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Excess Volumes for Binary Liquid Mixtures of 1-Chlorobutane with Normal Alkanes

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Abstract

Excess volumes for binary mixtures of 1-chlorobutane with hexane, heptane, octane and nonane were measured dilatometrically at 303·15 K. Excess volumes are positive over the entire range of composition in the four mixtures. Further, it is observed that increase in chain length increases the magnitude of the excess function.

Introduction

New experimental data for the excess volumes of four binary liquid mixtures are reported. The mixtures include 1-chlorobutane as a common component and a homologous series of normal alkanes (from C_6 to C_9) as non-common components. The experimental results are analysed in terms of dipolar effects and size differences. The effect of chain length on the excess volume has also been examined.

Experimental

Excess volumes for the binary liquid mixtures were measured by using a single composition per loading type of dilatometer described by Rao and Naidu.[1] Four dilatometers with different capacities were used to cover the entire mole fraction range. The dilatometers were kept in a thermostat maintained to ±0·01 K. The values of V^E were accurate to ±0·003 cm^3 mol^{-1}.

1-Chlorobutane was refluxed with concentrated sulfuric acid, washed several times with water, dried over two portions of calcium chloride and finally fractionated.[2] Hexane (B.D.H.) 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 fractionally distilled.[3] Heptane (B.D.H.) was shaken twice with concentrated sulfuric acid, washed with water, dilute potassium hydroxide solution and again with water. The sample was kept over potassium hydroxide pellets and finally fractionated.[4] Octane (Veb.) was passed through silica gel and then fractionated.[5] Nonane (Veb.) was fractionally distilled. All fractionations were carried out on a column that contained 20–30 theoretical plates. The purity of the samples was checked by comparing the measured densities with those reported in the literature.[6] The data are given in Table 1.

[1] Rao, M. V. P., and Naidu, P. R., *Can. J. Chem.*, 1976, **54**, 2280.
[2] Smyth, C. P., and McAlpine, K. B., *J. Chem. Phys.*, 1935, **3**, 347.
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[4] Herold, W., and Wolf, K. L., *Z. Phys. Chem. (Leipzig) B*, 1932, **18**, 265.
[5] Pomerantz, P., and Fookson, A., *J. Res. Nat. Bur. Stand.*, 1954, **52**, 59.
[6] Timmermans, J., 'Physico-Chemical Constants of Pure Organic Compounds' (Elsevier: Amsterdam 1950).

Table 1. Densities (in g cm^{-3}) of the pure component liquids at 303·15 K

Liquid	This work	Lit.	Liquid	This work	Lit.
1-Chlorobutane	0·87543	0·87549[A]	octane	0·69457	0·69450[D]
Hexane	0·65064	0·65070[B]	nonane	0·70998	0·70999[C]
Heptane	0·67530	0·67538[C]			

[A] Timmermans, J., and Hennaut-Roland, Mme, *J. Chim. Phys. Phys.-Chim. Biol.*, 1930, **27**, 401.
[B] Dornte, R. W., and Smyth, C. P., *J. Am. Chem. Soc.*, 1930, **52**, 3546.
[C] Bruylants, A., unpublished data.
[D] Quayle, O. R., Day, R. A., and Brown, G. M., *J. Am. Chem. Soc.*, 1944, **66**, 938.

Table 2. Excess volumes for mixtures of 1-chlorobutane (BuCl) and n-alkanes (C_nH_{2n+2})
V^E in cm^3 mol^{-1}. x_1 is the mole fraction of 1-chlorobutane

BuCl + C_6H_{14}		BuCl + C_7H_{16}		BuCl + C_8H_{18}		BuCl + C_9H_{20}	
x_1	V^E	x_1	V^E	x_1	V^E	x_1	V^E
0·0868	0·032	0·0968	0·092	0·1265	0·127	0·1035	0·115
0·1471	0·053	0·1665	0·152	0·1842	0·180	0·1921	0·192
0·2288	0·072	0·2531	0·207	0·2749	0·241	0·2868	0·262
0·3071	0·095	0·3287	0·245	0·3551	0·278	0·3707	0·298
0·4134	0·118	0·4507	0·278	0·4736	0·304	0·5068	0·317
0·5059	0·123	0·5696	0·263	0·5928	0·295	0·5740	0·308
0·5940	0·113	0·6105	0·249	0·6342	0·285	0·6517	0·295
0·6839	0·098	0·7116	0·202	0·7252	0·245	0·7421	0·248
0·7819	0·075	0·8067	0·152	0·8162	0·176	0·8352	0·181
0·9018	0·036	0·9125	0·072	0·9143	0·097	0·9250	0·093

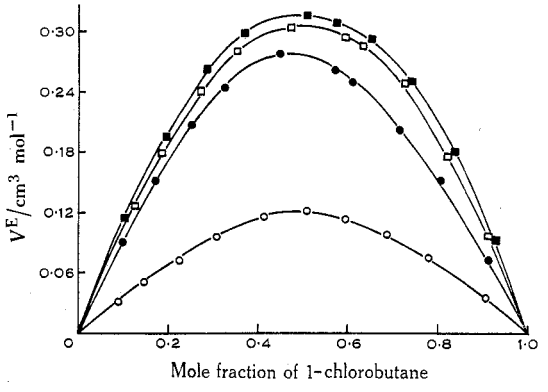

Fig. 1. Mixtures of 1-chlorobutane and
○ n-hexane;
● n-heptane;
□ n-octane;
■ n-nonane
at 303·15 K.

Table 3. Values of parameters for equation (1) and the standard deviation, $\sigma(V^E)$
a_0, a_1, a_2 and $\sigma(V^E)$ in cm^3 mol^{-1}

System	a_0	a_1	a_2	$\sigma(V^E)$
1-Chlorobutane + hexane	0·475	0·005	−0·113	0·004
1-Chlorobutane + heptane	1·090	−0·103	−0·166	0·004
1-Chlorobutane + octane	1·221	0·028	−0·052	0·003
1-Chlorobutane + nonane	1·274	0·051	0·021	0·003

Results and Discussion

The experimental excess volumes for the mixtures of 1-chlorobutane with hexane, heptane, octane and nonane at 303·15 K are presented in Table 2. The dependence of V^E on mole fraction is represented graphically in Fig. 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 and x_2 denote mole fractions of 1-chlorobutane and normal alkanes respectively. a_0, a_1 and a_2 are empirical constants. The values of the constants, obtained by the method of least squares, are given in Table 3 along with the standard deviations, $\sigma(V^E)$.

The experimental excess volumes are positive over the entire range of composition in the four binary mixtures. This may be ascribed to two factors: (i) reduction in the dipolar interaction between molecules of 1-chlorobutane on dilution with normal alkanes and (ii) size differences between unlike molecules. The plots of V^E against mole fraction in Fig. 1 show that the values of V^E for the four mixtures fall in the order:

$$\text{nonane} > \text{octane} > \text{heptane} > \text{hexane}$$

This order suggests that an increase in chain length leads to an increase in positive excess volume. Finally, the effect of chain length is maximum between hexane and heptane.

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