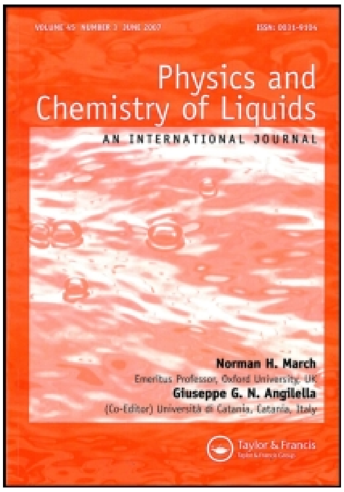

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Volumetric, ultrasonic and viscometric studies of molecular interactions in binary mixtures of aromatic+aliphatic alcohols at different temperatures

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Volumetric, ultrasonic and viscometric studies of molecular interactions in binary mixtures of aromatic + aliphatic alcohols at different temperatures

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The densities, ρ, ultrasonic speeds, u and viscosities, η of pure benzyl alcohol, 1-propanol, 2-propanol and those of their binary mixtures, with benzyl alcohol as a common component, have been measured at 298.15, 303.15, 308.15 and 313.15 K over the entire composition range. The excess molar volume, V^E, deviation in isentropic compressibility, Δk_s, excess thermal expansivity, α^E, deviations in ultrasonic speed, Δu and viscosity, $\Delta \eta$, partial molar volume and compressibility, $\bar{V}^o_{\phi,2}$ and $\bar{K}^o_{\phi,2}$ of 1-propanol/2-propanol in benzyl alcohol at infinite dilution have been evaluated from the experimental data. The results have been used to discuss the nature and strength of intermolecular interactions in these mixtures. The V^E values have also been calculated theoretically by using the Flory's statistical theory and Prigogine–Flory–Patterson theory. The calculated V^E values were found in good agreement with the experimental V^E values. The thermal expansivity, α and isothermal compressibility, k_T have been calculated theoretically by using Flory's theory and various hard sphere models, and were compared with experimental α and k_T values.

Keywords: Density; Ultrasonic speed; Viscosity; Thermal expansivity; Isothermal compressibility

1. Introduction

The studies on volumetric, ultrasonic and viscometric properties of liquid mixtures and their dependence on composition and temperature are of importance in many fields of applied research and find applications in many important chemical, industrial and biological processes [1,2]. As a part of our ongoing research focusing on experimental and theoretical studies of several thermodynamic, acoustic and transport properties of non-aqueous binary liquid mixtures containing alcohols [3–5], here we report the results of our study on the binary mixtures of benzyl alcohol (BA) with

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isomers of propanol over the entire composition range. It is well-known that alcohols are self-associated in the pure state [6]. Despite the extensive studies on binary mixtures of alcohols [7,8], so far relatively less attention has been given to the mixtures containing an aromatic alcohol [9]. The mixtures of BA with aliphatic alcohols are interesting to study because of the possibility of weak $\pi \cdots H$ bonding, in addition to the hydrogen bonding between unlike molecules. The weak $\pi \cdots H$ bonding of aromatic rings with proton donors appears to play an important role in the structure of certain biomolecules [10]. These considerations led us to undertake the present study.

The present work reports the densities, ρ, ultrasonic speeds, u and viscosities, η of the binary mixtures of BA with 1-propanol and 2-propanol, including those of pure liquids, at 298.15, 303.15, 308.15 and 313.15 K, over the whole composition range expressed by the mole fraction, x_1 of BA. The experimental values of ρ, u and η have been used to evaluate the excess molar volume, V^{E}, deviation in isentropic compressibility, Δk_s, excess thermal expansivity, α^{E}, deviations in ultrasonic speed, Δu and viscosity, $\Delta \eta$, partial molar volume and compressibility, $\bar{V}^{o}_{\phi,2}$ and $\bar{K}^{o}_{\phi,2}$ of 1-propanol/2-propanol in BA at infinite dilution. The composition and temperature dependences of these evaluated parameters have been used to interpret the nature and extent of intermolecular interactions in these mixtures.

The experimental values of V^{E} were analysed and compared with the theoretically calculated V^{E} values by using Flory's statistical theory [11,12] and Prigogine–Flory–Patterson theory [13,14]. The thermal expansivity, α and the isothermal compressibility, k_T were evaluated theoretically by using Flory's statistical theory [11,12] and various hard sphere models compiled by Pandey *et al.* [15–17]; and were compared with the experimental α and k_T values.

2. Experimental

Benzyl alcohol, 1-propanol and 2-propanol (all s.d. fine chemicals, India, AR grade) were purified by using the standard procedures described in the literature [18]. Before use, the liquids were stored over 0.4 nm molecular sieves to reduce the traces of water, if any, and were degassed. The mixtures were prepared by mass in a dry box and were kept in special airtight bottles. The weighings were done on Precisa XB-220A, Swiss make electronic balance with precision of ±0.1 mg.

The densities of pure liquids and their binary mixtures were measured by using single capillary pycnometer (made of Borosil glass) having a bulb capacity of $8 \times 10^{-6}\,\mathrm{m}^3$. 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. The densities of pure water at required temperatures were taken from the literature [19]. The accuracy in density measurements was found to be $\pm 0.0001\,\mathrm{g\,cm^{-3}}$. The ultrasonic speeds in pure liquids and in their mixtures were measured by using a single-crystal variable-path ultrasonic interferometer operating at 3 MHz with an accuracy of ±0.05%. The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde-type suspended level viscometer. The viscometer was allowed to stand in a thermostatic water bath for 30 min so that the thermal fluctuations in viscometer were minimised. The viscosity data were reproducible within ±0.0005 cP. The reliability of the experimental measurements of ρ, u and η were checked by comparing the experimental data of pure liquids

Table 1. Comparison of experimental density, ρ, ultrasonic speed, u and viscosity, η of pure liquids with the corresponding literature values at different temperatures.

		ρ (kg m^{-3})		u (m s^{-1})		η (10^{-3} N s m^{-2})	
Liquid	T (K)	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
BA	298.15	1040.1	1040.11[a]	1528.4	–	4.9365	4.928[a] 4.935[b]
	303.15	1036.5	–	1510.8	–	4.2011	–
	308.15	1033.0	1032.9[c]	1496.3	1496.3[c]	3.6601	3.664[b]
	313.15	1029.2		1483.6		3.1210	3.181[b]
1-Propanol	298.15	799.5	799.54[d] 799.6[f]	1208.1	1206.5[e]	1.9324	1.922[f] 1.915[g]
	303.15	795.5	795.58[g]	1192.6	1192.0[h]	1.7185	1.7843[i] 1.714[g]
	308.15	791.4	791.62[g] 791.29[j]	1178.1	–	1.5252	1.560[g]
	313.15	787.4	787.47[i] 787.5[k]	1160.2	–	1.3203	1.397[i]
2-Propanol	298.15	780.7	780.5[l] 781.02[n]	1145.5	1140.6[m]	1.9850	2.0436[f] 2.0377[o]
	303.15	776.5	776.59[p]	1126.3	1126.0[h]	1.7345	1.7618[o] 1.740[q]
	308.15	772.3	772.2[q]	1111.2	1105.3[m]	1.4824	1.5193[o]
	313.15	768.2	–	1091.3	–	1.2809	1.3112[o]

[a]Ref. [20]; [b]Ref. [21]; [c]Ref. [3]; [d]Ref. [22]; [e]Ref. [23]; [f]Ref. [18]; [g]Ref. [24]; [h]Ref. [25]; [i]Ref. [26]; [j]Ref. [27]; [k]Ref. [28]; [l]Ref. [29]; [m]Ref. [30]; [n]Ref. [31]; [o]Ref. [32]; [p]Ref. [33], [q]Ref. [34].

with the corresponding literature values, which were available at the investigated temperatures (table 1). The comparison shows that the experimental values of ρ, u and η are in good agreement with the literature values [3,18,20–34]. The temperature of the test samples during the measurements was maintained to an accuracy of ±0.02 K in an electronically controlled thermostatic water bath (JULABO, Model-MD, Germany).

3. Results and discussion

The experimental values of ρ, u and η of pure BA, 1-propanol, 2-propanol and those of their 18 binary mixtures as a function of mole fraction, x_1 of BA and temperature are listed in table 2. From these experimental data, the excess functions V^{E}, Δk_s, α^{E}, Δu, and $\Delta\eta$, have been calculated by using the following relations:

$$V^{\mathrm{E}} = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{1}$$

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

$$\alpha^{\mathrm{E}} = \alpha - (\phi_1 \alpha_1 + \phi_2 \alpha_2) \tag{3}$$

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \tag{4}$$

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{5}$$

where ϕ is the volume fraction; M is the molar mass; R is the universal gas constant; T is the absolute temperature; the subscripts 1 and 2 stand for pure components,

Table 2. Experimental values of densities, ρ, ultrasonic speeds, u and viscosities, η of binary mixtures as a function of mole fraction, x_1 of benzyl alcohol at different temperatures.

	T (K)			
x_1	298.15	303.15	308.15	313.15
ρ (kg m^{-3})				
BA + 1-Propanol				
0.0000	799.5	795.5	791.4	787.4
0.0744	825.6	821.8	818.0	814.2
0.1531	851.2	847.5	843.8	840.1
0.2366	876.2	872.6	869.0	865.4
0.3252	900.7	897.1	893.5	889.9
0.4196	924.8	921.2	917.6	914.0
0.5203	948.5	944.9	941.3	937.7
0.6278	971.9	968.3	964.7	961.1
0.7431	995.0	991.4	987.8	984.2
0.8668	1017.7	1014.1	1010.5	1006.9
1.0000	1040.1	1036.5	1033.0	1029.2
BA + 2-Propanol				
0.0000	780.7	776.5	772.3	768.2
0.0760	809.1	805.0	800.9	796.8
0.1562	836.8	832.8	828.8	824.8
0.2409	863.8	859.9	856.0	852.1
0.3305	890.4	886.5	882.6	878.7
0.4254	916.6	912.8	908.9	905.0
0.5262	942.2	938.4	934.6	930.8
0.6334	967.3	963.6	959.8	956.0
0.7476	992.0	988.3	984.6	980.9
0.8695	1016.2	1012.5	1008.8	1005.1
1.0000	1040.1	1036.5	1033.0	1029.2
u (m s^{-1})				
BA + 1-Propanol				
0.0000	1208.1	1192.6	1178.1	1160.2
0.0744	1258.8	1245.0	1232.2	1216.8
0.1531	1303.1	1290.3	1278.1	1264.2
0.2366	1342.1	1329.5	1317.7	1304.2
0.3252	1375.5	1363.3	1352.2	1339.0
0.4196	1405.1	1392.5	1380.5	1368.1
0.5203	1432.8	1419.7	1408.1	1396.2
0.6278	1459.1	1445.1	1433.4	1421.1
0.7431	1483.5	1468.3	1456.0	1444.4
0.8668	1505.4	1489.5	1476.4	1464.5
1.0000	1528.4	1510.8	1496.3	1483.6
BA + 2-Propanol				
0.0000	1145.5	1126.3	1111.2	1091.3
0.0760	1206.6	1190.2	1176.0	1157.2
0.1562	1259.2	1243.1	1229.5	1212.4
0.2409	1305.1	1288.5	1275.8	1260.2
0.3305	1346.5	1331.1	1318.1	1303.5
0.4254	1383.3	1367.3	1355.4	1341.4
0.5262	1415.8	1400.1	1388.1	1375.1
0.6334	1446.4	1431.2	1419.9	1407.5
0.7476	1475.0	1460.3	1448.5	1436.5
0.8695	1502.2	1485.5	1473.6	1463.0
1.0000	1528.4	1510.8	1496.3	1483.6

(*continued*)

Table 2. Continued.

	T (K)			
x_1	298.15	303.15	308.15	313.15
η (10^{-3} N s m^{-2})				
BA + 1-Propanol				
0.0000	1.9324	1.7185	1.5252	1.3203
0.0744	2.0383	1.7957	1.5875	1.3675
0.1531	2.1970	1.9184	1.6868	1.4468
0.2366	2.4005	2.0832	1.8275	1.5620
0.3252	2.6513	2.2882	2.0020	1.7089
0.4196	2.9318	2.5200	2.2010	1.8770
0.5203	3.2496	2.7835	2.4288	2.0700
0.6278	3.5934	3.0706	2.6780	2.2815
0.7431	3.9902	3.4045	2.9675	2.5300
0.8668	4.4334	3.7762	3.2922	2.8070
1.0000	4.9365	4.2011	3.6601	3.1210
BA + 2-Propanol				
0.0000	1.9850	1.7345	1.4824	1.2809
0.0760	2.0333	1.7760	1.5321	1.3381
0.1562	2.1671	1.8957	1.6493	1.4320
0.2409	2.3659	2.0599	1.7956	1.5562
0.3305	2.6065	2.2582	1.9745	1.7009
0.4254	2.8795	2.4865	2.1715	1.8705
0.5262	3.2025	2.7558	2.4062	2.0702
0.6334	3.5701	3.0605	2.6754	2.3031
0.7476	3.9750	3.4003	2.9752	2.5568
0.8695	4.4230	3.7849	3.3036	2.8283
1.0000	4.9365	4.2011	3.6601	3.1210

BA and 1-propanol/2-propanol, respectively; V, k_s and α are the molar volume, isentropic compressibility and thermal expansivity, respectively, and were calculated by using the following standard relations:

$$V = \frac{(x_1 M_1 + x_2 M_2)}{\rho} \tag{6}$$

$$k_s = \left(\rho u^2\right)^{-1} \tag{7}$$

$$\alpha = \left(\frac{1}{\rho}\right)\left(\frac{\partial \rho}{\partial T}\right)_p \tag{8}$$

The values of V^{E}, Δk_s, α^{E}, Δu, and $\Delta\eta$ of the binary mixtures, at each investigated temperature, were fitted to a Redlich–Kister [35] type polynomial equation

$$F^{\mathrm{E}} = x_1 x_2 \sum_{i=1}^{5} A_i (1 - 2x_1)^{i-1} \tag{9}$$

where F^{E} stand for V^{E} or Δk_s or α^{E} or Δu or $\Delta\eta$. A_i are the polynomial coefficients and x_2 is the mole fraction of 1-propanol/2-propanol. The coefficients, A_i evaluated by using least-squares method with all points weighed equally, together with the standard deviations, σ (F^E) are given in table 3. The variations of V^E, Δk_s, α^E, Δu, and $\Delta\eta$ with mole fraction, x_1 of BA and temperature for the binary mixtures are shown graphically in figures 1–5.

Table 3. Coefficients, A_i of equation (9) and standard deviations, σ (F^E) for the binary mixtures at different temperatures.

T (K)	A_1	A_2	A_3	A_4	A_5	σ (F^E)
BA + 1-Propanol						
V^E (10^{-6} m^3 mol^{-1})						
298.15	−1.7966	−0.7664	−0.5185	−0.0955	0.2123	0.0004
303.15	−1.9099	−0.8592	−0.6328	−0.1511	0.2503	0.0012
308.15	−2.0257	−0.9895	−0.6911	−0.3151	0.1726	0.0021
313.15	−2.1837	−1.0412	−0.8781	−0.2949	0.1682	0.0031
Δk_s (10^{-11} m^2 N^{-1})						
298.15	−3.4665	−1.6144	−0.9392	−0.2494	0.3573	0.0004
303.15	−3.7415	−1.7834	−1.0136	−0.2931	0.2718	0.0009
308.15	−4.0034	−1.9193	−1.1129	−0.3962	0.1764	0.0038
313.15	−4.3284	−2.1017	−1.3842	−0.5417	0.1930	0.0035
α^E (10^{-4} K^{-1})						
298.15	−1.5752	−1.5817	−2.7815	4.1613	6.6579	0.0188
303.15	−1.5956	−1.6013	−2.8168	4.1798	6.7083	0.0189
308.15	−1.6188	−1.6206	−2.8321	4.1813	6.7297	0.0191
313.15	−1.6430	−1.6393	−2.8672	4.2096	6.7685	0.0192
Δu (m s^{-1})						
298.15	2.3715	1.1178	0.8677	0.3855	−0.5535	0.0012
303.15	2.5147	1.2026	0.8813	0.3711	−0.4580	0.0010
308.15	2.6275	1.2068	0.9972	0.4740	−0.4948	0.0038
313.15	2.7524	1.2764	0.9509	0.4892	−0.1935	0.0036
$\Delta\eta$ (10^{-3} N s m^{-2})						
298.15	−1.0027	−0.2834	−0.5795	−0.3241	0.3023	0.0016
303.15	−0.9221	−0.2674	−0.5284	−0.2844	0.2837	0.0012
308.15	−0.8421	−0.2624	−0.4686	−0.2407	0.2887	0.0011
313.15	−0.7605	−0.2401	−0.4469	−0.2267	0.3232	0.0010
BA + 2-Propanol						
V^E (10^{-6} m^3 mol^{-1})						
298.15	−2.3201	−0.8064	0.0766	−0.2448	−0.6462	0.0019
303.15	−2.4004	−0.8469	−0.0664	−0.3414	−0.4063	0.0019
308.15	−2.4629	−0.9082	−0.1801	−0.4843	−0.1364	0.0028
313.15	−2.5530	−0.9266	−0.4952	−0.3745	0.3011	0.0039
Δk_s (10^{-11} m^2 N^{-1})						
298.15	−4.9419	−2.3198	−0.9051	−0.5997	−0.4715	0.0023
303.15	−5.3206	−2.4500	−1.0294	−1.0337	−0.8012	0.0046
308.15	−5.6531	−2.5768	−1.2781	−1.0557	−0.7284	0.0038
313.15	−6.1165	−2.8469	−1.5375	−0.8773	−0.6505	0.0039
α^E (10^{-4} K^{-1})						
298.15	−1.6044	−1.0377	−3.7170	0.2983	6.6523	0.0292
303.15	−1.6252	−1.0522	−3.7603	0.3004	6.7205	0.0294
308.15	−1.6459	−1.0667	−3.7907	0.2975	6.7751	0.0297
313.15	−1.6681	−1.0768	−3.8285	0.3156	6.8366	0.0300
Δu (m s^{-1})						
298.15	2.8450	1.3529	0.3816	0.1712	0.3775	0.0024
303.15	2.9643	1.2945	0.3450	0.4970	0.6653	0.0051
308.15	3.0788	1.2323	0.4640	0.4657	0.6333	0.0046
313.15	3.1921	1.2392	0.7065	0.2629	0.4706	0.0037

(*continued*)

Table 3. Continued.

T (K)	A_1	A_2	A_3	A_4	A_5	σ (F^E)
$\Delta\eta$ (10^{-3} N s m^{-2})						
298.15	−1.3771	−0.6043	−0.0947	−0.2280	−0.8087	0.0014
303.15	−1.1430	−0.4529	0.0320	−0.3892	−0.6611	0.0010
308.15	−0.9109	−0.3665	0.1636	−0.3000	−0.6953	0.0017
313.15	−0.7364	−0.3970	0.2204	−0.0167	−0.4947	0.0020

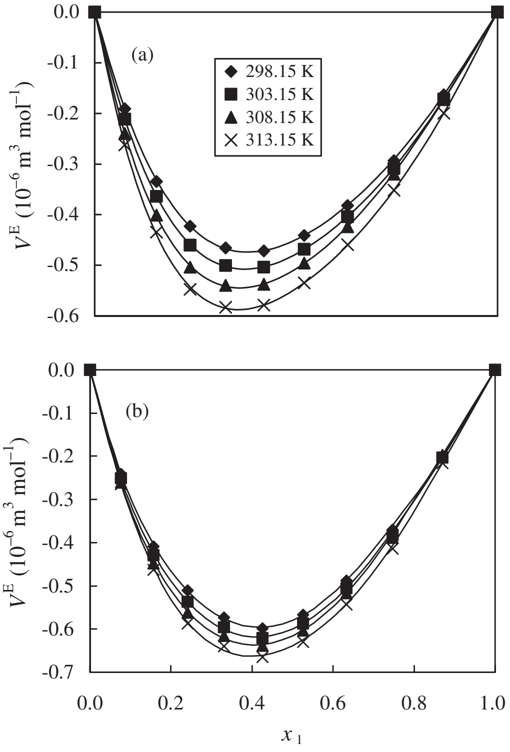

Figure 1. Plots of excess molar volume V^E against mole fraction x_1 of BA for (a) BA + 1-propanol and (b) BA + 2-propanol binary mixtures at different temperatures. Points show experimental values and lines show smoothed values calculated by using equation (9).

The curves in figures 1 and 2 show that the values of V^E and Δk_s are negative over the whole composition range at all the investigated temperatures for both the systems under study. The behaviour of V^E and Δk_s with composition may be qualitatively examined. As stated above, both the components (BA and 1-propanol/2-propanol) of these mixtures are self-associated in the pure state [7]. The mixing of BA with 1-propanol/2-propanol would induce mutual breaking of hydrogen-bonded structures in these liquids resulting in expansion in volume, making V^E and Δk_s values positive. On the other hand, there is a possibility of subsequent formation of (new) hydrogen bonds between unlike molecules resulting in contraction in volume and decrease in compressibility of the mixture. The observed negative V^E and Δk_s values indicate that BA–alkanol interaction is stronger than BA–BA or alkanol–alkanol interactions

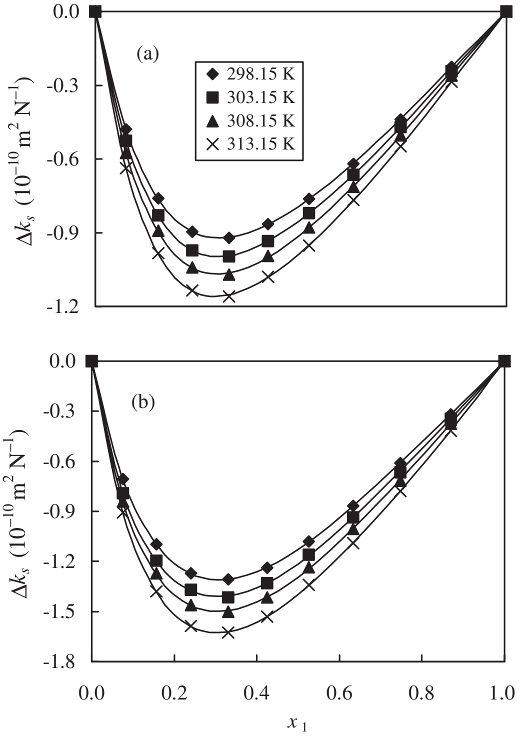

Figure 2. Plots of deviations in isentropic compressibility Δk_s against mole fraction x_1 of BA for (a) BA + 1-propanol and (b) BA + 2-propanol binary mixtures at different temperatures. Points show experimental values and lines show smoothed values calculated by using equation (9).

in both the systems under study. Negative V^E and Δk_s values for the present mixture are indicative of strong interactions (mainly due to H-bonding) between unlike molecules, as suggested by Fort and Moore [36]. Apart from the strong H-bonding, relatively weak hydrogen bonding ($\pi \cdots$H) between π-electrons of benzene ring of BA and proton of alkanol may also exist. This is supported by the fact that recently Larsen *et al.* [37] have also predicted the existence of weak $\pi \cdots$H bonding between benzene and tert-butyl alcohol molecules. Further, it is clear from figures 1 and 2 that V^E and Δk_s values for BA + 2-propanol mixtures are more negative than those for BA + 1-propanol mixtures, suggesting that the strength of interaction between unlike molecules in BA + 2-propanol system is greater than that in BA + 1-propanol system. This may be due to +I effect of two methyl groups attached to α-carbon atom in 2-propanol (as compared to only one ethyl group at α-carbon in 1-propanol), which enhance the proton-accepting ability of oxygen atom of hydroxyl group of 2-propanol than in 1-propanol. Thus, stronger H-bonds are formed between 2-propanol and BA molecules than between 1-propanol and BA molecules and, hence, more negative V^E and Δk_s values for BA + 2-propanol system are observed. Further, it is also evident from figures 1 and 2 that V^E and Δk_s values become more negative with increase in temperature of the mixtures for both the systems. Increase in temperature promotes the breaking up of associates present in the pure liquids releasing more and more free dipoles of unlike molecules in the

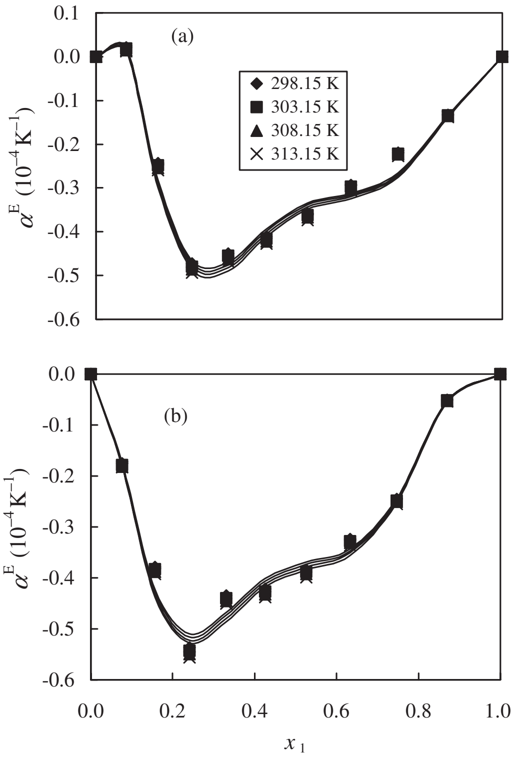

Figure 3. Plots of excess thermal expansivity α^E against mole fraction x_1 of BA for (a) BA + 1-propanol and (b) BA + 2-propanol binary mixtures at different temperatures. Points show experimental values and lines show smoothed values calculated by using equation (9).

mixture which interact with each other forming greater number of BA-1-propanol/2-propanol H-bonds. As a result, V^E and Δk_s become more negative with rise in temperature.

The values of excess thermal expansivity, α^E are negative (figure 3) over the whole composition range for both the systems under study at all investigated temperatures. In general, negative α^E values indicate the formation of new interactions between unlike molecules and positive α^E values are attributed to self-association of components in the mixtures [38]. The trends observed in α^E values for the present mixtures suggest the formation of H-bonding between unlike (BA and propanol) molecules. The increasingly negative α^E values with increase in temperature indicate enhanced A-B type interaction between components of the mixture.

Figure 4 shows that the values of Δu are positive over the entire composition range for both the systems at all the studied temperatures. This suggests the presence of strong interaction between unlike molecules in the mixture. These trends in Δu strongly support the behaviours of V^E, Δk_s and α^E values. Kawaizumi *et al.* [39] suggested that the concentration at which Δu versus x_1 curves exhibit a maximum indicates strong interaction between unlike molecules in the mixtures. Δu values become more positive (figure 4) with rise in temperature for both the systems under study. This again supports increased interaction between unlike molecules in the mixture as the temperature of the mixture increases.

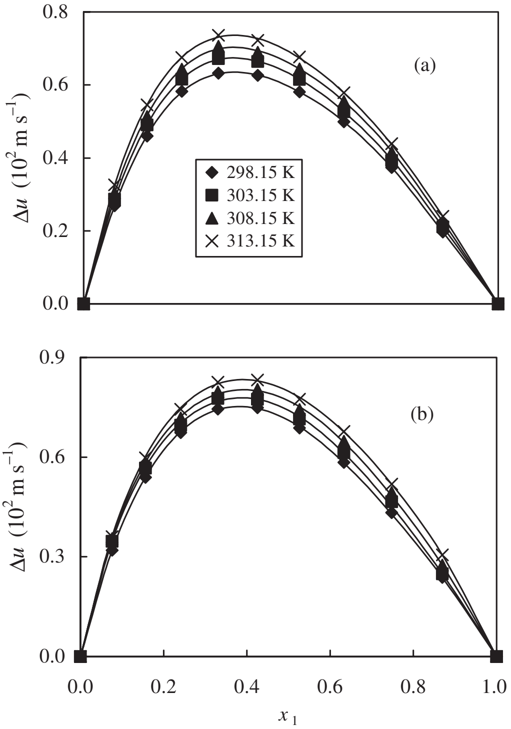

Figure 4. Plots of deviations in ultrasonic speed Δu against mole fraction x_1 of BA for (a) BA + 1-propanol and (b) BA + 2-propanol binary mixtures at different temperatures. Points show experimental values and lines show smoothed values calculated by using equation (9).

The curves in figure 5 indicate that $\Delta\eta$ values are negative over the whole composition range for both the systems at all the studied temperatures. These trends in $\Delta\eta$ values indicate the presence of dispersion forces in these mixtures. Also, negative $\Delta\eta$ values are observed for the mixtures having component molecules of different molecular size [4,40], as in the present mixtures.

The apparent molar volume, $V_{\phi,2}$ and apparent molar compressibility, $k_{\phi,2}$ of 1-propanol/2-propanol in BA, at all the temperatures investigated, were calculated by using the relations [41,42]

$$V_{\phi,2} = V_2^* + \frac{V^{\mathrm{E}}}{x_2} \tag{10}$$

$$K_{\phi,2} = K_{\phi,2}^* + \frac{K_s^{\mathrm{E}}}{x_2} \tag{11}$$

where $K_S^{\mathrm{E}}[=(K_sV)^{\mathrm{E}}]$ is the excess molar compressibility of the mixture; V_2^* and $K_{\phi,2}^*$ are the molar volume and molar isentropic compressibility of 1-propanol/2-propanol, respectively. The partial molar volume, $\bar{V}_{\phi,2}^o$ and partial molar compressibility, $\bar{K}_{\phi,2}^o$ of 1-propanol/2-propanol in BA at infinite dilution were obtained by the method

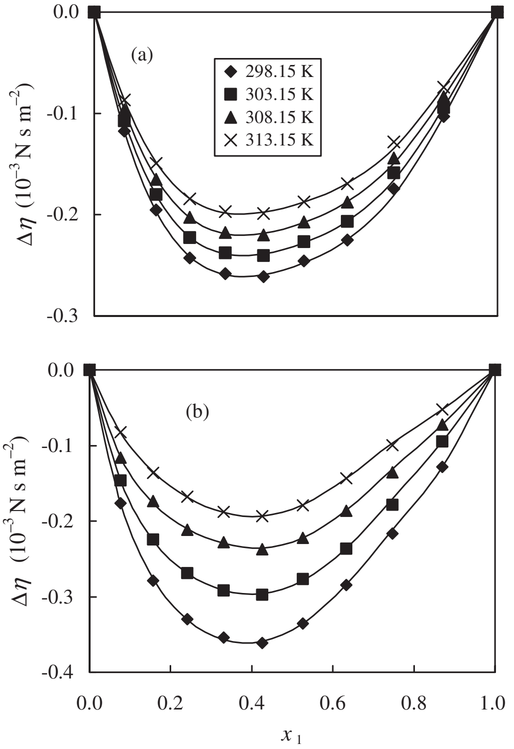

Figure 5. Plots of deviations in viscosity $\Delta\eta$ against mole fraction x_1 of BA for (a) BA + 1-propanol and (b) BA + 2-propanol binary mixtures at different temperatures. Points show experimental values and lines show smoothed values calculated by using equation (9).

described elsewhere [23,41]. The deviations in $V_{\phi,2}$ and $K_{\phi,2}$ at infinite dilution, ΔV and ΔK, respectively, were calculated by using the relations [41]

$$\Delta V = \bar{V}^{o}_{\phi,2} - V^{*}_{2} \tag{12}$$

$$\Delta K = \bar{K}^{o}_{\phi,2} - K^{*}_{\phi,2} \tag{13}$$

The values of $\bar{V}^{o}_{\phi,2}$, V^{*}_{2}, ΔV, $\bar{K}^{o}_{\phi,2}$, $K^{*}_{\phi,2}$, and ΔK are listed in table 4. A close perusal of table 4 indicates that the deviations ΔV are negative at each investigated temperature for both the systems under study. This clearly suggests that on mixing there is contraction in volume of the mixture. The deviations in ΔK are also negative (table 4) for both the systems, at all the studied temperatures. This further suggests that the molar compressibilities of 1-propanol and 2-propanol molecules in the mixture at infinite dilution, $\bar{K}^{o}_{\phi,2}$ are less than their molar compressibility in the pure state. This, again, suggests a contraction in volume of the mixture. Negative values for both ΔV and ΔK at each investigated temperatures suggest that BA–alkanol interactions are stronger than BA–BA or alkanol–alkanol interactions. It is interesting to note that ΔV and ΔK values (table 4) are more negative for BA + 2-propanol mixtures than for BA + 1-propanol mixtures, thereby indicating that the strength of BA – 2-propanol interaction is greater than that BA – 1-propanol interaction.

Table 4. The values of $\bar{V}^o_{\phi,2}$, $V^*_{\phi,2}$, ΔV, $\bar{K}^o_{\phi,2}$, $K^*_{\phi,2}$ and ΔK of alkanols in BA for the binary mixtures at different temperatures.

	$(10^{-6}\,\mathrm{m^3\,mol^{-1}})$			$(10^{-14}\,\mathrm{m^5\,N^{-1}\,mol^{-1}})$		
T (K)	$\bar{V}^o_{\phi,2}$	$V^*_{\phi,2}$	ΔV	$\bar{K}^o_{\phi,2}$	$K^*_{\phi,2}$	ΔK
BA + 1-Propanol						
298.15	73.913	75.172	−1.529	4.541	6.442	−1.901
303.15	74.245	75.550	−1.305	4.624	6.677	−2.053
308.15	74.618	75.941	−1.323	4.706	6.914	−2.208
313.15	74.865	76.250	−1.462	4.793	7.187	−2.394
BA + 2-Propanol						
298.15	75.371	76.982	−1.611	4.785	7.515	−2.730
303.15	75.774	77.399	−1.624	4.904	7.857	−2.953
308.15	76.221	77.820	−1.599	4.974	8.161	−3.187
313.15	76.554	78.235	−1.681	5.052	8.551	−3.499

Thus, the behaviours of V^{E}, Δk_s, Δu, α^{E}, $\Delta\eta$, ΔV and ΔK for the systems investigated support each other.

4. Theoretical analysis

4.1. *Excess molar volume*

The Flory statistical theory [11,12], which is generally valid for non-polar liquids and their mixtures, and its modified form known as Prigogine–Patterson–Flory (PFP) theory [13,14], which is applicable to both non-polar and polar molecules in liquids and their mixtures, have been successfully employed to estimate and analyse excess thermodynamic functions of binary liquid mixtures by a number of workers in recent years. In the present work we have applied both the theories to predict the excess molar volume, V^{E} for the mixtures under study. According to the Flory equation of state [11,12], V^{E} is given by the equation

$$V^{\mathrm{E}} = \left[\sum_{i=1}^{2} x_i V_i^*\right]\left[\frac{(\tilde{V}^o)^{7/3}}{(4/3) - (\tilde{V}^o)^{1/3}}\right](\tilde{T} - \tilde{T}^\circ) \tag{14}$$

The modified version of Flory's theory known as Prigogine–Flory–Patterson theory [11–13] has been successfully applied to the liquid mixtures containing non-polar as well as polar molecules to predict the excess properties of solutions. According to the PFP theory, V^{E} can be calculated from the equation

$$\begin{aligned}\frac{V^{\mathrm{E}}}{x_1V_1^* + x_2V_2^*} &= \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2\chi_{12}}{[(4/3)\tilde{V}^{-1/3} - 1]P_1^*} \\ &\quad - \frac{(\tilde{V}_1 - \tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3} - 1]}{[(4/3)\tilde{V}^{-1/3} - 1]\tilde{V}}\psi_1\psi_2 \\ &\quad + \frac{(\tilde{V}_1 - \tilde{V}_2)}{P_1^*\psi_2 + P_2^*\psi_1}(P_1^* - P_2^*)\psi_1\psi_2\end{aligned} \tag{15}$$

The first term on the right-hand side of equation (15) represents the interaction contribution, V^E (int.), the second term accounts for the free volume contribution, V^E (fv.), and the third term is the internal pressure (ip.) contribution, V^E (P^*); ψ, θ and P^* are the contact energy fraction, surface site fraction and characteristic pressure, respectively, and are calculated by using the equations

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \tag{16}$$

$$\theta_2 = 1 - \theta_1 = \frac{\phi_2}{\left[\phi_2 + \phi_1 (V_1^*/V_2^*)^{1/3}\right]} \tag{17}$$

$$P^* = \frac{T\tilde{V}^2 \alpha}{k_T} \tag{18}$$

The notations and terms used in equations (14–18) are the same as given in the literature [11–14,43–45]. The other parameters pertaining to pure liquids and the mixtures are obtained by using the expressions given in the literature [11–14] and are listed in table 5. The contact interaction parameter, χ_{12} required for the calculation of V^E from PFP theory has been derived by fitting the V^E expression to the experimental equimolar value of V^E for each system under study.

The values of χ_{12}, θ_2, three PFP contributions (V^E (int.), V^E (fv.) and V^E (P^*)), along with the experimental and calculated V^E values by using Flory and PFP theory (at near equimolar composition) are given in table 6. It is clear from table 6 that the calculated values of V^E (Flory) and V^E (PFP) by using Flory's statistical theory and PFP theory,

Table 5. Physical constants and characteristic parameters for pure liquids used in Flory and PFP theories.

Parameter	BA	1-Propanol	2-Propanol
C_p ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	217.9	143.9	156.5
α ($10^{-3}\,\mathrm{K^{-1}}$)	0.696	0.943	1.068
k_T ($10^{-10}\,\mathrm{m^2\,N^{-1}}$)	4.805	9.955	11.435
k_s ($10^{-10}\,\mathrm{m^2\,N^{-1}}$)	4.116	8.570	9.762
V ($10^{-6}\,\mathrm{m^3\,mol^{-1}}$)	103.97	75.172	76.982
$\tilde{V}$	1.1819	1.2359	1.2615
V^* ($10^{-6}\,\mathrm{m^3\,mol^{-1}}$)	87.969	60.823	61.022
P^* ($10^6\,\mathrm{J\,cm^{-3}}$)	603.34	431.44	443.27
T^* (K)	6503	5405	5047
T_c (K)	715.0	536.8	508.3

Table 6. Values of χ_{12}, θ_2, experimental and calculated V^E (using Flory and PFP theories) and three PFP contributions for near equimolar composition at 298.15 K.

			V^E ($10^{-6}\,\mathrm{m^3\,mol^{-1}}$)					
						PFP contributions		
BA+	θ_2	χ_{12} ($\mathrm{J\,mol^{-1}}$)	Expt.	Flory	PFP	int.	fv.	ip.
1-Propanol	0.4143	−6.457	−0.4410	−0.3811	−0.4726	−0.0942	−0.0700	−0.3084
2-Propanol	0.4137	−2.180	−0.5671	−0.5757	−0.6032	−0.0315	−0.1530	−0.4187

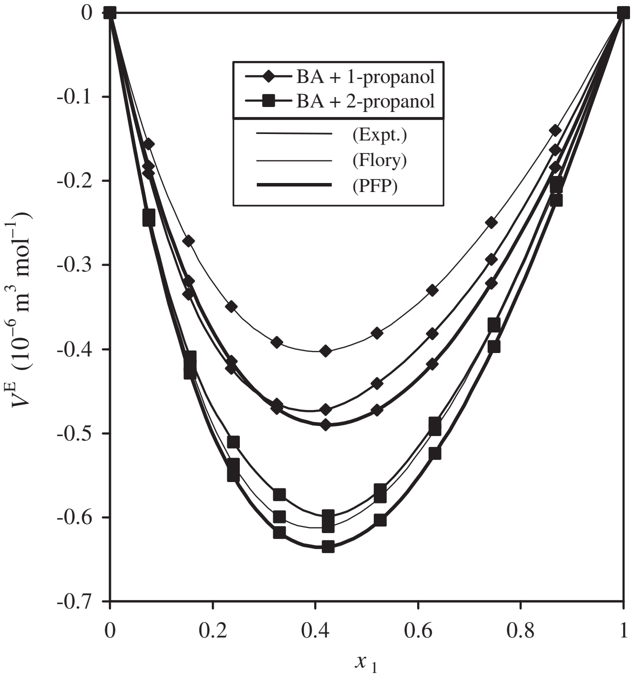

Figure 6. Comparison of experimental V^E values with those calculated from Flory and PFP theories for the binary mixtures at 298.15 K.

respectively, agree reasonably well with the experimental V^E values for both the systems under study, with PFP theory providing slightly better results for BA + 1-propanol system, whereas Flory theory provides slightly better results for BA + 2-propanol system. It is also clear from table 6 that all the three contributions of PFP theory, viz., interactional, free volume and internal pressure, are negative for both the systems under study, with internal pressure contributing major part and, hence, plays dominant role in deciding the sign and magnitude of V^E (PFP) values. Furthermore, the composition dependence of calculated V^E (PFP) values has been checked by comparing the V^E (PFP) values obtained using χ_{12} value over the entire mole fraction range. The V^E (PFP) and V^E (Flory) values have been plotted against mole fraction, x_1 of BA for comparison with V^E (expt.) for the binary mixtures at 298.15 K (figure 6). Figure 6 indicates that both PFP and Flory theories predict the trend of dependence of V^E on composition quite successfully.

4.2. *Thermal expansivity*

Thermal expansivity, α is an important thermodynamic property which is useful in calculating a number of thermodynamic parameters. But, surprisingly no attention has been paid by the researchers to the theoretical prediction of α of binary liquid mixtures, except a recent study by Pandey *et al.* [15], who have computed the values of α for some binary and ternary liquid mixtures by using Flory's statistical theory [11,12] and various hard sphere models and compared these α values with the experimental α values. In the present work an attempt has been made to evaluate and compare the theoretical α values of pure liquids and their binary mixtures by using Flory's statistical theory [11,12] and seven hard sphere models [15–17] with the experimental α values calculated from the density data using equation (8) at 298.15 K.

Flory's statistical theory [11,12] gives an α value as

$$\alpha = \frac{3(\tilde{V}^{1/3} - 1)}{T[1 - \{3(\tilde{V}^{1/3} - 1)\}]} \tag{19}$$

where $\tilde{V}$ is the reduced volume and is obtained for the binary mixtures.

The values of α were calculated theoretically by using the following equations of state derived from various hard sphere models.

Thiele–Lebowitz Model:

$$\alpha = \frac{1}{T} \cdot \frac{(1 - y^3)}{(1 + 2y)^2} \tag{20}$$

Thiele Model:

$$\alpha = \frac{1}{T} \cdot \frac{(1 + 2y + 3y^2)(1 - y)}{(1 + 5y + 9y^2 - 3y^3)} \tag{21}$$

Carnhan–Starling Model:

$$\alpha = \frac{1}{T} \cdot \frac{(1 + y + y^2 - 3y^3)(1 - y)}{(1 + 4y + 4y^2 - 4y^3 + y^4)} \tag{22}$$

Guggenheim Model:

$$\alpha = \frac{1}{T} \cdot \frac{(1 - y)}{(1 + 3y)} \tag{23}$$

Scaled-particle theory Model:

$$\alpha = \frac{1}{T} \cdot \frac{(1 - y)}{(1 + y)} \tag{24}$$

Henderson Model:

$$\alpha = \frac{1}{T} \cdot \frac{(8 + y^2)(1 - y)}{(8 + 8y + 3y^2 - y^3)} \tag{25}$$

Hoover–Ree Model:

$$\alpha = \frac{1}{T} \cdot \frac{(1 + 4y + 10y^2 + 18.36y^3 + 28.2y^4 + 39.5y^5)}{(1 + 8y + 30y^2 + 73.44y^3 + 141.0y^4 + 237.0y^5)} \tag{26}$$

where y is the packing fraction calculated by using the relation

$$y = \frac{\pi d^3 N}{6V} \tag{27}$$

where d is the rigid sphere diameter of the molecules of pure liquids and liquid mixtures and N is the Avogadro's number. The values of d were calculated by using the relation [45]

$$d^{5/2} = \left[\frac{1}{(7.21 \times 10^{19})}\right] \cdot \frac{(V\gamma^{1/4})}{T_c^{1/4}} \tag{28}$$

where T_c is the critical temperature and γ is the surface tension of liquids and their mixtures. The values of γ were evaluated from ultrasonic speed by using the relation [46]

$$\gamma = 6.3 \times 10^{-4} \rho u^{3/2} \tag{29}$$

The values of T_c for the mixtures were evaluated as

$$T_c = x_1 T_{c1} + x_2 T_{c2} \tag{30}$$

The theoretically predicted values of α (by using Flory's theory and seven hard sphere models), experimental α values calculated using equation (8) and average standard percentage error, σ (%) in the predicted values for the mixtures under study are given in table 7. It is clear from table 7 that the Flory's statistical theory with minimum σ (%) value predicts the α values well followed by the Guggenheim model, while the Scaled particle theory [25] gives the maximum σ (%) value.

4.3. *Isothermal compressibility*

Literature survey indicates that there have been very few studies [16,17] on the theoretical prediction of isothermal compressibility, k_T of liquid mixtures by using Flory's statistical theory [11,12] and various hard sphere models [15–17]. In the present study the values of k_T have been evaluated by using equation (18) based on Flory theory and various rigid sphere equations based on hard sphere models. The following rigid sphere equations were used

Lebowitz–Frisch–Helford Model:

$$k_T = \frac{V}{RT} \cdot \frac{(1 - y)^4}{(1 + 2y)^2} \tag{31}$$

Table 7. The experimental values of thermal expansivity, α, theoretically calculated values of α by using Flory theory and various hard sphere models and average percentage deviations, σ (%) in the calculated values for the binary mixtures at 298.15 K.

	α (10^{-3} K^{-1})								
x_1	Expt.	Flory	Equation (20)	Equation (21)	Equation (22)	Equation (23)	Equation (24)	Equation (25)	Equation (26)
BA + 1-Propanol									
0.0000	0.943	0.943	0.816	1.032	1.076	0.861	1.370	1.346	1.069
0.0744	0.921	0.905	0.787	1.006	1.048	0.832	1.333	1.310	1.051
0.1531	0.869	0.871	0.763	0.984	1.024	0.807	1.301	1.278	1.035
0.2366	0.822	0.840	0.741	0.964	1.002	0.785	1.273	1.249	1.022
0.3252	0.799	0.813	0.723	0.947	0.983	0.766	1.248	1.225	1.010
0.4196	0.779	0.789	0.706	0.931	0.965	0.750	1.225	1.202	1.000
0.5203	0.759	0.767	0.691	0.917	0.949	0.734	1.204	1.181	0.991
0.6278	0.741	0.747	0.677	0.904	0.934	0.719	1.185	1.162	0.983
0.7431	0.724	0.728	0.663	0.891	0.920	0.706	1.167	1.144	0.975
0.8668	0.707	0.712	0.652	0.880	0.907	0.694	1.150	1.128	0.968
1.0000	0.696	0.696	0.640	0.869	0.895	0.682	1.134	1.111	0.961
σ (%) =		−0.61	10.08	−18.41	−22.70	4.57	−55.76	−52.84	−27.16
BA + 2-Propanol									
0.0000	1.068	1.068	0.827	1.042	1.087	0.872	1.384	1.360	1.076
0.0760	1.013	1.007	0.794	1.013	1.055	0.839	1.342	1.318	1.055
0.1562	0.956	0.955	0.767	0.988	1.028	0.811	1.307	1.283	1.038
0.2409	0.903	0.908	0.744	0.967	1.004	0.788	1.276	1.253	1.023
0.3305	0.876	0.867	0.724	0.948	0.983	0.767	1.249	1.226	1.011
0.4254	0.840	0.831	0.706	0.931	0.965	0.749	1.225	1.202	1.000
0.5262	0.807	0.798	0.690	0.916	0.949	0.733	1.204	1.181	0.991
0.6334	0.775	0.769	0.676	0.903	0.933	0.719	1.184	1.161	0.982
0.7476	0.746	0.743	0.663	0.891	0.920	0.706	1.166	1.143	0.975
0.8695	0.728	0.718	0.651	0.879	0.907	0.693	1.149	1.127	0.968
1.0000	0.696	0.696	0.640	0.869	0.895	0.682	1.134	1.111	0.961
σ (%) =		0.53	15.65	−11.08	−15.10	10.48	−46.11	−43.37	−19.31

Theil–Wertheim Model:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^3}{(1+5y+9y^2-3y^3)} \tag{32}$$

Carnahan–Starling Model:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^5}{(1+3y)} \tag{33}$$

Guggenheim Model:

$$k_T = \frac{V}{RT} \cdot \frac{(1-y)^4}{(1+4y+4y^2-4y^3+y^4)} \tag{34}$$

Hoover–Ree Model:

$$k_T = \frac{V}{RT} \cdot (1+8y+30y^2+73.44y^3+141.0y^4+273.0y^5)^{-1} \tag{35}$$

Table 8. The experimental values of isothermal compressibility, k_T, theoretically calculated values of k_T by using Flory theory and various hard sphere models and average percentage deviations, σ (%) in the calculated values for the binary mixtures at 298.15 K.

	k_T ($10^{-10}\,\mathrm{m^2\,N^{-1}}$)						
x_1	Expt.	Flory	Equation (31)	Equation (32)	Equation (33)	Equation (34)	Equation (35)
BA + 1-Propanol							
0.0000	9.955	9.955	10.129	13.243	10.991	8.800	9.853
0.0744	8.932	9.208	9.396	12.485	10.241	8.083	8.711
0.1531	8.044	8.267	8.815	11.889	9.647	7.514	7.810
0.2366	7.325	7.451	8.353	11.421	9.174	7.058	7.093
0.3252	6.791	6.929	7.995	11.070	8.811	6.703	6.532
0.4196	6.344	6.466	7.712	10.802	8.524	6.418	6.080
0.5203	5.954	6.054	7.475	10.587	8.287	6.176	5.697
0.6278	5.609	5.684	7.276	10.417	8.089	5.970	5.370
0.7431	5.307	5.352	7.118	10.296	7.934	5.802	5.098
0.8668	5.045	5.051	7.007	10.232	7.830	5.677	4.883
1.0000	4.805	4.805	6.905	10.181	7.735	5.559	4.683
σ (%) =		−0.16	−29.10	−87.68	−44.58	−4.56	−1.87
BA + 2-Propanol							
0.0000	11.435	11.435	10.771	13.999	11.668	9.392	10.658
0.0760	9.973	10.246	9.840	13.022	10.713	8.486	9.234
0.1562	8.841	9.164	9.132	12.283	9.986	7.796	8.157
0.2409	7.950	8.234	8.584	11.717	9.424	7.262	7.328
0.3305	7.273	7.623	8.142	11.267	8.972	6.829	6.664
0.4254	6.689	6.996	7.794	10.921	8.616	6.485	6.139
0.5262	6.204	6.444	7.529	10.669	8.348	6.219	5.730
0.6334	5.782	5.955	7.312	10.474	8.130	5.998	5.389
0.7476	5.414	5.519	7.141	10.332	7.960	5.819	5.109
0.8695	5.109	5.200	7.008	10.237	7.831	5.675	4.877
1.0000	4.805	4.805	6.905	10.181	7.735	5.559	4.683
σ (%) =		−0.30	−22.09	−77.82	−36.82	1.26	3.52

The theoretically calculated values of k_T for the binary mixtures at 298.15 K by using Flory theory equation (18) and hard sphere equations of state equations (31–35) have been compared with the experimental k_T values calculated by using the equation [45]

$$k_T = k_s + \frac{T\alpha^2 V}{C_p} \tag{36}$$

where C_p is the heat capacity. The values of C_p for pure liquids have been taken from literature [47] and for the mixtures the values of C_p were calculated by using the additive relation

$$C_p = x_1 C_{p1} + x_2 C_{p2} \tag{37}$$

The predicted values of k_T (using Flory theory and five hard sphere equations), experimental values of k_T (using equations (36)) and average percentage error in the predicted values for the systems under study are given in table 8.

A close perusal of table 8 reveals that, again, Flory's theory predicts the k_T values well, for both the systems under study, followed by Hoover–Ree equation and then by Guggenheim equation for BA + 1-propanol binary mixtures, whereas Guggenheim equation predicts the data better than Hoover–Ree equation for BA + 2-propanol binary mixtures. However, the remaining three equations do not predict the k_T values well and show very large deviations in k_T from experimental values for both the mixtures under study.

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