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Excess Volumes of Binary Mixtures of 1,2-Dichlorobenzene with 1-Alkanols (C_4–C_8)

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New experimental data for excess volumes of binary mixtures of 1,2-dichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol have been measured at 303.15 K. V^E is negative in mixtures rich in alcohols and positive in those rich in 1,2-dichlorobenzene. The results have been ascribed to the dominant nature of the structure-making effect of unlike molecules. The results have also been used to show that the structure-making effect becomes pronounced due to the introduction of a second chloro function into the benzene nucleus.

Introduction

A survey of the literature showed that excess volumes of binary mixtures of chlorobenzene with 1-alkanols (*1*) and iso alcohols (*2*) have been measured at 303.15 K. The data were interpreted in terms of strong hydrogen bond interaction between unlike molecules. When a second chloro function is introduced into the benzene nucleus, it may alter both the nature and degree of interaction between the components. We report here new experimental data at 303.15 K for the excess volumes of five binary mixtures. The mixtures included are 1,2-dichlorobenzene + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, and + 1-octanol.

Experimental Section

Excess volumes were measured by using a single composition per loading type dilatometer described by Rao and Naidu (*3*). The dilatometer was made up of two bulbs of different capacities that were connected through a U-tube. Mercury in the U-tube separated the two bulbs. One end of the first bulb was fitted with a capillary outlet, and the opposite end of the second bulb was closed with a ground-glass stopper. Four dilatometers of the aforesaid type 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. Measurements were made employing a thermostatic bath maintained to 303.15 ± 0.01 K. Values of V^E were accurate to ± 0.003 cm^3/mol^{-1}.

Purification of Materials

1,2-Dichlorobenzene, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol were purified by the methods described by Reddick and Bunger (*4*). 1,2-Dichlorobenzene (S.D. Fine Chemicals) was passed through alumina in a 30 × 2 cm column and fractionally distilled. 1-Butanol (S.D. Fine Chemicals) was refluxed over freshly ignited calcium oxide for 6 h and distilled by employing a fractionating column. 1-Pentanol (Fluka AG) and 1-hexanol (Merck) were dried over Drierite and fractionally distilled. 1-Heptanol (S.D. Fine Chemicals) and 1-octanol (SISCO) were fractionated.

The purities of the samples were checked by comparing the measured densities of the components with those reported in the literature (*5*). Densities of pure liquids were measured with a bicapillary pycnometer described by Rao (*6*). The method affords an accuracy of 2 parts in 10^5. The measured densities and the literature data are presented in Table I. The purity of the liquids was further confirmed in terms of GLC single sharp peaks.

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

component	ρ/(g cm^{-3}) this work	 lit.
1,2-dichlorobenzene	1.299 20	1.299 22
1-butanol	0.802 06	0.802 06
1-pentanol	0.807 60	0.807 64
1-hexanol	0.812 05	0.812 01
1-heptanol	0.815 72	0.815 74
1-octanol	0.821 88	0.821 92

Table II. Excess Volumes of 1,2-Dichlorobenzene + 1-Alkanols at 303.15 K

x^a	V^E/(cm^3 mol^{-1})	x^a	V^E/(cm^3 mol^{-1})
	1,2-Dichlorobenzene + 1-Butanol		
0.1000	−0.080	0.6354	−0.050
0.2050	−0.130	0.7342	−0.009
0.3101	−0.151	0.8194	+0.031
0.4333	−0.126	0.9253	+0.035
0.5627	−0.090		
	1,2-Dichlorobenzene + 1-Pentanol		
0.1212	−0.107	0.5904	−0.093
0.1947	−0.141	0.6357	−0.060
0.3888	−0.170	0.6964	−0.033
0.4814	−0.152	0.8532	+0.031
0.5423	−0.120	0.9224	+0.020
	1,2-Dichlorobenzene + 1-Hexanol		
0.1222	−0.118	0.6195	−0.089
0.2009	−0.157	0.6834	−0.055
0.3050	−0.179	0.7430	−0.027
0.3904	−0.175	0.8017	+0.006
0.5158	−0.139	0.9013	+0.020
	1,2-Dichlorobenzene + 1-Heptanol		
0.1476	−0.090	0.5927	−0.095
0.2140	−0.126	0.6380	−0.069
0.3132	−0.156	0.7038	−0.015
0.4296	−0.160	0.7933	+0.030
0.5286	−0.139	0.8915	+0.060
	1,2-Dichlorobenzene + 1-Octanol		
0.0930	−0.043	0.6152	−0.006
0.1994	−0.080	0.7023	+0.050
0.2849	−0.098	0.7926	+0.095
0.4023	−0.086	0.8664	+0.098
0.4455	−0.074	0.9215	+0.076
0.5337	−0.039		

[a] x, mole fraction of 1,2-dichlorobenzene.

Results and Discussion

Excess volumes for binary mixtures of 1,2-dichlorobenzene with 1-butanol, 1-pentanol, and 1-hexanol along with those for mixtures of chlorobenzene with the three alcohols, reported in the literature (*1*), are graphically presented in Figure 1. V^E data for the binary mixtures of 1,2-dichlorobenzene with 1-

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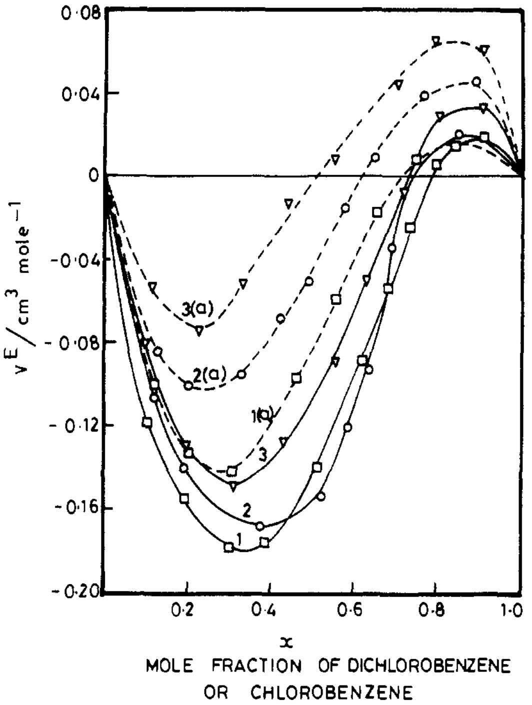

Figure 1. Excess volumes, V^E, plotted against mole fraction of (A) 1,2-dichlorobenzene at 303.15 K (—) for 1,2-dichlorobenzene mixtures with 1-alkanols (1) 1-butanol, (2) 1-pentanol, (3) 1-hexanol; and (B) chlorobenzene at 303.15 K (---) for chlorobenzene mixtures with 1-alkanols (1a) 1-butanol, (2a) 1-pentanol, (3a) 1-hexanol.

Table III. Values of Parameters for Eq 1 Calculated by the Method of Least Squares with the Standard Deviation

system	a^a	b^a	c^a	$\sigma(V^E)$
1,2-dichlorobenzene + 1-butanol	−0.4557	0.8071	0.3557	0.005
1,2-dichlorobenzene + 1-pentanol	−0.5347	0.8027	0.2762	0.006
1,2-dichlorobenzene + 1-hexanol	−0.5565	0.8476	0.1454	0.006
1,2-dichlorobenzene + 1-heptanol	−0.5757	0.8089	0.8971	0.004
1,2-dichlorobenzene + 1-octanol	−0.2161	0.8906	0.7126	0.004

^{a}Units: cm^3 mol^{-1}.

heptanol and 1-octanol are included in Figure 2. The results for mixtures of 1,2-dichlorobenzene with the five alcohols are given in Table II.

The reduction of excess volume data has been carried out by using a polynomial of the form

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)[a + b(2x-1) + c(2x-1)^2] \qquad (1)$$

where a, b, and c are adjustable parameters and x is the mole fraction of 1,2-dichlorobenzene. The values of the parameters, computed by the least-squares method, are given in Table III along with the standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$ were determined by employing the equation

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

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

The curves in Figures 1 and 2 show that the V^E is negative in mixtures rich in alcohols and positive in mixtures rich in 1,2-dichlorobenzene. Sign inversion in V^E occurs beyond the mole fraction of 0.6 for the 1,2-dichlorobenzene. Further, the introduction of a second chloro group into the benzene nucleus renders V^E more negative and it leads to a shift in the range of mole fraction, wherein the sign inversion of V^E occurs. This suggests that the interactions between molecules of 1,2-dichlorobenzene and those of alcohols are stronger than those between chlorobenzene and the alcohols.

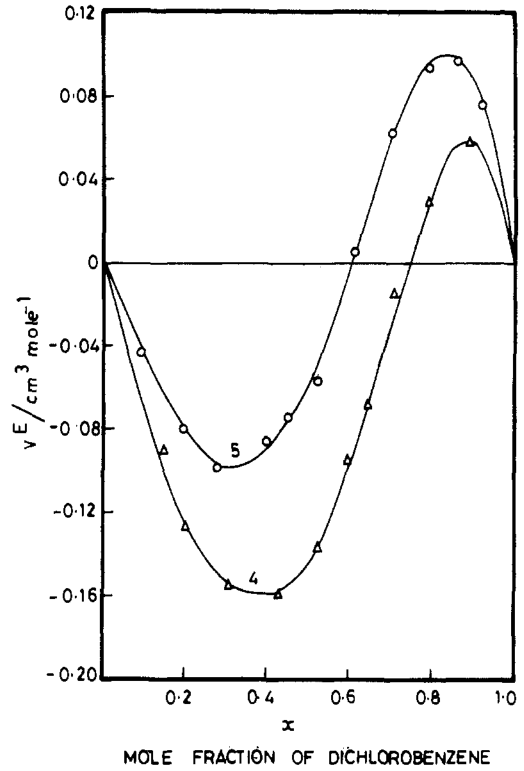

Figure 2. Excess volumes V^E plotted against mole fraction of 1,2-dichlorobenzene at 303.15 K for mixtures of 1,2-dichlorobenzene with 1-alkanols (4) 1-heptanol and (5) 1-octanol.

Glossary

V^E	excess volume
$\sigma(V^E)$	standard deviation in V^E
x	mole fraction
a, b, c	constants in excess volume–mole fraction equation (1)
n	number of results
p	number of parameters

Registry No. 1,2-Dichlorobenzene, 95-50-1; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5.

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