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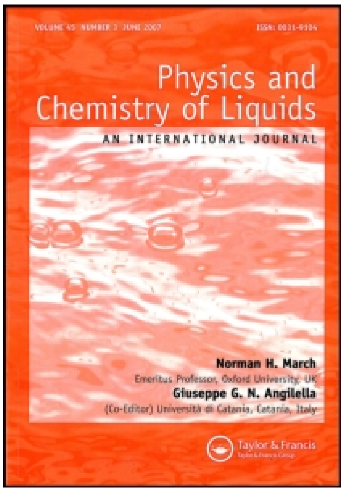

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ULTRASONIC STUDIES OF BINARY MIXTURES OF *p*-CHLOROTOLUENE WITH *l*-ALCOHOLS AT 303.15 K

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Ultrasonic sound velocities and densities were measured for the binary mixtures of *p*-chlorotoluene with *l*-alcohols. The alcohols included: *l*-propanol, *l*-butanol, *l*-pentanol, *l*-hexanol and *l*-heptanol. Isentropic compressibilities, k_s and deviation in isentropic compressibility, K_s from ideal behaviour have been calculated from the results. The deviation in isentropic compressibility has been ascribed to competition between structure-breaking and structural effects to different extents.

KEY WORDS: Isentropic compressibility, volume fraction, sound speed, binary mixtures

INTRODUCTION

Attempts$^{1-3}$ have been made to use ultrasonic sound velocity and density data to compute isentropic compressibility. A survey of the literature showed that isentropic compressibilities of binary mixtures of toluene^{4} with *l*-alcohols have been measured at 303.15 K. However, no attempt has been made to measure isentropic compressibilities of binary mixtures of *p*-chlorotoluene with *l*-alcohols. Introduction of a chloro group into the toluene molecule may influence both the sign and magnitude of deviation in isentropic compressibility. Hence we report here new experimental sound velocity data for five binary mixtures of *p*-chlorotoluene with *l*-alcohols.

EXPERIMENTAL

Apparatus

Ultrasonic sound velocities were measured with a single crystal interferometer at a frequency of 2 MHz and were accurate to ±0.15%. The temperature of the experimental liquid in the cell was maintained by circulating water from a thermostatic bath through the double walled liquid container. All the measurements were made

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Table 1 Densities of pure components.

Compound	*Density ρ, gcm^{-3}*	
	Experimental	*Literature*
p-chlorotoluene	1.06514*	1.06510*
l-propanol	0.79562	0.79567
l-butanol	0.80203	0.80206
l-pentanol	0.80762	0.80764
l-hexanol	0.81205	0.81201
l-heptanol	0.81572	0.81574

* At 298.15 K.

at a constant temperature that could be maintained to ±0.01 K. Densities of the mixtures were computed from experimental excess volumes data using the relation

$$\rho = \frac{X_1 M_1 + X_2 M_2}{V^0 + V^E} \tag{1}$$

where X_1, X_2 denote the mole fractions of the two components and M_1 and M_2 stand for the molecular weights. V^0 represents the ideal molar volume of the mixture. V^E denotes the excess molar volume.

Materials

p-Chlorotoluene and the alcohols were purified by the methods described by Vogel[5] and Riddck and Bunger[6] respectively. *p*-chlorotoluene (Fluka) was washed successively with 30 ml of 10% sodium hydroxide solution and equal amount of concentrated sulphuric acid and water. It was dried over anhydrous calcium chloride, decanted and distilled. *l*-propanol (BDH) and *l*-butanol (BDH) was refluxed over freshly ignited calcium oxide for four hours and then distilled by employing a fractionating column. *l*-pentanol (Fluka) and *l*-hexanol (Merck), dried over Drierite, was fractionally distilled. *l*-Heptanol (S.D. Fine Chemicals) was fractionated. The purity of the samples was checked by comparing the measured densities of the samples with those reported in the literature.[7,8] Densities of the pure components were determined using a bicapillary type pyknometer which gave an accuracy of 2 parts in 10^5. The measured densities and the literature data are presented in Table 1.

RESULTS AND DISCUSSION

Isentropic compressibility (k_s) was calculated from the expression

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

Table 2 Volume fraction ϕ_1 of *p*-chlorotoluene, density ρ, sound velocity u, isentropic compressibility k_s from Eq. (2) and K_s from Eq. (3) for *p*-chlorotoluene + *l*-alcohols at 303.15 K.

ϕ_1	$\rho\ gcm^{-3}$	$u\ msec^{-1}$	$k_s\ TPa^{-1}$	$K_s\ TPa^{-1}$
		p-chlorotoluene + *l*-propanol		
0.0000	0.79596	1190	887	—
0.0999	0.82313	1205	837	−20
0.1816	0.84528	1213	804	−28
0.2351	0.85962	1215	788	−29
0.3854	0.89938	1223	743	−26
0.4512	0.91664	1226	726	−23
0.5688	0.94740	1236	691	−17
0.6609	0.97127	1246	663	−9
0.7175	0.99379	1242	652	−5
0.8194	1.01251	1248	634	−2
0.8960	1.03267	1258	612	−1
1.0000	1.06056	1274	581	—
		p-chlorotoluene + *l*-butanol		
0.0000	0.80203	1224	832	—
0.1283	0.83578	1236	783	−16
0.1656	0.84562	1240	769	−21
0.2830	0.87601	1244	738	−23
0.3875	0.90289	1245	714	−21
0.4461	0.91783	1246	702	−18
0.5058	0.93315	1241	696	−15
0.5538	0.94534	1243	685	−12
0.6458	0.96889	1248	663	−7
0.7569	0.99749	1250	642	0
0.8349	1.01769	1254	625	3
1.0000	1.06056	1274	581	—
		p-chlorotoluene + *l*-pentanol		
0.0000	0.80762	1258	782	—
0.0968	0.83260	1265	751	−12
0.1639	0.84175	1270	736	−13
0.2209	0.86416	1264	724	−14
0.3021	0.88467	1263	709	−12
0.4077	0.91117	1261	690	−10
0.4935	0.93296	1261	674	−8
0.5824	0.95754	1256	662	−3
0.6397	0.96933	1257	653	0
0.7599	0.99983	1257	633	4
0.8304	1.01767	1258	621	6
1.0000	1.06056	1274	581	—
		p-chlorotoluene + *l*-hexanol		
0.0000	0.81205	1288	742	—
0.0976	0.83657	1285	724	−4
0.1508	0.84999	1284	714	−6
0.2319	0.87025	1281	700	−5
0.3461	0.89713	1276	685	−3
0.4211	0.91918	1271	673	−1
0.5169	0.94074	1268	661	2
0.5995	0.96110	1265	650	5

(*continued*)

Table 2 (*continued*)

ϕ_1	ρ gcm^{-3}	$u\,m\,sec^{-1}$	k_s TPa^{-1}	K_s TPa^{-1}
		p-chlorotoluene + *l*-hexanol		
0.6591	0.97571	1265	640	6
0.7304	0.99324	1263	631	7
0.8764	1.02930	1265	607	6
1.0000	1.06056	1274	581	—
		p-chlorotoluene + *l*-heptanol		
0.0000	0.81572	1310	713	—
0.0689	0.83297	1308	702	−2
0.1458	0.85200	1304	690	−4
0.2263	0.87170	1297	682	−1
0.3404	0.89955	1288	670	2
0.3929	0.91227	1283	665	5
0.4791	0.93320	1278	656	6
0.5674	0.95462	1274	645	7
0.6617	0.97751	1272	632	9
0.7474	0.99838	1269	623	8
0.8343	1.01960	1267	611	8
1.0000	1.06056	1274	581	—

where u and ρ denotes sound velocity and density respectively. The values of isentropic compressibilities are accurate to $\pm 2\ TPa^{-1}$. The deviation in isentropic compressibility (K_s) has been calculated from the equation

$$K_s = k_s - \phi_1 k_{s_1} - \phi_2 k_{s_2} \tag{3}$$

where k_s, k_{s_1} and k_{s_2} are the isentropic compressibilities of mixture and the components 1 and 2 respectively. ϕ_1 and ϕ_2 are volume fractions. The volume fractions can be calculated using the equation

$$\phi_1 = \frac{X_1 V_1^0}{X_1 V^0 + X_2 V_2^0} \tag{4}$$

Densities, sound velocities, isentropic compressibilities, and deviations in isentropic compressibility for all the binary systems are listed in Table 2. The experimental K_s values against volume fraction ϕ_1 are also graphically presented along with those for mixtures of the *l*-alcohols with toluene in Figures 1, 2 and 3. The dependence of K_s on volume fraction is expressed by an empirical equation

$$K_s = \phi_1\phi_2[a_0 + a_1(\phi_1 - \phi_2) + a_2(\phi_1 - \phi_2)^2] \tag{5}$$

where a_0, a_1 and a_2 are adjustable parameters obtained by the method of least squares and are given in Table 3 along with the standard deviation σ (K_s).

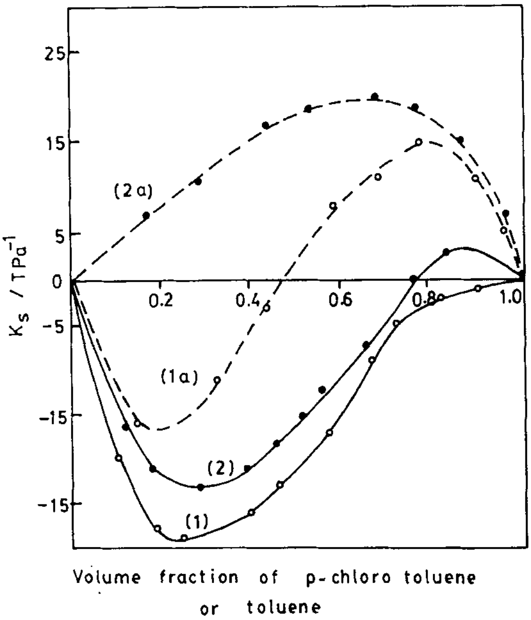

Figure 1 K_s plotted against volume fraction (ϕ_1) at 303.15 K for (1) *p*-chlorotoluene + *l*-propanol, (2) *p*-chlorotoluene + *l*-butanol (1a) toluene + *l*-propanol, (2a) toluene + *l*-butanol.

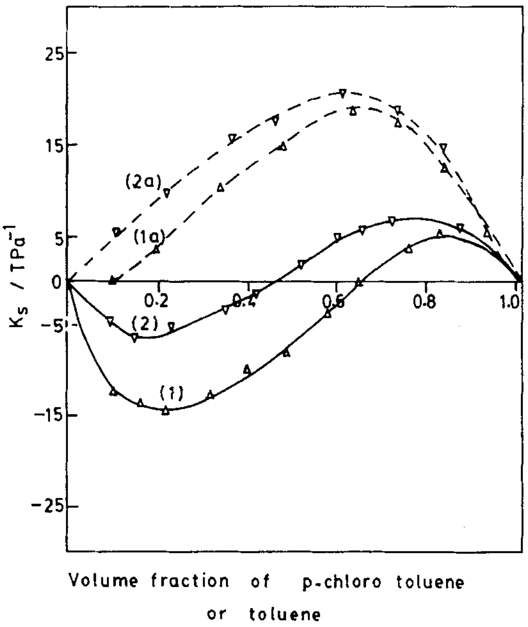

Figure 2 K_s plotted against volume fraction (ϕ_1) at 303.15 K for (1) *p*-chlorotoluene + *l*-pentanol, (2) *p*-chlorotoluene + *l*-hexanol, (1a) toluene + *l*-pentanol, (2a) toluene + *l*-hexanol.

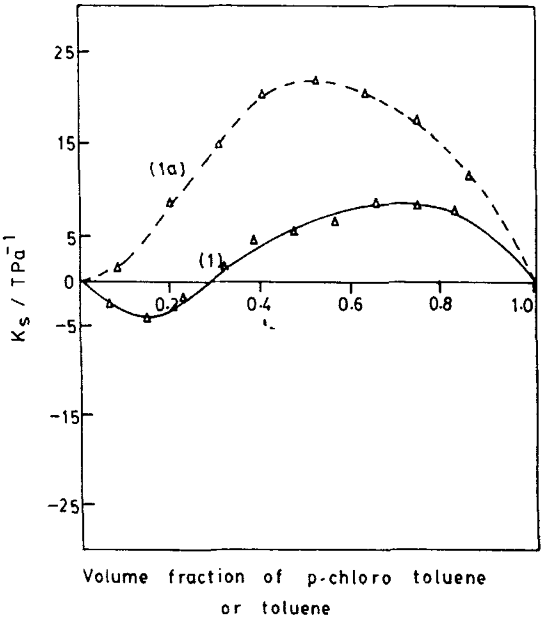

Figure 3 K_s plotted against volume fraction (ϕ_1) at 303.15 K for (1) *p*-chlorotoluene + *l*-heptanol, (1a) toluene + *l*-heptanol.

The data in Table 2 show that K_s is, in general negative in mixtures of *p*-chlorotoluene with *l*-propanol, *l*-butanol and *l*-pentanol. The quantity, on the other hand, exhibits inversion in sign in the remaining two mixtures. Further, the magnitude of deviation is 3 to 4 times the experimental error in these two mixtures. This suggests that the two mixtures are nearly ideal in terms of compressibility.

The deviations may be examined in the light of structure-breaking and structural effects (Eq. 1). Loss of dipolar association of the components and break-up of hydrogen bonds in alcohol aggregates are considered structure-breaking factors, will increase free spaces, defined by Jacobson[9] and contribute to a positive deviation in isentropic compressibility. Structural effects like interstitial accommodation of mole-

Table 3 Least square parameters in Eq. (5) and the standard deviation $\sigma(K_s)$ at 303.15 K.

System	a_0	a_1	a_2	$\sigma(K_s)$
		TPa^{-1}		
p-chlorotoluene + *l*-propanol	−78.2589	133.9960	−56.5740	1
p-chlorotoluene + *l*-butanol	−62.2895	121.0518	3.1729	1
p-chlorotoluene + *l*-pentanol	−23.0129	103.5071	−23.8417	1
p-chlorotoluene + *l*-hexanol	6.4195	66.3906	−2.5417	0
p-chlorotoluene + *l*-heptanol	26.2574	53.2926	−20.5623	1

cules of *p*-chlorotoluene in alcohol aggregates and an intermolecular hydrogen bonding of the type, cl ... H—O, in between unlike molecules may lead to decrease in free spaces and consequently a negative deviation in compressibility. The actual value of deviation would depend on the balance between the two opposing contributions. The results included in Table 2 suggest that structural effects are dominant in the mixtures of *p*-chlorotoluene with *l*-propanol, *l*-butanol and *l*-pentanol. The opposing effects cancel each other in the remaining two mixtures.

Finally an examination of K_s curves included in Figures 1, 2 and 3 show that the algebraic values of K_s decrease when toluene is replaced by *p*-chlorotoluene.

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