

Thermodynamic Properties of Serine in Aqueous Sodium Chloride Solutions AT 303.15, 308.15 and 313.15K.”

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Abstract: Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for serine in aqueous sodium chloride at 303.15, 308.15 and 313.15K. Using the experimental values, thermodynamic parameters such as adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f), relative association (R_A) have been estimated using the standard relations. The results have been analyzed on the basis of variations of thermodynamic parameters. These parameters have been interpreted the molecular interactions in terms of solute-solute and solute-solvent interaction present in the given solutions

Keywords: Serine, sodium chloride mixture, ultrasonic velocity(u), density(ρ), viscosity (η),acoustical parameters

1. Introduction

Ultrasound can be viable technology because it is readily available and can be used for wide range of application in different fields like consumer industries, pharmaceuticals, medical field process industries, chemical industries, physics etc. [1-3]. In chemistry, ultrasound velocity along with related thermo acoustic parameters have been extensively used in the recent past to study molecular interactions in binary and ternary liquid mixtures by a number of researchers [4-7]. Many researchers have used ultrasound to investigate the ion-solvent interactions in aqueous solutions containing electrolytes. Literature survey on ultrasound velocity measurement shows that very little work has been done for solid organic compounds [8-10]. Thus, in present paper we have used this technique for the better understanding of the molecular interactions in some solutions. Thus, in continuation of previous work [11-13], the density, viscosity and ultrasonic velocity of electrolytes solutions in aqueous amino acids are measured a 303.15, 308.15 K&313.15K over a wide concentration range. The experimental data is used for the evaluation of various thermodynamic and acoustical parameters by which molecular interactions in solutions are interpreted.

2. Materials and Methods

All the chemicals used were of AR grade and dried over anhydrous CaCl_2 in desiccators before use. All solutions were prepared in deionized and distilled water (degassed by boiling), having specific conductivity 10^{-6} S cm^{-1} . The stock solutions of 1M concentration were prepared by weighing NaCl and MgCl_2 on a digital balance with an accuracy of 1×10^{-5} g Solutions were kept in the special air tight bottles and were used within 12 hrs. The ultrasonic velocities in pure solvent as well as in mixed solutions were measured using single frequency ultrasonic interferometer (Model-F-81, supplied by Mittal Enterprises, New Delhi) at a constant frequency 2 MHz. The temperature of the solutions placed in the interferometer cell changed through 5°C (from 303.15.15K to 313.15K) by circulating water around the cell

from a thermostat. The interferometer was calibrated against the ultrasonic velocity of water used at $T = 303.15\text{K}$. The present experimental value is 1508.80 ms^{-1} which is in good agreement with literature value 1509.55 ms^{-1} . Accuracy in the velocity measurement was 1.0 ms^{-1} . The viscosity of the solutions at different temperatures and concentrations were measured with Ostwald's viscometer apparatus. The density measurements were made by a 25 ml specific gravity bottle, the accuracy in density measurements was found to be $\pm 0.001 \text{ g/cc}$.

3. Theory and calculations

Various acoustic and thermodynamic parameters used in the present study are computed [14] using following relations.

$$\text{Ultrasonic velocity } u = n \times \lambda \text{ ms}^{-1} \quad (1)$$

$$\text{Adiabatic compressibility } \beta_a = 1/u^2 \rho \text{ m}^2 \text{N}^{-1} \quad (2)$$

Where u and ρ are ultrasonic velocity and density of aqueous solution of electrolytes

$$\text{Acoustic impedance } Z = u \rho \text{ kg m}^{-1} \text{s}^{-1} \quad (3)$$

$$\text{Intermolecular free } L_f = K / u \cdot \rho \text{ A}^0 \quad (4)$$

Where k is Jacobson's temperature dependent constant

$$\text{Temp } 303 \quad 308 \quad 313 \quad 318$$

$$k \times 10^4 \quad 6.31 \quad 6.36 \quad 6.42 \quad 6.47$$

$$\text{Relative association } R_A = (\rho / \rho_0) \cdot (u_0 / u)^{1/2} \quad (5)$$

ρ_0 , ρ and u_0 , u are the density and ultrasonic velocity of solvent and solution respectively

4. Results and Discussions

The experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) of the solutions and calculated values of acoustical parameters such as adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A) are reported in Table -1 for the systems (water + NaCl + serine) and the graph plotted for ultrasonic velocity (u), adiabatic

compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A) at different temperatures and various concentrations at 2 MHz frequency for the systems (water + NaCl + serine) are shown in Fig.1 to Fig.5.

Table 1: Variation of thermodynamic parameters at different mole fractions (x) and different temperatures for the system (Water + NaCl + Serine) at 2MHz.

m mol kg ⁻¹	u ms ⁻¹	ρ Kg m ⁻³	η Nm ⁻² s	$\beta \times 10^{-10}$ m ² N ⁻¹	$z \times 10^{-6}$ Nm ⁻²	L_f A ⁰	R_A
303.15K							
0.000	1551.80	1058.11	1.06195	3.92502	1.64180	0.41120	1.05285
0.008	1564.88	1064.54	1.16268	3.83071	1.66816	0.40623	1.05785
0.017	1593.18	1078.71	1.37615	3.65472	1.71745	0.39679	1.06339
0.026	1601.16	1081.52	1.55944	3.60831	1.73085	0.39426	1.06458
0.034	1618.12	1087.01	1.61528	3.51368	1.75890	0.38905	1.06674
0.043	1651.64	1094.01	1.87772	3.35085	1.80689	0.37994	1.06630

m mol kg ⁻¹	u ms ⁻¹	ρ Kg m ⁻³	η Nm ⁻² s	$\beta \times 10^{-10}$ m ² N ⁻¹	$z \times 10^{-6}$ Nm ⁻²	L_f A ⁰	R_A
308.15 K							
0.000	1560.51	1055.11	0.98731	3.89242	1.64634	0.41319	1.05255
0.008	1574.20	1063.22	1.07613	3.79621	1.67697	0.40805	1.06534
0.017	1603.15	1068.12	1.09777	3.64314	1.71219	0.39974	1.06552
0.026	1613.80	1080.25	1.18695	3.55532	1.74290	0.39489	1.07749
0.034	1628.30	1086.42	1.42941	3.47906	1.76833	0.39029	1.08348
0.043	1664.20	1090.24	1.45927	3.31264	1.81398	0.38117	1.08747

m mol kg ⁻¹	u ms ⁻¹	ρ Kg m ⁻³	η Nm ⁻² s	$\beta \times 10^{-10}$ m ² N ⁻¹	$z \times 10^{-6}$ Nm ⁻²	L_f A ⁰	R_A
313.15K							
0.000	1583.60	1053.38	0.95536	3.78693	1.66753	0.41060	1.04796
0.008	1587.80	1061.78	0.94504	3.73852	1.68466	0.40797	1.05499
0.017	1609.83	1064.25	1.08785	3.62665	1.71286	0.40182	1.05313
0.026	1615.76	1079.66	1.16157	3.54591	1.74341	0.39556	1.06667
0.034	1648.04	1083.70	1.27930	3.39967	1.78482	0.38904	1.06360
0.043	1695.10	1088.39	1.36861	3.19889	1.84427	0.37738	1.05854

Where m , mole fraction; ρ , density of the solution; η , viscosity of solution; u , ultrasonic velocity; β_a , adiabatic compressibility; z , acoustic impedance; L_f , intermolecular free length; R_A , relative association.

1) Ultrasonic Velocity (u):

From Table it is seen that ultrasonic velocity increases with increase in concentration of solutes serine. The variation of ultrasonic velocity in a solution depends on the intermolecular free length (L_f). Intermolecular free length is a predominant factor, as it determines the sound velocity in fluid state. Presence of an ion alters the intermolecular free length. Therefore, ultrasonic velocity of a solution will be different from that of the solvent.

According to model proposed by Eyring and Kincaid [15,16] the increase in ultrasonic velocity with the decrease in intermolecular free length (L_f) and vice versa, Consequently ultrasonic velocity of system increases depending on the structural properties of solutes. The solute that increases the ultrasonic velocity is of structure maker type (SM). The variations in ultrasonic velocity with molar concentrations of NaCl in 1M serine are given in Tables 1. From Tables 1 & Fig.1 (water + NaCl + serine), it is seen

that ultrasonic velocity in aqueous NaCl solution increases with increase in concentration of solutes serine. The ultrasonic velocity in aqueous NaCl is maximum at temperature 313.15K and minimum at 303.15K. Such an increase in ultrasonic velocity clearly shows that molecular association is being taking place in this liquid system. Such type of variation in the sound velocity is attributed to different types of interactions taking place in the solutions. These interactions are as follows.

- Ionic group of serine i.e. zwitter ionic centers of serine with Na⁺, Cl⁻ and Mg⁺⁺ ions.
- NH₂ group (hydrophilic) of serine through H-bonding.
- CH₃-CH-OH group (hydrophobic) of serine, non polar molecules.
- COO⁻ and NH₃ or NH₂ of serine and ions of solvents.

These different types of interactions affect the solute solvent interactions. The ultrasonic velocity increases with molar concentration of solute as well as rise in temperature. The increase in ultrasonic velocity in water, in aqueous NaCl may be attributed to the overall increase in cohesion brought about by the solute-solute, solute-solvent and solvent-solvent interactions²¹.

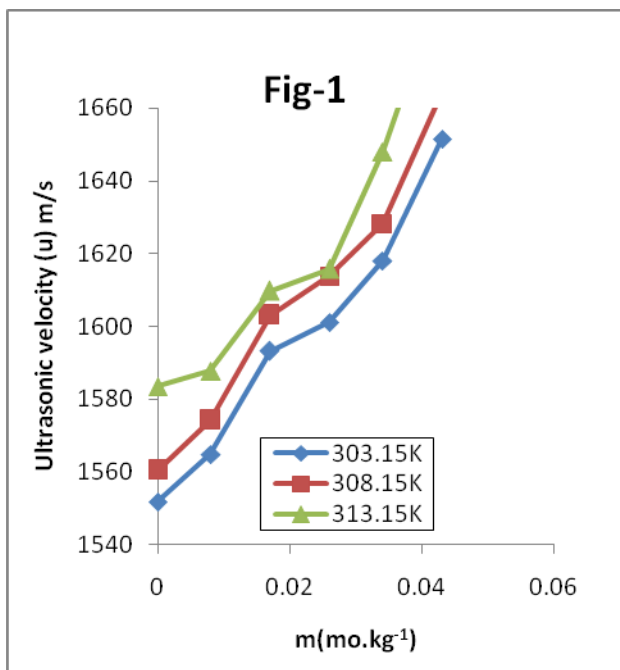


Figure 1: Plot of ultrasonic velocity (u) against mole fraction (m) for the system (water + NaCl + serine) at 2MHz and at 303.15, 308.15 and 313.15K temperatures.

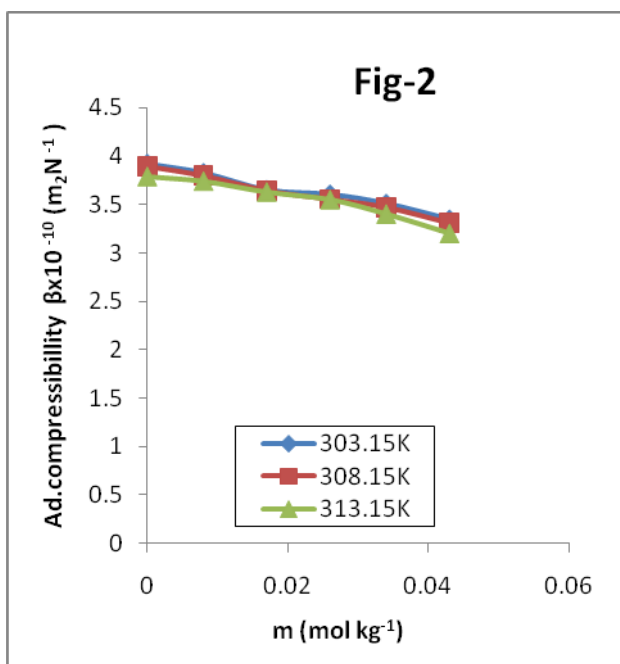


Figure 2: Plot of adiabatic compressibility (β_a) against mole fraction for the system (water+ NaCl + serine) at 2MHz and at 303.15, 308.15 and 313.15K temperatures.

2) Adiabatic Compressibility (β_a):

In the present case, adiabatic compressibility (β_a) decreases with increase in concentrations of serine as shown in Fig.2 (water + NaCl +serine). This is because as the concentrations of solute increases, a larger portion of water molecules are electrostatic and the amount of bulk water decreases causing the compressibility to decrease [17]. When an amino acid is added to a solvent, its compressibility decreases and this decrease is due to the interaction between the ions and the water molecules. The values of adiabatic compressibility are maximum in water, moderate in aqueous NaCl.

3) Acoustic Impedance (z):

Acoustic impedance is calculated by using Eq. (5). From Table - 1(water + NaCl +serine) and Fig.3(water + NaCl +serine), it is observed that for a given concentration, the values of acoustic impedance (z) increases with increase in concentrations. The increase in acoustic impedance (z) with the increase in concentration of solution can be explained on the basis of hydrophobic interaction between solute and solvent molecules [18, 19]which increases the intermolecular distance, making relatively wider gap between the molecules. This also indicates significant interactions in the systems of serine in aqueous NaCl as a co-solvent. The values of acoustic impedance are moderate in water and minimum in NaCl.

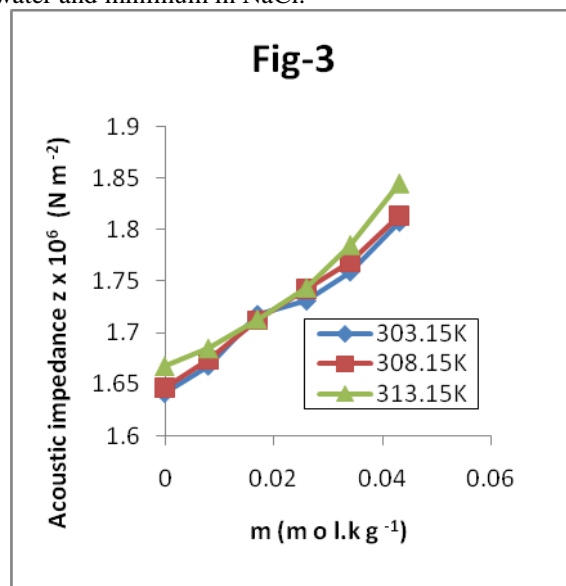


Figure 3: Plot of acoustic impedance (z) against mole fraction for the system (water +NaCl +serine) at 2MHz and at 303.15, 308.15 and 313.15K temperatures

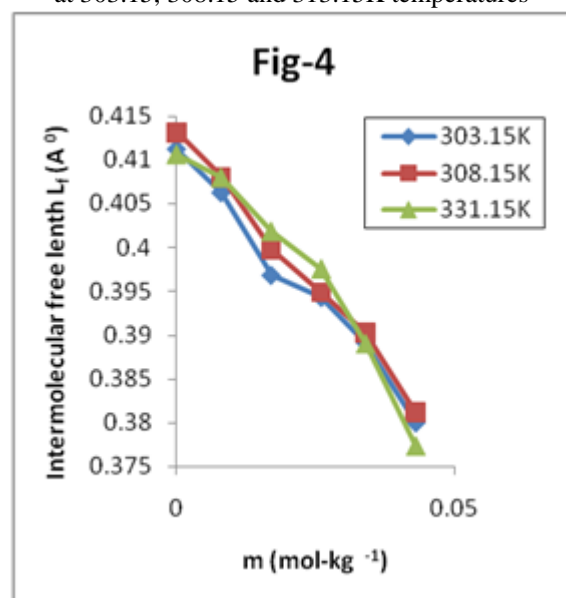


Figure 4: Plot of intermolecular free length (L_f) against mole fraction for the system (water +NaCl +serine) at 2MHz and at 303.15, 308.15 and 313.15K temperatures

4) Intermolecular Free Length (L_f)

The values of intermolecular free length for (water+ NaCl+serine) system have been calculated using Eq.(6). From

Table-1 & Fig.1 (water + NaCl + serine), it has been observed that, in the present investigation, intermolecular free length decreases linearly on increasing concentrations of solutes [20]. The decrease in L_f with increase of solutes concentrations in solution indicates that there are significant interactions between solute and solvent suggesting the structure promoting behavior of solutes. The decrease in intermolecular free length may be due to the gain of dipolar association, making up of hydrogen bonds in the molecules of the liquid mixtures. The values of intermolecular free length are maximum in water and minimum in aqueous NaCl.

5) Relative Association (R_A)

The values of relative association (R_A) for (water + NaCl + serine) system were calculated using Eq. (7). The property which can be studied to understand the molecular interaction is the relative association (R_A). It is influenced by two factors: (i) Breaking up of the associated solvent molecules on addition of solute in it and (ii) The solvation of solute molecule. The former leads to the decrease and later to the increase of relative association. From Table 1 (water + NaCl + serine), it is observed that, R_A increases with increase in the solute concentrations (serine) in the NaCl solution. The graphs for (R_A) versus mole fraction (m) of these systems were plotted as shown in Fig.5 (water + NaCl + serine). The values of relative association (R_A) are minimum in water, and maximum in aqueous NaCl.

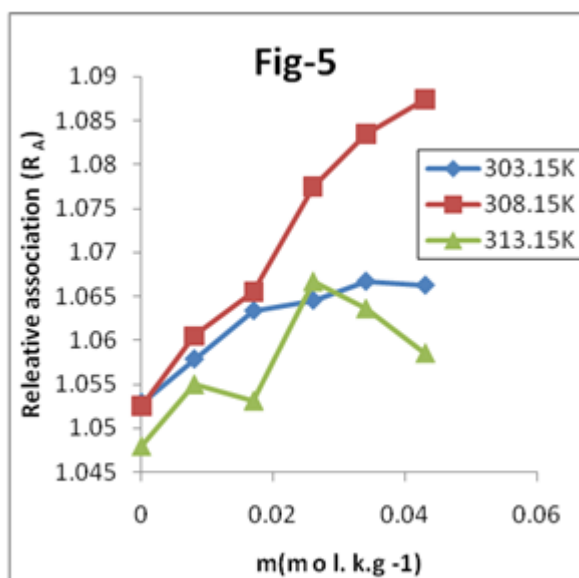


Figure 5: Plot of relative association (R_A) against mole fraction for the system (water + NaCl) + serine at 2MHz and at 303.15, 308.15 and 313.15K temperatures

5. Applications

The thermodynamic properties of a binary mixture such as viscosity and density are important for practical and theoretical points of view to understand liquid theory. Their properties are extremely useful for the design of process equipment in chemical industries and the data on some of the properties associated with the liquids and liquid mixtures

like density and viscosity find extensive application in solution theory and molecular dynamics.

6. Conclusions

Ultrasonic velocity, density and viscosity have been measured for serine in aqueous NaCl and $MgCl_2$ solution at 303.15, 308.15 and 313.15K. The variation in ultrasonic velocity, density and viscosity and other related thermodynamic parameters such as adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A), of serine at various concentrations and temperatures in both the NaCl – based system, shows the non-linear increase or decrease behavior. The non linearity confirms the presence of solute-solvent, ion-ion, dipole-dipole, ion-solvent interactions. The observed molecular interaction, complex formation, hydrogen bond formation are responsible for the heteromolecular interaction in the liquid mixture. This provides useful information about inter and intra molecular interactions of liquid systems.

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