



Studies of Acoustic and Thermodynamic Properties of Binary Liquid Mixtures at 308K

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ABSTRACT

The ultrasonic velocity, density and viscosity at 308K have been measured in the binary systems of 1,4-dioxane with ethanol and methanol. From the experimental data, various acoustical parameters such as adiabatic compressibility (β_a), specific acoustical impedance (Z), relaxation time (τ), Rao's constant (R), were calculated. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Keywords: Ultrasonic velocity, acoustical parameters, molecular interactions, specific acoustical impedance, molar volume, Rao's constant and binary liquid mixtures, Molecular interaction.

INTRODUCTION

Ultrasonic study finds extensive applications for characterizing aspects of Physico-chemical behavior such as the nature of molecular interactions in pure liquids as well as liquid mixtures. In the recent years, the ultrasonic study of properties of liquid mixtures and solutions finds direct applications in chemical and biochemical industry [1, 2]. Liquid mixtures consisting of polar and non-polar components are of considerable importance in industries. Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality [3-6]. The measurements of ultrasonic velocity and density have been adequately employed in understanding the molecular interactions in the liquid mixtures [7-11]. The measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids [12]. The 1, 4-dioxane is selected as a solvent in the present work since it finds a variety of applications. Alcohol plays an important role in many chemical reactions due to the ability to undergo self-association with internal structures [13].

EXPERIMENTAL SECTION

All the chemicals used were of Analytical Reagent (AR) grade with minimum assay of 99.9%. The ultrasonic velocity (U) in liquid and liquids mixtures have been measured using an ultrasonic interferometer (Mittal type, Model F-83) working at 2 MHz fixed frequency with an accuracy of $\pm 0.1 \text{ ms}^{-1}$. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature. The density (ρ) of pure liquids and liquid mixtures was determined using pycnometer by relative measurement method with an accuracy of $\pm 0.1 \text{ Kg m}^{-3}$. An Ostwald's viscometer was used for the viscosity (η) measurement of pure liquids and liquid mixtures with an accuracy of $\pm 0.0001 \text{ N Sm}^{-2}$. The temperature around the viscometer and pycnometer was maintained within $\pm 0.1 \text{ K}$ in an electronically operated constant temperature water bath. All the precautions were taken to minimize the possible experimental error.

The various acoustical parameters such as adiabatic compressibility (β_a), specific acoustical impedance (Z), relaxation time (τ), Rao's constant (R) have been calculated from the measured data using the following standard expressions :

$$\beta_a = (U^2 \rho)^{-1} \quad \dots\dots (1)$$

$$Z = U \rho \quad \dots\dots (2)$$

$$\tau = 4/3 \eta \beta_a \quad \dots\dots (3)$$

and

$$R = U^{1/3} V \quad \dots\dots (4)$$

Where, $M_{\text{eff}} = \sum x_i m_i$, where x_i is the mole fraction and m_i is the molecular weight of the component.

RESULTS AND DISCUSSION

The experimentally measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), adiabatic compressibility (β_a), at 308K are listed in **Table-1** for the **system-I: 1,4-dioxane+ ethanol** and **system-II: 1,4-dioxane+ methanol**.

The calculated values of relaxation time (τ), molar volume (V), Rao's constant (R) of binary liquid at 308K are presented in **Table-2** for the **system-I: 1,4-dioxane+ ethanol** and **system-II: 1,4-dioxane+ methanol**. The variation of specific acoustical impedance (Z), relaxation time (τ), molar volume (V), Rao's constant (R) against mole fraction at 308K for the **system-I** and **system-II** are shown in **fig.1** respectively.

Table-1 shows that, for 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 has been 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).

Table 1: Velocity (U), Density (ρ), Viscosity (η), Adiabatic compressibility (β_a), specific acoustical impedance (Z), relaxation time (τ), Rao's constant (R) of 1,4-dioxane + Ethanol at 308K.

X	U (m/s)	ρ (kg/m ³)	$\eta \cdot 10^{-3}$ (Ns/m ²)	$\beta_a \cdot 10^{-10}$ (Pa ⁻¹)	Z (kg/m ² s)	$\tau \cdot 10^{-12}$ (s)	R (m ³ /mol) (m/s) ^{1/3}
0.0	1229.6	769.46	0.715	8.5958	946128.0	0.8195	0.6412
0.1	1228.8	781.43	0.702	8.4752	960221.2	0.7933	0.6889
0.2	1233.6	790.4	0.670	8.3139	975037.4	0.7427	0.7390
0.3	1237.6	796.4	0.636	8.198	985624.6	0.6952	0.7910
0.4	1241.6	805.4	0.594	8.0544	999959.8	0.6379	0.8391
0.5	1245.0	814.4	0.562	7.9221	1013891	0.5936	0.8861
0.6	1249.3	832.3	0.527	7.6975	1039855	0.5409	0.9224
0.7	1253.0	853.3	0.491	7.4645	1069172	0.4887	0.9538
0.8	1256.0	889.2	0.457	7.1287	1116860	0.4344	0.9670
0.9	1261.6	958.1	0.433	6.5578	1208714	0.3786	0.9462
1.0	1273.6	1015	0.401	6.0741	1292666	0.3248	0.9409

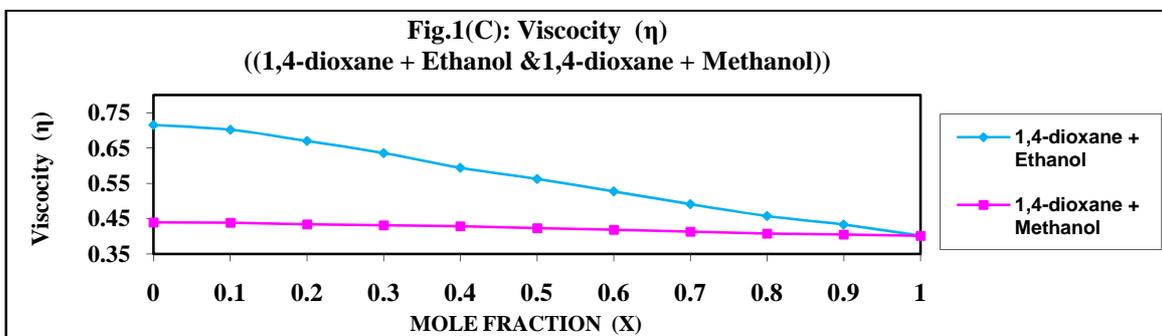
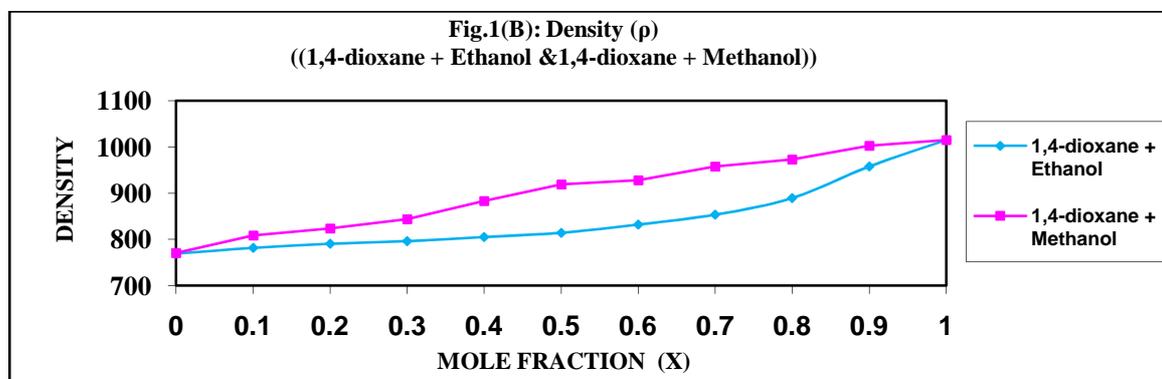
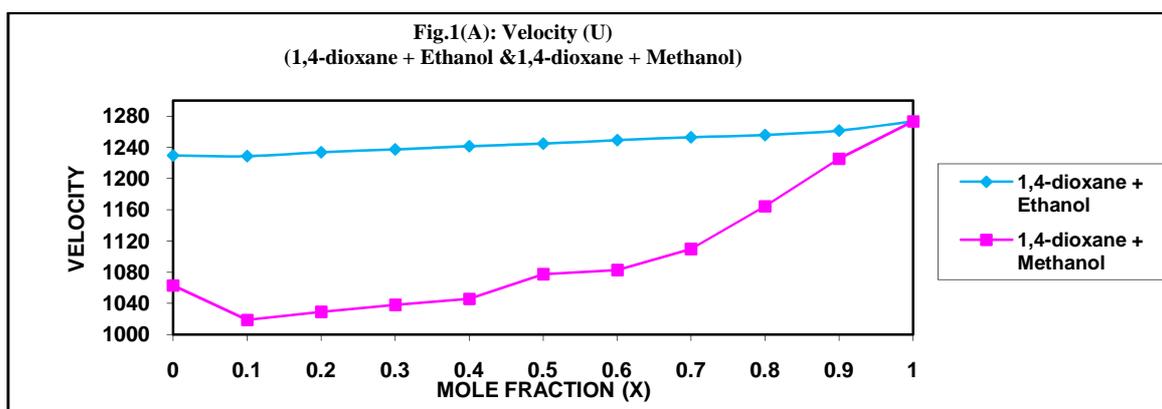
In **Table-2**, the acoustic impedance (Z), which is the product of ultrasonic velocity and density of the solution, increases with increase in concentration of dioxane, but relaxation time (τ) have completely reverse trend with that of velocity. This also indicates significant interactions in the system-I and system-II. The decrease in L_f and increase of Z with the concentration of 1,4-dioxane, suggest the presence of solvent-solute interactions in system-I and system-II. Rao's constant (R) is increasing linearly with molality of 1, 4-dioxane indicating the solute-solvent interactions may occur [14-17] in the system-I and system-II.

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.

The variations of specific acoustical impedance (Z), relaxation time (τ), Rao's constant (R) with respect to compositions **X** of 1, 4-dioxane + Ethanol are shown in **Fig. 2(A), 2(B) and 2(C)** respectively.

Table 2: Velocity (U), Density (ρ), Viscosity (η), Adiabatic compressibility (β_a), specific acoustical impedance (Z), relaxation time (τ), Rao's constant (R) of 1,4-dioxane + Methanol at 308K.

X	U (m/s)	ρ (kg/m ³)	$\eta \cdot 10^{-3}$ (Ns/m ²)	$\beta_a \cdot 10^{-10}$ (Pa ⁻¹)	Z (kg/m ² s)	$\tau \cdot 10^{-12}$ (s)	R (m ³ /mol) (m/s) ^{1/3}
0.0	1063.2	770.35	0.439	11.484	819036.1	0.6722	0.4244
0.1	1019.0	808.4	0.438	11.913	823739.2	0.6957	0.4686
0.2	1029.0	823.4	0.434	11.471	847227.2	0.6638	0.5303
0.3	1038.0	844.3	0.431	10.993	876393.8	0.6317	0.5859
0.4	1046.0	883.2	0.428	10.348	923858.6	0.5905	0.6260
0.5	1077.3	919.2	0.423	9.3737	990238.6	0.5287	0.6700
0.6	1082.7	928.1	0.418	9.1918	1004860	0.5123	0.7266
0.7	1109.3	958.1	0.413	8.4816	1062827	0.4671	0.7702
0.8	1164.8	973.1	0.408	7.5746	1133409	0.4121	0.8314
0.9	1225.6	1003	0.405	6.6375	1229265	0.3584	0.8802
1.0	1273.6	1015	0.401	6.0741	1292666	0.3248	0.9409



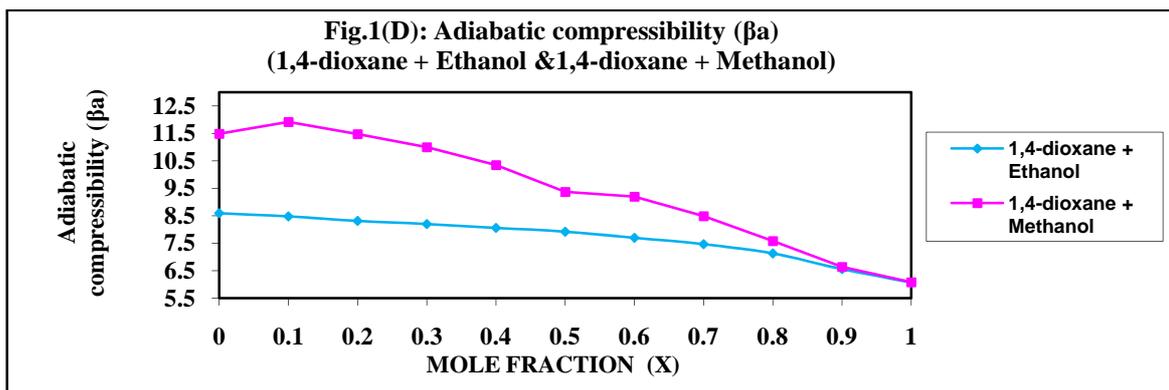
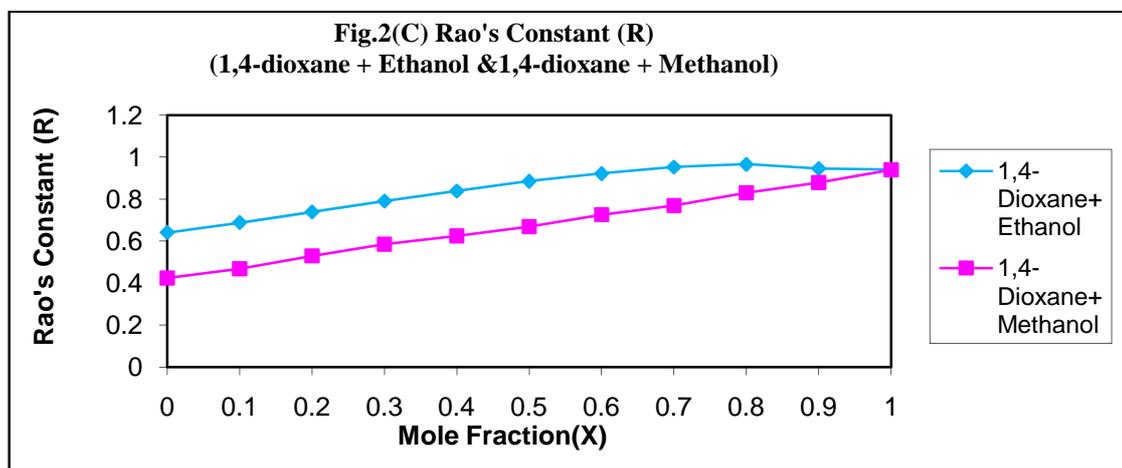
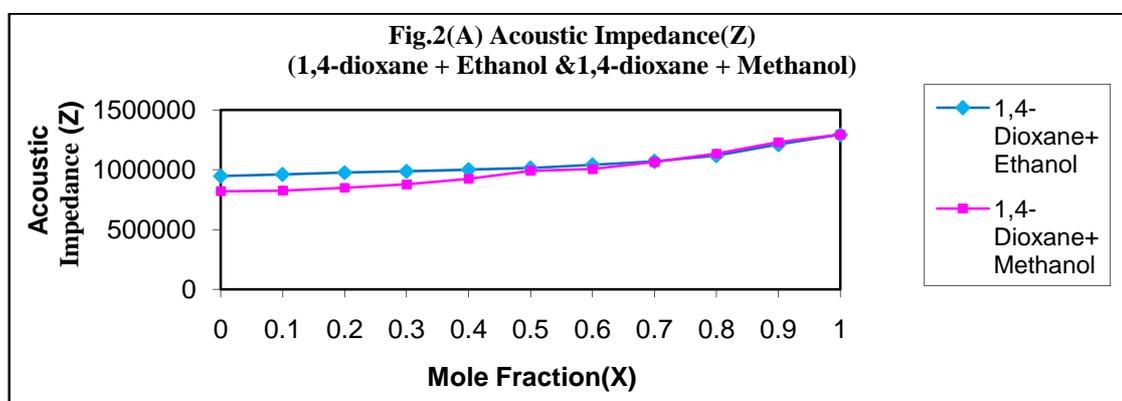


Fig. 1: The variations of Velocity (U), Density (ρ), Viscosity (η) and Adiabatic compressibility (β_a) with respect to compositions X of 1,4-dioxane + Ethanol & 1,4-dioxane + Methanol are shown in Fig.1(A), Fig.1(B), Fig.1(C) & Fig.1(D) respectively



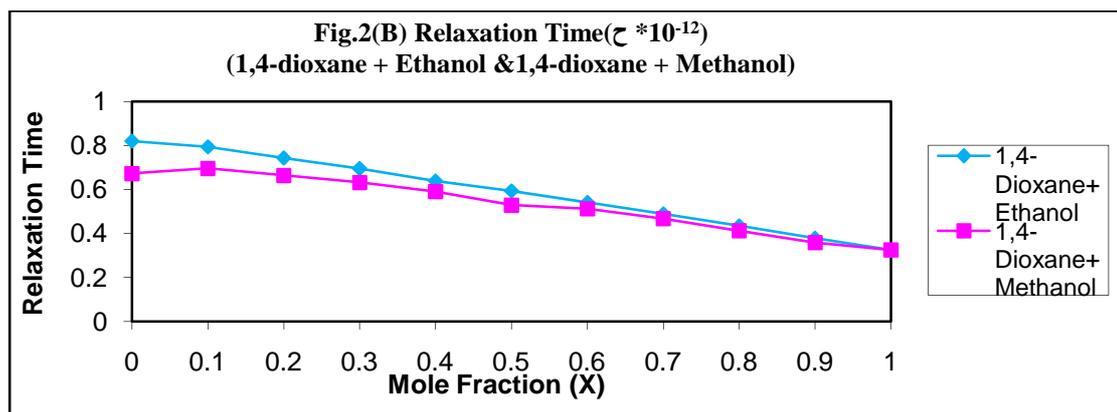


Fig. 2: The variations of specific acoustical impedance (Z), relaxation time (ζ), Rao's constant (R) with respect to compositions X of 1, 4-dioxane + Ethanol and 1, 4-dioxane + Methanol are shown in Fig. 2(A), 2(B) and 2(C) respectively.

CONCLUSION

Weak dispersive type intermolecular interactions are confirmed in the present systems. Dipole induction is found to be more in methanol system. Components maintain their individuality in the mixture. All the experimental determinations of adiabatic compressibility are strongly correlated with each other.

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