Molecular Interaction Study of Two Aliphatic Alcohols with 1,4-dioxane at 298 °K

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ABSTRACT

Sound velocity, density and viscosity values have been measured at 298 °K in the two binary systems of 1,4-dioxane with ethanol and methanol. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been estimated using the standard relations. The results are interpreted in terms of molecular interaction between the components of the mixtures. It has been observed that, the molecular interactions existing in the system is highly disturbed by the polar alcohol molecules and dispersive type interactions are existing in the system.

Keywords: Ultrasonic velocity, Adiabatic compressibility, free length, molecular interactions, dipolar and dispersive interactions.

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INTRODUCTION

The ultrasonic study of liquids is very important in understanding the nature and strength of molecular interactions. In many industrial applications liquid mixtures, rather than single component liquid system, are used in processing and product formulations[1,2]. Liquid mixtures consisting of polar and non-polar components are of considerable importance in industries such as petrochemical, pharmaceutical and dye. The formation and destruction of azeotropes in petrochemical industries[3], the biological activity of drug molecules[4] and the activation energy of the metabolic process[5] basically depend on the type and strength of the intermolecular interactions. Various methods are available to identify these interactions and ultrasonic study is one such more reliable and commonly used study.

Thermodynamic and transport properties of liquid mixtures have been extensively used[6-8] to study the departure of a real liquid mixture behaviour from ideality. Further, these properties have been widely used to study the intermolecular interactions between the various species present in the mixture [9-12].

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As alcohols are highly polar, they can easily form azeotropes of binary complexes. Ethanol is reported[13] to form azeotropic mixture with 1,4 dioxane at 337.8 ^{o}K whereas methanol at 347.7 ^{o}K and the separation is a major task in petrochemical industries.

In the present work, the measurement of ultrasonic velocity, density, viscosity and computation of related parameters at 298°K in two non-ideal binary mixtures of 1,4-dioxane + ethanol and 1,4-dioxane + methanol have been studied.

MATERIALS AND METHODS

2. Experimental Details:

The ultrasonic velocity (U) in liquid mixtures which prepared by taking purified AR grade samples, have been measured at 298 ^{o}K using an ultrasonic interferometer (Mittal type, Model F-83) working at 2 MHz frequency with an accuracy of $\pm$ 0.1 ms^{-1}. The density (ρ) and viscosity (η) are measured using a pycknometer and an Ostwald's viscometer respectively with an accuracy of 3 parts in 10^5 for density and 0.001 Nsm^{-2} for viscosity.

Sound velocity, density and viscosity values have been measured at 298 ^{o}K in the two binary systems of 1,4-dioxane with ethanol and methanol. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been calculated using the following standard expressions:

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

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

$$V_f = (M_{eff} U/\eta K)^{3/2} \qquad\qquad \ldots.. \quad (3)$$

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

Where, K_T is the temperature dependent constant having a value 205.8336*10^{-8} in MKS system at 298 ^{o}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.

RESULTS AND DISCUSSION

The measured values of sound velocity (U), density (ρ) and viscosity (η) for the two binary systems of 1,4-dioxane + methanol and 1,4-dioxane + ethanol at 298 ^{o}K are presented in Table 1and Adiabatic compressibility (β_a), free length (L_f), free volume(V_f) and internal pressure(Π_i) of 1,4-dioxane + Methanol and 1,4-dioxane + Ethanol at 298 ^{o}K are presented in Table 2.

The perusal of these Tables shows that the viscosity shows decreasing trend in both systems with the increase in mole fraction of 1,4-dioxane. As regards sound velocity and density, ethanol shows a continuous increase, whereas in methanol system, it initially decreases, exhibit a minimum at 0.1 mole fraction and then continually increasing with increase in mole fraction of 1,4-dioxane.

As per Edward Peters[14], a higher density or viscosity of a component molecule is a reflection of higher intramolecular interactions. So, among the three components taken here, methanol is

having higher intra interactions. A molecule having higher intra interaction is also expected to show high degree of intermolecular interactions. Thus among the two binaries, in any given mole fraction, ethanol records more velocity that reflects the existence of more intermolecular interactions.

Comparing the two alcohols, ethanol is a good solvent that can dissolve both the polar and nonpolar components. The hydrophilic –OH group of ethanol can dissolve the polar whereas the short hydrophobic hydrocarbon group can dissolve the nonpolar.

In the ethanol mixture, the 1,4-dioxane is completely dissolved and so no chances of hydrogen bond ruptures and only the interaction with the 1,4-dioxane ring and the active groups of ethanol, which are mostly dispersive in nature. The increase in mole fraction of 1,4- dioxane increases the net dispersive interactions and hence the velocity continuously increases as observed. The case of methanol mixture is different due to the less salvation tendency of methanol. It is to be remembered that the methyl group becomes more nonpolar with increase in chain length. Further the –OH group can dissolve preferably the polar component. So, in the lower mole fraction ranges the added 1,4-dioxane has practically no interaction with the methyl or hydroxyl group of methanol. As the mole fraction of 1,4-dioxane increases, the hydrogen bond rupture of the boat form is of considerable extent and they leads to additional dipole type interactions.1,4- dioxane being non-polar the predominant dispersive type interactions with temporary dipolar type are existing as a net result of intermolecular forces in both systems, but more in methanol system. The observed non-linear change in all these measured parameters indicates the existence of specific interactions[16].

A reduction in viscosity with increase in mole fraction of 1,4-dioxane suggests that the existing intermolecular interactions are weakening in magnitude. However, the increasing sound velocity and density with increasing mole fraction of 1,4-dioxane leads to a notion that the system is getting more and more compact, which is not true as the interactions due to 1,4-dioxane are dispersive in nature. This is indicated by the existence of minimum sound velocity in methanol system. However, as 1,4-dioxane mole fraction is increased, sound velocity exhibits increasing trend in methanol system.

The calculated parameters of adiabatic compressibility (β_a) and free length (L_f) are listed in Table 2. These tables suggests that for both systems β_a and L_f are of similar nature and in decreasing trend. In general, a continuously decreasing trend of β_a with increasing mole fraction of 1,4-dioxane in these systems lends support to the idea that the systems are in a more compressed state. The ruptured hydrogen bonds create many new dipoles in the medium and thereby increase the compactness. The reduction in L_f indicates that the components are much more closer. This confirms the existence of specific interactions between the components.

The perusal of methanol system shows that β_a and L_f are almost unaltered in intermediate mole fraction range, i.e., the addition of 1,4-dioxane in the mole fraction range of 0.2 to 0.8 has very small influence on compressibility and free length. This is clear evidence that interactions of weak nature, that too in very small magnitude, are existing in the system. As the dipole moment value of 1,4-dioxane is zero, it can offer only dispersive type interactions, whereas methanol can exhibit dipoles and can support induced dipoles. But, this inducement of dipoles in 1,4-dioxane seems to be highly restricted, as β_a and L_f almost remain unaltered. At higher mole fraction of 1,4-dioxane, because of its inherent compact structure, β_a and L_f are decreasing.

1,4-dioxane is a ring type molecule, whereas alcohol is a linear molecule. The reduction of alcohol reduces the straight chain type and the system is more and more occupied by ring-structured molecules, which occupies comparatively less space. In the two components, one is non-polar and the other is strong polar, attractive type interactions are feeble and so molecules are not in a closed shield or cage-like formation. Each component still maintains their identity and at the same time, the collective molecular influence is reduced. The increase in free space between the components offer a support to stabilize their independent nature and hence mutual force (attractive/repulsive) retains their original value, i.e., the interactive forces decrease.
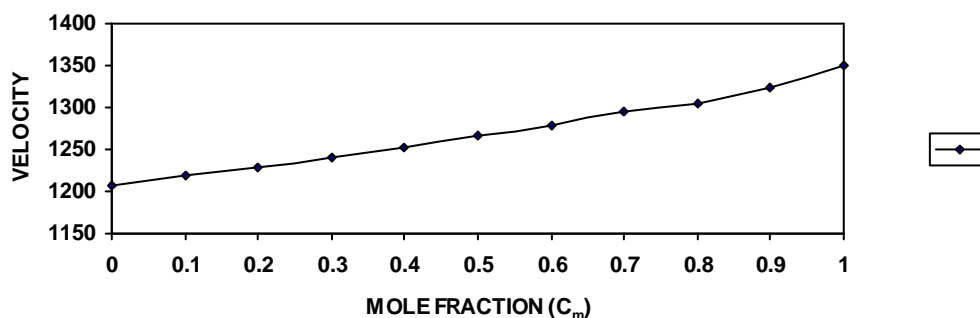
Table 1: Velocity (U), Density (ρ) and Viscosity (η), of 1,4-dioxane + Ethanol and 1,4-dioxane + Methanol at 298 ^{o}K.

X	U(m/s)		ρ (kg/m^3)		$\eta*10^{-3}$ (Ns/m^2)	
	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol
0.0	1208.00	1108.00	801.10	780.10	0.895	0.550
0.1	1218.10	1100.80	811.23	809.22	0.844	0.546
0.2	1229.00	1111.00	828.14	839.35	0.796	0.543
0.3	1241.33	1144.00	846.24	858.12	0.732	0.538
0.4	1253.00	1152.00	866.56	877.22	0.673	0.533
0.5	1266.67	1168.00	881.10	895.00	0.631	0.525
0.6	1279.00	1172.67	896.23	911.10	0.607	0.517
0.7	1295.10	1184.00	910.16	932.12	0.570	0.512
0.8	1305.00	1207.00	931.36	949.31	0.541	0.508
0.9	1325.00	1241.00	947.00	968.10	0.523	0.503
1.0	1350.00	1350.00	1030.0	1030.0	0.500	0.500

Table 2: Adiabatic compressibility (β_a), free length (L_f), free volume(V_f) and internal pressure(Π_i) of 1,4-dioxane + Ethanol and 1,4-dioxane + Methanol at 298 ^{o}K.

X	β_a*10^{-10} (Pa^{-1})		L_f*10^{-10} (m)		$V_{f*}10^{-7}$ (m^{3}mol^{-1})		Π_i*10^8(P$_a$)	
	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol
0.0	8.5542	10.4417	0.6020	0.6651	0.5535	0.5856	8.7282	10.7195
0.1	8.3078	10.1980	0.5932	0.657	0.6978	0.7467	7.6869	9.0971
0.2	7.9945	9.6522	0.5819	0.6394	0.8710	0.9402	6.8607	7.8694
0.3	7.6688	8.9043	0.5700	0.6142	1.1209	1.1960	6.0895	6.7955
0.4	7.3502	8.5898	0.5580	0.6032	1.4305	1.4425	5.4463	6.0257
0.5	7.0737	8.1901	0.5474	0.5890	1.7649	1.7450	4.9178	5.3690
0.6	6.8208	7.9814	0.5375	0.5815	2.0792	2.0536	4.5224	4.8489
0.7	6.5505	7.6528	0.5268	0.5694	2.5372	2.3905	4.1155	4.4314
0.8	6.3046	7.2306	0.5168	0.5534	3.0105	2.7890	3.8075	4.0513
0.9	6.0147	6.7071	0.5048	0.5330	3.5001	3.2797	3.5380	3.7105
1.0	5.3271	5.3271	0.4750	0.4750	4.1439	4.1439	3.4236	3.4236

Fig.2(A): Velocity (1,4-dioxane +Ethanol)

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

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

Fig.1(D): Adiabatic compressibility (βa)
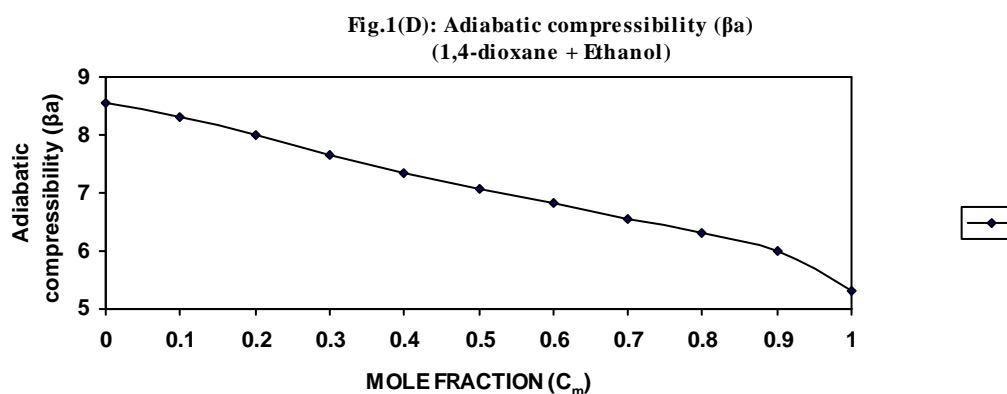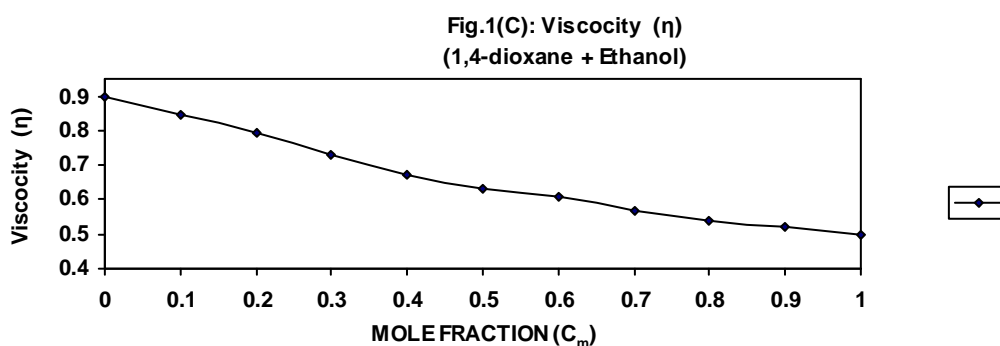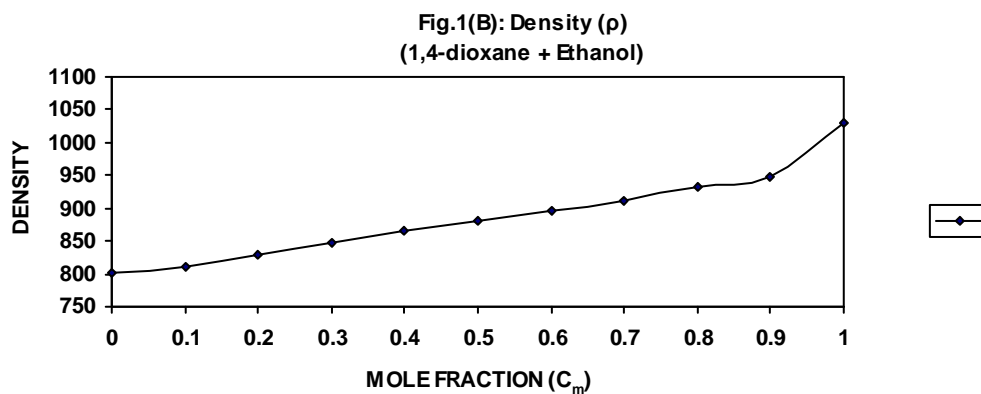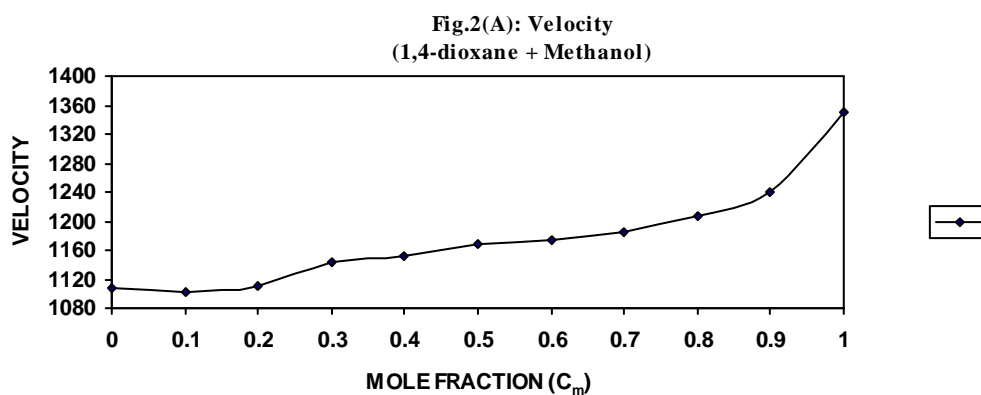**(1,4-dioxane + Ethanol)**

Fig. 1: The variations of Velocity (*U*), Density (ρ), Viscosity (η) and Adiabatic compressibility (β$_a$) with respect to compositions (C$_m$) of 1,4-dioxane + Ethanol are shown in Fig. 1(A), 1(B), 1(C) and 1(D) respectively.
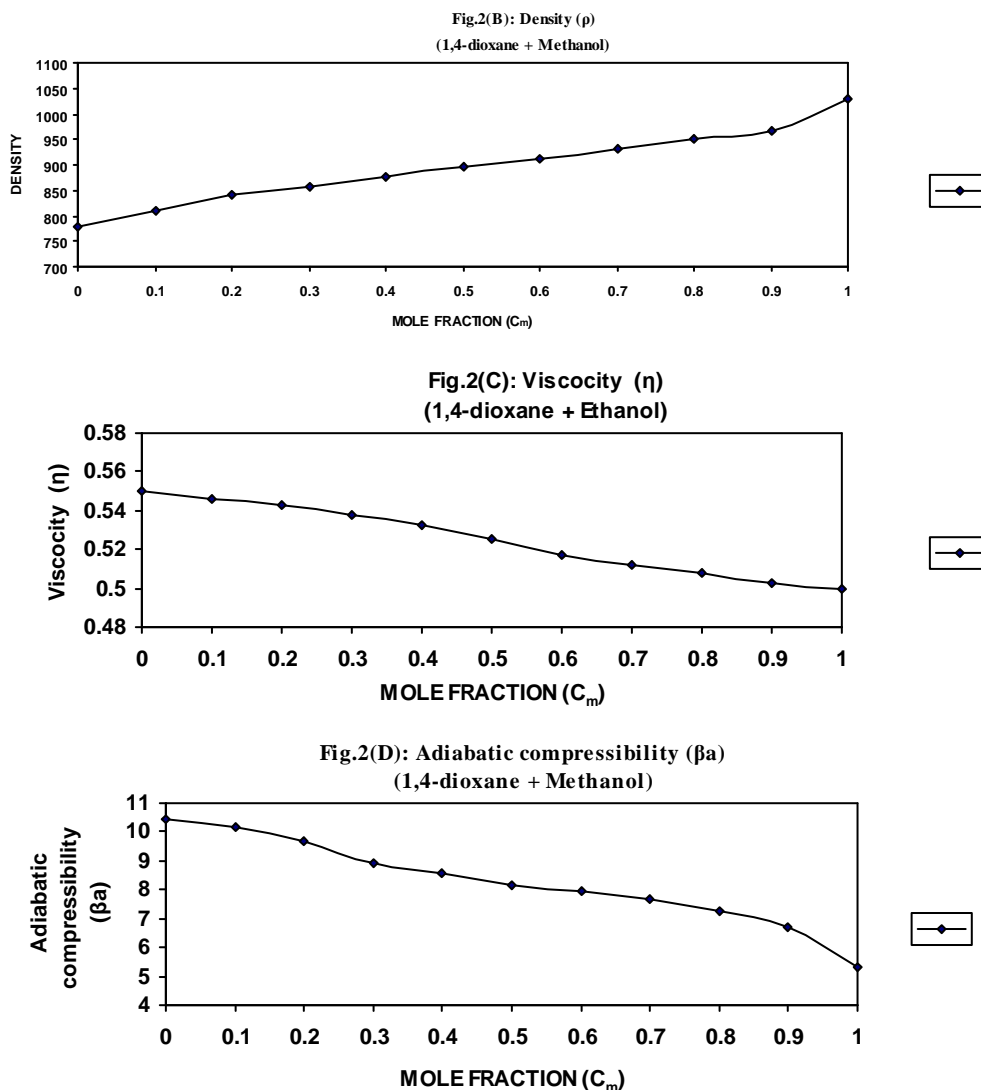
Fig.2(A): Velocity
(1,4-dioxane + Methanol)

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Fig.2(B): Density (ρ)
(1,4-dioxane + Methanol)

Fig.2(C): Viscocity (η)
(1,4-dioxane + Ethanol)

Fig.2(D): Adiabatic compressibility (βa)
(1,4-dioxane + Methanol)

Fig. 2: The variations of Velocity (*U*), Density (ρ), Viscosity (η) and Adiabatic compressibility (β$_a$) with respect to compositions (C$_m$) of 1,4-dioxane + Methanol are shown in Fig. 2(A), 2(B), 2(C) and 2(D) respectively.

The variations of Velocity (*U*), Density (ρ), Viscosity (η) and Adiabatic compressibility (β$_a$) with respect to compositions (C$_m$) of 1,4-dioxane + Methanol are shown in Fig. 1(A), 1(B), 1(C) and 1(D) respectively and the variations of Velocity (*U*), Density (ρ), Viscosity (η) and Adiabatic compressibility (β$_a$)with respect to compositions (C$_m$) of 1,4-dioxane + Ethanol are shown in Fig. 2(A), 2(B), 2(C) and 2(D) respectively.

CONCLUSION

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

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