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Note

Enthalpy of mixing of hexafluorobenzene with some pyridines

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Recent studies of fluorocarbons with various compounds indicate the possibility of a complex formation[1-6].

In a previous work Armitage and Morcom[6] have determined the excess enthalpy of hexafluorobenzene with pyridine, 2,6-dimethyl pyridine and 2,4,6-trimethyl pyridine. This work has been extended to a mixture of hexafluorobenzene with 2-methyl pyridine, 4-methyl pyridine, 3,5-trimethyl pyridine. These pyridines were chosen in order to study the effect of the position of a substituant on the ring.

EXPERIMENTAL

The calorimeter used was a C.R.M.T. already described[7]. The hexafluorobenzene obtained from the Imperial Smelting Corporation was distilled and stored over freshly molecular sieve. Pyridines were dried, distilled and stored out of contact with air in the dark. All samples showed a purity greater than 99 moles per cent.

RESULTS AND DISCUSSION

The enthalpies of mixing were fitted by a least squares computer program to the expression:

$$H^E/x_1(1-x_1) = \sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \qquad (1)$$

where x_1 is the mole fraction of hexafluorobenzene.

The values of the coefficients A_i together with the standard deviation σ of the results are given in Table 1.

The experimental results are given in Table 2. The excess enthalpies of mixtures of pyridine, 2,6-dimethyl pyridine, 2,4,6-trimethyl pyridine with hexafluorobenzene have been measured by Armitage and Morcom[6] at different temperatures. Their

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TABLE 1

VALUES OF THE LEAST SQUARES PARAMETERS A_i IN EQN (1)

Mixture	A_1	A_2	A_3	A_4	A_5	*Standard deviation of* $H^E/x_1(1-x_1)$, σ (*cal*^{a} *mol*$^{-1}$)
C_6F_6 + 2-methyl pyridine	−510	319.1	96.6	71.9		7.9
Standard deviation of parameters	3.7	14	12.9	2.5		
C_6F_6 + 4-methyl pyridine	−43.1	355.3		−162.3	51.5	3.8
Standard deviation of parameters	2	8.8		20	12.5	
C_6F_6 + 3,5-dimethyl pyridine	−482.5	130.9	330.5			2.9
Standard deviation of parameters	1.3	3.2	1.7			

[a] Throughout this paper 1 $\text{cal}_{\text{ther}} = 4.184$ J.

results showed that pyridine and its homologues act essentially as π donors, the heat evolved increases with substitution.

This work has now been extended to mixtures of hexafluorobenzene with 2-methyl pyridine, 4-methyl pyridine, 3,5-dimethyl pyridine. The behaviour of pyridine mixtures is very similar to that of the corresponding aromatic compounds, except that the 2 position of heterocyclic compounds appears to be privileged.

We have considered two sets of mixtures: 2-methyl pyridine, 2,6-dimethyl pyridine, 2,4,6-trimethyl pyridine and pyridine, 4-methyl pyridine, 3,5-dimethyl pyridine. For each set the H^E becomes more negative as the number of methyl groups on the pyridine ring increases. If we plot H^E $(x_1 = 0.5)$ against the number of methyl groups we obtain approximately a straight line. In every case the excess enthalpies for the C_6F_6–pyridines mixtures are less negative than for C_6F_6–aromatic hydrocarbon mixtures. While the curves for C_6F_6 + 2-methyl pyridine and C_6F_6 + 3,5-dimethyl pyridine are negative over the entire mole fraction range, the excess enthalpy for 4-methyl pyridine is S-shaped with H^E negative at low mole fraction of base and positive at low mole fraction of hexafluorobenzene.

In recent publications[1,4,8,9] it was suggested that the decrease in H^E which accompanies the addition of methyl groups on the benzene ring is caused by the increase in polarizability leading to stronger 1–2 interactions, a similar situation is evident in the present study. There is evidence that weak complex formation does take place in C_6F_6 + pyridines systems[6,10,11], but the nature of the complexes formed is a

TABLE 2

EXCESS ENTHALPY H^E OF C_6F_6 (1) WITH PYRIDINES (2) AT 318.15 K

x_1	H^E (*exp.*) (*cal mol*$^{-1}$)	H^E (*calc.*) (*cal mol*$^{-1}$)	x_1	H^E (*exp.*) (*cal mol*$^{-1}$)	H^E (*calc.*) (*cal mol*$^{-1}$)
C_6F_6 + 2-methyl pyridine					
0.1534	−34.57	−34.57	0.5923	−138.31	−136.45
0.2352	−58.99	−58.37	0.6244	−137.8	−136.57
0.4230	−111.27	−111.97	0.8140	−97.46	−99.10
0.4365	−112.88	−115.11	0.9550	−28.49	−28.58
0.4620	−117.69	−120.59	0.9743	−16.75	−16.61
0.5362	−134.6	−132.43			
$\sigma = (\Sigma\, H^E$ (exp.) $- H^E$ (calc.)$/m-n)^{1/2} = 1.95$ cal mol^{-1} where m = number of measurement and n = number of parameters into eqn (1)					
C_6F_6 + 4-methyl pyridine					
0.8267	−31.97	−31.58	0.3914	7.73	7.74
0.8473	−28.62	−28.89	0.3474	13.02	13.86
0.717	−37.01	−36.97	0.2821	20.66	20.28
0.50	−9.6	−10.77	0.165	22.3	21.53
0.4655	−5.23	−4.64	0.1389	19.37	19.89
0.4202	2.87	3.16			
$\sigma = 0.73$ cal mol^{-1}					
C_6F_6 + 3,5-dimethyl pyridine					
0.0816	−8.61	−8.55	0.5905	−130.36	−130.10
0.1691	−28.81	−28.99	0.6875	−126.17	−126.37
0.4443	−110.04	−109.59	0.733	−119.46	−119.02
0.4544	−111.97	−111.87	0.861	−77.68	−78.08
0.4887	−118.69	−118.69	0.8727	−72.52	−72.83
0.5603	−127.58	−128.19	0.892	−64.24	−63.47
$\sigma = 0.47$ cal mol^{-1}					

matter of speculation. The lack of confirmatory non thermodynamic evidence has led to the suggestion that the interactions between the unlike molecules arise principally from electrostatic forces[1,6,12] of type C–F bond dipoles π electrons.

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