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Solvation of complexes with strong symmetric H bonds in the methanesulfonic acid—2-pyrrolidone system

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Multiple Attenuated Total Reflectance (MATR) IR spectra of solutions of methanesulfonic acid (MSA) in 2-pyrrolidone (Pyr) (0—100 % MSA) were examined at 30 °C. Depending on the ratio of components, two types of species with strong symmetric H bonds are formed: uncharged quasi-ion pairs of 1 : 1 composition and anions $(AHA)^-$. The solvation of quasi-ion pairs by base molecules and of the $(AHA)^-$ anions by acid molecules was detected. The data on the influence of the hydrogen bond donor and acceptor on the IR spectra of the quasi-ion pairs and $(AHA)^-$ anions are presented.

Key words: acid-base interactions, hydrogen bond; solutions, complexes; methanesulfonic acid, 2-pyrrolidone.

The physicochemical and catalytic properties of acid (HA) solutions are determined, in many cases, by the presence of charged and uncharged species with strong symmetric hydrogen bonds.[1,2] In aqueous solutions these species are charged proton disolvates $H_5O_2^+$ and $(AHA)^-$. The $(AHA)^-$ anions are formed in solutions containing excess acid. In organic aprotic solvents positively charged protons disolvates are not virtually formed and the acid-base equilibrium is often restricted by the formation of uncharged quasi-ion pairs with a strong quasi-symmetric H bond. When solutions of acids with different strengths[3—7] (H_2SO_4, HCl, CH_3SO_3H, CF_3COOH) form compositions ranging from 0 to 50 mol.% HA, acids are almost completely bound to give these uncharged complexes. In excess acid negatively charged proton disolvates $(AHA)^-$ with a strong symmetric H bonds are formed

$$\mathrm{B...H...A + HA \Leftrightarrow BH^+ + (AHA)^-},$$

where B are base molecules, B...H...A are quasi-ion pairs; B...H...A and $(A...H...A)^-$ are catalysts of homogeneous acid-catalyzed reactions in solutions formed by acids and aprotic solvents. The study of the influence of the nature of the A and B ligands and the subsequent solvation of the B...H...A and $(A...H...A)^-$ complexes on their properties is an important problem.

This work is devoted to IR spectroscopic studies of the complex formation and solvation of species formed in the methanesulfonic acid (MSA)—2-pyrrolidone (Pyr) system, 0—100% HA.

Experimental

MSA ("puriss," content of H_2O < 0.05%) and Pyr ("purum," Fluka) were used. Solutions were prepared by weight. Densities of solutions were measured for the calculation of molar concentrations (Table 1).

Table 1. Stoichiometric composition and densities of MSA solutions in 2-pyrrolidone

C^0_{MSA} (%)	C^0_{MSA}	C^0_{Pyr}	ρ /g cm^{-3}
	mol L^{-1}		
0	0	13.04	1.110
4.43	0.52	12.68	1.129
7.20	0.86	12.44	1.142
10.30	1.24	12.17	1.154
14.07	1.72	11.83	1.172
22.38	2.81	11.02	1.208
27.88	3.58	10.44	1.232
32.37	4.22	9.95	1.252
36.21	4.78	9.50	1.268
40.11	5.36	9.03	1.283
45.00	6.10	8.41	1.302
49.95	6.86	7.76	1.320
53.12	7.36	7.33	1.332
55.06	7.67	7.07	1.338
59.95	8.46	6.38	1.356
65.04	9.29	5.64	1.373
67.75	9.74	5.23	1.382
69.43	10.01	4.98	1.386
75.10	10.98	4.11	1.405
80.04	11.83	3.33	1.420
85.22	12.72	2.49	1.435
90.24	13.62	1.66	1.450
94.93	14.47	0.73	1.464
100.0	15.42	0	1.482

IR spectra of MSA solutions in Pyr were recorded on a Multiple Attenuated Total Reflectance[8] (MATR) attachment in the composition range from 0 to 100% MSA (see Table 1) in the 900—3700 cm^{-1} frequency region at 30 °C. A Ge prism with an incident angle of 30° and a number of reflections of

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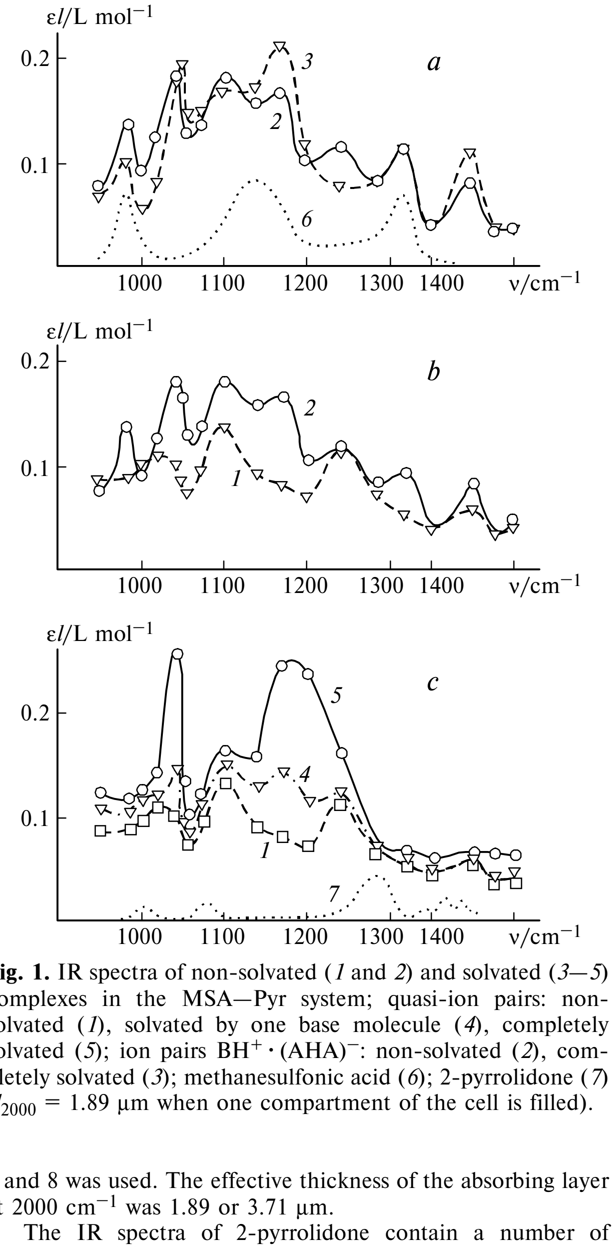


Fig. 1. IR spectra of non-solvated (*1* and *2*) and solvated (*3*—*5*) complexes in the MSA—Pyr system; quasi-ion pairs: non-solvated (*1*), solvated by one base molecule (*4*), completely solvated (*5*); ion pairs $BH^+\cdot(AHA)^-$: non-solvated (*2*), completely solvated (*3*); methanesulfonic acid (*6*); 2-pyrrolidone (*7*) (l_{2000} = 1.89 μm when one compartment of the cell is filled).

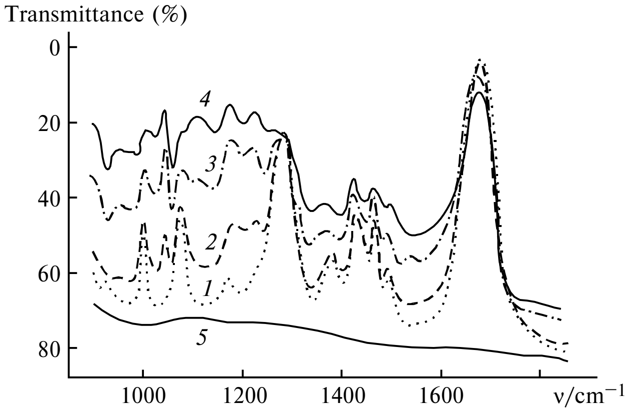


Fig. 2. IR spectra of 2-pyrrolidone (*1*) and solutions of methanesulfonic acid in 2-pyrrolidone at acid : base component ratios: 0.0411 (*2*); 0.145 (*3*); and 0.342 (*4*); spectrum of the empty cell (*5*).

4 and 8 was used. The effective thickness of the absorbing layer at 2000 cm^{-1} was 1.89 or 3.71 μm.

The IR spectra of 2-pyrrolidone contain a number of strong bands[9,10] at 997 (ν(C—C)), 1072 (ν(N—CH$_2$)), 1283 (ν(C—N)), 1375, 1426, and 1462 (δ(CH$_2$)), 1680 (ν(C=O)), 3250 (ν(N—H)) cm^{-1}. The spectra of MSA exhibit intense bands[11] at 990 (ρ_{s+as}(CH$_3$)), 1146 (ν_s(S=O)$_2$), 1332 (ν_{as}(S=O)$_2$), and 3035 (ν(O—H)) cm^{-1}. Unlike the IR spectra of the components, the spectra of MSA solutions in Pyr contain the intense continuous absorption (CA) in the 950—3000 cm^{-1} region, against which several new maxima appear (Fig. 1) and absorption coefficients of bands of the components change. The changes in the spectra do not allow construction of single basic lines for bands of the components and formed complexes (Fig. 2). Therefore, optical densities of CA and individual bands were measured relatively to the absorption of the empty cell.

Results and Discussion

As in earlier studies on the HCl—DMF,[6] HCl—1-methyl-2-pyrrolidone (*N*-MP),[7] and MSA—DMF [4] systems, two types of species with strong central H bonds are formed in MSA solutions in Pyr. Species of the first type are presented by uncharged quasi-ion pairs B...H...A, which are characterized by the incomplete proton transfer to the O atom of a base molecule. Species of the second type are $(AHA)^-$ anions. The complexes formed in solutions can be solvated by the component present in excess. The structure of the quasi-ion pairs of HCl with DMF Me$_2$NC(H)O...H...Cl was established by their IR spectra[6] and confirmed by X-ray diffraction studies.[12] The strong hydrogen bond O...H...Cl is virtually linear (O—H—Cl angle 178.8°). When a quasi-ion pair is formed, all bond lengths and angles in the basic ligand[12] change significantly compared to the geometric parameters of the DMF molecule.[13] Acid-base interactions in these systems correspond to Scheme 1.

Scheme 1

B + HA ⇔ B...H...A (0—66.7 mol.% HA)

B...H...A + B ⇔ $(B...H...A)_{solv}$ (0—50 mol.% HA)

B...H...A + HA ⇔ $BH^+ + (AHA)^-$ (50—100 mol.% HA)

$(AHA)^- + HA ⇔ (AHA)^-_{solv}$ (66.7—100 mol.% HA)

The intense CA in the IR spectra[1] at frequencies from 900 to ~3000 cm^{-1} is an intrinsic property of species with strong symmetric or quasi-symmetric H bonds. The presence of CA in IR spectra indicates the formation of species with quasi-symmetric H bonds in a solution.[1] The values of CA coefficients in the 2000—2200 cm^{-1} range suggest the charge of the complexes formed.[2] The IR spectra of the B...HA molecular complexes do not virtually contain continuous absorption.[14] The spectrum of CA is a continuum with several diffuse maxima. The spectra of CA of un-

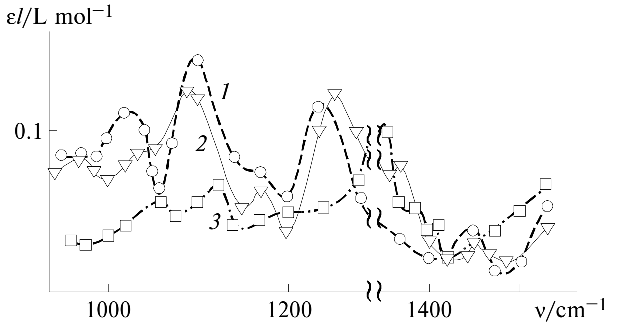


Fig. 3. IR spectra of non-solvated quasi-ion pairs in different acid-base systems: MSA—Pyr (*1*); MSA—DMF (*2*); and HCl—DMF (*3*).

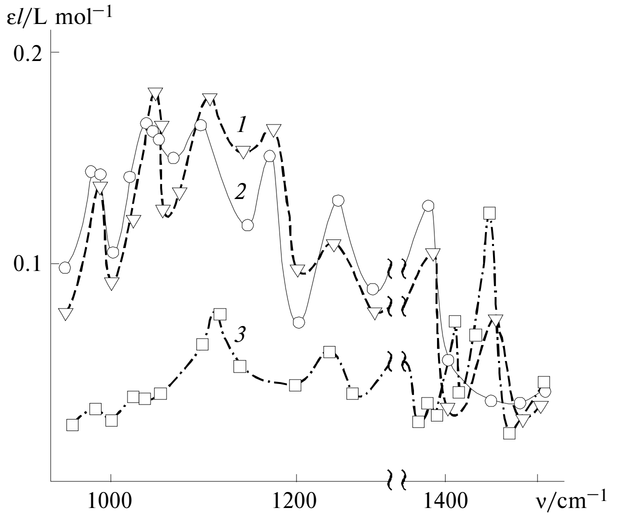


Fig. 4. IR spectra of non-solvated ion pairs $BH^+ \cdot (AHA)^-$ in different acid-base systems: MSA—Pyr (*1*); MSA—DMF (*2*); and HCl—*N*-MP (*3*).

charged and charged species with strong symmetric H bonds for several acid-base systems are presented in Figs. 1, 3, and 4.

The CA spectrum is formed by tens and hundreds of bands of component vibrations and overtones, a considerable part of which is comparable in intensity with bands of the main vibrations.[1,15] This is a consequence of electrooptical anharmonism of the O...H...O fragments in the B...H...A and $(A...H...A)^-$ complexes and a result of the strong interaction of coordinates of the hydrogen bridge and internal coordinates of the A and B ligands. The position of maxima in the CA spectrum corresponds to that of the most intense bands, and the absorption in the maxima is the total absorption of many bands. Therefore, the CA spectrum is usually characterized by an array of absorption coefficients at several frequencies relatively to the absorption of an empty cell. It is impossible to assign the observed maxima against the background of continuous absorption in the CA spectrum without results of quantum-mechanical calculations. To date these calculations have been performed for few simplest charged proton disolvates with strong symmetric H bonds.[1] It follows from the principle of CA spectrum formation that its shape depends on the nature of ligands that form complexes with strong H bonds and on the character of subsequent solvation of these species (see Figs. 1, 3, and 4).

The IR spectra of the non-solvated and solvated uncharged quasi-ion pairs B...H...A (complex of type **1**) (curves *1*, *4*, and *5*) and ion pairs $BH^+ \cdot (AHA)^-$ (complex of type **2**) (curves *2* and *3*) formed in MSA solutions in Pyr are presented in Fig. 1. The spectra of non-solvated complexes of types **1** and **2** were obtained from the analysis of the concentration plots of the optical densities of CA in solutions containing 50—66.7 mol.% of acid. In these solutions, the components are completely bound to form complexes of types **1** and **2** and the material balance equations are fulfilled

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

$$C^0_{\mathrm{Pyr}} = C_1 + C_2,$$

where C^0_{MSA} and C^0_{Pyr} are the analytical concentrations of the components, and C_1 and C_2 are the equilibrium concentrations of complexes **1** and **2**. In the indicated composition range, the absorption coefficients are constant at all frequencies in IR spectra. This conclusion is based on the linear character of the plots described by the following equation:

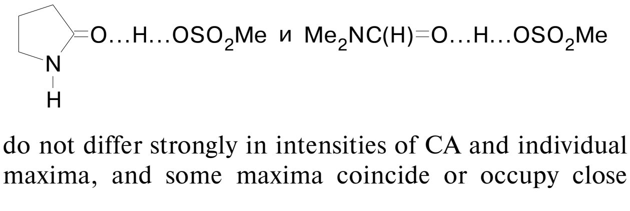
$$D_\nu/C_1 = \varepsilon^\nu{}_1 \cdot l_\nu + \varepsilon^\nu{}_2 \cdot l_\nu \cdot (C_2/C_1), \qquad (1)$$

where $\varepsilon^\nu{}_1$ and $\varepsilon^\nu{}_2$ are the molar absorption coefficients of the complexes of types **1** and **2** at the frequency ν, and l_ν is the thickness of the absorbing layer for the frequency ν.[8] Equation (1) is valid when the absorbance D_ν at each frequency ν is the sum of contributions of absorbances of individual complexes

$$D_\nu = \varepsilon^\nu{}_1 \cdot l_\nu \cdot C_1 + \varepsilon^\nu{}_2 \cdot l_\nu \cdot C_2.$$

Correlation (1) is fulfilled in all systems in which acid-base equilibria occur according to Scheme 1.[4,6,7] In Fig. 1, curves *1* and *2* are the experimental spectra of solutions with an acid concentration of 50 and 66.7 mol.% reduced to the unity concentration of the corresponding complexes. The spectra of MSA (curve *6*) and Pyr (curve *7*) are presented in Fig. 1 for comparison.

The influence of an acid (MSA, HCl) and base (DMF, Pyr) on the CA spectra of uncharged quasi-ion pairs is shown in Fig. 3. The spectra of the complexes of type **1** with the O...H...O bridge between MSA molecules and various bases



=O...H...OSO$_2$Me и Me$_2$NC(H)=O...H...OSO$_2$Me

do not differ strongly in intensities of CA and individual maxima, and some maxima coincide or occupy close positions. This is due to the contribution to CA resulted from interactions of vibrations of the central bridge with vibrations of the polyatomic acidic ligand. The transition from the polyatomic MSA molecule to diatomic acid HCl, $Me_2NC(H)=O...H...Cl$, noticeably decreases the intensities in the CA spectrum and number of maxima against its background. This is due to a lower number of bands that form the CA spectrum of the quasi-ion pairs of HCl with DMF. The spectra presented in Fig. 3 agree with the theory of CA spectra formation for species having a strong symmetric H bond.[1] For the quasi-ion pairs of MSA with Pyr, the absorption coefficient at 2000 cm^{-1} ε_1 = 67 L mol^{-1} cm^{-1} corresponds to the range of values of coefficients for uncharged complexes with strong quasi-symmetric H bonds.[2]

The $(MeO_2SO...H...OSO_2Me)^-$ anions with a strong symmetric H bond contribute mainly to the spectra of the complexes of type **2** in MSA solutions in Pyr and DMF (see Fig. 4, curves *1* and *2*). Some differences in CA intensities are due to the influence of the BH^+ counterion. In HCl solutions in *N*-MP, the CA spectrum is formed by the simple $(Cl...H...Cl)^-$ anion (see Fig. 4, curve *3*) and, hence, the CA intensity decreases substantially.

The solvation of the $(AHA)^-$ anions by MSA molecules involving OH groups has previously[4] been detected by spectra in MSA solutions in DMF in excess acid (more than 66.7 mol.% MSA). Solvation changes the absorption coefficients at several CA frequencies and the absorption coefficient of the band of stretching O—H vibrations of MSA molecules. In the MSA—Pyr system, the absorption of the intense band of N—H vibrations of the BH^+ ion is superimposed on the ν(OH) band of vibrations. Therefore, only changes in the CA spectra of the anions provide evidence of the solvation of the $(AHA)^-$ ion. As in the MSA—DMF system, the spectra of MSA solutions in Pyr indicate that anion solvation by acid molecules brings about changes in the CA coefficients. To obtain the spectrum of the completely solvated $(AHA)^-$ anions (see Fig. 1, curve *3*, Table 2) in concentrated MSA solutions in Pyr (>66.7 mol.% HA), we used concentration plots (2) in the coordinates of Eq. (3)

$$D_\nu = \varepsilon^\nu{}_{MSA} \cdot l_\nu \cdot C_{MSA} + \varepsilon^\nu{}_2 \cdot l_\nu \cdot C_2, \qquad (2)$$

where $C_{MSA} = C^0{}_{MSA} - 2C_2$.

$$D_\nu/(C^0{}_{MSA} - 2C_2) = \\ = \varepsilon^\nu{}_{MSA} \cdot l_\nu + \varepsilon^\nu{}_2 \cdot l_\nu \cdot (C_2/(C^0{}_{MSA} - 2C_2)) \qquad (3)$$

On deriving Eq. (2) it was accepted that acid molecules contribute to the total absorption, whereas the absorption coefficients of both anion-solvating and nonsolvating MSA molecules are the same. At most frequencies for which plots (3) were obtained, the contribution of the absorption from the MSA molecules to the absorbance is much lower than the absorption of the anions. Therefore, we believe that the violation of correlation linearity in the coordinates of Eq. (3) is related to a change in the $\varepsilon^\nu{}_2$ coefficients due to the influence of solvation on the array of frequencies that form the CA spectrum of the $(AHA)^-$ anions. If the acid concentration exceeds that of the complexes of type **2** at least threefold, the absorption coefficients of the anions at all CA frequencies are constant.

Table 2. Continuous absorption coefficients for quasi-ion neutral complexes (**1**) and ion pairs (**2**) formed by MSA with 2-pyrrolidone for frequencies higher than 1800 cm^{-1}

ν /cm^{-1}	$\varepsilon \cdot l$*/L mol^{-1}			
	1(solv)	**1**	**2**	**2**(solv)
1850	0.038	0.042	0.058	0.051
2000	0.025	0.025	0.040	0.043
2200	0.018	0.024	0.050	0.054
2450	0.023	0.023	0.064	0.071
2600	0.019	0.019	0.046	0.054

* l_{2000} = 3.71 μm when two compartments of the cell are filled.

Solvation by acid molecules changes the IR spectra of the $(AHA)^-$ anions and the protonated form of the base as well. This is most pronounced at frequencies near 1700 cm^{-1}. The spectrum of BH^+ changes continuously until the ratio of concentrations of acid and $(AHA)^-$ anions increases fivefold. The solvation of BH^+ is accompanied by the shift of the maximum of the band of the protonated carbonyl group from 1680 to 1705 cm^{-1}. Figure 1 (curve *3*) presents the spectrum of completely solvated $(AHA)^-$ and BH^+, and the absorption of the anions contributes mainly to this spectrum. A comparison of curves *2* and *3* in Fig. 1 shows that the solvation of complexes **2** changes the absorption coefficients of the CA spectrum and an array of maxima in this spectrum. It has been shown for the HCl—1,1,2,2-tetrachloroethane—*N*-MP system that the presence of a neutral solvent decreases the absorption coefficients of CA but does not change the shape of the spectrum.[16] Solvation results in insignificant changes in the CA coefficients of complexes **2** at frequencies ν > 1800 cm^{-1} (see Table 2). At a frequency of 2000 cm^{-1} ε_2 = 116 L mol cm^{-1}, this value corresponds to the range of coefficients characteristic of negatively charged proton disolvates.[2]

Solvation by base molecules substantially changes the IR spectra of quasi-ion pairs at the frequencies <1800 cm^{-1}. Similar changes were observed for solutions of HCl in DMF,[6] HCl in *N*-MP,[7] and MSA in DMF.[4] The CA coefficients of solvated quasi-ion pairs for these systems were obtained as follows. At $C^0{}_{HA} < C^0{}_B$ the contribution to the absorption D_ν is made by quasi-ion pairs and base molecules

$$D_\nu = \varepsilon^\nu{}_1 \cdot l_\nu \cdot C^0{}_{HA} + \varepsilon^\nu{}_B \cdot l_\nu \cdot (C^0{}_B - C^0{}_{HA}), \qquad (4)$$

the concentration of the quasi-ion pairs being equal to the acid concentration.

Depending on the ratio of components, the quasi-ion pairs are partially or completely solvated. The relative absorption coefficients $\varepsilon^{\nu}{}_{\mathbf{1}(\mathrm{solv})} \cdot l_{\nu}$ were determined from the correlation

$$\varepsilon^{\nu}{}_{\mathbf{1}(\mathrm{solv})} \cdot l_{\nu} = (D_{\nu} - \varepsilon^{\nu}{}_{\mathrm{B}} \cdot l_{\nu} \cdot (C^0{}_{\mathrm{B}} - C^0{}_{\mathrm{HA}}))/C^0{}_{\mathrm{HA}}. \quad (5)$$

The coefficients obtained from Eq. (5) for solvated quasi-ion pairs and calculated from the IR spectra with equimolar ratios of components for non-solvated ion pairs differ. It was accepted on deriving Eq. (5) that the absorption coefficients of the base molecules, which solvate and so not solvate quasi-ion pairs, are the same. This assumption is confirmed by linear correlations in the coordinates of Eq. (6) obtained from Eq. (4)

$$D_{\nu}/C^0{}_{\mathrm{HA}} = \varepsilon^{\nu}{}_{\mathbf{1}} \cdot l_{\nu} + \varepsilon^{\nu}{}_{\mathrm{B}} \cdot l_{\nu} \cdot (C^0{}_{\mathrm{B}} - C^0{}_{\mathrm{HA}})/C^0{}_{\mathrm{HA}}. \quad (6)$$

Curves *4* and *5* in Fig. 1 were plotted using Eq. (5) and the spectra of solutions with different concentrations of MSA. The solvation of quasi-ion pairs by base molecules is strongest in the MSA—Pyr system. Figure 1 presents the spectra of the non-solvated (*1*) and quasi-ion pairs MSA · Pyr solvated to different extents (*4* and *5*). These data indicate that several base molecules participate in solvation. Solvation can result in the formation of two H bonds between the N—H groups of the Pyr molecules and S=O groups of the acidic ligand of the quasi-ion pair, the H bond between the C=O group of Pyr and N—H group of the basic ligand of the quasi-ion pair, as well as in the coordination of the C=O group with the hydrogen atom of the O...H...O bridge of the quasi-ion pair. Noticeable changes in the CA spectrum are induced already by the interaction of **1** with one Pyr molecule. New maxima at 1043 and 1170 cm^{-1} appear and the CA intensity in the 950—1250 cm^{-1} frequency range increases. In the region of higher frequencies, the CA spectra of the solvated and non-solvated quasi-ion pairs virtually coincide (see Fig. 1, curves *1* and *4*). Curve *4* represents the IR spectrum of the quasi-ion pair solvated by at most one base molecule. Further solvation changes the spectrum still more strongly. The intensity of the appeared bands increases substantially and the CA coefficients somewhat change at frequencies from 1250 to 1600 cm^{-1} (see Fig. 1, curve *5*). The coefficients in the CA spectra of solvated quasi-ion pairs remain unchanged in dilute acid solutions until a ratio of the components reaches a value close to 0.2. This corresponds to an approximately fourfold excess of Pyr with respect to the concentration of quasi-ion pairs.

The concentration dependence of the absorbance of the band of stretching N—H vibrations at 3250 cm^{-1} indicates the formation of H bonds involving the N—H groups of the Pyr molecules. In the coordinates of Eq. (6), the linear plot for this frequency is observed for moderately concentrated solutions. In these solutions not more than two base molecules are associated with each quasi-ion pair (Fig. 5, curve *1*). In dilute solutions the linear character of the plot is violated (see Fig. 5, curve *2*). The absorption of the quasi-ion pairs and base molecules, which form H bonds with the S=O groups of the acidic ligand (>N—H...O=S=) contributes to the absorbance of the IR spectra of solutions, which obey the plot presented in Fig. 5 (curve *1*). Linearity indicates a constant character of the absorption coefficients of the species ($\varepsilon_1 l$ = 0.020, $(\varepsilon_{\mathrm{Pyr}})_{\mathrm{solv}} l$ = 0.023 L mol^{-1}). The absorption coefficient of the quasi-ion pair ε_1 remains unchanged during solvation by base molecules and coincides with the value of this coefficient calculated from the spectrum of the solution with an acid concentration of 50 mol.%. The absorption coefficient at 3250 cm^{-1}, obtained from the spectrum of Pyr, is equal to 0.029 L mol^{-1}. Linearity is violated at a high excess of the base. This is related to the presence of base molecule in solutions, some of which solvate and others do not solvate the quasi-ion pairs. The absorption coefficients of these molecules are different.

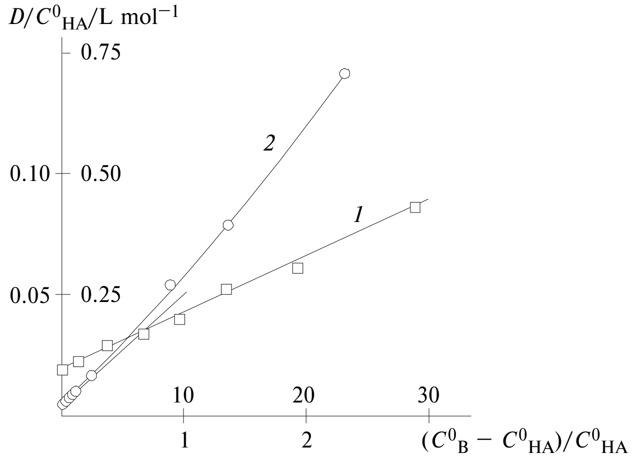


Fig. 5. Graphic solution of Eq. (6) for the band of 2-pyrrolidone at 3250 cm^{-1} in the MSA—Pyr system: 22.38—53.19% MSA (*1*), 0—53.19% MSA (*2*).

The absorption coefficients of the solvated and non-solvated quasi-ion pairs of MSA with Pyr for frequencies higher than 1800 cm^{-1} are presented in Table 2. In other studied systems,[4,6,7] the solvation of quasi-ion pairs by base molecules does not change the absorption coefficients at the frequencies presented in Table 2. Some decrease in the CA coefficients near frequencies of 1850 and 2200 cm^{-1} is observed for solutions of MSA in Pyr during solvation. This can be related to a change in symmetry of the central O...H...O bridge in solvated quasi-ion pairs. These changes are stipulated, most likely, by the formation of H bonds between the N—H groups of Pyr molecules and S=O groups of the acidic ligand of the quasi-ion pair. Base molecules (DMF, *N*-MP) do not form similar H bonds in other studied systems.[4,6,7]

Thus, we obtained the complete scheme of acid-base interactions in the MSA—Pyr (0—100%) system (see

Scheme 1). It is established that, depending on the ratio of components, two types of species with strong symmetric hydrogen bonds are formed: uncharged 1 : 1 quasi-ion pairs $(CH_2)_3N(H)CO...H...OSO_2Me$ and anions $(MeO_2SO...H...OSO_2Me)^-$. The IR spectra of both types of species contain an intense continuous absorption in the 950—2600 cm^{-1} frequency range, which is characteristic of structures with strong symmetric H bonds. The CA spectra change during the solvation of quasi-ion pairs by base molecules and of $(AHA)^-$ anions by acid molecules. The influence of the nature of the acidic and basic ligands in the continuous absorption of quasi-ion pairs and anions was demonstrated.

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