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ULTRASONIC VELOCITY AND VISCOSITY OF BINARY LIQUID MIXTURES

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ABSTRACT

Density, ρ, and viscosity, η, of binary mixtures of (a) benzyl alcohol + iso-amyl alcohol and (b) benzyl alcohol + isopropyl alcohol, and their pure components, have been measured as functions of concentration and temperature. Theoretical values of sound velocity, U, for the above mixtures are evaluated using Jacobson's relation, based on the free length theory, and that of Schaffs, based on the collision factor theory. The excess volume, V^E, the excess adiabatic compressibility, β_s^E, the excess viscosity, η^E, and the excess molar free energy of activation of flow, $G^{\star E}$ are found to be negative over the entire range of concentrations and temperatures in both systems, indicating strong interactions.

INTRODUCTION

Alcohols are self associated [1–4] in pure state, and when mixed with other liquids they partially dissociate as a result of the breaking of hydrogen bonds to form another kind of hydrogen bonding with unlike molecules [5,6]. The degree of such a dissociation depends upon the proton accepting ability of the functional group of approaching molecules. It has been found [7,8] that there may be two possible contributions towards the total excess properties of mixing: (i) the breaking up of alcohol structure into fragments or molecules and (ii) the geometrical adjustments or the cooperative accommodation of the second component into the remaining alcohol structure. The first factor contributes to positive values while the second has a negative contribution towards the excess properties. Recently, it has been found that the changes in the thermodynamic parameters derived from the ultrasonic sound velocities as functions of mole fraction and temperature for binary

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associated liquid mixtures [9–12] have been attributed to the molecular interactions. An attempt has been made to study the above for binary solutions of aliphatic and aromatic alcohols. This interesting idea based on similar intermolecular interactions, the role played by the difference in the size, shape, polarity, orientations, the charge density including the π electrons and the self association of molecules of the two components has prompted us to undertake the present investigation with carefully chosen binary liquid mixtures to predict the extent and the type of molecular interactions in them. The binary systems chosen were (a) benzyl alcohol + isoamyl alcohol (*i*-AmOH) and (b) benzyl alcohol + isopropyl alcohol (*i*-PrOH).

Therefore, the excess volume, V^E, the excess isentropic compressibility, β_s^E, the excess viscosity, η^E, and the excess free energy, $G^{\star E}$, have been computed as functions of temperature and concentration. The significance of these parameters has been emphasized in understanding the intermolecular interactions in such mixtures.

MATERIALS AND METHODS

Purified [13] and redistilled amyl alcohol, benzyl alcohol and isopropyl alcohol (BDH) of Analar grade were used in preparing the binary mixtures. Density and viscosity measurements were made using a dilatometer [14] (1 division = 0.005 cm^3) and a modified Cannon Ubbelohde viscometer [15] (viscometer constant, 0.0037 cSt s^{-1}), respectively, in a thermostated water bath of ± 0.01 K thermal stability. The observed values of density and viscosity were compared with those reported earlier [16] and are found to be in agreement within ± 0.001 and $\pm 0.1\%$, respectively. Ultrasonic sound velocity was measured using the continuous wave interferometric technique in a manner described earlier [17].

THEORETICAL EVALUATION OF SOUND VELOCITY

The intermolecular free length, L_f, of pure liquid has been evaluated by the thermodynamic method using the Eyring and Hirschfelder [18] relation:

$$L_f = 2V_a/Y \tag{1}$$

where $V_a = V_T - V_0$

and $V_0 = V_T\left(1 - \frac{T}{T_c}\right)^{0.3}$

in which V_a, V_T and V_0 are the available volume, molar volume at absolute temperature and absolute zero temperature, respectively. T_c anbd Y are the critical temperature and surface area per mole.

This concept of free length has been extended to the binary liquid mixtures [19] and expressed as

$$L_{f_{\text{mix}}} = \frac{2[V_m - (x_1V_{01} + x_2V_{02})]}{x_1Y_1 + x_2Y_2} \tag{2}$$

where x is the mole fraction, V_m, the molar volume of the mixture, while the subscripts 1 and 2 refer to the pure components. The ultrasonic velocity, u, in the mixture can be evaluated by the free length theory (FLT) using Jacobson's formula [20,21]

$$u_{\text{mix}} = \frac{K}{L_{\text{mix}}\rho_{\text{mix}}^{1/2}} \tag{3}$$

where ρ_{mix} and K are the density of the mixture and the temperature dependent constant [21], respectively.

Schaffs [22], on the basis of the collision factor theory (CFT), gave the following relation for the ultrasonic velocity in pure liquids:

$$u = u_\alpha S r_j = u_\alpha S \frac{B}{V} \tag{4}$$

where $u_\alpha = 1600$ m s^{-1}, S is the collision factor and $r_j = B/V$ is the space filling factor in which V is the molar volume of the pure liquid and B is the actual volume of the molecule per mole and is given by

$$B = \frac{4\pi}{3} r_m^3 \mathrm{N} \tag{5}$$

where r_m stands for the molecular radius and N is the Avogadro number. Schaffs [22] and Rao et al. [23] have used the following relations for the calculation of molecular radius

$$r_{m_{\text{Schaffs}}} = \alpha\left[1 - \beta\left\{\left(1 + \frac{1}{3\beta}\right)^{1/2} - 1\right\}\right]^{1/3} \tag{6}$$

$$r_{m_{\text{Rao}}} = \alpha\left[1 - \beta\left\{\left(1 + \frac{1}{\beta}\right)^{1/2} - 1\right\}\right]^{1/3} \tag{7}$$

where $\alpha = (3V/16\pi\mathrm{N})^{1/3}$, $\beta = (\gamma \mathrm{R}T/Mu^2)$, γ is the ratio of principal specific heats, R is the gas constant and M the molecular weight. This concept was applied to binary liquid mixtures by Nutsch-Kuhnkies [19] for calculating the ultrasonic velocity in mixtures using the relation

$$u_{\text{mix}} = u_\alpha[x_1S_1 + x_2S_2]\frac{x_1B_1 + x_2B_2}{V_m} \tag{8}$$

where the terms have their usual meaning.

RESULTS AND DISCUSSION

The experimental values of density, ρ, viscosity, η, and sound velocity, U, for pure liquids at various temperatures are given in Table 1. Using eqns. 1–3 the theoretical values of sound velocities for the above liquids are also evaluated and included in Table 1 for comparison. It is seen that the theoretical values are very close to those of the experimental, which reinforces the applicability of Jacobson's formula.

Similarly, the measured values of molar volume, V, and viscosity, η, for binary mixtures of (a) benzyl alcohol + *i*-AmOH and (b) benzyl alcohol + *i*-PrOH as functions of temperature and concentration are given in Table 2. The theoretical values of sound velocities for binary mixtures are evaluated using Jacobson's (eqns. 1–3) and Schaffs formulae (eqns. 4–8). The temperature-dependence data of molar volume, viscosity and sound velocity for all the binary mixtures are least squares fitted to a linear equation and their temperature coefficient, du/dT, are given.

TABLE 1

Density, ρ, viscosity, η, and sound velocity, U, for pure liquids as functions of temperature

T (K)	ρ (kg m^{-3})	η (N m^{-2} s)	U (m s^{-1}) theoretical	U (m s^{-1}) experimental	Δ (%)
i-AmOH					
298.15	808.1	3.497	–	–	–
303.15	804.4	3.064	1128.7	1137.6	0.7
308.15	800.7	2.637	1116.4	1114.6	0.2
313.15	796.9	2.295	1103.8	1089.6	1.3
318.15	793.2	2.004	1092.0	1068.8	2.2
323.15	789.3	1.719	–	–	–
				Average deviance	1.1%
i-PrOH					
298.15	781.7	1.983	–	–	–
303.15	777.6	1.717	1059.0	1063.4	0.4
308.15	773.5	1.494	1048.1	1048.0	0.0
313.15	769.3	1.310	1037.4	1028.8	0.8
318.15	765.2	1.161	1027.1	1010.7	1.6
323.15	761.3	1.041	–	–	–
				Average deviance	0.7%
Benzyl alcohol					
293.15	1043.4	4.935	–	–	–
303.15	1039.6	4.211	1419.5	1409.6	0.7
308.15	1035.7	3.664	1402.0	1395.2	0.5
313.15	1031.9	3.181	1385.9	1378.6	0.5
318.15	1028.0	2.795	1368.9	1365.3	0.3
323.15	1024.2	2.487	–	–	–
				Average deviance	0.5%

TABLE 2
Molar volume, V, viscosity, η, sound velocity, U, and their temperature coefficients and interaction, d, for binary liquid mixtures

$x_{C_6H_5OH}$	V (m^3 $\times 10^3$)	$\frac{dV}{dT} \times 10^2$	$\eta \times 10^3$ (N m^{-2} s)	$\frac{d\eta}{dT} \times 10^2$	U (m s^{-1})	dU/dT	d
(a) Benzyl alcohol + *i*-AmOH							
0.105	0.1081	9.95	2.994	−8.048	1175.8	−4.496	−0.606
					(1110.8)	(−2.333)	
0.210	0.1078	9.68	3.010	−8.047	1202.7	−4.297	−0.509
					(1132.5)	(−2.384)	
0.310	0.1074	9.42	3.060	−8.076	1226.8	−4.137	−0.469
					(1155.6)	(−2.770)	
0.412	0.1068	9.08	3.129	−8.203	1255.5	−3.962	−0.454
					(1190.8)	(−2.544)	
0.512	0.1063	8.93	3.241	−9.111	1282.5	−3.720	−0.428
					(1224.5)	(−2.693)	
0.612	0.1057	8.63	3.380	−9.326	1300.4	−3.631	−0.406
					(1261.3)	(−2.803)	
0.710	0.1052	8.36	3.510	−9.357	1335.8	−3.643	−0.438
					(1300.1)	(−3.202)	
0.810	0.1048	8.54	3.710	−9.964	1361.7	−3.303	−0.470
					(1340.3)	(−3.402)	
0.904	0.1045	7.77	3.929	−10.698	1384.8	−3.122	−0.491
					(1375.5)	(−3.392)	
(b) Benzyl alcohol + *i*-PrOH							
0.078	0.0784	7.94	1.823	−4.62	1104.4	−3.522	
					(1186.6)	(−2.630)	
0.155	0.0806	7.80	1.936	−4.86	1128.9	−3.456	−0.142
					(1199.8)	(−2.624)	
0.240	0.0827	7.64	2.098	−5.23	1160.0	−3.362	−0.147
					(1229.6)	(−2.680)	
0.330	0.0854	7.60	2.269	−5.63	1188.0	−3.362	−0.120
					(1243.2)	(−2.697)	
0.424	0.0879	7.37	2.503	−6.35	1220.5	−3.256	−0.076
					(1270.3)	(−2.711)	
0.525	0.0901	7.58	2.870	−7.51	1262.7	−3.254	−0.017
					(1326.4)	(−3.046)	
0.633	0.0934	7.86	3.167	−8.17	1293.3	−3.213	0.061
					(1337.3)	(−3.176)	
0.747	0.0967	7.71	3.430	−9.12	1329.9	−3.121	0.109
					(1364.5)	(−3.182)	
0.878	0.1040	7.73	3.794	−10.11	1368.9	−3.892	0.048
					(1384.7)	(−3.210)	

The values of U given in parentheses are those obtained by free length theory.

Although some degree of association is expected in these systems, the interaction should be stronger in isoamyl alcohol than in isopropyl alcohol, as is shown by the higher values of the interaction parameter d [24,25] (Table 2), computed by least squares fitting the viscosity data to the

Grunberg–Nissan equation [26]:

$$\eta_{\mathrm{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \tag{9}$$

where η_{mix} is the viscosity of the mixture while η_1 and η_2 are the viscosities of the two pure components.

Using the above results the V^{E}, β_s^{E}, η^{E} and $G^{\star\mathrm{E}}$ of mixing are calculated with the help of the following relations:

$$V^{\mathrm{E}} = V - (x_1 V_1 + x_1 V_2) \tag{10}$$

$$\beta_s^{\mathrm{E}} = \beta_s - \left(x_1 \beta_{s(1)} + x_2 \beta_{s(2)}\right) \tag{11}$$

$$\eta^{\mathrm{E}} = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{12}$$

$$G^{\star\mathrm{E}} = \mathrm{R}T\left[\ln V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)\right] \tag{13}$$

Excess volume (V^E*)*

The excess volume of mixing of both the systems are negative over the entire range of concentration and temperature, as has been observed by

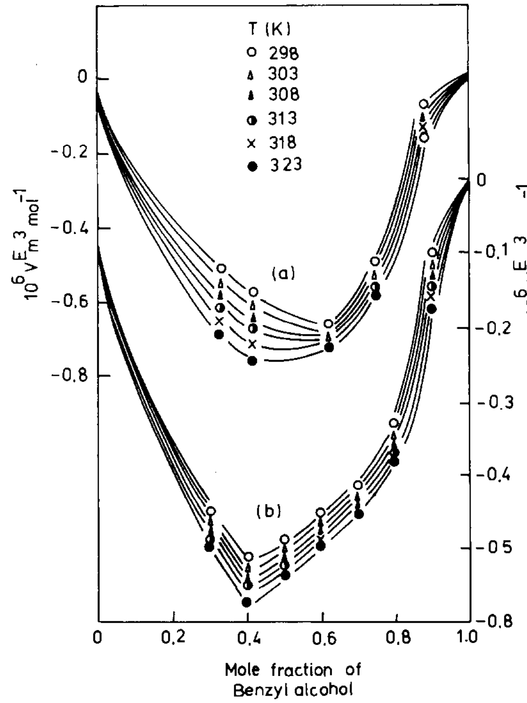

Fig. 1. Excess volume, V^{E}, as a function of mole fraction and temperature for (a) benzyl alcohol + *i*-AmOH and (b) benzyl alcohol + *i*-PrOH.

others [7,27]. The negative contribution to V^E appears to have been caused mainly by the changes in the free volume of the mixture, as well as the presence of π electrons in benzyl alcohol, resulting in the formation of weak intermolecular complexes. Furthermore, the V^E values of benzyl alcohol + *i*-AmOH mixtures (Fig. 1a) are more positive, compared to those of benzyl alcohol + *i*-PrOH mixtures (Fig. 1b). This may be due to the fact that self association in alcohols varies in the order [3,4,27,28] ethyl alcohol > n-propyl alcohol > butyl alcohol > amyl alcohol. In other words, the addition of aromatic alcohol would cause an appreciable O–H · · · O bond rupture in isoamyl alcohol compared to isopropyl alcohol. The observed V^E values in both the systems become more negative with the increase in temperature. Their temperature coefficients, dV^E/dT, being negative, may be attributed to the expansion of their free volume.

Excess adiabatic compressibility (β_s^E)

The variation of β_s^E (Fig. 2) in both cases being negative over the entire concentration range indicates the presence of AB type interactions. In both cases, a significantly large minimum in β_s^E at about 0.4 mole fraction suggests a strong AB type interaction which eventually results in complexation. The relative values of β_s^E show that the strength of the AB type interaction decreases in the order isoamyl alcohol < isopropyl alcohol. Also, the values of β_s^E become more negative with increasing temperature. In the present case, the observed values of V^E and β_s^E indicate that the association between the unlike molecules predominates over the dissociation of aromatic alcohol molecules.

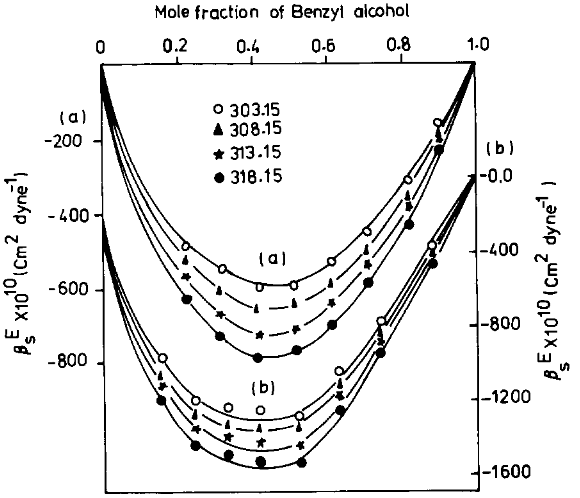

Fig. 2. Excess adiabatic compressibility, β_s^E, as a function of mole fraction and temperature.

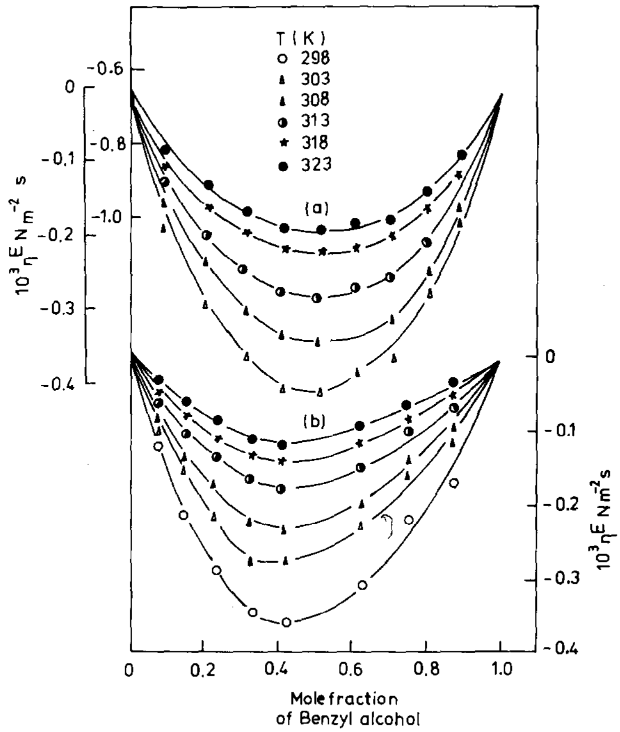

Fig. 3. Excess viscosity, η^E, as a function of mole fraction and temperature.

Excess viscosity (η^E)

The viscosity values for both the systems are negative over the entire range of concentration, indicating that the dispersion forces are dominant, as expected, [29,30]. In the case of benzyl alcohol + *i*-AmOH mixtures (Fig. 3a) the values of η^E are more negative than those of benzyl alcohol + *i*-PrOH mixtures (Fig. 3b). This seems to be due to weak *n*–π type of interaction between the aliphatic and the aromatic alcohols, as the values of Grunberg–Nissan's parameter *d* [13] (Table 2) are not very large. The η^E value passes through a minimum at $\simeq$ 0.5 mole fraction in the system benzyl alcohol + *i*-AmOH and at $\simeq$ 0.45 mole fraction in that of benzyl alcohol + *i*-PrOH. This may be due to complex formation [31] in the ratio of 1 : 1. An increase in temperature decreases the values of η^E, as well as those of *d*, i.e. the systems tend towards ideal behaviour.

Excess molar free energy of flow ($G^{\star E}$)

The negative sign of $G^{\star E}$ values in the case of benzyl alcohol + *i*-AmOH mixtures indicates that the process of complex formation is spontaneous, as is evident from the plots of $G^{\star E}$ versus mole fraction of benzyl alcohol (Fig.

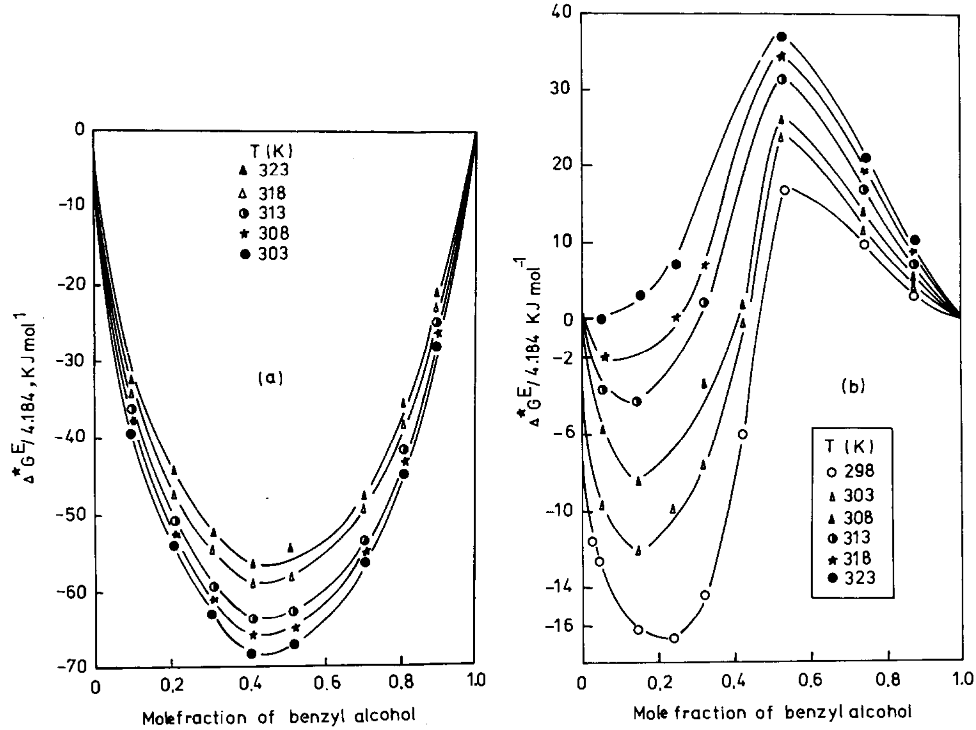

Fig. 4. Excess free energy of mixing, $G^{\star E}$, as a function of mole fraction and temperature.

4a). The behaviour in the benzyl alcohol + *i*-AmOH system appears to be typical (Fig. 4b). The values of $G^{\star E}$ initially decrease and pass through a sharp minimum at $\simeq 0.2$ mole fraction of benzyl alcohol and then increase with a steep maximum at $\simeq 0.53$ mole fraction of benzyl alcohol and finally decrease, reaching the values of the pure benzyl alcohol. Therefore, the process of free energy change seems to proceed through a three step mechanism. In the first step the free-energy decrease may be ascribed to complex formation, which starts dissociating as the free energy is increased in the second step, due to specific interaction, and, finally, self association predominates when the concentration of benzyl alcohol is high. Moreover, the extent of complex formation is hindered by the temperature increase, as the temperature coefficient of $G^{\star E}$ has been found to be positive in this case. Such a trend of free energy change has also been reported by Jain et al. [32] for the methyl benzene + carbon tetrachloride system.

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