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THERMODYNAMICS OF BINARY MIXTURES: EXCESS GIBBS FREE ENERGIES OF 1,2-DIBROMOETHANE MIXTURES WITH BENZENE, CYCLOHEXANE, CARBON TETRACHLORIDE AND DIOXANE, AT 20°C

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ABSTRACT

The excess Gibbs free energies of 1,2-dibromoethane mixtures with benzene, cyclohexane, carbon tetrachloride and dioxane have been determined by a static vapour pressure method at 20°C. The results have been analysed in the light of the current theories of solutions due to Prigogine and Flory. Both the theories fail to fit the results with useful accuracy.

INTRODUCTION

Recently, it has been shown[1–3] that useful estimates of the excess functions of binary mixtures, which are characterized by some specific interactions, can be derived from their excess enthalpies, through an empirical application of the Flory theory of mixtures[4], despite the fact that the original development of the theory specifically excluded hydrogen bonds and strong dipolar interactions[5]. It is the purpose of this paper to examine theories of solutions[4,6] due to Prigogine and Flory for binary mixtures in which one of the components is slightly polar.

MATERIALS AND METHODS

Benzene, cyclohexane, carbon tetrachloride and dioxane were purified and their purity checked as reported earlier[7,8]. 1,2-Dibromoethane was purified by fractional crystallization. Its density at 20°C agreed within 0.00002 g cm^{-3} with those in the literature[9].

Vapour pressures of pure components and their mixtures were determined by a static method as already reported[10]. The temperature was controlled within ±0.01°C by toluene regulator. The vapour pressures of pure compounds were reproducible within 0.02 mm Hg. The equilibrium mole fraction x_1 of 1,2-dibromoethane in the liquid phase was determined from the refractive index n, measured with a Carl Zeiss refractometer maintained at 20±0.01°C, and was computed from the relation

$$n = a + bx_1 + cx_1^2$$

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

TABLE 1

TOTAL VAPOUR PRESSURES AND EXCESS FREE ENERGIES FOR THE SYSTEMS AT 20°C

Mole fraction x_1	P (*mm Hg*)	G^E (*cal mol*$^{-1}$)
1,2-dibromoethane(1) + benzene(2)		
0.0000	74.35	—
0.0815	69.26	10.90
0.1100	67.45	14.42
0.2390	59.51	27.34
0.3200	54.59	32.96
0.3815	50.89	35.89
0.4625	46.26	37.88
0.4950	44.50	38.06
0.6095	37.03	36.07
0.7350	28.62	29.09
0.7890	24.73	24.67
0.8815	17.98	15.18
1.0000	8.05	—
1,2-dibromoethane(1) + cyclohexane(2)		
0.0000	76.92	—
0.1385	71.76	96.98
0.1825	69.92	119.84
0.3375	64.14	175.01
0.4825	59.82	195.11
0.5695	56.10	193.41
0.6100	53.96	189.01
0.6935	49.88	172.23
0.7975	43.12	135.31
0.8975	32.28	80.31
0.9350	24.83	53.97
0.9565	22.11	37.33
1.0000	8.05	—
1,2-dibromoethane(1) + carbon tetrachloride(2)		
0.0000	89.38	—
0.1450	80.23	55.38
0.2310	74.35	78.06
0.3522	67.26	98.95
0.4375	62.13	106.56
0.5535	55.46	107.82
0.6470	48.13	101.06
0.6900	44.65	95.96
0.7585	38.76	83.21
0.8275	32.57	66.22
0.9200	21.74	35.28
1.0000	8.05	—

TABLE 1 (*continued*)

Mole fraction x_1	*P* (*mm Hg*)	G^E (*cal mol*$^{-1}$)
1,2-dibromoethane(1)+1,4-dioxane(2)		
0.0000	26.16	—
0.0725	24.97	0.91
0.1945	22.48	8.82
0.2350	21.79	12.25
0.3275	20.81	21.27
0.4255	18.03	30.44
0.5375	17.52	38.30
0.6025	16.32	40.67
0.7180	14.31	39.50
0.7875	13.06	35.07
0.8700	11.43	25.43
0.9410	9.94	13.13
1.0000	8.05	—

RESULTS

The total vapour pressures at different mole fractions are given for the four mixtures in Table 1, together with the excess Gibb's free energies G^E computed by Barker's method[11]. The second virial coefficients of the pure substances were calculated from the Berthelot equation[12] except for benzene for which Allen et al.'s[13] value was used. It was assumed that $B_{12} = (B_{11}+B_{22})/2$. The parameters A, B and C of the equation:

$$G^E/RT = x_1 x_2[A+B(x_1-x_2)+C(x_1-x_2)^2] \tag{1}$$

are given in Table 2 together with the standard deviations $\sigma(P)$ of the observed vapour pressures from those calculated. The errors in G^E were estimated to be of the order of ± 1.5 cal mol^{-1} in the mixtures studied here.

DISCUSSION

The values of G^E are positive for these mixtures and lie in the sequence cyclohexane > carbon tetrachloride > benzene > dioxane. The values of G^E for 1,2-dibro-

TABLE 2

VALUES OF PARAMETERS OF EQN (1) AT 20°C

System	*A*	*B*	*C*	σP (*mm Hg*)
1,2-Dibromoethane(1)+benzene(2)	0.2616	0.0025	−0.0173	0.12
1,2-Dibromoethane(1)+cyclohexane(2)	1.3439	−0.0553	0.1762	0.51
1,2-Dibromoethane(1)+carbon tetrachloride(2)	0.7457	−0.0259	0.0792	0.35
1,2-Dibromoethane(1)+1,4-dioxane(2)	0.2482	−0.2219	−0.0479	0.32

moethane+benzene have also been reported by Neckel and Volk[14], but are consistently more positive than ours, the greatest difference being 2.5 cal mol^{-1}. The results were examined in the light of the average potential model of Prigogine et al.[15] and the statistical theory of Flory[4].

According to the refined theory of Prigogine et al.[15]

$$G^E/x_1x_2 = -\{h_1(-2\theta+9\rho^2)-\tfrac{1}{2}TC_{p_1}(\theta^2-\tfrac{3}{4}\delta^2+\delta\theta(1+2x_2))- -\tfrac{3}{4}kT\rho[\theta(x_1-x_2)+\tfrac{1}{2}\delta+5\rho]\}$$

The various parameters have the same significance as discussed by Prigogine[6] and have been calculated as described earlier[3].

TABLE 3

COMPARISON OF THE CALCULATED AND EXPERIMENTAL G^E VALUES AT 20°C AT EQUIMOLAR COMPOSITION

System	G^E *(cal mol^{-1})*		
	Exptl.	*Prigogine*	*Flory*
1,2-Dibromoethane+benzene	37.95	15.21	141.23
1,2-Dibromoethane+cyclohexane	194.75	49.66	314.04
1,2-Dibromoethane+carbon tetrachloride	108.50	8.80	42.24
1,2-Dibromoethane+1,4-dioxane	36.00	15.06	89.85

G^E values for an equimolar composition computed in this way by taking a non-polar component as the reference are recorded in Table 3. The contributions due to dipolar and inductive effects to the excess function G^E have not been considered as they were found to be very small for these systems. It is obvious from Table 3 that G^E_{calc} for these mixtures agree well with G^E_{obs} so far as sign is concerned but this theory is unable to predict the results qualitatively.

The results were also examined for Flory's theory[4]. The experimental values[16] of V^E for equimolar compositions were used to calculate $\tilde{T}$ which was substituted in the equation

$$\tilde{T} = \left[\frac{\phi_1 P_1^*\tilde{T}_1+\phi_2 P_2^*\tilde{T}_2}{\phi_1 P_1^*+\phi_2 P_2^*}\right]\left[1-\frac{\phi_1\theta_2 x_{12}}{\phi_1 P_1^*+\phi_2 P_2^*}\right]^{-1}$$

from which $\theta_2 x_{12}$ was evaluated at 20°C and substituted in the expression

$$G^E = 3T[x_1(P_1^*V_1^*/T_1^*)\ln(\tilde{v}_1^{1/3}-1)/(\tilde{v}_{calc}^{1/3}-1)+ +x_2(P_2^*V_2^*/T_2^*)\ln(\tilde{v}_2^{1/3}-1)/(\tilde{v}_{calc}^{1/3}-1)]+ +x_1P_1^*V_1^*(\tilde{v}_1^{-1}-\tilde{v}_{calc}^{-1})+x_2P_2^*V_2^*(\tilde{v}_2^{-1}-\tilde{v}_{calc}^{-1})+ +x_1V_1^*\theta_2x_{12}\tilde{v}_{calc}^{-1}$$

to get G^E. The various quantities needed for this purpose were calculated as previously described[3]. The values of G^E_{calc} for the various systems at 20°C obtained in this manner are compared with the experimentally determined quantities in Table 3. The values of G^E_{calc} for all the systems thus obtained, agree in sign with the experimental values. However, even Flory's theory does not correctly predict the magnitude of G^E for these mixtures. The failure of Flory's theory might be attributed to the uncertainty in the evaluation of $\theta_2 x_{12}$ from V^E values; it might have been better to have evaluated it from H^E values, as was pointed out by Benson and Singh[17]. Thus none of these theories of solutions of non-electrolytes explain satisfactorily the excess function studied here for the present systems.

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