Monatshefte für Chemie 110, 639—645 (1979)

Monatshefte für Chemie

Excess Volumes of 1,2-Dichloroethane With Acetone, Chloroform, Carbon Tetrachloride, 1,4-Dioxane, and Tetrahydrofuran at 293.15 K

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(Received 2 October 1977. Accepted 16 December 1977)

Excess volumes of mixtures of 1,2-dichloroethane with acetone, chloroform, carbon tetrachloride, 1,4-dioxane, and tetrahydrofuran have been measured at 293.15 K. The data have been analysed in the light of the cell model theory and *Flory*'s theory.

(Keywords: Cell model theory; Excess volumes; Thermodynamic parameters)

Überschuß-Volumina von 1,2-Dichlorethan mit Aceton, Chloroform, Tetrachlorkohlenstoff, 1,4-Dioxan und Tetrahydrofuran bei 239,15 K

Es wurden Überschuß-Volumina von Mischungen von 1,2-Dichlorethan mit Aceton, Chloroform, Tetrachlorkohlenstoff, 1,4-Dioxan und Tetrahydrofuran bei 239,15 K gemessen. Die Daten wurden im Licht der Zellenmodell-Theorie und der Theorie nach *Flory* analysiert.

Introduction

Excess volumes of dihaloethanes with aromatic hydrocarbons have been reported earlier[1–3]. In this paper, we report excess volumes of 1,2-dichloroethanes with acetone, chloroform, carbon tetrachloride, 1,4-dioxane, and tetrahydrofuran. Excess volume data can be used to check the statistical theory of *Flory*[4,5] and the cell model theory of *Prigogine*[6,7].

Experimental

Acetone (A.R. grade) was refluxed with successive small quantities of potassium permanganate (until violet colour persists), dried over anhydrous potassium carbonate, filtered and distilled. Carbon tetrachloride (A.R. grade)

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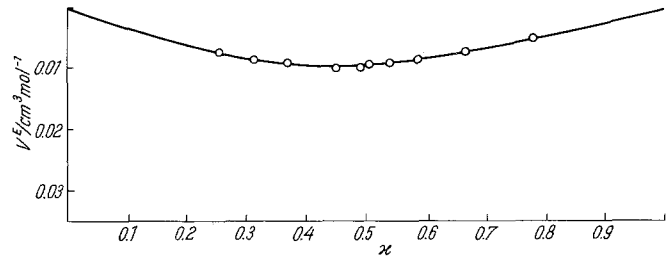

Fig. 1. Excess volume V^E vs. mole fraction x for x acetone + $(1-x)$ 1,2-dichloroethane

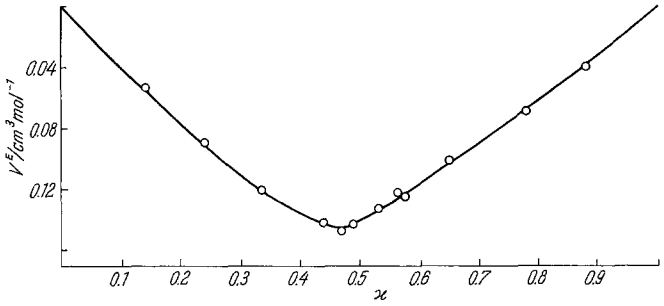

Fig. 2. Excess volume V^E vs. mole fraction x for x chloroform + $(1-x)$ 1,2-dichloroethane

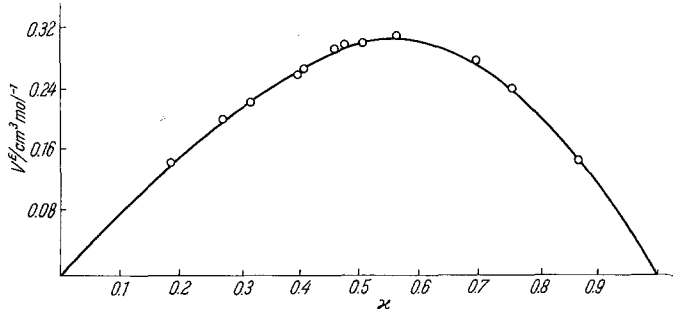

Fig. 3. Excess volume V^E vs. mole fraction x for x carbon tetrachloride + + $(1-x)$ 1,2-dichloroethane

was treated with potassium hydroxide dissolved in 50 % ethanol and vigorously shaken. The aqueous layer was removed, ethanol was removed by shaking with water and small amounts of sulphuric acid; then it was washed with water, dried over anhydrous calcium chloride and distilled.

Chloroform (A.R. grade) was shaken with water, dried over anhydrous calcium chloride and distilled.

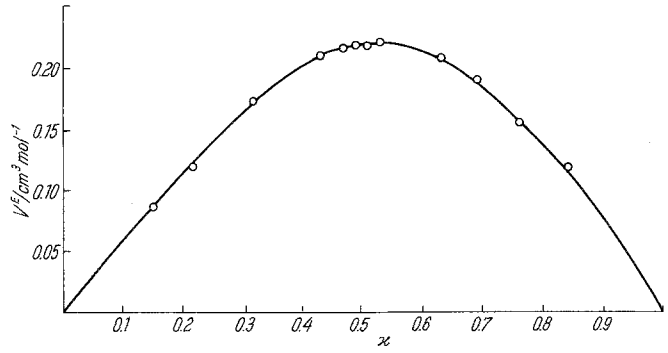

Fig. 4. Excess volume V^E vs. mole fraction x for x dioxane + $(1-x)$. 1,2-dichloroethane

Fig. 5. Excess volume V^E vs. mole fraction x for x tetrahydrofuran + $(1-x)$ 1,2-dichloroethane

1,4-Dioxane (B.D.H. grade): Nitrogen gas was bubbled through it, treated with potassium hydroxide solution, the aqueous layer was removed, then refluxed over sodium metal and distilled.

Tetrahydrofuran (B.D.H. grade) was kept over sodium hydroxide pellets for 24 hours, refluxed three times over sodium metal for ten hours and distilled.

1,2-Dichloroethane (Reidel) was fractionally distilled over P_2O_5. The purities of the samples were checked by measuring their densities, the results agreed to within 0.00002 g cm^{-3} with those in literature[8,9]. The excess volumes were measured in a water-filled thermostat controlled to within 0.01 K at 293.15 K. Measured excess volumes are correct to within 0.001 cm^3 mol^{-1}. Excess volumes were measured using a dilatometer described earlier[10].

The coefficients of cubical expansion were measured in a pyknometer specially designed for this purpose.

Table 1. *The values of parameters for equation (1) and standard deviations*

System	A	B	C	$\sigma(V^E)/\mathrm{cm^3\,mol^{-1}}$
x acetone + $(1-x)$ 1,2-dichloroethane	−0.0364	0.0106	−0.0011	0.000
x chloroform + $(1-x)$ 1,2-dichloroethane	−0.5476	0.0610	0.2394	0.007
x carbon tetrachloride + $(1-x)$ 1,2-dichloroethane	1.2301	0.2695	−0.3928	0.008
x 1,4-dioxane + $(1-x)$ 1,2-dichloroethane	0.8739	0.1503	−0.2107	0.003
x tetrahydrofuran + $(1-x)$ 1,2-dichloroethane	0.3871	0.0541	−0.1323	0.002

Results

Excess volumes of 1,2-dichloroethane with acetone, chloroform, carbon tetrachloride, 1,4-dioxane, and tetrahydrofuran at 293.15 K as a function of composition have been plotted in Fig. 1 to 5.

Excess volumes were least square fitted to the equation

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

The values of the parameters A, B, and C along with their standard deviations $\sigma(V^E)$ are given in Table 1.

The coefficients of cubical expansion of liquids are recorded in Table 2.

Discussion

Calculations Based on Flory's Theory

According to *Flory*'s theory the excess volumes V^E of mixing are related to characteristic parameters. The values for the components are listed in Table 3.

There is a difficulty in computing V^E from *Flory*'s theory; the reduced temperature $\tilde{T}$ of the mixture is a dependent on parameters which can be evaluated from knowing other excess functions of the system. Since excess functions other than excess volumes for these systems are not known, a departure has been made from *Flory*'s original method of evaluating $\tilde{T}$. The reduced temperature $\tilde{T}$ of the mixture was obtained from the relation $\tilde{T} = \varphi_1 \tilde{T}_1 + \varphi_2 \tilde{T}_2$ which is a reasonable approximation to the original equation[4,5]. In calculating

Table 2. *Molar volumes and coefficients of volume expansion of pure components*

Compound	V/ $cm^3 mol^{-1}$	V'/ $cm^3 mol^{-1} deg^{-1}$	V'' $cm^3 mol^{-1} deg^{-2}$	$\alpha \cdot 10^3/deg^{-1}$
acetone	73.3502	0.124	0.0003	1.2420
chloroform	80.1746	0.122	0.0003	1.2416
carbon tetrachloride	96.4994	0.106	0.0002	1.2488
1,4-dioxane	85.2375	0.119	0.0003	1.2368
tetrahydrofuran	81.7574	0.115	0.0003	1.2532
1,2-dichloroethane	78.2160	0.136	0.0004	1.1846

Table 3. *Values of the characteristic parameters ($\tilde{V}$ reduced volume, V^* characteristic volume, T reduced temperature) according to Flory*[4,5]

Compound	$\tilde{V}$	V^* /$cm^3 mol^{-1}$	$\tilde{T}$
acetone	1.2914	56.7989	0.06327
chloroform	1.2913	62.0883	0.06326
carbon tetrachloride	1.2926	74.6553	0.06343
1,4-dioxane	1.2904	66.0551	0.06314
tetrahydrofuran	1.2935	63.2063	0.06355
1,2-dichloroethane	1.2805	61.0872	0.06178

the values of the parameters, experimental determined values for the coefficients of volume expansion and densities have been used. Excess volumes were calculated at equimolar compositions and are recorded in Table 5.

Calculations Based on the Cell Model Theory

Excess volumes of mixing were also calculated using the refined version of *Prigogine* theory [6,7].

The characteristic parameters for the pure components were calculated from the critical constants using the relations

$$\delta = (P_c^B V_c^B / P_c^A V_c^A) - 1 \tag{2}$$

$$\rho = (V_c^B / V_c^A)^{1/3} - 1 \tag{3}$$

assuming that each component of the mixture obeys the theorem of corresponding states (Table 4). The values of the critical constants were

Table 4. *Values of the parameters* δ, θ, *and* ρ (ref. [4,5])

System 1,2	δ_1	δ_2	ρ_1	ρ_2	θ_1	θ_2
1,2-dichloroethane (2) + acetone (1)	0.1750	—0.1490	0.0216	—0.0212	—0.0038	—0.0028
chloroform (1)	—0.0199	0.0203	—0.0213	0.0218	—0.0000	—0.0000
carbon tetrachloride (1)	0.4793	—0.3240	0.1372	—0.1206	—0.0287	—0.0131
1,4-dioxane (1)	—0.0981	0.1083	—0.0186	0.0189	—0.0012	—0.0015
tetrahydrofuran (1)	0.0416	—0.0399	0.0015	—0.0015	—0.0002	—0.0002

Table 5. *Calculated and experimental* V^E *values at equimolar compositions*

System 1,2	V^E/cm^3 mol^{-1}			
	Experimental	*Flory* theory	Cell model theory	
			1st component as reference	2nd
1,2-dichloroethane (2) + acetone (1)	—0.009	—0.103	0.000	0.020
chloroform (1)	—0.137	—0.042	0.038	0.044
carbon tetrachloride (1)	0.308	—0.187	2.465	1.536
1,4-dioxane (1)	0.218	—0.075	0.039	—0.042
tetrahydrofuran (1)	0.097	—0.173	—0.003	—0.004

taken from the literature[11–14]. In computing V^E, a simplified for dispersion forces was introduced, i.e. $\theta = -\delta^2/_8$. The V^E values were calculated taking either component as reference at equimolar compositions and are recorded in Table 5.

It is evident from Table 5 that both *Flory*'s theory and the cell model theory fail to predict accurately the sign and magnitude of excess functions. The reason (concerning *Flory*'s theory) may be due to the assumption that dispersion forces are operating between the components of these mixtures. This amounts to assuming that $\tilde{T} = \varphi_1 \tilde{T}_1 + \varphi_2 \tilde{T}_2$ for the interaction pair potential, which may not be strictly valid for these systems.

Excess volumes of 1,2-dichloroethane with acetone and chloroform are negative due to the presence of dipolar interactions. Excess volumes of 1,2-dichloroethane with carbon tetrachloride, 1,4-dioxane and tetrahydrofuran are positive indicating the presence of dispersion forces in these mixtures.

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