"STUDY OF SOLVENT-SOLVENT INTERACTION IN A AQUEOUS MEDIUM AT DIFFERENT TEMPERATURES BY ULTRASONIC TECHNIQUE"

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ABSTRACT

The basic parameters like viscosity (η), density(ρ) and velocity (U) can be measured by ultrasonic Interferometer. From these three parameters various thermo dynamical and acoustical parameters such as specific acoustic impedance (Z), Intermolecular free length (L$_f$), adiabatic compressibility (β) etc have been estimated using standard relations from measured values of Ultrasonic viscosities, densities and velocities in the wide range of concentrations at 35^0 C, 40^0C and 45^0C temperatures for Acetone + Propanol-2 +Toluene tertiary system. The solvent-solvent interactions are studied on the basis of increase or decrease in ultrasonic velocity, density, viscosity and other derived acoustical parameters in terms of structure making and structure breaking tendencies of various solvent molecules.

Keywords: density, ultrasonic interferometer, ultrasonic velocity, viscosity, water bath

I. INTRODUCTION

Developments which are taking place in this field have found great use of ultrasonic energy in the field of medicine, engineering, agriculture, technology and industry [5,6]. In chemical industries, ultrasonic energy is found useful in studying the chemical processes as well as different types of reactions in synthesis of chemical substances. Wong and Zhu [7] have studied the speed of sound in seawater as a function of salinity, temperature and pressure. Skumiel and Labowski [8] have given a theoretical analysis of the effect of an external constant magnetic field on the propagation of ultrasonic waves in electrically conducting liquids as well as the results of measurements carried out in mercury. Hanel[9] has analytically deduced an equation for the longitudinal sound velocity of thin film samples and the velocities of the tertiary liquid mixtures have been calculated. 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. Ultrasonic waves with low amplitude have been used by many researcher to investigate the nature of molecular interactions and physio-chemical behavior of pure, binary, ternary and quaternary liquid mixtures. A survey of literature indicates that excess values of acoustical parameters are useful in understanding the nature

and strength of the molecular interaction in the pure, binary, ternary and quaternary liquid mixtures . 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.

II. EXPERIMENTAL STUDIES

Ultrasonic velocity was measured using single crystal ultrasonic interferometer of 2 MH_z frequency (Model M81) supplied by Mittal Enterprises, New Delhi, that has a reproducibility of 0.4ms^{-1} at 25°C.The temperature was maintained constant by circulating water from a thermostatically controlled water bath (accuracy 0.1^{0}C).The temperature of the cell was measured using a thermocouple (at the crystal) and found to be accurate to 0.25^{o}C. The densities of various concentrations have been measured using 25 ml capacity gravity bottle and digital balance (Shinko, model HTR-220E, made in Japan)with an accuracy of 0.0001 gm. The viscosities have been determined by using Ostwald's Viscometer with an accuracy of 0.001 Nsm $^{-2}$.

The chemicals used were of AR grade, procured from BDH. All the chemicals were purified by standard procedures discussed by Armarigo and Perrin before use. Tertiary system is studied at different temperatures, 35^0 C, 40^{0}C and 45^{0}C with different concentrations of the system such as 1.4 mole,1.6 mole,1.8 mole,2.0 mole,2.2 mole,2.4 mole ,2.6mole,2.8 mole , 3.0 mole,3.2mole and 3.4mole.

III. THEORY

Various physical parameters were evaluated from the measured values of ultrasonic velocity (U) and density (ρ) using the following standard formulae:

$$\text{Intermolecular free length } (L_f) = K\beta^{1/2} \qquad (1)$$

$$\text{Adiabatic compressibility } (\beta) = \frac{1}{U^2\rho} \qquad (2)$$

Where k values for different temperatures were taken from the work of Jacobson; at 35,40 and 45° C the K values are 637, 642 ,647 respectively.

$$\text{Molar sound velocity } (R) = U^{1/3} V \qquad (3)$$

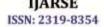$$\text{Molar compressibility}(B) = \beta^{-1/7} \qquad (4)$$

where V and M are the molar volume and molecular weight of the mixtures, respectively.

$$\text{Specific acoustic impedance } (Z) = \rho U \qquad (5)$$

and the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) can evaluated by the following expressions:

$$B^E = \beta_{exp} - \beta_{ideal} \qquad (6)$$

$$(L_f^E) = L_{f.exp} - L_{f.ideal} \qquad (7)$$

For β_{ideal} and $L_{f.ideal}$, the densities and the ultrasonic velocities of various components in pure state at the three given temperatures have been measured. Further, the velocities of both the systems at different concentrations and temperatures have been evaluated theoretically using volume additive rule as :

$$U \, ideal = U_1.\emptyset_1 + U_2.\emptyset_2 + U_3.\emptyset \qquad (8)$$

Where U_1, U_2, and U_3 are the velocities of the three components of the ternary liquid mixture in pure state and , and are their volume fractions.

Simillarly ideal density is evaluated using:

$$P \, ideal = \rho_1.\emptyset_1 + \rho_2.\emptyset_2 + \rho_3.\emptyset \qquad (9)$$

$$L_{f.ideal} = K\beta_{ideal}^{1/2} \qquad (10)$$

TABLE 1

Ultrasonic Velocity and related parameters for Acetone+ Propanol-2 + Toluene

T(^{o}C)	Conc /Mole	U ms^{-1}	P Kgm^{-3}	η / 10^{-3} Nsm^{-2}	Z / 10^6 $Kgm^{-2}S^{-1}$	B / 10^{-10} $Kg^{-1}ms^2$	L_f / 10^{-10} m
35	1.4	1450.5	825.2	4.259	1.196	5.762	4.958
	1.6	1414	827.2	4.278	1.161	6.090	5.170
	1.8	1416.5	829.0	4.322	1.167	6.048	5.152
	2.0	1416	832.6	4.563	1.166	6.055	5.155
	2.2	1446	835.6	4.573	1.193	5.792	5.041
	2.4	1421	838.0	4.586	1.171	6.007	5.134
	2.6	1414.5	840.6	4.610	1.170	6.039	5.148
	2.8	1415	843.8	4.620	1.169	6.040	5.148
	3.0	1402	843.6	4.630	1.157	6.162	5.200
	3.2	1409	845.8	4.635	1.164	6.092	5.170
	3.4	1402	848.2	4.637	1.159	6.151	5.195
40	1.4	1429	830.3	4.712	1.174	5.957	5.162

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	1.6	1401	833.8	4.720	1.142	6.245	5.285
	1.8	1411	837.1	4.725	1.156	6.126	5.234
	2.0	1407	841.9	4.722	1.152	6.167	5.252
	2.2	1419	845.2	4.727	1.168	6.032	5.194
	2.4	1395	848.3	4.730	1.144	6.264	5.293
	2.6	1409	853.8	4.747	1.159	6.121	5.232
	2.8	1396.5	855.8	4.750	1.149	6.231	5.279
	3.0	1399.5	858.1	4.752	1.149	6.218	5.273
	3.2	1388.5	860.6	4.755	1.140	6.293	5.305
	3.4	1385	862.5	4.760	1.147	6.312	5.313
45	1.4	1471.5	850.5	4.762	1.217	5.584	5.045
	1.6	1481.5	854.7	4.765	1.211	5.601	5.052
	1.8	1428.5	858.4	4.770	1.167	5.628	5.064
	2.0	1439	863.1	4.775	1.172	5.654	5.076
	2.2	1509	865.5	4.776	1.151	5.701	5.097
	2.4	1455	867.5	4.780	1.189	5.778	5.132
	2.6	1443	869.5	4.782	1.178	5.881	5.177
	2.8	1440.5	872.7	4.785	1.176	5.900	5.185
	3.0	1440	875.2	4.785	1.173	5.916	5.192
	3.2	1500.5	880.3	4.790	1.172	5.925	5.196
	3.4	1427	885.1	4.795	1.198	5.945	5.205

TABLE 2

Conversion of CGS units to SI units.

No	Parameter	CGS units	SI units
1	Ultrasonic velocity (U)	1 cms^{-1}	10^{-2}ms^{-1}
2	Density (ρ)	1 g cm^{-3}	10^3 Kg m^{-3}
3	Adiabatic compressibility (β)	$1 \text{dyn}^{-1} \text{ cm}^2$	$10 \text{ N}^{-1}\text{m}^2$
4	Intermolecular free length(L_f)	1A^o	10^{-10} m
5	Molar sound velocity (R)	$1 \text{ cm}^3 \text{ mol}^{-1} (\text{cm s}^{-1})^{1/3}$	$10^{-20/3} \text{ m}^3 \text{ mol}^{-1} (\text{ms}^{-1})^{1/3}$
7	Molar compressibility (B)	$1 \text{ cm}^3 \text{ mol}^{-1} (\text{dyn}^{-1} \text{ cm}^2)^{-1/7}$	$10^{-43/7} \text{ m}^3 \text{ mol}^{-1} (\text{N}^{-1}\text{m}^2)^{-1/7}$
8	Wave number (λ)	1 cm^{-1}	10 m^{-1}

IV. RESULTS

Ultrasonic velocity, density, viscosity ,adiabatic compressibility and specific acoustic impedance for the acetone-propanol-2 and Toluene have been listed in table 1.The appropriate conversion of CGS units to SI units have been provided in Table 2 .

V. DISCUSSION

It is seen from the data that in Acetone, Propanol-2 and Toluene system ultrasonic velocity increases initially as a function of increasing concentration for each temperature of the solution. The non-monotonous behavior of ultrasonic velocity indicates occurrence of complex formation between unlike molecules. The molecular association becomes maximum at those concentrations where a velocity maximum occurs. This is due to the formation of strong hydrogen bonding results into complex formation producing displacement of electrons and nuclei. The chemical interaction is due to dipole-dipole interaction, hydrogen bonding etc. Hydrogen bonding in the system is confirmed by spectroscopic characterization.

At 35° C, the ultrasonic velocity is maximum at 1.4 M concentration solution and subsequent decrease of velocity with further increase in concentration. At 40 and 45° C also , the ultrasonic velocity is maximum at 1.4 M concentration solution and subsequent decrease of velocity with further increase in concentration. This can be explained as follows: at 1.4M concentration, at low temperature Acetone+ Propanol-2 + Toluene are broken into their monomers and the hydrogen bonds are formed between the O atom of Acetone and H of the propanol-2. At low temperature, these molecules may stay in associated form. The associated molecules are fairly in large size as compared to Propanol -2 and Acetone and Toluene may cause some structural changes resulting in the weakening of the intermolecular forces. The adiabatic compressibility (β) and intermolecular free length (L_f) both have an inverse relationship with ultrasonic velocity. The decrease in β with increase in concentration is an indicative fact that intermolecular forces are increasing which brings the molecules to a closer packing resulting into a decrease in L_f. The specific acoustic impedance is governed by the initial and elastic properties of the medium. Therefore it is important to examine specific acoustic impedance in relation to concentration and temperature.

When the temperature is increased the velocity maxima shifts towards lower concentration. This is because of the thermal energy which facilitates the breaking of bonds between the associated molecules of Acetone, Propanol-2 and Toluene. The increase in thermal energy weakens the molecular forces and hence decrease in velocity is expected. The observed acoustical parameters and their variation and temperature clearly indicate that the formation of complex between unlike molecules through hydrogen bonding.

From Table 1 it is observed that density and viscosity of aqueous solutions of Acetone, Propanol-2 and Toluene increases with increase in temperature except ultrasonic velocity. The increase in density with increasing concentration of solvent suggests a moderate strong electrolyte nature in which Acetone molecules tends to attract water molecules. The decrease in adiabatic compressibility with increase in concentration confirms the presence of solvent-solvent interactions through dipole-dipole interactions between Acetone,Propanol-2 and Toluene molecules. The compressibility of solvent is higher than that of solution and it decreases with increase in concentration of the solution.

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VI. CONCLUSION

Ultrasonic investigations of molecular interactions in aqueous solutions have carried out at which wide range of concentrations at different temperatures. The results of the present study indicate that the thermodynamic parameters are sensitive to the molecular interactions present in the liquid mixtures. The experimental parameters such as ultrasonic velocity, density and other properties gives valuable information regarding solvent –solvent interactions in aqueous solutions.

The Ultrasonic studies provide comprehensive investigations between Acetone+ Propanol-2 + Toluene molecules arising dipole-dipole interactions.

VII. ACKNOWLEDGEMENT

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