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Note

Excess Gibbs free energies of some binary mixtures of 1,2-dichloroethane and hydrocarbons

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Excess volumes V^E and excess enthalpies H^E for 1,2-dichloroethane+benzene, +toluene, +*o*-, *m*-, and *p*-xylenes have already been reported in the literature[1,2]. In this work, we report the excess Gibbs free energies for the same systems at 30°C to analyse the data in the light of the refined version of the cell model theory[3] and Flory's theory[4].

MATERIALS AND METHODS

The materials were purified and their purity checked as reported earlier[5,6]. Vapour pressures and mole fractions in the liquid phase were determined by a static method. The equilibrium mole fraction x_1 of 1,2-dichloroethane in the liquid phase was determined from the refractive index measured with a Carl Zeiss refractometer maintained at 30°C and computed from the relation.

$$\eta = a + bx_1 + cx_1^2 \tag{1}$$

where *a*, *b* and *c* were determined from the refractive indices of mixtures of known compositions by the method of least squares. An uncertainty of 0.0001 in η leads to an error of about 0.001 in x_1.

RESULTS AND DISCUSSION

The vapour pressures as a function of composition of 1,2-dichloroethane+aromatic hydrocarbons are given in Table 1, together with G^E values computed by Barker's method[8]. The second virial coefficients of pure components were calculated from the Berthelot equation[9]. It was assumed that $\beta_{12} = (\beta_{11} + \beta_{22})/2$. The coefficients of equation:

$$G^E/RT = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \tag{2}$$

are given in Table 2, together with the standard deviations $\sigma(P)$ of the observed vapour pressures from those calculated.

TABLE 1

MOLE FRACTIONS x_1, VAPOUR PRESSURES P AND EXCESS GIBBS FREE ENERGIES G^E FOR THE MIXTURES CONTAINING 1,2-DICHLOROETHANE AT 30°C

x_1	P (*mm Hg*)	G^E (*cal mol*$^{-1}$)
1,2-Dichloroethane (1) + benzene (2)		
0.0000	118.70	
0.1894	115.32	1.02
0.2925	113.48	2.22
0.3475	112.50	2.65
0.3860	111.83	2.89
0.4290	111.07	3.16
0.5300	109.20	3.44
0.6500	106.93	3.40
0.6830	106.28	3.21
0.7285	105.39	2.92
0.7980	103.95	2.42
0.9312	101.12	0.96
1.0000	99.64	
1,2-Dichloroethane (1) + toluene (2)		
0.0000	37.74	
0.1310	44.56	−2.85
0.1675	47.08	−2.87
0.2515	52.80	−1.96
0.3235	57.76	−0.02
0.4080	63.66	2.70
0.5025	70.10	6.39
0.6040	76.68	9.98
0.6700	80.68	11.67
0.7050	82.96	12.27
0.7625	86.49	12.49
0.7850	87.82	12.42
0.9390	96.60	5.74
1.0000	99.64	
1,2-Dichloroethane (1) + o-xylene (2)		
0.0000	8.75	
0.0665	15.22	4.23
0.1640	24.77	8.95
0.2600	34.12	12.22
0.3240	39.77	14.16
0.4035	47.80	16.10
0.5060	56.19	17.97
0.6230	67.58	19.09
0.7515	78.65	17.75
0.7560	79.03	17.66
0.8670	88.40	12.78
1.0000	99.64	

(*Table continued on p. 126*)

TABLE 1 (*continued*)

x_1	P (*mm Hg*)	G^E (*cal mol*$^{-1}$)
1,2-Dichloroethane (1)+m-xylene (2)		
0.0000	10.92	
0.1500	24.93	4.43
0.2670	36.05	8.35
0.3525	44.09	11.27
0.4750	55.21	14.81
0.5903	65.24	16.72
0.6260	68.27	16.96
0.7275	76.92	16.29
0.8301	85.52	13.09
0.9250	93.44	7.06
1.0000	99.64	
1,2-Dichloroethane (1)+p-xylene (2)		
0.0000	11.49	
0.0580	17.05	3.18
0.1840	28.81	8.80
0.2735	37.05	11.29
0.2750	37.23	11.36
0.4020	49.87	14.78
0.4670	54.75	16.10
0.5815	64.90	18.01
0.6715	73.08	18.49
0.7440	78.74	17.89
0.7670	80.75	17.34
0.8575	88.13	13.61
1.0000	99.64	

TABLE 2

PARAMETERS A, B AND C OF EQN (2) AT 30°C AND STANDARD DEVIATIONS $\sigma(P)$ OF THE VAPOUR PRESSURES

System	A	B	C	$\sigma(P)$ (*mm Hg*)
Benzene+1,2-dichloroethane	0.0226	−0.0085	−0.0075	0.01
1,2-Dichloroethane+toluene	0.0415	0.1289	0.0216	0.15
1,2-Dichloroethane+*o*-xylene	0.1186	0.0513	0.0527	0.36
1,2-Dichloroethane+*m*-xylene	0.1023	0.0704	0.0112	0.12
1,2-Dichloroethane+*p*-xylene	0.1115	0.0614	0.0573	0.24

The G^E data were analysed in terms of Flory's theory[4] and Prigogine's theory[3]. According to the refined version of Prigogine's theory

$$G^E/x_1x_2 = -[h_1(-2\theta+9\zeta^2)-\tfrac{1}{2}TC_{p1}\{\theta^2-\tfrac{3}{4}\delta^2+\delta\theta(1+2x_2)\}- -\tfrac{3}{2}kT\zeta\{\theta(x_1-x_2)+\tfrac{1}{2}\delta+5\zeta\}] \tag{3}$$

where the terms have the significance as given by Prigogine[3,9]. The various parameters were evaluated as described earlier[10] and are reported in Table 4. Heat capacities, h and configurational enthalpies, C_p for the pure components are given in Table 3 at 30°C. G^E thus calculated at equimolar composition, by taking a non-polar component as reference are given in Table 5.

TABLE 3

THE VALUES OF THE PARAMETERS FOR PURE COMPONENTS AT 30°C

Compound	$\alpha \times 10^3$ *deg*$^{-1}$	$-h$ *(cal)*	C_p *(cal mol*$^{-1}$*)*
1,2-Dichloroethane	1.194	—	—
Benzene	1.243	7981	12.33
Toluene	1.079	8917	20.54
o-xylene	0.990	10361	11.88
m-xylene	1.050	10244	10.78
p-xylene	1.055	10118	12.64

TABLE 4

PARAMETERS OF THE MIXTURES

System	δ	ζ	$\theta_2 X_{12}$
Benzene + 1,2-dichloroethane	−0.030	−0.048	5.757
Toluene + 1,2-dichloroethane	−0.062	−0.109	7.292
o-Xylene + 1,2-dichloroethane	−0.104	−0.152	2.572
m-Xylene + 1,2-dichloroethane	−0.090	−0.157	3.683
p-Xylene + 1,2-dichloroethane	−0.081	−0.159	1.048

TABLE 5

EXPERIMENTAL AND COMPUTED G^E VALUES AT EQUIMOLAR COMPOSITIONS AT 30°C

System	G^E *(cal mol*$^{-1}$*)*		
	Exptl.	*Prigogine*	*Flory*
Benzene + 1,2-dichloroethane	3.40	40.99	118.05
Toluene + 1,2-dichloroethane	26.14	278.18	110.70
o-Xylene + 1,2-dichloroethane	17.88	537.59	44.95
m-Xylene + 1,2-dichloroethane	15.42	573.67	65.92
p-Xylene + 1,2-dichloroethane	16.80	578.35	6.99

According to Flory's theory:

$$\begin{aligned}G^{E} = {} & 3T[x_1(P_1^* V_1^*/T_1^*)\ln(\tilde{v}_1^{1/3}-1)/(\tilde{v}_{\mathrm{calc}}^{1/3}-1)+\\ & + x_2(P_2^* V_2^*/T_2^*)\ln(\tilde{v}_2^{1/3}-1)/(\tilde{v}_{\mathrm{calc}}^{1/3}-1)]+\\ & + x_1 P_1^* V_1^*(\tilde{v}_1^{-1}-\tilde{v}_{\mathrm{calc}}^{-1})+x_2 P_2^* V_2^*(\tilde{v}_2^{-1}-\tilde{v}_{\mathrm{calc}}^{-1})+x_1 V_1^* \theta_2 X_{12}\tilde{v}_{\mathrm{calc}}^{-1}\end{aligned} \tag{4}$$

the various quantities have been calculated as described by Abe and Flory[4]. The coefficients of thermal expansions for pure components are given in Table 3, isothermal compressibilities being taken from the literature[11,12]. The adjustable parameter $\theta_2 X_{12}$ was evaluated from V^E values[1]. The calculated G^E for the various systems are recorded in Table 5.

The G^E values for all the systems thus obtained by both theories agree in sign with the experimental values. But the qualitative agreement is poor. Both theories predict comparatively larger values for the present systems as compared to their corresponding experimental values. The failure of the theories is due to the fact that the specific interactions[2] between the components of these mixtures is not taken into account.

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