Ultrasonic Investigation of Thermodynamic Parameters in Binary Liquid Mixture of Acetonitrile in 2- Propanol at 301.15K

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ABSTRACT:

The ultrasonic velocity (u), density (ρ) and viscosity (η) and related thermo-acoustic parameters are the important tools in understanding the nature and extent of pattern of molecular interactions between components of liquid mixture. The ultrasonic velocity, density and viscosities of binary liquid mixture containing Acetonitrile in 2- Propanol over whole concentration range have been measured at 305.15K. This measured data have been used to compute derived thermo-acoustic parameters like adiabatic compressibility (β_{ad}), free length (L_f)), free volume (V_f), internal pressure (π_i), and acoustic impedance (Z). The variation of these parameters with concentration and temperature are also used to correlate with the structural changes observed in binary liquid mixture.

Keywords: Binary liquid mixture, ultrasonic velocity (u), density (ρ) and viscosity (η), adiabatic compressibility (β_{ad}), free length (L_f), free volume (V_f),internal pressure (π_i), molar volume(Vm).

INTRODUCTION

The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures [1-4]. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids [5-10]. The study of molecular association in binary liquid mixture having alcohol as one of component is of particular interest since alcohols are strongly self associated liquids having three dimensional network of hydrogen bonding and can be associate with any other group having some degree of polar attraction[11-16]. In the present paper, an attempt has been made to determine the densities and ultrasonic velocities of the above said title binary mixtures. The result is interpreted in terms of molecular interaction such

as dipole-dipole interaction through hydrogen bonding between components of mixtures.

EXPERIMENTAL

The chemicals Acetonitrile and 2-Propanol used were of analytical grade and obtain from Merck chemicals private Ltd. (Purity 99.5%). The densities of pure components and binary mixtures were measured by hydrostatic sinker method with an accuracy 1 part in10^{+5}. Special attention was given to avoid the vaporization of solution. Comparing their density with literature values checked the purity of chemicals. The mixtures of various concentrations in mole fraction were prepared. The ultrasonic velocities in pure liquids and their mixtures have been measured by ultrasonic interferometer supplied by Mittal Enterprises, New Delhi at a central frequency of 5 MHz with accuracy ± 0.01 m/s. The viscosity of pure liquids and their mixtures is measured by an Ostwald/s Viscometer with accuracy ± 0.001Nm−2s. The temperature of pure liquids and their mixtures is maintained constant using temperature controlled water bath with an accuracy of ± 0.01K.. The time of flow was measured using a digital racer stop watch with an accuracy of 0.1 sec.

THEORY:

The *Density* was measured using the formula

$$\rho_2 = \left(\frac{W_2}{W_1}\right)\rho_1 \quad \text{---------- (1)}$$

Where, w_1 = weight of distilled water,

w_2 = Weight of experimental liquid,

ρ_1 = Density of water, ρ_2 = Density of experimental liquid.

The *Viscosity* was determined using the relation.

$$\eta_2 = \left(\frac{t_2}{t_1}\right)\left(\frac{\rho_2}{\rho_1}\right)\eta_1 \quad \text{---------- (2)}$$

Where, η_1 = Viscosity of water, η_2 = Viscosity of mixture, ρ_1 = Density of water, ρ_2 = Density of mixture, t_1 = Time of flow of water, t_2 = Time of flow of mixture.

The *Adiabatic Compressibility* (β) has been calculated from sound velocity '*U*' and the density (ρ) of the medium using the relation

$$\beta_{ad} = \frac{1}{\rho\, U^2} \quad \text{---------- (3)}$$

Intermolecular free length (L_f) has been determined by the equation:

$$L_f = K_T\sqrt{\beta_{ad}} \quad \text{---------- (4)}$$

Where K_T is a Jacobsen's constant. (K_T = 93.875 + 0.375 T) X 10^{-8} and T being the absolute temperature.

The *Free Volume* (V_f) in terms of ultrasonic velocity (U) and the viscosity (η) of a liquid is

$$V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{3/2} \text{--------- (5)}$$

Where Meff is the effective molecular weight

$$Meff = \Sigma\, mi\, xi$$

In which mi & xi are the molecular weights and mole fraction of individual constituents respectively and K is a temperature dependent constant equal to 4.28 × 10^9 for all liquids in MKS system.

The *Specific Acoustic Impedance* is given by:

$$Z = U.\rho \text{ ---------- (6)}$$

Where '*U*' is the velocity and 'ρ' is the density of the mixture.

Relaxation Time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. The relaxation time can be calculated from the relation.

$$\tau = 4/3.\ (\beta.\eta) \text{ ----------(7)}$$

Internal Pressure (Πi): The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant force of attraction and force of repulsion between the molecules. It is calculated by using the relation:

$$\Pi i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{Meff^{7/6}}\right) \text{ ----------(8)}$$

RESULT AND DISCUSSION:

Ultrasonic velocity (*u*), density (ρ), viscosity (η) and other related thermodynamic parameters are evaluated for binary Acetonitrile in 2- Propanol over whole concentration at 301.15K

Table 1: For binary liquid mixture containing Acetonitrile in 2- Propanol at 301.15K

Mole fraction (X)	*U* (ms^{-1})	$\rho \times 10^3$ $(Kg\ m^{-3})$	$\eta\ x\ 10^{-3}$ $(Nm^{-2}\ s)$	$\beta \times 10^{-10}$ (m^2N^{-1})	$L_f\ X\ 10^{-11}$ *m*	$V_f x10^{-7}$ m^3	$Z\ X\ 10^5$ $Kg\ m^{-2}s^{-1}$	$\prod i$ $10^8\ Pa$
0	1217.3	0.7773	1.8803	8.6824	6.0937	0.2741	9.4618	9.1465
0.1	1220.5	0.7776	1.3602	8.6326	6.0762	0.4262	9.4909	8.0685
0.2	1224.7	0.7779	1.0661	8.5704	6.0543	0.5873	9.5271	7.4152
0.3	1227.5	0.7781	0.848	8.5289	6.0396	0.7889	9.5515	6.8776
0.4	1231.5	0.7787	0.7298	8.4683	6.0181	0.9411	9.5893	6.6442
0.5	1239.4	0.7794	0.6732	8.3530	5.9770	1.0147	9.6596	6.6453
0.6	1244.8	0.7797	0.5954	8.2769	5.9497	1.1592	9.7058	6.5232
0.7	1249.5	0.7799	0.4963	8.2122	5.9264	1.4429	9.7452	6.2289
0.8	1251.5	0.7801	0.4696	8.1851	5.9166	1.4762	9.7626	6.3565
0.9	1256.7	0.7803	0.4033	8.1145	5.8911	1.7489	9.8062	6.1846
1	1260.0	0.7806	0.4018	8.0692	5.8746	1.6492	9.8356	6.5022

Fig-1: Ultrasonic Velocity Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

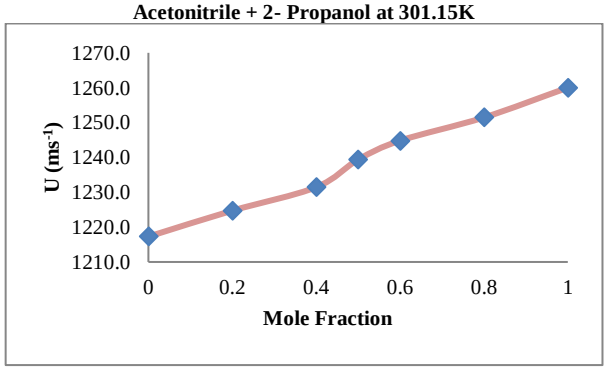


Fig-2: Density Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

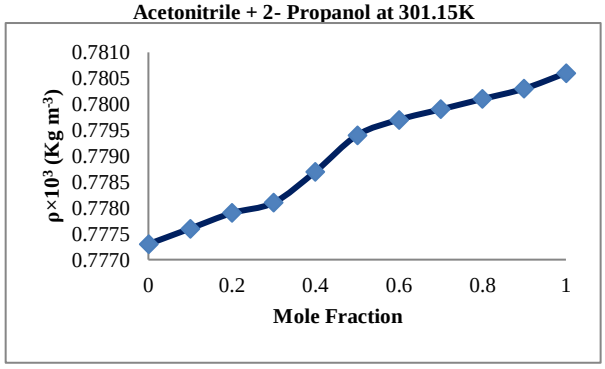


Fig-3: Viscosity Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

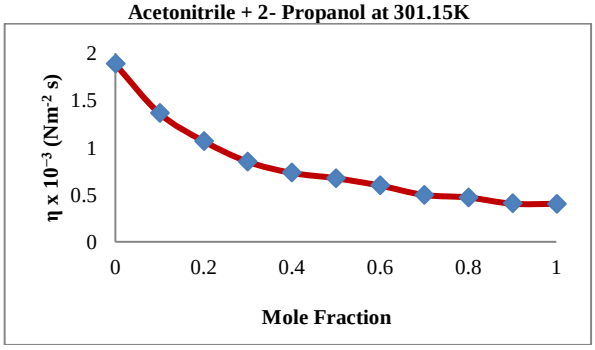


Fig-4: Adiabatic Compressibility Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

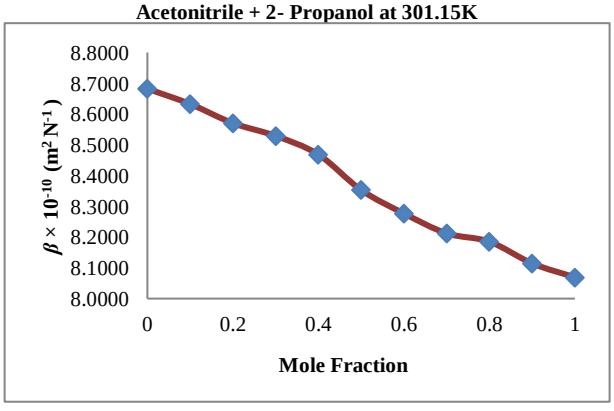


Fig-5: Free Length Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

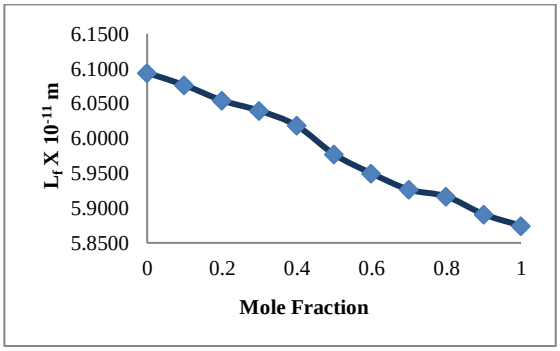


Fig-6: Free Volume Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

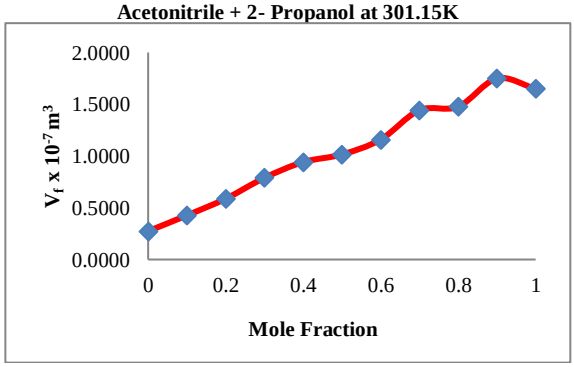


Fig-7: Acoustic Impedance Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K

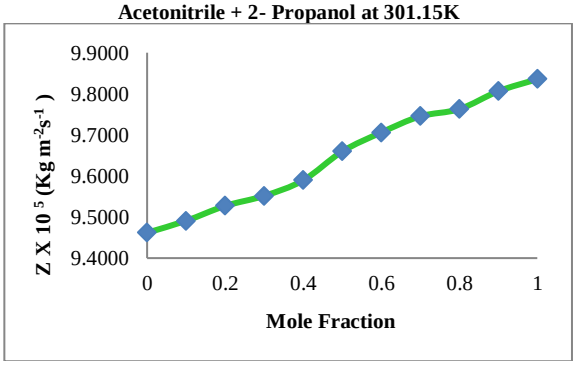
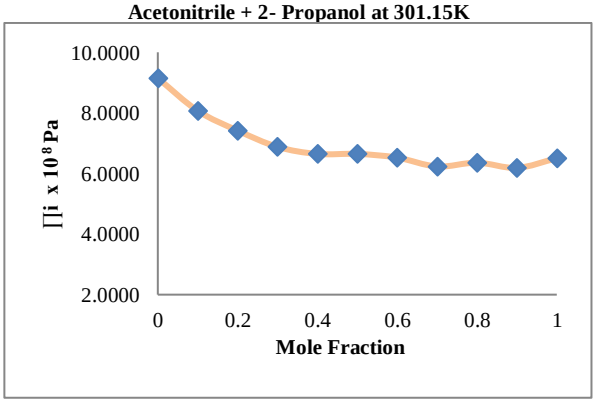


Fig-8: Internal Pressure Vs Mole fraction of Acetonitrile + 2- Propanol at 301.15K



From the table1 is noted that the Ultrasonic velocity and density increases with

increase in mole fraction for all the cases. Viscosity decreases with increase in mole fraction of the solute in all the systems. The increase in velocity is due to the decrease in free length and adiabatic compressibility of the liquid mixtures. It is observed that for a given concentration as the number of CH group or chain length increases, the sound velocity increases. The adiabatic compressibility and free length decrease with increase of mole fraction in the system. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in liquid system. The internal pressure decrease and free volume increases with increasing mole fraction. The internal pressure may give information regarding the nature and strength of forces existing between the molecules. The decrease in free volume shows that the strength of interaction decreases gradually with the increase in solute concentration. It represents that there is weak interaction between the solute and solvent molecules. Acoustic impedance increases with increase of mole fraction in the system.

In the binary liquid systems (Acetonitrile in 2- Propanol) under investigation, the variation of ultrasonic velocity (U), density(ρ), viscosity(η), adiabatic compressibility (β), free length(Lf),free volume (Vf), acoustic impedance (Z) and internal pressure(∏i) are shown in Fig-1 to Fig-8. The variation of these acoustic parameters indicate existence of molecular interaction between solvent and solute and indicate that the intermolecular interaction at specific concentration and it may leads to formation weak hydrogen bonded complex in binary liquid mixture. Beyond this optimum concentration, addition of solute in a solvent tries to break this weak complex structure and tends towards the values of pure components.

CONCLUSION:

The computed acoustical parameters and their values point to the presence of specific molecular interaction in the mixtures. Hence it is concluded that the interaction between the molecules of two liquids takes place because of the presence of various forces like a dispersive force, charge transfer, hydrogen bonding and dipole induced dipole interactions.

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