Molecular Interaction Studies of Aqueous Acetonitrile Solutions Using Ultrasonic Technique

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Abstract Density (ρ), viscosity (η) and ultrasonic velocity (u) of aqueous acetonitrile solutions were measured as functions of concentration at 308.15K. The measured data of ρ, η and u have been used to calculate various acoustical and thermodynamic parameters viz. adiabatic compressibility (β_{ad}), intermolecular free length (L_f), acoustic impedance (Z), relaxation time (τ), rao's constant (R_M), wada's constant (W), free volume (V_f), absorption coefficient (α/f^2), gibb's free energy (ΔG), relative association (R_A) and available volume (V_a). These parameters help out in elucidating the molecular association in the mixture. The variation of these parameters with concentration of solute indicates the nature of interaction present in the binary mixture.

1. INTRODUCTION

In recent years, measurement of ultrasonic investigations found extensive applications in determining the physicochemical behavior of liquid mixtures (Pandey et al., 1999; Pandey et al., 2005; Rao et al., 2005; Vasantharani et al., 2008; Sumathi and Maheswari, 2009). Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. Ultrasonic velocities of the liquid mixtures consisting of polar and non-polar (Mehra and Pancholi, 2007) components are of considerable significance in understanding intermolecular interaction between component molecules and find applications in numerous industrial and technological processes (Pal and Kumar, 2004); Rao et al., 2005). Ultrasonic velocity measurement provides a significant tool to study the liquid state (Mirikar et al., 2011). Ultrasonic and

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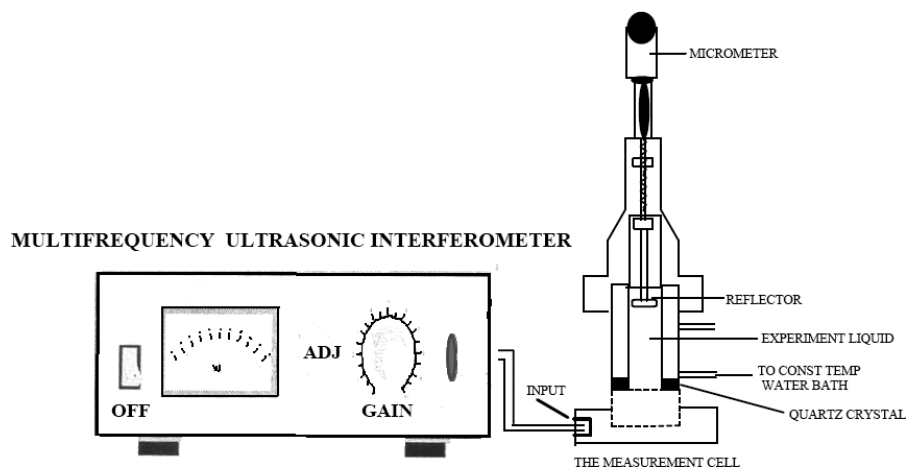**MULTIFREQUENCY ULTRASONIC INTERFEROMETER**

Figure 1: Ultrasonic Interferometer.

thermodynamic parameters derived from these measurements are extremely used to study the molecular interactions in liquid systems, aqueous solutions and liquid mixtures. There has been considerable progress in the determination of thermodynamic, acoustic and transport properties of liquid systems from density and viscosity measurements in recent years. Viscosity, density measurements and the properties derived from these are excellent tools to detect solute – solute and solute – solvent interactions. It is used in so many fields of scientific researches in physics, chemistry, biology, medicines and industry. Even though the ultrasonic velocity data as such do not provide sufficient information about the native and the relative strength of various types of intermolecular /interionic interactions between the components, their derived parameters such as acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), relative association (R_A), relaxation amplitude (α/f^2) and relaxation time (τ) provide information on the type and strength of interactions presently. In view of above we have carried out a systematic experimental investigations of the ultrasonic velocity, density and viscosity measurements of aqueous solutions of acetonitrile of different concentrations. Here we report the result of our study on aqueous acetonitrile system.

2. MATERIALS AND METHODS

The chemicals used in the present work were of analytical grade. In all systems, the various concentrations of the binary mixtures were prepared in terms of % (w/w). Triply distilled water was used for preparation of solutions. A special thermostatic water bath arrangement was made for density, ultrasonic velocity

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and viscosity measurements, in which temperature variation was maintained within ± 0.01°C. The density of aqueous solutions is measured using a 10 mL specific gravity bottle. These values were accurate up to ± 0.1 kg/m³. The viscosity of the aqueous solutions is measured using an Ostwald's viscometer calibrated with doubly distilled water. An electronic stop watch was employed to measure the time of flow. The accuracy of viscosity in this method is ±0.001 Nsm⁻². An ultrasonic interferometer is a simple and direct device, Figure 1 to determine the ultrasonic velocity in pure liquids and liquid mixtures with high degree of accuracy. Ultrasonic velocity was measured by determining the wavelength of sound with the help of multi frequency ultrasonic interferometer (M-82S, Mittal Enterprises, India) at 6 MHz.

3. RESULTS AND DISCUSSION

The experimentally dvalues of density (ρ), viscosity (η) and ultrasonic velocity (u) of the system at 308.15 K are represented in Table 1.

From the observed values the adiabatic compressibility (β_{ad}), intermolecular free length (L_f), acoustic impedance (Z), relaxation time (τ), rao's constant (R_M), wada's constant (W), free volume (V_f), absorption coefficient (α/f^2), gibb's free energy (ΔG), relative association (R_A) and available volume (V_a) were calculated. By using ultrasonic velocity data, the adiabatic compressibility of the liquid was determined by using the relation as,

$$\beta_{ad} = \frac{1}{u^2 \rho} \qquad (kg^{-1}ms^{-2}) \tag{1}$$

Where, u = velocity & ρ = density

Intermolecular free length is determined using the following formula given by Jacobson (Jacobson, 1951;1952)

$$L_f = K_T \beta_{ad}^{1/2} \qquad (m) \tag{2}$$

Table 1: Experimental parameters (ρ, η and u) for the system at 308.15 K.

Concentration (%) (w/w)	Density $\rho \times 10^{-3}$ (Kgm⁻³)	Viscosity $\eta \times 10^3$ (Kgm⁻¹s⁻¹)	Ultrasonic velocity $u \times 10^{-3}$ (ms⁻¹)
5%	0.9836	0.7530	1.542
10%	0.9763	0.7851	1.5468
15%	0.9666	0.8147	1.5516
30%	0.9318	0.6340	1.4964
40%	0.9093	0.5625	1.4544

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Table 2: Derived parameters (β_{ad}, L_f, Z, τ and R_M) for the system at 308.15 K.

Concentration (%) (w/w)	Adiabatic compressibility $\beta_{ad} \times 10^{10}$ ($N^{-1}m^2$)	Intermolecular free length $L_f \times 10^{11}$ (m)	Acoustical Impedance $Z \times 10^{-6}$ ($Kgm^{-2}s^{-1}$)	Relaxation time $\tau \times 10^{12}$ (s)	Rao's constant $R_M \times 10^3$ ($m^{10/3}s^{-1/3}mol^{-1}$)
5%	4.2758	4.3320	1.5167	0.4293	0.2175
10%	4.2810	4.3347	1.5101	0.4481	0.2259
15%	4.2973	4.3429	1.4998	0.4668	0.2354
30%	4.7927	4.5864	1.3943	0.4051	0.2657
40%	5.1990	4.7769	1.3225	0.3916	0.2892

Acoustic impedance is determined from equation,

$$Z = u \times \rho \qquad (kg\ m^{-2}s^{-1}) \qquad (3)$$

The relaxation time (τ) can be calculated from the relation (Hildebrand, 1959),

$$\tau = \left(\frac{4}{3}\right)\beta\eta \qquad (s) \qquad (4)$$

Rao's constant is calculated by using following equation,

$$R_M = \left(M_{eff}/\rho\right)u^{\frac{1}{3}} \qquad (m^{10/3}s^{-1/3}mol^{-1}) \qquad (5)$$

The values of adiabatic compressibility, intermolecular free length, acoustic impedance, relaxation time and rao's constant for aqueous solutions of acetonitrile at different concentrations & at a constant temperature of 308.15 K are shown in Table 2.

Further, wada's constant, free volume, absorption coefficient, gibb's free energy, relative association and available volume were calculated using following relations,

$$W = \left(M_{eff}/\rho\right)\beta_{ad}^{-1/7} \qquad (m^3/mole(N/m^2)^{1/7}) \qquad (6)$$

$$V_f = \left(\frac{M_{eff}u}{K\eta}\right)^{3/2} \qquad (m^3) \qquad (7)$$

$$\left(\alpha/f^2\right) = 4\pi^2\ \tau/2u \qquad (s^2m^{-1}) \qquad (8)$$

$$\Delta G = RT\ln\left(kT\tau/h\right) \qquad (Jmol^{-1}) \qquad (9)$$

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Table 3: Derived parameters (W, V_f, α/f^2, ΔG, R_A, V_a) of the system at 308.15 K.

Concentration (%) (w/w)	Wada's constant $W \times 10^3$ ($m^3/mole$ $(N/m^2)^{1/7}$)	Free volume $V_f \times 10^8$ (m^3mol^{-1})	Absorption coefficient $\alpha/f^2 \times 10^{15}$ (s^2m^{-1})	Gibb's free energy $\Delta G \times 10^{21}$ ($Jmol^{-1}$)	Relative Association R_A	Available volume $V_a \times 10^7$ (m^3)
5%	0.4104	2.6376	5.4899	4.3105	0.9805	6.8252
10%	0.4257	2.6008	5.7126	4.4928	0.9722	6.4946
15%	0.4429	2.5863	5.9325	4.6667	0.9615	6.1507
30%	0.4981	4.1231	5.3383	4.0637	0.9382	15.0390
40%	0.5410	5.2495	5.3094	3.9195	0.9242	23.2254

$$R_A = \rho/\rho_o \left(u_o/u\right)^{1/3} \qquad (10)$$

$$V_a = V_m \left(1 - u/u_\infty\right) \qquad (m^3) \qquad (11)$$

Table 3 represents wada's constant (W), free volume (V_f), absorption coefficient (α/f^2), Gibb's free energy (ΔG), relative association (R_A) and available volume (V_a) for the present system.

In the present investigation, the value of density decreases with increase of concentration. The results of density are in agreement with the weak structure breaking tendency of acetonitrile. There is an increase in viscosity and ultrasonic velocity up to 15% (mole fraction 0.07), there after it decreases. This is because ACN in water forms clathrates which are supposed to contain "monomeric" H_2O molecules (i.e., not hydrogen-bonded with the infinite network). So this suggests formation of clathrate-like hydrates with water (Jerie, et al., 2005) which resulted in decrease in solute-solvent interactions and is in accordance with the observed variation of ultrasonic velocity. Adiabatic compressibility increases for the present system with increase in concentration of the solution. This is because the value of adiabatic compressibility shows an inverse behavior as compared to the ultrasonic velocity. The free length is the distance between the surfaces of the neighboring molecules. It increases with increase in concentration of the solution. The results are in accordance with the fact that ultrasonic velocity and intermolecular path length have been reported to vary inversely of each other with the composition of the mixture as in the present system (Eyring and Kincaid, 1938; Ali et al., 1996; Ali et al., 1998; 2000). Acoustic impedance decreases whereas relaxation time first increases and then decreases with increase in concentration of solution. This is clearly due to the increasing free space between the molecules and the weakening of intermolecular forces.

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The increasing trends of Rao's constant or molar sound velocity with concentration suggest the availability of more number of components in a given region thus leads to a close packing of the medium and thereby increase the interactions. The increasing trends of Wada's constant are in accordance with the observed variation of Rao's constant with concentration. Formation of clathrate like hydrates by acetonitrile with water is also supported by other acoustical parameters such as relaxation time, gibb's free energy, available volume and absorption coefficient. Free volume first decreases and then increases with increase in concentration of solution whereas absorption coefficient first increases and then decreases with increase in concentration of solution. Again, this is in agreement with the observed ultrasonic velocity and viscosity data. Gibb's free energy first increases and then decreases with increase in concentration of solution which indicates weak structure breaker nature of acetonitrile. Relative association decreases with increase in concentration of solution for aqueous solution of acetonitrile. It is the measure of extent of association of the component in the mixture. Available volume first decreases and then increases with increase in concentration of solution. The absorption coefficient trend and available volume trend confirms the earlier conclusions.

From figure 2, it is seen that adiabatic compressibility increases for the present system with increase in concentration of the solution. The values of intermolecular free length and free volume for aqueous solutions of acetonitrile at different concentration have been presented in the figure 3 & 4. The values of intermolecular free length increase with increase in concentration of the solution. Free volume first decreases and then increases with increase in concentration of solution. As can be seen from figure 5 the variation of Gibb's free energy versus concentration for the present system. Gibb's free energy first increases and then decreases with increase in concentration of solution. These results are in accordance with clathrate like structure of acetonitrile.
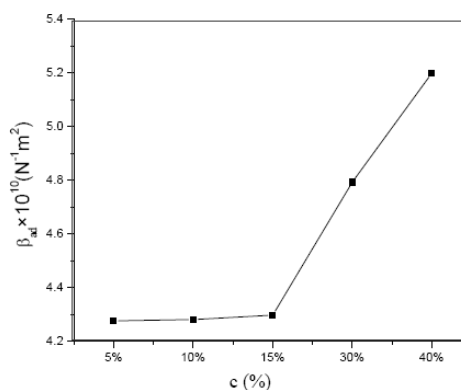

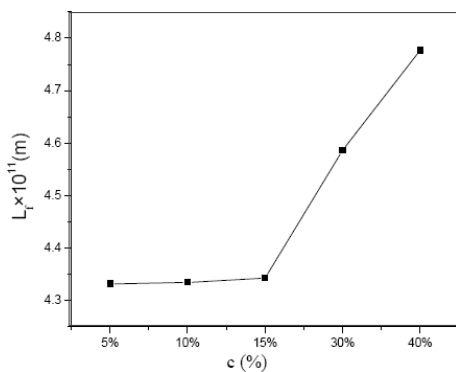**Figure 2:** A plot of adiabatic compressibility versus concentration.

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Figure 3: A plot of intermolecular free length versus concentration.

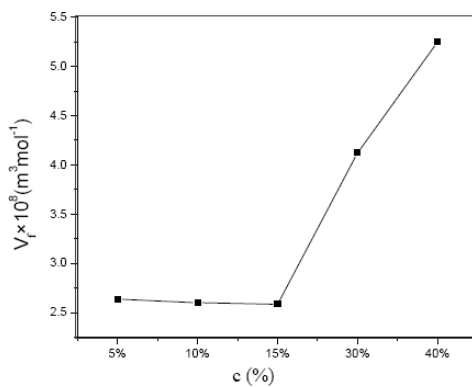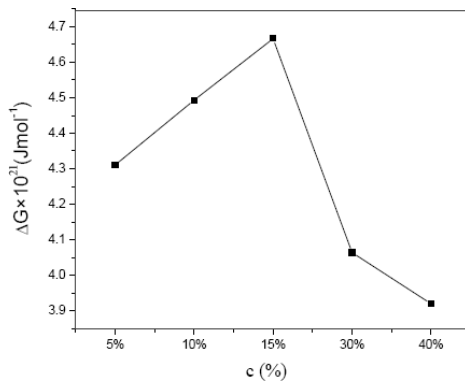**Figure 4:** A plot of free volume versus concentration.

Figure 5: A plot of Gibb's free energy versus concentration.

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CONCLUSION

A systematic study of acetonitrile in water has been carried out at different concentrations using ultrasonic experiments. Viscosity increases initially with addition of ACN to water up to solute mole fraction of about 0.07 and after it decreases monotonically. It may be due to the formation of suspension of solvates in the solution with no enhancement or breakdown of hydrogen bonded network after mole fraction of 0.07. From ultrasonic velocity and related acoustical parameter values for the binary liquid mixture of acetonitrile in water at 308.15 K, it is concluded that acetonitrile is too weak hydrophobic agent to stabilize typical clathrate hydrates. It is a weak structure-breaker also.

ACKNOWLEDGEMENTS

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