Kinetics and Catalysis, Vol. 45, No. 3, 2004, pp. 367–371. Translated from Kinetika i Kataliz, Vol. 45, No. 3, 2004, pp. 393–397.

Compositions and Structures of Methanesulfonic Acid Complexes with Acetonitrile According to IR Spectroscopic Data

I. S. Kislina, V. D. Maiorov, S. G. Sysoeva, and N. B. Librovich

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia
e-mail: proton@chph.ras.ru

Received February 20, 2003

Abstract—IR spectra of solutions of methanesulfonic acid in acetonitrile are recorded and analyzed at 30°C at methanesulfonic acid concentrations ranging from 0 to 100%. Molecular 1 : 1 complexes with the coordination of the acid proton at the nitrogen atom of the acetonitrile molecule are formed over a wide range of acid concentrations. When the base is in excess, the whole amount of the acid is bound in these complexes. In solutions with excess acid, the solvation of the 1 : 1 complexes by several methanesulfonic acid molecules produces associates containing a structure fragment in which the acetonitrile molecule acts as both the donor and acceptor of hydrogen bonds. Hydrogen bonds involving CH_3 groups of acetonitrile can be formed when the 1 : 1 complexes are solvated by several acid molecules.

INTRODUCTION

The efficiency of aqueous solutions of an acid in a series of homogeneous acid-catalyzed systems is determined by the high protonating ability of the $H_5O_2^+$ ions with a strong symmetric hydrogen bond [1]. In aprotic organic solvents (B), a positively charged proton disolvate $(BHB)^+$ with this type of hydrogen bonds is not formed. Acid–base complexes with different degrees of proton transfer can be formed in organic solvents, depending on their basic properties. Stronger bases (DMF or 2-pyrrolidone) form quasi-ionic pairs with the strong symmetric hydrogen bond or (in excess acid) protonated forms (BH^+) and negatively charged protons disolvate [2]. When weaker bases (for example, esters) are used as solvents, molecular complexes with a hydrogen bond are formed over a wide range of acid concentrations. Complexes with an ionic or quasi-ionic structure can also be formed in solutions with a significant acid excess [3]. These are the molecular complexes which possess a high ionizing ability, comparable with that of the $H_5O_2^+$ ions [4].

In this work, we study the specific features of molecular interactions in the methanesulfonic acid (MSA)–acetonitrile (AN) system. The chosen solvent is less basic than diethyl ether and much less basic than amides. It is not protonated even in concentrated solutions of H_2SO_4 [5]. In CCl_4 solutions, trifluoroacetic acid with acetonitrile forms 1 : 1 molecular complexes [6] of the type

$$CH_3–C\equiv N\cdots H–OOC–CF_3.$$

I

Multiple attenuated total reflectance (MATR) IR spectroscopy was used to study the complex formation of methanesulfonic acid with acetonitrile [7].

EXPERIMENTAL

Methanesulfonic acid ("puriss", ≥99%) and acetonitrile ("puriss", ≥99.5%, $[H_2O] \le 0.001$, Fluka) were used.

MATR IR spectra of solutions of MSA in acetonitrile (0–100% acid) were recorded in the frequency interval from 900 to 3600 cm^{-1} at 30°C. A germanium cell with a MATR unit was used, the incident angle being 30°, and the number of reflections were 4 and 8 when one or two cavities adjacent to the crystal, respectively, were filled. The effective thicknesses of the absorbing layer (l) at a frequency of 2000 cm^{-1} were 2.02 and 4.06 μm, respectively.

The IR spectra of methanesulfonic acid contain intense absorption bands with maxima at 987 ($\rho_{s+as}(CH_3)$), 1146 ($\nu_s(S=O)_2$), 1332 ($\nu_{as}(S=O)_2$), and 3035 ($\nu(O–H)$) cm^{-1} [8]. In this spectral region, the IR spectrum of acetonitrile contains seven weak absorption bands at 917 ($\nu(C–C)$), 1040 ($\rho(CH_3)$), 1375 ($\delta_s(CH_3)$), 1410–1450 ($\delta_{as}(CH_3)$), 2254 ($\nu(C\equiv N)$), 2944 ($\nu_s(CH_3)$), and 3002 ($\nu_{as}(CH_3)$) cm^{-1} [9, 10]. In solutions of methanesulfonic acid, its intense absorption is superimposed on all bands of acetonitrile, except for the $\nu(C\equiv N)$ band at 2254 cm^{-1}.

When recording the spectra in the frequency interval from 900 to 1800 cm^{-1}, one cavity of the cell was filled (l_{2000} = 2.02 μm). At frequencies higher than 2000 cm^{-1}, two cavities of the cell were filled (l_{2000} = 4.06 μm) to increase the contrast of the spectrum.

The absorbances (D) of the acetonitrile band at 2254 cm^{-1} were determined relative to the basis line, and the D values at other frequencies were determined relative to the spectrum of the empty cell. The accuracy of measuring D was ±7%.

The concentrations of the components and densities (ρ) of the solutions are presented in Table 1.

0023-1584/04/4503-0367 © 2004 MAIK "Nauka/Interperiodica"

Table 1. Stoichiometric composition and densities of the methanesulfonic acid (MSA)–acetonitrile (AN) system at 30°C

ρ, g/cm^3	$[MSA]_0$, mol/l	$[AN]_0$, mol/l	ρ, g/cm^3	$[MSA]_0$, mol/l	$[AN]_0$, mol/l	ρ, g/cm^3	$[MSA]_0$, mol/l	$[AN]_0$, mol/l
1.482	15.41	0	1.295	11.07	5.63	1.003	4.57	13.74
1.445	14.53	1.18	1.244	9.88	7.18	0.964	3.76	14.68
1.421	13.96	1.95	1.192	8.70	8.68	0.913	2.66	16.01
1.395	13.67	2.69	1.134	7.41	10.27	0.861	1.57	17.31
1.355	12.46	3.85	1.069	5.98	12.05	0.782	0	19.05

RESULTS AND DISCUSSION

In the MSA concentration interval from 0 to 50 mol %, the spectra of solutions contain all observable bands of molecules of the components. The $\nu_s(S{=}O)_2$ band maximum shifts from 1146 to 1170 cm^{-1}, a new band appears at 2280 cm^{-1}, and the absorbance in the 2000–2600 cm^{-1} frequency range increases. The continuous absorption coefficient (ε) at 2000 cm^{-1} (calculated per 1 mol of the acid) is equal to 17 l mol^{-1} cm^{-1}, indicating that the solutions contain acid–base molecular complexes. Acid–base complexes with an ionic or quasi-ionic structure are characterized by much higher ε_{2000} values [11].

It follows from the D_ν–$[MSA]_0$ concentration plots that the interaction between MSA and acetonitrile changes the ε_ν coefficients for most bands compared with the absorption coefficients in the spectra of pure components. Some plots obtained for the frequencies at 987, 2200, and 3100 cm^{-1} are shown in Fig. 1. These plots are linear in the acid concentration interval from 0 to 8.7 mol/l (the equimolar solution). This indicates that methanesulfonic acid was completely bound to form complexes. Solvation of the resulting complexes by acetonitrile molecules in solutions with a base excess does not induce noticeable changes in the IR spectra.

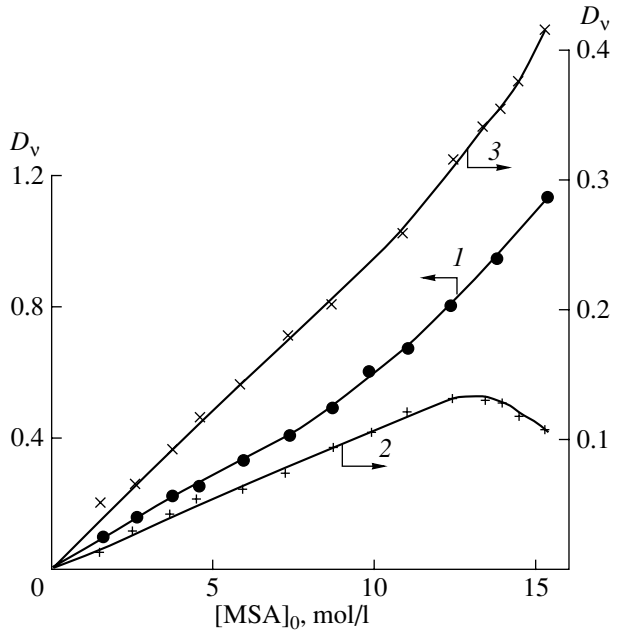

Fig. 1. Plots of D_ν vs. analytical concentration of acid ($[MSA]_0$) at 30°C for the frequencies (*1*) 987, (*2*) 2280, and (*3*) 3100 cm^{-1}.

When 1 : 1 complexes (C1, $[C1] = [MSA]_0$) are formed in solutions, the D_{2254} absorbance is the sum of the absorbances of acetonitrile molecules in the C1 composition and absorbances excessive with respect to the C1 concentration

$$\begin{aligned} D_{2254} &= \varepsilon_{K1} l_\nu [C1] + \varepsilon_{AH} l_\nu [AN], \\ [AN] &= [AN]_0 - [MSA]_0, \\ D_{2254}/([AN]_0 - [MSA]_0) &= \varepsilon_{AH} l_\nu + \varepsilon_{K1} l_\nu [C1]/([AN]_0 - [MSA]_0), \end{aligned} \quad (1)$$

where l_ν is the effective thickness of the absorbing layer at the frequency ν, and $[MSA]_0$ and $[AN]_0$ are the analytical concentrations of the components.

The plot in the coordinates of Eq. (1) for the frequency $\nu(C{\equiv}N) = 2254$ cm^{-1} is presented in Fig. 2a. Using this linear correlation, we calculated the coefficients as $\varepsilon_{AN} l_\nu = 12 \times 10^{-3}$ l/mol and $\varepsilon_{C1} l_\nu = 8.1 \times 10^{-3}$ l/mol. Their values virtually coincide with the coefficients obtained from the spectra of acetonitrile (12.8×10^{-3} l/mol) and a 1 : 1 solution (7.6×10^{-3} l/mol), respectively. A considerable decrease in the absorption coefficient of the $\nu(C{\equiv}N)$ vibration of acetonitrile is evidence for the formation of 1 : 1 molecular complexes in MSA solutions in acetonitrile (to 50 mol % acid)

$$H_3C{-}S(O_2)O{-}H{\cdots}N{\equiv}C{-}CH_3.$$

II

The structures of the AN complexes with acids of different strengths (methanesulfonic and trifluoroacetic acids) [6] are similar. When these complexes are formed in MSA solutions, the absorbance of the band at 2280 cm^{-1} increases in proportion to the acid concentration, and the absorption coefficient of ν(O–H) at

3100 cm^{-1} (εl) somewhat decreases from 0.0273 (for 100% MSA) to 0.0235 l/mol (for C1).

Bands of skeletal vibrations of MSA molecules change in different manners upon complex formation. The position of the band at 987 cm^{-1} remains unchanged, and its absorption coefficient decreases by ~25%. The band maximum at 1135 cm^{-1} shifts to 1170 cm^{-1}, and ε_{1170} for C1 is ~12% higher than ε_{1135} in pure acid. A noticeable short-wave broadening of the band at 1330 cm^{-1} is observed without changes in the intensity of the maximum. This indicates a change in the symmetry of the (SO_2OH) fragment in the C1 complex compared to the MSA molecules in pure acid. Similar changes are observed for the spectra of solutions of CH_3SO_3Na in MSA in the frequency range 1100–1400 cm^{-1} when the $[CH_3SO_2O\cdots H\cdots OSO_2CH_3]^-$ anions are formed [12]. The spectra of methanesulfonic acid and a solution with equimolar concentrations of MSA and acetonitrile are presented in Fig. 3.

Changes in the IR spectra of solutions with excess acid ($[MSA]_0 > 50$ mol %) indicate the solvation of the C1 complexes by MSA molecules. For several frequencies (1040, 2000, 2200, and 2440 cm^{-1}), the absorbances reach maximum values at MSA concentration of about 12.5 mol/l ($[AN]_0 \cong 3.85$ mol/l) (see Fig. 1). This could indicate that the solvation of C1 by several acid molecules in solutions is accompanied by the formation of associates whose spectra differ from those of the C1 complexes. The spectra of both MSA and acetonitrile change upon solvation. In the region of skeletal vibrations, the maximum changes are observed for the band at 987 cm^{-1}. A new band with a maximum near 1040 cm^{-1} appears at the wing of the band at 1170 cm^{-1}. The band of acetonitrile at 2254 cm^{-1} is absent from the spectra of the most concentrated solutions ($[AN]_0 <$ 2 mol/l). We believe that these changes in the spectra are related to the formation of MSA complexes with acetonitrile whose structures differ from those of the C1 complexes. Let us denote them as C2. It should be emphasized that C2 is a C1 complex associated with several acid molecules. Also note that the solvation of C1 has a strong effect on the IR spectrum of the acetonitrile molecule. Therefore, the changes in the spectra cannot be explained by sole solvation of the MSA molecule in the composition of the C1 complex.

Depending on the component ratio, acetonitrile can partially or completely be bound in C2 associates. The concentration plots of the absorbances show that at $[AN]_0 \le 2$ mol/l the solutions contain only C2 and MSA molecules, while more dilute acid solutions additionally contain the C1 complexes. The concentrations of C1 and C2 were determined as follows. The $D_\nu - \varepsilon_{MSA} l_\nu [MSA] - [AN]_0$ concentration plots were obtained for the series of frequencies. One of these plots for ν = 2000 cm^{-1} is presented in Fig. 4. It was assumed that $[MSA] = [MSA]_0 - [AN]_0$, that is, the absorbance of the MSA molecules, whose OH groups are not involved in the formation of hydrogen bonds with the nitrogen

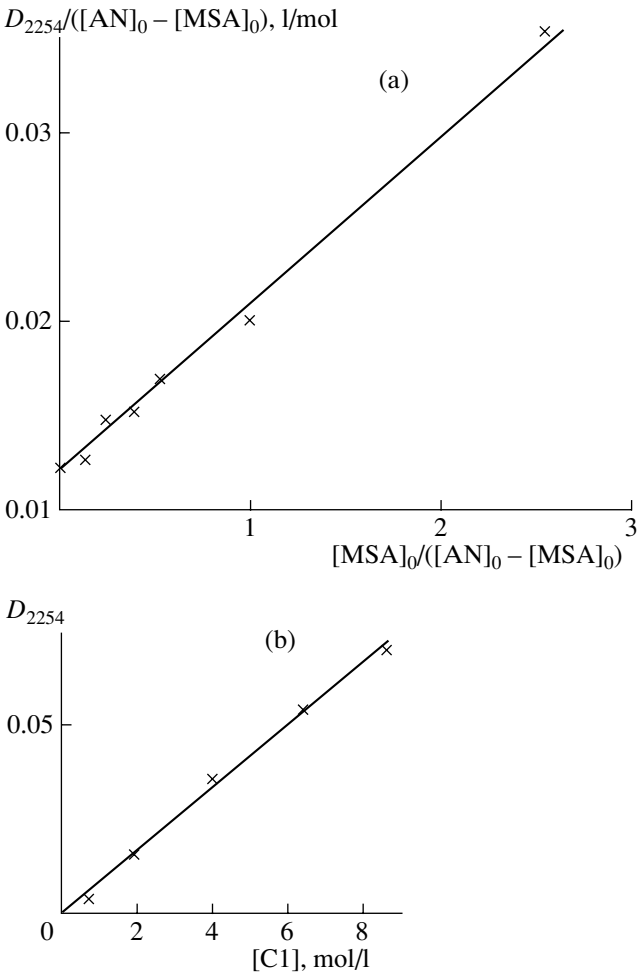

Fig. 2. (a) Graphical solution of Eq. (1) for the acetonitrile band at 2254 cm^{-1} in the MSA–AN system (0–50 mol % MSA). (b) Plot of D_{2254} vs. [C1] in the concentration interval from 50 to 100 mol % MSA. 30°C.

atoms of the acetonitrile molecule, was subtracted from the total absorbance at the ν frequency. The initial segment of the plot ($[AN] \le 2$ mol/l) in Fig. 4 is linear, indicating that acetonitrile is completely bound to C2 associates. The absorption coefficient of C2 associates can be determined from the linear segment (ε = 37 l mol^{-1} cm^{-1} for ν = 2000 cm^{-1}). The linearity is violated in solutions containing both C1 and C2 complexes. The concentrations of C1 and C2 complexes were determined in the composition interval from 8.7 to 2 mol/l of acetonitrile using the equation

$$\begin{aligned} D_{2000} - \varepsilon_{MSA} l_\nu [MSA] \\ = \varepsilon_{C1} l_\nu [C1] + \varepsilon_{C2} l_\nu [C2], \\ [C1] + [C2] = [AN]_0. \end{aligned} \quad (2)$$

The ε_{C1} values determined from the IR spectra of the 1 : 1 solution and ε_{C2} from the linear segments of the plots similar to that presented in Fig. 4 were used in the calculations. The averaged concentrations of C1 and C2

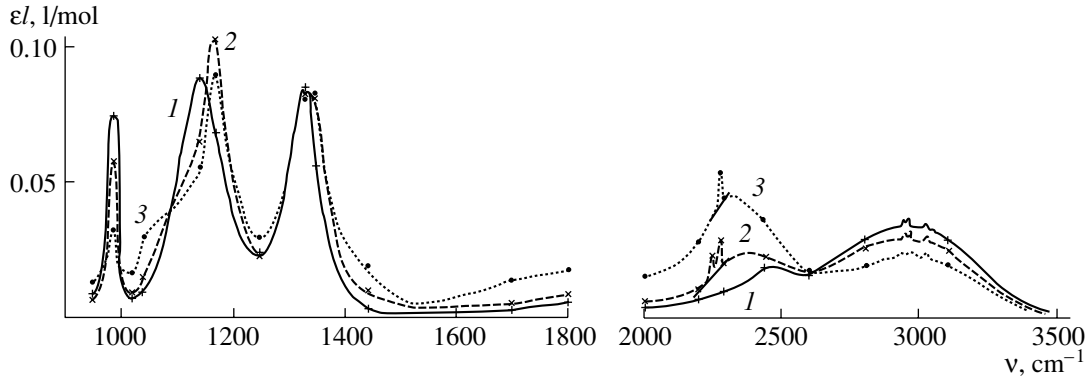

Fig. 3. IR spectra of (*1*) MSA, (*2*) C1 complexes, and (*3*) C2 complexes in the methanesulfonic acid–acetonitrile system at 30°C. Points mark the frequencies for which the plots of the absorbances (D_ν) vs. composition of the system were examined.

obtained by Eq. (2) for frequencies of 987, 2000, 2200, and 2290 cm^{-1} are presented in Table 2. The spectrum of the C2 complex for the studied frequency interval is presented in Fig. 3 (curve *3*).

The absence of the band at 2254 cm^{-1} (ν(C≡N)) from the spectra of concentrated MSA solutions also indicates that acetonitrile is completely bound in C2. The absorbance at this frequency in solutions with an acid excess changes in proportion to the C1 concentration (Fig. 2b). For the absorption band at 2280 cm^{-1}, the absorption coefficients of C1 and C2 complexes are almost the same. When C2 is formed, the hydrogen bond between the OH group of the MSA molecule and the nitrogen atom of acetonitrile is strengthened. This is indicated by a decrease in the absorption coefficient of the ν(OH) band at 3100 cm^{-1} ($\varepsilon_{3100}l_{3100}$) from 0.0235 l/mol for nonsolvated C1 complexes to 0.017 l/mol for the solvation of C1 by several MSA molecules and by a significant (almost twofold) decrease in the coefficient of the $\rho_{s+as}(CH_3)$ band at 987 cm^{-1}. Changes in other bands of skeletal vibrations of the MSA molecule are much smaller compared to changes in the spectrum of C1. The IR spectra of C1 and C2 differ significantly (Fig. 3) in the frequency range from 2000 to 2600 cm^{-1}.

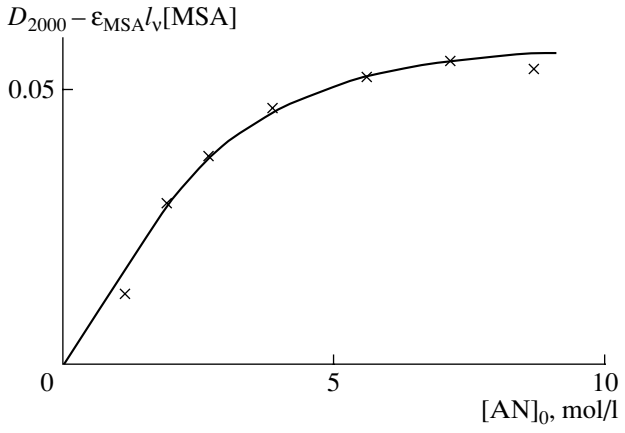

Fig. 4. Plot of ($D_{2000} - \varepsilon_{MSA}l_\nu$[MSA]) vs. $[AN]_0$ in the MSA concentration interval from 50 to 100 mol % at 30°C. $[MSA] = [MSA]_0 - [AN]_0$.

The data in Table 2 show that several acid molecules are involved in the formation of the C2 associates. Some of these molecules are linked by hydrogen bonds with the SO groups of the MSA molecule in C1. Therefore, at the component ratios $[MSA]_0 : [AN]_0 = 2 : 1$, only 20% of the complexes formed have the C2 structure. We believe that the addition of one more MSA molecule to the C1 complex solvated by one or two acid molecules results in the formation of a hydrogen bond involving the CH_3 group of acetonitrile. These associates are designated as C2. The involvement of the hydrogen atom of the CH_3 group in hydrogen bond formation agrees with a noticeable increase in the absorption coefficients near the maxima of the bands of stretching (1385, 1450 cm^{-1}) and torsional (1040 cm^{-1}) vibrations of the methyl group of acetonitrile (see Fig. 3, curve *3*). According to the data presented in [13], acetonitrile solutions with iodide and thiocyanate ions contain H-complexes involving CH_3 groups. The formation of C–H···O bonds involving the solvent molecule (acetone or dimethyl sulfoxide) and the hydrogen atoms of the CH_3 group of acetonitrile was established by calorimetry and IR spectroscopy [9]. On this basis, we believe that acetonitrile complexes with MSA solvated by several acid molecules (C2) contain the structural fragment

$$CH_3SO(OH)O\cdots HCH_2{-}C{\equiv}N\cdots H{-}OS(O_2)CH_3,$$

III

in which acetonitrile forms two hydrogen bonds.

In our opinion, conclusions made in [14] confirm that CH_3 groups of acetonitrile can be involved in hydrogen bond formation. The authors of [14] established by calculating the vibrational spectrum of the solvated $(CH_3OH)_2H^+$ ion and the data on charges on its atoms and the equilibrium composition of the system that each CH_3 group of the ion formed two C–H···O bonds with a strength of ~12.5 kJ/mol. Calcu-

Table 2. Concentrations of nonsolvated 1 : 1 complexes (C1) and C1 complexes solvated by several MSA molecules and containing structure **III** (C2) in solutions of methanesulfonic acid in acetonitrile for the composition range from 50 to 100 mol % of acid at 30°C

$[MSA]_0^*$, mol/l	$[AN]_0^*$, mol/l	[C1], mol/l	[C2], mol/l
8.70	8.68	8.68	0
9.88	7.18	6.6	0.6
11.07	5.63	4.4	1.2
12.46	3.85	2.1	1.7
13.67	2.69	0.7 ± 0.3**	2.0 ± 0.3**
13.96	1.95	0	1.95

* $[MSA]_0$ and $[AN]_0$ are the analytical concentrations of the components in solutions.

** The accuracy of determination of other concentrations is at least ±0.2 mol/l.

lations [14] explain the low-frequency shift of the ν(CH) bands observed in the IR spectra when the $(CH_3OH)_2H^+$ ions are solvated by methanol molecules.

Thus, based on analysis of the IR spectra, we believe that 1 : 1 molecular complexes with structure **II** (C1) are formed between the components of the MSA–AN system. When these complexes are solvated by several (at least two) MSA molecules in solutions with excess acid, associates with the structural fragment **III** are formed in which the acetonitrile molecule acts as both the donor and acceptor of hydrogen bonds. Hydrogen bonds involving the CH_3 groups of acetonitrile can be formed when the C1 complexes are solvated by several acid molecules.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 02-03-32174.

REFERENCES

1. Librovich, N.B., *Khim. Fiz.*, 1992, vol. 11, no. 5, p. 627.
2. Kislina, I.S., Maiorov, V.D., and Sysoeva, S.G., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 6, p. 965.
3. Burdin, V.V., Maiorov, V.D., and Librovich, N.B., *Izv. Akad. Nauk, Ser. Khim.*, 2000, no. 2, p. 292.
4. Kislina, I.S. and Sysoeva, S.G., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 6, p. 961.
5. Arnett, E.M., *Progress in Physical Organic Chemistry*, Cohen, S., Streitwieser, A., and Taft, R.W., Eds., New York: Wiley, 1963, p. 237.
6. Perelygin, I.S. and Afanas'eva, A.N., *Zh. Prikl. Spektrosk.*, 1973, vol. 19, no. 3, p. 500.
7. Harrick, N.J., *Internal Reflection Spectroscopy*, New York: Wiley, 1967.
8. Simon, A. and Kriegsmann, H., *Chem. Ber.*, 1956, vol. 89, p. 2384.
9. Stolov, A.A., Borisover, M.D., Solomonov, B.N., *et al.*, *Zh. Fiz. Khim.*, 1992, vol. 66, no. 3, p. 620.
10. Tanabe, K. and Hiraishi, J., *Spectr. Chim. Acta*, 1980, vol. 36, no. 7, p. 665.
11. Librovich, N.B., Burdin, V.V., Maiorov, V.D., and Kislina, I.S., *Khim. Fiz.*, 2000, vol. 19, no. 4, p. 41.
12. Kirilova, A.P., Maiorov, V.D., Serebryanskaya, A.I., *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, no. 12, p. 2724.
13. Perelygin, I.S., *Ionnaya sol'vatatsiya* (Ion Solvation), Krestov, G.A., Ed., Moscow: Nauka, 1987, p. 320.
14. Tarakanova, E.G., Maiorov, V.D., and Yukhnevich, G.V., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 2, p. 306.