Excess Volumes of Binary Mixtures of *p*-Chlorotoluene with 1-Alkanols (C_3–C_7) and Ternary Mixtures with *n*-Hexane and 1-Pentanol, 1-Hexanol, or 1-Heptanol at 303.15 K

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Excess molar volumes V^E of *p*-chlorotoluene with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol have been measured at 303.15 K. V^E is negative in mixtures rich in alkanol and positive in those rich in *p*-chlorotoluene. A comparison of these results with those for mixtures of the alkanols with toluene showed that the algebraic values of V^E are smaller in the former group. V^E for three ternary mixtures were also measured at 303.15 K. *p*-Chlorotoluene and *n*-hexane served as common components in the mixtures. 1-Pentanol, 1-hexanol, and 1-heptanol were noncommon components. V^E is negative at all the investigated compositions. The experimental results were also compared with those predicted by empirical equations using the binary data.

Introduction

A survey of the literature showed that excess molar volumes V^E of binary mixtures of toluene with 1-alkanols have been measured at 303.15 K (*1*). However, no attempt has been made to measure V^E of binary mixtures of *p*-chlorotoluene with 1-alkanols. Introduction of a chloro group into the toluene molecule may influence both the sign and magnitude of V^E. Hence, we report here new experimental data for five binary mixtures of *p*-chlorotoluene with 1-alkanols, and we also report V^E for three ternary mixtures which included *p*-chlorotoluene and *n*-hexane as common components and the three 1-alkanols as noncommon components. The ternary data have been used to check the capability of predictive expressions (*2*).

Experimental Section

Apparatus and Procedure. Excess volumes of binary and ternary mixtures were measured by using the single composition per loading type dilatometers described by Rao and Naidu (*3*) and Naidu and Naidu (*4*), respectively. The binary data were obtained in a two-limbed dilatometer. This was made up of two bulbs of different capacities that were connected through a U-tube. Mercury in the U-tube separates the two bulbs. One end of the first bulb was fitted with a capillary (i.d. 1.0 mm), and the other end of the second bulb was closed with a ground-glass stopper. Excess volumes of ternary mixtures have been determined using a three-limbed dilatometer. The three limbs, which differ in their capacities, were connected through a W-tube. Mercury is used in the bottom to separate the three components. One of the bulbs was fitted with a capillary, and the other two were closed with ground-glass stoppers. Four dilatometers of the aforesaid types were used to cover the entire range of composition. The composition of each mixture was determined directly by weighing. All weights were corrected for buoyancy. The measurements were made employing a thermostatic bath maintained to ±0.01 K. The excess volumes measured were accurate to ±0.003 $cm^3 mol^{-1}$.

Table I. Densities, ρ, of Pure Liquids at 303.15 K

component	ρ/(g cm^{-3})	
	this work	literature
p-chlorotoluene	1.065 14[a]	1.065 10[a]
1-propanol	0.795 62	0.795 67
1-butanol	0.802 03	0.802 06
1-pentanol	0.807 62	0.807 64
1-hexanol	0.812 05	0.812 01
1-heptanol	0.815 72	0.815 74
n-hexane	0.650 63	0.650 70

[a] At 298.15 K.

Table II. Excess Molar Volumes V^E for Binary Mixtures of *p*-Chlorotoluene (1) + 1-Alkanols (2) as a Function of Mole Fraction x_1 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})
		1-Propanol			
0.0656	−0.070	0.3421	−0.129	0.7416	0.028
0.1231	−0.121	0.4549	−0.094	0.8450	0.041
0.1628	−0.139	0.5521	−0.046		
0.2840	−0.142	0.6164	−0.018		
		1-Butanol			
0.1023	−0.066	0.3841	−0.052	0.7068	0.025
0.1332	−0.088	0.4421	−0.040	0.7965	0.020
0.2341	−0.091	0.4900	−0.016		
0.3288	−0.076	0.5854	0.010		
		1-Pentanol			
0.0892	−0.066	0.3862	−0.052	0.7431	0.030
0.1535	−0.091	0.4721	−0.021	0.8174	0.022
0.2058	−0.086	0.5711	0.008		
0.2835	−0.080	0.6187	0.015		
		1-Hexanol			
0.1023	−0.040	0.4421	−0.060	0.7406	0.041
0.1576	−0.069	0.5299	−0.031	0.8819	0.062
0.2413	−0.083	0.6120	−0.008		
0.3518	−0.081	0.6707	0.016		
		1-Heptanol			
0.0812	−0.062	0.4358	−0.051	0.7793	0.041
0.1692	−0.096	0.5233	−0.024	0.8573	0.046
0.2587	−0.092	0.6102	0.004		
0.3812	−0.070	0.7000	0.025		

Materials. All the chemicals used were of analytical grade. *p*-Chlorotoluene was purified by the method described by Vogel (*5*). Alkanols and *n*-hexane were purified by the methods described by Riddick and Bunger (*6*). *p*-Chlorotoluene (Fluka) was washed successively with an aqueous 10% solution of sodium hydroxide, concentrated sulfuric acid,

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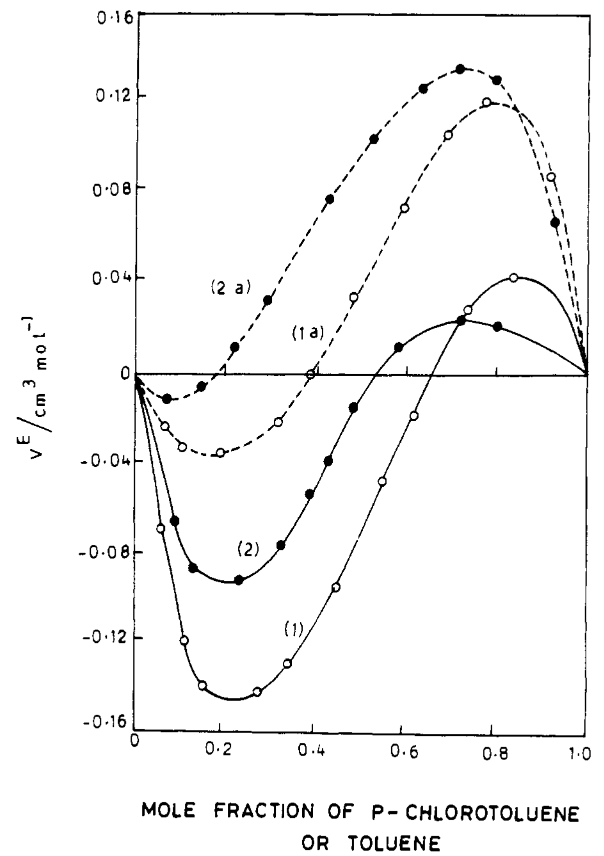

Figure 1. Excess molar volumes V^E at 303.15 K plotted against the mole fraction x_1 for (1) *p*-chlorotoluene + 1-propanol, (2) *p*-chlorotoluene + 1-butanol, (1a) toluene + 1-propanol, and (2a) toluene + 1-butanol.

and water. It was dried with anhydrous calcium chloride, decanted, and distilled. 1-Propanol (BDH) was refluxed over freshly ignited calcium oxide for 4 h and then fractionated. 1-Butanol (S.D. Fine Chemicals) was refluxed over freshly ignited calcium oxide for 6 h and then distilled employing a fractionating column. 1-Pentanol (Fluka) and 1-hexanol (Merck) were dried over Drierite and fractionally distilled. 1-Heptanol (S.D. Fine Chemicals) was fractionated. *n*-Hexane (BDH) was shaken several times with concentrated sulfuric acid, then with a 0.1 N solution of potassium permanganate in 10% sulfuric acid, and finally with a 0.1 N solution of permanganate in 10% sodium hydroxide. The sample was washed with water, dried over sodium wire, and distilled.

The purities of the samples were checked by comparing the measured densities of the components with those reported in the literature (*7, 8*). Densities of pure liquids were measured with a bicapillary pycnometer which offered an accuracy of ±0.000 02 g cm^{-3}. The measured densities and the literature data are presented in Table I.

Results and Discussion

The experimental V^E data for five binary mixtures are given in Table II. The results are also graphically presented along with those for mixtures of the 1-alkanols with toluene in Figures 1–3.

The results in Table II show that V^E exhibits inversion in sign in the mixtures of *p*-chlorotoluene with all the 1-alkanols. However, the algebraic values of V^E decrease when toluene is replaced by *p*-chlorotoluene.

The measured V^E data for ternary mixtures of *p*-chlorotoluene and *n*-hexane with 1-pentanol, 1-hexanol, and 1-heptanol are given in Table III.

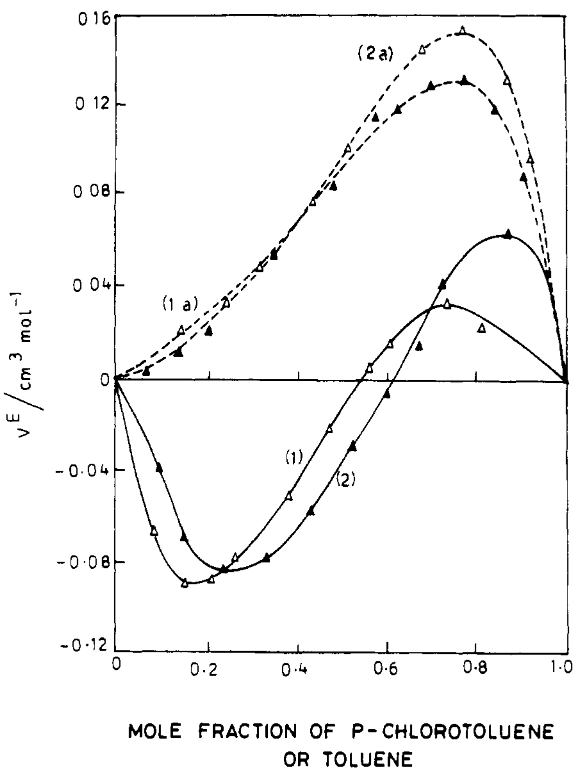

Figure 2. Excess molar volumes V^E at 303.15 K plotted against the mole fraction x_1 for (1) *p*-chlorotoluene + 1-pentanol, (2) *p*-chlorotoluene + 1-hexanol, (1a) toluene + 1-pentanol, and (2a) toluene + hexanol.

The results in Table III show that the ternary excess volume is negative at all the investigated compositions in the three mixtures.

The binary V^E data were fitted to the polynomial

$$V^E_{\mathrm{calcd}}/(\mathrm{cm^3\ mol^{-1}}) = x_1(1 - x_1)[a + b(2x_1 - 1) + c(2x_1 - 1)^2] \quad (1)$$

where a, b, and c are adjustable parameters and x_1 is the mole fraction of *p*-chlorotoluene. The values of the parameters, computed by the least-squares method, are given in Table IV along with the standard deviation $\sigma(V^E)$:

$$\sigma(V^E) = [(V^E_{\mathrm{calcd}} - V^E_{\mathrm{exptl}})^2/(n - p)]^{1/2} \quad (2)$$

where n is the number of experimental data and p is the number of parameters.

Similarly, the ternary molar excess volumes V^E were fitted to the polynomial

$$V^E = V^E_{12} + V^E_{13} + V^E_{23} + x_1x_2x_3[A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2] \quad (3)$$

where V^E_{ij} is the molar excess volume of the binary mixture $i + j$, as given by Eq 1, and x_1, x_2, and x_3 are, respectively, the mole fractions of *p*-chlorotoluene, 1-alkanol, and *n*-hexane. The values of the adjustable parameters A, B, and C obtained by the least-squares method are given in Table V along with the standard deviations $\sigma(V^E)$.

The binary V^E data of *p*-chlorotoluene with *n*-hexane and of *n*-hexane with 1-alkanols were taken from the literature (*9, 10*). The least-squares parameters for these systems are given in Table IV. The excess volume data for the mixtures of *n*-hexane with 1-alkanols are graphically represented in Figure 4.

A comparison between experimental excess volumes and those predicted by Redlich-Kister, Kohler, and Tsao-Smith

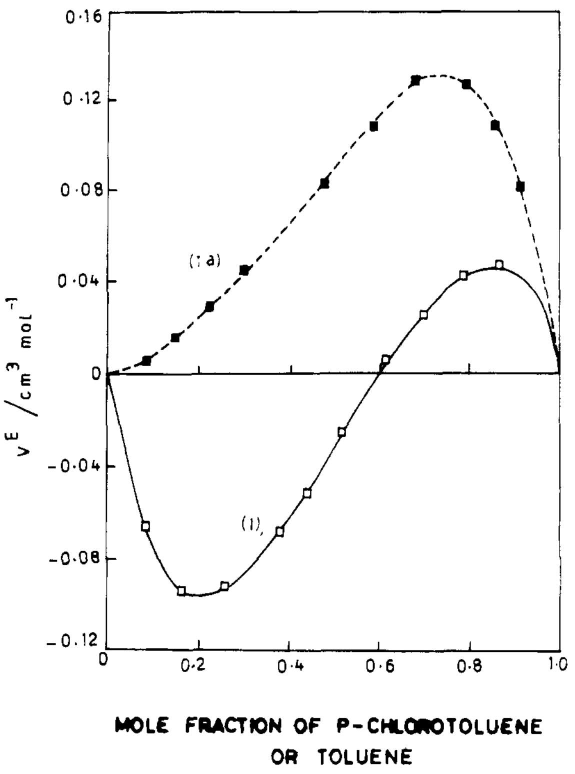

Figure 3. Excess molar volumes V^E at 303.15 K plotted against the mole fraction x_1 for (1) *p*-chlorotoluene + 1-heptanol and (1a) toluene + 1-heptanol.

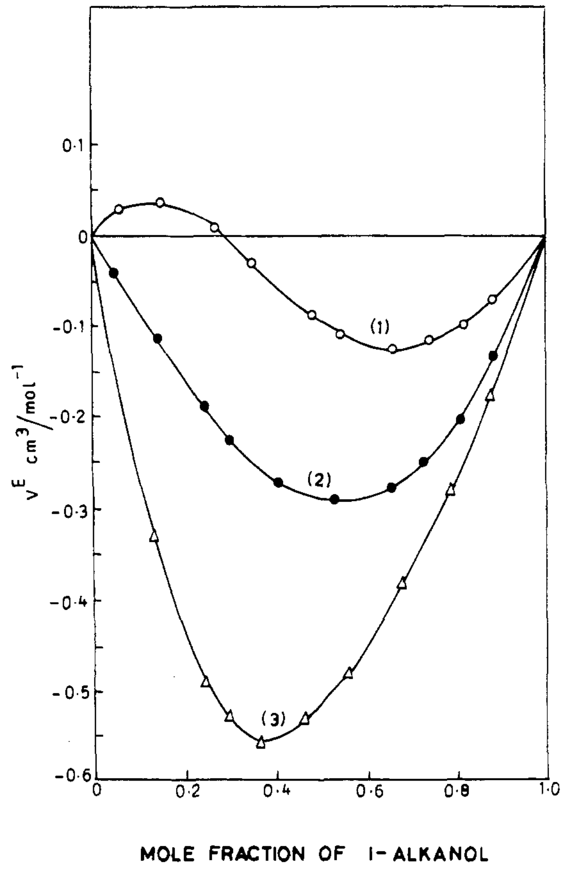

Figure 4. Excess molar volumes V^E at 303.15 K plotted against the mole fraction x_1 for (1) hexane + 1-pentanol, (2) hexane + 1-hexanol, and (3) hexane + 1-heptanol.

points out that the former data differ from the latter to a considerable degree in all mixtures. Hence, it may be concluded that the predictive expressions give only a crude estimate of V^E in the mixtures.

Table III. Excess Molar Volumes V^E of Ternary Systems: *p*-Chlorotoluene (1) + 1-Alkanol (2) + *n*-Hexane (3)

x_1	x_3	$V^E/(cm^3\ mol^{-1})$	x_1	x_3	$V^E/(cm^3\ mol^{-1})$
		1-Pentanol			
0.1744	0.6382	−0.216	0.2120	0.2934	−0.271
0.1884	0.5813	−0.224	0.1600	0.2811	−0.244
0.1489	0.5840	−0.195	0.1827	0.2011	−0.246
0.1291	0.5357	−0.189	0.1884	0.1331	−0.212
0.1880	0.4152	−0.241	0.1989	0.0997	−0.199
		1-Hexanol			
0.1698	0.5889	−0.305	0.1648	0.2828	−0.297
0.2514	0.5953	−0.363	0.1983	0.2063	−0.295
0.1897	0.6067	−0.319	0.1958	0.1990	−0.291
0.1738	0.5198	−0.306	0.1961	0.1950	−0.291
0.1806	0.3689	−0.306	0.1331	0.1148	−0.198
		1-Heptanol			
0.2136	0.6258	−0.356	0.1980	0.2511	−0.477
0.2309	0.5689	−0.337	0.1820	0.2316	−0.462
0.1551	0.5920	−0.405	0.2050	0.1609	−0.474
0.1538	0.5426	−0.414	0.1348	0.1410	−0.339
0.1449	0.4684	−0.433	0.1116	0.1395	−0.299

Table IV. Values of Parameters *a*, *b*, and *c* (Equation 1) and Standard Deviations $\sigma(V^E)$ (Equation 2) at 303.15 K

system	*a*	*b*	*c*	$\sigma(V^E)/(cm^3\ mol^{-1})$
p-chlorotoluene + 1-propanol	−0.2865	0.9502	−0.1150	0.004
1-butanol	−0.0725	0.5915	−0.3773	0.006
1-pentanol	−0.0512	0.5996	−0.4199	0.003
1-hexanol	−0.1956	0.6900	0.4253	0.005
1-heptanol	−0.1276	0.7385	−0.1088	0.004
n-hexane	−2.2284	−0.1913	−0.6959	0.005
1-pentanol + *n*-hexane	−0.3630	−0.7090	0.3910	0.003
1-hexanol	−1.1620	−0.2690	0.0640	0.003
1-heptanol	−2.0460	0.9160	−0.3350	0.007

Table V. Values of Parameters *A*, *B*, and *C* (Equation 3) and Standard Deviations $\sigma(V^E)$ (Equation 2) at 303.15 K

system	$A/(cm^3\ mol^{-1})$	$B/(cm^3\ mol^{-1})$	$C/(cm^3\ mol^{-1})$	$\sigma(V^E)/(cm^3\ mol^{-1})$
p-chlorotoluene + 1-pentanol + *n*-hexane	−0.038	−23.764	−18.469	0.002
1-hexanol	2.604	−22.269	−160.719	0.001
1-heptanol	3.611	−89.106	−297.188	0.002

Glossary

a,*b*,*c*	binary constants in eq 1
A,*B*,*C*	ternary constants in eq 3
$\sigma(V^E)$	standard deviation, eq 2, $cm^3\ mol^{-1}$
V	molar volume, $cm^3\ mol^{-1}$
V^E_{ij}	molar excess volume of any two components in a ternary mixture
x	mole fraction

Subscripts

1,2,3	components

Superscript

E	excess property

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Received for review November 14, 1991. Revised June 15, 1992. Accepted August 25, 1992.