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Complexes with strong symmetric hydrogen bonds and their solvation in the trifluoroacetic acid—*N*,*N*-dimethylformamide system studied by IR spectroscopy

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Complex formation in the trifluoroacetic acid (TFA)—DMF system containing TFA from 0 to 100 mol.% was studied by IR multiple attenuated total reflectance (MATR) spectroscopy at 30 °C. The formation of uncharged 1 : 1 TFA—DMF complexes with a quasi-ion structure and partial proton transfer to the O atom of the DMF molecule (quasi-ion pairs) were observed in the TFA—DMF system with the TFA content from 0 to 90 mol.%. Depending on the ratio of the components, the quasi-ion pairs are solvated by the DMF or TFA molecules. The solvation of the quasi-ion pairs slightly changes the parameters of the central strong H bond. When the acid concentration reaches 80 mol.%, the proton adds to the DMF molecule to form the ion pair $(DMF)H^+ \cdot (A...H...A)^-$, whose anion contains a strong symmetric H bond.

Key words: IR spectra; acid-base interaction, hydrogen bond; solutions, solvation; trifluoroacetic acid, *N*,*N*-dimethylformamide.

Ions, quasi-ion pairs, or molecular complexes[1–4] can be formed in nonaqueous solutions of acids with a base excess. For strong acids (HCl, H_2SO_4, methanesulfonic acid (MSA)), the degree of completeness of acid-base interaction is determined by the nature of the organic base. Disolvates of a proton form in alcohol solutions, being similar to analogous $H_5O_2^+$ ions in aqueous systems[1] as far as the structure and IR spectral parameters. These solvates are characterized by a strong symmetric central H bond. The IR spectra of all systems containing the proton disolvates with these H bonds exhibit intense continuous absorption (CA)[1] in the region from ~800 to 3500 cm^{-1}. According to calculations, the spectra of these ions in the CA region exhibit many (40—300) bands of combined vibrations and overtones, the majority of which (up to 60%) are comparable in intensity to the bands of fundamental vibrations.[1] The most intense of these bands that form the CA spectrum can be detected as individual maxima against the background of the CA. Intense CA is also observed in the IR spectra of negatively charged proton disolvates formed by the strong symmetric H bond and of uncharged complexes with the quasi-ion structure.[2] The mechanism of CA appearance has been considered in the review.[1] The strong quasi-symmetric H bond with an incomplete transition of a proton to the heteroatom of the base molecule is observed in the quasi-ion pairs.[5,6] The formation of molecular acid—base complexes whose spectra do not exhibit CA was observed for the MSA—ethyl acetate and MSA—propylenecarbonate systems.[3]

Quasi-ion pairs have been observed to date in many aprotic acid-base systems. The HCl complexes with DMF have been characterized[4–6] most completely by IR spectroscopy, Raman spectroscopy, and X-ray structural analysis. In an excess of the acid, a proton can completely transfer to the base molecule (*i.e.*, protonation of the base) with the simultaneous formation of the negatively charged proton disolvate.[4,5,7]

$$AH + B \rightleftharpoons A...H...B \qquad (0-50 \text{ mol.\% HA}),$$

$$A...H...B + HA \rightleftharpoons BH^+ \cdot (A...H...A)^- \quad (>50 \text{ mol.\% HA}). \qquad (1)$$

This work is aimed at studying the acid-base interaction of DMF with the weaker trifluoroacetic acid[8] (TFA).

Experimental

Reagents. DMF ("puriss" grade) with H_2O content <0.01% and TFA ("purum" grade, Fluka) were used. The salt CF_3COONa was prepared by TFA neutralization with sodium bicarbonate followed by evaporation on a rotary evaporator and washing the precipitate with ethanol.

Procedure of measurements. IR MATR spectra were recorded on a UR-20 spectrophotometer at 30 °C. An MNPVO-3 attachment (designed at the Institute of Chemical Physics of the Russian Academy of Sciences) was used (a germanium working prism, incident angle 30°, four or eight reflections for filling one or two cavities of the cell). The effective thicknesses at ν = 2000 cm^{-1} were 1.77 and 3.30 μm, respectively.[9]

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Table 1. Stoichiometric composition and density (ρ) of TFA solutions in DMF at 30 °C

C^0_{TFA} (mol.%)	C^0_{TFA}	C^0_{DMF}	ρ /g cm^{-3}
	mol L^{-1}		
100.00	12.98	0.00	1.480
92.13	12.29	1.05	1.477
81.39	11.02	2.52	1.441
74.89	10.14	3.40	1.405
66.52	9.20	4.63	1.360
63.20	8.52	4.96	1.334
59.23	7.96	5.48	1.308
54.90	7.34	6.03	1.278
50.37	6.73	6.63	1.252
42.55	5.60	7.56	1.190
39.82	5.24	7.92	1.176
33.21	4.37	8.79	1.141
24.14	3.15	9.90	1.084
23.83	3.10	9.91	1.078
11.49	1.49	11.48	1.010
0	0	12.91	0.948

Experimental data. IR spectra of TFA solutions in DMF with different concentrations of the components in the 0—100% composition range and solutions of CF_3COONa in TFA (Table 1) were recorded in the frequency region of 900—3800 cm^{-1}. The concentration dependences of the optical densities (*D*) of the bands of the components and complexes that formed and CA were examined. The *D* bands were measured relative to the basic lines, and CA was measured relative to the absorption of the empty cell.

The solutions for the study were prepared by the weighing method. The densities of the solutions (see Table 1) were measured for the calculation of molar concentrations.

Results and Discussion

The spectra of individual DMF[5,10] and TFA[11] contain several intense bands (Fig. 1) and no CA. The changes in the spectra on going to solutions of both TFA and MSA[7] in DMF in the interval of acid concentrations of 0—50 mol.% are similar. The intensity of the DMF bands decreases strongly. New broad bands and an intense CA (see Fig. 1) appear. The conclusions about the composition of the DMF complex with TFA are based on the analysis of the concentration dependences of the absorbances of the DMF bands at 1255 cm^{-1} ($\nu_{as}(N-CH_3)$), 1383 cm^{-1} ($\nu(C-N)$), and 1660 cm^{-1} ($\nu(C=O)$) and the bands of the acid at 1770 cm^{-1} ($\nu(C=O)$) and 3200 cm^{-1} ($\nu(O-H)$). With a base excess, the band attributed to ν(OH) vibrations of the acid molecules at 3200 cm^{-1} is almost absent, *i.e.*, the solutions do not contain acid molecules that are not bound in complexes with DMF. The absorption of both free and bound in complexes TFA molecules appears at 1770 cm^{-1} in the spectra of the solutions. The absorbance at this frequency changes proportionally to the acid concentration to a ratio of the components of 1 : 1.

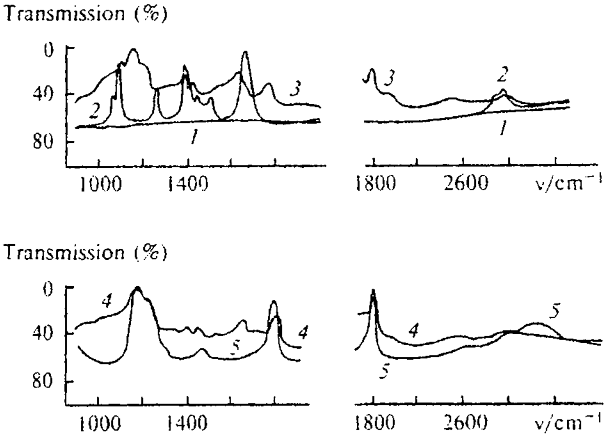

Fig. 1. IR MATR spectra: *1*, empty cell; *2*, DMF; and *3*—*5*, solutions of trifluoroacetic acid in DMF with concentrations of 50.37 (*3*), 66.52 (*4*), and 100 mol.% TFA (*5*).

The absorptivity of the acid molecules bound in the complexes (150 L mol^{-1} cm^{-1}) is much lower than that of 100% TFA (275 L mol^{-1} cm^{-1}). These data indicate that with a base excess the acid is completely bound in 1 : 1 complexes with DMF molecules (**1**). The formation of complex **1** is accompanied by substantial changes in the spectrum of the DMF molecules. The bands at 1093 (δ(NCH)), 1255, 1438, 1500, and 1660 cm^{-1} are absent from the spectrum of the complexes. New bands, which are shifted relative to these bands by 20—30 cm^{-1}, with lower absorptivity appear. We estimated the content of DMF molecules that are not bound in the complexes as <0.5 mol L^{-1} from the absorbance of the highest-intensity band at 1660 cm^{-1} in the spectrum of the 1 : 1 solution.

The concentration dependence of the absorbance of the DMF band at 1383 cm^{-1} is described by the equation

$$D = \varepsilon_{DMF} l C_{DMF} + \varepsilon_1 l C_1,$$

$$D/C_1 = \varepsilon_{DMF} l C_{DMF}/C_1 + \varepsilon_1 l, \qquad (2)$$

which was obtained under the assumption that each acid molecule is bound to one DMF molecule (Fig. 2). The absorptivity at this band is summated of the absorptivities of complexes **1** and DMF molecules free of these complexes, $C_1 = C^0_{TFA}$, $C_{DMF} = C^0_{DMF} - C^0_{TFA}$, where C^0_{DMF} and C^0_{TFA} are the analytic concentrations of the components, and *l* is the effective thickness of the absorbing layer at 1383 cm^{-1}. The coefficients ε_{DMF} and ε_1 are equal to 175 and 117 L mol^{-1} cm^{-1}, respectively. In pure DMF ε_{1383} = 184 L mol^{-1} cm^{-1}.

The spectrum of complex **1** contains CA from 900 to 2700 cm^{-1}, and against this background several broad maxima at 930, 1010, 1320, and 1950 cm^{-1} and a diffuse wing at 1500—1600 cm^{-1} appear. These specific features of the spectrum indicate[4,7] a quasi-ionic structure of the

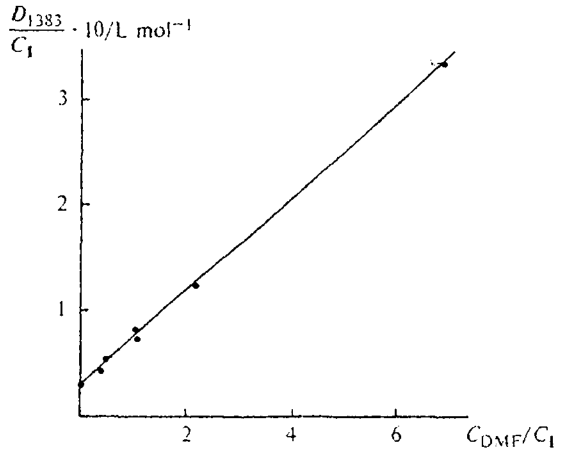

Fig. 2. Graphical representation of the solution of Eq. (2) for the frequency of 1383 cm^{-1}.

1 : 1 DMF—TFA complexes. The spectrum of complexes **1** is presented in Fig. 3.

The concentration dependence of the CA in the TFA—DMF system indicates the solvation of complexes **1** with quasi-ionic structure by the base molecules (at an excess of the base) to form $\mathbf{1}_{solv}$. As in other systems,[4,7] for frequencies exceeding 1600 cm^{-1}, the CA intensity is proportional to the acid concentration for a ratio of the components of at most 1 : 1. At lower frequencies no proportionality is observed. The proportionality coefficients for the majority of frequencies decrease with an increase in the acid concentration. For some frequencies (for example, 1330 cm^{-1}), the dependences are linear when the component ratio changes to 2 : 1. For other frequencies (900, 940, 1200, and 1220 cm^{-1}), the proportionality is violated in more dilute solutions. These data indicate that complex **1** can be solvated by more than one DMF molecule. As in solutions of other acids,[4,7] in a DMF solution the solvation of **1** enhances the absorptivity at the frequencies indicated. The $(\varepsilon_1)_{solv}$ values presented in Table 2 were obtained from the linear regions of the D_ν — C^0_{TFA} plots. The spectra of the DMF molecules participating in the formation of the quasi-ionic structure and those of the DMF molecules solvating complex **1** are different.

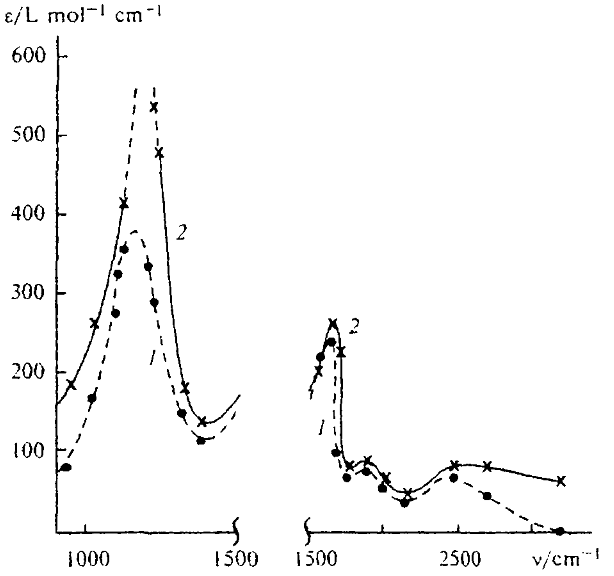

Fig. 3. Continuous absorption spectra (ε) of complexes **1** (*1*) and **2** (*2*).

Table 2. Coefficients of continuous absorption of complexes of trifluoroacetic acid with DMF **1** and **2**

ν	$(\varepsilon_1)_{solv}$*	ε_1	ε_2	ε**
/cm^{-1}	L mol^{-1} cm^{-1}			
900	91	68	154	154
940	92	79	187	187
1020	85	171	263	263
1093	—	277	329	329
1110	332	363	420	420
1200	458	340	541	540
1220	331	295	488	488
1330	181	159	187	234
1383	240	122	145	226
1600	228	228	218	360
1650	—	248	268	—
1705	—	108	232	553
1770	83	72	84	115
1900	98	86	93	124
1940	92	96	84	121
2000	72	69	76	103
2150	45	45	51	85
2470	73	80	96	164
2700	52	52	92	125
3200	20	8	79	—

Note. The accuracy of the determination of ε is ~10%.

* The data of solvated complex **1**.

** The coefficients were obtained from the spectrum of a TFA solution with the concentration of 1.4 mol L^{-1} DMF.

The highest concentration of complex **1** is achieved at an equimolar ratio of the complexes. This composition is characterized by maxima of the concentration dependences of the CA for several frequencies (1330, 1600, 1900, 1940, 2000, 2150, and 2470 cm^{-1}). For other frequencies (940, 1020, 1200, 1705, and 2700 cm^{-1}), the highest intensity is achieved in more concentrated solutions of the acid. In our opinion, this can be related to the further interaction of complex **1** with the TFA molecules. Under the assumption that in the composition interval from 50 to 66.7 mol.% acid the components are bound in the 1 : 1 and 2 : 1 complexes (**2**), we may write

$$C^0_{DMF} = C_1 + C_2,$$

$$C^0_{TFA} = C_1 + 2C_2.$$

The changes in the optical densities of the CA correspond to the equation

$$D_\nu = \varepsilon^\nu{}_1 l_\nu C_1 + \varepsilon^\nu{}_2 l_\nu C_2. \qquad (3)$$

$$D_\nu/C_1 = \varepsilon^\nu{}_1 l_\nu + \varepsilon^\nu{}_2 l_\nu (C_2/C_1). \qquad (4)$$

All experimental data are described by linear equation (4). The obtained coefficients $\varepsilon^\nu{}_2$ are presented in Fig. 3. The $\varepsilon^\nu{}_1$ values calculated from Eq. (3) and the spectrum of the 1 : 1 solution coincide.

In the HCl–DMF and MSA–DMF systems, the interaction of complex **1** with the second TFA molecule substantially changes the structure of the complexes[4,7] (see Eq. (1)), which is reflected in the difference of the spectra of the HA · DMF and (2HA) · DMF complexes in these systems. For the TFA–DMF system, the spectra of complexes **1** and **2** (see Fig. 3) differ only in intensities. In our opinion, this indicates that complex **1** is solvated by the acid molecules with the retention of the quasi-ionic character of the central H bond. Two TFA molecules in complex **2** are not equivalent. The solvation of complex **1** with the acid molecules increases the absorptivity of the CA (see Fig. 3, Table 2).

The changes in the spectra of the concentrated acid solutions (>80 mol.% TFA) indicate an equilibrium between the species with the quasi-ionic and ionic structures:

$$\underset{\mathbf{2}}{(\mathrm{A...H...B})\cdot\mathrm{HA}} \rightleftharpoons \mathrm{BH^+\cdot(A...H...A)^-}. \qquad (5)$$

The spectra of solutions with DMF concentration ≤~2.5 mol L^{-1} contain a band with a maximum at 1720 cm^{-1}. It is assigned[4,5,7] to the protonated DMF molecules. At ν > 1300 cm^{-1}, the CA coefficients in these solutions are noticeably higher than those for complexes **2**. If equilibrium (5) is entirely shifted to the right, the CA spectrum corresponds to that of the proton disolvate $(A...H...A)^-$. The $(A...H...A)^-$ disolvates formed by the anions of several acids (H_2SO_4, MSA, CH_3COOH) have[2] similar values of the CA coefficients at 2000 cm^{-1} in the interval of 100–130 L mol^{-1} cm^{-1}. The spectra of the solutions with equal concentrations (1.4 mol L^{-1}) of DMF and CF_3COONa in TFA were compared. The spectra of the salt system indicate the formation of proton disolvates by the equilibrium (ε_{2000} = 100 L mol^{-1} cm^{-1})

$$\mathrm{NaA + HA \rightleftharpoons (A...H...A)^-\cdot Na^+}. \qquad (6)$$

Almost the same CA coefficient was obtained for a solution of DMF in TFA (ε_{2000} = 103 L mol^{-1} cm^{-1}). The CA spectra of these solutions with equal concentrations of the salt and DMF coincide. The formation of the $(A...H...A)^-$ anions by reactions (5) and (6) is accompanied by a decrease in the concentration of the free TFA molecules. In the DMF-containing system, two TFA molecules are required for the formation of the proton disolvate, whereas only one TFA molecule is needed in the salt system. This agrees with the decrease in the absorbances of the band of the ν(C=O) vibrations of the TFA molecule at 1770 cm^{-1} in the corresponding spectra.

The concentrations of the $BH^+\cdot(A...H...A)^-$ complexes at different DMF concentrations were estimated from the band at 1720 cm^{-1} attributed to vibrations of the protonated DMF molecule. When the DMF content >2.5 mol L^{-1}, this band is absent from the spectra, *i.e.*, equilibrium (5) is completely shifted to the left. In more concentrated acid solutions, the protonated DMF form BH^+ appears, and equilibrium (5) is completely shifted to the right at DMF concentrations <1.4 mol L^{-1}.

Thus, the following scheme of acid-base interactions was determined for the TFA (HA)–DMF (B) system:

$$\mathrm{B + HA \rightleftharpoons B...H...A}, \qquad (7)$$

$$\mathrm{B...H...A + B \rightleftharpoons (B...H...A)\cdot B} \quad \text{(0–50 mol.\% HA)}, \qquad (8)$$

$$\mathrm{B...H...A + HA \rightleftharpoons (B...H...A)\cdot HA} \quad \text{(50–90 mol.\% HA)}, \qquad (9)$$

$$\mathrm{(B...H...A)\cdot HA \rightleftharpoons BH^+\cdot(A...H...A)^-} \quad \text{(80–100 mol.\% HA)}. \qquad (10)$$

With a base excess in the system, as in solutions of HCl[4] and MSA[7] in DMF, complex **1** with quasi-ionic structure is formed (stage (7)), which is solvated by the base molecules (stage (8)). In the interval of TFA–DMF compositions from 1 : 1 to ~4 : 1, complex **1** is solvated by the TFA molecule (stage (9)). This equilibrium was not observed in solutions of HCl and MSA. The protonation of DMF accompanied by the formation of the $(A...H...A)^-$ anion with a strong symmetric H bond (stage (10)) occurs at a considerable excess of the acid in the solution. Equilibrium (10) is completely shifted to the right at TFA concentrations >90 mol.%. In solutions of HCl and MSA, the $BH^+\cdot(A...H...A)^-$ ion pairs form even at a minor HA excess (reaction (1)). In TFA solutions in DMF, the solvation of the B...H...A quasi-ion pairs by DMF or acid molecules was found from changes in the intensity of the CA spectrum. Solvation slightly changes the parameters of the central H bond.

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