

MOLECULAR INTERACTION IN BINARY MIXTURES OF BENZYL ALCOHOL WITH ETHANOL, PROPAN-1-OL AND OCTAN-1-OL AT 303 K: AN ULTRASONIC AND VISCOMETRIC STUDY

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Densities, ultrasonic speeds and viscosities have been measured for benzyl alcohol, ethanol, propan-1-ol, octan-1-ol and for their binary mixtures with benzyl alcohol as common component at 303 K. From the experimental data, isentropic compressibility, relative association, acoustic impedance, molar sound velocity, excess volume, excess isentropic compressibility, deviations of viscosity and ultrasonic speed from linear dependence on composition, excess acoustic impedance and molecular association for all the three binary mixtures were obtained. These parameters have been interpreted in terms of intermolecular interactions. The experimental viscosity data of the three binary mixtures were used to test the validity of the empirical relations of Grunberg–Nissan, Tamura–Kurata, Hind–Mclaughlin, Katti–Chaudhary and Heric. The experimental values of ultrasonic speeds have been compared with those predicted on the basis of the Nomoto empirical relation, collision factor theory, free length theory and van Dael and Vangeel ideal mixing relation. The relative merits of these theories and relations are discussed.

Keywords: Binary mixtures; Alcohols; Thermodynamics; Viscosity; Density; Ultrasonic speeds; Mixing.

Mixed solvents are extensively used in industrial and chemical processes as they provide a wide range of solvents with various physical properties. A deeper knowledge of the influence of the solvent at a molecular level is essential for the understanding of many chemical and biological processes in solution. As a part of our ongoing research^{1–3} to attain deeper insight into the molecular interactions in non-aqueous binary systems, we report here the results of our study on binary mixtures of benzyl alcohol (BA) with ethanol, propan-1-ol and octan-1-ol at 303 K. Pure alkanols are strongly associated due to hydrogen bonding through OH groups⁴. The degree of association of alkanols decreases as their carbon chain length increases⁵. Mixtures of aromatic alcohols with alkanols are interesting to study because, apart from strong hydrogen bonding, they also exhibit relatively

weak hydrogen bonding of the π -H type involving π -electrons of the benzene ring of aromatic alcohol and proton of OH group of alkanols⁶. The components of these binary mixtures have both proton donating as well as proton accepting ability, as a result, significant interaction through hydrogen bonding between unlike molecules in these binary mixtures is expected. Moreover, alkanols are a class of compounds of wide distinction and great economic, social and physiological importance⁷. BA forms esters which are used in perfumery⁸. Alkanols are important not only for their practical use but also as starting material for further synthesis *e.g.* of alkanes, aldehydes, ketones *etc.*⁷ Although binary mixtures of alkanols have been extensively studied, there are only few studies on aromatic alcohol-alkanol binary mixtures⁹. These considerations led us to undertake the present study.

In this paper we report values of the density ρ , ultrasonic speed u and viscosity η of mixtures of BA with ethanol, propan-1-ol or octan-1-ol including nest liquids at 303 K over the entire composition range. Variations of ultrasonic speed, viscosity and those of derived parameters such as isentropic compressibility K_s , relative association R_A , acoustic impedance Z , molar sound velocity R_m , excess volume V^E , excess isentropic compressibility K_s^E , viscosity deviation $\Delta\eta$, ultrasonic speed deviation Δu , excess acoustic impedance Z^E and molecular association M_A with composition of the mixtures reveal the nature of interactions between the component molecules. This study will also provide a test of various empirical equations to correlate viscosity data of binary mixtures containing polar components. Moreover ultrasonic speeds for all the binary mixtures have been calculated theoretically as a function of composition using the Nomoto (NOM) empirical relation¹⁰, collision factor theory¹¹ (CFT), free length theory¹² (FLT) and van Dael and Vangeel (VDV) ideal mixing relation¹³. The suitability of these theories and relations was checked by comparing theoretical values of ultrasonic speeds with those obtained experimentally.

EXPERIMENTAL

Benzyl alcohol, ethanol, propan-1-ol and octan-1-ol (all of AR grade) were purified using standard procedures described in literature¹⁴. The solutions were prepared by weight over the whole composition range with precision of ± 0.05 mg and were kept in special airtight bottles. All the solutions were prepared in a dry box. Density measurements (accuracy $\pm 10^{-4}$ g cm⁻³) were performed using a standard pycnometer. Marks on the stem of the pycnometer were calibrated using known densities of triply distilled water. For the viscosity measurements, we employed a standard Cannon Ubbelohde viscometer mounted in a suitable constant-temperature water bath stable within ± 0.02 K. The viscosities were averaged

from three readings for each solution: the data were reproducible within $\pm 0.5\%$. The ultrasonic speed was determined using a single-crystal variable-path interferometer working at 2 MHz with accuracy of $\pm 0.05\%$. The measured density, ultrasonic speed and viscosity data of nest compounds were compared with the corresponding values reported in the literature^{1-3,9,15-20}, as shown in Table I.

RESULTS AND DISCUSSION

The measured density ρ , ultrasonic speed u , and viscosity η of pure liquids and of their binary mixtures as a function of mole fraction x of BA at 303 K are given in Table II. The values of K_s , R_A , Z , R_m and M_A have been calculated using the Eqs (1) to (5)

$$K_s = u^{-2} \rho^{-1} \quad (1)$$

$$R_A = (\rho/\rho_0)(u_0/u)^{1/3} \quad (2)$$

$$Z = up \quad (3)$$

$$R_m = u^{1/3} V \quad (4)$$

$$M_A = (u^2/u_{lm}^2) - 1, \quad (5)$$

TABLE I

Measured values of density ρ , ultrasonic speed u and viscosity η of pure compounds and their comparison with literature data at 303 K

Compound	ρ , kg m ⁻³		u , m s ⁻¹		η , 10 ⁻³ N m ⁻² s	
	exp.	lit.	exp.	lit.	exp.	lit.
Ethanol	781.6	780.6 (ref. ¹⁵) 781.8 (ref. ¹)	1 132.2	1 132.2 (ref. ¹) 1 133.3 (ref. ²)	1.0090	0.9985 (ref. ⁷) 1.0090 (ref. ²)
Propan-1-ol	796.0	796.02 (ref. ¹⁶) 796.0 (ref. ¹⁷)	1 192.6	1 192.0 (ref. ¹⁶) 1 194.4 (ref. ¹⁵)	1.7183	1.7140 (ref. ¹⁸)
Octan-1-ol	817.7	817.4 (ref. ⁴) 818.05 (ref. ¹⁹)	1 333.1	1 330.0 (ref. ²⁰) 1 327.5 (ref. ³)	6.4931	6.4931 (ref. ²)
Benzyl alcohol	1 039.1	-	1 516.6	-	4.4255	-

TABLE II
 Measured values of density ρ , ultrasonic speed u and viscosity η for binary mixtures BA-ethanol, BA-propan-1-ol and BA-octan-1-ol at 303 K

$x(\text{BA})$	ρ , kg m^{-3}	u , ms^{-1}	η , $10^{-3} \text{ N m}^{-2} \text{ s}$
BA-ethanol			
0.0000	781.6	1 132.2	1.0090
0.1780	860.4	1 231.4	1.4541
0.3074	902.9	1 305.7	1.7943
0.4193	933.7	1 352.0	2.1498
0.5317	960.5	1 395.1	2.5599
0.6131	976.9	1 420.8	2.8775
0.6933	992.0	1 444.8	3.2230
0.7795	1 006.8	1 469.0	3.5798
0.8624	1 019.7	1 486.0	3.9121
0.9401	1 030.8	1 503.0	4.2012
1.0000	1 039.1	1 516.6	4.4255
BA-propan-1-ol			
0.0000	796.0	1 192.6	1.7183
0.0875	826.0	1 233.6	1.8842
0.1563	848.3	1 260.0	2.0167
0.2255	869.4	1 285.7	2.1724
0.3133	894.0	1 315.6	2.3713
0.4075	918.7	1 348.0	2.6051
0.4874	938.2	1 375.4	2.8262
0.5573	953.9	1 398.2	3.0350
0.6714	978.3	1 432.0	3.4087
0.7895	1 001.5	1 463.7	3.7767
1.0000	1 039.1	1 516.6	4.4255
BA-octan-1-ol			
0.0000	817.7	1 333.1	6.4931
0.1209	836.4	1 343.1	5.5803
0.2075	850.6	1 351.1	5.2203
0.3464	875.1	1 367.0	4.8845
0.4470	894.5	1 380.2	4.6537
0.5470	915.2	1 396.8	4.5162
0.6474	938.2	1 415.1	4.3775
0.7378	960.7	1 436.0	4.3191
0.8287	985.4	1 459.1	4.2265
0.9150	1 011.1	1 485.8	4.2909
1.0000	1 039.1	1 516.6	4.4255

where ρ , ρ_0 and u , u_0 are the densities and ultrasonic speeds of the mixture and nest solvent (ethanol, propan-1-ol and octan-1-ol), respectively, V is the molar volume of the mixture and u_{im} is the ultrasonic speed of ideal mixture obtained using the method given by van Dael and Vangeel¹³. The calculated values of K_s , R_A , Z , R_m and M_A of nest liquids and their binary mixtures as a function of x are listed in Table III. It is evident that the values of K_s decrease while those of R_A and Z increase with increasing mole fraction of BA in all the mixtures investigated. R_A is defined as a measure of the extent of interaction between the component molecules in a real mixture relative to that in an ideal one. The values of R_m increase for BA-ethanol/propan-1-ol, while a decrease in R_m is observed for BA-octan-1-ol. The observed increase/decrease in K_s , R_A , Z and R_m with composition of the mixture is an evidence of the presence of interaction between the component molecules of the binary liquid mixtures under study^{21,22}. The deviation of the ratio (u^2/u_{im}^2) from unity is a measure of M_A and its variation with composition of the mixture is a direct measure of the non-ideality of the system as a result of intermolecular association. M_A shows large deviations for the mixtures of BA with ethanol followed by those of propan-1-ol and then by octan-1-ol. This suggests that the non-ideality of the systems follows the order ethanol > propan-1-ol > octan-1-ol which is also the order of increasing length of carbon chains of these alkanols.

The strength of interaction between the component molecules of binary mixtures is well reflected in deviations of the excess functions from ideality. The excess functions are found to be more sensitive to intermolecular interactions in binary liquid mixtures. The excess molar volumes V^E and excess isentropic compressibilities K_s^E were calculated using the Eqs (6) and (7)

$$V^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (6)$$

$$K_s^E = K_s - (\phi_1 K_{s1} + \phi_2 K_{s2}), \quad (7)$$

where x , M , ρ and ϕ are the mole fraction, molar mass, density and volume fraction, respectively; subscripts 1 and 2 stand for BA and ethanol/propan-1-ol/octan-1-ol, respectively. The viscosity and ultrasonic speed deviations from additivity based on mole fraction were calculated using the Eqs (8) and (9)

TABLE III
 Calculated values of isentropic compressibility K_s , relative association R_A , specific acoustic impedance Z , molar sound velocity R_m and molecular association M_A for given binary mixtures at 303 K

$x(\text{BA})$	$10^{-10} \frac{K_s}{\text{m}^2 \text{N}^{-1}}$	R_A	$10^6 \frac{Z}{\text{kg m}^{-2} \text{s}^{-1}}$	$10^{-3} \frac{R_m}{\text{m}^3 \text{mol}^{-1}} (\text{ms}^{-1})^{1/3}$	M_A
BA-ethanol					
0.0000	9.9809	1.0000	0.8849	0.61434	0.0000
0.1780	7.6648	1.0704	1.0595	0.71158	0.2675
0.3074	6.4964	1.1016	1.1789	0.78867	0.4399
0.4193	5.8592	1.1260	1.2624	0.85379	0.5180
0.5317	5.3492	1.1463	1.3400	0.91989	0.5494
0.6131	5.0709	1.1588	1.3880	0.96809	0.5312
0.6933	4.8292	1.1701	1.4332	1.01543	0.4844
0.7795	4.6027	1.1810	1.4790	1.06646	0.3998
0.8624	4.4411	1.1916	1.5153	1.11463	0.2749
0.9401	4.2945	1.2000	1.5493	1.16042	0.1307
1.0000	4.1841	1.2060	1.5759	1.19569	0.0000
BA-propan-1-ol					
0.0000	8.8328	1.0000	0.9493	0.80068	0.0000
0.0875	7.9556	1.0261	1.0190	0.83489	0.0790
0.1563	7.4252	1.0464	1.0689	0.86081	0.1269
0.2255	6.9583	1.0652	1.1178	0.88716	0.1687
0.3133	6.4627	1.0870	1.1761	0.92111	0.2088
0.4075	5.9903	1.1080	1.2384	0.95806	0.2407
0.4874	5.6344	1.1239	1.2904	0.98995	0.2570
0.5573	5.3624	1.1365	1.3337	1.01835	0.2601
0.6714	4.9847	1.1563	1.4009	1.06403	0.2393
0.7895	4.6606	1.1751	1.4659	1.11133	0.1838
1.0000	4.1841	1.2049	1.5759	1.19569	0.0000
BA-octan-1-ol					
0.0000	6.8815	1.0000	1.0901	1.7528	0.0000
0.1209	6.6278	1.0203	1.1234	1.6827	-0.0141
0.2075	6.4402	1.0356	1.1492	1.6330	-0.0233
0.3464	6.1151	1.0613	1.1963	1.5546	-0.0341
0.4470	5.8686	1.0813	1.2346	1.4981	-0.0401
0.5470	5.6004	1.1020	1.2784	1.4431	-0.0419
0.6474	5.3227	1.1248	1.3276	1.3873	-0.0421
0.7378	5.0478	1.1461	1.3796	1.3380	-0.0369
0.8287	4.7667	1.1693	1.4378	1.2883	-0.0298
0.9150	4.4801	1.1926	1.5023	1.2416	-0.0173
1.0000	4.1841	1.2173	1.5759	1.1957	0.0000

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (8)$$

$$\Delta u = u - (x_1u_1 + x_2u_2). \quad (9)$$

The excess acoustic impedance was calculated using Eq. (10)

$$Z^E = Z - (x_1Z_1 + x_2Z_2). \quad (10)$$

The values of V^E , K_s^E , $\Delta\eta$, Δu and Z^E were fitted to the Redlich–Kister²³ polynomial equation (11)

$$Y^E = x_1x_2 \sum_{i=0}^4 A_i(1 - 2x_1)^i, \quad (11)$$

where Y^E is V^E or K_s^E or $\Delta\eta$ or Δu or Z^E . The values of the A_i coefficients together with standard deviations $\sigma(Y^E)$ calculated from Eq. (12)

$$\sigma(Y^E) = \left[\sum (Y_{\text{obs}}^E - Y_{\text{cal}}^E)^2 / (m - n) \right]^{1/2}, \quad (12)$$

where m is the total number of experimental points and n is the number of A_i coefficients considered ($n = 5$ in the present calculation). The values of the constants A_i and standard deviations of Y^E are listed in Table IV. The variations of V^E , K_s^E , $\Delta\eta$, Δu and Z^E with mole fraction x of BA are presented graphically in Figs 1–5.

The curves in Fig. 1 show that V^E values are entirely negative for BA–ethanol and BA–propan-1-ol mixtures and change from small negative to small positive for BA–octan-1-ol binary mixtures. K_s^E values (Fig. 2) are large negative for BA–ethanol followed by propan-1-ol and become small negative for BA–octan-1-ol mixtures. $\Delta\eta$ values (Fig. 3) are negative for all the three systems. As expected, the values of both Δu and Z^E (Figs 4 and 5) are positive for BA–ethanol and BA–propan-1-ol and become negative for BA–octan-1-ol binary mixtures. Positive or negative deviations of these functions from a rectilinear dependence on composition of the mixtures indicate the extent of dissociation or association between unlike molecules. Dissociation refers to breaking up of hydrogen bonded network of alkanols and association refers to formation of new hydrogen bonds between unlike molecules.

A qualitative interpretation of the behaviour of the above parameters with composition may be proposed. As mentioned earlier, the molecules of alcohols are associated in the neat state through hydrogen bonding. Mixing of BA with other alcohols would induce mutual dissociation of associated

structures in these alcohols. This facilitates the release of dipoles of unlike molecules in the mixture. As a result, the free dipoles of unlike molecules interact with each other forming strong hydrogen bonds³ leading to contraction in volume and reduction in compressibility of the mixtures. Apart from the strong O...H-O hydrogen bonding, relatively weak hydrogen-bonding (π -H) between π -electrons of the benzene ring of BA and protons of alkanols is quite obvious. Recently, Larens *et al.*⁶ have discussed the importance of π -H bonding between benzene and *tert*-butyl alcohol molecules. The strength of hydrogen bond formed between BA and alkanol molecules should follow the order: ethanol > propan-1-ol > octan-1-ol. This

TABLE IV

Values of coefficient A_i of polynomial expression according to Eq. (11) along with standard deviations σ (Y^E) for the binary systems at 303 K

Function	A_1	A_2	A_3	A_4	A_5	σ (Y^E)
BA-ethanol						
$V^E, 10^{-5} \text{ m}^3 \text{ mol}^{-1}$	-0.2342	-0.1873	-0.2351	0.0225	0.0254	0.0013
$K_s^E, 10^{-10} \text{ m}^2 \text{ N}^{-1}$	-3.1683	-2.3796	-1.4041	0.5441	1.5690	0.0115
$\eta^E, 10^{-3} \text{ N m}^{-1} \text{ s}^{-1}$	-1.1399	-0.5778	1.3474	0.1206	-1.1327	0.0035
$u^E, 10^2 \text{ m s}^{-1}$	2.3466	0.4220	0.0130	-0.9192	-1.6198	0.0119
$Z^E, 10^5 \text{ kg m}^{-2} \text{ s}^{-1}$	3.4991	0.6758	0.3188	-0.8330	-1.8817	0.0128
BA-propan-1-ol						
$V^E, 10^{-5} \text{ m}^3 \text{ mol}^{-1}$	-0.1563	-0.0916	-0.0091	0.0346	0.0573	0.0009
$K_s^E, 10^{-10} \text{ m}^2 \text{ N}^{-1}$	-2.2170	-0.8645	-0.4538	-1.3065	-0.4636	0.0034
$\eta^E, 10^{-3} \text{ N m}^{-1} \text{ s}^{-1}$	-0.8314	-0.4289	-0.5318	0.1565	-0.3464	0.0023
$u^E, 10^2 \text{ m s}^{-1}$	0.9762	-0.0981	0.1226	0.9037	0.2017	0.0027
$Z^E, 10^5 \text{ kg m}^{-2} \text{ s}^{-1}$	1.4008	-0.0516	0.1161	0.7613	-0.0282	0.0036
BA-octan-1-ol						
$V^E, 10^{-5} \text{ m}^3 \text{ mol}^{-1}$	-0.0029	-0.0826	-0.0663	-0.0002	0.0867	0.0007
$K_s^E, 10^{-10} \text{ m}^2 \text{ N}^{-1}$	-0.3536	0.1325	-0.0381	-0.0045	-0.0483	0.0025
$\eta^E, 10^{-3} \text{ N m}^{-1} \text{ s}^{-1}$	-3.2734	-0.8713	-4.3149	-1.0582	1.9616	0.0137
$u^E, 10^2 \text{ m s}^{-1}$	-1.4381	0.4626	-0.2088	0.0647	0.0999	0.0036
$Z^E, 10^5 \text{ kg m}^{-2} \text{ s}^{-1}$	-3.0420	1.0100	-0.1333	0.1022	-0.2641	0.0028

is due to the fact that molecular size of ethanol (molar volume = $5.8943 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) is much smaller than those of propan-1-ol (molar volume = $7.5503 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) and octan-1-ol (molar volume = $1.5926 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$) which would allow a closer approach, hence, stronger association occurs between BA and ethanol molecules than between BA and propan-1-ol or

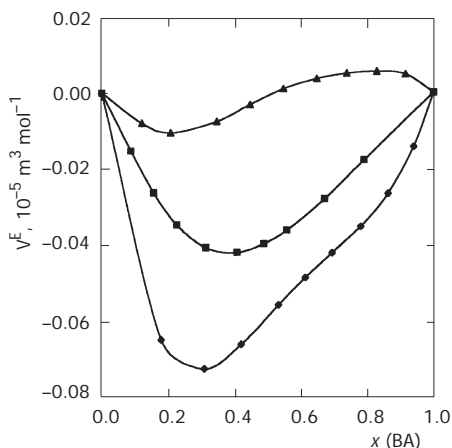


FIG. 1

Plots of excess volume V^E , against mole fraction x of BA for the studied binary systems at 303 K.

◆ Ethanol, ■ propan-1-ol, ▲ octan-1-ol

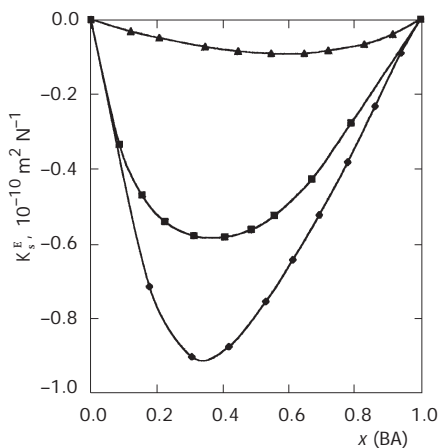


FIG. 2

Plots of excess isentropic compressibility K_s^E against mole fraction x of BA for the studied binary systems at 303 K.

◆ Ethanol, ■ propan-1-ol, ▲ octan-1-ol

octan-1-ol molecules. A similar explanation for the decrease in V^E and K_s^E with composition for a liquid mixture has also been suggested by Ali *et al.*¹ The negative $\Delta\eta$ (Fig. 3) deviations observed in all the three systems over the whole composition range are attributed to the presence of dispersion forces, particularly for the systems having different molecular size^{24,25} as in

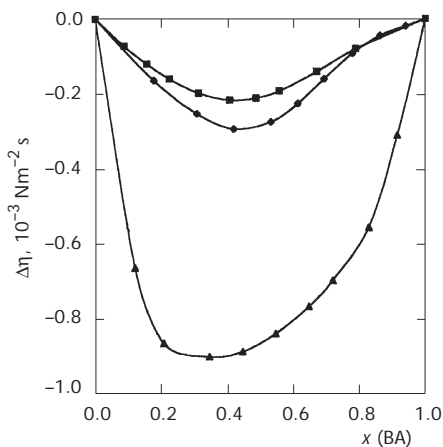


FIG. 3

Plots of viscosity deviations $\Delta\eta$ against mole fraction x of BA for the studied binary systems at 303 K. ♦ Ethanol, ■ propan-1-ol, ▲ octan-1-ol

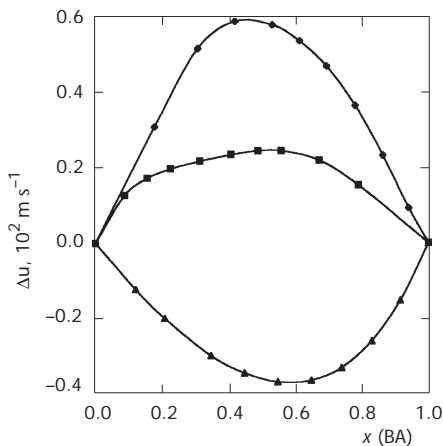


FIG. 4

Plots of deviations in ultrasonic speed Δu against mole fraction x of BA for the binary systems at 303 K. ♦ Ethanol, ■ propan-1-ol, ▲ octan-1-ol

the present case. It should be noted that BA–octan-1-ol exhibits more pronounced negative $\Delta\eta$ followed by BA–ethanol and BA–propan-1-ol. The relative difference in molar volumes between BA and ethanol/propan-1-ol/octan-1-ol reinforces the above view.

The observed trends in the behaviour of Δu (Fig. 4) and opposite trends in K_s^E where $K_s = 1/u^2\rho$, for the systems under study, are in good agreement with the behaviour of the rest of the properties discussed above. Thus, we may conclude that factors responsible for the variation of Δu with x are the same as for K_s^E . It has been suggested²⁶ that excess acoustic impedance, Z^E , becomes increasingly positive/negative as the interaction between unlike molecules increases/decreases. The positive Z^E values for BA–ethanol and BA–propan-1-ol (Fig. 5) over the whole composition range are attributed to the presence of significant interaction between unlike molecules. Negative values of Z^E for BA–octan-1-ol suggest the presence of weak interaction between BA and octan-1-ol molecules. Thus, the sign and magnitude of V^E , K_s^E , $\Delta\eta$, Δu and Z^E deviations from the linear dependence on composition for the present liquid mixtures clearly suggest that the strength of interaction between BA and alkanol molecules decrease in the order: ethanol > propan-1-ol > octan-1-ol.

The experimental viscosities were used to estimate the theoretical viscosity of liquid mixtures in terms of pure-component data using several empirical relations. We examined equations of Grunberg and Nissan²⁷, Tamura and Kurata²⁸, Hind *et al.*²⁹, Katti and Chaudhri³⁰ and Heric³¹.

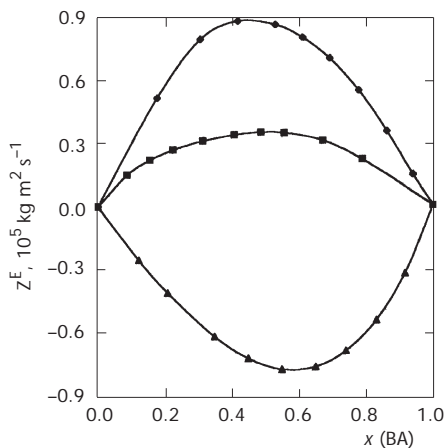


FIG. 5

Plots of excess acoustic impedance Z^E against mole fraction x of BA for the studied binary systems at 303 K. \blacklozenge Ethanol, \blacksquare propan-1-ol, \blacktriangle octan-1-ol

The Grunberg–Nissan²⁷ equation, based on the Arrhenius relation for the viscosity of a liquid mixture reads

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}, \quad (13)$$

where G_{12} is a parameter proportional to the interchange energy, which reflects the non-ideality of the system. It represents a measure of the strength of interactions between the components of the mixture.

Tamura and Kurata²⁸ proposed the Eq. (14)

$$\eta = x_1 V_1 \eta_1 + x_2 V_2 \eta_2 + 2(x_1 x_2 V_1 V_2)^{1/2} T_{12}, \quad (14)$$

where T_{12} is the interaction parameter which depends on temperature and composition of the mixture, V_i is the molar volume of nest component.

Hind *et al.*²⁹ proposed the following Eq. (15)

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12}, \quad (15)$$

where H_{12} is attributed to unlike pair interactions.

Katti–Chaudhri³⁰ derived Eq. (16) which is of the form

$$\ln \eta V = x_1 \ln V_1 \eta_1 + x_2 \ln V_2 \eta_2 + x_1 x_2 W_{\text{vis}}/RT, \quad (16)$$

where W_{vis}/RT is an interaction parameter.

Heric³¹ suggested Eq. (17)

$$\ln \eta + x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln (x_1 M_1 + x_2 M_2) + \Delta_{12}, \quad (17)$$

where M_1 is the molar mass of BA and M_2 is that of ethanol, propan-1-ol and octan-1-ol, respectively; Δ_{12} ($= \alpha_{12} x_1 x_2$) is a function representing molecular interaction and $\alpha_{12} = \alpha_{21}$ is the interaction parameter. Heric expressed α_{12} or α_{21} as a linear function of composition.

Values of calculated parameters of Eqs (13)–(17) and values of their standard percentage deviations were obtained by using experimental viscosity data and least-squares method, with equal weights assigned to each point, as described by Oswal and Desai³², are compiled in Table V. The parameter G_{12} can assume both positive and negative values and is characteristic of the system. Table V shows that G_{12} is positive for ethanol and propan-1-ol while it turns negative for octan-1-ol indicating the presence of interaction between unlike molecules in the mixtures. Garcia *et al.*⁴ pointed out that positive G_{12} values reflect the behaviour of liquid systems that deviate negatively from Raoult's law. The observed G_{12} decreases in the order:

ethanol > propan-1-ol > octan-1-ol. This order should be taken as the strength of interaction between BA and alkanol molecules. This observation substantiates our earlier finding based on the variation of Y^E with composition of the mixtures.

The values of σ (%) shown in Table V suggest that they are in the range of 0.80–1.78% for Eq. (13), 15.84–53.33% for Eq. (14), 0.84–2.58% for Eq. (15), 0.80–1.82% for Eq. (16) and 0.61–1.79% for Eq. (17). Out of the five aforementioned empirical relations, the Grunberg–Nissan and Heric models provide best description of the present mixtures whereas Tamura–Kurata model yields maximum deviations. Garcia *et al.*⁴ have also reported a reasonably good result for the binary mixtures formamide–C₁–C₅ alkanols using the Grunberg–Nissan and Heric models.

Theoretical values of ultrasonic speed in all studied binary mixtures were evaluated using the following relations and theories:

Nomoto's (NOM) empirical relation¹⁰

$$u(\text{NOM}) = [(x_1 R_1 + x_2 R_2)/(x_1 V_1 + x_2 V_2)]^3, \quad (18)$$

collision factor theory¹¹ (CFT)

$$u(\text{CFT}) = u_\infty (x_1 S_1 + x_2 S_2) [(x_1 B_1 + x_2 B_2)/V], \quad (19)$$

free-length theory¹² (FLT)

$$u(\text{FLT}) = K/(L_f \rho^{1/2}), \quad (20)$$

van Dael and Vangeel (VDV) relation¹³

$$u(\text{VDV}) = u_1 u_2 \{M_1 M_2 / [(x_1 M_2 u_2^2 + x_2 M_2 u_1^2)(x_1 M_1 + x_2 M_2)]\}^{1/2}. \quad (21)$$

TABLE V

Values of the parameters of Eqs (13)–(17) and corresponding standard percentage deviations in correlating viscosities of the binary mixtures at 303 K

Binary mixture	Eq. (13)		Eq. (14)		Eq. (15)		Eq. (16)		Eq. (17)	
	G_{12}	σ , %	T_{12}	σ , %	H_{12}	σ , %	W_{vis}/RT	σ , %	Heric	σ , %
BA–ethanol	0.6262	0.84	48.0660	53.33	2.2975	2.30	0.7529	0.80	0.9692	0.87
BA–propan-1-ol	0.1516	0.80	35.1692	15.84	2.6715	0.84	0.1846	0.84	0.3294	0.61
BA–octan-1-ol	-0.7405	1.78	44.9898	19.74	3.3999	2.58	-0.6492	1.82	-0.7232	1.79

TABLE VI
Theoretical values of ultrasonic speed calculated from NOM, CFT, FLT and VDV relations along with experimental ultrasonic speed and percentage error for the binary systems at 303 K

<i>x</i> (BA)	<i>u</i> , ms ⁻¹					Error, %			
	Exp.	NOM	CFT	FLT	VDV	NOM	CFT	FLT	VDV
BA-ethanol									
0.0000	1 132.2	1 132.2	1 132.2	1 132.2	1 132.2	0.00	0.00	0.00	0.00
0.1780	1 231.4	1 231.1	1 211.3	1 161.9	1 093.8	0.03	1.63	5.64	11.18
0.3074	1 305.7	1 291.9	1 261.8	1 180.9	1 088.1	1.06	3.36	9.56	16.66
0.4193	1 352.0	1 338.4	1 304.3	1 204.1	1 097.3	1.01	3.53	10.94	18.84
0.5317	1 395.1	1 380.3	1 346.5	1 237.0	1 120.8	1.06	3.48	11.33	19.66
0.6131	1 420.8	1 408.1	1 375.8	1 258.8	1 148.2	0.90	3.17	11.40	19.19
0.6933	1 444.8	1 433.5	1 405.1	1 290.8	1 185.9	0.78	2.75	10.66	17.92
0.7795	1 469.0	1 459.0	1 436.5	1 334.3	1 241.6	0.68	2.21	9.17	15.48
0.8624	1 486.0	1 481.9	1 466.5	1 386.0	1 316.0	0.28	1.31	6.73	11.44
0.9401	1 503.0	1 501.9	1 494.5	1 447.9	1 413.4	0.07	0.56	3.67	5.96
1.0000	1 516.6	1 516.6	1 516.6	1 516.6	1 516.6	0.00	0.00	0.00	0.00
BA-propan-1-ol									
0.0000	796.0	1 192.6	1 192.6	1 192.6	1 192.6	0.00	0.00	0.00	0.00
0.0875	826.0	1 227.8	1 223.4	1 194.9	1 187.6	0.47	0.83	3.13	3.73
0.1563	848.3	1 254.3	1 247.4	1 200.2	1 187.0	0.45	1.00	4.75	5.80
0.2255	869.4	1 280.1	1 271.2	1 207.1	1 189.3	0.43	1.13	6.11	7.50
0.3133	894.0	1 311.6	1 300.1	1 215.4	1 196.6	0.31	1.18	7.62	9.04
0.4075	918.7	1 343.8	1 331.0	1 229.5	1 210.2	0.31	1.26	8.79	10.22
0.4874	938.2	1 370.0	1 356.8	1 244.7	1 226.8	0.39	1.36	9.51	10.81
0.5573	953.9	1 392.1	1 378.5	1 257.3	1 245.6	0.44	1.41	10.08	10.92
0.6714	978.3	1 426.6	1 414.3	1 290.4	1 286.4	0.37	1.23	9.89	10.17
0.7895	1 001.5	1 460.5	1 451.0	1 339.3	1 345.3	0.22	0.87	8.5	8.09
1.0000	1 039.1	1 516.6	1 516.6	1 516.6	1 516.6	0.00	0.00	0.00	0.00
BA-octan-1-ol									
0.0000	1 333.1	1 333.1	1 333.1	1 333.1	1 333.1	0.00	0.00	0.00	0.00
0.1209	1 343.1	1 347.6	1 356.0	1 332.8	1 352.7	0.34	0.96	0.77	0.71
0.2075	1 351.1	1 358.9	1 372.0	1 331.6	1 367.1	0.58	1.55	1.44	1.18
0.3464	1 367.0	1 378.8	1 397.3	1 329.1	1 390.9	0.86	2.22	2.77	1.75
0.4470	1 380.2	1 394.7	1 415.5	1 328.8	1 408.8	1.05	2.56	3.72	2.07
0.5470	1 396.8	1 412.1	1 433.2	1 328.7	1 427.0	1.09	2.60	4.88	2.16
0.6474	1 415.1	1 431.2	1 451.4	1 336.9	1 445.8	1.14	2.57	5.52	2.17
0.7378	1 436.0	1 450.2	1 467.8	1 350.5	1 463.3	0.99	2.21	5.96	1.90
0.8287	1 459.1	1 471.1	1 484.4	1 376.2	1 481.3	0.82	1.73	5.68	1.52
0.9150	1 485.8	1 492.9	1 500.3	1 422.2	1 498.9	0.48	0.98	4.28	0.88
1.0000	1 516.6	1 516.6	1 516.6	1 516.6	1 516.6	0.00	0.00	0.00	0.00

The details of derivations and terms used in the above relations may be obtained from the literature^{10-13,20}. The theoretically calculated values of ultrasonic speeds using NOM, CFT, FLT and VDV equations along with the experimental ultrasonic speeds and percentage errors in the calculated values for all the three binary systems as a function of composition are listed in Table VI. The results given in Table VI clearly indicate that for the mixtures of BA with ethanol and propan-1-ol, NOM relation shows lowest minimum deviations followed by CFT, FLT and VDV relations. For the mixture of BA with octan-1-ol, NOM relation again gives the best result, while FLT shows maximum deviation. It can be thus concluded that NOM relation is the best one from the relations studied. The linearity of molecular sound speed and additivity of molar volume, as envisaged in Nomoto's empirical relation (18), is well obeyed by the present liquid mixtures. The CFT relation is also reasonably good in predicting the experimental ultrasonic speed in the present systems. This may be due to the presence of two empirical factors S_1 , and S_2 contained in the Schaaffs equation (19). These factors are known as collision factors and are in fact correction terms which can be adjusted to give better results. The success of the NOM and CFT relations in predicting the experimental ultrasonic speeds for polar-polar liquid mixtures, as in the present case, have also been reported by others^{33,34}.

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