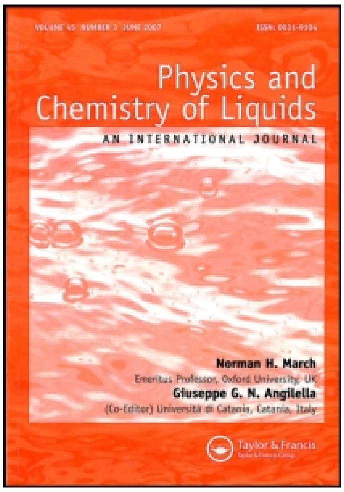

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CALORIMETRIC INVESTIGATIONS OF COMPLEX FORMATION OF 2,3,4,5,6-PENTAFLUOROANILINE WITH PROTON ACCEPTORS IN CCl_4

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Solution enthalpies of 2,3,4,5,6-pentafluoraniline in CCl_4 as well as in the solutions of tetrahydrofuran and hexamethylphosphoric triamide have been measured. From the obtained data and spectroscopically determined equilibrium constants the enthalpies of the complex formation of 2,3,4,5,6-pentafluoroaniline with one and two molecules of tetrahydrofuran and hexamethylphosphoric triamide have been calculated. The results yielded from the combination of calorimetric and spectroscopic data have been compared with those obtained using the i.r. method only.

KEY WORDS: 2,3,4,5,6-pentafluoroaniline solutions, enthalpies of solution, enthalpies of the complex formation of PFA, tetrahydrofuran, hexamethylphosphoric triamide.

INTRODUCTION

Spectroscopic investigations of 2,3,4,5,6-pentafluoroaniline (PFA) + organic base (THF and HMPT) system showed that two types of hydrogen bonded complexes, AB and AB_2 (where A denotes PFA and B-organic base molecule), exist in CCl_4 solution. Moreover, it was found that the H-bonds present in AB_2 complexes are not equivalent energetically.[1]

Determination of a complex formation energy by the use of spectroscopic method only gives the results with a relatively large uncertainty. Since calorimetry is only one method which allows to measure directly energetical effects of different processes it seemed advisable to examine the above mentioned systems calorimetrically. It is possible to determine the enthalpy (ΔH_A) and the equilibrium constant (K_A) of the complex formation only from the calorimetric data. However it is rather difficult and often gives ambiguous results. That is why we decided to calculate the enthalpy of the complex formation from the calorimetric data using the literature data concerning the equilibrium constants of the formation of complexes under discussion.

EXPERIMENTAL

Enthalpy of solution measurements (ΔH_s) for 2,3,4,5,6-pentafluoroaniline in pure CCl_4 and in solutions of THF and HMPT in CCl_4 were made using a consecutive dissolution method in a calorimeter described elsewhere.[2] Six to fifteen measurements were performed in each investigated solution concentration of 0.1, 0.2, 0.3 and 0.4 mol (only for HMPT) of organic base per dm^3 of CCl_4. The concentration range of PFA was within 0.0025–0.06 $mol \cdot dm^{-3}$.

Carbon tetrachloride (POCh-Poland),[3] tetrahydrofuran (Merck)[3] and hexamethylphosphor triamide (Fluka AG)[4] were purified and dried using the methods described in the literature.[3,4] 2,3,4,5,6-pentafluoroaniline (Aldrich) dried under vacuum was stored in a dessicator over molecular sieves. Its melting temperature was 36.5–36.7°C.

RESULTS AND DISCUSSION

The measured dissolution enthalpies, (ΔH_s) of 2,3,4,5,6-pentafluoroaniline in CCl_4 are presented as a function of the PFA concentration in Table 1. Tables 2 and 3 contain the transfer enthalpies (ΔH_t) of the PFA from pure CCl_4 to solutions of THF and HMPT in CCl_4. As it can be seen from the presented data, the solution enthalpy of PFA in CCl_4 in the concentration range 0.005–0.14 $mol \cdot dm^{-3}$ does not depend on the aniline concentration. The enthalpic effect of the PFA dissolution in CCl_4 solutions of THF as well as HMPT is lower than in pure CCl_4 and becomes less endothermic when the organic base concentration increases. The slope of the ΔH_t curve in the solution of more basic HMPT (DN = 38.8)[5] is steeper than that in the

Table 1 Dissolution enthalpy of 2,3,4,5,6-pentafluoroaniline in CCl_4 at 298.15 K

c $mol \cdot dm^{-3}$	ΔH_s $cal \cdot mol^{-1}$	c $mol \cdot dm^{-3}$	ΔH_s $cal \cdot mol^{-1}$
0.00506	5119	0.00939	5030
0.01145	5098	0.01723	5056
0.01390	5121	0.02686	5073
0.01692	5125	0.03723	5116
0.01994	5142	0.04585	5108
0.02300	5153	0.05539	5100
0.02773	5154	0.06244	5096
0.03252	5154	0.06817	5110
0.03743	5168	0.07420	5106
0.04245	5159	0.08136	5088
	$\Delta H_s = 5138$	0.08756	5084
		0.09564	5088
		0.10568	5092
		0.11581	5089
		0.12546	5086
		0.13593	5077
			$\Delta H_s = 5087$

Table 2 Molar transfer enthalpies, ΔH_t (cal · mol^{-1}) of 2,3,4,5,6-pentafluoroaniline (PFA) from CCl_4 to the solutions of THF in CCl_4 at 298.15 K, and degree of association (α) of PFA in the solution[a]; c_A^0-concentration of PFA, c_B^0-concentration of THF, both in mol · dm^{-3}

c_A^0	ΔH_t	α_1	α_2	α
		$c_B^0 = 0.09898$		
0.00366	−272	0.1712	0.0397	0.08134
0.00789	−261	0.1702	0.0397	0.08083
0.01271	−283	0.1690	0.0390	0.08025
0.01992	−309	0.1672	0.0386	0.07939
0.02775	−338	0.1654	0.0381	0.07848
		$c_B^0 = 0.20047$		
0.00428	−682	0.2949	0.0772	0.1520
0.00875	−671	0.2936	0.0767	0.1511
0.01351	−644	0.2921	0.0761	0.1502
0.01918	−625	0.2904	0.0755	0.1491
0.02667	−659	0.2882	0.0747	0.1477
		$c_B^0 = 0.29343$		
0.00569	−900	0.3795	0.1089	0.2076
0.01207	−904	0.3776	0.1080	0.2061
0.01845	−921	0.3756	0.1072	0.2046
0.02504	−881	0.3736	0.1063	0.2031
0.03263	−898	0.3714	0.1052	0.2014
0.04045	−900	0.3690	0.1042	0.1997
		$c_B^0 = 0.31299$		
0.00765	−952	0.3943	0.1151	0.2179
0.01606	−953	0.3917	0.1139	0.2160
0.03600	−954	0.3858	0.1111	0.2113
0.04590	−955	0.3829	0.1097	0.2091
0.05687	−955	0.3796	0.1091	0.2066

[a] For explanation, see into the text.

solution of THF, that has a lower donicity (DN = 20.0).[5] The observed decrease of the PFA dissolution effect along with the increase of the organic base content in CCl_4 is connected with the creation of the PFA-base mixed complexes in the solution.

As it was mentioned earlier 2,3,4,5,6-pentafluoroaniline forms with the Lewis bases in apolar solvent (e.g. in CCl_4) associates of 1:1 and 1:2 type:[1]

$$A + B \rightleftharpoons AB \qquad (1)$$

$$AB + B \rightleftharpoons AB_2 \qquad (2)$$

where: A – PFA molecule, B – base molecule. Therefore, the observed heat effect, (q) of the dissolution of n_{PFA} moles of PFA in CCl_4 solution of B can be presented as a sum:

$$-q = n_{PFA}\Delta H_s + n_{AB}\Delta H_{AB} + n_{AB_2}\Delta H_{AB_2} + Q \qquad (3)$$

Table 3 Molar transfer enthalpies, ΔH_t (cal · mol^{-1}) of 2,3,4,5,6-pentafluoroaniline (PFA) from CCl_4 to the solutions of HMPT in CCl_4 at 298.15 K, and degree of association (α) of PFA in the solution[a]; c_A^0-concentration of PFA, c_B^0-concentration of HMPT, both in mol · dm^{-3}

c_A^0	ΔH_t	α_1	α_2	α
$c_B^0 = 0.10295$				
0.00567	−3153	0.8052	0.08598	0.7912
0.00877	−3148	0.8011	0.08385	0.7825
0.01261	−3105	0.7960	0.08123	0.7710
0.01591	−3077	0.7914	0.07901	0.7605
0.01967	−3031	0.7861	0.07651	0.7478
0.02292	−3001	0.7813	0.07438	0.7362
0.02657	−2973	0.7757	0.07203	0.7224
0.02928	−2947	0.7714	0.07031	0.7118
0.03283	−2927	0.7657	0.06808	0.6974
0.03837	−2889	0.7564	0.06469	0.6738
0.04203	−2849	0.7500	0.06251	0.6577
0.04583	−2816	0.7431	0.06029	0.6407
$c_B^0 = 0.19946$				
0.00298	−4005	0.8921	0.1586	0.8867
0.00648	−3975	0.8905	0.1562	0.8835
0.01157	−3920	0.8882	0.1526	0.8784
0.01675	−3885	0.8858	0.1490	0.8728
0.02359	−3845	0.8824	0.1443	0.8648
0.02838	−3825	0.8799	0.1410	0.8587
0.03293	−3805	0.8775	0.1379	0.8525
0.03693	−3790	0.8753	0.1351	0.8466
0.04190	−3775	0.8725	0.1318	0.8389
$c_B^0 = 0.29835$				
0.00375	−4320	0.9253	0.2202	0.9216
0.00761	−4280	0.9244	0.2176	0.9198
0.01144	−4245	0.9236	0.2151	0.9179
0.01508	−4225	0.9228	0.2127	0.9160
0.01868	−4205	0.9219	0.2104	0.9142
0.02228	−4180	0.9211	0.2080	0.9122
0.02555	−4165	0.9203	0.2058	0.9103
0.02798	−4150	0.9197	0.2042	0.9089
0.03527	−4125	0.9178	0.1994	0.9044
$c_B^0 = 0.37736$				
0.00388	−4455	0.9401	0.2635	0.9372
0.00482	−4450	0.9400	0.2630	0.9369
0.01393	−4420	0.9387	0.2573	0.9341
0.01941	−4400	0.9378	0.2539	0.9322
0.02505	−4380	0.9370	0.2504	0.9302
0.03152	−4365	0.9359	0.2464	0.9278
0.03810	−4350	0.9349	0.2423	0.9252
0.04481	−4340	0.9337	0.2381	0.9224

[a] For explanation, see into the text.

where n_{AB} and n_{AB_2} denote the number of moles of AB and AB_2 type complexes, ΔH_{AB} and ΔH_{AB_2} are the molar enthalpies of the AB and the AB_2 type complex formation respectively, and ΔH_s is the molar enthalpy of PFA solution in pure CCl_4. Q denotes the thermal effect of other specific or non-specific interactions. The enthalpy of self-association of PFA in CCl_4 was not included into Eq. (3) since spectroscopic data suggest that PFA in CCl_4 exists only in a monomeric form.[1]

From the expression (3) we obtain:

$$\Delta H_s' = -q/n_{PFA} = \Delta H_s + \alpha_1 \Delta H_{AB} + \alpha_2 \Delta H_{AB_2} + Q' \tag{4}$$

$$\Delta H_t = \Delta H_s' - \Delta H_s = \alpha_1 \Delta H_{AB} + \alpha_2 \Delta H_{AB_2} + Q' \tag{5}$$

where: ΔH_t – molar enthalpy of transfer of PFA from CCl_4 to the solution of B in CCl_4,

α_1 and α_2 denote the 1st and the 2nd degree of association respectively (see Eq. 1 and 2).

The values of α_1 and α_2 can be calculated as a function of the concentration from the values of the equilibrium constants of the AB and the AB_2 type complexes formation. For the AB type complex we have:

$$K_1 = \frac{[AB]}{[A]\cdot[B]} \tag{6}$$

where [A] and [B] are the PFA and the Lewis base concentrations in mol·dm^{-3} respectively, and [AB] is a concentration of the complex. Denoting initial concentrations of the components as c_A^0 and c_B^0 and the degree of association referring to the formation of AB complex as α_1 we obtain:

$$[A] = c_A^0 - [AB]$$

$$[B] = c_B^0 - [AB]$$

$$[AB] = c_A^0 \alpha_1$$

and next

$$K_1 = \frac{c_A^0 \alpha_1}{(c_A^0 - c_A^0 \alpha_1)(c_B^0 - c_A^0 \alpha_1)} \tag{7}$$

and

$$\alpha_1 = \frac{(K_1 c_A^0 + K_1 c_B^0 + 1) - \sqrt{(K_1 c_A^0 + K_1 c_B^0 + 1)^2 - 4K_1^2 c_A^0 c_B^0}}{2K_1 c_A^0} \tag{8}$$

For the AB_2 type complex formation from the associates of AB (Eq. 2) we have:

$$K_2 = \frac{[AB_2]}{[AB'][B']} \tag{9}$$

Following the foregoing procedure we obtain:

$$[AB_2] = [AB]\alpha_2$$

$$[B'] = [B] - [AB_2] = c_B^0 - c_A^0\alpha_1 - c_A^0\alpha_1\alpha_2$$

$$[AB'] = [AB](1 - \alpha_2)$$

$$K_2 = \frac{[AB]\alpha_2}{[AB](1 - \alpha_2)(c_B^0 - c_A^0\alpha_1 - c_A^0\alpha_1\alpha_2)} \tag{10}$$

and

$$\alpha_2 = \frac{(K_2c_B^0 + 1) - \sqrt{(K_2c_B^0 + 1)^2 - 4K_2^2c_A^0\alpha_1(c_B^0 - c_A^0\alpha_1)}}{2K_2c_A^0\alpha_1} \tag{11}$$

The values of association degree, α_1 and α_2, that refer to PFA-THF and PFA-HMPT complexes, calculated from the equations (8) and (11) are presented in Tables 2 and 3. In order to calculate the enthalpy of formation of the AB and AB_2 associates for PFA-THF and PFA-HMPT systems we solved Eq. 5 using the multiparametric linear regression method.

2,3,4,5,6-pentafluoroaniline-tetrahydrofuran system

The experimental transfer enthalpies of PFA from CCl_4 to THF-CCl_4 mixtures can be presented as:

$$\Delta H_t = (203 \pm 60) - (2859 \pm 1038)\alpha_1 - (344 \pm 3115)\alpha_2$$

$$\text{for } n = 20 \text{ dysp.} = 23.5;\ r = 0.997$$

Therefore:

$$\Delta H_1 = -(2859 \pm 1038)\ \text{cal}\cdot\text{mol}^{-1} \text{ and } \Delta H_2 = -(344 \pm 3115)\text{cal}\cdot\text{mol}^{-1}.$$

The ΔH_2 value is statistically unimportant ($T = 0.1$) in ΔH_t value estimation and it can be neglected. The best fit for the experimental data is obtained for the expression: $\Delta H_t = (209 \pm 19) - (2975 \pm 60)\alpha_1$ for $n = 20$ dysp. = 22.8; $r = 0.997$. The enthalpic effect of bonding of one PFA molecule to one molecule of THF, $\Delta H_1 =$

-3.0 kcal · mol^{-1} is very close to the value obtained from spectroscopy ($\Delta H_1^{sp} = -3.3$ kcal · mol^{-1}).[1]

2,3,4,5,6-pentafluoroaniline-hexamethylphosphoric triamide system

The ΔH_t data that refer to the PFA-HMPT system could not be fitted to the three-parameter equation as it was done for the PFA-THF system. The correlation coefficient (r) was less than 0.9 and ΔH_1 and ΔH_2 assumed values without any physical sense. Moreover, the use of the three-parameter equation exclusively for the data concerning a HMPT solution, concentration of 0.1 mol · dm^{-3} and next independently for solutions of 0.2 and 0.3 mol HMPT per dm^3 gave the values of the adjustable parameters Q, ΔH_1 and ΔH_2 that differed significantly from one another depending on the HMPT concentration. Neglecting the AB$_2$ complex formation in a solution with concentration of HMPT $c_B^0 = 0.1$ mol · dm^{-3} we got an expression:

$$\Delta H_t = (1210 \pm 133) - (5407 \pm 172)\alpha_1$$

$$\text{for } n = 12 \quad r = 0.995$$

which means that $\Delta H_1 = -5.4$ kcal · mol^{-1}. The calculated value of ΔH_1 is very close to that obtained from the spectroscopic measurements ($\Delta H_1^{sp} = -5.3$ kcal · mol^{-1}).[1]

As it can be seen from the presented analysis the enthalpy of the complex formation of the AB type can be calculated with a relatively high accuracy by a combination of appropriate calorimetric and spectroscopic data. However, it was not possible to calculate in the same way the enthalpy of formation of the second H-bond that leads to creation of the AB$_2$ type complex. Relatively small changes of α_2 values in a series of measurements caused by the low value of the K_2 constant seem to be the main reason of the observed behaviour. For instance the total change of the transfer enthalpy produced by the formation of the AB$_2$ type complex from the AB one in PFA-HMPT system amounts only to about 50 calories (calculated from the spectroscopic data—Table 4) and so it is within the experimental uncertainty limits ((50/5000) × 100 = 1%). Since it was impossible to determine independently the

Table 4 Equilibrium constants and enthalpies of associate formation of AB and AB$_2$ type for PFA-THF and PFA-HMPT in CCl$_4$

	K_1	K_2	ΔH_1	ΔH_2	ΔH	
PFA-THF	2.1	0.42	−3.3	−2.8	−6.1	[a]
			−3.0	−2.0	−5.0	[b]
PFA-HMPA	42	0.96	−5.3	−3.2	−8.5	[a]
			−5.4(b$_1$)	−2.9(b$_2$)	−8.3(b$_2$)	[b]

[a] Spectroscopic data.[1]

[b] Calorimetric results:

b$_1$ for $c_B^0 = 0.1$ mol · dm^{-3}, b$_2$ for $c_B^0 = 0.2$, 0.3 and 0.4 mol · dm^{-3}.

ΔH_1 and ΔH_2 values in the examined systems we decided to calculate the enthalpy of formation of the AB_2 complex from the monomers (ΔH) according to the equation:

$$A + 2B \rightleftharpoons AB_2 \tag{12}$$

In this case: $\Delta H = \Delta H_1 + \Delta H_2$ and

$$K = K_1 \cdot K_2 = \frac{[AB_2]}{[A] \cdot [B]^2} \tag{13}$$

whereas the degree of association α can be calculated from the formula:

$$\alpha = \frac{(2Kc_A^0 + Kc_B^0 + 1) - \sqrt{(2Kc_A^0 + Kc_B^0 + 1)^2 - 8K^2c(_A^0c_B^0}}{4Kc_A^0} \tag{14}$$

The values of the total degrees of association α in PFA-THF and PFA-HMPT systems are presented in Tables 2 and 3. The molar enthalpy of AB_2 complex formation $\Delta H = \Delta H_1 + \Delta H_2$ was determined using the multiple linear regression method. For the system PFA-THF we obtain:

$$\Delta H_t = (112 \pm 18) - (5013 \pm 102)\alpha \quad r = 0.996$$

which means that $\Delta H = -5.0\ \text{kcal} \cdot \text{mol}^{-1}$. Taking into account the value of $\Delta H_1 = -3.0\ \text{kcal mol}^{-1}$ determined earlier for this system we can easily calculate the ΔH_2:

$$\Delta H_2 = \Delta H - \Delta H_1 = -5.0 - (-3.0) = -2.0\ \text{kcal} \cdot \text{mol}^{-1} \qquad \text{(Table 4)}$$

The values of the total enthalpy ΔH and the enthalpy of formation of the second H-bond in the PFA-HMPT system were calculated from the calorimetric data referring to the HMPT solutions, concentration of 0.2, 0.3 and 0.4 mol · dm^{-3}, in the same manner as presented above. They are also given in Table 4 which presents additionally the analogous data obtained spectroscopically. The results shown here seem to confirm the conclusion about a different energy of hydrogen bonds in the AB_2 type complex formed by 2,3,4,5,6-pentafluoroaniline with the Lewis bases.

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References

1. G. S. Denisov, L. A. Kuzina, A. L. Smolyansky, and G. G. Furin, *Zh. Prikl. Spektrosk.*, **51**, (3), 476 (1990).
2. S. Taniewska-Osińska and A. Piekarska, *J. Chem. Soc., Faraday Trans. I*, **81**, 1913 (1985).
3. S. Taniewska-Osińska and P. Góralski, *J. Chem. Soc., Faraday Trans. I*, **77**, 969 (1981).
4. J. F. Coetzee "Purification of solvents and tests impurities" IUPAC, Pergamon Press, p. 38 (1983).
5. V. Gutman, "The Donor-Acceptor Approach To Molecular Interactions", pp. 13–33. Plenum Press, New York (1978).