

Ultrasonic and Volumetric Study of Binary Mixtures of Benzyl Alcohol with Amides

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The density (ρ) and ultrasonic speed (u) in binary mixtures of benzyl alcohol (BA) with formamide (FA), *N*-methylacetamide (NMA), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA), including those of pure liquids, were measured at 35 °C over the entire composition range. The isentropic compressibility (k_s), deviations in isentropic compressibility (Δk_s) and ultrasonic speed (Δu) from linear dependence on the composition, excess volume (V^E), apparent molar isentropic compressibility ($K_{\phi,s}$) and apparent molar volume (V_ϕ) of amides in benzyl alcohol were calculated. The variation of these parameters with composition of the mixtures suggests that the strength of interaction (BA–FA) $<$ (BA–BA) or (FA–FA), whereas the interaction (BA-substituted amide (NMA, DMF, and DMA)) $>$ (BA–BA) or (amide–amide). Moreover, the values of Δk_s are found to depend on the positions of the methyl groups, while those of V^E seem to depend on the number of such groups in the amide molecule.

Alcohol + amide mixed solvents are interesting liquid systems for studying molecular interactions, since amides and alcohols are the most common solvents used in chemical reactions and in many industrial processes. Moreover, amides are convenient model systems for investigating peptide and protein interactions in biological systems. In previous papers[1–3] we have reported on studies of the thermodynamic, acoustic and transport properties of binary mixtures of amides with aliphatic alcohols. The results were explained by considering the specific interactions between the amide and alcohol molecules. The present work focused on the study of molecular interactions in binary mixtures of benzyl alcohol (BA), an aromatic alcohol, with formamide (FA), *N*-methylacetamide (NMA), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA), over the entire composition range. The molecules of BA are polar (dipole moment, $\mu = 1.66$ D) and self-associated through hydrogen bonding, while the molecules of FA, NMA, DMF, and DMA ($\mu = 3.37$, 4.39, 3.86, and 3.72 D, respectively, at 298 K)[4] are highly polar; the first two amides are strongly associated through hydrogen bonding in the pure state,[4] and this association decreases with increase in the number of methyl groups in the molecule. Thus, DMF and DMA are practically unassociated.[5,6] A survey of the literature indicates that there has been no study of these systems from the view point of their ultrasonic behavior. Although studies on the aliphatic alcohol + amide interaction have been extensively carried out by many workers,[1,2,7–9] no attention has been paid to the interaction of an aromatic alcohol, rich in π-electrons, with amide. Recently, Kim et al.[10] studied the substituent effect of *N*,*N*-dialkylamides on intermolecular hydrogen bonding with thioacetamide using near-infrared absorption spectroscopy. Benzyl alcohol is a compound having commercial applications in the production of many useful medicines, cosmetics, and synthetic resins. The study of molecular interactions in binary mixtures of BA with protein-like compounds (amides) will be useful owing to their biological importance. Moreover, the effect of an electron-rich benzene ring in BA and the number and position of the methyl groups in amides on the interaction between BA and amide molecules in binary mixtures will be investigated. Therefore, the present study was expected to reveal the extent and nature of new interactions between the component molecules in these binary mixtures.

In the present paper, we report on the densities (ρ) and ultrasonic speeds (u) of binary mixtures of BA with FA, NMA, DMF, and DMA, including those of pure liquids at 35 °C, covering the entire composition range, expressed by the mole fraction (x_1) of BA. The experimental data on the densities and ultrasonic speeds were used to calculate the isentropic compressibility (k_s), the deviations in isentropic compressibility (Δk_s) and the ultrasonic speed (Δu) from the linear dependence on the mole fraction, excess volume (V^E), apparent molar isentropic compressibility ($K_{\phi,s}$) and apparent molar volume (V_ϕ). These functions offer a convenient method to study the thermodynamic properties of liquids and their mixtures not easily obtained by other means.

Experimental

Materials. Benzyl alcohol, formamide, and *N*-methylacetamide (s.d.fine, India) of analytical grade were purified according to standard procedures.[11,12] DMF and DMA were the same as those used in our previous studies.[2,13] All of the chemicals were kept in special air-tight bottles. Before use, they were stored over 0.4 nm molecular sieves to reduce the water content as much as possible, and were degassed at low pressure. The mixtures were prepared by mass in a dry box, while taking precaution to prevent evaporation. The masses were measured by an electronic balance (Afcoset ER-120A) precisely up to 1.0×10^{-4} g.

Instrumental. The densities of pure liquids and their binary mixtures were measured using a single-capillary pycnometer made of Borosil glass having a bulb capacity of 8×10^{-6} m^3. The

capillary, with graduated marks, had a uniform bore, and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triple-distilled water at 35 °C. The pycnometer was kept for about 25 min in an electronically controlled thermostated water bath (±0.02 °C), and the position of the liquid level on the capillary was noted. The density of pure water at 35 °C was taken from the literature.[14] The ultrasonic speeds in pure liquids and in their mixtures were measured using a single-crystal variable-path interferometer operating at 3 MHz by a method described elsewhere.[1–3,14,15] The accuracies of the density and ultrasonic speed measurements were ascertained by comparing the experimental values of these properties of pure liquids for which the corresponding values are available in the literature at 35 °C. For instance, the obtained experimental values of the densities of pure FA, DMF, and DMA were 1121.1, 935.7, and 927.6 kg m^{-3}, respectively, at 35 °C (corresponding literature values are: 1121.1,[16] 935.8[7]/934.7,[14] and 927.4[14] kg m^{-3}); the observed values of the ultrasonic speeds in pure DMF and DMA were found to be 1428.5 and 1420.2 m s^{-1}, respectively, at 35 °C (literature values: 1428.5[13]/1424.2[17] and 1418.9[14] m s^{-1}). The temperature of the test liquids and their binary mixtures was maintained at 35 ± 0.02 °C in an electronically controlled thermostatic water bath.

Results and Discussion

The experimental results of density (ρ) and ultrasonic speed (u) measurements of pure BA, FA, NMA, DMF, and DMA, and those of thirty six binary mixtures of BA with FA, NMA, DMF, and DMA over the whole composition range, expressed in the mole fraction (x_1) of BA ($0 \leq x_1 \leq 1$), at 35 °C together with the values of the isentropic compressibility (k_s) of the mixtures calculated by using the relation

$$k_s = (\rho\, .u^2)^{-1}, \tag{1}$$

are listed in Table 1. The sign and magnitude of the deviations in isentropic compressibility (Δk_s), ultrasonic speed (Δu) and excess volume (V^E) from rectilinear dependence on the mole fraction depends on the strength of the intermolecular interaction between the component molecules in the mixture. These parameters were computed using the following equations[1,19,20]

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}), \tag{2}$$

$$\Delta u = u - (x_1 u_1 + x_2 u_2), \tag{3}$$

$$V^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2), \tag{4}$$

where k_s, u, and ρ are the isentropic compressibility, ultrasonic speed, and density of the solution; k_{s1}, k_{s2}, u_1, u_2, ρ_1, and ρ_2 are the corresponding properties for the pure components, 1 and 2; M_1, M_2, ϕ_1, ϕ_2 , x_1, and x_2 are the molar masses, volume fractions and mole fractions of the pure components, 1 and 2, respectively. The values of Δk_s, Δu, and V^E were smoothed for each mixture by a Redlich–Kister[21] type polynomial equation

$$Y^E = x_1 x_2 \sum_{i=1}^{5} A_i (1 - 2x_1)^{i-1}, \tag{5}$$

where Y^E is Δk_s or Δu or V^E. The values of the coefficients (A_i) and corresponding standard deviations ($\sigma(Y^E)$) were calculated as

$$\sigma(Y^E) = [\Sigma(Y^E_{expt} - Y^E_{cal})^2/(m-n)]^{1/2}, \tag{6}$$

where m is the number of experimental data points and n is the number of coefficients considered ($n = 5$ in the present calculation) in Eq. 5, by the method of least-squares with all points weighed equally. The values are given in Table 2. The variations of Δk_s, V^E, and Δu with mole fraction x_1 of BA are graphically presented in Figs. 1–3.

The observed Δk_s, Δu and V^E values depend upon several contributions, which are of physical and/or chemical nature.[4,9] The physical contributions comprise the dispersion forces and non-specific physical (weak) interactions that lead to positive values in Δk_s and V^E, or negative Δu values; the physical contribution is also due to a geometrical effect allowing the fitting of molecules of very different sizes into each other's structure, resulting in negative Δk_s and V^E values. However, liquids of not very different molecular sizes usually mix to give positive Δk_s and V^E values.[26] Chemical contributions involve breaking up of the hydrogen-bonded structure(s), resulting in positive Δk_s and V^E values or negative Δu values and specific interactions, such as the formation of (new) hydrogen bonds, the formation of charge-transfer complexes and strong dipole–dipole interactions between component molecules, resulting in negative Δk_s and V^E values or positive Δu values.

The curves in Fig. 1 show that the values of Δk_s are positive for mixtures of BA with FA, become negative for mixtures with other amides, and that these negative values follow the sequence DMF < DMA < NMA over the entire composition range. A plausible qualitative interpretation of the behavior of these mixtures with composition has been suggested. As stated earlier, the molecules of BA are self-associated through hydrogen-bonding. The hydrogen bonding in FA becomes significant due to the presence of a strong proton-acceptor[22] group, C=O, in the molecule. Mixing BA with FA induces a mutual dissociation of hydrogen bonds in the component liquids, and the subsequent formation of a (new) hydrogen bond (O–H···O=C) between the hydrogen atom of the –OH group of BA and a proton-acceptor oxygen atom (with its two lone pair of electrons) of the C=O group of FA. The observed positive values of Δk_s (Fig. 1) indicate that the BA–FA interaction is weaker than the BA–BA or FA–FA interactions. There is evidence involving weaker hydrogen bonding between FA and water[23,24]/1,2-ethanediol[25] molecules than between like molecules (FA–FA, water–water and 1,2-ethanediol–1,2-ethanediol), all of the liquids being polar, protic, and hydrogen bonded in the pure state,[4] as in our case. Moreover, there is the possibility of an interaction of hydrogen atoms in FA (because FA possesses three hydrogen-bond donors: three hydrogen atoms in addition to a proton acceptor group C=O)[9] with the π-electron cloud of the aromatic ring of BA. This is supported by the fact that in their recent studies Rodham et al.[27] and Larsen and co-workers[28] have predicted the existence of weak π···H bonding between the π-electrons of the benzene ring and the hydrogen atoms of ammonia and that of the –OH group of tert-butyl alcohol. Thus, it is concluded that the observed positive values of Δk_s, over the whole composition range (Fig. 1) for the BA + FA mixture may be due to a breaking up of the hydrogen-bonded structures in the component liquids, which is not compensated by a decrease in Δk_s due to the combined ef-

Table 1. Values of Density (ρ), Ultrasonic Speed (u), and Isentropic Compressibility (k_s) of Binary Mixtures of Benzyl Alcohol with Amides at 35 °C

x_1 (BA)	ρ / kg m^{-3}	u / m s^{-1}	k_s / 10^{-10} m^2 N^{-1}
		BA + FA	
0.0000	1121.1	1577.2	3.5858
0.0932	1100.8	1563.7	3.7152
0.1929	1084.2	1550.6	3.8361
0.2617	1075.6	1540.0	3.9202
0.3422	1067.3	1533.1	3.9863
0.4235	1060.4	1526.6	4.0465
0.5131	1054.1	1521.1	4.1002
0.6271	1047.8	1516.0	4.1526
0.7432	1042.3	1509.7	4.2095
0.8895	1036.3	1502.0	4.2773
1.0000	1032.9	1496.3	4.3242
		BA + NMA	
0.0000	945.9	1351.1	5.7913
0.0889	957.4	1372.3	5.5464
0.1618	966.3	1390.0	5.3562
0.2608	977.4	1410.3	5.1440
0.3517	986.9	1429.4	4.9593
0.4459	996.1	1446.3	4.7993
0.5500	1005.3	1461.1	4.6596
0.6490	1013.2	1475.4	4.5340
0.7613	1021.3	1487.4	4.4258
0.8634	1027.4	1493.7	4.3625
1.0000	1032.9	1496.3	4.3242
		BA + DMF	
0.0000	935.7	1428.5	5.2372
0.0933	948.4	1439.7	5.0870
0.1663	958.3	1451.4	4.9536
0.2699	971.4	1464.6	4.7991
0.3559	981.3	1475.4	4.6814
0.4398	990.5	1484.6	4.5806
0.5221	998.7	1492.3	4.4963
0.6413	1009.4	1498.3	4.4131
0.7709	1019.7	1502.6	4.3435
0.8735	1026.6	1502.0	4.3178
1.0000	1032.9	1496.3	4.3242
		BA + DMA	
0.0000	927.6	1420.2	5.3449
0.1213	943.3	1441.4	5.1025
0.2159	955.6	1458.6	4.9187
0.3391	971.0	1474.9	4.7343
0.4397	982.8	1486.6	4.6041
0.5441	994.6	1497.1	4.4859
0.6408	1004.6	1502.6	4.4088
0.7277	1012.6	1506.3	4.3525
0.8283	1021.4	1507.4	4.3087
0.9058	1027.4	1503.7	4.3047
1.0000	1032.9	1496.3	4.3242

fect of (weak) hydrogen bonding between BA and FA molecules (via O–H···O=C and π···H interactions) and the fitting of smaller FA molecules into the voids created by the bigger BA molecules. The values of Δk_s (Fig. 1) being negative for mixtures of BA with NMA, DMF, and DMA, over the whole composition range, suggest that BA-substituted amide interactions are stronger than BA–BA or amide–amide interactions. Further, the extent of the negative deviation in Δk_s clearly indi-

Table 2. Coefficients (A_i) of Eq. 5 and Standard Deviations ($\sigma(Y^E)$) of Binary Mixtures

Properties	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
			BA + FA			
$\Delta k_s/10^{-10}$ m^2 N^{-1}	0.5511	0.4240	−0.1098	−0.3236	0.1257	0.0041
$V^E/10^{-6}$ m^3 mol^{-1}	0.6303	0.5767	0.2178	−0.6532	−0.0911	0.0058
Δu/m s^{-1}	−59.958	−59.566	29.373	59.771	−24.182	0.8900
			BA + NMA			
$\Delta k_s/10^{-10}$ m^2 N^{-1}	−1.3440	−0.1151	−0.0572	0.0164	−0.0685	0.0052
$V^E/10^{-6}$ m^3 mol^{-1}	−1.8325	0.7039	−0.1818	0.7937	−0.8946	0.0055
Δu/m s^{-1}	123.269	−18.386	7.825	−15.161	−2.246	0.3940
			BA + DMF			
$\Delta k_s/10^{-10}$ m^2 N^{-1}	−1.0395	0.0129	0.0966	0.2985	0.0509	0.0019
$V^E/10^{-6}$ m^3 mol^{-1}	−1.8877	0.6313	−0.1855	0.9799	0.1017	0.0043
Δu/m s^{-1}	110.063	−21.621	−24.636	−35.857	5.998	0.2770
			BA + DMA			
$\Delta k_s/10^{-10}$ m^2 N^{-1}	−1.2073	0.0567	−0.0345	0.1511	0.0018	0.0024
$V^E/10^{-6}$ m^3 mol^{-1}	−2.6916	1.0914	0.8256	0.7836	−1.5690	0.0073
Δu/m s^{-1}	138.820	−27.320	7.417	−15.579	−7.995	0.3940

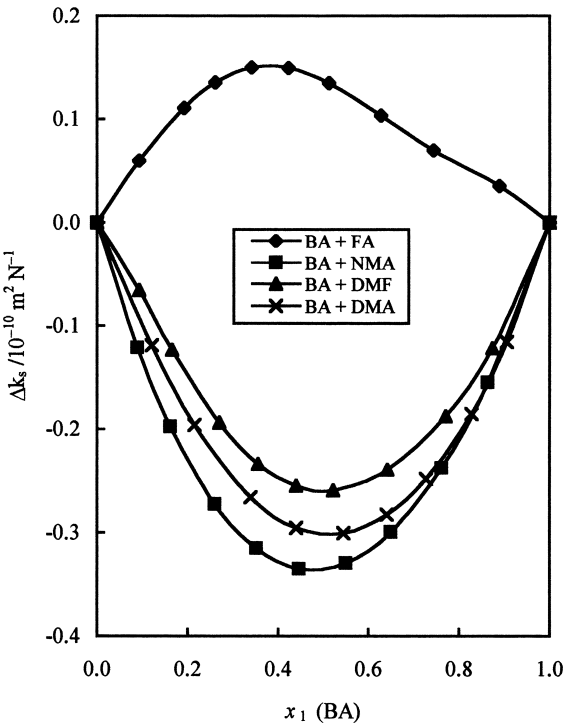

Fig. 1. Variation of deviations in isentropic compressibility (Δk_s) with mole fraction (x_1) of benzyl alcohol (BA) for the binary mixtures at 35 °C.

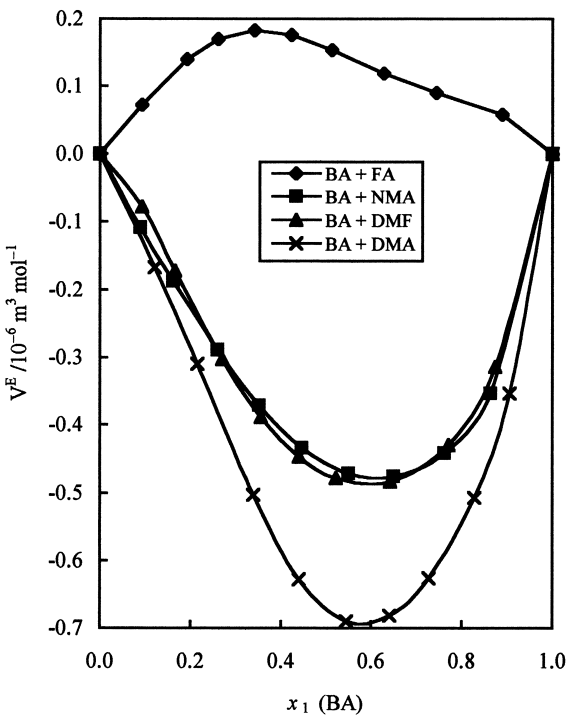

Fig. 2. Variation of excess volume (V^E) with mole fraction (x_1) of benzyl alcohol (BA) for the binary mixtures at 35 °C.

cates that the strength of the BA–amide interaction should be in the order NMA > DMA > DMF > FA. This finding is in accordance with a view proposed by Fort and Moore[26] and others,[18,19,29] that Δk_s becomes increasingly negative as the strength of the interaction between unlike molecules increases. The strength of the interaction between BA and NMA/DMA/DMF molecules seems to strongly depend on the positions of the methyl groups in the amide molecules. Kim et al.[10] and Spencer and co-workers[30] have reported that the methyl group present at the carbonyl carbon of acetamides, as in NMA and DMA, makes the C=O group a stronger proton-acceptor than the C=O group of formamides, as DMF, without a methyl group at the carbonyl carbon. Consequently, stronger hydrogen bonding between the proton of the –OH group of BA and the oxygen atom of the C=O group of NMA/DMA is quite obvious. Also, NMA being more polar than DMA, the dipolar

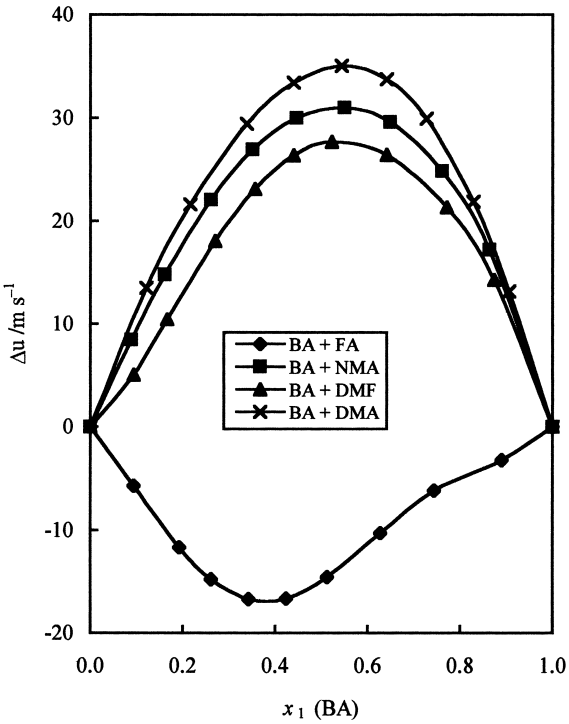

Fig. 3. Variation of deviations in ultrasonic speed (Δu) with mole fraction (x_1) of benzyl alcohol (BA) for the binary mixtures at 35 °C.

interaction BA–NMA is anticipated to be stronger than BA–DMA. As a result, the observed larger negative Δk_s values (Fig. 1) for BA + NMA than for BA + DMA suggest a greater interaction between the BA and NMA molecules than that between the BA and DMA molecules. In their recent study on *N*,*N*-dialkylamides, Kim et al.[10] observed that the proton affinity of the oxygen site of DMA (= 216.07 kcal/mol) is larger than that of DMF (= 210.09 kcal/mol); this makes DMA to form a stronger hydrogen bond with the proton of the –OH group of BA than DMF. Moreover, there is a possibility of weak π···H bonding between π-electrons of the benzene ring of BA and the H-atom of N–H of the NMA molecule.

As expected, the curves in Fig. 2 show that the values of V^E are positive for BA + FA, become negative for BA + NMA/DMF and become more so for BA + DMA mixtures over the entire composition range. This reinforces our earlier contention that the strength of the interaction BA-FA < BA–BA or FA–FA, while the interaction BA-substituted amide (NMA, DMF, and DMA) > BA–BA or amide–amide interactions. Positive values of V^E for 1,2-ethanediol + FA[25] and negative values for toluene/chlorobenzene + DMF,[31] ethanol + DMF,[13] toluene/chlorobenzene + DMA[32] and BA + isoamyl/isopropyl alcohol[33] further support our view. Further, the V^E values decrease and become increasingly negative as the number of methyl groups in the amide molecule increase form FA to DMA. From this, it emerges that for mixtures of BA with amides (FA, NMA, DMF, and DMA) the values of V^E are strongly influenced by the number of methyl groups, irrespective of their positions in the amide molecule. Thus, it is interesting to note that the results obtained so far suggest that the values of Δk_s and V^E, for the present mixtures, are essentially influenced by two different factors: the Δk_s values are dependent mainly on the position of the methyl groups, while those of V^E seem to depend on the number of methyl groups in the amide molecule. Almost equal values of V^E for NMA and DMF at all compositions (Fig. 2), with two methyl groups in each molecule, substantiate our finding. Further, Garcia et al.[8] report that the nature of amide has little effect on the V^E values for aliphatic alkanol + amide mixtures.

A plausible explanation for the variation of V^E with the composition may be proposed by considering the specific acid-base interaction between BA and amide (FA, NMA, DMF, and DMA) molecules. Such an acid-base interaction can be assumed by considering benzyl alcohol to be a Lewis acid and amides as a Lewis base. Del Bene[34] and Prakash and Sinha[35] observed that the presence of an electron-repelling $-CH_3$ group(s) in amides is primarily responsible for the increased basicity of the amide carbonyl. Consequently, the basicity of the amides increases with increasing number of $-CH_3$ groups from FA to DMA. As a result, the acid–base interaction between BA and amide molecules should vary in the order FA < NMA ≈ DMF < DMA, making V^E to decrease in the same sequence (Fig. 2). Recently, Ho-Nam Tran[36] emphasized the importance of the acid–base interaction between the *tert*-butyl alcohol and DMF/DMA in order to evaluate the interaction energy in alcohol + amide mixtures. Apart from this effect, the values of V^E are generally influenced by the difference in the sizes of the component molecules of a liquid mixture.[8,12] However, inspite of a considerable difference in the molecular sizes of BA and amide molecules, particularly FA and NMA, the size effect seems to be insignificant in deciding the magnitude of V^E for the liquid mixtures under study. Also, the pattern of the variation of Δu with x_1 (Fig. 3) strongly supports the behaviors of Δk_s and V^E with the compositions for these mixtures. Kawaizumi et al.[14] and Prakash et al.[35] suggested that the concentration at which the Δu versus x_1 curve exhibits a maximum indicates strong interactions between the component molecules, leading to the formation of a complex.

The apparent molar compressibility ($K_{\phi,2}$) of amide in benzyl alcohol, which reflects the extent of the interaction between the component molecules in the mixture, was calculated using the following equation[18,37]

$$K_{\phi,2} = (K_s^E/x_2) + k^*_{s2}\, V^*_2, \tag{7}$$

where K_s^E [= $(K_sV)^E$] is the excess molar compressibility of the mixture; x_2, k^*_{s2}, and V^*_2 are, respectively, the mole fraction, isentropic compressibility, and molar volume of component 2, i.e., amide; V is the molar volume of the mixture. The partial molar compressibility of the amide ($\overline{K}^\circ_{\phi,2}$) in benzyl alcohol at infinite dilution was obtained graphically[18,19] and the decrease in K at infinite dilution (ΔK) was evaluated using the following equation[18]

$$\Delta K = \overline{K}^\circ_{\phi,2} - K^*_{\phi,2}, \tag{8}$$

where $K^*_{\phi,2}$ is the molar isentropic compressibility of the amide. The values of $\overline{K}^\circ_{\phi,2}$, $K^*_{\phi,2}$, and ΔK are given in Table 3. The partial molar compressibility ($\overline{K}^\circ_{\phi,2}$) of the amide in

Table 3. The Values of $\overline{K}^{\circ}_{\phi,2}$, $K^{*}_{\phi,2}$, ΔK, $\overline{V}^{\circ}_{2}$, V^{*}_{2}, and ΔV of Amides in Benzyl Alcohol for the Binary Mixtures

Amide	$\overline{K}^{\circ}_{\phi,2}$	$K^{*}_{\phi,2}$	ΔK	$\overline{V}^{\circ}_{2}$	V^{*}_{2}	ΔV
	10^{-14} m^5 N^{-1} mol^{-1}			10^{-5} m^3 mol^{-1}		
FA	1.4299	1.4406	−0.0107	4.0628	4.0175	0.0453
NMA	3.6236	4.4756	−0.7683	7.5249	7.7281	−0.2032
DMF	3.3227	4.0910	−0.8520	7.6086	7.8113	−0.2027
DMA	3.7655	5.0199	−1.2544	9.0175	9.3920	−0.3205

benzyl alcohol characterizes the compressibility of its molecules in the solution. When $\overline{K}^{\circ}_{\phi,2}$ of amide is compared with the molar compressibility of pure liquid ($K^{*}_{\phi,2}$), it is observed that the ΔK (Eq. 8) is according to the sequence FA < DMF < NMA < DMA. This, in turn, clearly suggests the order of the strength of the interaction between BA and the amide molecules in the solution. This further supports our view regarding the intermolecular interaction in the mixtures under study. For FA, $\overline{K}^{\circ}_{\phi,2} \approx K^{*}_{\phi,2}$ implies that after dissolution its compressibility is practically unaffected. For other amides, DMA exhibits the largest deviation, followed by NMA, and then by DMF. Such deviations can be analyzed in terms of the structural and geometrical compressibility, as suggested by Hall[38] and others,[39] and recently by Mehta and Chauhan.[19] Structural compressibility results from a breakdown of the associated structure (upon the addition of BA in amide, as in the present case) while geometrical compressibility is due to the simultaneous compression of the molecules (due to formation of hydrogen-bond between BA and amide molecules) leading to a contraction in volume and a decrease in the average intermolecular distance.

The apparent molar volume ($V_{\phi,2}$) of amide in benzyl alcohol was calculated using the following equation[18]

$$V_{\phi,2} = V^{*}_{2} + (V^{E}/x_2), \tag{9}$$

The partial molar volume ($\overline{V}^{\circ}_{2}$) which characterizes the behavior of the amide in BA at infinite dilution was obtained graphically, as described by others.[12,18] The decrease in the volume at infinite dilution was calculated using the following equation[18]

$$\Delta V = \overline{V}^{\circ}_{2} - V^{*}_{2}, \tag{10}$$

The values of $\overline{V}^{\circ}_{2}$, V^{*}_{2}, and ΔV are listed in Table 3. It should be noted that the partial molar volume of FA in BA is greater, while those of DMF, NMA, and DMA are lower than their corresponding molar volumes. Accordingly, the value of ΔV is positive, i.e., an increase in volume for FA and for the rest of amides, there is volume loss in the order DMF ≈ NMA < DMA. This, again, reinforces our earlier view that the magnitude of V^{E} and, hence, the interaction between BA and amide molecules depends upon the number of –CH_3 groups present in the amide molecule.

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References

1 A. K. Nain, A. Ali, and M. Alam, *J. Chem. Thermodyn.*, **30**, 1275 (1998); A. K. Nain and A. Ali, *Z. Phys. Chem.*, **210**, 185 (1999).

2 A. Ali, S. Hyder, and A. K. Nain, *J. Mol. Liq.*, **79**, 89 (1999).

3 A. Ali, K. Tewari, A. K. Nain, and V. Chakravortty, *Phys. Chem. Liq.*, **38**, 459 (2000).

4 Y. Marcus, "Introduction to Liquid State Chemistry," Wiley-Interscience, New York (1977).

5 R. Gopal, S. Aggarwal, and D. K. Aggarwal, *J. Chem. Thermodyn.*, **8**, 1205 (1976).

6 R. C. Petersen, *J. Phys. Chem.*, **64**, 184 (1960).

7 F. Corradini, L. Marcheselli, A. Marchetti, M. Tangliazucchi, L. Tassi, and G. Tosi, *Bull. Chem. Soc. Jpn.*, **65**, 503 (1992).

8 B. Garcia, R. Alcalde, J. M. Leal, and J. S. Matos, *J. Chem. Soc., Faraday Trans.*, **92**, 3347 (1996); **93**, 1115 (1997).

9 H. Iloukhani and R. Ghorbani, *J. Solution Chem.*, **27**, 141 (1998).

10 N. K. Kim, H. J. Lee, K. H. Choi, J. A. Yu, C. J. Yoon, J. Park, and Y. S. Choi, *J. Phys. Chem.*, **104**, 5572 (2000).

11 A. I. Vogel, "Text Book of Practical Organic Chemistry," 5th ed., Longman Green, London (1989).

12 P. Assarson and F. R. Eirich, *J. Phys. Chem.*, **72**, 2710 (1968).

13 A. Ali, A. K. Nain, and M. Kamil, *Thermochim. Acta*, **274**, 209 (1996).

14 F. Kawaizumi, M. Ohno, and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, **50**, 2229 (1977).

15 S. V. Subrahmanyam and N. Murthy, *J. Solution Chem.*, **4**, 347 (1975).

16 A. Ali and A. K. Nain, *Indian J. Chem.*, **35A**, 751 (1996).

17 V. K. Syal, B. S. Patil, and S. Chauhan, *Indian J. Pure Appl. Phys.*, **37**, 366 (1999).

18 B. Hawrylak, K. Gracie, and R. Palepu, *J. Solution Chem.*, **27**, 17 (1998).

19 S. K. Mehta and R. K. Chauhan, *J. Solution Chem.*, **26**, 295 (1997).

20 A. G. Camacho and M. A. Postigo, *J. Solution Chem.*, **27**, 719 (1998).

21 O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).

22 L. Pauling, "The Nature of Chemical Bond," 2nd ed., Cornell Univ. Press, Ithaca, New York (1948).

23 P. Rohdewald and M. Moldner, *J. Phys. Chem.*, **77**, 373 (1973).

24 C. D. Visser, W. J. M. Heuvelsland, L. A. Dunn, and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1159 (1978).

25 A. Ali and A. K. Nain, *Indian J. Pure. Appl. Phys.*, **35**, 729 (1996).

26 R. J. Fort and W. R. Moore, *Trans. Faraday Soc*., **61**, 2102 (1965).
27 D. A. Rodham, S. Suzuki, R. D. Suenram, F. J. Lovas, S. Dasgupta, W. A. Goddard, and G. A. Blake, *Nature*, **362**, 735 (1993).
28 G. Larsen, Z. K. Ismail, B. Herreros, and R. D. Parra, *J. Phys. Chem.*, **102**, 4734 (1998).
29 P. S. Nikam, V. M. Kapade, and M. Hasan, *Indian J. Pure Appl. Phys*., **38**, 170 (2000).
30 J. N. Spencer, R. C. Gerrati, F. J. Mayer, J. E. Merkle, C. R. Powell, W. T. Tran, and S. K. Berger, *Can. J. Chem*., **58**, 1372 (1980).
31 T. M. Aminabhavi, S. S. Joshi, and R. H. Balundgi, *Can J. Chem*., **69**, 1028 (1990).
32 A. Ali, S. Hyder, and A. K. Nain, *Acoust. Lett*., **21**, 77 (1997).
33 M. R. Islam and S. K. Quadri, *Thermochim. Acta*, **115**, 335 (1987).
34 J. Del Bene, *J. Am. Chem. Soc*., **100**, 1387 (1978).
35 O. Prakash and S. Sinha, *Acustica*, **54**, 223 (1984).
36 H. Nam-Tran, *J. Phys. Chem*., **98**, 5362 (1994).
37 A. Cipiciani, G. Onori, and G. Savelli, *Chem. Phys. Lett*., **143**, 505 (1988).
38 L. Hall, *Phys. Rev*., **73**, 775 (1948).
39 W. Slie, A. Donofor, and T. Litovit, *J. Chem. Phys*., **14**, 1106 (1946).