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Note

Heats of mixing of some binary methylene chloride solutions

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ABSTRACT

Heats of mixing of pyridine, α-picoline, aniline, *o*-toluidine and cyclohexane with methylene chloride have been measured at 298.15 K. The results have been considered in terms of molecular interactions between the components of these mixtures and possible structures of the complexes have been described.

INTRODUCTION

Pyridine and substituted pyridines both act as N and π-electron donors and as such they form intermolecular complexes of the electron donor–acceptor type. One could thus visualize such type of interactions between pyridines and methylene chloride. A knowledge of the thermodynamic properties of these mixtures would, therefore, be of interest when studying weak interactions in them. In this paper we report the heats of mixing of pyridine, α-picoline, aniline, *o*-toluidine and cyclohexane with methylene chloride.

EXPERIMENTAL

Methylene chloride, pyridine, α-picoline, aniline and *o*-toluidine were purified and their purities were checked as described earlier[1].

Measurements of heats of mixing as a function of composition were made in an adiabatic calorimeter reported earlier[2].

RESULTS

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

$$H^{E}/x_1(1-x_1)\ \text{cal mol}^{-1} = A+B(2x_1-1)+C(2x_1-1)^2 \qquad (1)$$

where x_1 is the mole fraction of component 1. The constants A, B and C were evaluated by fitting $H^{E}/x_1(1-x_1)$ to expression (1) by the method of least squares. These constants together with the standard deviations $\sigma(H^{E})$ are recorded in Table 2.

TABLE 1

EXCESS HEATS OF MIXING, H^E, AT 298.15 K AND AT MOLE FRACTIONS X_1 OF COMPONENT 1. THE QUANTITY δH^E IS THE DIFFERENCE BETWEEN THE OBSERVED H^E AND THAT CALCULATED ACCORDING TO EQN 1

X_1	H^E *(cal mol^{-1})*	δH^E *(cal mol^{-1})*
Methylene chloride (1) + cyclohexane (2)		
0.1397	140.60	−1.15
0.1851	170.84	−0.70
0.2252	194.05	0.69
0.3500	238.25	0.46
0.3850	245.00	−0.02
0.4497	254.35	1.06
0.5582	255.00	1.02
0.6705	234.00	−0.50
0.7000	226.80	−0.33
0.8449	156.20	0.50
0.9198	96.80	−0.24
Methylene chloride (1) + aniline (2)		
0.1650	49.00	−0.25
0.2298	62.02	−0.06
0.2902	71.98	0.47
0.3448	78.00	−0.21
0.3949	83.01	0.14
0.4450	86.10	−0.22
0.6250	86.98	−0.42
0.6602	85.70	0.37
0.7051	80.80	−0.48
0.7448	76.00	−0.25
0.8152	63.70	0.30
0.8600	52.30	−0.40
Methylene chloride (1) + *o*-toluidine (2)		
0.1608	16.02	−0.05
0.2100	19.80	0.11
0.2550	22.05	−0.37
0.3452	26.00	−0.48
0.4398	28.50	−0.32
0.5500	29.00	−0.11
0.6302	27.00	−0.25
0.6848	25.62	−0.21
0.7450	23.00	0.00
0.7952	20.20	0.24
0.8298	17.50	0.21
Methylene chloride (1) + pyridine (2)		
0.1800	−42.02	0.22
0.2552	−55.20	−0.41
0.3168	−63.15	−0.50
0.4149	−69.87	0.44
0.4852	−71.83	0.28
0.5650	−69.98	0.44
0.6549	−64.01	−0.13

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TABLE 1 (*continued*)

X_1	H^E (*cal mol*$^{-1}$)	δH^E (*cal mol*$^{-1}$)
Methylene chloride (1) + pyridine (2)		
0.7288	−55.02	0.11
0.7704	−49.00	−0.19
0.8148	−40.92	−0.51
Methylene chloride (1) + α-picoline (2)		
0.1598	−96.95	0.10
0.1901	−110.25	0.60
0.2708	−146.20	0.54
0.3402	−175.00	0.67
0.4847	−201.05	0.40
0.5279	−206.10	−0.36
0.5848	−204.96	−0.20
0.7190	−185.80	0.72
0.7602	−170.00	0.70
0.8298	−139.55	−0.86
0.8675	−116.20	0.51

TABLE 2

VALUES OF THE PARAMETERS OF EQN (1) AND OF $\Delta H_{1\overset{*}{-}2}$ FOR THE VARIOUS MIXTURES AT 298.15 K

System	$\sigma(H^E)$ (*cal mol*$^{-1}$)	*A*	*B*	*C*	$\Delta H_{1\overset{*}{-}2}$ (*Kcal mol*$^{-1}$)
Methylene chloride (1) + pyridine (2)	0.47	−288.3249	11.2500	22.8017	−1.60
Methylene chloride (1) + α-picoline (2)	0.64	−812.2220	−192.1800	−87.6820	−2.03
Methylene chloride (1) + aniline (2)	0.14	394.3000	53.4400	86.6740	−0.84
Methylene chloride (1) + *o*-toluidine (2)	0.34	117.2000	3.1333	9.7410	−1.20
Methylene chloride (1) + cyclohexane (2)	0.88	1022.2000	19.7170	321.7800	

DISCUSSION

Heats of mixing for methylene chloride + pyridine and methylene chloride + α-picoline are all negative; exothermicity being larger for the latter than for the former. On the other hand for methylene chloride + aniline and methylene chloride + *o*-toluidine, the results indicate endothermic mixing; methylene chloride + *o*-toluidine being less endothermic than methylene chloride + aniline. The exothermic mixing for pyridine + methylene chloride suggests an interaction between pyridine and methylene chloride which becomes stronger for α-picoline and methylene chloride. The curves of

H^E against the mole fraction of methylene chloride are almost symmetrical which suggests[3] that we are dealing with 1:1 complexes in solution. We are unaware of any data of H^E with which to compare our results.

A general increase in the amount of heat evolved with the introduction of a $-CH_3$ substituent in pyridine is to be expected. However, the less endothermic mixing for *o*-toluidine+methylene chloride as compared to that of the aniline+methylene chloride mixture indicates that there may be some type of interaction between the components of the former mixture. This gets further support if it is supposed[4] that the experimental H^E values are composed of (i) contributions arising from the spherical field of force, i.e. size effect; 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 pyridine, α-picoline, aniline and *o*-toluidine, H^E_{size} values were taken to be H^E_{expt} for methylene chloride+cyclohexane mixtures. $H^E_{\text{interaction}}$ values for these mixtures at an equimolar composition are

System	$H^E_{\text{interaction}}$ (cal mol^{-1})
Methylene chloride+aniline	−157.00
Methylene chloride +*o*-toluidine	−226.30

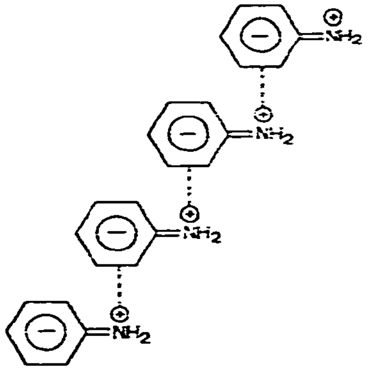
The $H^E_{\text{interaction}}$ values thus indicate that aniline and *o*-toluidine interact with methylene chloride.

The endothermic mixing for mixtures of aniline and *o*-toluidine with methylene chloride may be accounted for if we suppose that they are partly associated (structure 1). The observed heat is then the result of an asymmetric endothermic term due to breaking up of this association and a symmetric exothermic term if a 1:1 complex is envisaged. Such a scheme would assume a slightly lesser degree of association in *o*-toluidine as compared with aniline because of the close proximity of the $-CH_3$ substituent and consequently the large asymmetric endothermic term due to breaking up of association would be slightly less in the former as compared to the latter. At the same time the symmetric exothermic term due to complex formation would be larger for *o*-toluidine+methylene chloride than for aniline+methylene chloride. The H^E_{exp} values for *o*-toluidine+methylene chloride would thus be less endothermic than aniline+methylene chloride mixture.

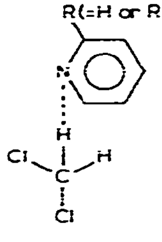
It would now be instructive to determine the enthalpy of formation at 25°C of the bond in a 1:1 complex between the components of these mixtures. The desired quantity was calculated from the difference between the partial molar heat of mixing of methylene chloride in pyridine, α-picoline, aniline and *o*-toluidine and in cyclohexane. The partial molar heat of mixing of methylene chloride at infinite dilution in the second component $h^E(x_1 \rightarrow 0)$ was obtained from the plot of H^E/x_1x_2 against x_1 whence the desired quantity was $A-B+C$ of expression (i). The enthalpy of formation (ΔH^*_{1-2}) of the bond between the components of these mixtures is recorded in Table 2. The data indicate that α-picoline forms a stronger bond with methylene chloride than *o*-toluidine.

Based on H^E and V^E data[1] we may now suggest possible structures of the complexes formed between the components of these mixtures.

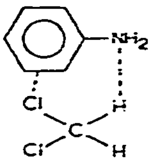
The high exothermic heats of mixing and greater contraction in volume in α-picoline + methylene chloride as compared to pyridine + methylene chloride may be explained if it is assumed that pyridine and α-picoline form hydrogen bonds with methylene chloride. The presence of a $-CH_3$ substituent at the α-position in α-picoline renders the lone pair of electrons on nitrogen to be more labile and so it will form a stronger hydrogen bond with methylene chloride. This causes the two components to come closer in α-picoline + methylene chloride than in pyridine + methylene chloride, thereby causing greater contraction of volume in the former as compared to the latter mixture. On the other hand whereas owing to resonance the lone pair of electrons on the nitrogen atom in aniline is less available for bond formation, the presence of a $-CH_3$ group at the *ortho* position in *o*-toluidine renders this lone pair to be more readily available for bond formation. *o*-Toluidine should thus interact strongly with methylene chloride. The smaller endothermic heats of mixing followed by lesser contraction in volume in *o*-toluidine + methylene chloride as compared to aniline + methylene chloride may be explained if we assume that they form hydrogen bonds with methylene chloride. However, the vacant $3d$ levels of chlorine in methylene chloride can also accommodate the increased π-electron charge on the benzene ring in aniline and so the complex of aniline + methylene chloride may have structure (III).



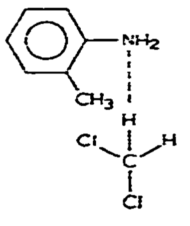
(I)



(II)



(III)



(IV)

But the proximity of the bulky $-CH_3$ group in *o*-toluidine prevents such accommodation of charge by the chlorine of methylene chloride. The complex of *o*-toluidine + methylene chloride should have structure (IV).

The structures indicate that the hydrogen bond in aniline + methylene chloride should be weaker than that in *o*-toluidine + methylene chloride. The enthalpy of formation data of the bond in a 1:1 complex supports these conclusions.

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