IR study of ion-molecular interactions in the system methanesulfonic acid—ethyl acetate

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The complex formation in the methanesulfonic acid (MSA)—ethyl acetate (EA) system was studied by Multiple Attenuated Total Reflection (MATR) IR spectroscopy at 30 °C. In solutions with excess EA, neither protonation of a base nor formation of complexes with a strong symmetrical H bond was observed. Molecular complexes EA · MSA are found in these solutions. Complexes formed by the strong symmetric H bond are observed in the system when the MSA content exceeds 50 mol.%.

Key words: acid-base interactions, hydrogen bond; solutions, complexes; methanesulfonic acid, ethyl acetate.

The ability of a proton to form ions and complexes *via* strong symmetrical hydrogen bonding is a fundamental property that characterizes its behavior in solutions.[1,2] The catalytic properties of solutions of acids are determined by the structure and concentration of these species. In excess of base aprotic solvents usually form quasi-ion pairs, *i.e.*, uncharged[3—5] 1 : 1 complexes with a strong symmetrical H bond. These complexes were detected, in particular, in the methanesulfonic acid (MSA)—DMSO[3] and MSA—DMF[6] systems. The interaction of weaker bases with an acid can be described by another mechanism.[7] This work is devoted to the study of complex formation in the MSA—ethyl acetate (EA) system, which is homogeneous in the whole range of compositions.

Experimental

EA and MSA ("puriss" grade, Fluka) were used for the preparation of solutions. The content of water in the starting EA and MSA did not exceed 0.01 and 0.05%, respectively. Sample dilutions were performed gravimetrically. Densities of solutions were measured to calculate molar concentrations (Table 1).

IR spectra of the MSA—EA system in the composition range of 0—100% MSA (see Table 1) in the frequency region of 900—4000 cm^{-1} were obtained at 30 °C on an UR-20 spectrophotometer equipped with an MNPVO-2 attachment[8] developed at the Institute of Chemical Physics of the Russian Academy of Sciences. A Ge prism with an incident angle of 30° was used. The samples of solutions were contained in one or two Teflon jackets adjacent to the edges of the prism. The number of reflections was 4 or 8, respectively. The effective thickness of the absorbing layer at a frequency of 2000 cm^{-1} was 1.68 or 3.20 μm, depending on the filling of the cell.

Intensities of bands were measured relative to the basic lines. In several cases, measurements were corrected by determining the relative intensity of the band at the lowest point in the vicinity of shoulders. Background absorption was measured relative to an empty cell.

Results and Discussion

Solutions containing 0—50 mol.% MSA. All bands characterizing the MSA molecule, including bands of vibrations of OH at 2450, 3035, and 986 cm^{-1}, appear in the

Table 1. Stoichiometric composition (n) and density (ρ) of solutions in the MSA—EA system, optical densities (D) of the band of ethyl acetate at 1738 cm^{-1}, and concentrations of ethyl acetate (C) unbound in complexes with MSA (C_{EA})

C^0_{MSA} (mol.%)	ρ /g cm^{-3}	C^0_{MSA}	C^0_{EA}	D_{1738}	C_{EA}	n_{1738}
		mol L^{-1}				
0	0.901	0	10.21	0.7811	10.21	—
9.60	0.944	1.02	9.60	0.6601	8.60	1.0
14.29	0.968	1.55	9.30	0.6090	7.96	0.9
17.30	0.982	1.90	9.08	0.5478	7.16	1.0
24.51	1.021	2.78	8.56	0.4713	6.16	0.9
28.02	1.038	3.22	8.27	0.4262	5.57	0.8
33.08	1.065	3.88	7.85	0.3969	5.19	0.7
36.50	1.083	4.34	7.55	0.3467	4.53	0.7
40.12	1.104	4.85	7.24	0.3146	4.11	0.65
44.02	1.126	5.41	6.88	0.3010	3.93	0.55
49.92	1.164	6.31	6.33	0.2243	2.93	0.55
56.57	1.205	7.36	5.65	0.1659	2.17	0.50
62.21	1.239	8.28	5.03	0.1112	1.45	0.4
66.49	1.265	9.01	4.54	0.0735	0.96	0.4
70.62	1.289	9.71	4.04			
74.79	1.321	10.50	3.54			
78.23	1.344	11.14	3.10			
81.96	1.364	11.81	2.60			
85.67	1.384	12.49	2.09			
88.72	1.408	13.13	1.67			
92.29	1.436	13.88	1.16			
93.58	1.444	14.13	0.97			
100	1.481	15.42	0			

Note: $n_{1738} = (C^0_{EA} - C_{EA})/C^0_{MSA}$.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 292—294, February, 2000.

spectra of EA solutions with a low (~1—2 mol L^{-1}) concentration of MSA. These bands are absent in the spectra of quasi-ion pairs $MeO_2SO^-...H^+...O(H)CNMe_2$, formed in solutions of MSA in DMF.[6] The optical densities of the bands at 986, 1335, and 2450 cm^{-1} and at 3035 cm^{-1}, increase linearly with the concentration of MSA in all solutions until the base : acid ratio reaches a value of 1, which corresponds to a concentration of MSA of 6.3 mol L^{-1} (Figs. 1 and 2). To avoid the superposition due to absorption of Me groups, the optical density of the band at 3035 cm^{-1} was measured at a frequency of 3100 cm^{-1} and on the shoulder at 2800 cm^{-1}. The absorption coefficients of the bands of skeletal vibrations at 986 and 1335 cm^{-1} are almost the same as those in the neat acid, and the absorption coefficients of stretching vibrations ν_{OH} in solutions with an MSA concentration of 0—50 mol.% are much lower than those in the neat acid (see Fig. 1). In addition, continuous absorption typical of species with a strong symmetric H bond is virtually absent. In the composition range of 0—50 mol.% MSA the absorption coefficient at 2000 cm^{-1} is equal to 20 L $mol^{-1}cm^{-1}$, which is much lower than the characteristic values (50—60 L $mol^{-1}cm^{-1}$) for quasi-ion pairs. This indicates that neither quasi-ion pairs nor other species with the strong symmetric H bond are formed in the solutions.

However, based on a considerable decrease in the absorption coefficient of the band of OH vibrations, the excess EA favors the formation of the molecular MSA · EA complexes. This is also indicated by a considerable decrease in the intensity of the band at 1738 cm^{-1} attributable to $\nu_{C=O}$ vibrations of EA molecules that is observed when the acid is added (see Table 1). In excess EA, the added acid is completely bound to form a 1 : 1 molecular complex. The complexation also follows from linear character of the dependences of D_{3100} and D_{2800} on the EA concentration (see Fig. 2) observed for concentrations of MSA ranging from 0 to 50%. The weakening of D_{1738} is accompanied by the appearance of a band at 1690 cm^{-1}, whose intensity increases with increase in the MSA concentration and, hence, which should be assigned to EA bound in the molecular complex.

Solutions containing 50—100 mol.% MSA. The bands of C=O vibrations of EA molecules are observed in the spectra of solutions with the MSA concentration reaching a ~75—80 mol.% level. The absence of these bands in the case of more concentrated acid solutions indicates either the protonation of the EA molecules or the formation of quasi-ion pairs with strong symmetrical H bonds. The characteristic bands[9] at 1510 and 1610 cm^{-1} and an intense band at 1050 cm^{-1} appear in the IR spectra. Quantitative analysis of this band of ionized MSA is difficult due to a strong superposition of the band at 1050 cm^{-1} attributed to vibrations of the C—O—C groups of the EA molecules.

The continuous coefficient of absorption at 2000 cm^{-1}, ε_{2000}, determined from the linear region of the plot of the optical absorption density on the EA concentration in the 70—100 mol.% range is equal to ~100 L $mol^{-1}cm^{-1}$. This value indicates the formation of complexes with a strong symmetric H bond in concentrated solutions of MSA.

Thus, in the binary MSA—EA liquid system, base—acid complexes with a strong symmetric H bond are formed only in concentrated solutions of MSA. Excess ether results in the formation of molecular acid : ether (1 : 1) complexes.

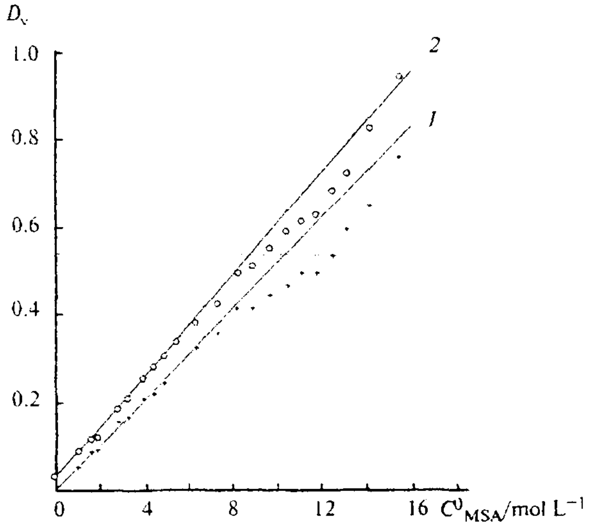

Fig. 1. Optical density of bands at 986 (*1*) and 1335 (*2*) cm^{-1} as a function of the concentration of MSA.

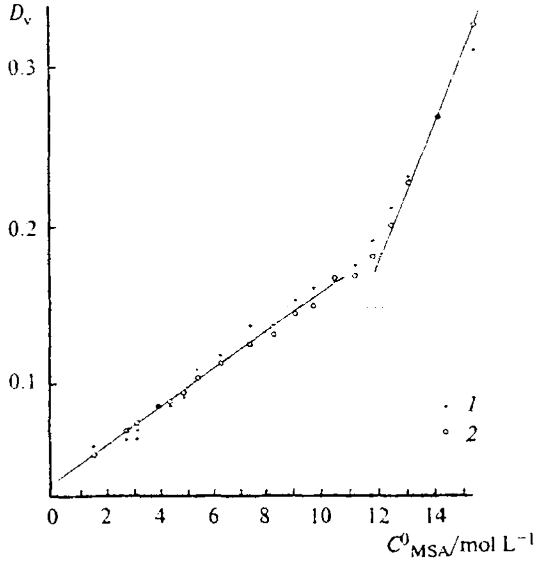

Fig. 2. Optical density of the band of ν_{OH} vibrations at frequencies of 2800 (*1*) and 3100 (*2*) cm^{-1} as a function of the concentration of MSA.

In the MSA—DMF system,[6] generation of quasi-ion pairs with a partial proton transfer from an acid molecule to a base molecule is observed even in MSA solutions with low concentrations. The degree of proton transfer from the acid molecule to the base molecule depends on the proton affinity of the base molecule and solvating ability of the solvent. The proton affinity of the EA molecule is equal[10] to 48.4 kJ mol^{-1}, which is ~3 kJ mol^{-1} lower than that of the DMF molecule. In addition, the EA molecule has a dipole moment of ~1.7 D, which is twice as low as that of the DMF molecule. An aprotic base with such a low dipole moment has a low solvating power. Therefore, excess EA favors the formation of molecular MSA · EA complexes rather than the generation of quasi-ion pairs with a strong symmetric H bond.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34144).

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Received June 1, 1999