Research Journal of Chemical and Environmental Sciences
Res J. Chem. Environ. Sci. Vol 3 [2] April 2015: 32-37
Online ISSN 2321-1040
CODEN: RJCEA2 [USA]

Website: www.aelsindia.com/rjces.htm

RJCES

ORIGINAL ARTICLE

Acoustical Studies on Binary Liquid Mixture of Biomolecule in Aqueous Electrolytes at 313.15 K Temperature

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ABSTRACT
Molecular interaction studies using ultrasonic technique in the binary liquid mixture of biomolecule (amino acid) in aqueous electrolytes(NaCl and $MgCl_2$) has been carried out at 313.15 K and at 2 MHz frequency. Using measured values of Density (ρ), Ultrasonic velocity (U) and Viscosity (η) acoustical parameters such as classical absorption factor (α/f^2), relaxation time (τ),relaxation strength (r) and Rao's molar sound function (F) are evaluated for the solutions of inorganic salts i.e. NaCl and $MgCl_2$ with amino acids at various concentrations and temperature. From the properties of these parameters, the nature and the strength of molecular interactions in this binary system are discussed.
Keywords: *Ultrasonic velocity, Acoustical properties, Molecular interactions, amino acid ,electrolytes and binary liquid mixture*

Received 10.01.2015 Accepted 23.03.2015

INTRODUCTION

In many industrial applications, rather than single component liquid system, liquid mixtures are used in processing and product formulations [1, 2]. Liquid mixtures consisting of polar and non-polar components are of considerable importance in industries such as petrochemical, pharmaceutical and dye. The ultrasonic study of liquids is of immense important in understanding the nature and strength of molecular interactions. The biological activity of drug molecules and the activation energy of the metabolic process [3, 4] basically depend on the type and strength of the intermolecular interactions. Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality [5, 6]. From the literature, the nature and degree of molecular interactions in different solutions changes, depending upon the nature of solvent, the structure of solute molecule and extent of solution taking place in the solution [7, 8]. In view of growing interest, the result of an ultrasonic velocity, density and viscosity to study the related acoustical parameters for the binary system of amino acid in aqueous eletrolytes at the temperature 313.15 K and at 2 MHz frequency have been reported in the present paper. The variations of these properties with composition at the temperature 313.15 K are studied in terms of molecular interactions between unlike molecules. Further, these properties have been widely used to study the intermolecular interactions between the various species present in the mixture. In the present work, the measurement of ultrasonic velocity, density and viscosity and computation of related parameters at 313.15 K in binary mixture of electrolytes with amino acid has been studied.

System I- Aqueous NaCl +serine
System II- Aqueous $MgCl_2$ + serine

The classical absorption factor (α/f^2), relaxation time (τ), relaxation strength (r) and Rao's molar sound function (F) were serine in aqueous solution of inorganic salts such as NaCl and $MgCl_2$ at 303.15, 308.15 &313.15K have been studied in the present paper. Such data are expected throw light on the interaction between inorganic salts and biomolecules.

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 the serine on a digital balance with an accuracy of ± 1 x 10^{-4} g. Solutions of NaCl & MgCl2 were made by mass on the mole fraction scale. Uncertainties in solution concentrations were estimated at ± 1 x 10^{-5} mol kg^{-1} in calculations. The solutions were kept in the special air tight bottles and were used within 12 hrs after preparation to minimize decomposition due to bacterial contamination. 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 ± 2x10^{-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 ± 0.1K 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 classical absorption factor (α/f^2), relaxation time (τ),relaxation strength (r) and Rao's molar sound function (F) were calculated by using the following relations[9-12]

Ultrasonic velocity $u = n \times \lambda$ _____(1)

Density $\rho = m / v$ _____(2)

Viscosity $\eta_2 = [t_2 / t_1].[\rho_2 / \rho_1] \times \eta_1$ _____(3)

Where, n & λ are frequency and wavelength; V is the volume of the solution; η_1 & η_2 are the viscosities of the water and solutions; t_1, t_2 are time of flow of water and solution and ρ_1, ρ_2 are the densities of water and solution.

Classical absorption factor (α/f^2) $\frac{\alpha}{f^2} = \frac{2\pi^2\eta}{3\rho c^2}$ _____(4)

Relaxation time $(\tau) = \frac{4\eta}{3\rho u^2}$ _____(5)

Relaxation strength $(r) = 1 - (u / u_\infty)$ _____(6)

Rao's molar sound function $(F) = M / \rho (u)^{1/3}$ _____ (7)

The experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) of the solutions and calculated values of acoustical parameters such as classical absorption factor (α/f^2), relaxation time (τ),relaxation strength (r) and Rao's molar sound function (F) are reported in Table -1 for the systems (water + NaCl +serine) and Table – 2 for the system (water+ $MgCl_2$ + serine) respectively, and the graph plotted for ultrasonic velocity(u), classical absorption factor (α/f^2), relaxation time (τ),relaxation strength (r) and Rao's molar sound function (F) at different temperatures and various concentrations at 2 MHz frequency for the systems (water + NaCl+ serine) and (water+ $MgCl_2$ + serine) are shown in Fig.1 to Fig. 10 respectively.

Table:-1 Variation of thermodynamic parameters at different mole fractions (x) and constant temperature for the system (Water + NaCl + Serine) at 2MHz. 313.15K

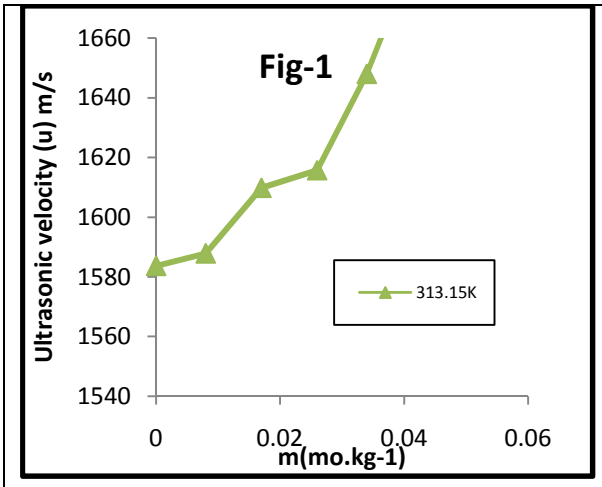
m mol kg^{-1}	u ms^{-1}	ρ Kg m^{-3}	η Nm-2s	α/f^2 x10^{-15} s^2m^{-11}	τ x 10^{-14} sec	r	F x10^{-3} (m/mol)m/s $^{1/3}$
0.000	1583.60	1053.38	0.95536	6.00624	4.82347	0.01025	2.993
0.008	1587.80	1061.78	0.94504	5.85002	4.71046	0.00763	2.967
0.017	1609.83	1064.25	1.08785	6.02849	4.92152	-0.00614	2.945
0.026	1615.76	1079.66	1.16157	6.13180	5.02430	-0.00985	2.901
0.034	1648.04	1083.70	1.27930	5.85370	4.98225	-0.00300	2.871
0.043	1695.10	1088.39	1.36861	5.79801	4.98408	-0.05944	2.831

Where m, mole fraction; ρ, density of the solution ; η,viscosity of solution; u, ultrasonic velocity; α/f^2 classical absorption factor; τ, relaxation time; r, relaxation strength; F, Rao's molar function.

Table:2-variation of thermodynamic parameters at different mole fractions (x) and constant temperature for the system (Water + $MgCl_2$ + Serine) at 2MHz. 313.15K

m mol kg^{-1}	u ms^{-1}	P Kg m^{-3}	η $Nm^{-2}s$	$\alpha/f^2 x10^{-15}$ s^2m^{-11}	τ x 10^{-14} sec	r	F $x10^{-3}$ $(m/mol)m/s^{1/3}$
0.000	1588.77	1053.14	0.95533	5.94800	4..79212	0.00702	6.127
0.008	1598.76	1068.21	1.03814	6.88204	5.57970	0.00077	6.028
0.017	1618.48	1078.95	1.11385	6.40759	5.25911	-0.01150	5.928
0.026	1630.10	1090.51	1.10846	6.92485	5.70319	-0.01500	5.876
0.034	1637.15	1100.25	1.37749	7.50291	6.22916	-0.02320	5.807
0.043	1657.00	1112.12	1.45346	7.55337	6.34708	-0.03560	5.721

Where m, mole fraction; ρ, density of the solution ; η,viscosity of solution; u, ultrasonic velocity; α/f^2 classical absorption factor; τ, relaxation time; r, relaxation strength; F, Rao's molar function.



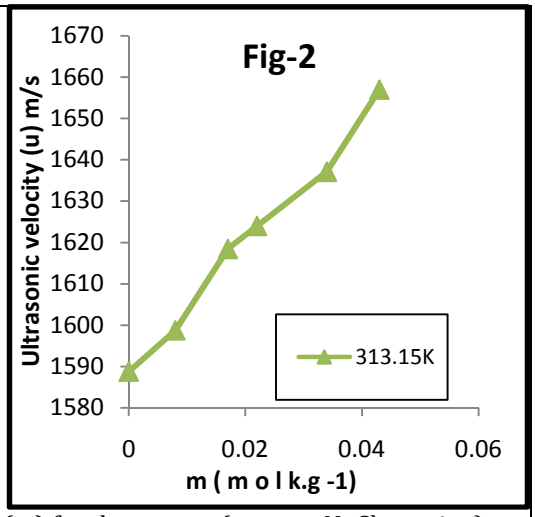


Fig.1- Plot of ultrasonic velocity (u) against mole fraction (m) for the system (water + NaCl + serine) at 2MHz and at 313.15K temperature.

Fig.2- Plot of ultrasonic velocity (u) against mole fraction (m) for the system (water +$MgCl_2$ +serine) at 2MHz and at 313.15K temperature.

The ultrasonic velocity (u), for amino acid electrolytes solutions at $2MH_z$ frequency, for different temperatures and various concentrations (m) have been determined using Eq. (1) and experimental values of u have been presented in Tables 1for the systems (water + NaCl +serine) and Table 2 for the system (water+ $MgCl_2$ + serine) .From Tables it is seen that ultrasonic velocity increases with increase in concentration of solutes serine.

The experimental results support the above statement in both the cases. 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 and $MgCl_2$ in 1M serine are given in tabls1&2. From Tables 1 -& Fig1 (water + NaCl + serine) and Table2 & Fig.-2 (water+ $MgCl_2$ + serine), it is seen that ultrasonic velocity in aqueous NaCl solution increases with increase in concentration of solutes serine. The value of ultrasonic velocity of serine in aqueous NaCl is less as compared to the value of serine in aqueous $MgCl_2$ .The ultrasonic velocity in aqueous NaCl is maximum at temperature 313.15K . Such an increases in ultrasonic velocity clearly shows that molecular association is being taking place in these liquid systems. The same results are observed for aqueous $MgCl_2$. The order of variation of ultrasonic velocity with increase in concentrations and temperatures is observed as follows;

u water < u NaCl < u $MgCl_2$

Density is a measure of solvent-solvent and ion-solvent interactions. Increase of density with concentration indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of

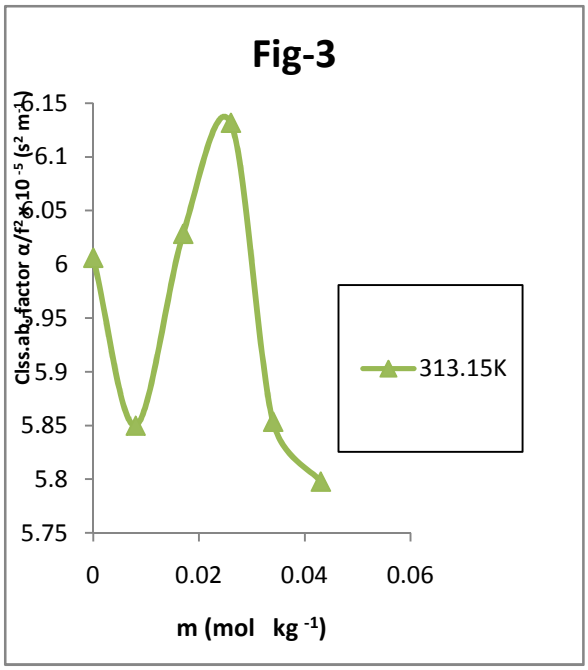
solute molecules. In other words, the increase in density may be interpreted to the structure-maker of the solvent due the added solute. Similarly, the decrease in density with concentration indicates structure-breaker of the solvent. It may be also true that solvent-solvent interactions bring about a bonding, probably H-bonding between them. So, size of the resultant molecule increases and hence there will be decrease in density. Density of the solution in both the systems increases with increase in concentration of serine .However, from Table-1(water + NaCl +serine) and Table- 2(water+ $MgCl_2$ + serine), density of the solution is less in aqueous NaCl for serine as compared to aqueous $MgCl_2$ for serine .The order of variation of density with increase in temperatures is observed as follows;

$$\rho_{MgCl2} > \rho_{NaCl} > \rho_{water}$$

Viscosity is an important parameter in understanding the structure as well as molecular interactions occurring in the solutions. The viscosities are determined for these systems at various concentrations of donor-acceptor mixtures. Increase in viscosity with concentration in all the systems suggests that the extent of complexation increases with increase in concentration. Also from the Tables- 1 (water + NaCl +serine)&Table- 2(water+ $MgCl_2$ + serine), it is observed that viscosity of the solutions shows a non-linear behavior in both the systems. The order of variation of viscosity with increase in concentrations in the three systems is observed as follows;

$$\eta_{water} < \eta_{NaCl} < \eta_{MgCl2}$$

This supports the association of molecules of serine in aqueous $MgCl_2$ is more than serine in aqueous NaCl and pure water.



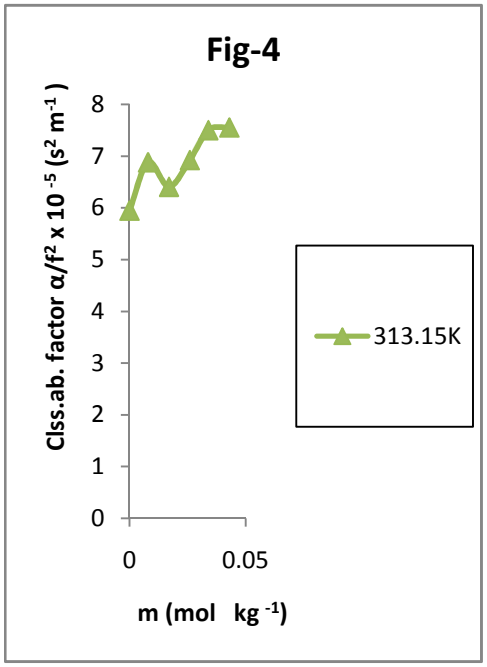
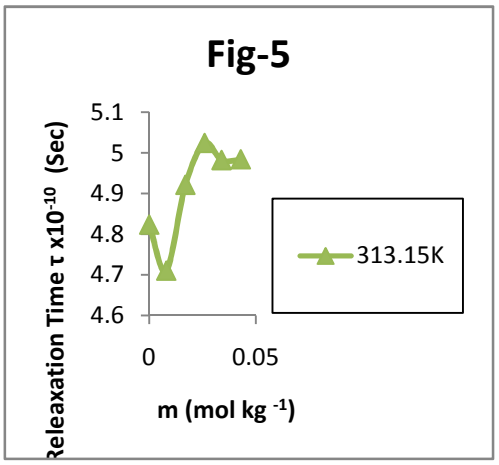


Fig.3- Plot of classical absorption factor (α/f^2) against mole fraction for the system (water + NaCl + serine) at 2MHz and at 313.15K temperature.
Fig.4- Polt of classical absorption factor(α/f^2) against mole fraction for the system (water +$MgCl_2$ +serine) at 2MHz and at 313.15K temperature.

The values of **classical absorption factor (α/f^2)** for (water + NaCl+ serine) and (water+ $MgCl_2$ + serine) systems were calculated using Eq. (4). From Tables.1 &2and Fig.3and Fig.4), it is observed that the classical absorption factor (α/f^2) decreases with increase in concentrations. This is due to aggregation of solvent molecules of ions suggesting strong solute-solvent interaction. The graph for classical absorption factor (α/f^2) versus mole fraction (m) of (water+ NaCl+ serine) and (water+ $MgCl_2$ + serine) were plotted as shown in the Fig-3and Fig4.

The values of classical absorption factor (α/f^2) are maximum in water, moderate in aqueous NaCl and minimum in aqueous $MgCl_2$



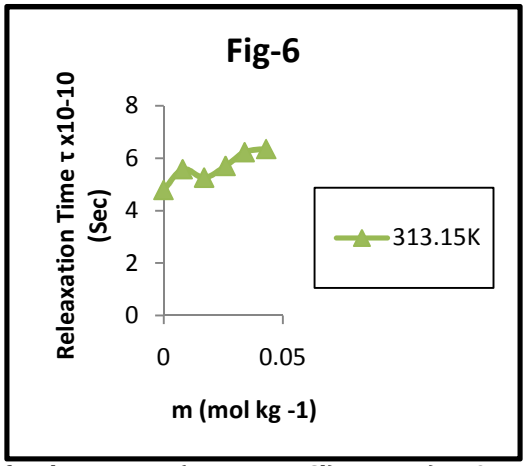
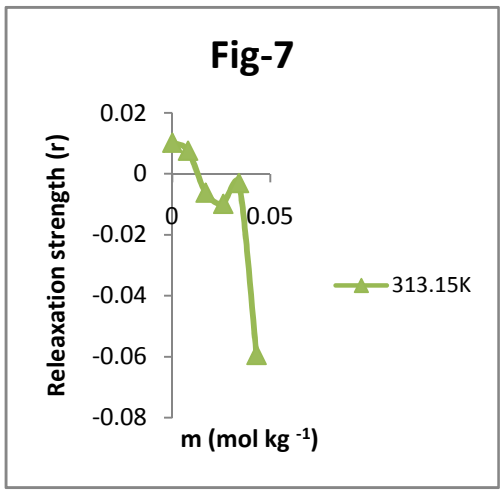


Fig.5- Plot of relaxation time (τ) against mole fraction for the system (water +NaCl) +serine) at 2MH$_z$ and at 313.15K temperature.

Fig.6- Plot of relaxation time (τ) against mole fractionfor the system (water +$MgCl_2$ +serine) at 2MHz and at 313.15K temperature.

The values of **relaxation time (τ)** for (water + NaCl+ serine) and (water+ $MgCl_2$ + serine) systems were calculated using Eq. (5). From Tables.1 & 2, and (Figs.5 &6), it is observed that the relaxation time (τ) decreases with increase in concentrations. This is due to aggregation of solvent molecules of ions suggesting strong solute-solvent interaction. The graph for relaxation time (τ) versus mole fraction (m) of (water + NaCl+ serine) and (water+ $MgCl_2$ + serine) was plotted as shown in the Fig.5and Fig.6.

The values of relaxation time (τ) are maximum in water, moderate in aqueous NaCl and minimum in aqueous $MgCl_2$. This also indicates the significant interactions in the system [13, 14].



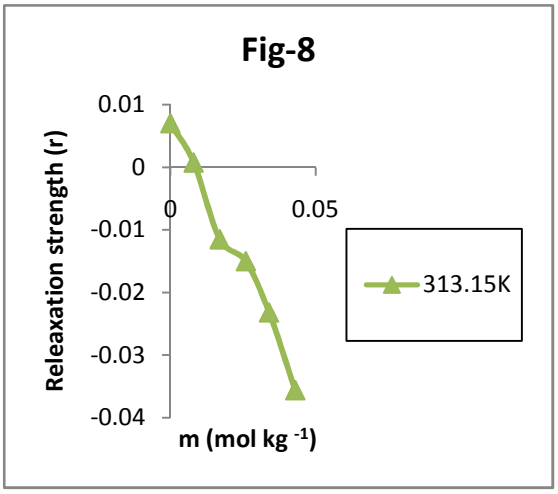


Fig.7-Plot of relaxation strength (r) against mole fraction for the system (water +NaCl +serine) at 2MHz and at 313.15K temperature.

Fig.8-Plot of relaxation strength (r) against mole fraction for the system (water +$MgCl_2$ +serine) at 2MHz and at 313.15K temperature.

The values of **relaxation strength (r)** for the systems (water + NaCl + serine) and (water+ $MgCl_2$ + serine) have been calculated using Equation (6). The experimental calculated data for different concentrations and temperatures for both the systems have been presented in Tables.1 and 2. From

Fig.7and Fig.8, it is clear that, in the present investigation, the relaxation strength (r) shows the increase and decrease non-linear behavior which indicates, there is significant interactions between the solutes and solvent. In present investigation positive values of relaxation strength (r)for some mole fractions confirms presence of strong molecular association in the system ,While for negative values of relaxation strength (r) for some mole fractions indicate presence of weak interaction between molecules of the compounds.

The values of relaxation strength (r) are maximum in water, moderate in aqueous NaCl and minimum in aqueous $MgCl_2$

Rao's molar sound function (F) for the (water +NaCl+ serine) and (water+ $MgCl_2$ + serine) systems have been computed using equation (7). The experimental computed values of F are presented in Tables.1 and2.It is observed that F decreases with increase in concentrations and with increase in temperatures. From Fig.9 and Fig. 10, it is clear that the values of F decrease as temperature increases and vice - versa.

The values of Rao's molar sound function (F) are maximum in water, moderate in aqueous $MgCl_2$ and minimum in aqueous NaCl.

CONCLUSION

The ultrasonic velocity, density, viscosity and other related parameters were calculated. The existence of type of molecular interaction in solute-solvent is favored in the system, The variation in ultrasonic velocity, density and viscosity and other related thermodynamic parameters such as classical absorption factor (α/f^2), relaxation time (τ),relaxation strength (r) and Rao's molar sound function (F), of serine at various concentrations and at 313.15K temperature in both the NaCl – based and $MgCl_2$ – based systems, shows the non-linear increase or decrease behavior. Weak dispersive type intermolecular interactions are confirmed in the systems investigated. Components maintain their individuality in the system investigated. All the experimental determinations of acoustic parameters are strongly correlated with each other. For the observed molecular interaction, hydrogen bond formations are responsible for the heteromolecular interaction in the liquid mixture. This provides useful information about inter and intra molecular interactions of the mixture as existing in the liquid system.

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S.A Mirikar, Govind K. Bichile. Acoustical Studies on Binary Liquid Mixture of Biomolecule in Aqueous Electrolytes at 313.15 K Temperature.Res. J. Chem. Env. Sci. Vol 3 [2] April 2015. 32-37

