Ultrasonic Study of Molecular Interactions in Binary Mixtures at 308 K

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ABSTRACT

The ultrasonic velocity, density and viscosity at 308 K have been measured in the binary systems of 1,4-dioxane and ethanol with methanol. From the experimental data, various acoustical parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), free volume (V_f), internal pressure (Π_i), were calculated. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Keywords: Ultrasonic velocity, Acoustical properties, Molecular interactions.
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INTRODUCTION

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interactions in pure liquid [1], 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 [12-17] measurements have been widely used in field of interactions and structural aspect evaluations studies. In the present work an attempt has been made to investigate the behaviour of binary solutions of methanol and ethanol in 1, 4-dioxane with regard to adiabatic compressibility, intermolecular free length, free volume and internal pressure from ultrasonic measurements at 308 K.

MATERIALS AND METHODS

Solutions of different molality (m) were prepared for each binary system. The ultrasonic velocity (U) in liquid mixtures which prepared by taking purified AR grade samples, have been measured at 308 K using an ultrasonic interferometer (Mittal type, Model F-83) working at 2 MHz frequency. The accuracy of sound velocity was ±0.1 ms-1. The density (ρ) and viscosity (η) were measured using a pycknometer and an Ostwald's viscometer respectively with an accuracy of 3 parts in 10^5 for density and 0.0001 Nsm^{-2} for viscosity.

RESULTS AND DISCUSSION

Various acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure, were calculated using the experimental data of ultrasonic sound velocity, density and viscosity by the following equations (1-4).

$$\beta_a = (U^2 \rho)^{-1} \qquad\qquad \text{..... (1)}$$

$$L_f = K_T \beta a^{1/2} \qquad\qquad \text{..... (2)}$$

$$V_f = (M_{eff} \, U/\eta K)^{3/2} \qquad\qquad \text{….. (3)}$$

$$Лi = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M_{eff}^{7/6}) \qquad \text{….. (4)}$$

Where, K_T is the temperature dependent constant having a value $209.5906*10^{-8}$ in MKS system at temperature 308 K, K is constant equal to $4.28*10^{9}$ in MKS system, b is a cubical packing fraction taken as 2 for all the liquids, R is the Universal gas constant, T is the experimental temperature, $M_{eff} = \Sigma \, x_i m_i$, where x_i is the mole fraction and m_i is the molecular weight of the component.

The measured parameters *viz.*, ultrasonic velocity (U), density (ρ) and viscosity (η) and calculated parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), free volume (V_f) and internal pressure ($Л_i$) for the **system I: 1,4-dioxane + Ethanol** at temperature 308 K are given in Table 1. Table 2 shows, the measured parameters *viz.*, ultrasonic velocity (U), density (ρ) and viscosity (η) and calculated parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), free volume (V_f) and internal pressure ($Л_i$) for the **system II: 1,4-dioxane + Methanol** at temperature 308 K. Table shows that, in both the system I and system II, velocity increases with concentration of 1,4-dioxane in ethanol and methanol. This indicates that strong interaction observed at higher concentrations of X. The density values also have the same trend with velocity in the system I and system II. Viscosity decreases in system I and system II, suggesting thereby more association between solute and solvent molecules.

From the same Table 1 and Table 2, it is observed that adiabatic compressibility (β_a) decreases with increase in concentration of 1,4-dioxane as expected. This increase in structural order of ethanol and methanol may result in more cohesion, and leads to a decrease in β_a. The decrease in β_a results in an increase in the value of U. The free length (L_f) is another parameter which is calculated using ultrasonic velocity and adiabatic compressibility. It is observed that L_f, decreases with the concentration of 1,4-dioxane in system I and system II. Decrease in intermolecular free length leads to positive deviation in sound velocity and negative deviation in compressibility. This indicates that the molecules are nearer in the system.

The computed other parameters like free volume (V_f) and internal pressure ($Л_i$) system I and system II are given in Table 1 and 2. The variation in free volume (V_f) increases with increases in molality of 1,4-dioxane in system I and system II. The free volume is the space available for the molecule to move in an imaginary unit cell. This reduces internal pressure. The variations in internal pressure are given in the same Table 1 and 2. As stated above the internal pressure ($Л_i$) decreases with increase in molality of 1,4-dioxane in both the systems I and II. An inverse trend, as expected, is seen in the free volume changes in both the systems. The observed decreases values of V_f in system I and II are due to close association between solute and solvent. Thus, a progressive decrease in free volume and increase in internal pressure in methanol-1,4-dioxane mixtures clearly indicates the existence of ion-solvent interaction, due to which the structural arrangement is considerably affected.
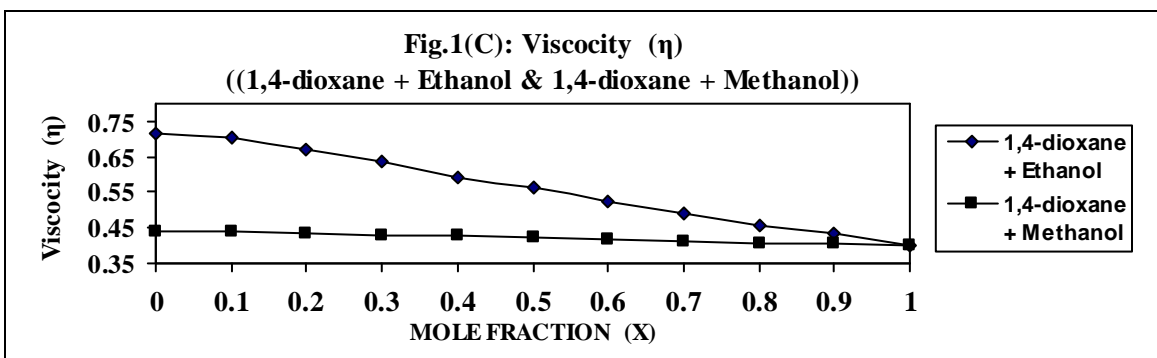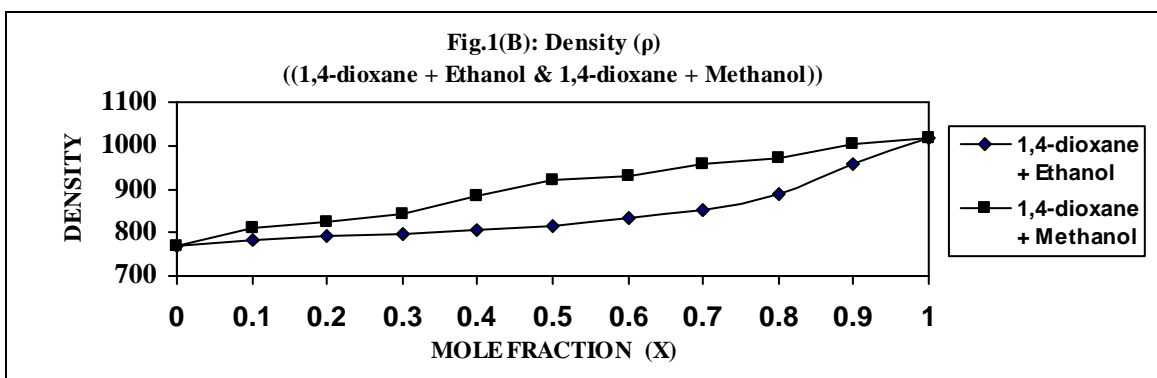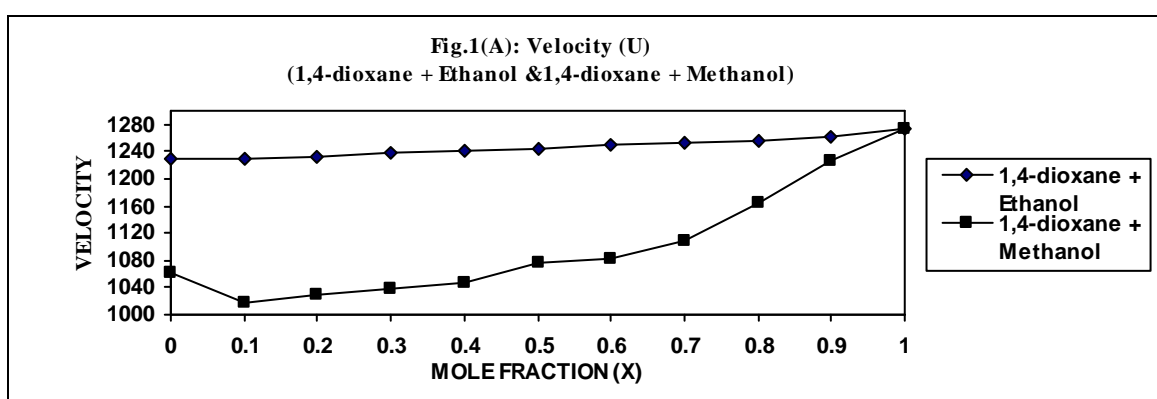
The variations of Velocity (*U*), Density (ρ), Viscosity (η) and adiabatic compressibility (β_a) with respect to compositions (X) of **1,4-dioxane + Ethanol** & **1,4-dioxane + Methanol** are shown in **Fig. 1(A), 1(B), 1(C) and 1(D)** respectively.
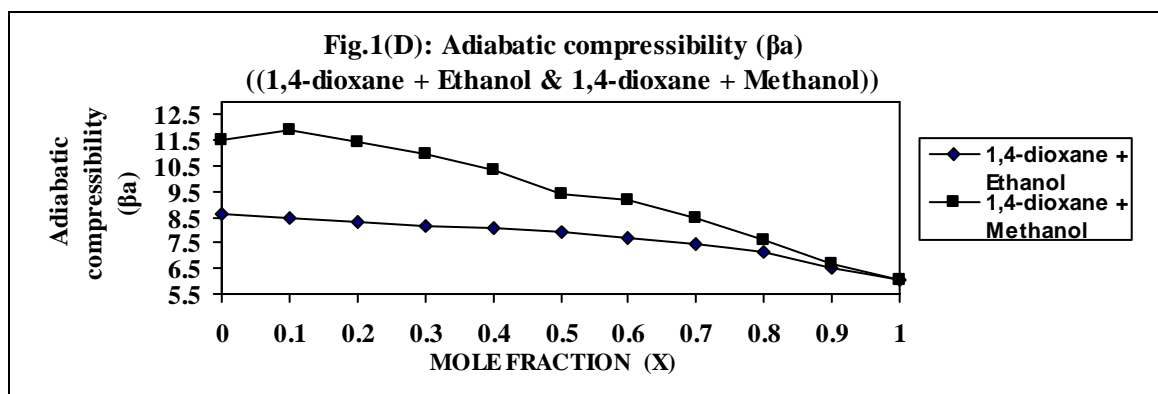
Table 1: Velocity (*U*), Density (ρ), Viscosity (η), Adiabatic compressibility (β_a), Intermolecular free length (L_f), Free volume (V_f) and Internal pressure ($Л_i$) of 1,4-dioxane + Ethanol at 308 K.

X	U (m/s)	ρ (kg/m³)	$\eta*10^{-3}$ (Ns/m²)	β_a*10^{-10} (Pa⁻¹)	L_f*10^{-10} (m)	V_f*10^{-7} (m³mol⁻¹)	$Лi*10^{8}$ (Pa)
0.0	1229.6	769.46	0.715	8.5958	0.6035	0.7962	7.53
0.1	1228.8	781.43	0.702	8.4752	0.5992	0.9321	6.81
0.2	1233.6	790.4	0.670	8.3139	0.5935	0.1134	6.09
0.3	1237.6	796.4	0.636	8.198	0.5893	0.1378	5.46
0.4	1241.6	805.4	0.594	8.0544	0.5842	0.1702	4.90
0.5	1245.0	814.4	0.562	7.9221	0.5793	0.2046	4.44
0.6	1249.3	832.3	0.527	7.6975	0.5711	0.2481	4.06
0.7	1253.0	853.3	0.491	7.4645	0.5624	0.3020	3.72
0.8	1256.0	889.2	0.457	7.1287	0.5496	0.3661	3.46
0.9	1261.6	958.1	0.433	6.5578	0.5271	0.4317	3.32
1.0	1273.6	1015	0.401	6.0741	0.5073	0.5287	3.13

Table 2: **Velocity (*U*), Density (ρ), Viscosity (η), Adiabatic compressibility (β$_a$), Intermolecular free length (*L$_f$*), Free volume (V$_f$) and Internal pressure (Л$_i$) of 1,4-dioxane + Methanol at 308 K.**

X	U (m/s)	ρ (kg/m^3)	η*10^{-3} (Ns/m^2)	β$_a$ *10^{-10} (Pa^{-1})	L$_f$*10^{-10} (m)	V$_{f*}$10^{-7} (m^{3}mol^{-1})	Л$_i$ *10^8 (P$_a$)
0.0	1063.2	770.35	0.439	11.484	0.6975	0.772	9.69
0.1	1019.0	808.4	0.438	11.913	0.7105	0.925	8.46
0.2	1029.0	823.4	0.434	11.471	0.6971	1.173	7.22
0.3	1038.0	844.3	0.431	10.993	0.6824	1.442	6.32
0.4	1046.0	883.2	0.428	10.348	0.6621	1.735	5.69
0.5	1077.3	919.2	0.423	9.3737	0.6302	2.137	5.11
0.6	1082.7	928.1	0.418	9.1918	0.6240	2.506	4.59
0.7	1109.3	958.1	0.413	8.4816	0.5995	2.993	4.19
0.8	1164.8	973.1	0.408	7.5746	0.5665	3.673	3.76
0.9	1225.6	1003	0.405	6.6375	0.5303	4.455	3.43
1.0	1273.6	1015	0.401	6.0741	0.5073	5.287	3.13

Fig.1(A): Velocity (U)
(1,4-dioxane + Ethanol &1,4-dioxane + Methanol)

Fig.1(B): Density (ρ)
((1,4-dioxane + Ethanol & 1,4-dioxane + Methanol))

Fig.1(C): Viscocity (η)
((1,4-dioxane + Ethanol & 1,4-dioxane + Methanol))

Fig. 1: The variations of Velocity (*U*), Density (ρ), Viscosity (η) and Adiabatic compressibility (β$_a$) with respect to compositions (X) of 1,4-dioxane + Ethanol & 1,4-dioxane + Methanol are shown in Fig. 1(A), 1(B), 1(C) and 1(D) respectively.

CONCLUSION

The ultrasonic velocity, density, viscosity and other related parameters were calculated. The observed increase of ultrasonic velocity indicates the solute-solvent interaction. The existence of type of molecular interaction is solute-solvent is favored in system I and II, confirmed from the U, ρ, η, βa, L_f, and Лi data.

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