Molecular Interactions in Binary Mixtures of Benzene with 1-Alkanols (C₅, C₇, C₈) at 35 °C: An Ultrasonic Study

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Densities and ultrasonic speeds have been measured in binary mixtures of benzene with 1-pentanol, 1-heptanol and 1-octanol, and in the pure components, as a function of composition at 35 ℃. The isentropic compressibility, intermolecular free length, relative association, acoustic impedance, isothermal compressibility, thermal expansion coefficient, deviations in isentropic compressibility, excess free length, excess volume, deviations in ultrasonic speed, excess acoustic impedance, apparent molar compressibility, apparent molar volume, partial molar volume of 1-alkanol in benzene have been calculated from the experimental data of densities and ultrasonic speeds. The variation of these parameters with composition indicates weak interaction between the component molecules and this interaction decreases in the order: 1-pentanol > 1-heptanol > 1-octanol. Further, theoretical values of ultrasonic speeds were evaluated using free length theory, collision factor theory, Nomoto's relation and Van Dael-Vangeel ideal mixing relation. The relative merits of these theories and relations were discussed for these systems.

Keywords   liquid mixtures, excess functions, density, ultrasonic speed, apparent molar properties

Introduction

The investigations on acoustic and volumetric properties of non-aqueous binary liquid mixtures have been found to provide useful information about the physical nature and strength of intermolecular interactions in these mixtures.[1-4] Moreover, mixed solvents, rather than single pure liquid, are of great practical importance in most chemical, industrial and biological processes, as they provide a wide range of mixtures in varying proportions. In continuation of our earlier studies on intermolecular interaction in non-aqueous binary liquid mixtures containing 1-alkanols,[5-7] here we report the results of our study on binary mixtures of benzene with 1-pentanol, 1-heptanol and 1-octanol at 35 ℃, covering the entire composition range. Benzene is a nonpolar and unassociated liquid, whereas 1-alkanols are self-associated through hydrogen bonding in the pure state.[8] The degree of association in 1-alkanols decreases as the carbon chain length in the molecule increases.[8] A survey of literature indicates that there has been no study of these systems from the point of view of their ultrason-

ic behaviour. The mixtures of benzene with 1-alkanols are interesting because of the possibility of weak hydrogen bonding involving π-electrons of benzene ring and proton of OH group of 1-alkanols. Weak hydrogen bonding of aromatic rings with proton donors, like 1-alkanols, appear to play a role in the structure of certain biomolecules.[9] The study of the behaviour of binary and ternary mixtures involving benzene and alcohols is an important field of research.[10,11] Moreover, the effect of increasing alkyl chain length on the intermolecular interactions will also be investigated. Therefore, the present study is expected to reveal the nature and extent of interaction between the component molecules in these mixtures.

In the present paper, we report densities, ρ and ultrasonic speeds, u in binary mixtures of benzene with 1-pentanol, 1-heptanol and 1-octanol, including those of pure liquids, at 35 ℃ covering the entire composition range. From these experimental data, the isentropic compressibility, k_s, intermolecular free length, L_f, relative association, R_A, acoustic impedance, Z, isothermal compressibility, β_T, thermal expansion coefficient, α, deviations in isentropic compressibility, Δk_s, excess free length, L_f^E, excess volume, V^E, deviations in ultrasonic speed, Δu, excess acoustic impedance, Z^E, apparent molar isentropic compressibility, $K_{\phi,2}$, and apparent molar volume, $V_{\phi,2}$ of 1-alkanols in benzene, partial molar compressibility, $\bar{K}^\circ_{\phi,2}$ and partial molar volume, $\bar{V}^\circ_{\phi,2}$ of 1-alkanols in benzene at infinite dilution have been calculated. These functions offer a convenient method for the study of thermodynamic properties of liquids and their mixtures not easily obtained by other means. Moreover, ultrasonic speeds in all the three binary mixtures were theoretically calculated with the help of different theories and empirical relations. Theoretical values of ultrasonic speed were compared with the experimental values and relative merits of these theories and relations were examined for the present systems.

Experimental

Benzene, 1-pentanol, 1-heptanol and 1-octanol (all

s. d. fine chemicals, India, analytical reagent grade) were purified by the methods described in the literature.[12,13] All the mixtures were prepared by weight on Afcoset ER-120A electronic balance with a precision of ± 0.1 mg. The probable error in mole fraction was estimated to be less than ± 0.0001.

The densities of the pure liquids and of their binary mixtures were measured using a single-capillary pycnometer (made of Borosil glass) with a bulb capacity of 8×10^{-6} m^3. The marks on the capillary were calibrated by using triple distilled water. The observed values of densities of pure benzene, 1-pentanol, 1-heptanol and 1-octanol at 35 °C were 864.2, 803.9, 811.7 and 814.1 kg·m^{-3}, respectively, which compare well with the corresponding literature values : 863.1,[14] 803.9[15]/804.1,[13] 813.5[16] and 814.4[16] kg·m^{-3}. The ultrasonic speeds were measured using single-crystal variable-path ultrasonic interferometer operating at 3 MHz with an accuracy of ± 0.05%. The temperature of the samples was maintained at (35 ± 0.02) °C in an electronically controlled thermostatic water bath.

Results and discussion

The experimental values of densities, ρ and ultrasonic speeds, u of pure liquids and of all the three binary systems, each at nine different compositions, at 35 °C are given in Table 1. The values of k_s, L_f, R_A, Z, β_T and α were evaluated using ρ and u of pure liquids and of their binary mixtures from the standard relations:[6,7,17,18]

$$k_s = 1/u^2\rho \tag{1}$$

$$L_f = K/u\rho^{1/2} \tag{2}$$

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

$$Z = u\rho \tag{4}$$

$$\beta_T = (1.71 \times 10^{-3})/(T^{4/9}u^2\rho^{4/3}) \tag{5}$$

$$\alpha = (0.0191 \times \beta_T)^{1/4} \tag{6}$$

where K is temperature-dependent constant [(93.875 + 0.375T) × 10^{-8}]; T is the absolute temperature; ρ_0 and u_0 are the density and ultrasonic speed of the pure solvent (1-alkanol), respectively. The values of ρ, u, k_s, L_f, R_A, Z, β_T and α for all the binary mixtures, including those of pure liquids, as a function of composition are listed in Table 2. It is evident from Table 2 that all the three systems (benzene + 1-pentanol/1-heptanol/1-octanol) exhibit nonlinear variation in k_s, L_f, R_A, Z, β_T and α values with composition. This indicates the presence of intermolecular interactions[19,20] between the component molecules of the mixtures.

Table 1 Densities, ρ and ultrasonic speeds, u of the binary mixtures as functions of mole fraction, x_1 of benzene at 35 °C

x_1	ρ (kg·m^{-3})	u (10^3 m·s^{-1})
Benzene + 1-pentanol		
0.0000	803.9	1.2457
0.1188	809.2	1.2403
0.2327	814.5	1.2357
0.3421	819.9	1.2314
0.4471	825.4	1.2274
0.5482	831.0	1.2256
0.6454	836.9	1.2270
0.7390	843.0	1.2299
0.8291	849.6	1.2357
0.9161	856.5	1.2443
1.0000	864.2	1.2571
Benzene + 1-heptanol		
0.0000	811.7	1.2971
0.1496	816.0	1.2840
0.2837	820.6	1.2720
0.4043	825.1	1.2615
0.5136	829.6	1.2521
0.6130	834.4	1.2448
0.7038	839.4	1.2403
0.7870	844.8	1.2396
0.8637	850.6	1.2414
0.9344	857.0	1.2463
1.0000	864.2	1.2571
Benzene + 1-octanol		
0.0000	814.1	1.3186
0.1643	818.2	1.2999
0.3067	822.3	1.2833
0.4313	826.4	1.2687
0.5413	830.7	1.2570
0.6390	835.3	1.2484
0.7264	840.3	1.2441
0.8051	845.6	1.2421
0.8762	851.2	1.2429
0.9409	857.2	1.2471
1.0000	864.2	1.2571

The deviations in isentropic compressibility, Δk_s, excess free length, L_f^E, excess volume, V^E, deviations in ultrasonic speed, Δu, and excess acoustic impedance, Z^E have been calculated by using the relation:

$$Y^E = Y_{\text{mixture}} - Y_{\text{ideal}} \tag{7}$$

and $$Y_{\text{ideal}} = x_1 Y_1 + x_2 Y_2 \tag{8}$$

Table 2 The values of isentropic compressibilities, k_s, intermolecular free lengths, L_f, relative associations, R_A, acoustic impedances, Z, isothermal compressibilities, β_T, and thermal expansion coefficients, α as functions of mole fraction, x_1 of benzene for the binary mixtures at 35 ℃

x_1	k_s $(10^{-10} \text{ m}^2 \cdot \text{N}^{-1})$	L_f (10^{-11} m)	R_A	Z $(10^6 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$	β_T $(10^{-10} \text{ m}^2 \cdot \text{N}^{-1})$	α (10^{-3} K^{-1})
			Benzene + 1-pentanol			
0.0000	8.0162	5.9296	1.0000	1.0014	1.1546	1.2186
0.1188	8.0332	5.9359	1.0081	1.0037	1.1546	1.2186
0.2327	8.0405	5.9386	1.0159	1.0065	1.1531	1.2182
0.3421	8.0434	5.9397	1.0238	1.0096	1.1510	1.2177
0.4471	8.0420	5.9391	1.0318	1.0131	1.1482	1.2169
0.5482	8.0113	5.9278	1.0393	1.0185	1.1412	1.2151
0.6454	7.9367	5.9001	1.0463	1.0269	1.1280	1.2115
0.7390	7.8421	5.8649	1.0531	1.0368	1.1118	1.2072
0.8291	7.7083	5.8146	1.0597	1.0499	1.0900	1.2012
0.9161	7.5409	5.7511	1.0658	1.0657	1.0635	1.1938
1.0000	7.3223	5.6671	1.0717	1.0864	1.0296	1.1842
			Benzene + 1-heptanol			
0.0000	7.3225	5.6672	1.0000	1.0529	1.0513	1.1904
0.1496	7.4333	5.7099	1.0087	1.0477	1.0654	1.1944
0.2837	7.5317	5.7476	1.0176	1.0438	1.0774	1.1977
0.4043	7.6159	5.7796	1.0260	1.0409	1.0875	1.2005
0.5136	7.6887	5.8072	1.0342	1.0387	1.0959	1.2028
0.6130	7.7344	5.8244	1.0422	1.0387	1.1003	1.2040
0.7038	7.7442	5.8281	1.0497	1.0411	1.0995	1.2038
0.7870	7.7034	5.8128	1.0566	1.0472	1.0914	1.2016
0.8637	7.6287	5.7845	1.0634	1.0559	1.0783	1.1980
0.9344	7.5123	5.7402	1.0700	1.0681	1.0592	1.1926
1.0000	7.3223	5.6671	1.0759	1.0864	1.0296	1.1842
			Benzene + 1-octanol			
0.0000	7.0647	5.5666	1.0000	1.0735	1.0133	1.1795
0.1643	7.2330	5.6325	1.0098	1.0636	1.0357	1.1860
0.3067	7.3844	5.6911	1.0193	1.0553	1.0556	1.1916
0.4313	7.5178	5.7423	1.0282	1.0485	1.0729	1.1965
0.5413	7.6188	5.7807	1.0368	1.0442	1.0855	1.1999
0.6390	7.6816	5.8045	1.0449	1.0428	1.0924	1.2019
0.7264	7.6887	5.8072	1.0524	1.0454	1.0912	1.2015
0.8051	7.6652	5.7983	1.0596	1.0503	1.0856	1.2000
0.8762	7.6049	5.7755	1.0664	1.0580	1.0747	1.1970
0.9409	7.5009	5.7359	1.0727	1.0690	1.0575	1.1922
1.0000	7.3223	5.6671	1.0786	1.0864	1.0296	1.1842

where Y^E stands for Δk_s, L_f^E, V^E, Δu and Z^E, respectively; x is the mole fraction; subscripts 1 and 2 refer to benzene and 1-alkanol (1-pentanol/1-heptanol/1-octanol), respectively. The molar volumes, V of binary mixtures were calculated using the relation:

$$V = (x_1 M_1 + x_2 M_2)/\rho \qquad (9)$$

where M is the molar mass. For each mixture, the values of Δk_s, L_f^E, V^E, Δu and Z^E were fitted to a Redlich-Kister[21] type polynomial equation:

$$Y^E = x(1-x) \sum_{i=1}^{5} A_i (1-2x)^{i-1} \qquad (10)$$

The values of coefficients, A_i, evaluated by the method of least-squares, along with the standard deviations $\sigma(Y^E)$ calculated using the relation:

$$\sigma(Y^E) = \left[\sum (Y_{\text{expt}}^E - Y_{\text{cal}}^E)^2 / (m-n) \right]^{1/2} \qquad (11)$$

where m is the number of experimental data points and n is the number of coefficients considered ($n = 5$ in the present

**Table 3**   Coefficients, A_i of Eq. (10) along with standard deviations $\sigma(Y^E)$ for the binary mixtures

Properties	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
Benzene + 1-pentanol						
Δk_s $(10^{-10}$ m$^2\cdot$N$^{-1})$	1.4414	− 0.7386	− 0.3642	0.1035	0.7065	0.0031
L_f^E $(10^{-11}$ m$)$	0.5439	− 0.2813	− 0.1073	0.0237	0.2403	0.0012
V^E $(10^{-6}$ m$^3\cdot$mol$^{-1})$	1.3838	− 0.7315	0.2026	− 0.1865	0.1905	0.0030
Δu $(10^2$ m$\cdot$s$^{-1})$	− 1.0062	0.5529	0.2123	− 0.0361	− 0.5001	0.0023
Z^E $(10^5$ kg$\cdot$m$^{-2}\cdot$s$^{-1})$	− 1.1309	0.5835	0.1280	0.0210	− 0.4498	0.0029
Benzene + 1-heptanol						
Δk_s $(10^{-10}$ m$^2\cdot$N$^{-1})$	1.4514	− 1.2293	0.1211	0.0214	0.8945	0.0019
L_f^E $(10^{-11}$ m$)$	0.5550	− 0.4649	0.0432	0.0000	0.3560	0.0007
V^E $(10^{-6}$ m$^3\cdot$mol$^{-1})$	1.6840	− 1.3048	0.4114	0.1882	0.8421	0.0029
Δu $(10^2$ m$\cdot$s$^{-1})$	− 0.9719	0.8627	− 0.0344	0.0218	− 0.7592	0.0015
Z^E $(10^5$ kg$\cdot$m$^{-2}\cdot$s$^{-1})$	− 1.2410	0.9531	− 0.1262	0.0581	− 0.7553	0.0014
Benzene + 1-octanol						
Δk_s $(10^{-10}$ m$^2\cdot$N$^{-1})$	1.5860	− 1.3724	− 0.3483	0.1595	1.7778	0.0021
L_f^E $(10^{-11}$ m$)$	0.6119	− 0.5166	− 0.1369	0.0513	0.6923	0.0008
V^E $(10^{-6}$ m$^3\cdot$mol$^{-1})$	1.9635	− 1.4414	− 0.9651	0.2808	2.7424	0.0013
Δu $(10^2$ m$\cdot$s$^{-1})$	− 1.0849	0.9385	0.2942	− 0.0825	− 1.3685	0.0016
Z^E $(10^5$ kg$\cdot$m$^{-2}\cdot$s$^{-1})$	− 1.3967	1.0642	0.2830	− 0.0495	− 1.5042	0.0015

calculation) are listed in Table 3. Y_{cal}^E has been obtained by equation (10) using the best-fit values of A_i. The variations of smoothed values of Δk_s, L_f^E, V^E, Δu and Z^E, using Eq. (10), with mole fraction x_1 of benzene at 35 ℃ are shown graphically in Figs. 1—5.
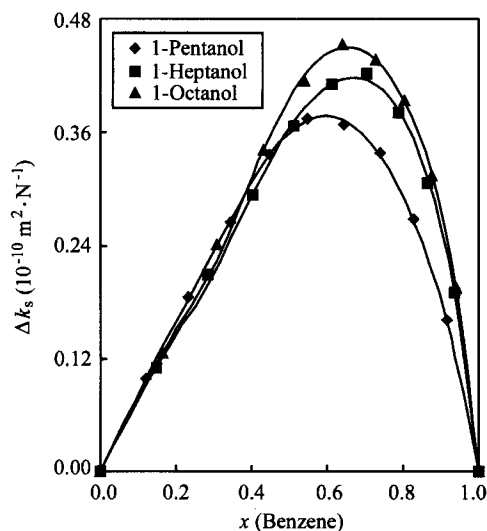
Fig. 1   Variation of deviations in isentropic compressibility, Δk_s with mole fraction x of benzene for the binary mixtures. Points show experimental values and curves show calculated values using Eq. (10).

Figs. 1, 2 and 3 show that Δk_s, L_f^E and V^E are positive for all the three binary systems (benzene + 1-pentanol/1-heptanol/1-octanol) under study over the whole composition range. The values of Δk_s, L_f^E and V^E can be qualitatively examined by considering the factors which influence these excess properties. In general, these excess properties depend
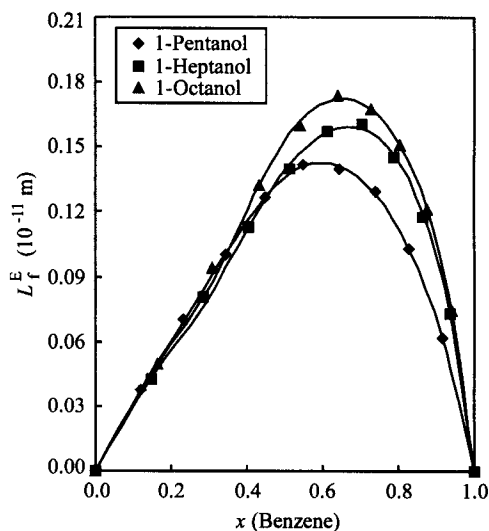
Fig. 2   Variation of excess intermolecular free length, L_f^E with mole fraction x of benzene for the binary mixtures. Points show experimental values and curves show calculated values using Eq. (10).

upon several contributions that are of physical and/or chemical nature.[1,4,8,22] The physical contributions comprise of dispersion forces or weak dipole-dipole interaction that lead to positive values in Δk_s, L_f^E and V^E. Chemical contributions include breaking up of the associates present in the pure liquids, resulting in positive Δk_s, L_f^E and V^E values, and specific interactions such as formation of (new) H-bonds, charge-transfer complexes and other complex forming interactions including strong dipole-dipole interactions between component molecules, resulting in negative Δk_s, L_f^E and V^E values. The physical contribution also includes the geometrical fitting of molecules of too different molecular size to fit into

each other's structure yielding negative Δk_s, L_f^E and V^E values.[16] However, liquids of not too different molecular size usually mix to give positive Δk_s, L_f^E and V^E values.[19]
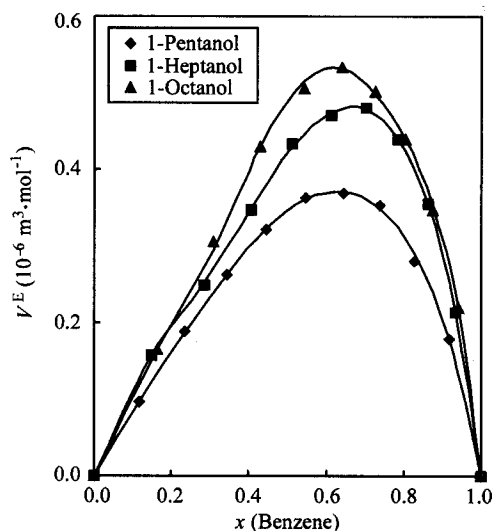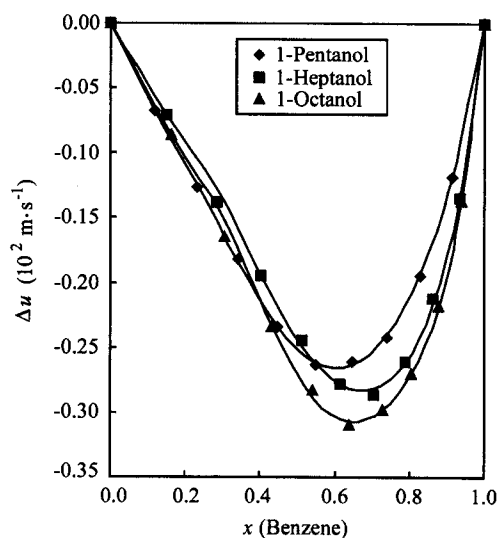

Fig. 3 Variation of excess volume, V^E with mole fraction x of benzene for the binary mixtures. Points show experimental values and curves show calculated values using Eq. (10).

A plausible qualitative interpretation of variations of Δk_s, L_f^E and V^E with composition has been suggested. As stated above, 1-alkanols are self-associated through hydrogen bonding in pure state.[8] The added benzene causes dissociation of self-associated structure of 1-alkanols (1-pentanol/1-heptanol/1-octanol) molecules leading to expansion in volume, and thus, making a positive contribution to Δk_s, L_f^E and V^E values. On the other hand, the accommodation of smaller benzene molecules (molar volume: 9.04×10^{-5} m$^3 \cdot$ mol^{-1}) into the spaces created by the bigger 1-pentanol, 1-heptanol and 1-octanol molecules (molar volumes: 10.97×10^{-5}, 14.32×10^{-5} and 16.00×10^{-5} m$^3 \cdot$ mol^{-1}, respectively) would cause a decrease in the values of Δk_s, L_f^E and V^E. Moreover, the formation of weak $\pi \cdots$ H bonding between π-electrons of benzene ring and hydrogen atom of OH group of 1-alkanols is quite obvious. Recently, Larsen et al.[23] also suggested the presence of weak $\pi \cdots$ H bonding involving π-electron cloud of benzene ring and hydrogen atom of OH group of tert-butyl alcohol. The observed positive trends in Δk_s, L_f^E and V^E values (Figs. 1, 2 and 3) clearly suggest that the disruption of associated structures of 1-alkanols dominates over the combined effect due to the accommodation of component molecules into each other's structure and electron donor-acceptor ($\pi \cdots$ H) interaction between unlike molecules. Further, it is interesting to note that despite of favourable packing of the component molecules into each other's structure the values of Δk_s, L_f^E and V^E become increasingly positive as the carbon chain length increases from 1-pentanol to 1-octanol. This trend suggests that the strength of $\pi \cdots$ H interaction between benzene and 1-alkanol molecules should follow the order: 1-pentanol > 1-heptanol > 1-octanol.

This is due to the fact that electron-accepting tendency of hydroxyl hydrogen of 1-alkanols towards π-electrons of the benzene ring decreases with increase in chain length of alkyl groups.[23,24] Also, a closer approach of unlike molecules in these mixtures is sterically hindered as the size of alkyl group becomes more bulky as we move from 1-pentanol to 1-octanol, resulting in weak interaction between benzene and 1-alkanol molecules. This is in good agreement with the view proposed by Fort and Moore[19] that Δk_s and V^E become increasingly positive as the strength of interaction between the component molecules decreases. Positive V^E values have also been reported for toluene + 1-alkanols[25] and butanol isomers + benzene/toluene[26] binary mixtures.

As expected, the curves in Figs. 4 and 5 show that Δu and Z^E values are negative throughout the composition range, and become more so as the length of carbon chain of 1-alkanols increases from 1-pentanol to 1-octanol. The increasingly negative values of Δu and Z^E with composition are indicative of decreasing strength of interaction between the component molecules in the mixtures.[27,28] The observed negative Δu and Z^E values support our earlier view that structure-breaking effect predominates over weak (electron donor-acceptor) interaction and accommodation of benzene molecules into the spaces created by 1-alkanol molecules. Negative deviations in Δu and Z^E have also been reported for toluene + dimethyl-sulphoxide[28] and toluene + cyclohexane[29] binary mixtures.

Fig. 4 Variation of deviations in ultrasonic speed, Δu with mole fraction x of benzene for the binary mixtures. Points show experimental values and curves show calculated values using Eq. (10).

The extent of interaction between the component molecules in a mixture is well-reflected in the parameters like apparent molar compressibility, apparent molar volume, partial molar compressibility and partial molar volume at infinite dilution.[30,31] The apparent molar compressibilities, $K_{\phi,2}$ of 1-alkanols in benzene were calculated using the relation:[30,31]
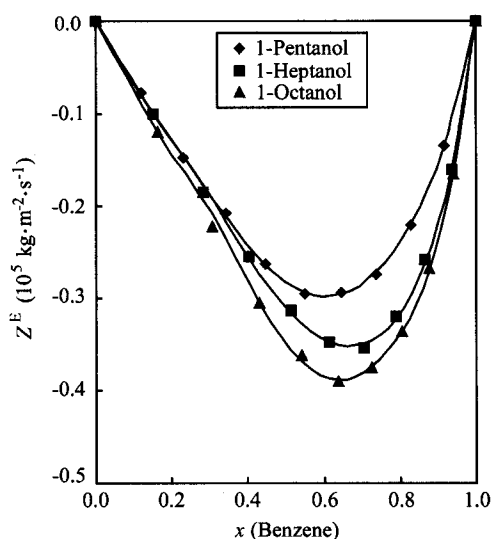
Fig. 5 Variation of excess acoustic impedance, Z^E with mole fraction x of benzene for the binary mixtures. Points show experimental values and curves show calculated values using Eq. (10).

$$K_{\phi,2} = K^*_{\phi,2} + (K^E_s/x_2) \qquad (12)$$

where $K^E_s[= (k_s V)^E]$ is the excess molar compressibility of the mixture; x_2 and $K^*_{\phi,2}$ are mole fraction and molar isentropic compressibility of 1-alkanol, respectively. The partial molar compressibility, $\bar{K}^\circ_{\phi,2}$ of 1-alkanol in benzene at infinite dilution was obtained graphically as suggested by others[30,32] and the deviation in K_ϕ at infinite dilution, ΔK was evaluated using the equation:[30]

$$\Delta K = \bar{K}^\circ_{\phi,2} - K^*_{\phi,2} \qquad (13)$$

The values of $\bar{K}^\circ_{\phi,2}$, $K^*_{\phi,2}$ and ΔK are listed in Table 4. The partial molar compressibility, $\bar{K}^\circ_{\phi,2}$ of 1-alkanol in benzene, at infinite dilution, characterises the compressibility of its molecules in the mixture, whereas molar isentropic compressibility, $K^*_{\phi,2}$ of pure 1-alkanol can be considered as partial molar compressibility of 1-alkanol when dissolved in itself. Table 4 indicates that the values of deviations ΔK are positive and follow the order: 1-octanol > 1-heptanol > 1-pentanol, which is also the order of the size of alkyl chain in 1-alkanols. Positive ΔK values are indicative of weak interactions between benzene and 1-alkanol molecules, and this interaction becomes more weak as the size of alkyl group increases from 1-pentanol to 1-octanol. The deviations ΔK may also be

analysed in terms of structural and geometrical compressibility as suggested by Hall[33] and others.[32] The trends in ΔK values suggest that breaking up of associated structures (*i. e.*, structural compressibility factor) dominates over that due to geometrical compressibility factor (due to formation of weak $\pi \cdots$H bond), leading to an expansion in volume. This supports our earlier view regarding interactions in these mixtures.

Apparent molar volumes, $V_{\phi,2}$ of 1-alkanols in benzene have been calculated using the equation:[30]

$$V_{\phi,2} = V^*_2 + (V^E/x_2) \qquad (14)$$

where V^*_2 is the molar volume of 1-alkanol. The partial molar volume, $\bar{V}^\circ_2$ of 1-alkanol in benzene at infinite dilution was obtained graphically.[30,34] The deviations in V_ϕ at infinite dilution, ΔV have been calculated using the equation:[30]

$$\Delta V = \bar{V}^\circ_2 - V^*_2 \qquad (15)$$

The values of $\bar{V}^\circ_2$, V^*_2 and ΔV are included in Table 4. It is evident from Table 4 that the values of ΔV are positive (*i. e.*, the partial molar volumes, $\bar{V}^\circ_2$ of 1-alkanols in benzene are greater than their corresponding molar volumes, V^*_2), and follow the order: 1-octanol > 1-heptanol > 1-pentanol. This suggests that mixing of benzene with 1-alkanols causes an expansion in the volume of the mixture, indicating that dissolution of associated structures of 1-alkanols dominates over that of the weak $\pi \cdots$H interaction between component molecules.

The theoretical values of ultrasonic speeds in all the three binary mixtures were calculated using the following theories and empirical relations:

Free length theory (FLT):[35]
$$u_{FLT} = K/(L_{f(theo)}\rho^{1/2}) \qquad (16)$$

Collision factor theory (CFT):[36]
$$u_{CFT} = u_\infty [x_1 S_1 + x_2 S_2][x_1 B_1 + x_2 B_2]/V \qquad (17)$$

Nomoto's relation (NOM):[37]
$$u_{NOM} = \{[x_1 R_1 + x_2 R_2]/[x_1 V_1 + x_2 V_2]\}^3 \qquad (18)$$

Van Dael and Vangeel ideal mixing relation (VDV):[38]
$$u_{VDV} = u_1 u_2 \{M_1 M_2[(x_1 M_2 u_2^2 + x_2 M_1 u_1^2)(x_1 M_1 + x_2 M_2)]\}^{1/2} \qquad (19)$$

Table 4 The values of $\bar{K}^\circ_{\phi,2}$, $K^*_{\phi,2}$, ΔK, $\bar{V}^\circ_2$, V^*_2 and ΔV of 1-alkanols in benzene for the binary mixtures

1-Alkanols	$\bar{K}^\circ_{\phi,2}$	$K^*_{\phi,2}$	ΔK	$\bar{V}^\circ_2$	V^*_2	ΔV
	(10^{-13} m$^5\cdot$N$^{-1}\cdot$mol^{-1})			(10^{-4} m$^3\cdot$mol^{-1})		
1-Pentanol	1.0339	0.8790	0.1609	1.1144	1.0965	0.0178
1-Heptanol	1.3082	1.0483	0.2599	1.4591	1.4316	0.0275
1-Octanol	1.4474	1.1301	0.3173	1.6306	1.5997	0.0309

The details of derivations and terms used may be obtained from the literature.[35-40] The theoretical values of ultrasonic speeds, evaluated using above theories and relations, along with the experimental values and percentage error in the calculated values are presented in Table 5 for comparison. On comparison, the results indicate that for benzene + 1-pentanol mixtures minimum deviations are observed in case of FLT followed by CFT and then by VDV relation, while NOM relation shows the maximum deviation. For the mixtures benzene + 1-heptanol/1-octanol, FLT and VDV seem to be equally good in predicting the data followed by CFT and NOM relation. Thus, it may be concluded that FLT and VDV fit the data better (hence, provide a satisfactory evaluation of ultrasonic speed in the binary mixtures under study) than NOM relation which shows maximum deviations.

Table 5 Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's ideal mixing relation along with the experimental values of ultrasonic speed and percentage error in calculated values for the binary mixtures

x_1	u (m·s^{-1})					Percentage error			
	Expt.	FLT	CFT	NOM	VDV	FLT	CFT	NOM	VDV
Benzene + 1-pentanol									
0.0000	1245.7	1245.7	1245.7	1245.7	1245.7	0.00	0.00	0.00	0.00
0.1188	1240.3	1242.1	1245.9	1246.8	1246.2	0.15	0.45	0.53	0.48
0.2327	1235.7	1238.6	1246.1	1248.0	1246.9	0.24	0.84	0.99	0.91
0.3421	1231.4	1235.9	1246.4	1249.1	1247.8	0.36	1.22	1.44	1.33
0.4471	1227.4	1233.8	1246.9	1250.3	1248.8	0.52	1.58	1.86	1.75
0.5482	1225.6	1232.4	1247.4	1251.4	1250.0	0.55	1.78	2.10	1.99
0.6454	1227.0	1232.8	1248.3	1252.5	1251.2	0.47	1.74	2.08	1.98
0.7390	1229.9	1234.5	1249.5	1253.7	1252.6	0.37	1.60	1.93	1.84
0.8291	1235.7	1239.2	1251.4	1254.8	1254.0	0.28	1.27	1.55	1.48
0.9161	1244.3	1245.7	1253.7	1256.0	1255.5	0.11	0.76	0.94	0.90
1.0000	1257.1	1257.1	1257.1	1257.1	1257.1	0.00	0.00	0.00	0.00
Benzene + 1-heptanol									
0.0000	1297.1	1297.1	1297.1	1297.1	1297.1	0.00	0.00	0.00	0.00
0.1496	1284.0	1285.9	1289.6	1293.1	1275.6	0.15	0.44	0.71	0.66
0.2837	1272.0	1277.2	1283.3	1289.0	1261.5	0.41	0.89	1.34	0.82
0.4043	1261.5	1268.2	1277.3	1285.0	1252.6	0.53	1.26	1.86	0.70
0.5136	1252.1	1259.4	1271.9	1281.0	1247.6	0.59	1.58	2.31	0.36
0.6130	1244.8	1252.9	1267.2	1277.0	1245.2	0.65	1.80	2.59	0.04
0.7038	1240.3	1247.9	1263.3	1273.0	1245.0	0.61	1.85	2.64	0.38
0.7870	1239.6	1245.4	1260.2	1269.0	1246.4	0.47	1.66	2.37	0.55
0.8637	1241.4	1245.4	1258.0	1265.0	1249.1	0.32	1.34	1.90	0.62
0.9344	1246.3	1249.0	1256.9	1261.1	1252.7	0.21	0.85	1.18	0.51
1.0000	1257.1	1257.1	1257.1	1257.1	1257.1	0.00	0.00	0.00	0.00
Benzene + 1-octanol									
0.0000	1318.6	1318.6	1318.6	1318.6	1318.6	0.00	0.00	0.00	0.00
0.1643	1299.9	1304.4	1307.1	1312.4	1279.3	0.35	0.55	0.96	1.58
0.3067	1283.3	1291.0	1296.9	1306.1	1256.2	0.60	1.06	1.78	2.11
0.4313	1268.7	1278.3	1287.9	1299.9	1243.1	0.75	1.51	2.46	2.02
0.5413	1257.0	1267.5	1280.1	1293.8	1236.5	0.84	1.84	2.92	1.63
0.6390	1248.4	1259.3	1273.5	1287.6	1234.4	0.87	2.01	3.14	1.12
0.7264	1244.1	1254.0	1268.2	1281.5	1235.4	0.80	1.93	3.00	0.70
0.8051	1242.1	1250.8	1263.8	1275.3	1238.7	0.70	1.75	2.68	0.27
0.8762	1242.9	1249.4	1260.3	1269.2	1243.7	0.52	1.40	2.12	0.07
0.9409	1247.1	1250.3	1257.8	1263.2	1249.9	0.26	0.86	1.29	0.23
1.0000	1257.1	1257.1	1257.1	1257.1	1257.1	0.00	0.00	0.00	0.00

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