Table VI. Binodal Compositions Estimated from the h^E Data

system	T, K	estimated x_1'	estimated x_1''	literature x_1'	literature x_1''
n-hexane (1) + methanol (2)	303.15	0.21	0.74	0.269	0.758
2-methylpropanoic acid (1) + water (2)	293.15		0.20	0.054	0.224
nitroethane (1) + 2,2,4-trimethylpentane (2)	293.15	0.20	0.83	0.236	0.834
nitromethane (1) + 1-butanol (2)	291.15	0.53	0.72	at CST	

Glossary

h^E	molar excess enthalpy (J/mol)
g^E	molar excess Gibbs free energy (J/mol)
R	molar gas constant [J/(mol·K)]
T	temperature (K)
x_i	mole fraction of component i
a_{ij}	adjustable parameter for $i-j$ interactions (J/mol)
H_{ij}	adjustable parameter for $i-j$ interactions (J/mol)
G_{ij}	nonrandomness weighting factor, defined by eq 2
b	adjustable parameter for $i-j$ interactions [J/(mol·K)]

Registry No. Hexane, 110-54-3; methanol, 67-56-1; 2-methylpropanoic acid, 79-31-2; nitroethane, 79-24-3; 2,2,4-trimethylpentane, 540-84-1; nitromethane, 75-52-5; 1-butanol, 71-36-3.

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Excess Volumes of Binary Mixtures of 1,3-Dichlorobenzene with 1-Alkanols at 303.15 K

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Excess molar volumes for binary mixtures of 1,3-dichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol have been determined at 303.15 K. V^E is negative in mixtures rich in alcohols and positive in mixtures rich in 1,3-dichlorobenzene.

Introduction

This forms a part of a study of excess thermodynamic properties of binary mixtures that include chlorinated benzenes as common components and a homologous series of alcohols as noncommon components. Excess volumes for mixtures of 1,2-dichlorobenzene with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol were reported earlier (*1*). We report here new experimental data for binary mixtures of 1,3-dichlorobenzene with the five alcohols. This work was undertaken to study the isomeric effect arising due to the replacement of 1,2-dichlorobenzene by 1,3-dichlorobenzene.

Table I. Densities ρ of Pure Liquid Components at 303.15 K

component	ρ/(g cm^{-3}) present work	ρ/(g cm^{-3}) literature
1,3-dichlorobenene	1.277 16	1.277 18 (*5*)
1-butanol	0.802 06	0.802 2 (*6*)
1-pentanol	0.807 60	0.807 9 (*6*)
1-hexanol	0.812 05	0.812 1 (*6*)
1-heptanol	0.815 72	0.814 8 (*6*)
1-octanol	0.821 88	0.818 4 (*6*)

Experimental Section

Excess volumes were measured as described previously (*1*) by using a single composition per loading type dilatometer described by Rao and Naidu (*2*). Measurements were made employing a thermostatic bath maintained to 303.15 ± 0.01 K.

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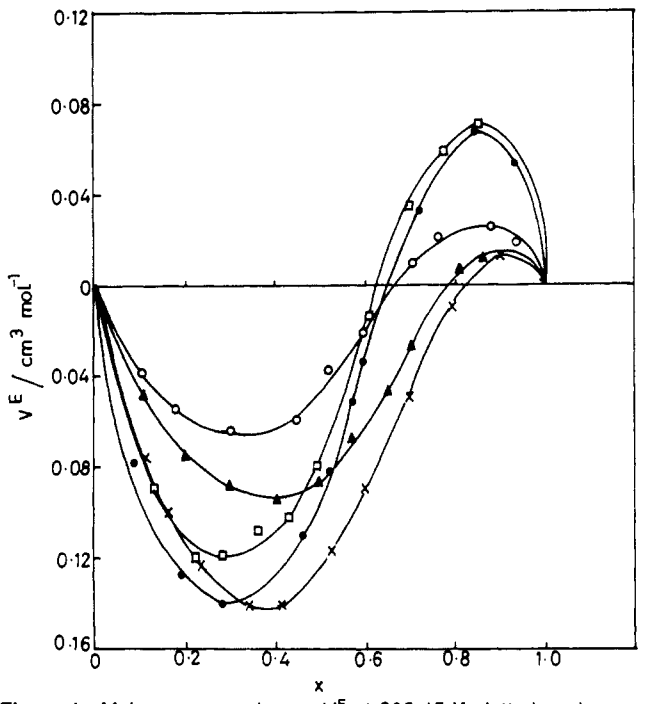

Figure 1. Molar excess volumes V^E at 303.15 K plotted against x, the mole fraction of 1,3-dichlorobenzene, for mixtures of 1,3-dichlorobenzene with (●) 1-butanol, (□) 1-pentanol, (×) 1-hexanol, (▲) 1-heptanol, or (○) 1-octanol.

Values of V^E were accurate to ±0.003 cm^3 mol^{-1}.

The five alcohols were purified by the methods described earlier (*1*); 1,3-dichlorobenzene was purified by the method described by Riddick et al. (*3*). 1,3-Dichlorobenzene was purified by washing repeatedly with 10% sodium hydroxide solution, and then with water, until the washings were neutral. It was dried over Drierite and fractionally distilled. The purities of the samples were checked by GLC and by comparing the densities of the components, measured using bicapillary pycnometer (*4*), with those reported in the literature (*5*, *6*) (cf. Table I).

Results and Discussion

The experimental V^E data for the five mixtures are given in Table II and are graphically presented in Figure 1. The data were fitted to the polynomial expression

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

where a, b, and c are adjustable parameters and x is the mole fraction of 1,3-dichlorobenzene. The values of the parameters, computed by the least-squares method, are given in Table II along with the standard deviations

$$\sigma = [\sum(V^E_{calc} - V^E_{exp})^2/(n-p)]^{1/2} \quad (2)$$

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

The results show that V^E is negative in mixtures rich in alcohols and positive in mixtures rich in 1,3-dichlorobenzene. The trend is similar to that observed for mixtures of 1,2-dichlorobenzene with the five alcohols. However, the V^E values for the mixtures with 1,3-dichlorobenzene are algebraically greater than those observed for the mixtures containing 1,2-dichlorobenzene. The inversion in sign of V^E occurs at higher mole fractions of 1,3-dichlorobenzene with 1-butanol, 1-pentanol, and 1-hexanol and at lower mole fractions with 1-heptanol and 1-octanol.

Table II. Molar Excess Volumes of 1,3-Dichlorobenzene + 1-Alkanols at 303.15 K as a Function of the Mole Fraction x of 1,3-Dichlorobenzene; Coefficients a, b, c, Equation 1; and Standard Deviation σ, Equation 2

x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})
	1,3-Dichlorobenzene + 1-Butanol		
0.0955	−0.078	0.5678	−0.051
0.1892	−0.127	0.5905	−0.033
0.3263	−0.140	0.7220	+0.033
0.4609	−0.111	0.8428	+0.068
0.5223	−0.082	0.9348	+0.053
a = −0.3589, b = 1.0335, c = 0.4269, σ = 0.004 cm^3 mol^{-1}			
	1,3-Dichlorobenzene + 1-Pentanol		
0.1312	−0.089	0.4919	−0.080
0.2201	−0.120	0.6105	−0.013
0.2816	−0.118	0.7008	+0.035
0.3597	−0.108	0.7785	+0.059
0.4285	−0.102	0.8539	+0.071
a = −0.2811, b = 0.9202, c = 0.3598, σ = 0.006 cm^3 mol^{-1}			
	1,3-Dichlorobenzene + 1-Hexanol		
0.1113	−0.075	0.5319	−0.117
0.1553	−0.099	0.6051	−0.090
0.2314	−0.121	0.7018	−0.049
0.3428	−0.140	0.7895	−0.009
0.4135	−0.139	0.8998	+0.013
a = −0.4923, b = 0.5580, c = 0.2934, σ = 0.004 cm^3 mol^{-1}			
	1,3-Dichlorobenzene + 1-Heptanol		
0.1124	−0.048	0.5729	−0.067
0.2008	−0.075	0.6525	−0.047
0.2970	−0.088	0.7039	−0.025
0.4114	−0.096	0.8054	+0.007
0.5009	−0.087	0.8635	+0.010
a = −0.3345, b = 0.3948, c = 0.2839, σ = 0.004 cm^3 mol^{-1}			
	1,3-Dichlorobenzene + 1-Octanol		
0.1052	−0.038	0.5990	−0.022
0.1769	−0.054	0.7056	+0.010
0.3055	−0.063	0.7618	+0.020
0.4541	−0.050	0.8861	+0.025
0.5184	−0.038	0.9263	+0.015
a = −0.1641, b = 0.3886, c = 0.1345, σ = 0.005 cm^3 mol^{-1}			

Glossary

a,b,c	constants in eq 1
V^E	molar excess volume, cm^3 mol^{-1}
x	mole fraction of 1,3-dichlorobenzene
ρ	density, g cm^{-3}
σ	standard deviation, eq 2

Registry No. 1,3-Dichlorobenzene, 541-73-1; 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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