Excess Volumes of Mixtures of Acetone, Chloroform, Carbon tetrachloride, 1,4-Dioxane and Tetrahydrofuran with o-Dichlorobenzene

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(Z. Naturforsch. **32 a**, 96–97 [1977];
received November 12, 1976)

Excess volumes of mixtures of o-dichlorobenzene with acetone, chloroform, carbon tetrachloride, 1,4-dioxane, and tetrahydrofuran have been measured at 293.15 K as a function of composition. The excess volume data have been used to check the one-fluid theory of mixtures with van der Waals's and Guggenheim's equations of state.

Introduction

The excess volumes, analysed in the light of the refined version of the cell model[1,2], of o-dichlorobenzene with aromatic hydrocarbons have been reported earlier[3]. In view of the revived interest[4–6] in n-fluid theories of liquid mixtures based on the principle of corresponding states[7–9], it seemed worth while to measure some more excess functions and make comparisons with theories. In this paper, we report the excess volumes of o-dichlorobenzene with acetone, chloroform, carbon tetrachloride, 1,4-dioxane, and tetrahydrofuran. The comparisons were made with the one-fluid theory using van der Waals's and Guggenheim's equations of state[10, 11].

Experimental

Acetone, chloroform, carbon tetrachloride (all A.R. grade), 1,4-dioxane, tetrahydrofuran, and o-dichlorobenzene (all B.D.H. grade) were purified as described earlier[12, 1]. The purities of the samples were checked by measuring their densities; the results agreed to within 0.00002 g cm^{-3} with those in the literature[13, 14]. The excess volumes were measured at 293.15 K as a function of composition in a water-filled thermostat controlled to within 0.01 K by a dilatometric method[15].

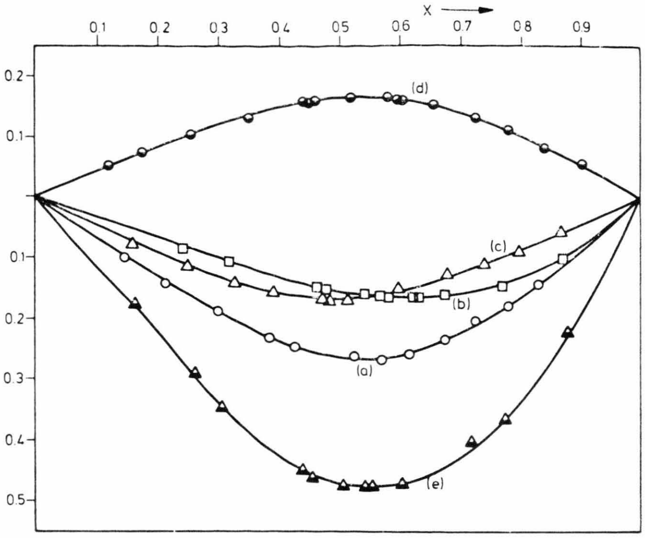

Fig. 1. Plots of excess volume V^E against mole fraction x.
(a) x acetone + $(1-x)$ o-dichlorobenzene ○○○;
(b) x chloroform + $(1-x)$ o-dichlorobenzene □□□;
(c) x carbon tetrachloride + $(1-x)$ o-dichlorobenzene △△△;
(d) x 1,4-dioxane + $(1-x)$ o-dichlorobenzene ●●●;
(e) x tetrahydrofuran + $(1-x)$ o-dichlorobenzene ▲▲▲.

Results

The results are reproducible to within 0.001 cm^3 mol^{-1} and are plotted in Figure 1. They were least squares fitted to the equation:

$$V^E/\text{cm}^3\,\text{mol}^{-1} = x(1-x)\,[A + B(2\,x-1) + C(2\,x-1)^2]\,. \tag{1}$$

Values of A, B and C are given with standard deviations $\sigma(V^E)$ in Table 1.

Discussion

Van der Waals's equation for a one-fluid mixture is given by[10]

$$p = R\,T/\{V_m(T,p,x) - b(x)\} - a(x)/\{V_m(T,p,x)\}^2 \tag{2}$$

where p denotes pressure, T temperature, V_m molar volume, x mole fraction of the substance B. At neg-

Table 1. Values of the parameters in Eq. (1) and standard deviations $\sigma(V^E)$.

o-dichlorobenzene +	A	B	C	$\sigma(V^E)/\text{cm}^3\,\text{mol}^{-1}$
acetone	−1.0271	−0.1766	0.1811	0.004
chloroform	−0.6382	−0.3190	−0.0719	−0.001
carbon tetrachloride	−0.6655	0.0329	0.2089	0.004
1,4-dioxane	0.6752	−0.1321	−0.1683	0.005
tetrahydrofuran	−1.9120	−0.6531	0.2719	−0.008

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ligible pressures the molar excess volume V^E is then given by:

$$V^E(T,x) = V_m(T,x) - (1-x)V_m(T,0) - x\,V_m(T,1) \quad (3)$$

where $V_m(T,x)$ denotes $V_m(T,p\rightarrow 0,x)$ and is given by:

$$V_m(T,x) = \{a(x)/2RT\}[1-\{1-4\,b(x)RT/a(x)\}^{1/2}]\,. \quad (4)$$

For one-fluid relations $a(x)$ and $b(x)$ are given by

$$a(x) = (1-x)^2 a_{AA} + 2x(1-x)\,a_{AB} + x^2 a_{BB}\,, \quad (5)$$

$$b(x) = (1-x)^2 b_{AA} + 2x(1-x)\,b_{AB} + x^2 b_{BB}\,. \quad (6)$$

Values of excess volumes were calculated at equimolar compositions from Eq. (3) and are recorded in Table 2. The quantities a and b for pure substances were taken as proportional respectively to $T_c V_c$ and to V_c, where T_c and V_c are the critical temperature and critical volume. The values of the critical constants were taken from the literature[17–20]. Guggenheim's equation in the one-fluid form for a liquid mixture is given by:

$$p = RT\{V_m(T,p,x)\}^3/\{V_m(T,p,x) - \beta(x)\}^4 - a(x)/\{V_m(T,p,x)\}^2\,. \quad (7)$$

At negligible pressures the molar excess volumes are then given by

$$V^E(T,x) = V_m(T,x) - (1-x)\,V_m(T,0) - x\,V_m(T,1) \quad (8)$$

where $V_m(T,x)$ again denotes $V_m(T,p\rightarrow 0,x)$ and is given by the relevant root of Eq. (7) with $p=0$.

The quantities α and β for pure substances were taken proportional respectively to $T_c V_c$ and to V_c. Values of excess volumes were calculated from Eq. (8) at equimolar compositions and are recorded in Table 2.

It is evident from Table 2 that both van der Waals's and Guggenheim's equation of state do not fit the experimental results, but nevertheless perdict the sign well. In calculating the excess volumes we have assumed that $\xi = 1$. The failure of the theories to perdict the magnitude is due to the fact that they are applicable to systems of simple, spherical and non-polar molecules. Secondly, the geometric mean rule may not be valid for these systems.

The negative excess volumes in the mixtures of o-dichlorobenzene with acetone and tetrahydrofuran, and the positive ones in the mixtures with 1,4-dioxane may be due to the presence and absence of dipolar interactions, respectively. On the other hand, the quite similar negative excess volumes in the mixtures of chloroform and carbon tetrachloride may be caused by an interaction of the π-electron cloud of the benzene ring of o-dichlorobenzene with the empty d-electrons of the chloro groups.

The author acknowledges his thanks to the German Academic Exchange for the award of a fellowship and to Guru Nanak Dev University Amritsar for leave of absence.

Table 2. Experimental and calculated excess volumes V^E in units cm³ mol⁻¹.

o-dichlorobenzene +	V^E at $x=0.5$			V^E at maximum
	Expt.	van der Waals	Guggenheim	Expt.
acetone	−0.257	−1.906	−1.625	−0.263
chloroform	−0.155	−1.045	−0.924	−0.166
carbon tetrachloride	−0.166	−1.094	−0.966	−0.167
1,4-dioxane	0.167	−1.831	−1.628	0.169
tetrahydrofuran	−0.478	−2.315	−2.041	−0.485

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