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Molecular interactions hexanol containing methyl benzoate and benzene at 301 K using ultrasonic measurements

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured in the binary (hexanol+ benzene) and ternary (hexanol + methyl benzoate + benzene) in all range of concentrations at 303K. From these measurements, related ultrasonic parameter were evaluated. The results confirmed solute – solvent interactions of hexanol and benzene due weak forces and strong interactions exist hexanol – methyl benzoate through hydrogen bonding.

Keywords: Ultrasonic velocity, molecular interactions, solute - solvent interactions, hydrogen bonding

INTRODUCTION

The ultrasonic properties of liquid mixtures find the various industrial and chemical applications [1, 2]. An ultrasonic measurement gives the extensive applications such as the nature of molecular interactions and solute solvent interactions. The organic liquid mixtures are of considerable importance in industrial and precursor. Thermodynamic properties of liquid mixtures have been widely used to identify the nature of the molecule interactions by the method of an ideal liquid mixture behavior from ideality [3-6]. The ultrasonic measurements frequently used to understanding type of molecular interactions in the liquid mixtures [7-11]. The excess properties are also important to finds the structural changes associated with the liquids [12]. The hexanol, methyl benzoate and benzene are selected in the investigations since it finds a variety of applications. The samples play an important role due to the ability to undergo self association with internal structures, hydrogen bonding [9-20]. The present work is an attempt to study the solute – solvent interactions of hexanol containing solvent benzene and hydrogen bonding interactions of hexanol – methyl benzoate using ultrasonic measurements.

MATERIALS AND METHODS

The ultrasonic measurements made the pure liquid and liquid mixtures discuss the following, Ultrasonic velocity measured using ultrasonic interferometer (Mital type M-80 series) at 2 MHz frequency with an accuracy of ± 0.1 ms⁻¹ at 301K. The densities were determined using the 5 ml specific gravity bottle immersed in the thermostat at the experimental temperature from the weight measurements and the accuracy in the measurements was ± 0.1 kgm⁻³. The liquid mixtures were prepared by mixing the calculated amount of pure liquids. The amount of pure liquid calculated from the relations $w_i = \frac{m_i x}{\sum m_i x}$. An Ostwald's viscometer was used find the viscosity with an accuracy of ± 0.0001 NSm⁻². The temperature around the ultrasonic interferometer, viscometer and specific gravity bottle was maintained at 303K with an error ± 0.1 using thermostatically water bath. All the safety measures were taken to reduce the possible experimental error.

Theory and Calculation

The ultrasonic parameters were evaluated using relations 1 to 11 from the experimental values of ultrasonic velocity (u), density (ρ) and viscosity (η). Ultrasonic relations discussed following

Adiabatic compressibility (β) and acoustic impedance (Z) can be find from the ultrasonic velocity and density given as

$$\beta = \frac{1}{u^2 \rho} \qquad \qquad \dots (1)$$

Intermolecular free length (L_f) evaluate from the adiabatic compressibility. L_f is inversely proportional to the square root of adiabatic compressibility. Since K_T is proportionality constant known temperature dependent constant.

i.e
$$L_{f} \alpha \frac{1}{\beta^{1/2}}$$

 $L_{f} = \frac{K_{T}}{\beta^{1/2}}$...(3)

Available volume (V_a) is related to molar volume (V_m) and ultrasonic velocity (u) given as

$$\mathbf{V}_{\mathbf{a}} = \mathbf{V}_{m} \left[1 - \left(\frac{\mathbf{u}}{\mathbf{u}_{\infty}} \right) \right] \qquad \dots (4)$$

Since V_m is the molar volume (m/ρ) and u_{∞} is velocity of water (1600 m/s), m is the effective molecular weight and ρ is the density of solution.

Relative association (R_a) is derived from the density of solution (ρ) solvent (ρ_0) and the ultrasonic velocity of the solution (u) and solvent (u_0).

$$\mathbf{R}_{a} = \left(\frac{\rho}{\rho_{0}}\right) \left(\frac{\mathbf{u}_{o}}{\mathbf{u}}\right)^{1/3} \dots (5)$$

Molecular association (α) find from experimental ultrasonic velocity and ideal mixture of of ultrasonic velocity. Ultrasonic velocity of ideal mixture find from these relations $u_{mix}=u_1X_1+u_2X_2$, since X and u are the mole fractions and ultrasonic velocity of the components 1 and 2, So interaction parameter can be written as

$$\alpha = \left(\frac{u_{exp}^2}{u_{mix}^2}\right) - 1 \qquad \dots (6)$$

Relaxation time (τ) find from viscosity and adiabatic compressibility given as

$$\tau = \frac{4}{3}\eta\beta \qquad \dots (7)$$

Rao's constant (R) obtained from the ultrasonic velocity and molar volume as

$$R = U^{1/3} V_m$$
 ...(8)

Wadas constant (W) obtained from the density and adiabatic compressibility can be written as

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$$w = \frac{m_{\text{eff}}}{\rho} \beta^{-1/7} \qquad \dots (9)$$

Where, $M_{eff} = \Sigma x_i m_i$, Where X_i is the mole fraction and mi is the molecular weight of the component.

The relation for free volume in terms of ultrasonic velocity (u) and viscosity (ρ) of the liquid as

$$:V_f = \left(\frac{M_{eff}U}{\eta K}\right)^{3/2} \dots (10)$$

Here M_{eff} is the effective molecular weight $M_{eff} = \sum m_i x_i$ which m_i and x_i are the molecular weight and mole fraction of the individual components respectively. K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

The Lennard - Jones potential is given by

$$LJP = \frac{6V_{\rm m}}{V_{\rm a}} \qquad \dots (11)$$

Where, V_m and V_a represent the molar volume and available volume of the mixtures.

The ultrasonic parameters were evaluated from the relations 1 to 11 and shown in table 2 and plotted the figure 2 to 11.

RESULTS AND DISCUSSION

The experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) at 301K for the binary (hexanol with benzene) and ternary (hexanol with methyl benzoate in benzene) systems are listed in table 1.

 $Table \ 1 \ Variation \ of \ ultrasonic \ velocity \ (u \ m/s) \ , \ density \ (\rho \ Kg/m^3) \ , \ viscosity \ (\eta \ 10^{^3} N sm^{^2}) \ with \ the \ mole \ fractions \ (X_2) \ of \ hexanol \ for \ the \ binary \ and \ ternary \ mixtures \ at \ 301 \ K$

X_2	U	ρ	η	X_2	u	ρ	Н		
	Ber	zene		Methyl benzoate + benzene					
0.1	1278	864	0.277	0.05	1340	971	0.424		
0.2	1280	858	0.403	0.1	1341	968	0.523		
0.3	1282	852	0.563	0.15	1342	965	0.636		
0.4	1284	846	0.761	0.2	1343	962	0.764		
0.5	1286	841	1.001	0.25	1344	959	0.908		
0.6	1288	835	1.285	0.3	1345	955	1.07		
0.7	1290	829	1.619	0.35	1346	952	1.25		
0.8	1292	823	2.007	0.4	1347	949	1.448		
0.9	1294	818	2.452	0.45	1348	946	1.667		

Table 2 reported the values of adiabatic compressibility ($\beta X 10^{-10} \text{ kg}^{-1} \text{ms}^{-2}$), free volume ($V_f 10^{-3} \text{m}^3$), relaxation time ($\mathbf{T} 10^{12}$ s), inter molecular free length ($L_f X 10^{-11} \text{ m}$), acoustic impedance ($ZX 10^6 \text{ kg m}^{-2} \text{ sec}^{-1}$), relative association (R_a), available volume ($V_a X 10^{-3} \text{ m}^3$), Linard John Potential (LJP 10²), Rao constant ($R \text{ m}^3/\text{mole}$)(m/s)^{1/3}, Wadas constant ($W (m^3/\text{mole})(nm^2)^{1/7}$) of binary and ternary mixtures also plotted in the figure 2 to 11.

X_2	β	V_{f}	τ	$\mathbf{L}_{\mathbf{f}}$	Ζ	RA	Va	LJP	R	W		
Hexanol + benzene												
0.10	7.09	25.57	26.19	5.67	1.10	0.09	18.75	2.98	1.01	1.89		
0.20	7.11	15.27	38.20	5.68	1.10	0.10	19.33	3.00	1.05	1.96		
0.30	7.14	9.67	53.60	5.69	1.09	0.10	19.91	3.02	1.09	2.03		
0.40	7.17	6.43	72.75	5.70	1.09	0.10	20.48	3.04	1.13	2.10		
0.50	7.19	4.46	95.87	5.71	1.08	0.11	21.04	3.06	1.17	2.17		
0.60	7.22	3.19	123.70	5.72	1.08	0.11	21.61	3.08	1.21	2.24		
0.70	7.25	2.35	156.50	5.74	1.07	0.11	22.19	3.10	1.25	2.32		
0.80	7.28	1.77	194.81	5.75	1.06	0.12	22.77	3.12	1.29	2.39		
0.90	7.30	1.36	238.66	5.75	1.06	0.12	23.33	3.14	1.33	2.46		
Hexanol + methyl benzoate + benzene												
0.05	5.74	5.13	32.45	5.10	1.30	0.04	6.74	3.69	0.46	0.87		
0.10	5.74	3.91	40.03	5.10	1.30	0.04	6.93	3.71	0.47	0.90		
0.15	5.75	3.05	48.76	5.11	1.30	0.04	7.13	3.72	0.49	0.92		
0.20	5.76	2.42	58.68	5.11	1.29	0.05	7.32	3.74	0.50	0.95		
0.25	5.77	1.95	69.86	5.12	1.29	0.05	7.52	3.75	0.52	0.98		
0.30	5.79	1.58	82.60	5.13	1.28	0.05	7.72	3.76	0.53	1.01		
0.35	5.8	1.31	96.67	5.13	1.28	0.05	7.92	3.78	0.55	1.04		
0.40	5.81	1.09	112.17	5.13	1.28	0.05	8.11	3.79	0.57	1.07		
0.45	5.82	0.92	129.36	5.14	1.28	0.05	8.31	3.81	0.58	1.10		

Table 2 hexanol+benzene mixtures at 301K



Figure 1 Plots of u versus X₂

Figure 2 Plots of β versus X_2



Figure 3 Plots of V_f versus X_2

Figure 4 Plots of τ versus X_2



Figure 7 Plots of u versus X₂

Figure 8 Plots of β versus X_2



Figure 11 Plots of W versus X₂

Figure 12 Plots of a versus X₂

Table 1 and figure 1 shows that velocity increases with concentration of hexanol for binary and ternary mixtures. This indicates that strong interaction observed at higher concentrations of X. The density values also have the reverse trend with velocity in the binary and ternary mixtures. Viscosity increases in binary and ternary mixtures, suggesting thereby more association between solute and solvent molecules. . On mixing several components the intermolecular free length and adiabatic compressibility are affected. This directly influences the speed of sound. On addition of greater proportions of hexanol, the mixture forms compact molecular aggregates and sound travels faster through the mixture by longitudinal waves. This shows the existence of strong intermolecular interactions highlighting the effect of a strong structure making effect of the binary solvent mixture. This fact is also represented in the present investigation of methyl benzoate in hexanol benzene mixtures. From the same table 2 and figure 2, it has been observed that adiabatic compressibility (β) increases with increase in concentration of hexanol as expected. This increase in structural order of hexanol may result in more cohesion, and leads to a increase in β . The increases β results in an increase in the value of u decreases with increase in concentration of hexanol. The intermolecular free length is considered as the distance between the surfaces of the adjacent molecules. The increase or decrease of the intermolecular free length is directly a result of the variation in ultrasonic velocity of a solution on mixing the several components Similar trend observed relaxation time (τ), intermolecular free length (L_t), available volume (V_a) Linard John Potential (LJP), Molar volume (V_m), Rao constant (R), Wadas constant (W), and interaction parameter (α) as shown in figures 4, 5, 8, 7, 9 10, 11 respectively. The free volume (V_f) have completely reverse trend with that of velocity as shown in figure 3 and also similar trend observed acoustic impedance (Z), available volume (V_a) and interaction parameter (α) as shown in figures 6, 8, 12 respectively. This also supports the significant interactions in the binary and ternary systems.

The variation of specific acoustic impedance (Z), relaxation time (τ) , molar volume (V_m), Rao's constant (R) and Wadas constant (W) against the mole fraction at 301K for the binary and ternary systems indicate existence of interaction between the molecules. The decrease in L_f and increase of Z with the concentration of hexanol, suggest the presence of solvent-solute interactions in binary and ternary systems. Rao's constant (R) is increasing linearly with molality of hexanol indicating the solute-solvent interactions may occur in the binary and ternary mixtures. The variations all the ultrasonic parameter supported one to each other binary mixtures exist solute – solvent interactions due weak kind of forces and ternary mixtures exist strong interactions due to the hydrogen bonding between the components also supported the variations interactions parameter, and relative association with the mole fractions of hexanol. From these parameter concluded that exit the molecular interactions between the components.

CONCLUSION

Intermolecular interactions are confirmed in the binary systems due to weak dispersive forces and strong interactions due to the hydrogen bonding. Polarity is increasingly found to be more in hexanol with methyl benzoate in benzene system compare than the hexanol benzene systems. The experimental ultrasonic velocity and other related ultrasonic parameter are strongly correlated with each other.

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