Thermochimica Acta, 12 (1975) 155–158

THERMODYNAMICS OF BINARY MIXTURES: EXCESS VOLUMES OF MIXING OF SOME BINARY 1,2-DICHLOROETHANE MIXTURES

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(Received 23 January 1975)

ABSTRACT

The excess volumes, V^E, of some binary 1,2-dichloroethane mixtures have been determined at 30°C. The data have been examined for Cell model theory of Prigogine and Flory's theory. Both theories have been found to fail to fit the results with useful accuracy.

INTRODUCTION

This communication reports the molar excess volumes of 1,2-dichloroethane + benzene, + carbon tetrachloride, + *p*-xylene, + dioxan, + n-hexane and + n-heptane at 30°C and at different mole fractions with an aim to examine the current theories of mixtures in which one of the components is slightly polar.

MATERIALS AND METHODS

Benzene, *p*-xylene, carbon tetrachloride, dioxan and n-hexane were purified as suggested by Vogel[1]. n-Heptane was distilled twice over sodium and the fraction distilling at 98.15°C was collected. 1,2-Dichloroethane was purified by fractional crystallisation[2] and their purities were checked by measuring their densities at 25°C. The densities of these chemicals compared well with the literature values[3].

Excess volumes were measured dilatometrically[4] as a function of composition at 30°C and the temperature was controlled within ±0.01°C.

RESULTS AND DISCUSSION

The results given in Table 1 were fitted by least squares to the expression:

$$\frac{V^E}{x(1-x)}(\text{cm}^3\ \text{mol}^{-1}) = A + B(2x-1) + C(2x-1)^2 \qquad (1)$$

where A, B and C are adjustable parameters and x denotes the mole fraction. The values obtained along with standard deviations are given in Table 2.

TABLE 1

MOLAR EXCESS VOLUMES V^E AT MOLE FRACTION x_1 OF COMPONENT (1) AT 30°C

x_1	V^E ($cm^3\ mol^{-1}$)	x_1	V^E ($cm^3\ mol^{-1}$)
1,2-dichloroethane(1) + benzene(2)		*1,2-dichloroethane(1) + dioxan(2)*	
0.1048	0.097	0.0901	0.060
0.2147	0.166	0.1493	0.096
0.3305	0.210	0.2525	0.146
0.4218	0.227	0.4104	0.185
0.5045	0.232	0.4521	0.189
0.6459	0.213	0.5928	0.178
0.7065	0.187	0.7510	0.128
0.7439	0.172	0.8293	0.093
0.8635	0.102	0.8805	0.065
1,2-dichloroethane(1) + carbon tetrachloride(2)		*1,2-dichloroethane(1) + n-hexane(2)*	
0.1050	0.120	0.1090	0.282
0.1889	0.201	0.1875	0.440
0.2945	0.288	0.2690	0.563
0.3652	0.323	0.3574	0.647
0.4913	0.339	0.3756	0.657
0.5951	0.315	0.5564	0.632
0.6074	0.311	0.6373	0.562
0.7555	0.218	0.6844	0.510
0.7986	0.182	0.8265	0.295
1,2-dichloroethane(1) + p-xylene(2)		*1,2-dichloroethane(1) + n-heptane(2)*	
0.0898	0.075	0.1850	0.560
0.1812	0.145	0.2596	0.706
0.2690	0.201	0.3235	0.797
0.3202	0.226	0.3626	0.846
0.4357	0.268	0.4077	0.882
0.5445	0.270	0.5855	0.851
0.6587	0.240	0.7125	0.698
0.7303	0.209	0.8379	0.451
0.8596	0.120	0.8482	0.425

TABLE 2

PARAMETERS FOR EQN (1) AND THE STANDARD DEVIATION $\sigma(V^E)$ OF THE MOLAR EXCESS VOLUMES AT 30°C

System	*A*	*B*	*C*	$\sigma(V^E)$ ($cm^3\ mol^{-1}$)
1,2-Dichloroethane(1) + benzene(2)	0.929	−0.088	0.015	0.003
1,2-Dichloroethane(1) + dioxan(2)	0.761	−0.072	−0.065	0.004
1,2-Dichloroethane(1) + carbon tetrachloride(2)	1.364	−0.168	−0.337	0.003
1,2-Dichloroethane(1) + *p*-xylene(2)	1.084	0.038	−0.165	0.003
1,2-Dichloroethane(1) + n-hexane(2)	2.657	−0.637	−0.350	0.004
1,2-Dichloroethane(1) + n-heptane(2)	3.571	−0.299	−0.092	0.004

The V^E data were examined on the basis of cell model theories[5] and the average potential model for these mixtures. According to the refined theory of Prigogine[6]:

$$\frac{V^E}{x_1 x_2} = \tfrac{3}{2} V_1 p[\theta(x_1 - x_2) + \tfrac{1}{2}\delta + \tfrac{11}{4}\rho] + \\ + TV_1'[-2\theta + 9\rho^2 + \theta^2 - \tfrac{3}{4}\delta^2 + \delta\theta(1 + 2x_2)] + \\ + \tfrac{1}{2} T^2 V_1''[\theta^2 - \tfrac{3}{4}\delta^2 + \delta\theta(1 + 2x_2)] \quad (2)$$

The values of the parameters δ, ρ and θ for these mixtures have been calculated as described earlier[7] and are recorded in Table 3. V_1 is the molar volume of the pure component used as the reference substance and V_1' and V_1'' refer to the first and second derivatives of V_1 with respect to temperature.

TABLE 3

VALUES OF PARAMETERS USED IN EQN (2)

System	δ	ρ	θ
1,2-Dichloroethane(1) + benzene(2)	−0.0298	−0.0477	−0.00011
1,2-Dichloroethane(1) + dioxan(2)	−0.0873	−0.0123	−0.00095
1,2-Dichloroethane(1) + carbon tetrachloride(2)	−0.0785	−0.0658	−0.00080
1,2-Dichloroethane(1) + *p*-xylene(2)	−0.0811	−0.1593	−0.00062
1,2-Dichloroethane(1) + n-hexane(2)	0.02405	−0.1528	−0.00007
1,2-Dichloroethane(1) + n-heptane(2)	−0.0376	−0.1956	−0.00018

The molar volumes were evaluated from the densities of the pure components and V_1' and V_1'' were calculated in the manner reported by Rastogi and Varma[8].

The values of equimolar compositions computed in this way by taking a non-polar component as a reference are recorded in Table 4. Examination of Table 4 shows that the theory correctly predicts the sign of V^E for the systems studied here but

TABLE 4

COMPARISON OF CALCULATED AND EXPERIMENTAL V^E VALUES AT 30°C AT EQUIMOLAR COMPOSITION

System	V^E ($cm^3\ mol^{-1}$)		
	Exptl.	*Prigogine*	*Flory*
1,2-Dichloroethane + benzene	0.230	0.429	−0.1201
1,2-Dichloroethane + dioxan	0.187	0.032	—
1,2-Dichloroethane + carbon tetrachloride	0.332	0.963	—
1,2-Dichloroethane + *p*-xylene	0.275	6.062	—
1,2-Dichloroethane + n-hexane	0.672	4.925	—
1,2-Dichloroethane + n-heptane	0.905	11.062	—

the quantitative agreement is poor except for 1,2-dichloroethane + benzene, + carbontetrachloride and + 1,4-dioxan systems wherein the agreement is reasonable. The theory predicts comparatively larger values for the 1,2-dichloroethane + *p*-xylene, + n-hexane and + n-heptane systems. This is not surprising because this theory would have given better agreement with the experimental results if the size of two components constituting the binary mixtures were almost similar. In the present investigation n-hexane, n-heptane and *p*-xylene have their molar volumes almost 50% larger than that of 1,2-dichloroethane. However, the size of the two components constituting 1,2-dichloroethane + benzene, + dioxan and + carbontetrachloride systems is almost the same and thus the agreement is satisfactory.

In the present work only one system 1,2-dichloroethane + benzene has been examined on the basis of Flory's theory[9] since the excess enthalpies for this system are already recorded in the literature[10]. The excess functions of the rest of the systems have not, however, been evaluated on similar lines, since the excess enthalpies are not known for these systems. The literature value[10] of the excess enthalpy at equimolar composition was used to evaluate $\theta_2\chi_{12}$. The coefficient of thermal expansion and isothermal compressibility being taken from the literature[2] to calculate the characteristic properties. The various quantities thus calculated were substituted in Flory's orginal expression[9] to get V^E. A comparison of the calculated and experimental results at equimolar composition, recorded in Table 4, shows that Flory's theory fails to predict the sign as well as magnitude of V^E for this system. This, however, is not surprising since Flory's theory does not hold for systems containing polar molecules.

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