Volumetric, Viscometric, and Ultrasonic Properties of Liquid Mixtures of Cyclohexane with Alkanols at Different Temperatures

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Z. Naturforsch. **65a,** 749 – 760 (2010); received August 17, 2009 / revised October 28, 2009

The densities (ρ), viscosities (η), and ultrasonic speeds (u) of pure cyclohexane, 1-butanol, 2-butanol, and those of their binary mixtures, with cyclohexane as common component, covering the whole composition range have been measured at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K. From the experimental data the excess molar volume (V^{E}), deviations in isentropic compressibility (Δk_{s}), deviations in viscosity ($\Delta\eta$), deviations in ultrasonic speed (Δu), deviations in acoustic impedance (ΔZ), deviations in internal pressure (ΔP_{i}), excess Gibbs free energy of activation ($\Delta G^{*\mathrm{E}}$), entropies (ΔS^{*}), and enthalpies (ΔH^{*}) of activation of viscous flow have been determined. The sign and magnitude of these parameters were found to be sensitive towards interactions prevailing in the studied systems. Partial molar volumes ($\bar{V}^{0}_{\phi,2}$) and partial molar compressibilities ($\bar{K}^{0}_{\phi,2}$) of 1-butanol and 2-butanol in cyclohexane have also been evaluated. Moreover, V^{E} values were theoretically predicted by using Flory's statistical theory. The variations of derived parameters mentioned above with composition offer a convenient method to study the nature and extent of interactions between the component molecules of the liquid mixtures, not easily obtained by other means.

Key words: Cyclohexane; Alkanols; Partial Molar Volume; Partial Molar Compressibility; Flory's Statistical Theory; Interactions.

1. Introduction

The present work is the continuation of our earlier studies [1 – 5] on molecular interactions of binary non-aqueous liquid mixtures using thermodynamic and transport properties. Here we extend our study to the binary mixtures containing 1-butanol and 2-butanol with cyclohexane at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K over the whole composition range. The mixtures studied are interesting from the experimental as well as from the theoretical point of view because cyclohexane is mixed with alkanols (1-butanol and 2-butanol) that have the same molar masses and similar functional group (-OH) but at different locations of the carbon chain. Cyclohexane is aprotic, unassociated, and has a globular structure [6], whereas alkanols are polar liquids, strongly self-associated by hydrogen bonding to the extent of polymerization that may differ depending on temperature, chain length, and position of the –OH group. It would be interesting to examine the mixing of cyclohexane with alkanols and also to observe the effect of the –OH group in alkanols on the molecular interaction in these binary mixtures.

Literature survey indicates that Gascon et al. [7] have measured the densities and speeds of sound of binary mixtures of cyclic ether with butanol isomers at different temperatures. Dewan et al. [8] have measured the excess volumes for mixtures of pyridine + 1-alkanol (C_1-C_{10}) at 298.15 K. Ali and co-workers [9] have reported the densities, viscosities, and ultrasonic speeds of cyclohexane + cyclohexanol, + 1-octanol, + 1-decanol at 308.15 K. To the best of our knowledge no volumetric, viscometric, and ultrasonic studies have been reported for the binary mixtures of cyclohexane with 1-butanol and 2-butanol at different temperatures, except the work of Bebek [10], who has studied only the densities and ultrasonic speeds of binary mixtures of cyclohexane with 1-butanol at one single temperature, 293.15 K. In view of these facts, the present study has been undertaken to have a better understanding of the intermolecular interactions in these systems.

This work reports the experimental densities (ρ), viscosities (η), and ultrasonic speeds (u) of pure cyclohexane, 1-butanol, 2-butanol and those of their binary mixtures over the entire composition range at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K. From the above experimental data of ρ, η, u, the excess

Component	T / K	ρ (kg · m^{-3})		η (mPa · s)		u (m · s^{-1})	
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Cyclohexane	303.15	768.8	766.2 [13] 768.8 [14]	0.822	0.820 [15]	1225.7	1229.1 [15] 1230.3 [16]
	308.15	764.4	764.3 [17] 764.46 [18]	0.751	...	1201.7	...
1-Butanol	303.15	802.1	801.94 [19] 801.91 [20]	2.287	2.285^g	1220.1	1222.7 [21]
	308.15	798.2	798.20 [20]	2.0138	...	1196.6	...
2-Butanol	303.15	796.9	795.89 [19]	2.484	2.417^g	1190.2	...
	308.15	792.6	793.90 [20]	2.0138	2.011 [22]	1165.8	1174.89 [22]

Table 1. Comparison of experimental densities ρ, viscosities η, and ultrasonic speeds u of pure components with literature values at 303.15 and 308.15 K.

molar volumes (V^E), deviations in isentropic compressibility (Δk_s), deviations in viscosity ($\Delta\eta$), deviations in ultrasonic speed (Δu), deviations in acoustic impedance (ΔZ), deviation in internal pressure (ΔP_i), excess Gibbs free energies of activation (ΔG^{*E}), entropies (ΔS^*), and enthalpies (ΔH^*) of activation of viscous flow have been determined. Partial molar volumes ($\bar{V}^0_{\phi,2}$) and partial molar compressibilities ($\bar{K}^0_{\phi,2}$) of 1-butanol and 2-butanol in cyclohexane have also been evaluated. Moreover, V^E values were theoretically evaluated by using Flory's statistical theory [11, 12]. The variations of derived functions, namely, V^E, k_s, $\Delta\eta$, Δu, ΔZ, ΔP_i, ΔG^{*E}, ΔS^*, ΔH^*, $\bar{V}^0_{\phi,2}$, $\bar{K}^0_{\phi,2}$ of the mixtures with composition are discussed in order to gain insight into the type and magnitude of the molecular interactions in binary mixtures of cyclohexane with alkanols, and also the effect of the position of the –OH group in alkanols on the molecular interactions has been discussed.

2. Experimental

Cyclohexane, 99.7%, 1-butanol and 2-butanol, 99.5% (E. Merk, Germany) were used as obtained but all the chemicals were stored over 0.4 nm molecular sieves to remove the traces of water, if any, and degassed just before use. The solutions were prepared by mass using a precisa XB–220 A (Swiss made) electronic balance with a precision of ±0.1 mg.

The densities of pure liquids and their binary mixtures were measured using a single-capillary pycnometer as described in the literature [1 – 5]. The ultrasonic speeds in liquid samples were measured by using a single crystal variable path interferometer (Mittal Enterprise, New Delhi, Model – M-82) at 2 MHz. The uncertainties in measured density and ultrasonic speed are ±0.0001 g · cm^{-3} and ±0.15 m · s^{-1}, respectively. The viscosities of pure liquids and their binary mixtures were measured using Ubbelohde-type suspended level viscometer, calibrated with triple-distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostated water bath (Julabo, Model-MD, Germany) having a precision of ±0.02 K in order to minimize thermal fluctuations. The uncertainty in viscosity measurement is ±0.003 mPa · s. A minimum of three readings were taken for each sample and the average values were used in all the calculations. Reliability of the experimental data and the purity of the solvents were ascertained by comparing their densities, ultrasonic speeds, and viscosities at different temperatures with the values reported in literature [13 – 22], see Table 1.

3. Results and Discussion

The experimental densities (ρ), ultrasonic speeds (u), and viscosities (η) of pure cyclohexane, 1-butanol, 2-butanol, and their binary mixtures over the entire composition range, expressed by the mole fraction x_1 of cyclohexane, at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K are presented in Table 2. Thermodynamic excess properties, which are the measure of the deviations from ideal behaviour, are found to be influenced by the factors such as: (i) structure of the components, i. e., different geometry of the unlike molecules, (ii) re-orientation of the component molecules in the mixture, and (iii) intermolecular interactions [23, 24]. Thus, excess molar volumes (V^E), deviations in isentropic compressibilities (Δk_s), viscosities ($\Delta\eta$), ultrasonic speeds (Δu), acoustic impedance (ΔZ), internal pressure (ΔP_i), and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}), were calculated with the help of the following standard relations:

$$V^E = V - (x_1 \cdot V_1 + x_2 \cdot V_2), \quad (1)$$

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

Table 2. Values of experimental density ρ, viscosity η, and ultrasonic speed u of binary liquid mixtures at different temperatures.

x_1	ρ (kg · m^{-3})	η (mPa · s)	u (m · s^{-1})
	Cyclohexane + 1-Butanol		
	T = 293.15 K		
0.0000	809.9	2.9252	1254.5
0.1019	804.7	2.4396	1255.8
0.2053	800.5	2.0439	1257.4
0.3095	796.7	1.7551	1259.3
0.4027	793.6	1.5516	1261.1
0.5223	789.8	1.3452	1263.4
0.6234	786.7	1.2067	1265.4
0.6990	784.6	1.1248	1267.0
0.8083	781.7	1.0336	1269.4
0.8925	779.8	0.9900	1271.3
1.0000	778.1	0.9728	1273.8
	T = 298.15 K		
0.0000	806.3	2.5778	1238.5
0.1019	801.2	2.1870	1239.1
0.2053	797.0	1.8520	1239.8
0.3095	793.1	1.6104	1240.8
0.4027	789.8	1.4380	1241.8
0.5223	785.9	1.2521	1243.1
0.6234	782.7	1.1216	1244.4
0.6990	780.5	1.0422	1245.4
0.8083	777.5	0.9629	1247.0
0.8925	775.5	0.9175	1248.2
1.0000	773.5	0.8886	1249.8
	T = 303.15 K		
0.0000	802.1	2.2871	1220.1
0.1019	797.1	1.9741	1220.2
0.2053	792.9	1.6958	1220.3
0.3095	789.0	1.4833	1220.7
0.4027	785.6	1.3251	1221.1
0.5223	781.6	1.1604	1221.8
0.6234	778.4	1.0502	1222.5
0.6990	776.2	0.9764	1223.1
0.8083	773.2	0.8960	1224.2
0.8925	771.0	0.8566	1225.0
1.0000	768.8	0.8215	1225.7
	T = 308.15 K		
0.0000	798.2	1.9975	1196.6
0.1019	793.3	1.7385	1196.8
0.2053	789.1	1.5280	1197.0
0.3095	785.1	1.3428	1197.1
0.4027	781.7	1.2022	1197.5
0.5223	777.7	1.0610	1198.2
0.6234	774.4	0.9608	1198.8
0.6990	772.1	0.8969	1199.4
0.8083	769.0	0.8285	1200.3
0.8925	766.8	0.7856	1201.1
1.0000	764.4	0.7509	1201.7
	T = 313.15 K		
0.0000	794.8	1.7693	1169.5
0.1019	789.9	1.5660	1170.2
0.2053	785.4	1.3899	1170.8
0.3095	781.3	1.2343	1171.3
0.4027	777.7	1.1145	1172.0
0.5223	773.4	0.9889	1173.0
0.6234	770.0	0.9035	1174.0
0.6990	767.5	0.8485	1174.9
0.8083	764.2	0.7815	1176.0
0.8925	761.9	0.7400	1176.8
1.0000	759.2	0.7075	1177.6
	T = 318.15 K		
0.0000	789.9	1.5269	1148.8
0.1019	785.1	1.3586	1149.2
0.2053	780.6	1.2108	1149.5
0.3095	776.4	1.0835	1149.6
0.4027	772.8	0.9891	1150.0
0.5223	768.5	0.8826	1150.6
0.6234	765.0	0.8049	1151.3
0.6990	762.5	0.7533	1151.9
0.8083	759.2	0.6900	1152.6
0.8925	756.7	0.6503	1153.1
1.0000	753.9	0.6176	1153.6
	Cyclohexane + 2-Butanol		
	T = 293.15 K		
0.0000	806.5	3.8200	1238.0
0.1132	801.4	2.4082	1241.4
0.1952	798.5	1.8930	1244.0
0.3278	794.2	1.5131	1248.4
0.4163	791.6	1.3536	1251.3
0.5303	788.3	1.1896	1255.3
0.6254	785.7	1.1012	1258.8
0.7405	782.8	1.0059	1263.3
0.8047	781.4	0.9701	1265.8
0.9023	779.3	0.9480	1269.8
1.0000	778.1	0.9728	1273.8
	T = 298.15 K		
0.0000	802.0	3.0100	1213.9
0.1132	797.2	1.9903	1217.1
0.1952	794.3	1.6096	1219.7
0.3278	789.9	1.3279	1224.0
0.4163	787.3	1.2002	1227.0
0.5303	784.0	1.0781	1231.0
0.6254	781.4	1.0015	1234.5
0.7405	778.6	0.9299	1238.9
0.8047	777.0	0.9005	1241.4
0.9023	774.9	0.8824	1245.4
1.0000	773.5	0.8886	1249.8
	T = 303.15 K		
0.0000	796.9	2.4841	1190.2
0.1132	792.4	1.7551	1193.1
0.1952	789.5	1.4348	1195.6
0.3278	785.2	1.1929	1199.9
0.4163	782.6	1.0848	1202.9
0.5303	779.4	0.9791	1206.9
0.6254	776.8	0.9206	1210.3
0.7405	774.0	0.8690	1214.6
0.8047	772.5	0.8532	1217.1
0.9023	770.5	0.8355	1221.1
1.0000	768.8	0.8215	1225.7
	T = 308.15 K		
0.0000	792.6	2.0138	1165.8
0.1132	788.2	1.4888	1168.4
0.1952	785.4	1.2581	1171.0

Table 2. (continued)

x_1	ρ (kg · m^{-3})	η (mPa · s)	u (m · s^{-1})
0.3278	781.1	1.0628	1175.4
0.4163	778.5	0.9828	1178.5
0.5303	775.2	0.9041	1182.5
0.6254	772.7	0.8515	1185.9
0.7405	769.8	0.8125	1190.2
0.8047	768.3	0.7946	1192.7
0.9023	766.3	0.7807	1196.7
1.0000	764.4	0.7509	1201.7
T = 313.15 K			
0.0000	788.5	1.7895	1141.8
0.1132	784.1	1.3800	1144.0
0.1952	781.2	1.1943	1146.6
0.3278	776.9	1.0098	1151.1
0.4163	774.1	0.9335	1154.2
0.5303	770.8	0.8639	1158.2
0.6254	768.1	0.8237	1161.7
0.7405	765.2	0.7837	1165.9
0.8047	763.6	0.7611	1168.4
0.9023	761.4	0.7352	1172.4
1.0000	759.3	0.7075	1177.6
T = 318.15 K			
0.0000	783.8	1.4235	1117.7
0.1132	779.5	1.1397	1119.5
0.1952	776.6	1.0100	1122.3
0.3278	772.1	0.8754	1126.8
0.4163	769.4	0.8091	1129.9
0.5303	765.9	0.7553	1133.9
0.6254	763.2	0.7262	1137.4
0.7405	760.1	0.6933	1141.6
0.8047	758.5	0.6735	1144.0
0.9023	756.2	0.6472	1148.0
1.0000	753.9	0.6176	1153.6

$$\Delta\eta = \eta - (x_1 \cdot \eta_1 + x_2 \cdot \eta_2), \tag{3}$$

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

$$\Delta Z = Z - (x_1 \cdot Z_1 + x_2 \cdot Z_2), \tag{5}$$

$$\Delta P_\mathrm{i} = P_\mathrm{i} - (x_1 \cdot P_{\mathrm{i}1} + x_2 \cdot P_{\mathrm{i}2}), \tag{6}$$

$$\Delta G^{*\mathrm{E}} = R \cdot T \cdot \left[\ln(\eta \cdot V) - x_1 \cdot \ln(\eta_1 \cdot V_1) - x_2 \cdot \ln(\eta_2 \cdot V_2)\right], \tag{7}$$

where x and ϕ are the mole fraction and volume fraction, respectively. Subscripts 1 and 2 stand for the pure components cyclohexane and 1-butanol / 2-butanol, respectively, k_s, V, and Z are the isentropic compressibility, molar volume, and acoustic impedance, respectively, and can be evaluated by the following relations:

$$k_\mathrm{s} = 1/(u^2 \cdot \rho), \tag{8}$$

$$V = (x_1 \cdot M_1 + x_2 \cdot M_2)/\rho, \tag{9}$$

$$Z = u\rho, \tag{10}$$

where M is the molar mass of the pure components. The internal pressure P_i can be obtained by using the ultrasonic speed data in conjunction with other thermodynamic parameters [25, 26] as:

$$P_\mathrm{i} = \frac{2^{1/6} \cdot R \cdot T}{2^{1/6} \cdot V - d \cdot N^{1/3} \cdot V^{2/3}}, \tag{11}$$

where N is the Avogadro number, V is the molar volume, and d is the molecular diameter of the mixture or pure components, which can be calculated using the following semi empirical relation [27]:

$$d^{5/2} = \frac{1}{7.21 \times 10^{19}} \cdot \frac{V \cdot \gamma^{1/4}}{T_\mathrm{C}^{1/4}}, \tag{12}$$

where γ and T_C are the surface tension and critical temperature, respectively. The surface tension of liquids, or their mixtures, is related to ultrasonic speed [27] as:

$$\gamma = 6.3 \times 10^{-4} \rho \cdot u^{3/2}. \tag{13}$$

The values of critical temperatures 553.5, 563.6, 536.2 K of cyclohexane, 1-butanol, and 2-butanol, respectively, were taken from the literature [28]. The critical temperature T_C of the mixtures was obtained from the following additive relation:

$$T_{\mathrm{c(mix)}} = \sum_{i=1}^{2} T_{\mathrm{C(i)}} \cdot x_i. \tag{14}$$

The values of V^E, Δk_s, $\Delta\eta$, Δu, ΔZ, ΔP_i, and $\Delta G^{*\mathrm{E}}$ of the binary mixtures were fitted to the Redlich and Kister type equation [29]:

$$Y^\mathrm{E} = x_1 \cdot x_2 \sum_{i=1}^{5} A_i \cdot (1 - 2 \cdot x_1)^{i-1}, \tag{15}$$

where Y^E stands for V^E, Δk_s, $\Delta\eta$, Δu, ΔZ, ΔP_i, and $\Delta G^{*\mathrm{E}}$. The coefficients A_i of (15), evaluated using least-squares method, and the standard deviations σ (Y^E), calculated as

$$\sigma(Y^\mathrm{E}) = \left(\sum[(Y^\mathrm{E}_\mathrm{expt} - Y^\mathrm{E}_\mathrm{cal})^2]/(m-k)\right)^{1/2}, \tag{16}$$

where m is the number of experimental data points and k is the number of A_i coefficients considered, have been listed in Table 3. The variations of V^E, Δk_s, $\Delta\eta$, Δu, ΔZ, ΔP_i, and $\Delta G^{*\mathrm{E}}$ with mole fraction x_1 of cyclohexane are shown graphically in Figures 1 – 7, at 298.15 K

Table 3. Values of A_i parameters along with standard error, σ (Y^E) of binary liquid mixtures at different temperatures.

Property	T / K	A_1	A_2	A_3	A_4	A_5	σ (Y^E)
				Cyclohexane + 1-Butanol			
$10^7 \cdot V^E$ ($m^3 \cdot mol^{-1}$)	293.15	11.2506	−0.1319	6.6243	0.2943	6.6197	0.0267
	298.15	10.0049	−0.9311	4.2760	1.9875	6.3714	0.0114
	303.15	8.9000	−0.6120	2.8390	1.6879	6.3669	0.0173
	308.15	7.7315	−0.5707	2.9004	1.8610	3.9472	0.0179
	313.15	6.7699	−0.9675	3.6856	1.7157	−0.9836	0.0104
	318.15	5.6174	−0.4010	4.2600	−0.1538	−2.3790	0.0232
$10^{11} \cdot \Delta k_s$ ($m^2 \cdot N^{-1}$)	293.15	17.9693	1.5399	9.4730	3.4018	2.2432	0.0327
	298.15	16.4110	1.3308	3.0334	2.9796	4.8390	0.0155
	303.15	14.6238	1.2155	2.2787	5.6580	−1.3496	0.0391
	308.15	13.0722	1.6986	3.7906	3.5339	−8.5755	0.0424
	313.15	12.0627	3.1732	−6.0930	−0.3600	2.3519	0.0557
	318.15	10.1099	4.1818	−6.8537	−4.2845	3.0478	0.0480
$10^2 \cdot \Delta\eta$ (mPa · s)	293.15	−22.7161	−5.4546	−9.6431	−12.3742	20.1975	0.0149
	298.15	−17.9797	−5.2363	−6.8715	0.2990	6.1343	0.0050
	303.15	−14.6220	−3.9399	−3.1080	1.1072	3.1863	0.0144
	308.15	−11.5636	−2.2205	−1.3738	−0.5457	0.1325	0.0109
	313.15	−9.1209	−1.6394	0.4870	0.7446	−1.6320	0.0022
	318.15	−6.8348	−1.3964	−1.6768	−0.7465	0.9104	0.0055
Δu ($m \cdot s^{-1}$)	293.15	−7.9671	−0.9176	−2.6996	−1.8250	1.5137	0.0095
	298.15	−6.9538	−1.3143	0.2644	−0.6156	0.4169	0.0187
	303.15	−5.9024	−1.1012	−0.0807	−2.6734	5.0261	0.0198
	308.15	−5.0510	−1.3879	−0.9223	−0.9679	8.2108	0.0136
	313.15	−4.4187	−2.4061	5.4214	1.3138	−1.3497	0.0401
	318.15	−3.6120	−2.5758	5.4712	2.4469	−1.8918	0.0416
$10^{-3} \cdot \Delta Z$ ($kg \cdot mol^{-1}$)	293.15	−21.0353	−1.8930	−10.0079	−3.1055	−4.1577	0.0340
	298.15	−20.2404	−1.5523	−4.0630	−3.3335	−6.1807	0.0040
	303.15	−19.0267	−1.6890	−2.7256	−4.4113	−2.5883	0.0293
	308.15	−17.0997	−1.8549	−3.4116	−2.9729	2.3973	0.0226
	313.15	−15.3496	−2.2585	1.3765	−0.6133	−1.0614	0.0230
	318.15	−14.0498	−2.8531	0.8973	2.00378	−0.0183	0.0103
$10^{32} \cdot \Delta P_i$ (T · Pa)	293.15	9.4769	1.3584	1.1366	0.4893	0.8296	0.0032
	298.15	9.4528	1.1772	0.6475	0.7081	1.1714	0.0033
	303.15	9.4335	1.2312	0.5716	0.5092	1.1529	0.0022
	308.15	9.5474	1.2235	0.5282	0.5500	1.0041	0.0035
	313.15	9.9373	1.2073	0.8507	0.4853	−0.0265	0.0033
	318.15	9.9537	1.2668	0.8383	0.2199	−0.1597	0.0058
ΔG^{*E} ($kJ \cdot mol^{-1}$)	293.15	−19.0318	2.1409	−5.7758	3.9260	3.3994	0.0080
	298.15	−15.7154	3.0060	−10.1865	1.4647	11.6830	0.0087
	303.15	−13.7235	2.6166	−4.9898	2.0508	6.6861	0.0297
	308.15	−11.8439	3.4923	−2.2029	−0.3624	0.9360	0.0275
	313.15	−10.0679	2.5875	2.1159	2.4856	−5.2259	0.0056
	318.15	−7.3370	1.5041	−4.1020	3.2627	1.5076	0.0137

only, to avoid overcrowding of data points at remaining temperatures.

Figure 1 shows the dependency of excess molar volumes V^E on the composition of cyclohexane + alkanol binary mixtures at 298.15 K. The observed V^E values exhibit positive deviations over the entire mole fraction range for the two binary systems. The positive deviations in excess molar volumes can be explained by considering the fact that mixing of cyclohexane with alkanols leads to (i) the loss of dipolar association between the alkanol–alkanol molecules which tends to make V^E positive, (ii) dipole-dipole or dipole-induced-dipole interactions between free alkanol-alkanol and cyclohexane-alkanol molecules, and (iii) geometrical fitting of smaller molecules of 1-butanol (molar volume $= 9.1517 \times 10^{-5}$ $m^3 \cdot mol^{-1}$) and 2-butanol (molar volume $= 9.1903 \times 10^{-5}$ $m^3 \cdot mol^{-1}$) molecules into the voids created by the bigger cyclohexane (molar volume $= 10.8161 \times 10^{-5}$ $m^3 \cdot mol^{-1}$) molecules. Thus, the observed positive V^E values suggest that the effect due to (i) dominates over that of (ii) and (iii) effects. It is worth to mention that V^E values (Fig. 1) are

Table 3. (continued)

Property	T / K	A_1	A_2	A_3	A_4	A_5	$\sigma\,(Y^E)$
				Cyclohexane + 2-Butanol			
$10^7 \cdot V^E$ ($m^3 \cdot mol^{-1}$)	293.15	9.9342	−0.0286	7.0077	−0.1641	4.1590	0.0106
	298.15	9.0225	0.3224	3.2120	−2.0559	5.6850	0.0219
	303.15	7.9957	−0.0557	2.8394	0.9961	2.0139	0.2220
	308.15	6.7496	−0.5050	2.4261	1.1646	0.7407	0.0182
	313.15	5.5949	−0.5995	2.1578	2.2937	−1.1603	0.0061
	318.15	4.3347	−0.6687	2.0247	2.2008	−3.6712	0.0118
$10^{11} \cdot \Delta k_s$ ($m^2 \cdot N^{-1}$)	293.15	22.6284	0.5310	1.3546	2.6352	7.6102	0.0093
	298.15	24.4018	0.9700	3.1352	−0.3653	8.2817	0.0222
	303.15	26.1580	0.3309	8.0415	0.8563	5.9834	0.0250
	308.15	27.7794	1.0381	12.1988	0.0379	9.5765	0.0257
	313.15	29.9902	0.7160	14.4365	3.3087	15.8106	0.0168
	318.15	32.4055	0.3676	15.2847	5.6312	29.6235	0.0259
$10^2 \Delta\eta$ ($mPa \cdot s$)	293.15	−9.1507	49.3339	−103.2509	−49.3849	130.9738	1.7246
	298.15	−33.4981	−22.5283	−25.0472	−19.7784	−7.2818	0.0671
	303.15	−25.8310	−17.3222	−15.9311	−10.5902	−0.5849	0.0537
	308.15	−18.4142	−12.9786	−10.9990	−7.5805	1.2713	0.0176
	313.15	−14.7340	−10.8804	−5.9103	−3.0162	−1.4535	0.0086
	318.15	−10.0939	−7.1991	−2.2021	−3.1492	−2.2096	0.0173
Δu ($m \cdot s^{-1}$)	293.15	−12.5288	0.2525	3.4249	−1.6178	−3.4384	0.0123
	298.15	−13.4531	0.1163	−0.2415	−0.4953	−2.8259	0.0057
	303.15	−14.2835	0.0531	−3.8038	0.4123	−2.9861	0.0057
	308.15	−15.0444	−0.391	−6.4037	1.1114	−5.8095	0.0060
	313.15	−15.9539	−0.2234	−7.4215	−0.2141	−10.1666	0.0110
	318.15	−16.8768	−0.0768	−7.3989	−1.3912	−18.6516	0.0011
$10^{-3} \cdot \Delta Z$ ($kg \cdot mol^{-1}$)	293.15	−19.9003	−0.7027	−4.5049	−1.9274	−6.6928	0.0062
	298.15	−19.3459	−1.0301	−3.4852	0.9395	−7.4519	0.0224
	303.15	−18.6022	−0.1724	−5.7121	−1.0418	−4.2429	0.0232
	308.15	−17.6707	−0.4740	−7.1950	−0.5658	−5.2931	0.0209
	313.15	−17.2231	−0.2508	−7.6335	−2.4565	−7.0527	0.0087
	318.15	−16.6792	−0.0326	−7.4683	−3.1467	−11.3205	0.0151
$10^{32} \cdot \Delta P_i$ ($T \cdot Pa$)	293.15	8.9569	1.3433	1.2884	0.3142	0.3836	0.0029
	298.15	8.9992	1.3670	0.6854	−0.0329	0.5032	0.0015
	303.15	8.9591	1.2233	0.4422	0.2615	0.1401	0.1600
	308.15	8.9735	1.1926	0.2553	0.2103	−0.1294	0.0026
	313.15	9.0821	11.627	0.0711	0.2333	−0.4383	0.0013
	318.15	9.1317	1.1534	−0.0088	0.0051	−1.1532	0.0018
ΔG^{*E} ($kJ \cdot mol^{-1}$)	293.15	−42.9853	−18.0133	−27.6095	−2.9422	3.0531	0.1123
	298.15	−37.2865	−16.5843	−24.5719	−6.7013	4.7906	0.0821
	303.15	−33.6861	−15.3236	−14.5363	−4.6117	8.8446	0.0760
	308.15	−29.0548	−15.8697	−13.7432	−6.7482	13.1066	0.0194
	313.15	−25.0548	−16.1222	−3.9348	0.4796	0.3420	0.0122
	318.15	−21.9850	−38.7901	64.8669	119.6608	−211.7094	0.1423

more positive for the cyclohexane + 1-butanol mixture than for the cyclohexane + 2-butanol mixture. This can be explained by considering the extent of association present in pure 1-butanol and 2-butanol molecules. It has been reported [30] that self-association in 1-butanol is more as compared to 2-butanol. As a result, addition of cyclohexane, a structure breaker [31], would cause more dissociation in 2-butanol than in 1-butanol, releasing large number of free 2-butanol molecules and relatively smaller number of free 1-butanol molecules in the solution. This would facilitate the greater fitting of large number of freely available 2-butanol molecules into the voids created by bigger cyclohexane molecules than the fitting of smaller number of freely available 1-butanol molecules into the structure of cyclohexane, resulting in larger positive V^E values for 1-butanol than for 2-butanol.

Like V^E the behaviour of Δk_s with x_1 (Fig. 2) shows positive deviations for both the systems investigated, whereby the deviation is larger for the cyclohexane + 1-butanol than for the cyclohexane + 2-butanol system. It should be noted that the extent of positive de-

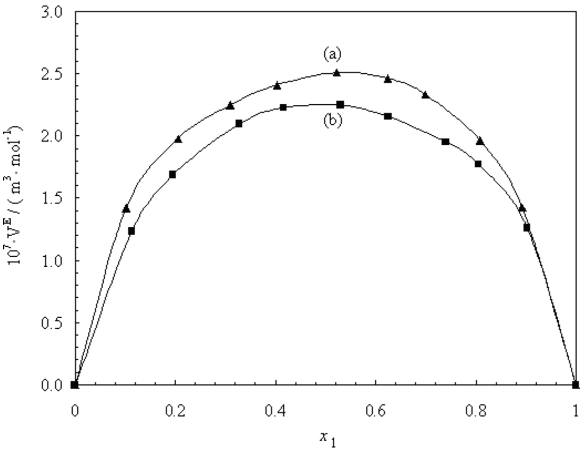

Fig. 1. Plots of excess molar volumes V^{E}, against mole fraction x_1, of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

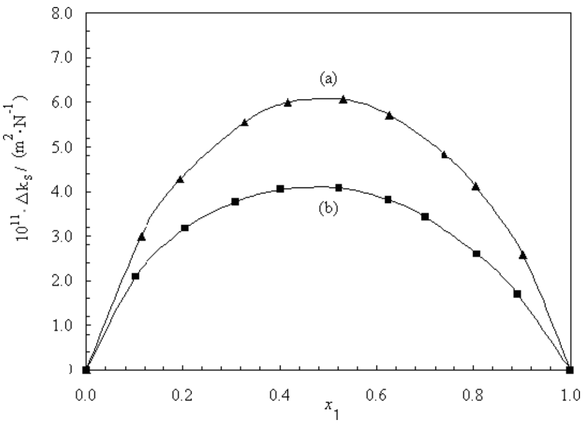

Fig. 2. Plots of deviations in isentropic compressibilities Δk_{S} against mole fraction x_1 of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

viation in Δk_{S} is more pronounced than in V^{E}. This is due to the fact that the compressibility is a more powerful thermodynamic parameter in sensing the presence of intermolecular interaction than does V^{E} [32]. The observed positive values of Δk_{S} (Fig. 2) for both the mixtures over the entire composition range indicate the presence of weak interactions between the component molecules. This is in accordance with the views suggested by Fort and Moore [33].

Figure 3 shows that $\Delta\eta$ values are entirely negative for both the binary systems and these negative values follow the sequence 2-butanol > 1-butanol over the complete composition range. Negative deviations in $\Delta\eta$ occur where dispersion and dipole-dipole forces are operative in the systems [34]. Garcia et al. [35] have also suggested similar deviations in $\Delta\eta$ from ideality for the binary mixtures N-methylpyrrolidine + alkanols ($C_1 - C_{10}$) at 298.15 K.

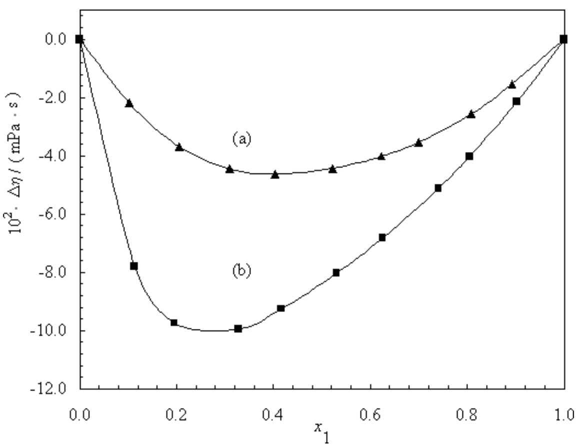

Fig. 3. Plots of deviations in viscosities $\Delta\eta$ against mole fraction x_1 of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

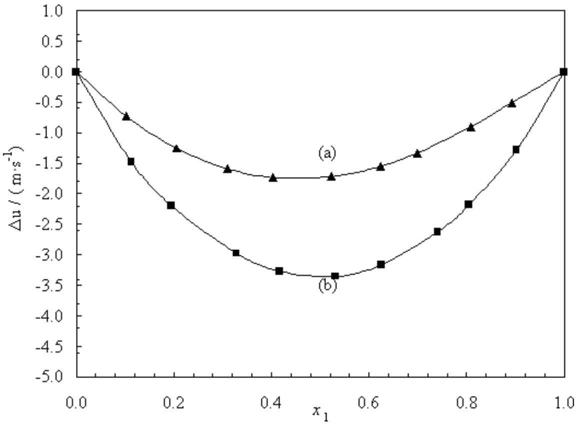

Fig. 4. Plots of deviations in ultrasonic speed Δu against mole fraction x_1 of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

The behaviour of Δu is similar to that of ΔZ (Figs. 4 and 5) and show negative deviation for both of the mixtures. Negative deviations in Δu and ΔZ indicate weak interaction between the component molecules in the mixtures [36] and that the strength of the interaction follows the sequence 1-butanol < 2-butanol. The observed negative deviation in ΔZ, where $Z = u\rho$, and an opposite trend in Δk_{S}, where $k = 1/u^2\rho$, over the whole composition range support our view regarding the structural order and, hence, intermolecular interactions in these mixtures. Similar conclusion regarding

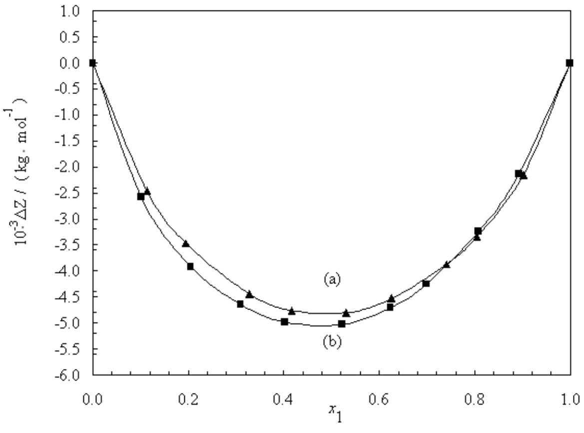

Fig. 5. Plots of deviations in acoustic impedance ΔZ against mole fraction x_1 of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

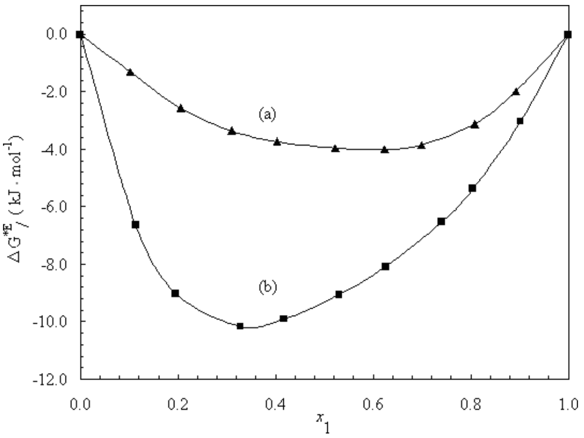

Fig. 6. Plots of deviations in free energy $\Delta G^{*\mathrm{E}}$ against mole fraction x_1, of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

the ΔZ values were also drawn by Ali et al. [37] for ethanol + 1-hexanol/1-octanol and acetonitrile + N,N-dimethylformamide binary mixtures.

The variations of $\Delta G^{*\mathrm{E}}$ with mole fraction x_1 of cyclohexane for both the binary mixtures are presented in Figure 6. The values of $\Delta G^{*\mathrm{E}}$, like $\Delta\eta$, are negative for both the binary mixtures. In general, the negative contribution to $\Delta G^{*\mathrm{E}}$ values are attributed to the presence of dispersion forces in the mixtures. Similar conclusion were also arrived at by Reed and Taylor [38] and Oswal and Rathnam [39] who ascribed negative $\Delta G^{*\mathrm{E}}$ values to the dispersion forces present in the liquid mixtures.

The ΔP_i values (Fig. 7) are positive for both the binary mixtures studied, which indicate that the attractive forces are greater than the repulsive forces. Similar results have also been reported by Aminabhavi et al. [27] for the binary mixtures of styrene with n-alkanes. This again reinforces our earlier view regarding the interactions between the component molecules of the liquid mixtures.

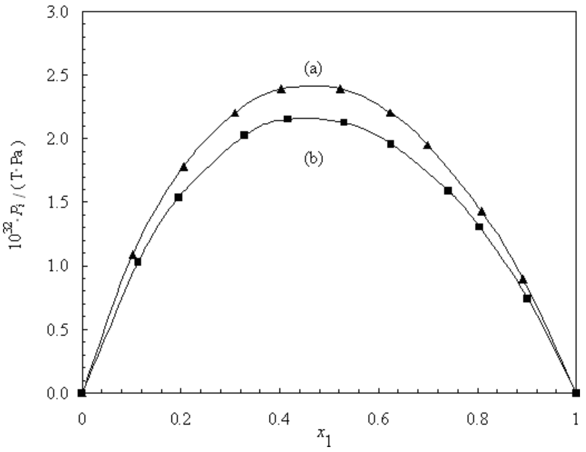

Fig. 7. Plots of deviations in internal pressure ΔP_i against mole fraction x_1 of cyclohexane for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

Further, by using the temperature dependence of viscosity data the activation parameters for viscous flow have been investigated. The Eyring viscosity equation [40, 41] is given as:

$$\eta = \left(\frac{h \cdot N}{V}\right) \exp\left(\frac{\Delta G^*}{R \cdot T}\right), \tag{17}$$

where h is Planck's constant, N is Avogadro's number, and ΔG^* is the Gibbs energy of activation of viscous flow. Combining (17) with $\Delta G^* = \Delta H^* - T\Delta S^*$ gives the equation

$$R \cdot \ln\left(\frac{\eta \cdot V}{h \cdot N}\right) = \left(\frac{\Delta H^*}{T}\right) - \Delta S^*, \tag{18}$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow, respectively. The plots of the left hand side of (18), i. e., $R \cdot \ln\left(\frac{\eta \cdot V}{h \cdot N}\right)$ against $\frac{1}{T}$ for both the binary mixtures at different compositions were found to show linear trend for each composition of the system under study. This indicates that ΔH^* values are almost constant in the investigated temperature range, i. e., ΔH^* is independent of temperature. Thus, the values of ΔH^* and ΔS^* were obtained as the slopes and intercepts of the above plots by using a linear regression procedure.

Table 4. Values of enthalpy ΔH^* and entropy ΔS^* of activation of viscous flow of binary liquid mixtures at each composition along with the linear correlation factor r.

x_1	ΔH^* ($\mathrm{kJ \cdot mol^{-1}}$)	ΔS^* ($\mathrm{kJ \cdot mol^{-1}}$)	r
	Cyclohexane + 1-Butanol		
0.0000	19.1918	4.6011	0.9988
0.1019	17.1674	5.1600	0.9976
0.2053	15.0525	5.7496	0.9958
0.3095	13.8208	6.0598	0.9952
0.4027	12.9352	6.2730	0.9958
0.5223	11.9901	6.4926	0.9954
0.6234	11.3402	6.6364	0.9938
0.6990	11.0751	6.6761	0.9931
0.8083	11.1343	6.6022	0.9917
0.8925	11.5854	6.4234	0.9915
1.0000	12.4836	6.1103	0.9933
	Cyclohexane + 2-Butanol		
0.0000	28.8559	1.5234	0.9975
0.1132	21.3251	3.7286	0.9953
0.1952	17.6252	4.8014	0.9932
0.3278	15.4209	5.3924	0.9950
0.4163	14.3070	5.6942	0.9943
0.5303	12.4748	6.2309	0.9928
0.6254	11.2732	6.5872	0.9910
0.7405	9.8953	7.0028	0.9886
0.8047	9.6993	7.0519	0.9869
0.9023	10.2231	6.8709	0.9850
1.0000	12.5064	6.1200	0.9934

The values of ΔH^* and ΔS^* along with the linear correlation factor r of (18) are given in Table 4. A close perusal of Table 4 indicates that for both the binary mixtures the values of ΔH^* and ΔS^* are positive, show a decrease in ΔH^* and an opposite trend in ΔS^* values with mole fraction x_1 of cyclohexane. It has been suggested earlier [42] that the enthalpy of activation of viscous flow may be regarded as a measure of the degree of cooperation between the species taking part in viscous flow. In a highly structured liquid there will be considerable degree of order and, hence, for cooperative movement of entities, a large heat of activation is needed for the flow process. Therefore, a perusal of Table 4 indicates that the formation of activated species necessary for viscous flow seems to be difficult in the 1-butanol rich region and relatively more difficult in 2-butanol rich region owing to the high values of ΔH^*, and become easy as the mole fraction of cyclohexane in the mixture increases. This is supported by the decreasing value of ΔS^* as the amount of cyclohexane in the mixture increases.

Furthermore, the extent of interaction between the component molecules in a mixture is well reflected in the parameters like apparent molar volume, apparent molar compressibility, partial molar volume and partial molar compressibility [43, 44]. The apparent molar volumes $V_{\phi,2}$ of 1-butanol and 2-butanol in cyclohexane were calculated by using the equation [43]

$$V_{\phi,2} = V_2^* + (V^{\mathrm{E}}/x_2), \tag{19}$$

where V_2^* is the molar volume of 1-butanol and 2-butanol and x_2 is their mole fraction. The partial molar volumes $\bar{V}^0_{\phi,2}$ of 1-butanol and 2-butanol in cyclohexane at infinite dilution were obtained by the method described earlier [43, 44]. The deviations in $\bar{V}^0_{\phi,2}$ at infinite dilution ΔV_2, were calculated by using the equation [43]

$$\Delta V_2 = \bar{V}^0_{\phi,2} - V_2^*. \tag{20}$$

The values of $\bar{V}^0_{\phi,2}$, V^* and ΔV_2 are listed in Table 5. It is clear from this table that the values of ΔV_2 are positive (i. e., the partial molar volumes $\bar{V}^0_{\phi,2}$ of 1-butanol/2-butanol in cyclohexane at infinite dilution are greater than their corresponding molar volumes in the pure state V_2^*), suggesting that on mixing there is an expansion in the volume of the mixture, which may be due to the presence of weak interactions between the component molecules as mentioned above. However, as the temperature increases, ΔV_2 becomes less positive, thereby, indicating that the effect of temperature is more pronounced for pure alkanols than in the mixture.

The apparent molar compressibilities $K_{\phi,2}$ of 1-butanol/2-butanol in cyclohexane were calculated using the relation [43, 44]

$$K_{\phi,2} = K_2^* + (K_{\mathrm{s}}^{\mathrm{E}}/x_2), \tag{21}$$

where $K_{\mathrm{s}}^{\mathrm{E}}$ [$= (k_{\mathrm{s}}V)^{\mathrm{E}}$] is the excess molar compressibility of the mixture; K_2^* is the molar isentropic compressibility of 1-butanol/2-butanol. The partial molar compressibilities $\bar{K}^0_{\phi,2}$ of 1-butanol/2-butanol in cyclohexane at infinite dilution were obtained by using the method described elsewhere [43, 44]. The deviations in $\bar{K}^0_{\phi,2}$ at infinite dilution ΔK_2 were obtained by using the relation [45]

$$\Delta K_2 = \bar{K}^0_{\phi,2} - K_2^*. \tag{22}$$

The values of $\bar{K}^0_{\phi,2}$, K_2^*, and ΔK_2 are also included in Table 5. The partial molar compressibilities $\bar{K}^0_{\phi,2}$ of 1-butanol/2-butanol in cyclohexane at infinite dilution characterize the compressibilities of their molecules in the mixture, whereas molar isentropic compressibilities K_2^* of pure components 1-butanol/2-butanol can be

Table 5. Values of $\bar{V}^0_{\phi,2}$, V_2^*, ΔV_2, $\bar{K}^0_{\phi,2}$, K_2^*, and ΔK_2 for the binary liquid mixtures at different temperatures.

T / K	$\bar{V}^0_{\phi,2}$	V_2^*	ΔV_2	$\bar{K}^0_{\phi,2}$	K_2^*	ΔK_2
	10^5 ($m^3 \cdot mol^{-1}$)			10^{-14} ($m^5 \cdot N^{-1} \cdot mol^{-1}$)		
			Cyclohexane + 1-Butanol			
293.15	9.2961	9.1517	0.1443	7.4973	7.1801	0.3171
298.15	9.3168	9.1926	0.1242	7.7074	7.4328	0.2746
303.15	9.3469	9.2407	0.1062	7.9624	7.7391	0.2234
308.15	9.3765	9.2859	0.0906	8.3196	8.1254	0.1943
313.15	9.4043	9.3256	0.0786	8.7729	8.5787	0.1943
318.15	9.4494	9.3835	0.0659	9.1955	9.0012	0.1943
			Cyclohexane + 2-Butanol			
293.15	9.3206	9.1903	0.1303	7.7821	7.4357	0.3464
298.15	9.3555	9.2419	0.1136	8.1913	7.8203	0.3710
303.15	9.3942	9.3010	0.0932	8.6315	8.2393	0.3922
308.15	9.4275	9.3515	0.0759	9.1008	8.6812	0.4196
313.15	9.4577	9.4013	0.0564	9.5648	9.1451	0.4196
318.15	9.4973	9.4595	0.0378	1.0077	9.6577	0.4196

considered as partial molar isentropic compressibilities of these molecules when dissolved in itself. It is worth mentioning that all the values of ΔK_2 (Table 5) for two binary mixtures studied are positive and decrease with temperature. Positive values of ΔK_2 are indicative of weak interaction between the component molecules in the mixture. This further supports our earlier finding.

In the present paper, the excess molar volume V^E has also been evaluated by using Flory's statistical theory [11, 12] (V_F^E). According to Flory's equation of state [11, 12] V_F^E is given as:

$$V_F^E = \left[\sum_{i=1}^{2} x_i \cdot V_i^*\right] \cdot [\tilde{V}^{07/3}/\{(4/3) - (\tilde{V}^0)^{1/3}\}] \cdot (\tilde{T} - \tilde{T}^0). \qquad (23)$$

The terms and notations used in (23) are the same as given in the literature [11, 12].

A comparison between the experimental V^E and the predicted V_F^E using Flory's theory is given in Figure 8. It is clear from this figure that Flory's statistical theory, though unable to predict excess molar volume quantitatively, seems to be satisfactory in predicting it qualitatively for the present systems studied.

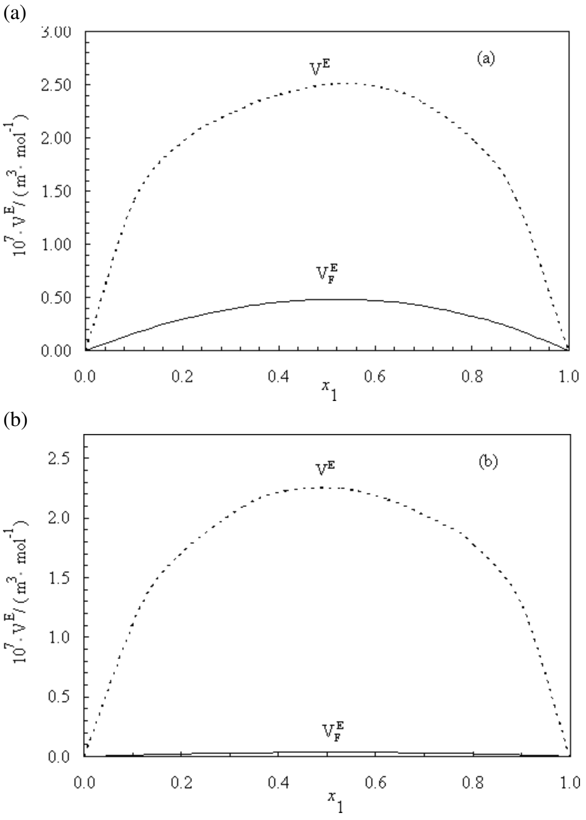

Fig. 8. Comparison of experimental value V^E (···) and V_F^E value of Flory statistical theory (—) of binary mixtures for (a) cyclohexane + 1-butanol and (b) cyclohexane + 2-butanol at 298.15 K.

4. Conclusion

The observed positive V^E values, over the entire composition range, for both the systems, cyclohexane + 1-butanol and + 2-butanol, at all the investigated temperatures indicate that disruption of associated structures of alkanols by cyclohexane molecules in the mixtures dominates over that of the combined effect due to dipole-dipole or dipole-induced-dipole interactions and fitting of smaller molecules of alkanols into the voids created by bigger cyclohexane molecules. Also, the positive values of Δk_s for both the systems under study support the behaviour of V^E.

Further, the positive deviations in Δk_s are more pronounced than in V^E for both the systems studied, thereby, suggesting that compressibility is a more powerful thermodynamic parameter than V^E in sensing the presence of molecular interaction in a mixture. The observed negative values of $\Delta\eta$, Δu, ΔZ, and ΔG^{*E} for both the binary mixtures clearly reinforce the behaviours of V^E and Δk_s. The positive deviations in ΔP_i indicate that the attractive forces are greater than the repulsive forces in both systems. Both systems have positive ΔH^* and ΔS^* values, show decrease in ΔH^* and reverse trend in ΔS^* values with mole fraction x_1 of cyclohexane. This indicates that the formation of activated species necessary for viscous flow is difficult in 1-butanol rich region and becomes more so more in 2-butanol rich rich. The positive values of ΔV_2 and also of ΔK_2 for alkanols in cyclohexane over the entire composition range for both binary mixtures clearly suggest the presence of weak interactions between the component molecules.

A comparison between the experimental V^E and the theoretically predicted V_F^E, using Flory's statistical theory, suggests that, though, Flory's theory is unable to predict excess molar volume quantitatively, is satisfactory in predicting it qualitatively for the systems investigated.

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