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THERMODYNAMICS OF ETHYL IODIDE + BENZENE MIXTURES

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ABSTRACT

The values of the excess Gibbs free energy of mixing G^E for ethyl iodide + benzene and ethyl iodide + cyclohexane at 298.15 K have been obtained from the measured vapour pressure data. Heats of mixing H^E of ethyl iodide + cyclohexane at 298.15 K have been measured over the entire composition range. The H^E and G^E values for ethyl iodide + benzene are positive throughout the ethyl iodide concentration range, and $H^E > G^E$. The results have been analysed in terms of the Flory, Sanchez and Lacombe and the ideal associated solution model theory of non-electrolyte solutions. It has been observed that the ideal associated model approach, which assumes the presence of AB and A_2B molecular species, describes well (within ± 10 J mol^{-1} at the worst) the general dependence of H^E on X_A (mole fraction of ethyl iodide) over the whole composition range for ethyl iodide + benzene mixtures. The equilibrium constants for $A + B \rightleftharpoons AB$ and $2A + B \rightleftharpoons A_2B$ reactions, along with the enthalpies of formation of AB and A_2B molecular species, have also been calculated.

INTRODUCTION

The study of excess heats of mixing and excess volumes of mixing of 1-haloalkane + *n*-alkane mixtures [1–3] and also of ethyl iodide + aromatic hydrocarbon mixtures [4,5] has revealed the interaction of two components on the one hand, and the disruption of the favourable orientational order of the pure components on the other. The presence of weak specific interactions of the electron donor–acceptor type between the ethyl iodide and benzene molecules (benzene behaves as a electron donor) has also been supported by dielectric and refractive index studies coupled with IR and proton NMR spectrophotometric measurements [6]. As an extension of this investigation, G^E and H^E data have been coupled to give an understanding of the exact nature of molecular interactions in ethyl iodide + benzene mixtures. It is hoped that this information will ultimately lead to a better understanding of the physicochemical behaviour and molecular interactions in these binary mixtures.

EXPERIMENTAL

Ethyl iodide, cyclohexane and benzene (all from Aldrich, AnalaR grade) were purified using standard procedures [7]. The purity of the final samples was checked by density determinations at 298.15 ± 0.01 K, which were within ±0.00005, g ml^{-1} of the corresponding literature values [8–10].

Heat of mixing measurements at 298.15 K were measured using a flow microcalorimeter (model L.K.B. 2107, L.K.B. Broma, Sweden) in the manner described previously [4,5]. The uncertainty in the H^E values is about 1%. Vapour pressures of ethyl iodide + benzene and ethyl iodide + cyclohexane mixtures were determined using a static method as described by Nigam and Mahl [11]. The heights of mercury in the manometer were read using a cathetometer which could read up to ±0.001 cm. All vapour pressure measurements were reproducible to better than ±0.02 Torr. The (liquid phase) compositions of the different mixtures were determined by capacitance measurements of a cell (fitted in the vapour pressure still) using a dipole meter (type RL 09, S&I Instruments, Indore, India). The error in the composition measurements is less than 0.01%. Our measured vapour pressures for cyclohexane, benzene and ethyl iodide at 298.15 K agree to within 0.30% with the values evaluated at 298.15 K from vapour pressure data reported in the literature [10] at various temperatures.

RESULTS

The excess heats of mixing for the system ethyl iodide + cyclohexane at 298.15 K are given in Table 1. The data have been fitted to

$$H^E = X_A X_B \left[h_0 + h_1 (X_A - X_B) + h_2 (X_A - X_B)^2 \right] \tag{1}$$

where X_A is the mole fraction of ethyl iodide and h_0, h_1 and h_2 are

TABLE 1

Experimentally measured heat of mixing values for ethyl iodide (A)+cyclohexane (B) at 298.15 K

X_A	$H^E_{\text{expt.}}$
0.1299	418.48
0.2239	631.70
0.4121	852.50
0.5639	972.85
0.5966	970.75
0.7317	824.85
0.8703	447.98
0.9309	254.45

$h_0 = 3875.93$; $h_1 = 297.37$; $h_2 = -126.21$; $\delta H^E = 11.30$ (J mol^{-1})

TABLE 2

Measured total vapour pressure P, partial pressures P_1 and P_2, activity coefficients r, residual vapour pressure $R = P_{\text{expt.}} - P_{\text{calc.}}$, excess Gibbs free energy of mixing G^E and the parameters of eqn. (2) for different mole fractions X_A of ethyl iodide at 298.15 K

X_A	P (Torr)	P_1 (Torr)	P_2 (Torr)	r_1	r_2	R (Torr)	G^E (J mol^{-1})
Ethyl iodide (A) + cyclohexane (B) [a]							
0.00	97.61						
0.1105	107.86	14.85	86.90	1.4419	0.9901	+0.41	78.39
0.2457	122.83	33.05	73.80	1.5327	0.9795	−0.14	221.34
0.4101	135.00	55.20	57.77	1.4172	1.0218	−1.43	385.90
0.5303	143.11	71.37	46.07	1.2796	1.1203	+0.17	456.14
0.6100	147.15	82.17	38.24	1.1933	1.2293	+0.56	466.77
0.6781	148.00	91.33	31.57	1.1300	1.3569	+0.68	448.96
0.7103	147.20	95.64	28.43	1.1043	1.4299	+0.93	431.36
0.8052	144.60	108.42	19.11	1.0451	1.6987	−1.18	343.97
0.8754	141.42	117.82	12.25	1.0176	1.9541	+0.58	244.83
1.0	134.60						
Ethyl iodide (A) + benzene (B) [b]							
0.00	94.20						
0.0987	98.80	13.24	84.93	1.0773	1.0010	−0.48	20.49
0.2117	105.40	28.40	74.32	1.0557	1.0047	+0.74	37.71
0.3599	110.60	48.30	60.37	1.0327	1.0136	−0.47	50.19
0.4755	115.70	63.83	49.49	1.0193	1.0232	−0.00	52.27
0.5847	119.60	78.15	39.20	1.0102	1.0330	−0.22	48.62
0.6344	121.80	85.20	34.51	1.0071	1.0383	+0.16	45.33
0.7233	125.30	97.16	26.13	1.0033	1.0468	+0.47	37.25
0.8126	127.90	109.17	17.70	1.0011	1.0543	−0.05	26.76
0.9027	130.60	121.29	9.19	1.0000	1.0599	−0.45	14.42
1.0	134.50						

[a] $G_0 = 0.71676$; $G_1 = 0.37697$; $G_2 = -0.16704$.

[b] $G_0 = 0.08376$; $G_1 = -0.01656$; $G_2 = -0.00644$.

adjustable parameters. These parameters were evaluated using the method of least-squares and are given in Table 1 together with the standard deviation of the molar heats of mixing $\delta(H^E)$.

Vapour pressure data for ethyl iodide + benzene and ethyl iodide + cyclohexane mixtures at 298.15 K were used to evaluate the molar excess Gibbs free energies of mixing G^E using the method of Barker [12]. The form of the function used for G^E following Redlich and Kister [13] is

$$G^E/RT = X_A X_B\left[G_0 + G_1(X_A - X_B) + G_2(X_A - X_B)^2\right] \tag{2}$$

where G_0, G_1 and G_2 are adjustable parameters. These parameters, along with the G^E data at 298.15 K for ethyl iodide + benzene and ethyl iodide + cyclohexane, are given in Table 2. In these calculations the virial coefficients required were obtained from Berthelot's equation [14], and the critical constant data were taken from the literature [15–17].

DISCUSSION

We are unaware of any G^E and H^E data for ethyl iodide + cyclohexane and G^E data for ethyl iodide + benzene mixtures at 298.15 K with which to compare our results.

G^E and H^E data (4) at 298.15 K were combined, giving TS^E values which are positive at all ethyl iodide mole fractions. The curve of TS^E values plotted against X_A is symmetrical (Fig. 1). At the simplest qualitative level, the observed H^E and G^E data for these mixtures may be accounted for if we assume (i) that there are specific interactions of the electron donor–acceptor type between ethyl iodide + benzene, and (ii) that there is disruption in the orientational order of the pure components.

As the orientational freedom of ethyl iodide and benzene molecules increases in the mixtures, the TS^E values should be strongly positive. On the other hand, since the measured H^E results from the cumulative effects of factors (i) and (ii) mentioned above, the positive H^E value for this mixture may be accounted for if it is assumed that the effects due to factor (ii) outweigh those due to factor (i). We next examined our results using the Flory theory [18,19], which takes the shape and size of the molecule into consideration, and Sanchez and Lacombe's theory [20,21], which is a lattice theory similar to the theory of Flory and Huggins [22] but which incorporates the idea of vacant sites or holes in the lattice fluids as suggested by Guggenheim [23,24]. According to the Flory theory, G^E is given by

$$\begin{aligned} G^E = 3T\big[&x_1\left(P_1^\star V_1^\star/T_1^\star\right)\ln\left(\tilde{V}_1^{1/3}-1\right)/\left(\tilde{V}_{\text{calc.}}^{1/3}-1\right) \\ &+x_2\left(P_2^\star V_2^\star/T_2^\star\right)\ln\left(\tilde{V}_2^{1/3}-1\right)/\left(\tilde{V}_{\text{calc.}}^{1/3}-1\right)\big] \\ &+H^E_{\text{theor.}} \end{aligned} \qquad (3)$$

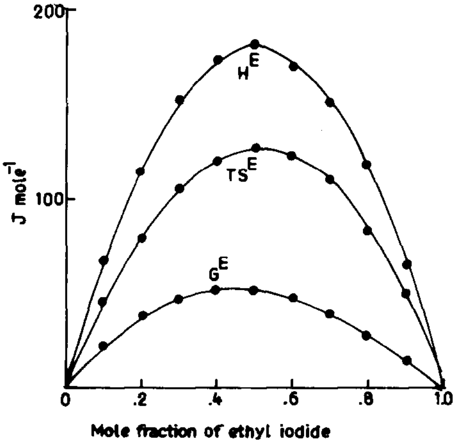

Fig. 1. Ethyl iodide + benzene system at 298.15 K.

TABLE 3

Comparison of G^{E} values calculated according to the Flory and Sanchez and Lacombe theories for the ethyl iodide + benzene and ethyl iodide + cyclohexane systems at 298.15 K

Mole fraction X_{A}	Expt. (J mol^{-1})	Flory (J mol^{-1})	Sanchez and Lacombe (J mol^{-1})
Ethyl iodide (A) + cyclohexane (B)			
0.1	68.77	236.35	2788.30
0.3	280.70	570.57	2710.68
0.5	444.17	691.49	2867.88
0.7	437.69	615.26	3261.09
0.9	203.33	275.09	3915.85
Ethyl iodide (A) + benzene (B)			
0.1	20.72	44.87	2299.6
0.3	46.51	105.27	2009.70
0.5	51.90	135.23	2021.92
0.7	39.61	108.91	2176.16
0.9	14.81	48.12	3045.45

where $\tilde{V}_{\mathrm{calc.}} = \tilde{V}^0 + \tilde{V}^{\mathrm{E}}_{\mathrm{calc.}}$, and according to the Sanchez and Lacombe theory by

$$\begin{aligned} G^{\mathrm{E}}(T,\ X_1) = H^{\mathrm{E}} - RT\Big\{ & \sum X_i \ln \phi_i + \gamma_{\mathrm{mix}}(V_{\mathrm{mix}} - 1) \ln(1 - P_{\mathrm{mix}}) \\ & + \ln \tilde{P}_{\mathrm{mix}} - \sum X_i\left[\gamma_1^0\left(\tilde{V}_1 - 1\right) \ln\left(1 - \tilde{P}_i\right) + \ln \tilde{P}_i\right]\Big\} \\ & - \left[X_i\left(\gamma_i^0\left(\tilde{V}_i - 1\right) \ln\left(1 - \tilde{P}_i\right) + \ln \tilde{P}_i\right)\right. \\ & \left. + X_j(V_i - 1) \ln\left(1 - \tilde{P}_j\right) + \ln P_j)\right] \end{aligned} \tag{4}$$

where all the parameters have the significance as described by Flory and Sanchez and Lacombe. For the ethyl iodide + benzene system these parameters have been calculated in a previous work [4]. G^{E} values at X_{A} (mole fractions of ethyl iodide) of 0.1, 0.3, 0.5, 0.7 and 0.9 have been calculated and are compared with the corresponding experimentally determined values in Table 3.

The H^{E} and activity coefficient data for these mixtures were then analysed in terms of an ideal associated solution model [25–27]. It is assumed that in binary solutions of ethyl iodide (A) + benzene (B), a mutual equilibrium of species $\mathrm{A}_m\mathrm{B}_n$, where $m = 1, 2, 3, \ldots, m$ and $n = 1, 2, 3, \ldots, n$, exists according to the reaction

$$m\mathrm{A} + n\mathrm{B} = \mathrm{A}_m\mathrm{B}_n \tag{5}$$

The equilibrium constants for the various association reactions represented by equation (5) are thus

$$K_{m,n} = a_{\mathrm{A}_m\mathrm{B}_n}/a_{\mathrm{A}}^m a_{\mathrm{B}}^n \tag{6}$$

where a denotes activity. If the activity coefficients of the various species represented in eqn. (5) are assumed to be unity [25,28] the mass balance equation for the system can be written as

$$a_A + a_B + \sum K_{m,n} a_A^m a_B^n = 1 \tag{7}$$

Two simple cases were then considered

case (i) $m = n = 1$

case (ii) $m = 1, 2$ and $n = 1$

Equation (7) thus reduces to eqns. (8) and (9) below for cases (i) and (ii) respectively.

$$(1 - a_A - a_B)/a_B = K_{11} a_A \tag{8}$$

$$(1 - a_A - a_B)/a_A a_B = K_{11} + K_{21} a_A \tag{9}$$

In order to evaluate the various K parameters in eqns. (8) and (9) for the two cases (1) and (ii) mentioned above, the observed activities of the components of these binary mixtures were corrected [29–31] for the dispersion concentrations using

$$a_A = r_A X_A / r_A^{\star} \tag{10}$$

and

$$a_B = \gamma_B X_B / r_B^{\star} \tag{11}$$

where $r_A^{\star}$ and $r_B^{\star}$ are the activity coefficients of a reference mixture. Since cyclohexane is inert in nature and has nearly the same volume as that of benzene, ethyl iodide (A) + cyclohexane (B) was taken as the reference system for the present analysis.

If AB molecular species only (case (i)) are present in the present system, a plot of $(1 - a_A - a_B)/a_B$ versus a_A should be a straight line passing through the origin. However, a non-linear curve was obtained. This shows that some other molecular species are also present along with AB. A plot of $(1 - a_A - a_B)/a_A a_B$ versus a_A yielded a straight line for all points except a few below $a_A = 0.1$. This suggests that these mixtures may be assumed to have both AB and A_2B molecular species in the solution. The K_{11} and K_{21} were evaluated from the intercept and slope of the line and are given in Table 4.

TABLE 4

Equilibrium constants K_{11} and K_{21} and enthalpies of formation ΔH_{11} and ΔH_{21} for the various molecular species present in ethyl iodide + benzene mixtures at 298.15 K

K_{11}	K_{21}	ΔH_{11} (kJ mol^{-1})	ΔH_{21} (kJ mol^{-1})
0.35	1.07	−11.142	−3.0529

Examination of H^E data for this mixture in terms of case (ii), which involved consideration of AB and A_2B molecular species in solution required that H^E is expressed as

$$H^E = \left[n_{AB}\ \Delta H_{AB} + n_{A_2B}\ \Delta H_{A_2B}\right]/N_A + N_B \tag{12}$$

where n_{AB} and n_{A_2B} are the amounts of species AB and A_2B present in solution at equilibrium, N_A and N_B are the stoichiometric amounts of A and B, and ΔH represents the enthalpy of formation of the various molecular species present in the mixture.

If the equilibrium mole fractions of A, B, AB and A_2B are represented by Z_A, Z_B, Z_{AB} and Z_{A_2B}, respectively, then for an ideal associated mixture of A + B containing AB and AB_2 molecular species

$$Z_A + Z_B + Z_{AB} + Z_{A_2B} = 1 \tag{13}$$

where

$$Z_{A_mB_n} = K_{m,n} Z_A^m Z_B^n \qquad (m = 1, 2 \text{ and } n = 1) \tag{14}$$

The experimental H^E values were again corrected for dispersion contributions by subtracting the H^E values for the ethyl iodide + cyclohexane system at 298.15 K from $H^E_{\text{expt.}}$. Consequently, in eqn. (12)

$$H^E = H^E_{\text{expt.}} - H^E_{(\text{ethyl iodide + cyclohexane})} \tag{15}$$

Algebraic manipulation of eqns. (12) and (13) and the mass balance equations

$$N_A = n_A + n_{AB} + 2n_{A_2B} \tag{16}$$

$$N_B = n_B + n_{AB} + n_{A_2B} \tag{17}$$

leads to

$$pH^E = (K_{11}\ \Delta H_{11} + K_{21}\ \Delta H_{21} + Z_A) \tag{18}$$

where

$$p = \left(1 + K_{11}Z_A + K_{21}Z_A^2\right)/Z_A(1 - X_A) \tag{19}$$

Further combination of eqns. (13), (16) and (17) leads to

$$X_A = \left[(1 + K_{11})Z_A + K_{21}Z_A^2(2 - Z_A)\right] \\ /\left[1 + K_{11}Z_A(2 - Z_A) + K_{21}Z_A^2(3 - 2Z_A)\right] \tag{20}$$

Using the values of K_{11} and K_{21} described above for a solution containing AB and A_2B molecular species, X_A values for various Z_A values were calculated. These quantities were combined with the corresponding H^E values in order to construct a graph of pH^E vs. Z_A. A straight line was observed over the entire range of composition. By the combination of the least-squares slope and intercept with K_{11} and K_{21}, ΔH_{11} and ΔH_{21} values

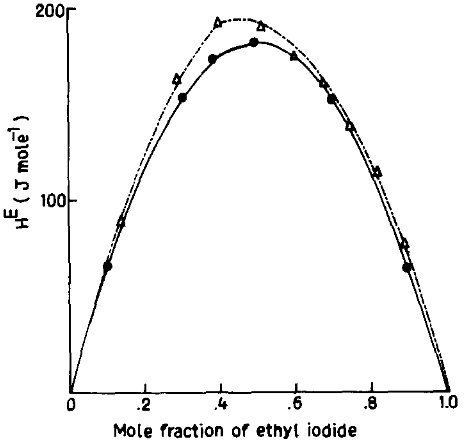

Fig. 2. Ethyl iodide + benzene system at 298.15 K: ●———●, experimental values; △·—·—·△, calculated values.

were calculated, and are given in Table 4. By using K_{11}, K_{21}, ΔH_{11} and ΔH_{21} values, calculated above using eqn. (18), H^{E} values at different mole fractions were obtained. These are compared with the corresponding $H^{\mathrm{E}}_{\mathrm{expt.}}$ values in Fig. 2. The agreement is satisfactory. The $H^{\mathrm{E}}_{\mathrm{calc.}}$ curve reproduces within (± 10 J mol^{-1}) in the worst case the corresponding experimental results. The analysis of H^{E} and G^{E} data for ethyl iodide + benzene mixtures thus suggests that the mixtures are characterized by the presence of AB and A_2B molecular species in solution.

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