d) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	a_0	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	S.D.$\times 10^2$
293.15	0.058	3.107	−4.497	−5.490	1.3
298.15	0.023	3.135	−2.535	−2.498	1.9
303.15	0.010	0.382	1.240	6.634	1.1
308.15	0.012	−0.061	1.565	1.565	0.7
313.15	0.001	1.380	1.617	1.820	0.3
318.15	0.005	4.130	1.231	−2.814	1.1

(e) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	a_0	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	S.D.$\times 10^2$
293.15	0.070	2.550	−6.470	−2.767	2.0
298.15	0.031	−3.146	3.431	5.641	0.8
303.15	0.032	−0.808	3.087	4.928	0.4
308.15	0.008	−2.198	−1.379	−1.709	0.5
313.15	0.014	−2.224	−1.928	−1.309	0.3
318.15	0.011	−4.860	0.122	−1.121	0.2

[4.4] $$[R] = \frac{M}{\rho} \eta^{1/8} = V\eta^{1/8}$$

The terms have their usual meanings.

The rheochor values have been found to decrease with increase in temperature as well as with increase in salt concentration. These values were fitted to the polynomial equation,

[4.5] $$[R] = \sum_{i=0}^{2} R_i x^i .$$

The least-squares fitted parameters are presented in Table 5 together with the corresponding standard deviations.

The excess rheochor function $[R^E]$ has been very sensitive to the molecular interactions and is defined as

[4.6] $$[R^E] = [R] - [R^{id}] = R - \{ x [R_1] + (1-x) [R_2]\}$$

like any of the excess properties. The $[R_1]$ and $[R_2]$ are the rheochor of the pure components. The $[R^E]$ values are given in Table 6 and are found to be generally positive. Fig. 3 displays the characteristic plots for the relative increase in interaction. The positive values of $[R^E]$ with small magnitudes suggests that the complex formation is either totally absent or weakly possible giving rise to unstable entities. The maximum in each of the curves lie between, x = 0.5-0.6 and gradually decreases with increase in salt concentration. The curves become somewhat flattened at higher temperatures.

In order to check the additivity of rheochor, the viscosity values were compued by using the following equation :

[4.7] $$\eta = \left\{\frac{R_1 x + R_2(1-x)}{V_1 x + V_2(1-x)}\right\}^8$$

TABLE 5 Correlation coefficients of equaiton 3 for the following systems :

(a) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

T(K)	$[R_0]$	$[R_1 \times 10^2]$	$[R_2 \times 10^2]$	$\sigma [R] \times 10^3$
293.15	10.287	-1.26	-6.55	12.7
298.15	10.137	-2.50	-4.22	3.0
303.15	9.997	-2.85	-3.51	4.1
308.15	9.882	-10.24	6.04	7.7
313.15	9.770	-2.30	-2.70	3.1

(b) x $NaCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	$[R_0]$	$[R_1 \times 10^2]$	$[R_2 \times 10^2]$	$\sigma [R] \times 10^3$
293.15	10.345	-8.85	-8.32	7.9
298.15	10.199	-7.83	-7.98	3.6
303.15	10.056	-4.14	-9.94	3.9
308.15	9.937	-0.03	-4.68	13.0
313.15	9.838	-9.70	-3.65	5.7

(c) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

T(K)	$[R_0]$	$[R_1 \times 10^2]$	$[R_2 \times 10^2]$	$\sigma [R] \times 10^3$
293.15	10.353	-15.27	9.96	3.0
298.15	10.201	-13.87	-1.24	3.4
303.15	10.062	-11.34	-1.20	6.8
308.15	9.942	-8.28	-3.53	6.0
313.15	9.838	-18.62	7.07	3.6

(d) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	$[R_0]$	$[R_1 \times 10^2]$	$[R_2 \times 10^2]$	$\sigma [R] \times 10^3$
293.15	10.455	–21.49	–5.49	4.2
298.15	10.297	–25.53	0.35	5.5
303.15	10.158	–25.76	1.40	4.1
308.15	10.038	–25.76	–0.24	5.7
313.15	9.935	–27.37	3.81	4.6

(e) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

T(K)	$[R_0]$	$[R_1 \times 10^2]$	$[R_2 \times 10^2]$	$\sigma [R] \times 10^3$
293.15	10.454	–16.23	–7.83	4.3
298.15	10.301	–17.78	–5.74	3.8
303.15	10.156	–15.58	–6.13	5.4
308.15	10.043	–21.32	–1.31	3.8
313.15	9.933	–18.14	–3.39	4.2

TABLE 6 Excess Rheochor ($|R^E| \times 10^2$) as functions of temperature and composition for the following systems

(a) x $NaCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	298.15	303.15	308.15	313.15	318.15
B	0.81	0.61	0.71	0.00	0.40
C	0.61	1.21	0.41	–0.04	0.80
D	0.41	1.81	1.07	0.68	1.21
E	1.21	1.41	0.82	0.32	1.60
F	1.20	1.61	1.51	0.41	1.01
G	1.81	1.62	1.37	0.36	1.00
H	1.61	1.20	0.91	0.02	0.81
I	0.41	0.81	0.61	0.05	0.21
J	0.21	0.40	0.30	0.00	0.20

(b) x $KCl_{(aq)}$ + (1 - x) $Glycine_{(aq)}$

x T(K)	298.15	303.15	308.15	313.15	318.15
B	0.82	0.62	0.52	0.20	0.14
C	0.62	1.23	1.02	0.78	0.81
D	1.42	1.82	1.52	0.52	0.22
E	1.22	1.42	2.01	0.67	0.61
F	2.01	2.01	2.52	1.02	1.02
G	1.82	1.62	3.02	1.20	1.42
H	2.62	1.83	2.52	0.97	1.81
I	2.41	1.82	2.02	0.83	2.21
J	0.23	0.40	1.51	0.61	0.61

(c) x $KCl_{(aq)}$ + (1 - x) $Leucine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		0.68	−0.41	0.31	0.20	0.12
C		0.82	−0.76	0.61	0.42	0.22
D		1.23	0.22	0.91	1.00	1.32
E		1.26	0.61	1.22	1.81	2.42
F		0.28	0.30	0.51	1.17	3.52
G		1.25	0.41	0.80	1.21	3.62
H		0.09	0.81	1.11	1.42	4.72
I		0.20	0.53	1.40	1.39	3.92
J		0.40	0.27	1.00	0.81	4.82

(d) x $NaCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		−0.16	−0.32	−0.42	−0.25	0.47
C		0.68	0.27	−0.07	0.40	0.87
D		0.48	−0.12	−0.42	−0.10	−0.73
E		1.27	−0.52	−0.93	1.18	−0.32
F		1.08	−0.07	−0.42	0.77	0.07
G		1.88	0.68	0.07	0.28	−0.53
H		1.68	0.28	0.58	0.98	−0.13
I		1.46	0.87	0.75	0.68	0.27
J		1.28	0.48	0.57	0.40	0.67

(e) x $KCl_{(aq)}$ + (1 - x) $Threonine_{(aq)}$

x	T(K)	298.15	303.15	308.15	313.15	318.15
B		1.06	0.37	0.40	0.27	0.16
C		1.06	1.67	0.67	0.48	1.26
D		1.06	1.25	0.97	0.66	1.36
E		0.06	1.26	1.26	0.87	1.46
F		0.07	1.06	1.57	0.92	0.56
G		0.06	0.88	1.87	0.27	0.66
H		−1.93	1.17	2.16	0.46	0.77
I		−1.93	0.90	2.46	0.65	−0.14
J		0.05	0.76	1.76	−0.13	−0.08

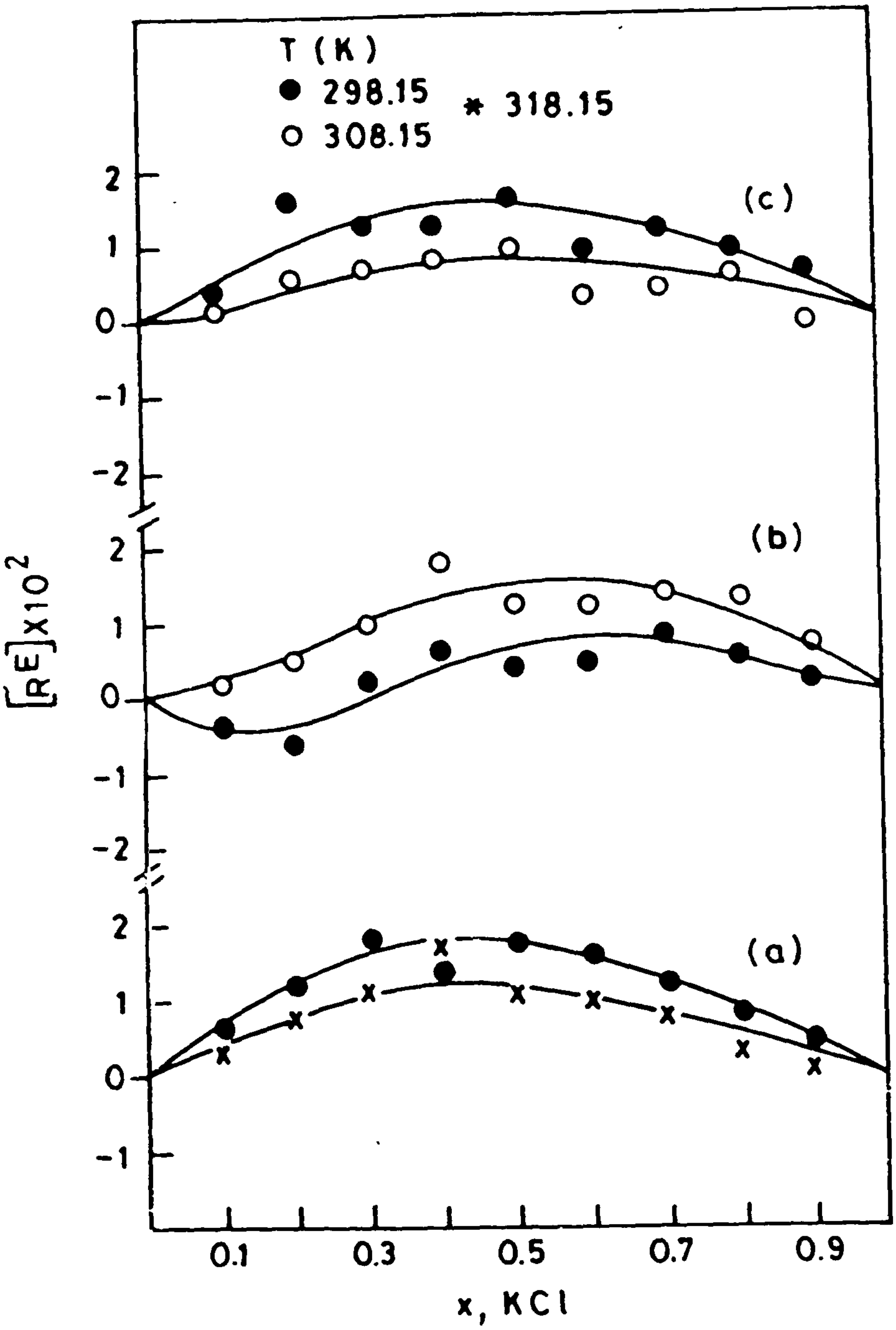
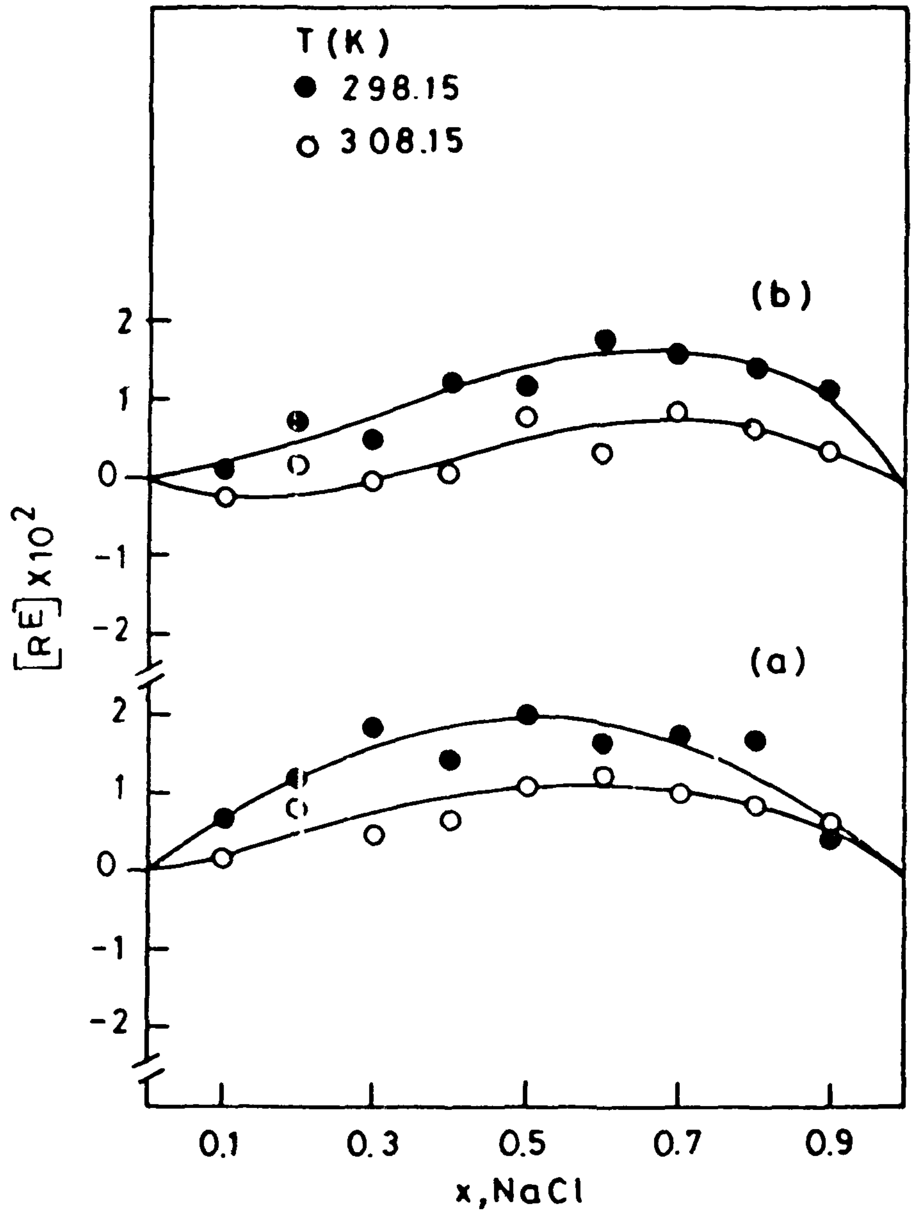


Fig. 3. (i) Plots of excess rheochor vs mole fraction of KCl of (a) x $KCl_{(aq)}$ + (1-x) $Glycine_{(aq)}$, (b) x $KCl_{(aq)}$ + (1-x) $Leucine_{(aq)}$ and (c) x $KCl_{(aq)}$ – (1-x) $Threonine_{(aq)}$ systems at several temperatures.



(ii) Plots of excess rheochor vs mole fraction of NaCl of (a) x $\mathrm{NaCl_{(aq)}}$ + (1-x) $\mathrm{Leucine_{(aq)}}$ and (b) x $\mathrm{NaCl_{(aq)}}$ + (1-x) $\mathrm{Threonine_{(aq)}}$ systems at several temperatures.

The results listed in Table 1 support the additive nature of rheochor values in all the systems under investigation.

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