



Research Article

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Ultrasonic Investigation of Molecular Interactions in Ternary Mixtures at 303 K

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ABSTRACT

The ultrasonic velocity, density and viscosity at 303 K have been measured in the ternary system Ethyl hydroxybenzoate + 1-Propanol with benzene. The acoustical parameters such as adiabatic compressibility, free length, free volume and acoustical impedance are calculated from the measured data at 303K. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Keywords: Ultrasonic velocity, Density, Viscosity, Acoustical parameters.

INTRODUCTION

In recent years ultrasonic investigation find extensive applications in probing in to the physicochemical behavior of binary liquid mixtures leading to an understanding of the liquid state [1-3]. Ultrasonic technique has been adequately employed to investigate the properties of any substance to understand the nature of molecular interactions in pure liquid liquid mixtures [2-5] and ionic interactions in electrolytic solutions [6, 7]. Though the molecular interactions studies can be best carried out through spectroscopic methods [8, 9] the other non spectroscopic techniques such as dielectric [10] magnetic [11] ultrasonic velocity and viscosity [12] measurements have been widely used in field of interactions and structural aspect evaluations studies. The measurements of ultrasonic velocity have been adequately employed in understanding the nature of molecular systems and physicochemical behavior in liquid mixtures [13-16].

EXPERIMENTAL SECTION

The Ultrasonic Velocity was measured using a single crystal variable path interferometer working at 2MHz by standard procedure. The accuracy of ultrasonic velocity determination in the solution is $\pm 0.001\%$. The velocities were measured at room temperature 303 K. The densities were measured using a specific gravity bottle by standard procedure and the viscosity was measured using Oswald's viscometer with an accuracy of $\pm 0.1\%$.

RESULTS AND DISCUSSION

The calculated parameters such as acoustic impedance (Z), adiabatic compressibility (β), inter molecular free length (L_f), relaxation time (τ), molar volume (V), internal pressure (π_i) and free volume (V_f) are calculated using the following relation (1- 7).

$$Z = \rho U \quad (1)$$

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

$$L_f = K_T \beta^{1/2} \quad (3)$$

$$\tau = \frac{4\eta}{3\rho U^2} \quad (4)$$

$$V = \frac{M_{eff}}{\rho} \quad (5)$$

$$\pi_i = bRT \left(\frac{K\eta}{U} \right)^{1/2} \left[\frac{\rho^{2/3}}{(M_{eff})^{7/6}} \right] \quad (6)$$

$$V_f = \left[\frac{UM_{eff}}{\eta K} \right]^{3/2} \quad (7)$$

The measured values such as ultrasonic velocity (U), density (ρ) and viscosity (η) of Ethyl hydroxybenzoate+1-Propanol with benzene are given in Table 1. It is clearly evident that measured parameters like sound velocity, density are decreasing where as viscosity follows increasing trend for decreasing concentration of X₂. The ultrasonic velocity studies carried out in the present investigation reveal that the velocity varies with concentration due to the solute –solvent interactions through molecular association. The existing particle-particle resistance initiates some more interactions and this is supported by the measured parameters. A keen look at the Table 1 suggest that the range of density, sound velocity, and their variation with concentration of EHB+1Propanol is appreciable, this liquid composition suggests the basis of structural changes as well as interaction between like molecules and unlike molecules. On comparing the concentrations of EHB+1Propanol with benzene it is evident that the ultrasonic velocity and density keep on decreasing. The shear viscosity increases with increase of concentration once again confirmed the existence of solute – solvent interaction.

Table 1. Measured Ultrasonic velocity (U), density (ρ) and viscosity (η) and calculate dacoustical impedance(Z), adiabatic compressibility (β), free length (L_f), relaxation time (τ) and for Ethyl hydroxybenzoate+1-Propanolwith benzene at 303 K.

X ₂	U ms ⁻¹	η mPa-s	ρ x10 ³ Kg.m ⁻³	Z x10 ³	β x10 ⁻¹⁰ m ² N ⁻¹	L _f x 10 ⁻¹¹ m	τ x 10 ⁻¹³ sec	V x 10 ⁻⁶ m ³ .mol ⁻¹
0.02% of EHB								
90%	1250.0	0.6755	0.8637	1079.6	7.4103	5.4011	6.6741	89.5836
80%	1241.2	0.7414	0.8597	1067.1	7.5500	5.4518	7.4633	82.1406
70%	1232.7	0.7800	0.8529	1051.4	7.7160	5.5114	8.0245	74.8859
60%	1224.2	0.8511	0.8477	1037.8	7.8714	5.5666	8.9327	67.3814
0.03% of EHB								
90%	1252.3	0.7028	0.8642	1082.2	7.3786	5.3895	6.9137	89.5287
80%	1242.6	0.7499	0.8603	1069.1	7.5278	5.4437	7.5268	82.0836
70%	1234.5	0.8042	0.8547	1055.2	7.6769	5.4974	8.2314	74.7238
60%	1228.1	0.8808	0.8488	1042.4	7.8116	5.5454	9.1739	67.2964
0.04% of EHB								
90%	1255.1	0.7157	0.8650	1085.6	7.3392	5.3751	7.0040	89.4494
80%	1245.3	0.7728	0.8609	1072.1	7.4901	5.4301	7.7174	82.0281
70%	1239.1	0.8363	0.8571	1062.0	7.5991	5.4695	8.4730	74.5189
60%	1232.4	0.8989	0.8527	1050.9	7.7216	5.5134	9.2540	66.9871
0.05% of EHB								
90%	1256.7	0.7384	0.8658	1088.0	7.3137	5.3658	7.2002	89.3663
80%	1251.2	0.8272	0.8616	1078.1	7.4135	5.4023	8.1769	81.9605
70%	1245.4	0.8988	0.8571	1067.4	7.5227	5.4419	9.0151	74.5224
60%	1238.2	0.9955	0.8527	1055.8	7.6494	5.4875	10.1531	66.9871

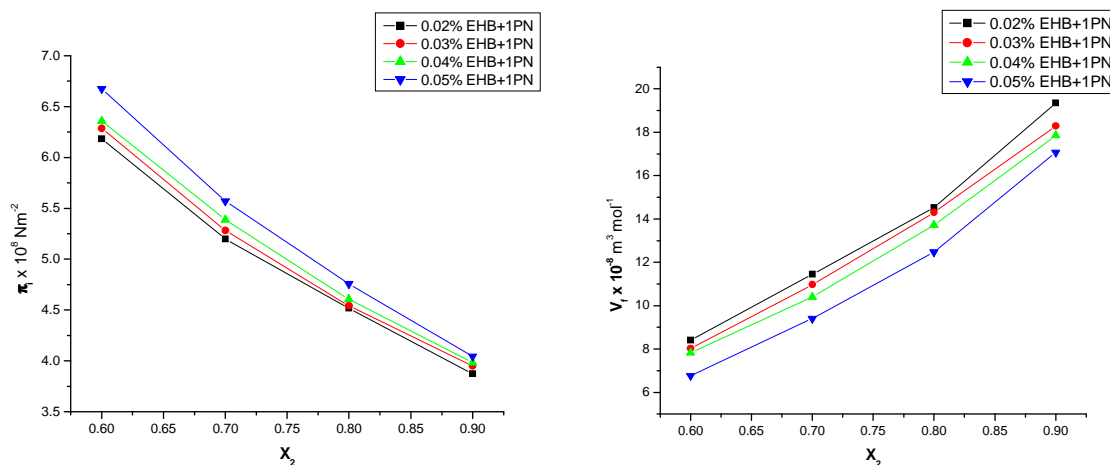


Fig.1 Variation of Internal pressure (π_i) and Free volume (V_f) with X_2 .

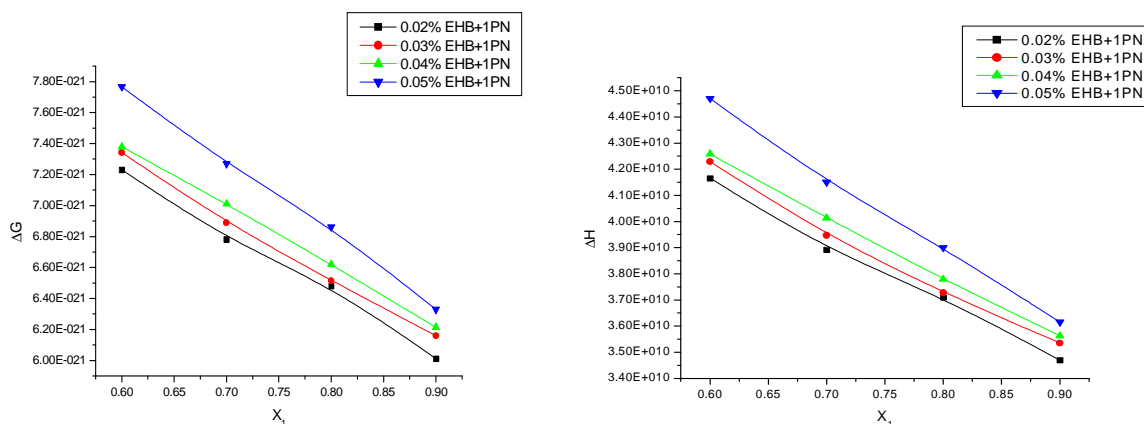


Fig.2 Variation of Gibbs free energy (ΔG) and Helmholtz free energy (ΔH) with X_2 .

The specific acoustic impedance Z is varied linearly with concentration of solution. Adiabatic compressibility (β) shows an increasing trend. The intermolecular free lengths L_f has been calculated by using semiempirical relation given by Jacobson [17]. The values of L_f reflect the same trend as that of β . According to Eyring and Kincaid [18], the ultrasonic velocity increases, if the L_f decreases and vice – a – versa in a result of mixing components. The decrease or increase in the values of L_f can be explained on the basis of interactions between the solute and solvent molecules.

Relaxation time shows an increasing trend and molar volume shows a decreasing trend. The computed other parameters like free volume and internal pressure are given in Fig 1. The values of V_f are decreasing in trend (for decreasing X_2) which suggest that there is a specific interaction between the components of the mixtures. An inverse trend is observed in case of internal pressure as expected. The observed decreasing values of V_f are due to close association between solute and solvent molecules. Similar trends were observed by earlier workers [19,20].

Similar trend was observed for relaxation time in our dielectric work²¹. Hence the formation of hydrogen bonding between hydroxyl group (-OH) of IPN and -CH group of hydroxyl benzoates restricts the free internal orientation of the molecules. Gibbs free energy and Helmholtz free energy also showed same trend [21]. This trend indicates the presence of interaction between the molecules of the mixture.

The increase in adiabatic compressibility and free length with decreasing concentrations of X₂ indicates significant interactions between Ethylhydroxybenzoate and the alkanol molecules forming hydrogen bonding through dipole-dipole interaction.

As alkanols are liquids which are associated through hydrogen bonding and in the pure state they exhibit equilibrium between multimer and monomer species.

The dipole-dipole interaction through hydrogen bonding between Ethyl hydroxybenzoate and alkanols clearly enhance the decrease in isentropic compressibility and free length. Similar results were observed by earlier workers in their liquid mixtures. Further, the increase in free volume and decrease in internal pressure with rise in concentrations of X₂ in all the systems clearly show the increasing magnitude of interactions [22].

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