



Full Length Research Article

ACOUSTICAL STUDIES ON MOLECULAR INTERACTIONS IN BINARY LIQUID SYSTEMS

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ABSTRACT

Molecular interaction studies using ultrasonic technique in binary liquid mixtures of amino acids with NaCl and MgCl₂ have been carried out at 303.15K. Using the measured values of ultrasonic velocity, density and viscosity, acoustical parameters and their excess values are evaluated. From the properties of these excess parameters the nature and strength of the interactions in these binary systems are discussed.

Key words:

Ultrasonic Velocity (u),
Density (ρ),
Viscosity (η),
Acoustical Parameters,
Binary Mixtures.

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INTRODUCTION

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behavior of liquid mixtures (Nikam *et al.*, 2001; Shipra Baluja and Swati Oza, 2001 and Ali *et al.*, 1996). This is because of its ability of characterizing physico-chemical behavior of liquid medium (Manisha Gupta and Shukla, 1996; Pankaj and Sharma, 1991 and Velmurugan *et al.*, 1987). The measurement of ultrasonic velocity have been adequately employed in understanding the molecular interactions in liquid mixtures. Molecular interaction studies can be carried out by both spectroscopic (Suryanarayana, 1983 and Fletcher, 1969) and non spectroscopic (Pimental and Maclellan, 1960 and Hobbs and Bates, 1952) techniques. However, ultrasonic velocity (Lin and Tsay, 1970) and viscosity (Kannappan *et al.*, 2008) measurements have been widely used in the field of interactions and structural aspect evaluation studies.

Experimental

All solutions were prepared in deionized and distilled water (degassed by boiling), having specific conductivity

$\sim 10^{-6}$ S cm⁻¹. The stock solutions of 1M concentration were prepared by weighing the serine on a digital balance with an accuracy of $\pm 1 \times 10^{-4}$ g. Solutions of NaCl and MgCl₂ were made by mass on the mole fraction scale. Ultrasonic velocity was measured with a single crystal interferometer (F- 81, Mittal Enterprises, New Delhi) at 2MHz. The interferometer was calibrated against the ultrasonic velocity of water used at T = 303.15K. 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 density measurements were performed with recalibrated specific gravity bottle with an accuracy of $\pm 2 \times 10^{-2}$ kg m⁻³. An average of triple measurements was taken into account. Sufficient care was taken to avoid any air bubble entrapment. Viscosity was measured with recalibrated Ostwald type viscometer. The flow of time was measured with a digital stop watch capable of registering time accurate to ± 0.1 s. An average of three or four sets of flow of times for each solution was taken for the purpose of calculation of viscosity. The accuracy of the viscosity measurements was ± 0.5 %. Accuracy in experimental temperature was maintained at ± 0.1 K by means of thermostatic water bath.

RESULTS AND DISCUSSION

From the measured values ultrasonic velocity (u), density (ρ) and viscosity (η) various acoustical parameters such as the

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adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A) were calculated by using the following relations¹³⁻¹⁶

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

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

$$\text{Acoustic impedance } (z) = u \cdot \rho \quad \text{--- (3)}$$

$$\text{Intermolecular free length } (L_f) = K / u \cdot \rho^{1/2} \quad \text{--- (4)}$$

$$\text{Relative association } (R_A) = (\rho / \rho_0) \cdot (u_0 / u)^{1/3} \quad \text{--- (5)}$$

Where, K is the temperature dependant Jacobson constant (Jacobson, 1952). The values of $K \times 10^4$ are taken as 207.556 $\times 10^{-8}$, 209.431 $\times 10^{-8}$ and 211.306 $\times 10^{-8}$ at 303.15, 308.15 and 313.15K. T is the absolute temperature, ρ_0 , ρ and u_0 , u are the density and ultrasonic velocity of solvent and solution respectively.

The excess parameters such as β_a^E , z^E , L_f^E , and R_A^E have been calculated using the following equations (Nikam *et al.*, 2000)

$$\text{Excess adiabatic compressibility } \beta_a^E = \beta_{\text{mix}} - [(1-x)\beta_{a1} + x\beta_{a2}] \quad \text{----- (6)}$$

$$\text{Excess acoustic impedance } z^E = z_{\text{mix}} - [(1-x)z_1 + xz_2] \quad \text{----- (7)}$$

$$\text{Excess intermolecular free length } L_f^E = L_{f\text{mix}} - [(1-x)L_{f1} + xL_{f2}] \quad \text{----- (8)}$$

$$\text{Excess relative association } R_A^E = R_{A\text{mix}} - [(1-x)R_{A1} + xR_{A2}] \quad \text{----- (9)}$$

Where, x- represents vol. fraction of the component and subscript 1 and 2 stands for components 1 and 2.

The experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) of the solutions are reported in Table 1 for the systems (water + NaCl +serine) and for the system (water+ MgCl₂ + serine) respectively.

(R_A^E) for liquid systems (1M NaCl+1M serine) and (1M MgCl₂+1M valine) at various volume fractions have been measured at constant frequency of 2 MHz and at different temperatures. From the Table 1, it is observed that as the concentration of liquid systems increases the ultrasonic velocity increases for both the systems studied.

Ultrasonic Velocity (u)

The ultrasonic velocity (u) for amino acid electrolytes solutions at 2MHz frequency and at different temperatures have been determined using relation (1) and presented in Tables 1. The variations in ultrasonic velocity in liquid mixtures depend on concentration (x) of solutes and temperatures Ultrasonic velocity (u) is related to, intermolecular free length. As the free length decreases due to the increase in concentrations of solutes, the ultrasonic velocity has to increase (Naidu *et al.*, 2001). The experimental results support the above statement in four liquid systems. Consequently, ultrasonic velocity of system increases depending on the structural properties of solutes.

The solute that increases the ultrasonic velocity is structure maker. Form Tables 1, ultrasonic velocity increases with increase in concentrations of solutes (1M serine, 1M valine) in liquid systems investigated such as (1M NaCl + 1M serine) and (1M MgCl₂ + 1M valine). The value of ultrasonic velocity of (1M NaCl + 1M serine) is less as compared to the value of (1M MgCl₂ + 1M valine). When NaCl or MgCl₂ is dissolved in solution, the sodium ion (Na⁺) or (Mg⁺⁺) has a structures breaking effect, would disrupt the water structure (Millero *et al.*, 1978 and Holiland, 1980). This makes the liquid medium less compressible and hence the ultrasonic velocity increases above that of pure value. The variation in ultrasonic velocity (u) in both systems with temperature shows following trend.

$$u_{1M MgCl_2} > u_{1M NaCl}$$

Table 1. Variation of thermodynamic parameters at different mole fractions (x) and different temperatures for the system (1MNaCl + 1Mserine) and (1MMgCl₂ + 1Mvaline) at 303.15K

m mol kg ⁻¹	u ms ⁻¹	ρ Kg m ⁻³	η Nm ⁻² s	$\beta^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	$z^E \times 10^{-6} \text{ Nm}^{-2}$	$L_f^E \text{ A}^0$	R_A^E
1MNaCl + 1MSerine							
0.0	1554.50	1056	1.0428	-0.51260	0.13784	-0.02467	0.05316
0.2	1561.70	1058	1.0507	-0.07836	0.02787	-0.00240	0.02372
0.4	1568.00	1060	1.0578	-0.06213	0.01178	-0.00167	0.01640
0.6	1570.04	1062	1.0605	0.43432	-0.13766	0.02564	-0.01719
0.8	1575.10	1064	1.0710	0.59783	-0.18526	0.03484	-0.01968
1.0	1586.08	1066	1.0810	0.89628	-0.25161	0.04331	-0.03554
1MMgCl ₂ + 1MSerine							
0.0	1558.80	1056	1.0628	-0.50800	0.14273	-0.02218	0.04931
0.2	1566.77	1063	1.0871	-0.20689	0.08034	-0.01089	0.04640
0.4	1586.08	1070	1.1492	-0.12382	0.05537	-0.00659	0.03516
0.6	1601.10	1080	1.1541	0.02560	0.01438	0.00156	0.03138
0.8	1608.20	1088	1.2688	0.04393	0.00035	0.00267	0.01987
1.0	1612.17	1096	1.3170	0.27404	-0.07238	0.01599	0.02014

Table 1 shows the values of ultrasonic velocity (u), density (ρ), the coefficient of viscosity (η) and excess adiabatic compressibility (β_a^E), excess acoustic impedance (z^E), excess intermolecular free length (L_f^E) and excess relative association

Excess Adiabatic Compressibility (β_a^E)

Excess thermodynamic parameters have been found to be highly useful in solute-solvent interactions in aqueous

solutions and binary mixtures. Excess adiabatic compressibility (β_a^E) for amino acid electrolytes solutions at 2MHz frequency and at different temperatures have been determined using relation (6) and presented in Tables 1. The variations in excess adiabatic compressibility (β_a^E) with volume fractions at different temperatures are presented in Tables 1, it is observed that the values of β_a^E are negative at the lower volume fraction up to $x=0.4$ whereas the sign inversion of the β_a^E values changes by increasing volume fraction $x=1.0$. The curves show that the positive values of excess compressibility reaches maximum at $x=1.0$ volume fraction of 1M serine. The values of excess compressibility become more negative in (1M MgCl₂ + valine) as compared to in (1M NaCl + 1M serine) system at the same temperature and same volume fractions, due to divalent nature of MgCl₂. The negative value of β_a^E suggests significant interaction between component molecules in the mixture forming donor-acceptor complex between amino acids and electrolytes. As a result there is contraction in volume resulting negative values of β_a^E with volume fraction (x). The variation in adiabatic compressibility (β_a^E) in both systems with temperature shows following trend.

$$\beta_a^E \text{ 1M NaCl} > \beta_a^E \text{ 1M MgCl}_2$$

Excess Acoustic Impedance (z^E)

Excess acoustic impedance for amino acid electrolytes solutions at 2MHz frequency and at different temperatures have been determined using relation (7) and presented in Tables 1. From Tables, it is clear that the values of z^E are positive at the beginning but becomes negative thereafter by increasing volume fractions of 1M serine and 1M valine in the liquid mixtures. The values of excess acoustic impedance are less negative in (1M MgCl₂ + 1M valine) as compared to (1M NaCl + 1M serine). More positive values of z^E indicates that the interactions between 1M MgCl₂ and 1M valine more strong than the 1M NaCl and 1M serine. The variation in excess acoustic impedance in both systems with temperature shows following trend.

$$z^E \text{ 1M MgCl}_2 > z^E \text{ 1M NaCl}$$

Excess Intermolecular Free Length (L_f^E)

The changes in excess intermolecular free length (L_f^E) have been calculated with the help of equation - (8). The values of L_f^E are mention in the Tables 1. From Tables, it is clear that, L_f^E values are negative at the beginning then become positive with increasing volume fraction (x) for all the systems at all temperatures suggesting strong specific interactions between amino acids and electrolytes molecules. L_f^E becomes more negative for 1M MgCl₂ as compared to 1M NaCl suggesting more of specific interaction of amino acids with divalent molecules (Palani and Geeta, 2007). For the mixtures of electrolytes with amino acids, L_f^E values are negative at lower vol. fraction of amino acids solution. And inversion in sign from negative to positive is found with increase in volume fraction for all the systems. The positive L_f^E arises due to breaking of H- bonds in the self associated amino acids. Again the values of L_f^E are negative for the system comprising NaCl as compared to the system comprising MgCl₂ suggests that the strong interactions occur between electrolytes and serine, while weak interactions occur between electrolytes and valine.

The variation in intermolecular free length in both systems with temperature shows following trend.

$$L_f^E \text{ 1M MgCl}_2 > L_f^E \text{ 1M NaCl}$$

Excess relative association (R_A^E)

The variation of excess relative association function with volume fraction (x) is mention in Tables 1 and have been determined using relation (9). From Table 1, it shows that R_A^E is more positive for the system (1M NaCl + 1Mserine). But the values of R_A^E are high and more positive for the system (1M MgCl₂+ 1M valine). At beginning values R_A^E is positive for liquid mixtures as the volume fraction increases up to $x=0.4$ as per Tables. The negative value of R_A^E suggests significant interactions between the component molecules in the mixture, forming donor – acceptor complex between amino acid and electrolytes molecules. As a result there is contraction in volume, resulting in negative values of R_A^E with x . Interactions between MgCl₂ and valine again stronger than NaCl and serine. The positive values of R_A^E for the system suggest the presence of weak interaction between unlike molecules. In case of MgCl₂ based system, the values of R_A^E are positive over the entire range of volume fraction suggest that there are weak interactions between MgCl₂ and valine. The values of R_A^E are positive for liquid mixture as the volume fraction increases. The variation in excess relative association in both systems with temperature shows following trend.

$$R_A^E \text{ 1M MgCl}_2 > R_A^E \text{ 1M NaCl}$$

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