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THERMODYNAMICS OF WEAK INTERACTIONS: EXCESS ENTHALPIES OF SOME BINARY BROMOFORM MIXTURES

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ABSTRACT

Excess enthalpies of bromoform + toluene, + *o*-xylene, + *m*-xylene and + *p*-xylene have been determined at 308.15 K. These compounds have been examined for Barker's theory in order to understand the magnitude and nature of various interactions between the components of these mixtures. It has been concluded that the H-atom and one bromine atom of bromoform interact with the π cloud of the aromatic ring. These conclusions have been supplemented by n.m.r. studies. An approximate distance of the bromoform proton from the plane of the aromatic ring has also been calculated and examined in the light of the proposed geometry of the molecular complexes. Equilibrium constants for the complexation reaction have also been determined.

INTRODUCTION

Recent heats of mixing studies[1] on the bromoform + benzene mixture have indicated that this mixture is characterized by specific interactions between its components. The present work forms part of a programme to establish how regular changes in the number and position of $-CH_3$ substituents in the aromatic ring modify their excess enthalpies, H^E, values, with bromoform.

EXPERIMENTAL

Toluene, *o*-, *m*- and *p*-xylenes and bromoform were purified as suggested by Vogel[2]. Purities of the final samples were checked by measuring their densities; the results agreed to within 0.00002 g cm^{-3} with those in the literature as reported earlier[3,4].

Excess enthalpies were measured in an adiabatic calorimeter described earlier[5].

Samples for n.m.r. studies were prepared by mixing bromoform and the aromatic hydrocarbons in the n.m.r. tubes followed by dilution with a fixed quantity of an inert solvent, cyclohexane. The inert solvent does not affect the nature of binary

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interactions and it also helps to exclude self-association of the interacting species. Immediately after preparation, a fixed quantity of tetramethylsilane (TMS), used as an internal reference, was added in each case and the proton chemical shift of the bromo-

TABLE 1

MEASURED HEATS OF MIXING AND COMPARISON OF VALUES CALCULATED ACCORDING TO BARKER'S THEORY WITH VALUES INTERPOLATED FROM THE MEASURED VALUES AT MOLE FRACTIONS X_1 OF COMPONENT 1

X_1	$H^E (J\ mol^{-1})$		X_1	$H^E (J\ mol^{-1})$	
	Exp.	*Barker*		*Exp.*	*Barker*
Bromoform (1) + toluene (2)					
0.1750	−115.40		0.5568	−252.85	
0.2987	−193.90		0.6348	−238.40	
(0.3000)	(−199.00)	−224.77	0.6546	−232.32	
0.3278	−209.82		(0.7000)	(−205.00)	−206.19
0.3770	−231.02		0.7017	−211.80	
0.4563	−252.97		0.7476	−188.54	
(0.5000)	(−260.00)	−264.60	0.8067	−146.70	
0.5044	−257.68		0.8512	−119.98	
Bromoform (1) + o-xylene (2)					
0.1368	−196.80		(0.5000)	(−420.00)	−422.67
0.2857	−354.05		0.5272	−424.10	
(0.3000)	(−350.00)	−362.17	0.5568	−418.50	
0.3133	−357.26		0.6711	−368.84	
0.3510	−387.70		(0.7000)	(−350.00)	−360.83
0.4264	−412.26		0.7063	−344.67	
0.4527	−420.34		0.7435	−315.12	
0.4915	−424.15		0.7801	−281.02	
			0.8554	−201.78	
Bromoform (1) + m-xylene (2)					
0.1502	−155.80		0.6000	−297.42	
0.2678	−250.98		0.6215	−288.88	
(0.3000)	(−275.00)	−262.14	0.6724	−263.02	
0.3240	−283.02		0.6960	−245.05	
0.3898	−309.15		(0.7000)	(−245.00)	−248.45
0.4719	−320.20		0.7054	−241.80	
(0.5000)	(−320.00)	−309.28	0.7318	−224.13	
0.5036	−319.11		0.7624	−202.66	
0.5534	−310.70		0.8368	−142.36	
Bromoform (1) + p-xylene (2)					
0.1479	−171.88		(0.5000)	(−380.00)	−372.66
0.2163	−240.03		0.5628	−371.67	
0.2578	−277.10		0.5807	−368.68	
(0.3000)	(−310.00)	−319.57	0.6398	−350.04	
0.3225	−319.87		(0.7000)	(−310.00)	−304.13
0.3560	−339.12		0.7080	−308.35	
0.4394	−369.01		0.7588	−270.12	
0.4604	−373.60		0.8064	−227.68	

TABLE 2

VALUES OF THE PARAMETERS OF EQN (1) AND INTERACTION ENERGIES U_1, U_2 FOR THE VARIOUS MIXTURES AT 308.15 K

	A	B	C	$\sigma(H^E)$ ($J\ mol^{-1}$)	U_1 ($J\ mol^{-1}$)	U_2 ($J\ mol^{-1}$)
Bromoform (1) + toluene (2)	−1032.68	−100.31	400.68	0.51	51.80	−169.02
Bromoform (1) + *o*-xylene (2)	−1693.98	−5.06	195.89	0.64	51.80	−257.42
Bromoform (1) + *m*-xylene (2)	−1278.88	150.21	302.02	0.66	51.80	−201.97
Bromoform (1) + *p*-xylene (2)	−1508.61	−50.23	205.85	0.61	51.80	−232.76

TABLE 3

CHEMICAL SHIFTS δ FOR BROMOFORM IN VARIOUS AROMATIC HYDROCARBONS

X_1	δ(ppm)	X_1	δ(ppm)
Bromoform (1) + toluene (2), $\delta_\infty = 6.295$ ppm, $K = 1.0$			
0.0378	6.362	0.1802	6.450
0.0726	6.350	0.2076	6.548
0.1430	6.459	0.2194	6.660
0.1681	6.482	0.2496	6.649
Bromoform (1) + o-xylene (2), $\delta_\infty = 6.200$ ppm, $K = 1.60$			
0.0517	6.320	0.1443	6.319
0.0768	6.240	0.1652	6.360
0.1091	6.308	0.1986	6.360
Bromoform (1) + m-xylene (2), $\delta_\infty = 6.255$ ppm, $K = 1.07$			
0.0435	6.358	0.1408	6.460
0.0678	6.380	0.1743	6.528
0.1071	6.458	0.1886	6.589
0.1266	6.360		
Bromoform (1) + p-xylene (2), $\delta_\infty = 6.285$ ppm, $K = 1.18$			
0.0402	6.340	0.1314	6.380
0.0614	6.349	0.1650	6.468
0.0906	6.358	0.2169	6.488

form proton relative to TMS was detected on a Varian A60D spectrometer using the side band method[6]. The chemical shifts were averaged over three determinations and were reproducible to within ±0.5 Hz.

RESULTS

The excess enthalpies, H^E, are recorded in Table 1. The data were fitted to the expression

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

where x_1 is the mole fraction of bromoform. The parameters h_0, h_1 and h_2, evaluated by fitting $H^E/x_1(1-x_1)$ to expression 1 by the method of least squares, are given together with the standard deviations $\sigma(H^E)$ in Table 2.

The proton chemical shifts of bromoform as a function of bromoform concentration at 298,15 K are recorded in Table 3. The total net shift of the bromoform at infinite dilution in the various solvents are listed in Table 3. All chemical shifts are upfield from TMS.

DISCUSSION

Heats of mixing for bromoform + toluene, +*o*-, *m*- and *p*-xylenes are all negative; exothermicity varies in the order toluene <*m*-xylene, <*p*-xylene <*o*-xylene. The curves of H^E against the mole fraction x_1 of bromoform are almost symmetrical indicating that we are dealing with 1:1 complexes in solution. We are unaware of any data of H^E at 308.15 K with which to compare our results. The present data combined with previously reported heats of mixing data[1] at 308.15 K for bromoform + benzene suggests that it is the π electron cloud of the aromatic hydrocarbons that is interacting with bromoform.

In an alternate attempt to understand the nature of interactions between the components of these mixtures, we examined our results for Barker's theory[7]. This generalized lattice model theory allows a molecule of type 1 occupying r_1 sites on a Z co-ordinated lattice to have $q_1^Z = r_1 Z - 2r_1 + 2$ neighboring contact sites, each of which has a specific interaction energy with the neighboring part of the surface of another molecule. These contact sites are further sub-divided into classes, the number in the μth class of molecule 1 denoted by $Q_{\mu 1}$. As bromoform has almost the same size as that of the various solvents used here, $r_1 = r_2 = 2$ and $Z = 4$ have been used throughout this paper. Further bromoform has 2 classes of contact sites, the hydrogen atom is assumed to have one contact point Q_H, of one class while the residual part has 5 contact points Q_R, of another class. The non-polar solvents are all assumed to have contact points of one type only. The interactions considered were specific (H–S), (Br–S) between the bromine atoms and hydrogen atom of bromoform with the various aromatic hydrocarbons (s), of strength u_2 and a non-specific (H–Br) interaction of strength u_1, for the remaining contact points. U_V^E (excess energy at constant volume) values were then calculated from

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

where the parameters X depend upon the number of interactions of various contact sites of different classes in molecules 1 and 2 of the binary mixture. These parameters were evaluated by solving the following simulataneous quadratic equations with certain assumed values of u_1 and u_2.

$$X_H[X_H + \eta_1 X_{Br} + \eta_2 X_S] = Q_H A \cdot x_A/2 \tag{3}$$

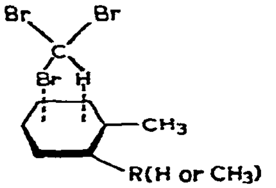
$$X_{Br}[\eta_1 X_H + X_{Br} + \eta_2 X_S] = Q_R A \cdot x_A/2 \tag{4}$$

$$X_S[\eta_2 X_H + \eta_2 X_{Br} + X_S] = Q_S x_S/2 \qquad (5)$$

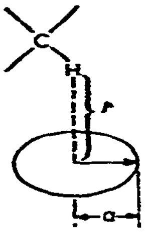
where $\eta_i = \exp(-u_i/RT)$ ($i = 1$ or 2), u_1 and u_2 are the interaction energies per mole and R is the universal gas constant. For strict comparison U_V^E values should be converted to measurements at constant pressure, H^E, but as even the indicated corrections[1] to H^E are small (<30 J mol^{-1}) for the bromoform + benzene mixture, this was neglected for all the present mixtures. In this way H^E values at $x_1 = 0.3$, 0.5 and 0.7 were calculated. These are recorded in Table 1 and they make an impressive agreement with their corresponding experimental values. The thermodynamic consistency of these values of u_1 and u_2 could be checked by measuring G^E for these mixtures; work for which is in progress. Nevertheless our u_1 and u_2 are comparable to their corresponding thermodynamic consistent values[1] for bromoform + benzene.

An examination of the interaction energy, u_2, of the mixtures of bromoform with those of the aromatic hydrocarbons indicates that both the hydrogen atom and bromine atoms of bromoform interact with the aromatics and that the interaction varies in the order toluene <*m*-xylene<*p*-xylene<*o*-xylene. As nuclear magnetic resonance is a valuable method of studying hydrogen bonding, it would now be instructive to examine n.m.r. data of these mixtures.

The total net shift of bromoform at infinite dilution in the various solvents are recorded in Table 3. It is evident that there is a large net shift of the n.m.r. signal of bromoform proton in each of these solvents towards higher magnetic fields. This is in sharp contrast to the corresponding shift to low fields observed in hydrogen bonding involving lone pair donors. A partial explanation of this different behaviour of the bromoform proton resonance in the aromatic solvents may be sought in the magnetic behaviour of the aromatic molecules themselves. The proton of bromoform may be visualized to allign itself along the six-fold axis of the aromatic ring and form a weak π complex with the π electron cloud of the ring, thereby causing shielding of the bromoform proton. The n.m.r. studies thus give additional support to our conjecture about the nature of interactions between the components of these mixtures. The interaction of the bromine atoms of bromoform with that of the aromatic hydrocarbons may be visualized as the accomodation of increased π charge on the ring of the aromatic hydrocarbons in the vacant d levels of one bromine atom of bromoform. The complexes may thus be assumed to have the following structure



The results of proton chemical shifts of bromoform in the various solvents were then utilized to obtain a rough measure of the distance of the bromoform proton from the plane of the aromatic ring in the molecular complexes. In the calculations it is assumed that in the molecular complex the hydrogen atom of bromoform is above the plane of the aromatic ring in the vicinity of the six-fold axis. Considering the aromatic ring as a circular loop of radius $a = 1.4$ Å, the applied field, H_0, induces a current expressed by[8]



$$i = 3e^2 H_0/2\pi mc \tag{6}$$

where e and m are the electronic charge and mass and c is the velocity of light. The small field ΔH on the axis of the circular coil of radius 'a' at a point p is given by

$$\Delta H = 2\pi i a^2/r^3 \tag{7}$$

so that

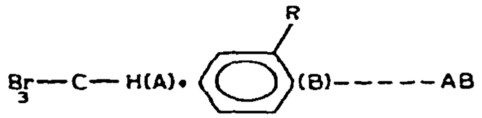
$$\frac{\Delta H}{H} = 3e^2a^2/mc^2r^3 = \delta \text{ (chemical shift in ppm)} \tag{8}$$

Averaging over all orientations of the molecule in the field introduces a factor of $\cos^2\theta = \frac{1}{3}$ so that

$$\delta = e^2a^2/mc^2r^3. \tag{9}$$

Thus the average distance of the bromoform proton from the plane of the ring in the various aromatic hydrocarbons is: bromoform + toluene, 2.06 Å; bromoform + *o*-xylene, 2.07 Å; bromoform + *m*-xylene, 2.06 Å; bromoform + *p*-xylene, 2.06 Å.

This distance is evidently smaller than the corresponding distance[9] of 3.1 Å of the chloroform proton from the plane of the benzene ring in the chloroform + benzene mixture. This may be taken to suggest a comparatively strong interaction of the bromine atom with the π cloud of the aromatic ring in bromoform + aromatic hydrocarbons than that in chloroform + benzene mixtures. The more electronegative chlorines in chloroform displace the charge on the C–H bond primarily towards the C atom thereby allowing only the proton of chloroform to interact (umbrella type) with the π cloud of the aromatic ring in the chloroform + benzene mixture. The less electronegative bromine atoms in bromoform are unable to cause such a strong charge displacement so that the 3d levels of the bromine atoms are also able to take some more charge. Consequently in bromoform + aromatic hydrocarbons mixture, the proton and one bromine atom of bromoform are interacting with the π cloud of the ring causing thereby a shortening of distance. Equilibrium constants were then calculated assuming that 1:1 complexes are formed according to the equation



(10)

The equilibrium constant K is related to the actual mole fractions of the acceptor ξ_A (bromoform), donor (aromatic hydrocarbons) ξ_D and complex ξ_{AD}, respectively, by

$$K = \xi_{AD}/\xi_A \xi_D \tag{11}$$

where ξ_{AD}, ξ_A and ξ_D were evaluated from the stoichiometric mole fractions x_A and x_D by the relations[10].

$$x_A = (\xi_{AD}+\xi_A)/(\xi_A+\xi_D+2\xi_{AD}) \tag{12}$$

and

$$\begin{aligned} x_D &= (\xi_{AD}+\xi_D)/(\xi_A+\xi_D+2\xi_{AD}) \\ &= (1+K)\xi_D/(1+K\xi_D(2-\xi_D)) \end{aligned} \tag{13}$$

The assumption that the ratio of activity coefficients $(\gamma_A\gamma_D/\gamma_{AD}) \approx 1$ has been shown[11] to be unlikely to lead to serious error in K. The observed chemical shift δ_{obs} may be taken as a weighted average of the shifts in the complexed state δ_{AD} and the uncomplexed state δ_A so that

$$\delta_{obs} = \delta_A\{\xi_A/(\xi_A+\xi_{AD})\}+\delta_{AD}\{\xi_{AD}/(\xi_A+\xi_{AD})\} = \delta_A+X(\delta_{AD}-\delta_A) \tag{14}$$

where

$$X = \xi_{AD}/(\xi_A+\xi_{AD}) = K\xi_D/(1+K\xi_D)$$

A series of K values were assumed and for each value of K was found by the method of least squares the best straight lines for δ_{obs} against X. The best value of K was then taken to be that for which $\sigma = \Sigma(\delta_{obs}-\delta_{calc})^2$ is minimum. The uncertainty in K is of the order of ±0.05. These K values are recorded in Table 3 and are consistent with the increased inductive effect of the methyl substituent in the aromatic ring.

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