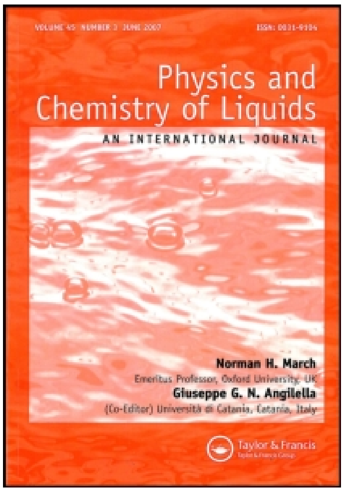

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CALORIMETRIC AND SPECTROSCOPIC STUDIES OF COMPLEX FORMATION OF 2,4,5-TRICHLOROANILINE WITH PROTON ACCEPTORS IN CCl_4

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Spectroscopic and calorimetric investigations of interactions between trichloroaniline (A) and organic base: tetrahydrofuran or hexamethylphosphoric triamide (B) in CCl_4 solution were carried out at 298.15 K. The equilibrium constants and the enthalpies for AB and AB_2 type complex formation processes were calculated from a combination of both calorimetric and spectroscopic data. The results obtained suggest that, as in the case of earlier investigated complexes of pentafluoroaniline with the same organic bases, the enthalpy of formation of the first hydrogen bond in the AB_2 type associates is higher than that of the second one.

KEY WORDS: Complex formation, hydrogen bonds.

INTRODUCTION

Recently, investigations of aniline halogen derivatives in solutions of organic bases in carbon tetrachloride as an inert solvent have been carried out in our laboratory. The 2,3,4,5,6-pentafluoroaniline (PFA) in solutions of tetrahydrofuran (THF) and hexamethylphosphortriamide (HMPT) was the former subject of these examinations [1]. The results of our calorimetric measurements for the above mentioned system were in good agreement with earlier spectroscopic observations [2], which pointed to the presence of two types of hydrogen bonded complexes in CCl_4 and indicated that the H-bonds present in AB_2 type complex are not equivalent energetically.

This paper is devoted to examination of another aniline derivative, 2,4,5-trichloroaniline (TChA) in solutions of the same organic bases (i.e. THF and HMPT) in CCl_4. Our aim was to determine both the enthalpies of association and the equilibrium constants of AB and AB_2 type complex formation. To this end, IR spectroscopy and solution calorimetry have been employed.

EXPERIMENTAL

Reagents: 2,4,5-trichloroaniline, (EGA-Chemie, Germany) was dried under vacuum at 300 K and stored in the dissicator over molecular sieves of 4A type. 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].

Enthalpies of solution ($\Delta_{sol}H_m$) of 2,4,5-trichloroaniline in pure CCl_4 and in solutions of THF and HMPT in CCl_4 were measured using a consecutive dissolution method in a calorimeter described in detail elsewhere [5]. Six to twelve measurements were performed in each solution of the organic base investigated; at concentrations of ca. 0.1, 0.2, 0.3 and 0.5 mol per dm^3 of CCl_4.

IR spectra were recorded on a Fourier transform spectrophotometer Bruker IFS 85 with a $1\,cm^{-1}$ resolution (128 scans). Infrasil quartz cells of 1 cm and 0,5 cm optical path-length were used. In the spectrometer compartment the cell was under thermostatic control at 25 ± 0,5°C.

The absorption spectra of 2,4,5-TChA in CCl_4 and in solutions of THF and HMPT in CCl_4 were examined within the frequency region corresponding to valence and deformation vibrations ($3600 - 3000\,cm^{-1}$). The 2,4,5-TChA concentration range was $0.002 - 0.05\,mol \cdot dm^{-3}$; the concentration of THF solutions varied from 0.05 to $0.3\,mol \cdot dm^{-3}$ and that for HMPT from 0.009 to $0.2\,mol \cdot dm^{-3}$. Each spectrum was deconvoluted. The bands were treated (assumed) as a sum of Gaussian and Lorentzian contributions.

RESULTS AND DISCUSSION

Spectroscopic data

The IR absorption spectra of 2,4,5-TChA in solutions of THF and CCl_4 exhibit, within the frequency range of $-NH_2$ group the bands of symmetrical (ν_s^f) and antisymmetrical (ν_{as}^f) vibrations of free $-NH_2$ group. Their maxima positions correspond with frequencies $\nu_s^f = 3402\,cm^{-1}$ and $\nu_{as}^f = 3500\,cm^{-1}$. Moreover, a band ν^f of the free $-NH$ group vibration in AB type complex was identified at $\nu^f = 3350\,cm^{-1}$. The analogous absorption bands of the free $-NH_2$ group, ν_s^f and ν_{as}^f at the same as above frequency have been observed for 2,4,5-TChA in solutions of HMPT in CCl_4. However, in this case a band of the free $-$ NH group in the AB type complex occur at ν^f (HMPT) $= 3476\,cm^{-1}$.

The AB type complex formation equilibrium constant (where A denotes 2,4,5-TChA and B-THF or HMPT) is defined as:

$$K_1 = c_{AB}/c_A \cdot c_B \tag{1}$$

The equilibrium concentration of the TChA (c_A) was calculated from the absorbance of the $3402\,cm^{-1}$ and $3500\,cm^{-1}$ peaks for the both systems. The concentration of the AB complex (c_{AB}) was obtained from the absorbance of the $3350\,cm^{-1}$ peak for the solutions containing THF and from the absorbance of $3476\,cm^{-1}$ peak for the solutions containing HMPT. Since in the systems under examination, apart of AB associates the formation of AB_2 type complexes is possible [1, 2] the equilibrium concentration of the organic base, c_B cannot be calculated as:

$$c_B = c_B^0 - c_{AB} \tag{2}$$

According to the proposal given in the mentioned earlier Denisov's paper [2] the c_B value should be calculated from the formula:

$$c_B^0 = c_B + c_{AB} + 2c_{AB_2} \tag{3}$$

where c_{AB_2} denotes a concentration of the AB_2 type complexes that can be determined from the Eq. (4):

$$c_A^0 = c_A + c_{AB} + c_{AB_2} \tag{4}$$

It was found that in the investigated solutions within the spectroscopically examined range of the proton acceptor content in CCl_4 the amount of the complexes of AB_2 type is very small and the determination of the equilibrium constant of this type associates formation appeared to be impossible. Therefore only K_1 values has been calculated from the obtained spectroscopic data and they are:

$K_1 = 1{,}2\ \mathrm{dm^3 \cdot mol^{-1}}$ for 2,4,5-TChA + THF complex, and
$K_1 = 60\ \mathrm{dm^3 \cdot mol^{-1}}$ for 2,4,5-TChA + HMPT complex in CCl_4.

The relative error of the calculated K_1 values is less than 20 per cent.

Calorimetric data

The measured dissolution enthalpies, $\Delta_{sol}H_m$ of 2,4,5-trichloroaniline in CCl_4 are presented as a function of the TChA concentration in Table 1. Tables 2 and 3 contain the transfer enthalpies $\Delta_{tr}H$ of the TChA 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 TChA in CCl_4 in the investigated concentration range does not depend on the aniline concentration within the experimental error limits.

The enthalpic effect of the TChA dissolution in CCl_4 solutions of THF as well as HMPT is lower than that in pure CCl_4 and becomes less endothermic when the organic

Table 1 Dissolution enthalpy of 2,4,5-trichloroaniline in CCl_4 at 298.15 K.

c_A^0 mol·dm^{-3}	$\Delta_{sol}H_m$ cal·mol^{-1}
0.00416	6025
0.00836	6027
0.01256	6024
0.01709	6024
0.02168	6017
0.02633	6012
0.03133	6004
0.03645	5999
0.03984	5998
0.04387	5992
0.04905	5988
0.05461	5985

Table 2 Molar transfer enthalpies, $\Delta_{tr}H_m$ (cal·mol^{-1}) of 2,4,5-trichloroaniline (TChA) from CCl_4 to the solutions of THF in CCl_4 at 298.15 K; c_A^0-concentration of TChA, c_B^0-concentration of THF, both in mol·dm^{-3}.

c_A^0 mol·dm^{-3}	$-\Delta_{tr}H_m$ cal·mol^{-1}	c_A^0 mol·dm^{-3}	$-\Delta_{tr}H_m$ cal·mol^{-1}
$c_B^0 = 0.1033$		$c_B^0 = 0.3099$	
0.00276	390	0.00198	822
0.00577	390	0.00405	818
0.00924	385	0.00645	810
0.01529	383	0.00898	809
0.01849	380	0.01196	805
0.02209	380	0.01515	804
0.02588	378	0.01836	800
0.03044	378	0.02145	797
0.03414	375	0.02469	795
		0.02817	790
$c_B^0 = 0.2066$		$c_B^0 = 0.5165$	
0.00356	610	0.00244	1150
0.00741	610	0.00610	1145
0.01177	608	0.01003	1140
0.01621	602	0.01427	1135
0.02066	595	0.01855	1131
0.02544	591	0.02285	1128
0.02877	587	0.02624	1125
0.03255	585	0.02969	1122
0.03657	585		
0.04053	580		

Table 3 Molar transfer ethalpies $\Delta_{tr}H_m$ (cal·mol^{-1}) of 2,4,5-trichloroaniline (TChA) from CCl_4 to the solutions of HMPT in CCl_4 at 298.15 K; c_A^0-concentration of TChA, c_B^0-concentration of HMPT, both in mol·dm^{-3}.

c_A^0 mol·dm^{-3}	$-\Delta_{tr}H_m$ cal·mol^{-1}	c_A^0 mol·dm^{-3}	$-\Delta_{tr}\mathrm{H}_m$ cal·mol^{-1}
$c_B^0 = 0.1018$		$c_B^0 = 0.3352$	
0.00213	4090	0.00298	4708
0.00435	4078	0.00660	4700
0.00743	4066	0.01029	4683
0.01056	4050	0.01400	4673
0.01408	4030	0.01781	4666
0.01762	4012	0.02167	4658
0.02137	3985	0.02588	4642
0.02520	3953	0.03004	4635
		0.03453	4625
		0.03934	4615
$c_B^0 = 0.2015$		$c_B^0 = 0.5572$	
0.00186	4467	0.00290	4870
0.00375	4458	0.00689	4862
0.00657	4434	0.01155	4852
0.00943	4414	0.01630	4846
0.01232	4398	0.02097	4840
0.01530	4379	0.02598	4835
0.01829	4361	0.03156	4830
0.02134	4342	0.03701	4829
0.02390	4332	0.04192	4821
0.02657	4323	0.04618	4818
		0.04973	4815

base concentration increases. The biggest changes of the $\Delta_{sol}H_m$ on the organic base concentration (C_B) are observed for the system containing HMPT. As it was mentioned earlier, the 2,4,5-trichloroaniline forms with the Lewis bases in apolar solvent (e.g. in CCl_4) associates of 1:1 and 1:2 type:

$$A + B \leftrightarrows AB \tag{5}$$

$$AB + B \leftrightarrows AB_2 \tag{6}$$

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

$$-q = n_{TChA}\Delta_{sol}H_m + n_{AB}\Delta H_{AB} n_{AB_2}\Delta H_{AB_2} + Q \tag{7}$$

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 AB_2 type complex formation respectively, and $\Delta_{sol}H_m$ is the molar enthalpy of TChA solution in pure CCl_4. Q denotes the thermal effect of other specific or non-specific interactions.

From the expression (3) we obtain

$$\Delta_{sol}H'_m = -q/n_{TChA} = \Delta_{sol}H_m + \alpha_1\Delta H_{AB} + \alpha_2\Delta H_{AB_2} + Q' \tag{8}$$

and

$$\Delta_{tr}H_m = \Delta_{sol}H'_m - \Delta_{sol}H_m = \alpha_1\Delta H_{AB} + \alpha_2\Delta H_{AB_2}Q' \tag{9}$$

where $\Delta_{sol}H'_m$ is the molar dissolution enthalpy of TChA in given solution of the organic base (B) in CCl_4, $\Delta_{tr}H_m$ denotes molar enthalpy of transfer of TChA from CCl_4 to the solution of B in CCl_4, and α_1 and α_2 are the 1st and the 2nd degree of association respectively (see Eqs. 5 and 6).

In order to solve the Eq. (9), the values of $\alpha_1, \alpha_2, \Delta H_{AB}, \Delta H_{AB_2}$ and Q' should be determined numerically what is impossible due to a very slight concentration dependence of the $\Delta_{sol}H'_m$ of the aniline (Tables 2, 3). As has been concluded from our spectroscopic results only small number of AB_2 type associates is formed in the investigated systems. Therefore it can be assumed that, at least in the solution of the lowest investigated base concentration ($c_B^0 = 0.1\ \mathrm{mol\cdot dm^{-3}}$) the number of AB_2 complexes is neglegible small and the energetic effect of their formation ($\alpha_2\Delta H_{AB_2}$) within the examined range of TChA content is constant. In such a case the Eq. (5) can be rewritten as:

$$\Delta_{tr}H_m = \alpha_1\Delta H_{AB} + Q_1 \tag{10}$$

where

$$Q_1 = Q' + \alpha_2\Delta H_{AB_2} = \text{const.}$$

The value of α_1 can be calculated as a function of concentration from the value of the equilibrium constant of the AB type complex formation only, determined spectroscopically in this work.

Since

$$K_1 = \frac{c_A^0 \alpha_1}{(c_A^0 - c_A^0 \alpha_1)(c_B^0 - c_A^0 \alpha_1)} \tag{11}$$

we obtain

$$\alpha_1 = \frac{(K_1 c_A^0 + K_1 c_B^0 + 1) - \sqrt{(K_1 c_A^0 + K_1 c_B^0 + 1)^2 - 4K_1^2 c_A^0 c_B^0}}{2K_1 c_A^0} \tag{12}$$

Applying the multiple linear regression method the "best" value of ΔH_{AB} and Q_1 have been determined and they are given in Table 4.

The formation of AB_2 type associates could not be neglected in the more concentrated solutions of the proton acceptor ($c_B^0 = 0.2$; 0.3 and 0.5 mol·dm^{-3}). Therefore the measured enthalpies of TChA transfer, $\Delta_{tr}H_m$ in these systems were fitted to the equation in form:

$$\Delta_{tr}H_m = \alpha \Delta H_{AS} + Q_2 \tag{13}$$

where ΔH_{AS} is the enthalpy of formation of the AB_2 complex from the monomers according to the equation:

$$A + 2B \rightleftharpoons AB_2 \tag{14}$$

In this case

$$\Delta H_{AS} = \Delta H_1 + \Delta H_2 \tag{15}$$

and

$$K = K_1 \cdot K_2 = \frac{[AB_2]}{[A][B]^2} \tag{16}$$

whereas the degree of association α can be expressed as:

$$\alpha = \frac{(2Kc_A^0 + Kc_B^0 + 1) - \sqrt{(2Kc_A^0 + Kc_B^0 + 1)^2 - 8K^2 c_A^0 c_B^0}}{4Kc_A^0} \tag{17}$$

Table 4 Equilibrium constants and enthalpies of associate formation of AB and AB_2 type for TChA-THF and TChA-HMPT in CCl_4*.

	K_1	K_2	ΔH_1	ΔH_2	ΔH_{AS}
TChA-THF	1.2	0.45	−3.0	−1.9	−4.9
TChA-HMPT	60	0.8	−5.0	−2.0	−7.0

*) K in dm^3·mol^{-1}; ΔH in cal·mol^{-1}.

Applying the method of consecutive approaching to Eqs. (13) and (17) we have determined the "best" values of K and ΔH_{AS} for TChA-HMPT and TChA-THF systems. They are given in Table 4. Taking into account the values of K_1, determined spectroscopically and calculated earlier the ΔH_1 we can easily calculate the values of K_2 and ΔH_2 (Eqs. 15 and 16). They are also given in Table 4. The presented results show that, similarly as examined earlier 2,3,4,5,6-pentafluoroaniline [1] also 2,4,5-trichloroaniline seems to form the AB_2 type complex with the hydrogen bonds of a different energy.

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