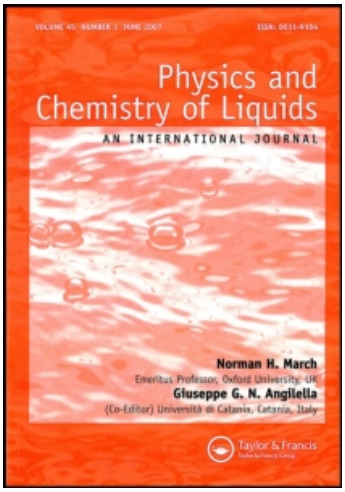

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Volumetric Behaviour of an Aromatic Hydrocarbon with 1-Chlorobutane

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Volumetric Behaviour of an Aromatic Hydrocarbon with 1-Chlorobutane

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Excess volumes (V^E) for the binary mixtures of 1-chlorobutane with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, nitrobenzene, chlorobenzene and bromobenzene have been measured directly by dilatometric method at 303.15 K. Values of V^E are negative in all eight binary liquid mixtures. The algebraic values of V^E increases from nitrobenzene to benzene. The results are ascribed to interactions between unlike molecules.

Key Words: Polarizability, dipole interaction.

1 INTRODUCTION

A survey of the literature has shown that many attempts have been made to measure excess volumes for the mixtures of 1-chlorobutane with *n*-alcohols,[1] alkanes,[2] and haloalkane with acids[3] and hydrocarbons.[4,5] But no attempt has been made to measure the excess volume for the binary mixtures of chlorobutane with benzene and substituted benzenes. Hence we studied the excess volume of chlorobutane with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and nitrobenzene at 303.15 K. The experimental results are analysed in terms of dipolar effects and size differences.

2 EXPERIMENTAL

Excess volumes were measured with the dilatometer as described by Rao and Naidu.[6] The mixing cell contained two bulbs of different

capacities which were connected through a U-tube having mercury to separate the two components. One end of the bulb was fitted with a capillary (1 mm id) and the other end of the second bulb was fixed with a ground glass stopper. The excess volumes were accurate to $\pm$ 0.003 cm^3 mol^{-1}.

Chlorobutane was purified by refluxing with concentrated sulphuric acid, washing several times with water, drying over two portions of calcium chloride and finally fractionated. Benzene and substituted benzenes were purified by standard methods described in the literature.[7] The purity of the samples was checked by comparing the measured densities with those reported in the literature.[8] Densities were determined with a bicapillary type pycnometer with accuracy of 2 parts in 10^5. The densities of the pure components are given in Table 1.

Table 1 Densities of pure components at 303.15 K.

Component	Density (ρ)/g cm^3 mol^{-1}	
	Present work	Literature
1-Chlorobutane	0.87560	0.87549
Benzene	0.86847	0.86850
Toluene	0.85764	0.85770
o-Xylene	0.87158	0.87160
m-Xylene	0.85552	0.85551
p-Xylene	0.85226	0.85230
Chlorobenzene	1.09547	1.09550
Bromobenzene	1.48146	1.48150
Nitrobenzene	1.19344	1.19341

3 RESULTS AND DISCUSSION

The experimental excess volumes for the mixtures of chlorobutane with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and nitrobenzene at 303.15 K are given in Table 2. The dependence of V^E on mole fraction is represented graphically in Figure 1. The values are fitted to an empirical smoothing equation of the form

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (1)$$

where x_1 denote mole fraction of chlorobutane, a_0, a_1 and a_2 are empirical constants. The values of the constants, obtained by the

Table 2 Excess volumes, V^E ($cm^3\ mol^{-1}$) of 1-chlorobutane with aromatic substituted hydrocarbons at 303.15 K (x_1 is mole fraction of 1-chlorobutane).

x_1	V^E	x_1	V^E	x_1	V^E	x_1	V^E
1-Chlorobutane + benzene		1-Chlorobutane + toluene		1-Chlorobutane + *o*-xylene		1-Chlorobutane + chlorobenzene	
0.1119	−0.030	0.0905	−0.082	0.0916	−0.088	0.0933	−0.161
0.2301	−0.052	0.1617	−0.115	0.1845	−0.148	0.1537	−0.225
0.3517	−0.067	0.2333	−0.140	0.2529	−0.184	0.2060	−0.260
0.4493	−0.075	0.3187	−0.154	0.3600	−0.224	0.3347	−0.298
0.4894	−0.077	0.4855	−0.167	0.4821	−0.240	0.4288	−0.308
0.5452	−0.079	0.5800	−0.160	0.5537	−0.238	0.5391	−0.302
0.6202	−0.078	0.6699	−0.145	0.6620	−0.214	0.6443	−0.286
0.7220	−0.070	0.7798	−0.116	0.7714	−0.168	0.7430	−0.260
0.8479	−0.048	0.8847	−0.070	0.8548	−0.116	0.8373	−0.210
0.9283	−0.032	0.9400	−0.040	0.9070	−0.080	0.9200	−0.126
1-Chlorobutane + *m*-xylene		1-Chlorobutane + *p*-xylene		1-Chlorobutane + bromobenzene		1-Chlorobutane + nitrobenzene	
0.0800	−0.095	0.1506	−0.098	0.0921	−0.137	0.1462	−0.270
0.1508	−0.140	0.2405	−0.152	0.1482	−0.206	0.2296	−0.346
0.2992	−0.167	0.3171	−0.184	0.2490	−0.302	0.3066	−0.390
0.3882	−0.176	0.3933	−0.203	0.3412	−0.369	0.3901	−0.430
0.5011	−0.166	0.4745	−0.208	0.4766	−0.424	0.4536	−0.450
0.5795	−0.153	0.5256	−0.205	0.5400	−0.427	0.5311	−0.475
0.6400	−0.140	0.6029	−0.190	0.6391	−0.408	0.6400	−0.488
0.7788	−0.103	0.6830	−0.160	0.7486	−0.345	0.7629	−0.460
0.8661	−0.070	0.7800	−0.114	0.8299	−0.270	0.8374	−0.390
0.9200	−0.045	0.8752	−0.054	0.9266	−0.134	0.9000	−0.290

method of least squares are given in Table 3 along with the standard deviation $\sigma(V^E)$.

The values of V^E are negative for all the systems over the whole mole fraction range of composition. The observed V^E values may be explained in terms of the following effects: (a) mutual loss of dipolar association due to the addition of the second component, (b) contributions due to difference in size and shape of the components, (c) dipole-π interactions and (d) dipole–dipole interaction. The observed excess volume is a resultant contribution of the above four effects. The negative V^E values indicate that the latter two effects are dominant over the former effects in all the systems. The algebraic values of V^E for the eight binary mixtures fall in order:

benzene > toluene > *m*-xylene > *p*-xylene > *o*-xylene > chlorobenzene > bromobenzene > nitrobenzene.

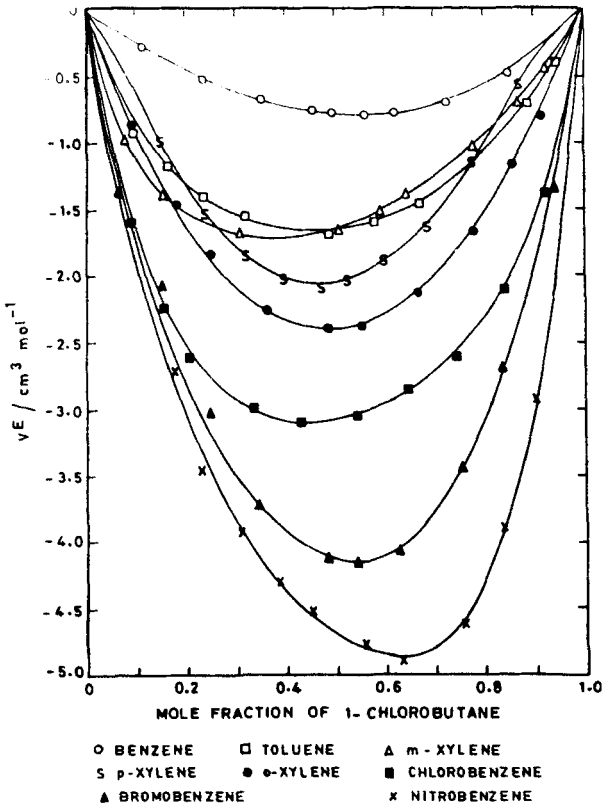

Figure 1 The values of V^E against Mole fraction for the binary mnixtures of 1-Chlorobutane with aromatic hydrocarbons at 303.15 K. ○—Benzene, □—Toluene, △—*m*-Xylene, S—*p*-Xylene, ●—*o*-Xylene, ■—Chlorobenzene, ▲—Bromobenzene, × —Nitrobenzene.

This order is in agreement with the polarizability[7] value of the components.

The methyl group in toluene and xylenes enhances the π-electrons density in aromatic nucleus due to hyperconjugation effect. Therefore dipole-interaction may be predominant in the mixtures of chlorobutane with benzene, toluene and xylenes.

The large negative values of V^E in the other three mixtures of chlorobutane with chlorobenzene, bromobenzene and nitrobenzene may be attributed to the existence of strong specific interactions of the type dipole-dipole interaction between unlike molecules. In contrast the values of V^E for mixtures of chlorobutane with alkanes[2] are highly

Table 3 Values of the parameters a_0, a_1 and a_2 of the Eq. (1) and the standard deviation of $\sigma(V^E)$ at 303.15 K

System	a_0	a_1	a_2	$\sigma(V^E)$
		$cm^3\ mol^{-1}$		
1-Chlorobutane + benzene	−0.2974	−0.0681	−0.01272	0.003
1-Chlorobutane + toluene	−0.6574	0.1459	−0.2545	0.004
1-Chlorobutane + *m*-xylene	−0.6545	0.3645	−0.4282	0.004
1-Chlorobutane + *p*-xylene	−0.8396	0.1564	0.3689	0.003
1-Chlorobutane + *o*-xylene	−0.9545	0.0537	−0.0420	0.002
1-Chlorobutane + chlorobenzene	−1.2038	0.1543	−0.9124	0.004
1-Chlorobutane + bromobenzene	−1.7093	−0.2050	−0.1133	0.003
1-Chlorobutane + nitrobenzene	−1.8575	−0.5743	−1.40427	0.002

positive, with alcohols[1] are positive and the present work chlorobutane with benzene and substituted benzenes are negative.

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