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Note

Thermodynamics of binary mixtures: excess enthalpies of 1,2-dibromoethane mixtures with benzene, cyclohexane, carbon tetrachloride and dioxane at 25 °C

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In previous communications[1,2], we reported the excess volumes of mixing and excess Gibbs free energies of mixing of the mixtures of 1,2-dibromoethane + benzene, + cyclohexane, + carbon tetrachloride and + 1,4-dioxane. In the present paper, we report excess enthalpies measurements for these systems at 25 °C with the aim to examine the cell model theory[3] of Prigogine and Flory's theory[4] for mixtures in which one of the components is slightly polar. The results have also been examined for molecular interactions in 1,2-dibromoethane + C_6H_6 and + dioxane mixtures.

MATERIALS AND METHODS

The materials were purified and their purity checked as reported earlier[5–7]. Excess enthalpies were measured in a previously described[8] calorimeter, the working of which was checked by measuring the excess enthalpies of mixing of carbon tetrachloride + benzene at 25 °C. The temperature of the water-bath in which the measurements were made was controlled better than ±0.001 °C.

RESULTS

The excess enthalpies of different mole fractions of these systems at 25 °C are given in Table 1 and were fitted to the expression:

$$\frac{H^E}{x_1x_2} = h_0+h_1(x_1-x_2)+h_2(x_1-x_2)^2+h_3(x_1-x_2)^3 \quad (1)$$

where h_0, h_1, h_2 and h_3 are the constants and x_1 and x_2 are the mole fractions of components 1 and 2 in the mixture. These constants were evaluated by fitting the experimental values of H^E to eqn (1) by the method of least squares. The values obtained along with the standard deviations are given in Table 2.

TABLE 1

ENTHALPIES OF MIXING H^E AT MOLE FRACTIONS x_1 OF 1,2-DIBROMOETHANE AT 25°C

x_1	H^E (*cal mol*$^{-1}$)	x_1	H^E (*cal mol*$^{-1}$)
1,2-Dibromoethane(1)+cyclohexane(2)		*1,2-Dibromoethane(1)+carbon tetrachloride(2)*	
0.1521	149.52	0.1710	63.14
0.2124	200.03	0.2335	80.96
0.2995	251.65	0.2975	94.93
0.3616	277.55	0.4473	110.84
0.4206	290.31	0.5274	112.34
0.4545	297.63	0.5821	110.60
0.5506	296.92	0.6066	108.95
0.6601	276.15	0.7511	86.57
0.7469	244.21	0.7719	81.70
0.8506	175.80	0.8491	58.50
1,2-Dibromoethane(1)+benzene(2)		*1,2-Dibromoethane(1)+1,4-dioxane*	
0.2227	37.11	0.1376	−32.51
0.2687	44.06	0.1965	−43.66
0.3484	52.72	0.2743	−57.96
0.4222	58.14	0.3305	−66.09
0.4665	59.70	0.4289	−72.80
0.5115	60.02	0.4784	−73.30
0.6464	55.90	0.5637	−70.81
0.6842	52.50	0.6505	−64.97
0.8765	27.21	0.7035	−59.37
		0.8559	−34.65

DISCUSSION

The results were examined for Flory's theory[4] and the cell model theory[3] of Prigogine. According to the refined theory of Prigogine et al.[9].

$$\frac{H^{\mathrm{E}}}{x_1 x_2} = \{(TC_{p1}-h_1)(-2\theta+9\rho^2)+\tfrac{1}{2}TC'_{p1}[\theta^2-\tfrac{3}{4}\delta^2+\delta\theta(1+2x_2)]\} \qquad (2)$$

The parameters δ, ρ and θ were evaluated from critical constant data, where C_{p_1} and h_1 are the heat capacities and configurational enthalpies for the pure components, and C'_{p_1} is the first derivative of C_{p_1} with respect to temperature. These parameters have been calculated as described earlier[10]. The H^{E} values for an equimolar composition computed in this way by taking a non-polar component as the reference are recorded in Table 3.

According to Flory's[4] theory, H^{E} is given by

$$H^{\mathrm{E}} = x_1 P_1^* V_1^* \left[\frac{1}{\tilde{v}_1}-\frac{1}{\tilde{v}_{\mathrm{calc}}}\right] + x_2 P_2^* V_2^* \left[\frac{1}{\tilde{v}_2}-\frac{1}{\tilde{v}_{\mathrm{calc}}}\right] + x_1 V_1^* \theta_2 \chi_{12} \tilde{v}_{\mathrm{calc}}^{-1} \qquad (3)$$

TABLE 2

VALUES OF THE CONSTANTS OF EQN (1) AND STANDARD DEVIATIONS (σH^E) AT 25 °C

System	h_0 (*cal mol^{-1}*)	h_1 (*cal mol^{-1}*)	h_2 (*cal mol^{-1}*)	h_3 (*cal mol^{-1}*)	(σH^E) (*cal mol^{-1}*)
1,2-Dibromoethane(1) + cyclohexane(2)	1198.38	22.00	166.67	278.50	1.38
1,2-Dibromoethane(1) + carbon tetrachloride(2)	451.87	16.00	11.32	−16.90	0.73
1,2-Dibromoethane(1) + benzene(2)	240.95	13.65	−33.40	45.13	0.24
1,2-Dibromoethane(1) + 1,4-dioxane(2)	−293.73	24.02	33.52	−63.25	0.59

TABLE 3

COMPARISON OF THE CALCULATED AND EXPERIMENTAL H^E VALUES AT 25 °C AT EQUIMOLAR COMPOSITION

System	H^E (*cal mol^{-1}*)		
	Exptl.	*Prigogine*	*Flory*
1,2-Dibromoethane + cyclohexane	229.6	109.33	376.9
1,2-Dibromoethane + carbon tetrachloride	112.9	51.13	152.9
1,2-Dibromoethane + benzene	60.3	67.69	173.4
1,2-Dibromoethane + 1,4-dioxane	−73.5	97.67	190.7

The various parameters have the same significance as discussed by Flory and were evaluated as described earlier[10]. $\theta_2 X_{12}$ was evaluated[2] from the experimental values[1] of V^E. H^E values were then calculated at equimolar compositions and have been recorded in Table 3. Examination of Table 3 shows that, but for qualitative agreement, both the theories correctly predict the sign of H^E for all the systems except for 1,2-dibromoethane + dioxane mixture.

The examination of the present data also gives an indication of the presence of weak interactions of 1,2-dibromoethane with benzene and dioxane. Ethylene dibromide is weakly polar and thus it has large positive heats with cyclohexane and carbon tetrachloride as is evident from Table 1. The values of H^E in 1,2-dibromoethane + benzene mixture is also positive but in this case the magnitude is comparatively small. The sharp decrease of H^E values of 1,2-dibromoethane with benzene as compared to that with cyclohexane (although their sizes are approximately the same) may be due to weak complex formation of 1,2-dibromoethane with benzene through its π-electron system. On the other hand, the negative H^E values of 1,2-dibromoethane with dioxane indicate the existence of some specific interactions in the system. The interaction in this system is probably due to the presence of the vacant *d*-orbital on the bromine atom in 1,2-dibromoethane which has the tendency to attract the lone pair of electrons on the oxygen atom in dioxane. However, it is difficult to comment specifically about the nature of these interactions in the absence of spectroscopic data.

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