IR spectroscopic study of ion-molecular interactions in the methanesulfonic acid—*N*,*N*-dimethylformamide system

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Complex formation in the methanesulfonic acid (MSA)—DMF system was studied by Multiple Attenuated Total Reflectance (MATR) IR spectroscopy at 30 °C within the composition range from neat MSA up to neat DMF. Depending on the ratio of components, two types of complexes with a strong quasi-symmetrical H bond (**1** and **2**) are formed. The uncharged complex **1** is a quasi-ion pair with the (O...H...O) bridge. Complex **2** is formed by a protonated DMF molecule and the $(A...H...A)^-$ anion bound as an ion pair. It is established that complexes **1** are solvated by DMF molecules in an excess of a base. Solvation of **2** in an excess of an acid corresponds to a change from contact to contact-separated ion pairs. Continuous absorption spectra of charged and uncharged complexes **1** and **2** were obtained. The schemes of acid-base interactions in the MSA—DMF and HCl—DMF systems were compared.

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

The formation of ions and complexes with a strong symmetrical bond is a fundamental property of protons in solutions.[1,2] Aprotic solvents in an excess of a base are characterized[3—5] by uncharged 1 : 1 complexes with a strong symmetrical H bond (quasi-ion pairs). The HCl · DMF complexes (**1**) have been characterized most completely.[6—8] The high solubility of HCl in DMF (up to 65 mol.% at 30 °C) is due to the formation of complexes **2** (2HCl · DMF) along with complexes **1**. These complexes consist of a protonated DMF molecule and the $(ClHCl)^-$ anion united in an ion pair.

This work is devoted to the study of complex formation in the methanesulfonic acid (MSA)—DMF system, which is homogeneous in the whole composition range. The data obtained make it possible to compare the schemes of acid-base interaction of DMF in solutions of two acids and spectral manifestations of O...H...Cl and O...H...O bridges in complexes **1** and to characterize complexes **2** in concentrated solutions in which MSA is not completely bound to DMF.

Experimental

N,*N*-Dimethylformamide (DMF) and methanesulfonic acid (MSA) (Fluka, "puriss" trade mark) were used for the preparation of solutions. Concentrations of water in starting DMF and MSA were not greater than 0.01 and 0.05%, respectively. Solutions were prepared by dilution by weight. Densities of solutions were measured for the calculation of molar concentrations (Table 1).

IR spectra of the MSA—DMF system in the 0—100% MSA composition range (see Table 1) in the 900—4000 cm^{-1} frequency range at 30 °C were recorded on a UR-20 spectrophotometer with a Multiple Attenuated Total Reflectance attachment (MATR-2)[9] produced in the N. N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences. A Ge prism with an incident angle of 30° was used. The solution under study was placed in one or two Teflon cavities adjacent to the prism facets, and the number of reflections was four or eight, respectively. The effective thickness of the absorbing layer at a frequency of 2000 cm^{-1} was 1.68 or 3.20 mm, depending on filling of the cell. Optical densities of bands were measured using base lines. In several cases, correctness of measurements was examined by determination of optical densities of the band compared to the minimum near one of its wings. The background absorption was measured relative to the empty cell.

Results and Discussion

Composition range from 0 to 67 mol.% MSA in DMF. Analysis of the concentration dependences of the optical density of the bands and background absorption of solutions of MSA in DMF indicates[6] that the schemes of acid-base equilibrium in the MSA—DMF and HCl—DMF systems are identical. Quasi-ion pairs **1** or complexes **2** are also formed in the MSA—DMF system depending on the ratio of components. In an excess of DMF, complexes **1** are solvated (1_{solv}).

The IR spectrum of DMF (Fig. 1) contains the following main bands[10] (ν/cm^{-1}): 1093 (δ(NCH)), 1255 ($\nu_{as}(N-CH_3)$), 1383 (ν(C—N)), and 1660 (ν(C=O)), as well as bands of stretching vibrations of C—H and CH_3 in the 2850—3000 cm^{-1} region. When MSA is added to

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DMF, the intensities of bands at 1383 and 1660 cm^{-1} decrease, and the background absorption appears. For complexes **I** and **I**$_{solv}$, we detected bands at 1290 cm^{-1} and also 1090 and 1250 cm^{-1}, which are superimposed

Table 1. Stoichiometric composition and densities of solutions of MSA in DMF. Optical densities (*D*) of bands at 1383, 1660, and 3200 cm^{-1} and equilibrium concentrations of components of the system at 30 °C

C^0_{MSA} (mol.%)	ρ /g cm^{-3}	C^0_{MSA}	C^0_{DMF}	3200 cm^{-1}			1383 cm^{-1}			1660 cm^{-1}		
		mol L^{-1}		D_{3200}	C_{MSA} /mol L^{-1}	$\frac{\Delta C_{MSA}}{C^0_{DMF}}$	D_{1385}	C_{DMF} /mol L^{-1}	$\frac{\Delta C_{DMF}}{C^0_{MSA}}$	D_{1660}	C_{DMF} /mol L^{-1}	$\frac{\Delta C_{DMF}}{C^0_{MSA}}$
0	0.948	0	12.97	—	—	—	0.588	12.97	—	1.300	12.97	—
6.31	0.993	0.84	12.48	—	—	—	0.533	11.75	0.9	1.180	11.77	0.8
10.86	1.024	1.47	12.06	—	—	—	0.446	9.85	1.5	0.996	9.94	1.4
17.26	1.066	2.39	11.46	—	—	—	0.389	8.58	1.2	0.853	8.51	1.2
24.42	1.112	3.45	10.68	—	—	—	0.296	6.53	1.2	0.708	7.07	1.0
33.45	1.167	4.83	9.61	—	—	—	0.199	4.40	1.1	0.523	5.22	0.9
37.46	1.190	5.45	9.10	—	—	—	0.167	3.68	1.0	0.426	4.25	0.9
44.45	1.230	6.57	8.21	—	—	—	0.087	1.92	1.0	0.195	1.94	1.0
47.40	1.246	7.03	7.80	—	—	—	0.030	0.66	1.0	0.141	1.41	0.9
49.97	1.261	7.45	7.46	—	—	—	0	0	1.0	0.109	1.09	0.9
53.28	1.278	7.97	6.99	—	—	—	—	—	—	≤0.5	≤0.5	—
56.42	1.294	8.48	6.55	—	—	—	—	—	—	—	—	—
60.65	1.316	9.17	5.95	—	—	—	—	—	—	—	—	—
63.90	1.333	9.70	5.48	—	—	—	—	—	—	—	—	—
66.71	1.347	10.16	5.07	≤0.007	≤0.5	1.9	—	—	—	—	—	—
71.72	1.371	10.98	4.33	0.028	1.86	2.1	—	—	—	—	—	—
76.98	1.396	11.84	3.54	0.048	3.18	2.4	—	—	—	—	—	—
81.93	1.419	12.65	2.79	0.073	4.88	2.8	—	—	—	—	—	—
87.21	1.434	13.43	1.97	0.125	8.31	2.6	—	—	—	—	—	—
90.46	1.457	14.04	1.48	0.146	9.70	2.9	—	—	—	—	—	—
94.41	1.474	14.68	0.87	0.185	12.30	2.7	—	—	—	—	—	—
100	1.482	15.42	0	0.232	15.42	—	—	—	—	—	—	—

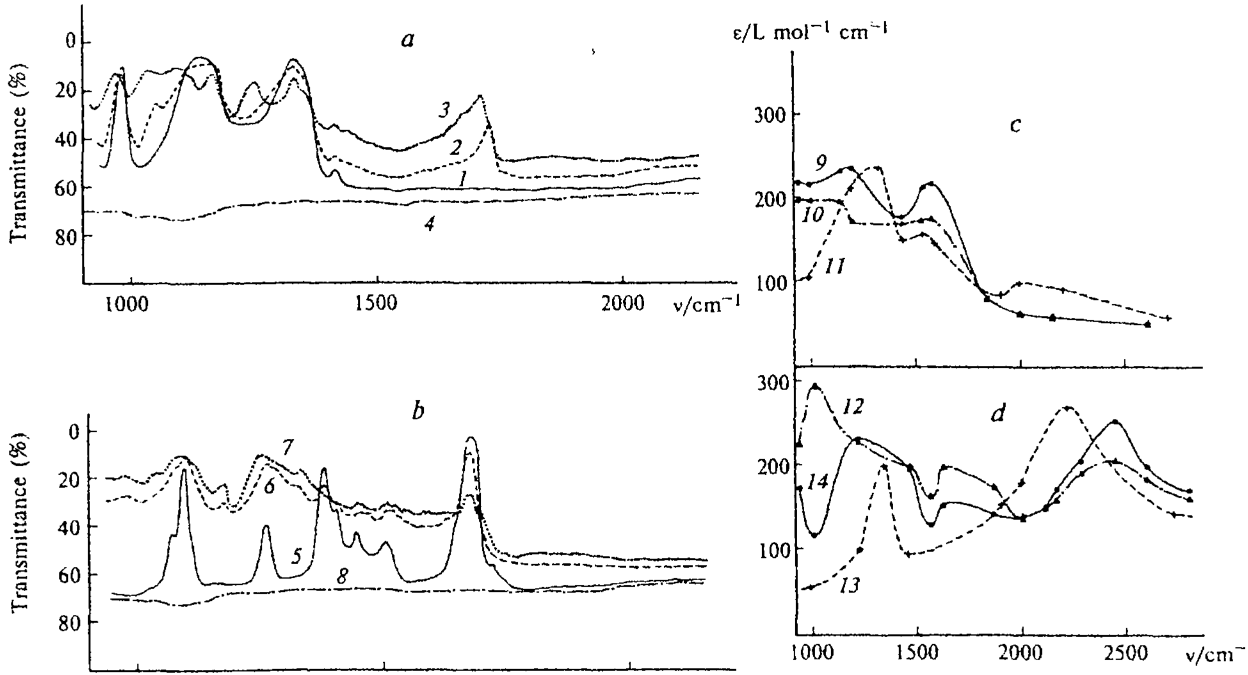

Fig. 1. MATR IR spectra of the MSA—DMF system in the range of MSA concentrations from 66.7 to 100 mol.% (*a*): *1*, 100; *2*, 81.2; *3*, 66.7 mol.% MSA; *4*, empty cell; and from 0 to 50 mol.% (*b*): *5*, 0 (100% DMF); *6*, 33.4; *7*, 50 mol.% MSA; *8*, empty cell. Spectra of background absorption (ε) of complex **I** (*c*): **I**$_{solv}$ (*9*) and **I** (*10*) in the MSA—DMF; **I** in the HCl—DMF (*11*); and complex **2** (*d*): **2** in the MSA—DMF (*12*) and HCl—DMF systems (*13*); **2**$_{solv}$ in the MSA—DMF system (*14*).

on bands of DMF molecules unbound in the complexes at 1093 and 1255 cm^{-1}.

The concentration dependences of the DMF bands at 1383 and 1660 cm^{-1} are described under the assumption that in an excess of DMF each MSA molecule binds a DMF molecule to form a structural unit DMF · MSA (**1**). The calculated concentrations of "free" (C_{DMF}) and "bound" ($\Delta C_{DMF}/C^0_{MSA} \equiv (C^0_{DMF} - C_{DMF})/C^0_{MSA}$) forms of DMF are presented in Table 1. In the spectrum of the 1 : 1 solution, no band is detected at 1383 cm^{-1} (ν(C—N)), and the intensity of the band at 1660 cm^{-1} (ν(C=O)) corresponds to a concentration of ~1 mol L^{-1} of free DMF molecules. Thus, the spectrum of complexes **1** contains no bands of vibrations of C—N and C=O bonds, which indicates their strong perturbation during the formation of these complexes. The absence of bands of protonated[4] DMF at 1720 cm^{-1} (ν(C=N)) and stretching vibrations ν(O—H) of MSA molecules in the 2400—3200 cm^{-1} region is evidence of a quasi-ion structure[4,6] of complex **1**: $(CH_3)_2N(H)C{=}O...H^+...O^-SO_2CH_3$. This is confirmed by the intense background absorption in the IR spectra (see Fig. 1), which is characteristic of species with strong quasi-symmetrical bonds with an intermediate position of the proton.[1]

Analysis of the concentration dependences of the optical density of the bands and background absorption in the 0—50 mol.% MSA composition region indicates that MSA is completely bound to quasi-ion pairs and solvated in an excess of DMF. The optical density of absorption at the ν frequency (D_ν) in an excess of DMF is the sum of the absorptions of complexes **1** and DMF molecules unbound in these complexes:

$$D_\nu = \varepsilon^\nu{}_{DMF} \cdot l_\nu \cdot C_{DMF} + \varepsilon^\nu{}_1 \cdot l_\nu \cdot C_1. \qquad (1)$$

Since each MSA molecule binds strongly one DMF molecule, we have

$$C_1 = C^0_{MSA}, \; C_{DMF} = C^0_{DMF} - C^0_{MSA}.$$

From Eq. (1) we obtain

$$D_\nu/C_{DMF} = \varepsilon^\nu{}_{DMF} \cdot l_\nu + \varepsilon^\nu{}_1 \cdot l_\nu \cdot (C_1/C^0_{DMF}). \qquad (2)$$

Linear dependence (2) is valid up to the equimolar ratio of components for bands at 1093 and 1255 cm^{-1} and frequencies of the background absorption at ν > 1800 cm^{-1} (Fig. 2). The 1800—2200 cm^{-1} region contains no frequencies of fundamental vibrations of DMF and MSA molecules. The intense background absorption in this region is formed by component vibrations due to the strong interaction of the central proton with vibrations of molecules in the quasi-ion pair, and its intensity is determined by the concentration of these protons.[1,4] The absorption coefficient at 2000 cm^{-1} is 58 L mol^{-1} cm^{-1}, which is substantially lower than that for charged ions with a strong quasi-symmetrical H bond. The values $\varepsilon_{2000} = 50 \pm 10$ L mol^{-1} cm^{-1} correspond to the absorption of quasi-ion pairs.[4] Thus, the analysis of the background absorption by Eq. (2) for frequencies of 1800—2200 cm^{-1} confirm the conclusion about the formation of uncharged complex **1** with an intermediate position of the proton. The structure suggested for complex **1** is also confirmed by the characteristic background absorption[6] in the 1400—1600 cm^{-1} region.

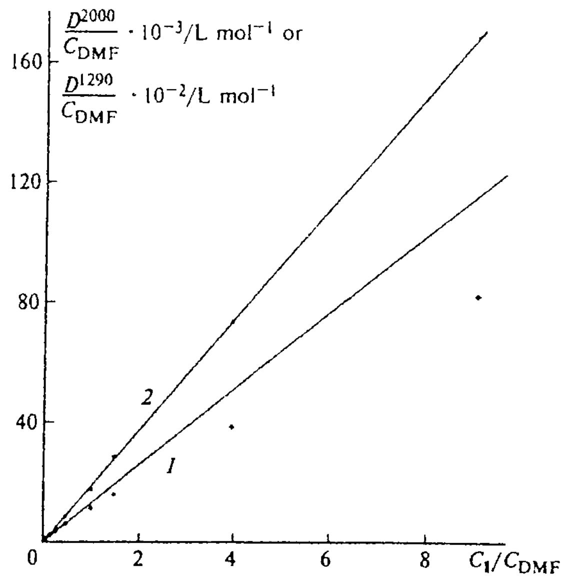

Fig. 2. Graphic solutions of Eq. (2) for frequencies of 1290 (*1*) and 2000 (*2*) cm^{-1}.

The dependences obtained from Eq. (2) for frequencies in the 1100—1800 cm^{-1} region are evidence of the solvation of complex **1** in an excess of DMF. DMF molecules solvating complex **1** almost do not differ in spectral parameters from free DMF molecules (see Table 1). The spectrum of complex **1** changes during solvation. Linear dependences (2) for ν < 1800 cm^{-1} are fulfilled at C_{MSA} < 3.5 mol L^{-1} (see Fig. 2).

The absorption coefficients obtained from the linear regions of the curve of change of $\varepsilon^\nu{}_{1solv}$ characterize complexes **1** solvated by DMF ($\mathbf{1}_{solv}$). In more concentrated solutions of MSA, the absorption coefficients decrease to $\varepsilon^\nu{}_1$. Complexes $\mathbf{1}_{solv}$ can be considered as a quasi-ion pair solvated by a DMF molecule. The bond between the solvating DMF molecule with complex **1** is much weaker than the quasi-symmetrical bond between MSA and DMF molecules in complex **1**, *i.e.*, two DMF molecules in complex $\mathbf{1}_{solv}$ are nonequivalent. The extinction coefficients of complexes **1** and $\mathbf{1}_{solv}$ for the 935—2800 cm^{-1} frequency region are presented in Table 2. For the HCl—DMF system, the conclusion about solvation of complexes **1** is also based on the analysis of the background absorption for ν < 1800 cm^{-1}. For solutions of both HCl and MSA, the solvation of complexes **1** by DMF molecules results in an increase in the background absorption.

Table 2. Coefficients of background absorption of MSA complexes with DMF

ν/cm^{-1}	ε_{1solv}	ε_1	ε_2	ε_{2solv}
	L mol^{-1} cm^{-1}			
935	220	201	225	175
1000	217	199	298	122
1150	229	195	—	—
1200	229	168	225	232
1440	176	167	201	197
1560	210	172	162	125
1600	214	176	200	152
1850	76	76	175	141
2000	58	58	135	138
2100	—	—	148	148
2150	—	—	151	170
2200	57	57	—	—
2280	—	—	185	203
2450	—	—	199	253
2600	46	46	162	187
2800	—	—	149	158

When the concentrations of MSA exceed the equimolar ratio of components, considerable changes in the spectra are observed (see Fig. 1). The intensities of the band at 1290 cm^{-1} of complex **1** and background absorption[6] in the 1400—1600 cm^{-1} region characteristic of **1** decrease. The intensity of the background absorption at ν > 1800 cm^{-1} increases. In addition, new bands at 980, 1035, 1170, 1330, and 1710 cm^{-1} appear in the spectra. These changes in the spectra indicate the formation of complexes **2**, whose structure differs substantially from that of complex **1**.

The spectra of the solutions with C_{MSA} = 50—67 mol.% contain no bands of individual DMF and MSA (see Fig. 1, Table 1). Therefore, the acid and base in these solutions are bound completely in complexes **1** and **2**. The optical density of absorption at the ν frequency (D_ν) is the sum of optical densities of these complexes:

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

where l_ν is the optical length of the absorbing layer at the ν frequency.

From this it follows that

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

The optical density of bands at 1050, 1170, and 1720 cm^{-1} and background absorption at 2000 cm^{-1} reaches a maximum at the ratio of components $C_{\mathrm{MSA}} : C_{\mathrm{DMF}} = 2 : 1$. The absorption of "free" MSA at 3200 cm^{-1} appears in the spectra at $C_{\mathrm{MSA}} > 67$ mol.%. This implies that complex **2** consists in fact of one DMF and two MSA molecules. The concentrations of **1** and **2** in Eqs. (3) and (4) satisfy the following equations:

$$C_1 + C_2 = C^0{}_{\mathrm{DMF}},\ C_1 + 2C_2 = C^0{}_{\mathrm{MSA}}.$$

Hence

$$C_2 = C^0{}_{\mathrm{MSA}} - C^0{}_{\mathrm{DMF}},\ C_1 = 2C^0{}_{\mathrm{DMF}} - C^0{}_{\mathrm{MSA}}.$$

The dependences of D_ν/C_1 on C_2/C_1 are linear in the whole frequency range studied, which confirms the conclusion about the composition of complex **2**. The absorption coefficients calculated from these dependences are presented in Table 2. The values of $\varepsilon^\nu{}_1$ determined from Eqs. (2) and (4) almost coincide for all frequencies. For example, for the frequency of 2000 cm^{-1}, they are equal to 58 and 64 L mol^{-1} cm^{-1}, respectively. The value $\varepsilon_2{}^{2000}$ = 135 L mol^{-1} cm^{-1} corresponds to the absorption of negatively charged complexes with a strong symmetrical H bond.[11] By analogy to the HCl—DMF system,[6] we can assume that complex **2** is a combination of two species (probably united in an ion pair): a protonated DMF molecule $(CH_3)_2N^+{=}C(H){-}OH$ and a $(CH_3O_2SO...H...OSO_2CH_3)^-$ anion formed by a strong symmetrical H bond. This structure of complex **2** is indicated by the fact that the spectra contain bands at 1710 cm^{-1} and 1035 and 1170 cm^{-1} assigned to vibrations $\nu(N{=}C)$ of the protonated DMF molecule[6,7] and vibrations $\nu_s(SO_3^-)$ and $\nu_{as}(SO_3^-)$ appearing in the IR spectrum of the $(CH_3O_2SO...H...OSO_2CH_3)^-$ anion,[12,13] respectively.

It follows from the concentration dependences at the frequencies of DMF (1660 cm^{-1}) and complexes **2** (980 and 1170 cm^{-1}) that in the MSA concentration range from 6.5 to 8.0 mol L^{-1}, the equilibrium

$$2\ \mathbf{1} \rightleftharpoons \mathbf{2} + \mathrm{DMF}$$

is partially shifted to the right. At the equimolar ratio of components, the concentration of **2** is ~1 mol L^{-1}. At $C_{\mathrm{MSA}} : C_{\mathrm{DMF}} = 2 : 1$, almost all acid is bound in complex **2** (see Table 1).

Composition range from 67 to 100 mol.% MSA in DMF. The MSA—DMF system is homogeneous in the whole composition range. The conclusions on the composition and structure of complex **2** in the HCl—DMF system were drawn from the data for the region of HCl concentrations where complexes **1** and **2** coexist and the free acid is absent.[6] In the MSA—DMF system, we also analyzed the concentration dependences of bands of complexes **2** and MSA in the range C_{MSA} = 67—100 mol.%.

The spectrum of 100% MSA contains the following bands[14] (ν/cm^{-1}): 990 ($\rho_{s+as}(CH_3)$), 1146 ($\nu_s(S{=}O)_2$), 1332 ($\nu_{as}(S{=}O)_2$), and 3035 ($\nu(OH)$). When DMF is added, the intensities of these bands decrease and new bands appear at 1050, 1170, and 1720 cm^{-1} as well as an intense continuous absorption. These bands correspond to the frequencies of 1035 ($\nu_s(SO_3^-)$), 1170 ($\nu_{as}(SO_3^-)$), and 1710 cm^{-1} ($\nu(C{=}N)$) in the spectra of more diluted solutions (50—67 mol.% MSA). The concentrations of "free" (C_{MSA}) and "bound" ($\Delta C_{\mathrm{MSA}} = C^0{}_{\mathrm{MSA}} - C_{\mathrm{MSA}}$) acids were determined by a change in the optical density of the wing of the band $\nu(OH)$ at

3200 cm^{-1} (see Table 1). In the maximum of this band, calculations are difficult due to superimposition of the methyl groups. It follows from the data in Table 1 that in concentrated solutions of MSA, each DMF molecule binds two MSA molecules, *i.e.*, complexes **2** are formed. The conclusion drawn is confirmed by the absence of the band of MSA at 1146 cm^{-1} at a content of MSA lower than 67 mol.%. The quantitative analysis of the concentration dependence for this band is difficult because of superimposition of the band of complex **2** at 1170 cm^{-1}. The absorptions of both "free" acids and acids bound in complexes **2** appear at 990 and 1332 cm^{-1}. These bands disappear at concentrations of MSA lower than 50 mol.% when complexes **1** predominate in solutions.

The optical density D_v at $C^0_{MSA}/C^0_{DMF} \geq 2:1$ corresponds to the sum of absorptions of "free" MSA molecules and complexes **2**:

$$D_v = \varepsilon^v_{MSA} \cdot l_v \cdot C_{MSA} + \varepsilon^v_2 \cdot l_v \cdot C_2. \qquad (5)$$

The dependences of the optical density of the bands at 1050 and 1720 cm^{-1} of the complex on the analytical concentration of DMF are presented in Fig. 3. Only the protonated form of DMF entering complex **2** absorbs at 1720 cm^{-1}:

$$D_{1720} = \varepsilon_2^{1720} \cdot l_{1720} \cdot C_2.$$

The frequency of 1050 cm^{-1} is on the wing of the band of MSA at 1146 cm^{-1}; therefore, according to Eq. (5), for D_2^{1050} we have

$$D_2^{1050} = \varepsilon_2^{1050} \cdot l_{1050} \cdot C_2 = D_{1050} - \varepsilon_{MSA}^{1050} \cdot l_{1050} \cdot C_{MSA},$$
$$C_{MSA} = C^0_{MSA} - 2C^0_{DMF}.$$

For the calculation of D_2^{1050}, we used the coefficient $\varepsilon_{MSA}^{1050} \cdot l_{1050}$ obtained from the spectrum of 100% MSA.

In concentrated solutions of MSA, D_2^{1720} and D_2^{1050} are proportional to the analytical concentration of DMF, which corresponds to the complete protonation of the base. We obtained from the linear regions of the dependences in Fig. 3 that $\varepsilon_2^{1050} = 320$ L mol^{-1} cm^{-1} and $\varepsilon_2^{1720} = 510$ L mol^{-1} cm^{-1}. The ε_2^{1050} value coincides within the measurement accuracy with the corresponding absorption coefficients[12,13] of the $(CH_3O_2SO...H...OSO_2CH_3)^-$ anions in the $CH_3SO_3Na-CH_3SO_3H$ and $CH_3SO_3H-H_2O$ systems. The high value of the ε_2^{1720} coefficient is characteristic of polar double bonds of the C=O and C=N types. These data confirm the conclusions about the composition and structure of complexes **2** in more diluted solutions of MSA and HCl—DMF system.[6]

In concentrated solutions of MSA, each DMF molecule is protonated ionizing one MSA molecule. At the same time, in the MSA—H_2O and MSA—DMSO systems, one acid molecule is ionized by two base molecules.[3] The $(CH_3O_2SO...H...OSO_2CH_3)^-$ anions are formed in all three systems, but the mechanisms of protonation are different. In the MSA—H_2O and MSA—DMSO systems, ions with a strong symmetrical H bond $(H_2O...H...OH_2)^+$ and $((CH_3)_2S{=}O...H...O{=}S(CH_3)_2)^+$ are formed. When DMF is protonated, the proton is completely transferred to the oxygen atom.

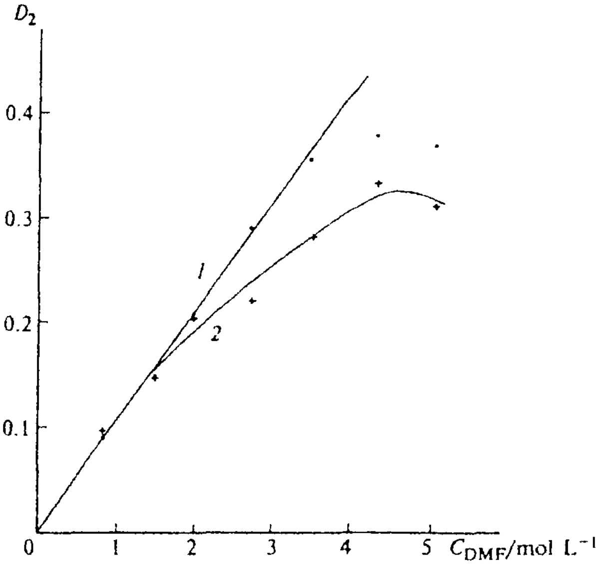

Fig. 3. Dependences of the optical density of bands of complex **2** at 1050 (*1*) and 1720 (*2*) cm^{-1} on the concentration of DMF.

In concentrated solutions in which all MSA is not bound in complex **2**, we observed spectral differences in solvated (2_{solv}) and nonsolvated complexes **2**. This effect appears in the continuous absorption spectra at $\nu <$ 1900 cm^{-1}.

Let us analyze the continuous background absorption of concentrated acid solutions. Let us transform Eq. (5):

$$D_v/C_{MSA} = \varepsilon^v_{MSA} \cdot l_v + \varepsilon^v_2 \cdot l_v \cdot (C_2/C_{MSA}). \qquad (6)$$

The dependences of D_v/C_{MSA} on C_2/C_{MSA} are linear for ν = 1900—2100 cm^{-1} (Fig. 4) in the 67—100 mol.% MSA range. For the ε_2^{2000} coefficient, we obtained a value of 138 L mol^{-1} cm^{-1}, corresponding to the absorption of anions with the O...H...O bridge and a strong symmetrical H bond.[11] This value coincides with the ε_2^{2000} value obtained by Eq. (4) for more dilute solutions of MSA. The absorption of complex **2** is the sum of absorptions of the $(CH_3O_2SO...H...OSO_2CH_3)^-$ anion and DMF-protonated $(CH_3)_2N^+{=}C(H)OH$. No bands of MSA and protonated DMF molecule are observed at 1900—2100 cm^{-1}, and the absorption is due only to component vibrations involving the central proton of the strong symmetrical H bond[1] of the anion. Therefore, the parameters of the $(O...H...O)^-$ bridge depend weakly on solvation. Therefore, ε_2^{2000} remains unchanged within the whole region $C^0_{MSA} : C^0_{DMF} \geq 2$.

By contrast, for several frequencies in the 1000—1900 cm^{-1} range, due to solvation of **2**, the dependences of D_v/C_{MSA} on C_2/C_{MSA} are linear in a more narrow

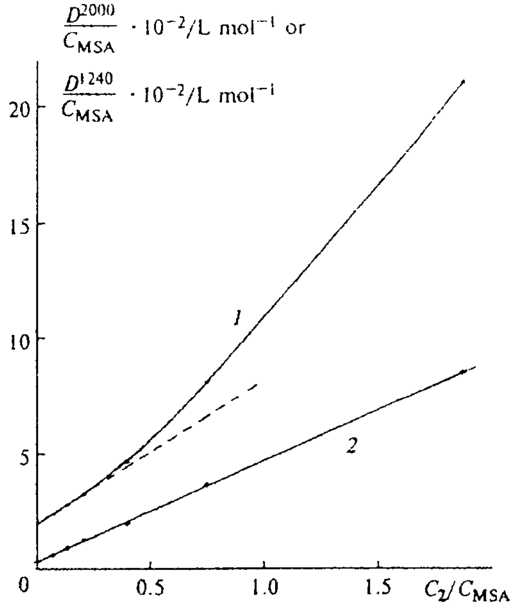

Fig. 4. Graphic solutions of Eq. (6) for frequencies of 1240 (*1*) and 2000 (*2*) cm^{-1}.

composition region, at $C^0{}_{MSA}$: $C^0{}_{DMF}$ ≥ 3—4 (see Fig. 4). The $\varepsilon^{v}{}_{2solv}$ coefficients obtained for the linear regions differ substantially from the $\varepsilon^{v}{}_2$ values (see Table 2 and Fig. 1, curves *12* and *14*). Most likely, this is associated with the fact that contact ion pairs **2** are transformed upon solvation into solvate-separated pairs $\mathbf{2}_{solv}$.

The distortion of the linear dependences of $D^{v}{}_2$ on C_2 for the bands of complex **2** at 1050 and 1720 cm^{-1} (see Fig. 3) is also related to the solvation of complex **2** in concentrated solutions of MSA. The band of the cationic part of complex **2** at 1720 cm^{-1} is more sensitive to solvation. Already at $C^0{}_{MSA}$: $C^0{}_{DMF}$ < 6, the low-frequency wing of this band is blurred, which reflects a decrease in the N=C bond order in protonated DMF. The most pronounced difference in the spectra of complexes $\mathbf{2}_{solv}$ and **2** is observed at 1240 cm^{-1}. Only the background absorption appears in the spectrum of $\mathbf{2}_{solv}$ at 1240 cm^{-1}. At $C^0{}_{MSA}$: $C^0{}_{DMF}$ < 4, a band at 1240 cm^{-1} is observed in the spectrum, which reflects the presence of complexes **2** in the solutions. This band is attributed to vibrations of nonsolvated protonated DMF molecules.

Thus, in the MSA—DMF system, depending on the ratio of components, two types of complexes with a strong symmetrical H bond are formed (**1** and **2**). The uncharged complex **1** is a quasi-ion pair with the (O...H...O) bridge. Complex **2** is formed by the protonated DMF molecule and the (A...H...A)$^-$ anion united in an ion pair. In an excess of a base, complexes **1** are solvated by DMF molecules. Solvation of **2** in an excess of an acid corresponds to the transition from contact to contact-separated ion pairs. The background absorption spectra of compounds **1**, $\mathbf{1}_{solv}$, **2**, and $\mathbf{2}_{solv}$ in the MSA—DMF system (curves *9*, *10*, *12*, and *14*) and complexes **1** and **2** in the HCl—DMF system (curves *11* and *13*) are compared in Fig. 1. The differences in the spectra of complexes **1** and **2** in two systems reflect the specific features of hydrogen O...H...Cl and O...H...O bridges in the uncharged complexes and (Cl...H...Cl)$^-$ and (O...H...O)$^-$ in the anions in solutions of HCl and MSA.

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