THERMODYNAMICS OF WEAK INTERACTIONS: EXCESS ENTHALPIES AND EXCESS GIBBS FREE ENERGIES OF MIXING

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ABSTRACT

Excess enthalpies of chloroform + n-hexane, bromoform + n-hexane, bromoform + pyridine and bromoform + benzene and excess Gibbs free energies of mixing for bromoform + pyridine, chloroform + pyridine, bromoform + n-hexane, chloroform + n-hexane and bromoform + benzene have been determined at 308.15 K and the same factors have been examined for Barker's theory to understand the magnitude and nature of various interactions between the components of these mixtures.

INTRODUCTION

It is the purpose of this paper to report excess enthalpies and excess Gibbs free energies of mixing for mixtures A + B some of which are assumed to have specific A–B interactions: chloroform + pyridine, chloroform + n-hexane; bromoform + pyridine, bromoform + benzene, and bromoform + n-hexane.

EXPERIMENTAL

Method

The liquids were purified and their purities checked as reported earlier[1].

Vapour pressures were measured by a static method[2]. The apparatus (excluding the manometric part) was placed in a water thermostat which in turn was placed in another water thermostat. The temperature of the outer thermostat was controlled to ±0.01 K and the temperature drift in the inner thermostat was of the order of ±0.002 K. The manometric part was maintained at a higher temperature 323.15 ±0.01 K to avoid condensation of liquid vapours. The pressure measurements for benzene + pyridine and benzene + bromoform mixtures were reproducible to within 0.001 torr while for n-hexane + chloroform and n-hexane + bromoform they were reproducible to ±0.03 torr. The equilibrium mole fraction in the liquid phase was determined from refractive index measurements as reported earlier[3].

Excess enthalpies were measured in an adiabatic calorimeter described earlier[4].

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RESULTS

Total vapour pressure, p, together with the excess Gibbs free energies, G^E, computed by Barker's method[5] for different mole fractions x_1 of component 1 are recorded in Table 1. The second virial coefficients of the pure substances except benzene and n-hexane were evaluated from the Berthelot equation[6] using critical constant data[7]; those for benzene and n-hexane were taken from the literature[8,9]. The critical constants, V_c, P_c and T_c of bromoform were evaluated from the Lyderson method, the Riedel method and the modified Guldberg rule, respectively, as reported[10]. It was further assumed that $B_{12} = (B_{11} + B_{22})/2$. The excess Gibbs free energy was assumed to have the form:

$$G^E/RT = x_1(1-x_1)[G_0 + G_1(2x_1-1) + G_2(2x_1-1)^2] \qquad (1)$$

where G_0, G_1 and G_2 were chosen by the method of least squares. It was found that only the three terms of expression (1) are sufficient to give results which are in agreement with the experimental vapour pressures.

The results for excess enthalpies were fitted to the expression

$$H^E = x_1(1-x_1)[h_0 + h_1(2x_1-1) + h_2(2x_1-1)^2] \qquad (2)$$

and the parameters h_0, h_1 and h_2 were evaluated by fitting $H^E/x_1(1-x_1)$ to expression (2) by the method of least squares. The parameters of expressions (1) and (2) together with the standard deviations $\sigma(H^E)$ of the excess enthalpy, and $\sigma(p)$ of the observed vapour pressure from those calculated, are given in Table 2. Further in bromoform(2) +pyridine(1), whereas no coloration was first observed, the solution gradually acquires a yellow colour on mixing. In several cases ($x_2 > 0.75$), the liquid was found to be opaque at the end of the experiment. Because of this no attempt was made to determine H^E and G^E for this mixture at $x_2 > 0.75$. The results tabulated in Table 1 correspond to those compositions in which opacity was not apparent. Following a similar observation[11] for carbontetrachloride + triethylamine, light was excluded from the experiment in a number of measurements but it had no effect on the color.

DISCUSSION

For bromoform + pyridine and bromoform + benzene, the results for H^E are negative suggesting[12] specific interactions between the components of these mixtures. On the other hand, there is endothermic mixing in bromoform + n-hexane and chloroform + n-hexane; the former being more endothermic than the latter. Moreover, whereas the curve of H^E against the mole fraction x_1 of bromoform is almost symmetrical about $x_1 = 0.5$ in bromoform + n-hexane, this is not so for chloroform + n-hexane; the curve is skewed towards the chloroform-rich end of the mole fraction scale.

Comparison of H^E values of bromoform + pyridine and bromoform + benzene with those of the earlier data[13,14] for chloroform + pyridine at 308.15 K and chloro-

TABLE 1

TOTAL VAPOUR PRESSURE, P, EXCESS GIBBS FREE ENERGIES OF MIXING, G^E, AND EXCESS ENTHALPIES, H^E, OF VARIOUS SYSTEMS AT 308.15 K FOR DIFFERENT MOLE FRACTIONS, X_1, OF COMPONENT 1

X_1	P (Torr)	G^E ($J\ mol^{-1}$)	H^E ($J\ mol^{-1}$)
Chloroform (1) + n-hexane (2)			
0.0598			67.03
0.1102			132.90
0.1803			228.25
0.2101	270.12	198.53	
0.3499			450.38
0.3503	286.17	332.25	
0.4201			518.17
0.4799	296.87	399.87	
0.5800			586.04
0.5900	300.84	398.08	
0.6297			572.11
0.6602	299.37	367.08	
0.7001	297.81	339.73	
0.7502			471.96
0.7700	293.34	278.71	
0.8001			405.06
0.8301	288.51	210.57	
0.8398			344.82
0.8802	284.31	149.86	
0.8903			249.78
0.9098	281.40	111.94	
0.9299			162.15
Chloroform (1) + pyridine (2)			
0.1300	46.50	−291.77	
0.2501	63.94	−463.15	
0.3199	76.03	−530.52	
0.4503	104.33	−603.01	
0.5398	127.15	−616.33	
0.6901	170.20	−564.59	
0.7602	192.28	−501.32	
0.8299	214.37	−406.53	
0.8997	237.95	−273.29	
0.9601	257.67	−122.19	
n-Hexane (1) + bromoform (2)			
0.0401	49.67	159.08	
0.0897			320.03
0.1300			450.34
0.1403	101.16	473.14	
0.2498	133.39	705.73	
0.2501			728.20
0.3100	146.38	729.32	
0.3499			879.88
0.4102			939.96
0.4401	167.61	899.14	
0.4798			960.10
0.5599	183.10	909.39	

TABLE 1 *(continued)*

X_1	P (Torr)	G^E (J mol^{-1})	H^E (J mol^{-1})
n-Hexane (1) + *bromoform* (2)			
0.6302	191.84	875.57	
0.6401			880.15
0.7097			785.24
0.7848	209.19	676.28	
0.8397	216.56	555.11	
0.8400			505.48
0.9102			300.07
0.9300	226.80	284.60	
Benzene (1) + *bromoform* (2)			
0.0399	15.29	9.99	
0.0598			−28.12
0.0897	22.29	21.77	
0.1200	26.45	28.18	
0.1501			−64.16
0.2802	48.59	59.17	
0.2899			−107.05
0.3498	58.02	70.96	
0.3503			−120.01
0.4499	71.32	84.79	
0.4800			−133.18
0.5302	81.64	93.24	
0.5503			−134.07
0.6297			−128.13
0.6498	96.66	97.86	
0.7101			−113.06
0.7403	107.62	92.22	
0.7502			−103.20
0.7898			−92.04
0.8598	121.99	66.60	
0.8699			−63.11
0.9201			−41.02
Pyridine (1) + *bromoform* (2)			
0.2300	12.05	−362.98	
0.2999	13.24	−422.28	
0.3250			−1420.36
0.3601	14.53	−456.49	
0.3997	15.49	−471.63	
0.4449			−1700.12
0.4900	17.85	−483.64	
0.5501			−1750.40
0.5698	20.12	−470.06	
0.5801			−1725.70
0.6198			−1671.08
0.6602	22.84	−428.56	
0.6804			−1541.98
0.7400	25.33	−367.60	
0.7601			−1265.73
0.8403			−915.05
0.8599	29.14	−232.34	
0.8899			−650.49
0.9502			−300.15

TABLE 2

VALUES OF THE PARAMETERS OF EQNS (1) AND (2) FOR THE VARIOUS MIXTURES AT 308.15 K

System	$h_0 (J\,mol^{-1})$	$h_1 (J\,mol^{-1})$	$h_2 (J\,mol^{-1})$	G_0	G_1	G_2	$\sigma(H^{E})(J\,mol^{-1})$	$\sigma(p)(Torr)$
Chloroform(1)+n-hexane(2)	2281.00	757.26	−571.06	0.6307	0.1161	−0.2855	3.79	1.17
Chloroform(1)+pyridine(2)				−0.9592	−0.1019	−0.2258		1.14
n-Hexane(1)+bromoform(2)	3841.00	130.20	−20.60	1.4287	0.0676	0.2982	4.73	1.97
Benzene(1)+bromoform(2)	−537.00	37.40	13.98	0.1414	0.0769	0.0376	0.474	0.13
Pyridine(1)+bromoform(2)	−7001.00	918.49	1849.82	−0.7545	0.0494	−0.0664	5.28	0.08

form + benzene at 298.15 K suggest that exothermicity decreases when chloroform is replaced by bromoform in the mixtures with pyridine and benzene. H^E values for bromoform + n-hexane and chloroform + n-hexane support this observation. We are unaware of any data at 308.15 K with which to compare our results for H^E and G^E for these systems. However, our H^E values for pyridine(1) + bromoform(2) are comparable to the H^E values at 298.2 K measured by Findlay and Kavanagh[15]. This mixture thus has positive C_p^E and so supports our conclusion that there are specific interactions between the components of this mixture. An interesting feature of this mixture is that a mixture containing $x_2 \geq 0.75$ on slow cooling in the dark, yields yellowish crystals (m.p. > 200 °C) after several hours. Further work on these crystals is in progress.

The crystallinity of the compound is clearly exhibited by excellent powder diffraction maxima obtained by using Ni-filtered Cu K_α-radiation ($\lambda = 1.5418$ Å) at 40 kV and 20 mA. The other experimental conditions are as follows: divergence slit = 1°; receiving slit = 0.1 mm; scatter slit = 1°; scanning speed = 1° min^{-1}; time constant = 10; counts per second = 2000; attenuation = 4.

The powdered sample was stuffed in an aluminum holder and X-rayed in a Philips PW 1050 goniometer. The peaks were recorded with a PW 1370 (flat bed) recorder.

The 2θ-angles, d-spacing (in Å) and the observed intensity of 34 peaks are given in Table 3.

The results of H^E were examined for Barker's theory[16]. The generalised lattice model theory allows a molecule to have contact points of several types; each type having a definite interaction energy. The total number of contacts which a molecule, occupying r_A sites on an A coordinated lattice, is capable of making is given by

$$q_A^Z = r_A Z - 2r_A + 2$$

As the molar volume of bromoform (A) is almost the same as that of the solvents (S), pyridine and benzene, used here, a value of $r_A = r_S = 2$ and $Z = 4$ has been used throughout this paper. For n-hexane a value of $r_S = 3$ has been used. Furthermore the non-polar component, benzene is assumed to have contact points of one type, while pyridine has one N contact point, Q_N^S, and ($q_S^Z - 1$) contact points, Q_R^S, for the residual molecule. n-Hexane is presumed to have 6 contact points of the same type for the terminal portions and 2 contact points of the same type for the remaining portion while bromoform is assumed to have one H contact point, Q_H^A, and 5 contact points, Q_{Br}^A, of another type for the residual part. For bromoform(A) + pyridine(S), the interactions considered were: hydrogen bond (N...H) of strength, u_2, and a non-specific interaction of strength, u_1, for all the remaining contact points. U_V^E (excess energy at constant volume) values were then calculated from

$$u_V^E = -2RT[(X_H X_{Br} + X_H X_R + X_R X_{Br} + X_{Br} X_H)\eta_1 \ln \eta_1 + X_H X_N \eta_2 \ln \eta_2] \quad (3)$$

where the parameters X_H, X_{Br}, X_R and X_N are solutions of

$$X_\mu A \sum_{B,\mu} \eta_{\mu\nu} ABX_\nu B = (Q_\mu A/2) x_A \quad (4)$$

and

$$\eta_i = \exp\left(-u_i/RT\right) \qquad (i = 1 \text{ or } 2) \tag{5}$$

The various symbols have their usual meanings[16]. With certain assumed values for u_1 and u_2, expression (4) was solved for X_H, X_{Br}, X_N and X_R at a particular value of x_A. The values so obtained were then used to calculate the corresponding value of U_V^E and hence of H^E from the relation

$$U_V^E = H^E - TV^E \alpha_m/(K_T)_m \tag{6}$$

where α_m, $(K_T)_m$, and V^E are, the expansivity isothermal compressibility and excess volumes of the mixture, respectively. The excess volumes of mixing values were taken from our previous publication while α_m and $(K_T)_m$ were calculated by assuming them to be additive functions of the corresponding functions[17–20] for the pure liquids. In this way H^E values at $x_1 = 0.3$, 0.5 and 0.7 were calculated and these are recorded in Table 4. The thermodynamic consistency of the values of u_1 and u_2 checked by calculating the G^E function for the mixture using the relation

$$G^E = \sum x_A u_A^E \tag{7}$$

where

$$u_A^E = RT\left[\sum_\mu Q_\mu A \ln\left(X_\mu A/x_A X_\mu' A\right) + r_A(Z/2 - 1)\ln\left(\sum_S x_S r_S/r_A\right)\right]$$

and the parameters $X_\mu' A$ are the solutions of expression (4) for pure liquids. Only those values of u_1 and u_2 were retained which reproduce the experimental H^E and G^E values as closely as possible. For chloroform + pyridine, H^E values were taken from our previous publication[13].

For benzene(S') + bromoform(A) the interactions considered were a specific bond (H...S) between the bromine atoms and hydrogen atom of bromoform on one side and the solvent benzene, of strength u_2 and a non-specific interaction of strength u_1 for all the remaining contact points. U_V^E values were then calculated as explained above from the expressions

$$U_V^E = -2RT\left[(X_H X_{Br})\,\eta_1 \ln \eta_1 + (X_H X_S + X_S X_{Br})\,\eta_2 \ln \eta_2\right] \tag{8}$$

G^E values were similarly calculated from expression (7). The calculated H^E and G^E values, where the interaction energies satisfy the consistency requirements, are recorded in Table 4.

For bromoform(A) + n-hexane(S) and chloroform(A) + n-hexane(S) a non-specific interaction of strength, u_1, was assumed for all the contact points. U_V^E values were obtained from the relation

$$U_V^E = -2RT\left[(X_R X_{R'} + X_R X_H + X_R X_{Br} + X_{R'} X_{Br})\,\eta_1 \ln \eta_1\right] \tag{9}$$

and G^E values were obtained from relation (7). These values are recorded in Table 4.

Nature of interactions

A consideration of the interaction energies, u_1 and u_2, would be instructive to understand the nature of the interactions between the compounds of these mixtures.

The N...H interaction energy (u_2) of chloroform+pyridine and bromoform +pyridine suggests that compared to bromoform, chloroform forms a stronger hydrogen bond with pyridine. This is justifiable as chlorine is more electronegative than bromine and the charge of the –C–H bond is displayed to a larger extent towards carbon in chloroform than in bromoform. The more polar proton of chloroform thus forms a stronger hydrogen bond with pyridine. It is interesting to observe that although the hydrogen bonded interaction in bromoform(2) + pyridine(1) is less than that in chlo-

TABLE 3

X-RAY POWDER DIFFRACTION DATA FOR THE PYRIDINE+BROMOFORM COMPLEX

Peak No.	2θ	d (Å)	Intensity
1	8.70	10.163	11
2	9.90	8.934	18
3	12.30	7.195	11
4	16.75	5.293	12
5	17.85	4.968	14
6	18.70	4.745	50
7	19.00	4.670	7
8	19.75	4.495	54
9	20.75	4.280	11
10	21.10	4.210	64
11	21.85	4.067	71
12	22.45	3.961	7
13	22.95	3.874	25
14	23.50	3.785	6
15	24.80	3.590	100
16	26.05	3.420	36
17	26.65	3.344	9
18	27.30	3.266	71
19	29.75	3.003	36
20	30.40	2.940	54
21	31.30	2.857	14
22	34.45	2.603	29
23	34.95	2.567	27
24	35.90	2.501	9
25	36.70	2.448	34
26	36.90	2.435	21
27	37.75	2.382	6
28	39.30	2.292	14
29	41.45	2.178	10
30	42.30	2.136	6
31	43.10	2.098	14
32	43.90	2.062	10
33	44.30	2.044	7
34	47.05	1.931	12

TABLE 4

INTERACTION ENERGIES AND THE COMPARISON OF H^E AND G^E VALUES CALCULATED ACCORDING TO THE EXPRESSIONS (3)–(6), (7), (8), (9) AND WITH VALUES INTERPOLATED FROM THEIR CORRESPONDING EXPERIMENTAL VALUES AT 308.15 K FOR THREE MOLE FRACTIONS X_1 OF COMPONENT 1
$U_i^* = U_i/8.30 \quad (i = 1 \text{ or } 2)$

X_1	H^E_{calc} ($J\ mol^{-1}$)	H^E_{expt} ($J\ mol^{-1}$)	G^E_{calc} ($J\ mol^{-1}$)	G^E_{expt} ($J\ mol^{-1}$)
n-Hexane (1)+bromoform (2), $U_1^* = 209.45\ J\ mol^{-1}$				
0.3	742.64	805.35	720.06	779.77
0.5	834.49	960.02	932.61	915.06
0.7	847.08	815.15	748.10	808.87
Chloroform (1)+n-hexane (2), $U_1^* = 150.15\ J\ mol^{-1}$				
0.3	425.70	375.25	318.24	289.76
0.5	618.51	570.36	422.58	403.96
0.7	495.72	535.76	333.67	339.73
Benzene (1)+bromoform (2), $U_1^* = 26.02\ J\ mol^{-1}$, $U_2^* = -63.00\ J\ mol^{-1}$				
0.3	−143.72	−107.51	77.08	62.76
0.5	−184.07	−137.50	93.52	90.57
0.7	−161.18	−116.73	110.24	95.86
Pyridine (1)+bromoform (2), $U_2^* = -3490.46\ J\ mol^{-1}$, $U_1^* = 9.05\ J\ mol^{-1}$				
0.3	−1360.58	−1350.07	−594.96	−422.28
0.5	−1719.54	−1750.30	−745.17	−483.25
0.7	−1405.56	−1450.21	−578.23	−401.01
Chloroform (1)+pyridine (2), $U_1^* = 9.05\ J\ mol^{-1}$, $U_2^* = -3886.76\ J\ mol^{-1}$				
0.3	−1712.60	−1430.00 (ref. 13)	−519.49	−513.57
0.5	−2278.65	−1909.00	−722.30	−614.37
0.7	−1716.18	−1600.00	−598.49	−557.43

roform + pyridine, a solid probably a 2:1 complex is formed in the former and not in the latter. This may be explained if it be supposed that a solid complex is formed from the lattice rearrangements, the new lattice probably has only a small energy difference as compared with the original one and that the lattice is maintained in tact by specific interactions. The size of bromoform is slightly larger than that of chloroform. Consequently in forming a 2:1 complex with pyridine by lattice rearrangements, the lattice deformations in bromoform + pyridine are less than those in a 1:1 complex of chloroform + pyridine. Moreover the specific interactions between bromoform + pyridine are of the same order of magnitude as in chloroform + pyridine and so no new lattice rearrangements appear in the latter system.

In benzene + bromoform the interaction energy, u_2, indicates that both the hydrogen atom and bromine atoms of bromoform interact with benzene. The proton of bromoform may be visualised to align itself along the six-fold axis of benzene and form a weak π complex with the π cloud of benzene. This, however, would cause shielding of the bromoform proton. Preliminary NMR studies[21] indicate that the proton resonance signal of bromoform is shifted upfield in its mixtures with benzene. At the same time the bromine atoms of bromoform may form a weak complex with

the planar hydrogen atoms of the benzene molecule, and as such the magnitude of the non-specific interactions, u_1, will also be appreciable.

Examination of u_1 interaction energy for bromoform + n-hexane and chloroform + n-hexane suggests that it is more repulsive in the former than in the latter. The larger repulsive interaction in bromoform + n-hexane than in chloroform + n-hexane may be explained by the fact that the bromine atom is larger than the chlorine atom. Consequently, the bromine atoms in bromoform experience greater steric repulsion in n-hexane + bromoform than the chlorine atoms in n-hexane + chloroform.

REFERENCES

1 B. R. Sharma and P. P. Singh, *J. Chem. Thermodyn.*, 5 (1973) 361.
2 A. A. Taha, R. D. Grigsby, J. R. Johnson, S. D. Christian and H. E. Affsprung, *J. Chem. Educ.*, 43 (1966) 432.
3 A. K. Adya, B. S. Mahl and P. P. Singh, *J. Chem. Thermodyn.*, 5 (1973) 393.
4 B. K. Nigam and B. S. Mahl, *J. Chem. Soc. Faraday Trans. I*, 8 (1972) 1508.
5 J. A. Barker, *Aust. J. Chem.*, 6 (1953) 207.
6 G. Scatchard and L. B. Ticknor, *J. Amer. Chem. Soc.*, 74 (1952) 3724.
7 J. Timmerman, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950.
8 P. W. Allen, D. H. Everett and M. F. Penny, *Proc. Roy. Soc.*, A212 (1952) 149.
9 K. R. Harris and P. J. Dunlop, *J. Chem. Thermodyn.*, 2 (1970) 805.
10 R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw Hill, New York, 1958.
11 D. V. Fenby, *Aust. J. Chem.*, 26 (1973) 1143.
12 K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, 62 (1966) 2063.
13 R. C. Phutela, P. S. Arora and P. P. Singh, *J. Chem. Thermodyn.*, 6 (1974) 801.
14 R. P. Rastogi, J. Nath and R. R. Misra, *J. Chem. Thermodyn.*, 3 (1971) 307.
15 T. J. V. Findlay and P. J. Kavanagh, *J. Chem. Thermodyn.*, 6 (1974) 367.
16 J. A. Barker, *J. Chem. Phys.*, 20 (1952) 1526.
17 R. K. Nigam and P. P. Singh, *Trans. Faraday Soc.*, 65 (1969) 950.
18 *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970.
19 *International Critical Tables*, McGraw-Hill, New York, 1933.
20 N. A. Lange, *Handbook of Chemistry*, McGraw-Hill, New York, 1967.
21 B. R. Sharma and P. P. Singh, *Z. Phys. Chem.*, communicated (1974).