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INTERACTION OF CHLOROFORM WITH ANILINE, *o*-TOLUIDINE AND N,N-DIMETHYL ANILINE

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ABSTRACT

Heats of mixing aniline, *o*-toluidine, and N,N-dimethyl aniline with chloroform have been determined by an adiabatic calorimeter. The results have been examined for molecular interactions between them, and they indicate that aniline and *o*-toluidine are associated through hydrogen bonds. Enthalpy of bond formation in a 1:1 complex has also been determined.

INTRODUCTION

Association in liquid aniline has been a subject of exhaustive IR[1–5] and NMR studies[6–8]. The purpose of the present study is to examine this problem from the point of view of thermodynamics of weak interactions and to report heats of mixing chloroform with aniline, *o*-toluidine, and N,N-dimethyl aniline at 308.15 K.

EXPERIMENTAL

Aniline, *o*-toluidine and chloroform were purified and their purities were checked as described earlier[9,10]. N,N-dimethyl aniline was purified as suggested by Vogel[11] and its purity at 298.15 K agreed within 0.00005 g cm^{-3} with that in the literature[12].

Measurements of heats of mixing as a function of composition were made in an adiabatic calorimeter described earlier[13].

RESULTS

The results of the measurements of heats of mixing are recorded in Table 1. The data were fitted to the expression

$$H^E/x_1(1-x_1)\ \mathrm{J\ mol^{-1}} = A+B(2x_1-1)+C(2x_1-1)^2 \tag{1}$$

where x_1 is the mole fraction of component 1. The constants A, B and C were evalu-

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together with the standard deviations $\sigma(H^E)$ are recorded in Table 2.

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 AT 308.15 K

x_1	H^E ($J\ mol^{-1}$)		x_1	H^E ($J\ mol^{-1}$)	
	Exp.	*Barker*		*Exp.*	*Barker*
Chloroform (1) + aniline (2)					
0.1621	89.05		0.5366	187.26	
0.2098	114.50		0.5472	189.04	
0.2316	124.70		0.5927	184.10	
(0.3000)	152.00	166.36	(0.6000)	182.00	156.19
0.3093	155.50		0.6329	176.14	
0.3562	166.72		(0.7000)	157.00	140.73
0.3826	174.90		0.7011	156.90	
(0.4000)	179.00	184.01			
0.4519	187.65		0.7782	126.12	
(0.5000)	190.00	181.83	0.8291	99.80	
0.5109	189.02		0.8920	66.70	
Chloroform (1) + o-toluidine (2)					
0.1423	−141.89		0.5200	−346.67	
0.2166	−208.92		0.5458	−347.04	
(0.3000)	−272.00	−304.13	(0.6000)	−339.00	−329.39
0.3002	−273.02		0.6102	−334.10	
0.3692	−315.20		0.6892	−302.98	
0.3815	−317.60		(0.7000)	−298.00	−296.12
(0.4000)	−324.00	−339.79	0.7269	−282.48	
0.4432	−337.34		0.7662	−252.98	
0.4855	−346.10		0.8196	−206.70	
(0.5000)	−347.00	−352.39	0.8528	−174.60	
0.5029	−347.90				
Chloroform (1) + N,N-dimethyl aniline (2)					
0.2015	−476.70		0.5128	−1243.84	
0.2962	−790.02		0.5871	−1252.02	
(0.3000)	−804.00	−1097.97	(0.6000)	−1243.00	−1229.89
0.3312	−900.11		0.6355	−1207.10	
0.3498	−950.97		(0.7000)	−1091.00	−1108.76
(0.4000)	−1079.00	−1268.04	0.7022	−1087.12	
0.4157	−1113.12		0.7532	−951.70	
0.4739	−1210.42		0.7954	−814.90	
(0.5000)	−1236.00	−1270.00	0.8428	−640.70	

TABLE 2

VALUES OF THE PARAMETERS OF EQN(I) AND OF ΔH_{1-2}^{*}, u_1, u_2 AND u_3 FOR THE VARIOUS MIXTURES AT 308.15 K

	A	B	C	$\sigma(H^{E})$ ($J\ mol^{-1}$)	ΔH_{1-2}^{*} ($KJ\ mol^{-1}$)	u_1 ($J\ mol^{-1}$)	u_2 ($J\ mol^{-1}$)	u_3 ($J\ mol$
Chloroform(1)+aniline(2)	758.37	29.85	−150.04	1.040	−1.33	25.10	−66.94	−418.
Chloroform(1)+o-toluidine(2)	−1389.24	−155.14	204.72	1.048	−2.94	41.84	−1029.26	−62.
Chloroform(1)+N,N-dimethyl aniline(2)	−4943.87	−1711.03	2700.01	1.374	−2.44	41.84	−2707.05	—

DISCUSSION

Heats of mixing for chloroform+o-toluidine and chloroform+N,N-dimethylaniline are all negative; exothermicity varies in the order N,N-dimethyl aniline >o-toluidine and is indicative of their interaction with chloroform. The results, however, indicate endothermic mixing for chloroform+aniline. The curves of H^E against the mole fraction of chloroform are almost symmetrical indicating[14] 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.

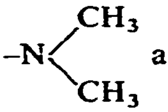
The exothermic mixing of chloroform with N,N-dimethyl aniline and o-toluidine indicates that there should also be some interaction between aniline and chloroform, which the heats of mixing data do not substantiate. The endothermic mixing for chloroform+aniline may be accounted for, if we suppose that aniline is self associated. The observed heat is then made up of an asymmetric endothermic term due to breaking up of this association and a symmetric exothermic term if a 1:1 complex is envisaged in solution. This would mean lesser association in o-toluidine as compared with aniline because of the close proximity of the $-CH_3$ substituent and as such the asymmetric endothermic contribution to H^E will be less in the former as compared to the latter. However, the symmetric exothermic contribution would be larger for o-toluidine+chloroform than for aniline+chloroform and so H^E_{exp} values for the o-toluidine +chloroform mixture would be less endothermic than for the aniline+chloroform mixture. The greater interaction in the former as compared to the latter gets further support if it is supposed[15] that the experimental H^E values are made up of: (i) contributions arising due to size; and (ii) contributions arising from molecular interactions. Since H^E values are not influenced by slight differences in the size of molecules and as cyclohexane has almost the same size as o-toluidine and aniline, H^E_{size} values were taken to be H^E_{exp} for the cyclohexane+chloroform mixture[16]. $H^E_{interaction}$ values at an equimolar composition are

System	$H^E_{interaction}$ (*J mol*$^{-1}$)
Chloroform+aniline	−434.34
Chloroform+o-toluidine	−975.24

The $H^E_{interaction}$ values thus support our conjecture that o-toluidine interacts strongly with chloroform.

In an alternate attempt to understand the nature of interactions between the components of these mixtures, we examined our results for Barker's[17] theory. This generalized lattice model theory allows a molecule to have contact points of several types; each type having a definite interaction energy. Further the total number of contacts which a molecule, occupying r_A sites on a Z-coordinated lattice, is capable of making is given by

$$q_A Z = r_A Z - 2r_A + 2 \tag{2}$$

It is further supposed that chloroform has one H contact point and ($Q^S_{Cl} = q_S Z - 1$) chlorine contact points while aniline and *o*-toluidine have one N contact point, 2I contacts for the 2 hydrogens on N in $-NH_2$ and 5 contact points for the residual molecule. N,N-dimethyl aniline is assumed to have one N contact, 2I contacts for the 2 CH_3 substituents on  $-\mathrm{N}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{smallmatrix}$ and 5I′ contact points for the residual molecule.

The interactions considered are for aniline (A)+chloroform (S) and *o*-toluidine (A)+chloroform (S): hydrogen bond (N ... H) of strength u_2; non-specific interaction of strength u_1, for all the remaining contact points; and self association interaction of strengths u_3 for aniline and *o*-toluidine. Heats of mixing values were then calculated from

$$H^E = -2RT[\eta_1 \ln \eta_1 (X_H X_I + X_I X_{Cl} + X_{I'} X_{I'} + X_{I'} X_{Cl} + X_N X_{Cl}) + + X_N X_H \eta_2 \ln \eta_2 + (X_N X_I - x_A X'_N X'_I) \eta_3 \ln \eta_3] \tag{3}$$

where X_H, X_I, X_{Cl}, X_N and $X_{I'}$ can be solved from:

$$X_{I'} [\eta_1 X_I + \eta_1 X_N + X_{I'} + \eta_1 X_H + \eta_1 X_{Cl}] = Q^A_{I'} x_A/2 \tag{4}$$

$$X_I [X_I + \eta_3 X_N + \eta_1 X_{I'} + \eta_1 X_H + \eta_1 X_{Cl}] = Q^A_I x_A/2 \tag{5}$$

$$X_N [\eta_3 X_I + X_N + \eta_1 X_{I'} + \eta_2 X_H + \eta_1 X_{Cl}] = Q^A_N x_A/2 \tag{6}$$

$$X_H [\eta_1 X_I + \eta_2 X_N + \eta_1 X_{I'} + X_H + \eta_1 X_{Cl}] = Q^S_H x_S/2 \tag{7}$$

$$X_{Cl} [\eta_1 X_I + \eta_1 X_N + \eta_1 X_{I'} + \eta_1 X_H + X_{Cl}] = Q^S_{Cl} x_S/2 \tag{8}$$

and X'_N and X'_I are solutions of the corresponding equations for the pure aniline and *o*-toluidine.

For N,N-dimethyl aniline (A)+chloroform (S) there is the hydrogen bond N ... H of strength u_2 and non-specific interactions for all the remaining contact points. For the sake of simplicity these non-specific interactions for all the remaining contact points are assumed to have the strength u_1. H^E values were then calculated from the expression

$$H^E = -2RT[(X_I X_H + X_I X_{Cl} + X_{I'} X_H + X_{I'} X_{Cl} + X_{Cl} X_N) \eta_1 \ln \eta_1 + + X_N X_H \eta_2 \ln \eta_2] \tag{9}$$

where X_I, X_H, X_{Cl}, X_N and $X_{I'}$ can be solved from:

$$X_{I'} [X_{I'} + \eta_1 X_I + \eta_1 X_N + \eta_1 X_H + \eta_1 X_{Cl}] = Q^A_{I'} x_A/2 \tag{10}$$

$$X_I [\eta_1 X_{I'} + X_I + \eta_1 X_N + \eta_1 X_H + \eta_1 X_{Cl}] = Q^A_I x_A/2 \tag{11}$$

$$X_N\,[\eta_1 X_{I'}+\eta_1 X_I+X_N+\eta_2 X_H+\eta_1 X_{Cl}] = Q_N^A\, x_A/2 \tag{12}$$

$$X_H\,[\eta_1 X_{I'}+\eta_1 X_I+\eta_2 X_N+X_H+\eta_1 X_{Cl}] = Q_H^S\, x_S/2 \tag{13}$$

$$X_{Cl}\,[\eta_1 X_{I'}+\eta_1 X_I+\eta_1 X_N+\eta_1 X_H+X_{Cl}] = Q_{Cl}^S\, x_S/2 \tag{14}$$

$$\text{and } \eta_1 = e^{-u_1/kT},\ \eta_2 = e^{-u_2/kT} \tag{15}$$

A value of $Z=4$, $r_S=2$ for chloroform and $r_A=2$ for aniline and 3 for N,N-dimethyl aniline and *o*-toluidine have been used throughout this paper.

Interaction energies and H^E values calculated according to this model for all the systems at $x_S=0.3$, 0.4, 0.5, 0.6 and 0.7 are recorded in Table 1 and these reproduce well the experimental curves of H^E against the mole fraction x_1 of chloroform. A consideration of the u_3 interaction energies thus clearly indicates that aniline and *o*-toluidine are self associated through hydrogen atoms on the $-NH_2$ group and that *o*-toluidine is less associated than aniline.

Further the present study suggests that it is the N atom in the $-NH_2$ group of aniline and *o*-toluidine that is involved in hydrogen bond formation with chloroform. Such a hypothesis is fully substantiated by the interaction of N,N-dimethyl aniline, in which the two hydrogen atoms of the $-NH_2$ group in aniline are replaced by two electron repelling $-CH_3$ substituents, with chloroform. Aniline and *o*-toluidine are thus associated in such a way that one of the two hydrogen atoms of the $-NH_2$ group is linked to the N atom of another aniline or *o*-toluidine molecule through a hydrogen bond while the second hydrogen atom is linked by weak specific interactions with the π electrons of the adjacent aniline or *o*-toluidine molecule leaving their nitrogen atom to form hydrogen bonds with chloroform. This modifies our earlier scheme[9] of association in aniline. Wolff and Mathias[18] have also arrived at a similar conclusion about the association in aniline from their IR spectral studies of pure aniline and its adducts with proton acceptors of varying basicity. The large exothermic N ... H interaction energy (u_2 in Table 2) in N,N-dimethyl aniline+chloroform as compared to *o*-toluidine+chloroform and aniline +chloroform indicates that the lone pair of electron on the N atom of N,N-dimethyl aniline is more easily available due to the electron repelling effect of the two $-CH_3$ substituents, to form hydrogen bonds with chloroform. In *o*-toluidine+chloroform the $-CH_3$ substituent increases the π electron density of the benzene ring thereby allowing the lone pair of electron on the N atom of *o*-toluidine to interact strongly, as compared to that of aniline, with chloroform.

It would now be instructive to determine the enthalpy of formation at 308.15 K of the bond in a 1:1 complex between the components of these mixtures. The desired quantity ΔH^*_{1-2} was calculated as described earlier[9] and these are recorded in Table 2. The data indicated that compared to aniline, *o*-toluidine and N,N-dimethyl aniline form stronger hydrogen bonds with chloroform. Nevertheless the enthalpy of bond formation in N,N-dimethyl aniline+chloroform is less than that in *o*-toluidine+chloroform which suggests that the hydrogen bond is stronger in the latter than that in the former. This may well be explained by taking into account steric hindrance.

In its attempt to form a hydrogen bond with the N-atom of N,N-dimethyl aniline, the chloroform proton experiences an appreciable steric repulsion because of the two bulky–CH_3 groups on its N-atom whereas no such steric hindrance is encountered in *o*-toluidine. This consequently does not allow the chloroform proton to come appreciably nearer to the N-atom in N,N-dimethyl aniline+chloroform than to that in *o*-toluidine+chloroform.

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