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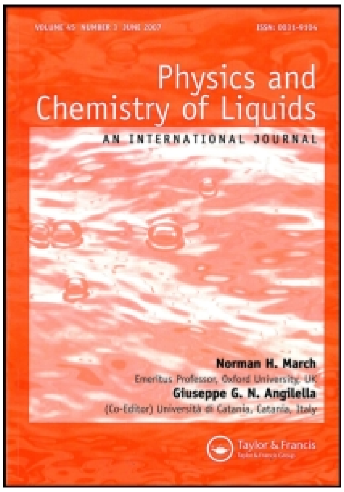

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Volumetric and Ultrasonic Behaviour of Acetophenone and Alcohol Mixtures

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VOLUMETRIC AND ULTRASONIC BEHAVIOUR OF ACETOPHENONE AND ALCOHOL MIXTURES

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Excess volumes and sound velocities for binary liquid mixtures of acetophenone with *n*-alcohols and *i*-alcohols are measured at 303.15 K. The sound velocity and density data are used to calculate the isentropic compressibilities (k_s) and deviations in isentropic compressibilities (Δk_s). The values of V^E are negative in all the systems except in the system, acetophenone + *n*-heptanol wherein the V^E values are positive. Deviations in isentropic compressibilities are negative in all the systems over the entire range of composition. The data are used to explain the possible intermolecular interactions between unlike molecules.

KEY WORDS: Sound velocity, compressibility.

1 INTRODUCTION

Several workers[1-3] have studied the interactions between aliphatic ketones and alcohols in terms of thermodynamic properties. Very few attempts[4] have been made to study the interactions in the mixtures containing acetophenone as a common component. Properties of these mixtures depend on (a) the structure breaking effect of the components and (b) the possible interaction between unlike molecules. We report here new experimental data on excess volume, sound velocity, density, isentropic compressibility and deviation in isentropic compressibility for the mixtures of acetophenone with *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *n*-pentanol, *i*-pentanol, *n*-hexanol and *n*-heptanol at 303.15 K.

2 EXPERIMENTAL SECTION

a) Materials

The component liquids were purified as described by Riddick and Bunger[5]. Acetophenone was kept over anhydrous calcium chloride for 3 days, filtered and fractionally distilled. Alcohols were refluxed over freshly ignited calcium oxide for 4 hrs. and fractionally distilled. The purity of the samples was checked by comparing the measured densities with the literature values[6]. The data are given in Table 1.

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Table 1 Densities of pure component liquids at 303.15 K.

Components	*Density* (ρ)/*g cm*$^{-3}$	
	Experimental	*Literature*
Acetophenone	1.01941	1.01940
n-propanol	0.79592	0.79600
i-propanol	0.77693	0.77690
n-butanol	0.80195	0.80206
i-butanol	0.79434	0.79437
n-pentanol	0.80758	0.80764
i – pentanol	0.80175	0.80179
n-hexanol	0.81196	0.81201
n-heptanol	0.81572	—

b) *Methods*

Excess volumes were measured using batch type dilatometer technique described by Rao and Naidu[7]. The values are accurate to ±0.003 cm^3 mol^{-1}. Isentropic compressibilities were calculated from the relation,

$$K_s = u^{-2}\rho^{-1} \tag{1}$$

where u and ρ denote sound velocity and density respectively. Sound velocities were measured with an ultrasonic interferometer at a frequency of 3 MHz. The sound velocities are accurate to ±0.03%. The measurements have been made at 303.15 K. Densities of mixtures were computed from experimental excess volume data using the equation,

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V^0 + V^E} \tag{2}$$

where x and M stand for mole fraction and molecular weight respectively. V^0 and V^E denote the ideal molar volume and excess molar volume respectively. Densities of pure components were determined experimentally using a bicapillary pycnometer. The deviations in isentropic compressibilities (ΔK_s) were obtained from the relation,

$$\Delta k_s = k_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \tag{3}$$

where k_s, $k_{s,1}$ and $k_{s,2}$ represent the isentropic compressibilities of the mixtures and pure components 1 and 2 respectively. ϕ indicates the volume fraction.

RESULTS AND DISCUSSION

Experimental excess volumes (V^E) along with the mole fraction are included in Table 2. Data on sound velocity (u), density (ρ), isentropic compressibility (k_s) deviation in isentropic compressibility (ΔK_s) as a function of volume fraction at 303.15 K for the

Table 2 Mole fraction (x_1) and excess volumes (V^E) for mixtures of acetophenone with normal and isoalcohols at 303.15 K

x_1	V^E $cm^3\ mol^{-1}$	x_1	V^E $cm^3\ mol^{-1}$	x_1	V^E $cm^3\ mol^{-1}$	x_1	V^E $cm^3\ mol^{-1}$
Acetophenone + *n*-propanol		Acetophenon + *i*-propanol		Acetophenone + *n*-butanol		Acetophenone + *i*-butanol	
0.1067	−0.096	0.1017	−0.076	0.1116	−0.034	0.1148	−0.042
0.1966	−0.153	0.1840	−0.122	0.2065	−0.058	0.1900	−0.063
0.2630	−0.170	0.2497	−0.140	0.3099	−0.085	0.2635	−0.082
0.3600	−0.188	0.3300	−0.159	0.3929	−0.009	0.3249	−0.095
0.4826	−0.186	0.4416	−0.163	0.4516	−0.103	0.3994	−0.099
0.5727	−0.163	0.4991	−0.158	0.5102	−0.102	0.4843	−0.092
0.6630	−0.136	0.6004	−0.120	0.5929	−0.096	0.6015	−0.075
0.7123	−0.112	0.6987	−0.085	0.7050	−0.073	0.6944	−0.057
0.7912	−0.083	0.7622	−0.053	0.7889	−0.052	0.7484	−0.045
0.8965	−0.040	0.8527	−0.022	0.8873	−0.029	0.8590	−0.028
Acetophenone + *n*-pentanol		Acetophenone + *i*-pentanol		Acetophenone + *n*-hexanol		Acetophenone + *n*-heptanol	
0.1403	−0.027	0.1630	−0.026	0.1174	−0.008	0.0958	0.026
0.2216	−0.046	0.2954	−0.044	0.2082	−0.013	0.2088	0.038
0.2910	−0.053	0.3619	−0.052	0.3025	−0.017	0.2510	0.041
0.3710	−0.061	0.4489	−0.056	0.3693	−0.020	0.3525	0.040
0.4308	−0.065	0.5014	−0.057	0.4400	−0.021	0.4370	0.038
0.5137	−0.063	0.5876	−0.054	0.5111	−0.022	0.5287	0.033
0.5748	−0.059	0.6533	−0.048	0.6019	−0.019	0.6052	0.028
0.6573	−0.052	0.7186	−0.042	0.7240	−0.014	0.6960	0.022
0.7716	−0.035	0.8058	−0.028	0.8072	−0.010	0.7625	0.017
0.8807	−0.020	0.8978	−0.016	0.8979	−0.005	0.8636	0.011

mixtures of acetophenone with *n*-alcohols and *i*-alcohols are included in Table 3. The dependence of V^E on mole fraction and Δk_s on volume fraction are graphically represented in Figures 1 to 4. The values of V^E are fitted to an empirical equation of the form

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad (4)$$

where a_0, a_1 and a_2 are adjustable parameters, obtained by the least square method, are included in Table 4 along with the standard deviation, $\sigma(V^E)$. Δk_s values are also fitted to Eq. (4), by replacing mole fraction by volume fraction and the values of a_0, a_1, a_2 and $\sigma(\Delta k_s)$ are included in Table 5.

The observed values of V^E and Δk_s are negative for all the systems except in the system, acetophenone + *n*-heptanol, wherein V^E values are positive. The observed V^E and ΔK_s values may be explained on the basis of the following factors: (1) depolymerization of self-associated alcohols by acetophenone and (2) hydrogen bonded interaction between unlike molecules. The former effect leads to expansion in volume and the latter effect results in contraction in volume. However, the sign and magnitude of V^E and ΔK_s of a particular system depends upon the resultant of the above said effects. The experimental data on V^E suggest that the latter effect may be dominant in all the systems except in acetophenone + *n*-heptanol, wherein the former

Table 3 Volume fractions (ϕ_1) densities (ρ), sound velocities (u), isentropic compressibilities (k_s) and deviation in isentropic compressibilities (Δk_s) of the mixture of acetophenone with normal and isoalcohols at 303.15 K.

ϕ_1	ρ $g\ cm^{-3}$	u ms^{-1}	k_s TPa^{-1}	Δk_s TPa^{-1}	ϕ_1	ρ $g\ cm^{-3}$	u ms^{-1}	k_s TPa^{-1}	Δk_s TPa^{-1}
	Acetophenone + *n*-propanol					Acetophenone + *i*-propanol			
0.0000	0.79595	1190.4	886.6	—	0.0000	0.77693	1126.5	1014.3	*M*
0.1572	0.83204	1232.4	791.3	−28.5	0.1471	0.81336	1174.3	891.5	−41.5
0.2764	0.85926	1266.8	725.3	−44.0	0.2557	0.84015	1211.4	811.0	−62.0
0.3578	0.87760	1290.0	684.4	−50.2	0.3365	0.85989	1238.4	758.3	−70.1
0.4675	0.90228	1321.3	634.8	−53.2	0.4287	0.88244	1269.9	702.6	−74.8
0.5928	0.93022	1355.7	584.9	−49.9	0.5465	0.91100	1309.8	639.9	−72.5
0.6766	0.94868	1377.4	555.6	−43.6	0.6029	0.92462	1328.6	612.7	−68.5
0.7544	0.96578	1396.6	530.8	−35.3	0.6960	0.94681	1359.1	571.8	−58.0
0.7944	0.79450	1406.2	518.9	−30.2	0.7794	0.96670	1385.8	538.7	−45.0
0.8554	0.98784	1421.0	501.3	−21.9	0.8300	0.97868	1402.1	519.7	−36.0
0.9311	1.00437	1439.7	480.4	−10.7	0.8982	0.99491	1424.4	495.4	−22.6
1.0000	1.01941	1457.4	461.8	—	1.0000	1.01941	1457.4	461.8	—
	Acetophenone + *n*-butanol					Acetophenone + *i*-butanol			
0.0000	0.80195	1225.4	830.6	—	0.0000	0.79434	1172.5	915.7	—
0.1381	0.83227	1260.1	756.7	−23.0	0.1408	0.82638	1213.8	821.3	−30.5
0.2492	0.85664	1290.0	701.5	−37.2	0.2286	0.84633	1241.1	766.9	−45.0
0.3641	0.88188	1319.7	651.1	−45.2	0.3112	0.86510	1266.5	720.6	−53.8
0.4521	0.90114	1341.2	616.9	−47.0	0.3781	0.88026	1286.6	686.3	−57.8
0.5122	0.91424	1354.6	596.1	−45.6	0.4565	0.89795	1308.9	650.0	−58.5
0.5705	0.92691	1367.4	577.0	−43.2	0.5426	0.91726	1333.2	613.3	−56.1
0.6500	0.94414	1383.7	553.2	−37.7	0.6559	0.94263	1363.1	571.0	−47.0
0.7529	0.96632	1404.0	525.0	−27.9	0.7416	0.96175	1384.7	542.3	−36.8
0.8266	0.98215	1417.5	506.7	−19.0	0.7898	0.97249	1397.2	526.7	−30.5
0.9094	0.99996	1435.3	485.4	−9.8	0.8850	0.99377	1421.5	498.0	−16.0
1.0000	1.01941	1457.4	461.8	—	1.0000	1.01941	1457.4	461.8	—
	Acetophenone + *n*-pentanol					Acetophenone + *i*-pentanol			
0.0000	0.80758	1257.3	783.3	—	0.0000	0.80175	1220.1	837.9	—
0.1498	0.83952	1282.2	724.5	−10.6	0.1727	0.83954	1271.1	748.9	−24.0
0.2351	0.85774	1298.8	691.1	−16.6	0.3101	0.86958	1295.0	685.8	−35.5
0.3071	0.87304	1312.9	664.5	−20.1	0.3781	0.88446	1311.6	657.2	−38.5
0.3891	0.89048	1330.5	634.4	−23.8	0.4662	0.90366	1332.9	622.9	−39.7
0.4497	0.90336	1343.1	613.6	−25.1	0.5188	0.91512	1345.3	603.8	−39.0
0.5328	0.92096	1359.8	587.2	−24.8	0.6043	0.93373	1364.0	575.6	−35.0
0.5934	0.93377	1372.5	568.5	−24.0	0.6689	0.94773	1378.7	555.1	−31.2
0.6744	0.95086	1388.8	545.3	−21.2	0.7324	0.96152	1392.6	534.0	−26.2
0.7844	0.97413	1410.8	515.8	−15.2	0.8164	0.97969	1411.5	510.4	−18.5
0.8885	0.99597	1431.7	489.8	−7.8	0.9040	0.99865	1433.2	487.5	−10.4
1.0000	1.01941	1457.4	461.8	—	1.0000	1.01941	1457.4	461.8	—
	Acetophenone + *n*-hexanol					Acetophenone + *n*-heptanol			
0.0000	0.81196	1284.6	746.3	—	0.0000	0.81572	1310.4	713.9	—
0.1108	0.83500	1299.4	709.3	−5.5	0.0806	0.83198	1319.3	690.6	−3.0
0.1976	0.85304	1313.7	679.3	−10.8	0.1792	0.85199	1332.3	661.2	−7.5
0.2889	0.87201	1328.1	650.2	−13.9	0.2172	0.85968	1337.5	650.3	−8.9
0.3542	0.88558	1339.8	629.0	−16.5	0.3105	0.87871	1350.3	624.2	−11.4
0.4239	0.90006	1351.9	607.9	−17.8	0.3911	0.89512	1361.9	602.3	−13.0
0.4947	0.91476	1364.4	587.2	−18.4	0.4814	0.91354	1374.9	579.1	−13.4
0.5861	0.93369	1378.8	563.4	−16.2	0.5591	0.92941	1385.9	560.2	−12.8
0.7107	0.95951	1401.0	531.0	−13.1	0.6545	0.94887	1399.8	537.9	−11.0
0.7968	0.97734	1416.6	509.9	−9.7	0.7265	0.96357	1410.1	521.9	−8.8
0.8917	0.99699	1433.5	488.1	−4.5	0.8397	0.98667	1428.4	496.7	−5.5
1.0000	1.01941	1457.4	461.8	—	1.0000	1.01941	1457.4	461.8	—

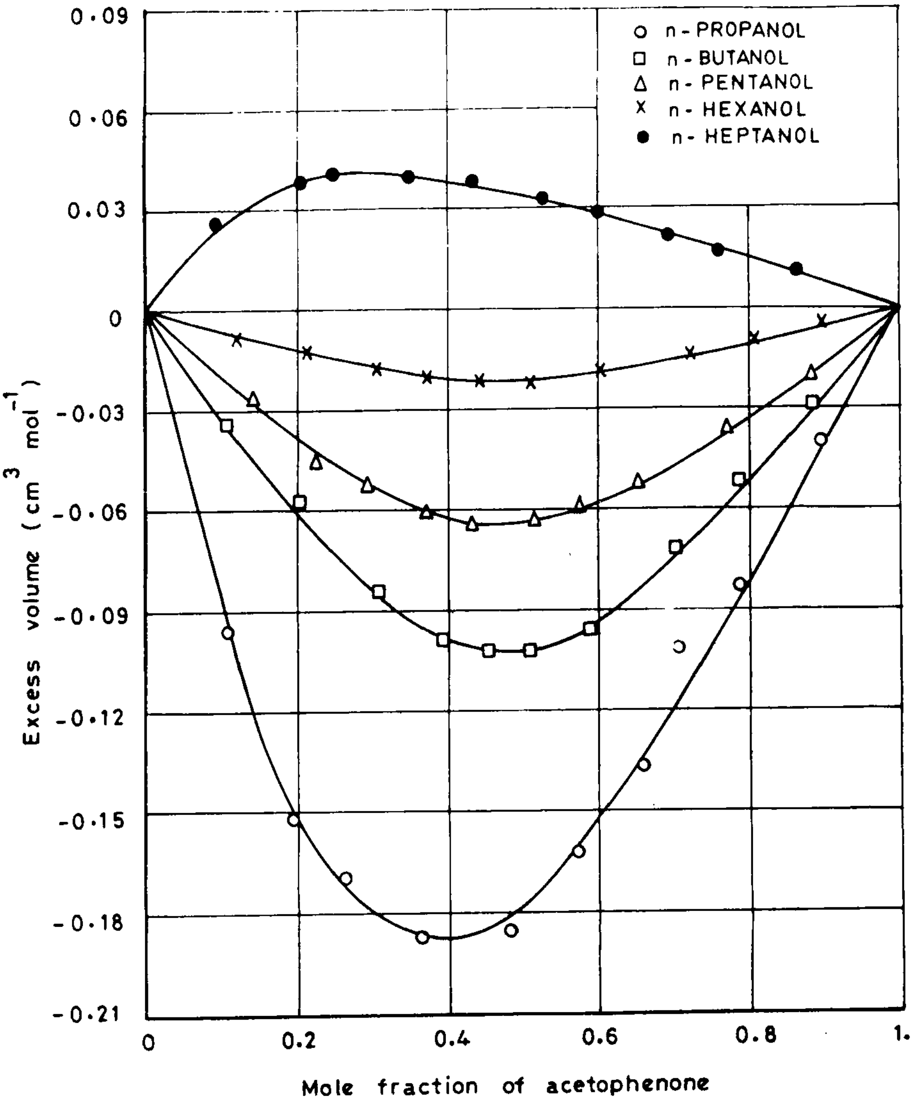

Figure 1 Acetophenone + *n*-alcohols at 303.15 K.

effect may contribute to excess volume. The negative values of ΔK_s support the contention that the hydrogen bonding interaction is dominant in all the systems. The existence of hydrogen bonding interaction between acetophenone and alcohols was confirmed by Bellamy and Pace[8], Sahini and Crain[9] and Singurel[10] on the basis of spectral studies.

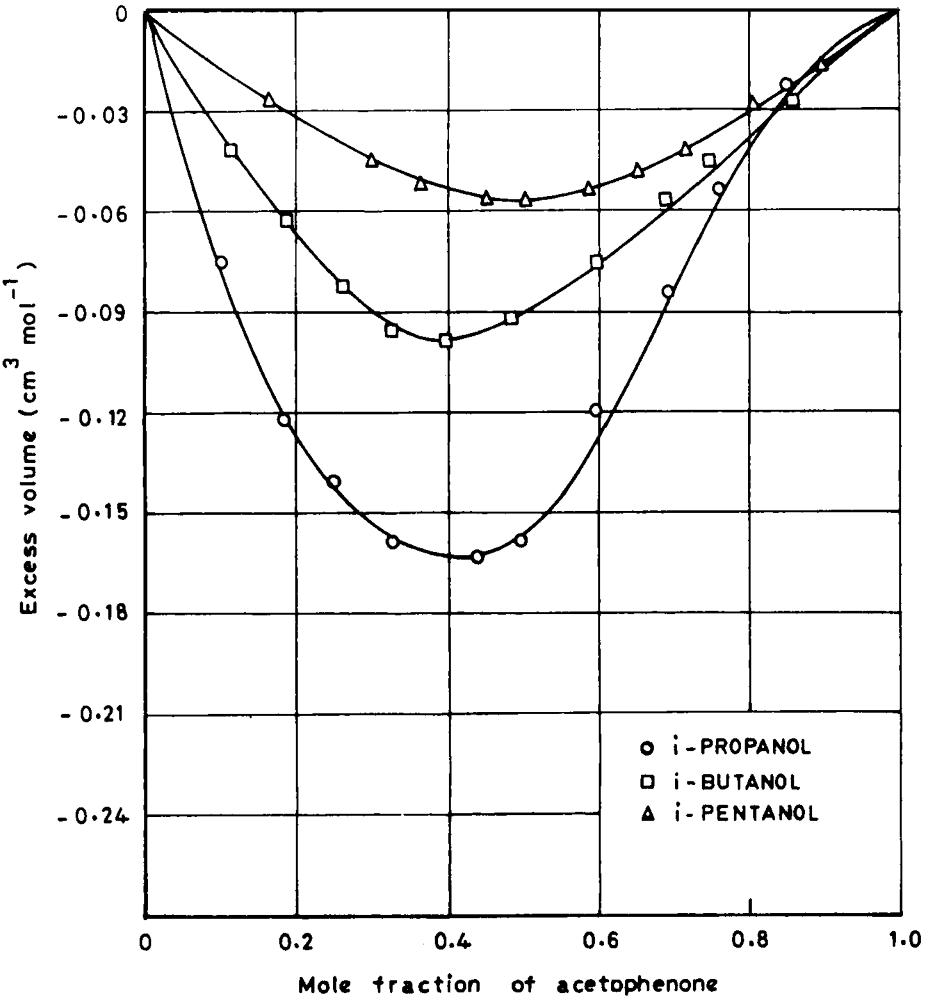

Figure 2 Acetophenone + *i*-alcohols at 303.15 K.

The negative values of V^E and ΔK_s for mixtures of acetophenone with *n*-alcohols fall in the order, *n*-heptanol < *n*-hexanol < *n*-pentanol < *n*-butanol < *n*-propanol. In the case of mixtures containing *i*-alcohols the order is as follows,

i-pentanol < *i*-butanol < *i*-propanol.

The order of V^E and ΔK_s suggests that increase in chain length of alcohols results in decrease of negative V^E and ΔK_s values. This indicates that the hydrogen bonding interaction between alcohols and acetophenone decreases with increase in chain length of alcohols. The V^E and ΔK_s values are more negative in the system containing *n*-alcohols than that of *i*-alcohols. This may be attributed to the steric effect. When the

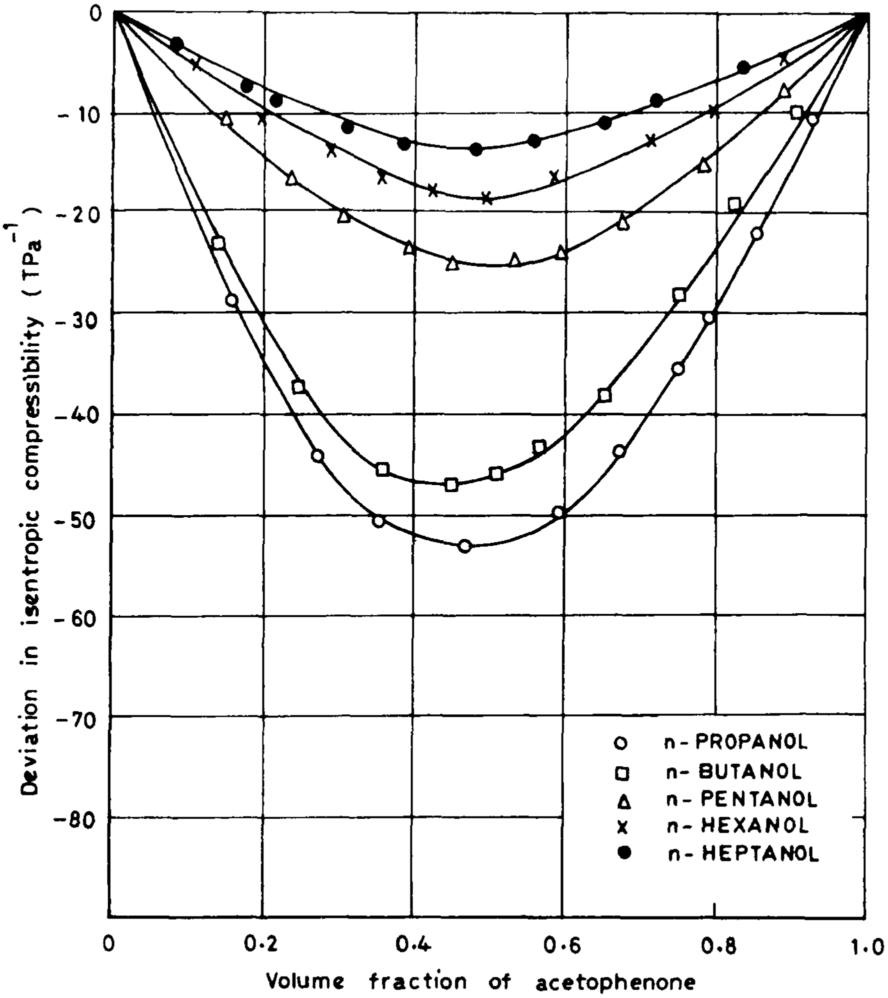

Figure 3 Acetophenone + *n*-alcohols at 303.15 K.

Table 4 Values of the parameters in Eq. (4) and the standard deviation, $\sigma(V^E)$ at 303.15 K.

System	a_0	a_1	a_2	$\sigma(V^E)$
Acetophenone + *n*-propanol	−0.719	0.371	−0.003	0.003
Acetophenone + *i*-propanol	−0.606	0.452	0.227	0.004
Acetophenone + *n*-butanol	−0.404	0.026	0.179	0.003
Acetophenone + *i*-butanol	−0.365	0.160	0.105	0.004
Acetophenone + *n*-pentanol	−0.255	0.037	0.081	0.002
Acetophenone + *i*-pentanol	−0.225	0.007	0.084	0.001
Acetophenone + *n*-hexanol	−0.084	0.013	0.031	0.001
Acetophenone + *n*-heptanol	0.136	−0.122	0.091	0.001

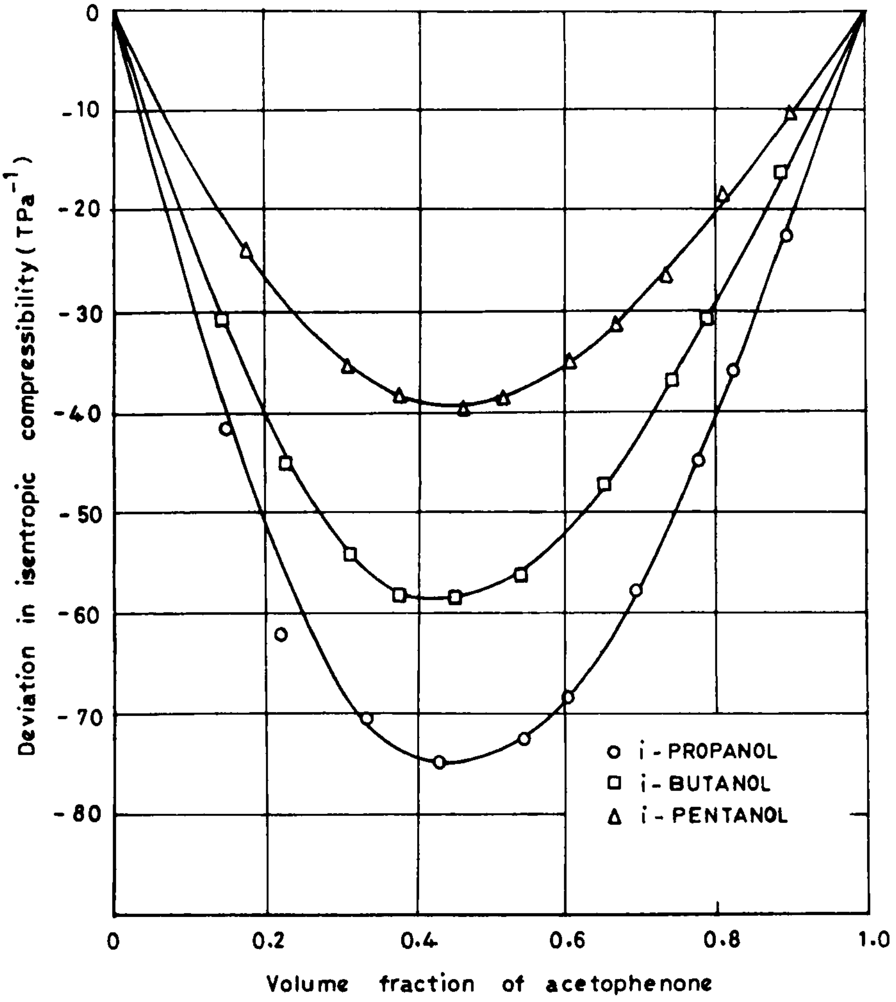

Figure 4 Acetophenone + *i*-alcohols at 303.15 K.

Table 5 Values of the parameters in Eq. (4) and the standard deviation, $\sigma(\Delta k_s)$ at 303.15 K.

System	a_0	a_1	a_2	$\sigma(\Delta k_s)$
Acetophenone + *n*-propanol	−212.0	25.7	27.5	0.3
Acetophenone + *i*-propanol	−298.3	59.0	11.9	0.3
Acetophenone + *n*-butanol	−185.0	47.8	45.2	0.3
Acetophenone + *i*-butanol	−232.4	61.3	41.3	0.3
Acetophenone + *n*-pentanol	−101.2	0.7	39.0	0.3
Acetophenone + *i*-pentanol	−155.9	33.3	23.5	0.4
Acetophenone + *n*-hexanol	−72.3	6.4	32.1	0.4
Acetophenone + *n*-heptanol	−52.6	5.8	17.4	0.3

alkyl group of the alcohol becomes more and more branced, the effect of interaction is more and more sterically hindered.

Acknowledgements

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