Excess Volumes and Speed of Sound for *m*-Chlorotoluene + 2-Propanol, + 2-Methyl-1-Propanol, and + 3-Methyl-1-Butanol at 303.15 K

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Excess volumes (V^E) and Isentropic compressibilities (k_s) of binary mixtures of *m*-chlorotoluene with 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol have been determined at 303.15 K. The excess volume exhibits inversion in sign in the three mixtures. The data are algebraically smaller than those for mixtures which include toluene in place of *m*-chlorotoluene. The deviation in isentropic compressibility is negative over the whole range of composition in the three mixtures. The deviation is algebraically smaller than that observed for mixtures of the three alcohols with toluene.

Introduction

A survey of the literature showed excess volumes (*1*) and isentropic compressibilities (*2*) for mixtures of toluene with 2-propanol and 2-methyl-1-propanol measured at 303.15 K. However, there appear to be no measurements of the excess volumes and isentropic compressibilities for mixtures of *m*-chlorotoluene with three isoalcohols. Introduction of a chloro function in the meta position may influence both volumetric and ultrasonic behavior. Hence, we report here experimental data for excess volumes and isentropic compressibilities of mixtures of *m*-chlorotoluene with 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol and for the mixture toluene with 3-methyl-1-butanol.

Experimental Section

Excess volumes were measured directly using the dilatometer described by Rao and Naidu (*3*). The mixing cell contained two bulbs of different capacities which were connected through a U-tube with mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.), and the other end of the second bulb was fitted with a ground-glass stopper. Four dilatometers of this type were used to cover the whole range of composition of the mixture studied. The composition of each mixture was determined by direct weighing. The dilatometer along with its contents was placed in a thermostat bath. The dilatometer was kept in the thermostat till it attained the temperature of the bath. The position of the constant liquid level was read relative to a reference mark on the capillary tube with the help of the traveling microscope. The dilatometer was removed from the bath, and the contents were thoroughly mixed by tilting the apparatus. The position of the liquid level relative to the reference mark was again read. The excess volumes were accurate to ±0.003 $cm^3\ mol^{-1}$.

Isentropic compressibilities were computed from measured sound speed data, and the density was calculated from the excess volumes.

The ultrasonic speed of sound was measured with a single-crystal interferometer at 4 MHz, and the results were accurate to ±0.15%. All the measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01 K.

Purification of Materials. All alcohols were purified by the methods described by Vogel (*4*). The alcohols were dried by refluxing with fused calcium oxide and finally distilled using a fractionating column.

Table I. Densities (ρ) of Pure Components at 303.15 K

component	$\rho/(g\ cm^{-3})$ lit. (*5*)	present study	accuracy
2-propanol	0.776 90	0.776 85	±0.000 05
2-methyl-1-propanol	0.794 37	0.794 34	±0.000 03
3-methyl-1-butanol	0.801 79	0.801 82	±0.000 03
toluene	0.857 70	0.857 76	±0.000 06

Table II. Excess Volumes (V^E) for the Binary Mixtures of *m*-Chlorotoluene (1) with Isoalcohols (2) at 303.15 K

x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$
m-Chlorotoluene (1) + 2-Propanol (2)					
0.1139	−0.055	0.3988	0.032	0.6680	0.160
0.2421	−0.040	0.5299	0.096	0.7423	0.182
0.3201	−0.010	0.5813	0.126	0.8186	0.172
m-Chlorotoluene (1) + 2-Methyl-1-propanol (2)					
0.1263	−0.022	0.3981	0.065	0.6138	0.139
0.1769	−0.010	0.4500	0.082	0.7176	0.153
0.2792	0.020	0.5449	0.120	0.7965	0.150
m-Chlorotoluene (1) + 3-Methyl-1-butanol (2)					
0.1144	−0.009	0.3864	0.049	0.6977	0.127
0.2384	0.003	0.4981	0.084	0.7951	0.125
0.2959	0.022	0.5722	0.105	0.8528	0.120
Toluene (1) + 3-Methyl-1-butanol (2)					
0.1364	0.042	0.3986	0.142	0.5931	0.185
0.2444	0.090	0.4938	0.169	0.6701	0.190
0.3320	0.112	0.5299	0.178	0.7698	0.177
				0.8697	0.136

The purity of the samples was checked by comparing the measured densities of the compounds with those reported in the literature (*5, 6*). Densities were determined with a bicapillary-type pycnometer which offered an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature (*5*) are given in Table I.

The purity of *m*-chlorotoluene was checked by GLC. The GLC system included a 1.5-μm capillary column, SE-30 (stationary phase, poly(methylsilane)), 2 m in length, and helium was the carrier gas. The system included an ECD (electron capture detector).

Results and Discussion

Excess volumes of mixtures of *m*-chlorotoluene (1) with 2-propanol (2), 2-methyl-1-propanol (2), and 3-methyl-1-butanol (2) are given in Table II. The results are also shown

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Table III. Standard Deviations $\sigma(V^E)$ and Values of the Constants from Redlich and Kister Equation 1 and Hwang et al. Equation 2

	eq 1				eq 2			
	a_0	a_1	a_2	$\sigma(V^E)/(\mathrm{cm^3\ mol^{-1}})$	b_0	b_1	b_2	$\sigma(V^E)/(\mathrm{cm^3\ mol^{-1}})$
m-chlorotoluene + 2-propanol	0.3426	1.1852	0.0975	0.006	0.3124	1.5333	−1.2807	0.003
m-chlorotoluene + 2-methyl-1-propanol	0.4204	0.7996	0.0193	0.004	0.412	0.9829	−0.9184	0.003
m-chlorotoluene + 3-methyl-1-butanol	0.3313	0.6825	0.1971	0.005	0.2661	1.0749	−0.5481	0.003
toluene + 3-methyl-1-butanol	0.6754	0.5364	0.1870	0.005	0.6159	0.8795	−0.3982	0.003

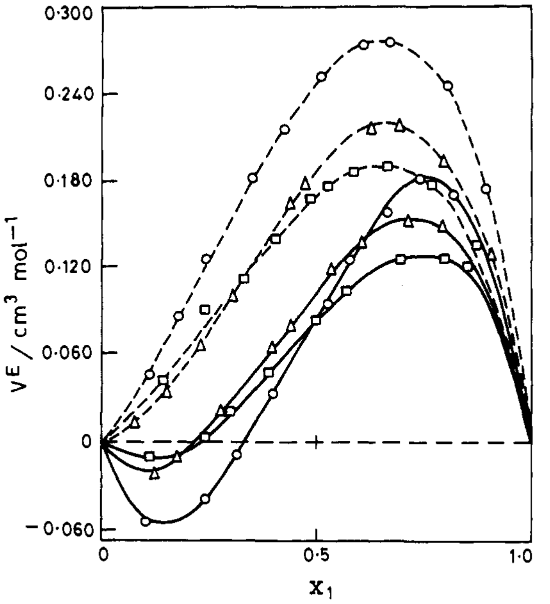

Figure 1. V^E plotted against the mole fraction (x_1) of *m*-chlorotoluene at 303.15 K (—) for *m*-chlorotoluene (1) (○) + 2-propanol (2), (△) + 2-methyl-1-propanol (2), and (□) + 3-methyl-1-butanol (2) and (- - -) for toluene (1) (○) + 2-propanol (2), (△) + 2-methyl-1-propanol (2), and (□) + 3-methyl-1-butanol (2).

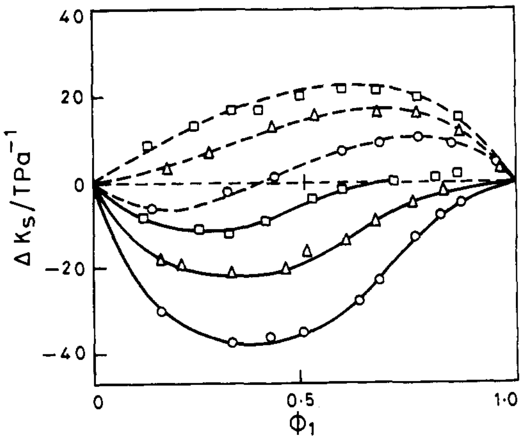

Figure 2. Δk_s plotted against the volume fraction (ϕ_1) of *m*-chlorotoluene at 303.15 K (—) for *m*-chlorotoluene (1) (○) + 2-propanol (2), (△) + 2-methyl-1-propanol (2), and (□) + 3-methyl-1-butanol (2) and (- - -) for toluene (1) (○) + 2-propanol (2), (△) + 2-methyl-1-propanol (2), and (□) + 3-methyl-1-butanol (2).

in Figure 1 along with those for toluene with the corresponding isoalcohols. The V^E results were fitted by the least-squares method to the polynomial proposed by Redlich and Kister (*7*):

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = [x_1x_2(a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{1}$$

where x_1 and x_2 denote the mole fractions of components 1 and 2 and a_0, a_1, and a_2 are constants.

Table IV. Volume Fractions (ϕ_1), Densities (ρ), Speed of Sound (u), Isentropic Compressibilities (k_s), and the Deviation in Isentropic Compressibilities (Δk_s) of *m*-Chlorotoluene with Isoalcohols at 303.15 K

ϕ_1	$\rho/(\mathrm{g\ cm^{-3}})$	$u/(\mathrm{m\ s^{-1}})$	$k_s/\mathrm{TPa^{-1}}$	$\Delta k_s/\mathrm{TPa^{-1}}$
	m-Chlorotoluene (1) + 2-Propanol (2)			
0.0000	0.776 85	1126	1015	
0.1649	0.824 96	1153	912	30
0.3292	0.872 18	1174	832	37
0.4197	0.897 98	1185	793	36
0.5047	0.922 08	1197	757	35
0.6339	0.958 73	1215	707	28
0.6808	0.971 97	1220	691	23
0.7555	0.993 23	1228	668	13
0.8157	1.010 38	1238	646	8
0.8739	1.027 29	1249	624	5
1.0000	1.065 24	1280	573	
	m-Chlorotoluene (1) + 2-Methyl-1-propanol (2)			
0.0000	0.794 34	1172	916	
0.1555	0.836 65	1189	845	18
0.2149	0.852 64	1194	823	19
0.3303	0.883 66	1203	782	21
0.4572	0.917 62	1214	739	20
0.5103	0.931 85	1217	725	16
0.6039	0.956 88	1226	695	14
0.6693	0.974 42	1231	677	9
0.7639	0.999 92	1241	649	5
0.8329	1.018 63	1250	628	2
1.0000	1.065 24	1280	573	
	m-Chlorotoluene (1) + 3-Methyl-1-butanol (2)			
0.0000	0.801 82	1220	838	
0.1225	0.834 16	1226	798	8
0.2528	0.868 39	1231	760	11
0.3124	0.883 93	1233	744	11
0.4050	0.908 12	1235	722	9
0.5176	0.937 47	1237	697	4
0.5911	0.956 66	1241	679	2
0.7139	0.988 78	1248	649	0
0.8075	1.013 45	1256	625	1
0.8623	1.027 92	1262	611	2
1.0000	1.065 24	1280	573	
	Toluene (1) + 3-Methyl-1-butanol (2)			
0.0000	0.801 82	1220	838	
0.1337	0.808 99	1221	829	9
0.2401	0.814 58	1224	819	13
0.3269	0.819 26	1227	811	17
0.3931	0.822 74	1231	802	17
0.4880	0.827 83	1234	793	20
0.5875	0.833 26	1240	781	22
0.6650	0.837 55	1245	770	21
0.7657	0.843 27	1253	755	20
0.8671	0.849 25	1264	737	15
1.0000	0.857 76	1287	704	

The V^E results were also fitted to the empirical equation recently proposed by Hwang et al. (*8*):

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x_1x_2(b_0 + b_1x_1^3 + b_2x_2^3) \tag{2}$$

where x_1 and x_2 represent the mole fractions of components 1 and 2 and b_0, b_1, and b_2 are constants. The values of the two sets of the constants are given in Table III along with standard deviations. The standard deviation values given under Table III point out that the Hwang et al. equation gives a better fit of the experimental data.

Table V. Standard Deviation, $\sigma(\Delta k_s)$, and values of the Constants Obtained by the Redlich and Kister Equation

system	b_0	b_1	b_2	$\sigma(\Delta k_B)$/TPa^{-1}
m-chlorotoluene + 2-propanol	−139.4	115.8	14.5	2
m-chlorotoluene + 2-methyl-1-propanol	−69.5	83.9	−6.4	1
m-chlorotoluene + 3-methyl-1-butanol	−22.7	61.7	−13.6	1
toluene + 3-methyl-1-butanol	80.4	35.7	42.9	1

Speed of sound (u) results and densities (ρ) are presented in Table IV. The density of the mixture was calculated using the relation

$$\rho = \frac{x_1M_1 + x_2M_2}{x_1V_1^\circ + x_2V_2^\circ + V^E} \qquad (3)$$

where M_i and V_i are the molar mass and molar volume of component i.

The isentropic compressibility k_s and the deviation in isentropic compressibility Δk_s are calculated using the equations

$$k_s = u^{-2}\rho^{-1} \qquad (4)$$

$$\Delta k_s = k_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \qquad (5)$$

$$\phi_1 = \frac{x_1V_1^\circ}{x_1V_1^\circ + x_2V_2^\circ} \qquad (6)$$

where k_s, $k_{s,1}$, and $k_{s,2}$ are the isentropic compressibilities of a mixture and pure components 1 and 2, respectively. ϕ_1 and ϕ_2 are the volume fractions of the components. The values of k_s and Δk_s are also given in Table IV. The results are shown in Figure 2 along with those for mixtures of toluene with the corresponding isoalcohols.

The isothermal compressibility results also have been fitted to an empirical equation of the form

$$\Delta k_s = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \qquad (7)$$

The values of the constants b_0, b_1, and b_2 are included in Table V along with the standard deviations $\sigma(\Delta k_s)$.

The results in Table II and the curves in Figure 1 show that the excess volume exhibits inversion in sign in all mixtures of *m*-chlorotoluene with the three isoalcohols. However, V^E is positive over the whole range of composition in mixtures of toluene with the three isoalcohols. This shows that replacement of toluene by *m*-chlorotoluene promotes a structure-making effect in mixtures rich in isoalcohols.

The deviation in isentropic compressibility included in Table IV and graphically represented in Figure 2 shows that replacement of toluene by *m*-chlorotoluene decreases the algebraic value of deviation. This also suggests that structural effects become dominant in mixtures which include *m*-chlorotoluene.

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