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Ultrasonic and Thermodynamic Studies in Ternary Liquid Systeam of Choline Chloride Urea+ L-Glutamine + Water at 298.15 And 308.15k

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ABSTRACT

The density(ρ), viscosity(η) and ultrasonic velocity(U) were measured for ternary system [choline chloride urea(1) + L-Glutamine(2) + water(3)] at 298.15 and 308.15K .Using Experimental values, the various acoustical parameters such as the adiabatic compressibility (ß),Intermolecular free length (L_f), Free volume (V_f), Internal pressure (Π_i), Acoustic impedance (Z) have been studied and have been estimated using the standard relations. The results have been analyses on the basis of variations of thermodynamic parameters. The presence of strong interactions is noticed in the ternary system.

Keywords : Ultrasonic Velocity, Adiabatic Compressibility, Intermolecular Free Length, Free Volume, Internal Pressure.

I. INTRODUCTION

Knowledge of thermodynamic and acoustical properties is of great significance in studying the physico-chemical behaviour and molecular interactions in a variety of liquid mixtures[1-3]. Considerable scientific and practical interest has been stimulated by the investigation of organic liquids using ultrasonic measurements[4, 5]. Such a type of study has been found to yield information regarding the intermolecular process and the structure of the liquid state[6]. The compositional dependence of thermodynamic properties has proved to be a very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from intermolecular interaction between components Acoustic and thermodynamic parameters have been used to understand different kinds of association, the molecular packing, molecular motion, and various types of intermolecular interactions and their strengths, influenced by the size in pure components and in the mixtures[7]. Theoretical evaluation of ultrasonic velocity in ternary liquid mixtures and its comparison with the experimental values reflects the molecular interactions in liquid mixtures. Ultrasonic velocities evaluated using Nomoto's relation[8] (NR), Impedance dependence relation[9] (IDR) and Collision factor theory[10] (CFT) have been compared with those obtained from the experimental values.

II. EXPERIMENTAL DETAILS

Chemicals used in this study (> 99.5% of purity) were supplied S.D. fine chem. Industries, Mumbai (purity 99%) used without further purification. The mixtures of the desired composition were prepared by weighting on a HR-120 (A & D Japan) electronic

balance with a precision of ± 0.0001 g. all mixed solvents were prepared by molality. The prepared solution was used within 12hrs. The densities of pure liquids and binary mixtures were measured by using 15cm^3 double arm pycnometer as describe earlier [11]. The Pycnometer was calibrated by using conductivity water with 0.9970 g/cm^3 as its density at 298.15 K. The pycnometer filled with air bubble free experimental liquid was kept in transparent walled water bath for 10-15 min. to attain thermal equilibrium. The position of liquid levels in the two arms was recorded.

The dynamic viscosities were measured using an Ubbelohde suspended level viscometer , calibrated with conductivity water. An electronic digital stopwatch with readability of ± 0.01 sec. was used for the flow time measurement, at least three repetitions of each data reproducible to ± 0.05 sec. were obtained and the result was averaged. Since all flow times were greater than 200 sec. and capillary radius (0.5 mm) was far less than its length (50 to 60mm.). The kinetic energy and corrections respectively were found to be negligible. The uncertainties in dynamic viscosities are of the order ± 0.003 m Pa s. The speed of sound waves was obtained by using ultrasonic interferometer, (Mittal Enterprises, New Delhi) at a fixed frequency of 2 MHz with an accuracy of ±2 ms^{1}. An electronically digital operated constant temperature bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement was ±0.1 K.

Theory

The various acoustical parameters such as adiabatic ompressibility (ß), free length (*Lf*), free volume (*Vf*), acoustic impedance (Z),Internal pressure (Πi) and their excess values were determined using the following equations:

$$ß = \frac{1}{U^2\rho} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$L_f = K_T\, ß^{1/2} \quad \ldots\ldots\ldots\ldots (2)$$

$$V_f = \frac{Meff}{\eta K} \quad \ldots\ldots\ldots\ldots..(3)$$

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)\left(\frac{\rho^{2/3}}{M_{eff}{}^{7/6}}\right) \quad \ldots\ldots\ldots\ldots (4)$$

$$Z = u\rho \quad \ldots\ldots\ldots\ldots (5)$$

where K_T is the temperature dependent constant, M_{eff} the effective molecular weight of the solution, K the temperature independent constant (K= 4.28×10^9), b a constant which is 2 for cubic packing, R the gas constant and T is the temperature in K.

III. RESULTS AND DISCUSSION

The experimentally measured values of Density (ρ), Ultrasonic velocity (U) and thermodynamic parameters adiabatic compressibility (ß), Intermolecular free length (L_f), Free volume (V_f), Acoustic impedance (Z) and Internal pressure (π_i) of ternary liquid system at temperature 298.15 K & 308.15 at frequency 2MHz are presented in table-1 and 2 respectively. Table-1 and 2 shows that, ultrasonic velocity, density, adiabatic compressibility (ß), Intermolecular free length (L_f), Free volume (V_f), Internal pressure (π_i), Acoustic impedance (Z) acoustic impedance and relative association increases while adiabatic compressibility and intermolecular free length decreases with concentration of ionic liquid with amino acid at temperature 298.15 and 303.15K.

The ultrasonic velocity (U) for ionic liquid and aqueous solution of L-Glutamine at 2MHz frequency and at 298.15 and 308.15 K temperature have been determined. The variations in ultrasonic velocity in liquid mixtures depend on concentrations (x) of solutes and temperature. 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. Ultrasonic velocity increases with increase in concentrations of solutes.

The increase in density with molal concentration suggests a solute solvent interaction exist between the electrolyte and water. In other words the increase in density may be interpreted to the structure makes of the solvent due to H-bonding.

The viscosity is an important parameter in understanding the structure as well as molecular interaction, occurring in the solutions. From above table, it is observed that viscosity of the solutions shows a non-linear behavior in the system. The increase in viscosity with concentration in all the system suggests that the extent of complexation increase with increase in concentration.

The adiabatic compressibility is calculated using equation (1). The calculated values of (ß) have been presented in table-1 and 2. From these tables it is clear that the compressibility of solvent is higher than that of a solution and it decreases with increase in concentrations.

The values of intermolecular free length for given system have been calculated using the equation (2). Increase in concentrations leads to decrease in gap between two species which is referred by intermolecular free length (L_f). With the increase in concentrations of solutes, intermolecular free length (L_f) has to decrease, intermolecular free length (L_f) is predominant factor in determining the variations of ultrasonic velocity in liquid mixtures. From table-1 and 2, it has been observed that, in the present investigation on increasing concentration. The decrease in Lf with increase of concentration in solution between solute and solvent suggesting the structure, promoting behavior of solutes, The value of free volume calculated using the equation (3).The calculated values of free volume (V_f) decreases whereas, the internal pressure (Π_i) increases due to the various degree of dispersive interaction and the columbic interaction existing between the component molecules. Internal pressure (Π_i) calculated using the equation (4). Acoustic impendence (z) calculated using equation (5), from table 1 and 2 it is observed that acoustic impendence increases with increase in concentrations. For a given concentration the values of acoustic impendence (z) increases with increase in concentration in liquid system .The increase in (z) with the increase in concentration of solutes can be explained in terms of inter and intra molecular interactions between the molecules of liquid mixtures.

IV. CONCLUSION

The observed trends and variations of thermo dynamical parameters with molar concentration of Ch Cl urea in aqueous amino acids provide useful information about the nature of intermolecular forces existing in the mixture. The existence of ion-solvent (or) solvent-solvent interaction resulting in attractive forces promote the structure-making tendency, An appreciable existence of solute-solute interactions present in the system with varying degrees hence it is evident that the ultrasonic velocity measurement in the given medium serves as a powerful probe in characterizing the physio-chemical properties of the media. The almost linear variation of acoustical parameters with temperature shows that there exist less intermolecular forces between the components of the ternary liquid mixtures.

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Table 1 : Density (ρ), viscosity (η) velocity (U), adiabatic compressibility (β), Intermolecular free length (L_f), Free volume (V_f), Internal pressure (π_i), Acoustic impedance (Z) of Ch-Cl-urea (1) + L-Glutamine (2) + Water (3) at 298.15 K

X_1	X_2	$\rho x10^3$ (kg/m^{-3})	$\eta x10^3$ (Nsm^{-2})	U ($msec^{-1}$)	$\beta x10^{-10}$ (Pa^{-1})	$L_f x10^{-10}$ (m)	$V_f x10^{-6}$ ($m^3 mol^{-1}$)	$\pi_i x10^{-6}$ (Pa^{-1})	$Zx10^6$ (Nm^{-2})
0.0001	0.0016	1.0100	2.5995	1445	4.756	0.431	2.413	0.4569	1.455
0.0002	0.0015	1.0068	2.5922	1447	4.743	0.430	2.410	0.4571	1.457
0.0003	0.0013	1.0069	2.5883	1449	4.727	0.430	2.409	0.4575	1.460
0.0004	0.0011	1.0074	2.5817	1450	4.717	0.429	2.403	0.4584	1.462
0.0005	0.0007	1.0083	2.5776	1455	4.684	0.428	2.407	0.4583	1.467
0.0005	0.0009	1.0085	2.5711	1458	4.663	0.427	2.405	0.4587	1.471
0.0006	0.0005	1.0089	2.5672	1461	4.642	0.426	2.402	0.4595	1.474
0.0007	0.0004	1.0092	2.5608	1463	4.626	0.425	2.400	0.4598	1.478
0.0008	0.0002	1.0122	2.5562	1467	4.590	0.423	2.402	0.4604	1.485

Table 2 : Density (ρ), viscosity (η) velocity (U), adiabatic compressibility (β), Intermolecular free length (L_f), Free volume (V_f), Internal pressure (π_i), Acoustic impedance (Z) of Ch-Cl-urea (1) + L-Glutamine (2) + Water (3) at 308.15 K

X_1	X_2	$\rho x10^3$ (kg/m^{-3})	$\eta x10^3$ (Nsm^{-2})	U ($msec^{-1}$)	$\beta x10^{-10}$ (Pa^{-1})	$L_f x10^{-10}$ (m)	$V_f x10^{-6}$ ($m^3 mol^{-1}$)	$\pi_i x10^{-6}$ (Pa^{-1})	$Zx10^6$ (Nm^{-2})
0.0001	0.0016	1.0048	2.3362	1408	5.020	0.450	2.566	0.4573	1.415
0.0002	0.0015	1.0052	2.3405	1413	4.982	0.448	2.571	0.4569	1.420
0.0003	0.0013	1.0057	2.3456	1417	4.952	0.447	2.572	0.4571	1.425
0.0004	0.0011	1.0065	2.3509	1422	4.913	0.445	2.574	0.4573	1.431
0.0005	0.0007	1.0067	2.3573	1425	4.892	0.444	2.571	0.4577	1.435
0.0005	0.0009	1.0072	2.3602	1426	4.882	0.444	2.569	0.4582	1.436
0.0006	0.0005	1.0076	2.3682	1428	4.867	0.443	2.560	0.4596	1.439
0.0007	0.0004	1.0083	2.3732	1431	4.843	0.442	2.561	0.4596	1.443
0.0008	0.0002	1.0103	2.3764	1433	4.820	0.441	2.560	0.4604	1.448