

Study of Acoustical Parameters of Binary Liquid Mixtures at 298K

Gajendra Bedare, Vivek Bhandakkar, and Bhagwat Suryavanshi

Abstract—Ultrasonic 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, relaxation time, specific acoustical impedance, molar volume, Rao's constant, Wada's constant and enthalpy are evaluated. From the properties of these acoustical parameters, the nature and the strength of interactions in these binary systems are discussed. It has been observed that, weak dispersive type intermolecular interactions are confirmed in the systems investigated. Dipole inducement is found to be more predominant in methanol system.

Index Terms—Molecular interactions, specific acoustical impedance, molar volume, Rao's constant, Wada's constant, enthalpy and binary liquid mixtures.

I. INTRODUCTION

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 [7-9]. The measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids [10]. 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 [11].

Manuscript received March 7, 2012; revised April 25, 2012.

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II. EXPERIMENTAL DETAILS

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 2MHz fixed frequency with an accuracy of $\pm 0.1 \text{ ms}^{-1}$. The density 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 measurement 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.

The various acoustical parameters such as adiabatic compressibility (β_a), free length (L_f), free volume (V_f), specific acoustical impedance (Z), relaxation time (τ), molar volume (V), Rao's constant (R), Wada's constant (W) and enthalpy (H) have been calculated using the following expressions :

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

$$V_f = (M_{\text{eff}} U / \eta K)^{3/2} \quad \dots\dots (3) \quad Z = U \rho \quad \dots\dots (4)$$

$$\tau = 4/3 \eta \beta_a \quad \dots\dots (5) \quad R = U^{1/3} V \quad \dots\dots (6)$$

$$W = \beta_a^{1/7} V \quad \dots\dots (7) \quad H = JI V \quad \dots\dots (8)$$

where, K_T is the temperature dependent constant having a value 205.8336×10^{-8} in MKS system at 298 K, K is constant equal to 4.28×10^9 in MKS system, $M_{\text{eff}} = \sum x_i m_i$, where x_i is the mole fraction and m_i is the molecular weight of the component.

III. RESULTS AND DISCUSSION

The experimentally measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), adiabatic compressibility (β_a), free length (L_f) and free volume (V_f) at 298K 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), Wada's constant (W) and enthalpy (H) of binary liquid at 298K are presented in Table-2 for the system-I: 1,4-dioxane+ ethanol and system-II: 1,4-dioxane+ methanol. The variation of these parameters is shown in fig. 1(A, B, C, D, E, F).

Table-1 shows that, in both the systems-I and II, viscosity shows decreasing trend with the increase in mole fraction of 1, 4-dioxane. As regards sound velocity and density, in 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.

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 [12].

From the same Table-1, it is observed that adiabatic compressibility (β_a) decreases with increase in concentration of dioxane as expected. This increase structural order of 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 . It is observed that L_f , decreases with the concentration of dioxane in system-I and II. Decrease in intermolecular free length (V_f) leads to positive deviation in sound velocity and negative deviation in compressibility. This indicates that the molecules are nearer in the system. The variation in V_f increases with increases in molality of dioxane in system-I and II. The free volume is the space available for the molecule to move in an imaginary unit cell.

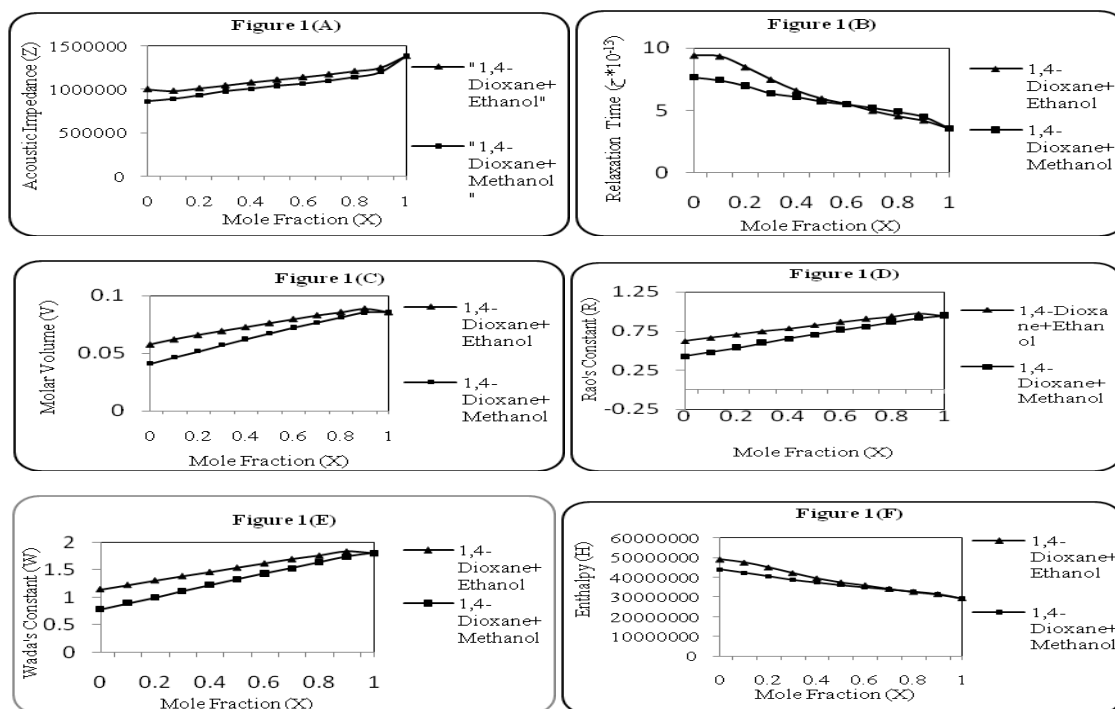
In Table-2, the acoustic impedance (Z) also increases with increase in concentration of dioxane, but relaxation time (τ) have completely reverse trend with that of velocity. This also indicates significant interactions in the system-I and II. Decrease in L_f and increase of Z with the concentration of 1,4-dioxane; suggest presence of solvent-solute interactions in system-I and system-II. The Rao's constant (R), Wada's constant (W) were increasing linearly with molality of dioxane and enthalpy (H) decreases with increase in composition of 1, 4-dioxane indicating the solute-solvent interactions may occur [13] in the system-I and II.

TABLE I: THE EXPERIMENTAL VALUES OF VELOCITY (U), DENSITY (ρ), VISCOSITY (η), ADIABATIC COMPRESSIBILITY (β_a), FREE LENGTH (L_f) AND FREE VOLUME (V_f) AT 298 K FOR THE SYSTEM-I AND SYSTEM-II.

	U (m/s)	ρ (kg/m ³)	$\eta \cdot 10^{-3}$ (Ns/m ²)	$\beta_a \cdot 10^{10}$ (Pa ⁻¹)	$L_f \cdot 10^{-10}$ (m)	$V_f \cdot 10^{-7}$ (m ³ mol ⁻¹)
System-I: 1,4-Dioxane + Ethanol						
0.0	1258.00	801.10	0.895	7.88	0.578	0.5883
0.1	1218.10	811.23	0.844	8.31	0.593	0.6978
0.2	1229.00	828.14	0.796	7.99	0.582	0.8710
0.3	1241.30	846.24	0.732	7.67	0.570	1.1209
0.4	1253.00	866.56	0.673	7.35	0.558	1.4306
0.5	1267.67	881.10	0.631	7.07	0.547	1.7649
0.6	1279.00	896.23	0.607	6.82	0.538	2.0792
0.7	1295.10	910.16	0.570	6.55	0.527	2.5372
0.8	1305.00	931.36	0.541	6.30	0.517	3.0105
0.9	1325.00	947.00	0.523	6.01	0.505	3.5002
1.0	1350.00	1030.0	0.500	5.33	0.475	4.1440
System-II: 1,4-Dioxane + Methanol						
0.0	1108.00	780.10	0.550	10.40	0.665	0.5856
0.1	1101.80	809.22	0.546	10.20	0.657	0.7468
0.2	1111.00	839.35	0.543	9.65	0.639	0.9402
0.3	1144.00	858.12	0.538	8.90	0.614	1.1960
0.4	1152.00	877.22	0.533	8.59	0.603	1.4426
0.5	1168.00	895.00	0.525	8.19	0.589	1.7450
0.6	1173.67	911.10	0.517	7.98	0.582	2.0537
0.7	1184.00	932.12	0.512	7.65	0.569	2.3905
0.8	1207.00	949.31	0.508	7.23	0.553	2.7890
0.9	1241.00	968.10	0.503	6.71	0.533	3.2798
1.0	1350.00	1030.0	0.500	5.33	0.475	4.1440

TABLE II: THE CALCULATED VALUES OF SPECIFIC ACOUSTICAL IMPEDANCE (Z), RELAXATION TIME (τ), MOLAR VOLUME (V), RAO'S CONSTANT (R), WADA'S CONSTANT (W) AND ENTHALPY (H) OF THE SYSTEM-I AND II AT 298K.

X	Z (kg/m ² s)	$\tau \cdot 10^{-13}$ (s)	V (m ³ /mol) (Kg ⁻¹ ms ²)	R (m ³ /mol) (m/s) ^{1/3}	W (m ³ /mol)	H (J/mol)
System-I: 1,4-Dioxane + Ethanol						
0.0	1007784	9.413	0.0575	0.620	1.148345	49176460
0.1	988159	9.349	0.0620	0.662	1.228393	47629180
0.2	1017784	8.485	0.0658	0.705	1.311157	45125505
0.3	1050463	7.485	0.0693	0.745	1.390403	42222199
0.4	1085800	6.596	0.0726	0.782	1.463957	39519915
0.5	1116063	5.951	0.0761	0.824	1.544519	37443169
0.6	1146278	5.520	0.0795	0.863	1.622037	35973562
0.7	1178748	4.978	0.0829	0.904	1.701222	34137297
0.8	1215425	4.548	0.0856	0.935	1.764716	32582177
0.9	1254775	4.194	0.0886	0.973	1.839469	31347091
1.0	1390500	3.551	0.0855	0.945	1.807067	29286703
System-II: 1,4-Dioxane + Methanol						
0.0	864351	7.657	0.0411	0.425	0.788089	44026577
0.1	890789	7.424	0.0465	0.480	0.895698	42322094
0.2	932518	6.988	0.0515	0.534	0.999985	40553323
0.3	981689	6.387	0.0569	0.596	1.117709	38693442
0.4	1010557	6.105	0.0621	0.651	1.225117	37415072
0.5	1045360	5.733	0.0671	0.707	1.333435	36038820
0.6	1068420	5.502	0.0721	0.760	1.437417	34956659
0.7	1103630	5.224	0.0765	0.809	1.534127	33892250
0.8	1145817	4.898	0.0810	0.862	1.638051	32816622
0.9	1201412	4.498	0.0852	0.916	1.741985	31621469
1.0	1390500	3.551	0.0855	0.945	1.807067	29286703



I. CONCLUSIONS:

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, free length, specific acoustical impedance, relaxation time, molar volume, Rao's constant, Wada's constant and enthalpy are strongly correlated with each

other.

ACKNOWLEDGEMENT

Authors (GRB and VDB) acknowledge the financial assistance from the UGC, in the form of Minor Research Project grant.

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