Acid-base interactions in the methanesulfonic acid—propylene carbonate system

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The methanesulfonic acid (MSA)—propylene carbonate (PC) system with component concentrations of 0—100% was studied at 30 °C using the Multiple Attenuated Total Reflection (MATR) IR spectroscopy. The formation of a strong 1 : 1 molecular complex of MSA with PC was established. In the presence of an excess of the acid, a second MSA molecule adds to this complex to give the molecular complex (2MSA) · PC. When excess propylene carbonate is used, the MSA · PC complex is solvated by a propylene carbonate molecule. No protonation of the base or formation of complexes with a strong symmetrical H bond was observed. Continuous absorption was not detected in IR spectra of the solutions.

Key words: IR spectra; acid-base interactions, complexes; methanesulfonic acid, propylene carbonate, solutions.

A fundamental property of a proton in solution is the formation of ions and complexes with a strong symmetrical H bond.[1—4]

The structure and concentration of these species largely determine the catalytic properties of acid solutions. The formation of noncharged 1 : 1 complexes with a strong symmetrical H bond (quasi ion pairs) is typical of nonaqueous systems.[5—8] Such complexes were detected in the methanesulfonic acid (MSA)—DMSO [5] and MSA—DMF systems. [9] For weaker bases, interac-

Table 1. Densities of solutions and the stoichiometric and equilibrium compositions of MSA—PC solutions, studied in the ν = 700—2000 cm^{-1} range (25 °C)

C^0_{MSA} (mol.%)	ρ /g cm^{-3}	C^0_{MSA}	C^0_{PC}	C_{C1}	C_{C2}	C_{C3}	C_{MSA}	C_{PC}
		mol L^{-1}						
100.00	1.480	15.4	0	—	—	—	15.4	—
94.48	1.462	14.33	0.84	—	0.84	—	12.65	—
91.38	1.452	13.73	1.30	—	1.30	—	11.13	—
84.80	1.432	12.51	2.24	—	2.24	—	8.03	—
80.60	1.420	11.77	2.83	—	2.83	—	6.11	—
76.78	1.407	11.07	3.34	—	3.34	—	4.39	—
74.40	1.392	10.26	3.54	—	3.54	—	3.18	—
68.64	1.382	9.69	4.42	—	4.42	—	0.85	—
59.40	1.357	8.42	5.58	2.74	2.84	—	—	—
57.10	1.346	7.81	5.85	3.89	1.96	—	—	—
51.00	1.331	6.85	6.58	6.31	0.20	—	—	—
43.95	1.308	5.78	7.37	4.19	—	1.59	—	—
39.25	1.295	5.11	7.92	2.30	—	2.81	—	—
35.34	1.288	4.56	8.33	0.79	—	3.77	—	—
31.40	1.275	4.00	8.75	—	—	4.00	—	0.75
27.10	1.266	3.42	9.19	—	—	3.42	—	2.35
24.00	1.258	3.00	9.50	—	—	3.00	—	3.50
20.30	1.248	2.51	9.87	—	—	2.51	—	4.85
14.83	1.232	1.74	10.43	—	—	1.74	—	6.95
10.85	1.225	1.31	10.76	—	—	1.31	—	8.14
7.80	1.216	0.93	11.04	—	—	0.93	—	9.18
0	1.200	0	11.76	—	—	0	—	11.76

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tion with an acid can follow a different pathway.

This work describes the complex formation in the MSA—propylene carbonate (PC) system containing a base with medium donor properties (DN_{SbCl_5} = 15.1) and a high dielectric constant[10] (ε = 70).

Experimental

Commercial MSA was purified by a known procedure.[3] Propylene carbonate was dried over calcium hydride and then distilled *in vacuo* over freshly calcined molecular sieves. The purity of PA was checked by chromatography. The solutions were prepared *in vacuo* using separate weighed portions. The multiple attenuated total reflection (MATR) cells were filled in an argon box. To calculate the molar concentrations, the densities of the solutions were measured (Tables 1 and 2).

IR spectra were recorded at 30 °C on a UR-20 spectrophotometer equipped with a MNPVO-2 [MATR] attachment,[11] produced at the Institute of Chemical Physics of the RAS. Ge prisms with angles of incidence of 45° (at frequencies of 700—2300 cm^{-1}) and 30° (2400—3400 cm^{-1}) were used. To compensate for the germanium bands in the 700—900 cm^{-1} range, an MNPVO-2 attachment was also mounted in the reference channel. The solution to be studied was placed into Teflon cavities adjacent to the prism faces. The numbers of reflections were 6 or 8, respectively. The effective thickness of the absorbing layer l_{2000} at a frequency of 2000 cm^{-1} was 1.33 μm for the 45° prism or 3.25 μm for the 30° prism. The effective thicknesses at other frequencies l_ν were determined from the relationship $l_\nu = l_{2000}(2000/\nu)$.

The optical densities of bands were measured in relation to base lines. In some cases, the correctness of the measurements was checked by determining the optical density of a band relative to the minimum located near one of its wings. The background absorption was measured in relation to an empty cell. The accuracy of determination of optical densities was 3—5%.

Table 2. Densities of solutions and the stoichiometric compositions of MSA—PC solutions, studied in the ν = 2000—3600 cm^{-1} range (25 °C)

C^0_{MSA} (mol.%)	ρ /g cm^{-3}	C^0_{MSA}	C^0_{PC}
		mol L^{-1}	
100.00	1.480	15.40	0
97.90	1.477	15.00	0.32
95.80	1.469	14.60	0.64
92.93	1.459	14.00	1.10
87.75	1.443	13.06	1.80
83.62	1.429	12.30	2.40
77.54	1.408	11.20	3.25
77.08	1.407	11.10	3.30
69.60	1.383	9.85	4.30
66.58	1.375	9.34	4.70
60.12	1.354	8.20	5.50
55.24	1.340	7.50	6.08
44.35	1.310	5.85	7.34
43.30	1.307	5.70	7.50
37.90	1.283	4.90	8.06
31.16	1.274	4.00	8.80

The MSA and PC bands were assigned in conformity with previous studies (see Ref. 12 and Refs. 13 and 14).

Results and Discussion

No ions or complexes with a strong symmetrical H bond are formed in the system under study. A typical continuous absorption is not observed; the spectra recorded near an equimolar ratio of the components remain contrasting, and the band for stretching vibrations of the OH groups in MSA is observed down to the most dilute solutions of the acid. However, the concentration dependences of the optical densities of some bands, the shift of some frequencies, and the appearance of a new band at 1736 cm^{-1} (Fig. 1) imply strong acid—base interaction, resulting in the formation of molecular complexes of various compositions.

The optical densities of some MSA bands, 987 cm^{-1} (ρ_{s+as}(Me)) and 1332 cm^{-1} (ν_{as}(SO)), and PC bands at 778 cm^{-1} (CH_2 rotat.) and 1050 cm^{-1} (skeletal) vary proportionally to the contents of MSA and PC in the solutions. The absorption coefficients of the other bands depend on the composition of the system.

The absorption coefficient of the ν(C=O) band of PC at 1783 cm^{-1} changes most appreciably upon complexation (see Figs. 1, 2). The addition of MSA to PC results in a band at 1736 cm^{-1}, which is absent in pure MSA and which reaches a maximum near the equimolar ratio of the components. The positions of the maxima of the bands at 1783 and 1736 cm^{-1} does not change over

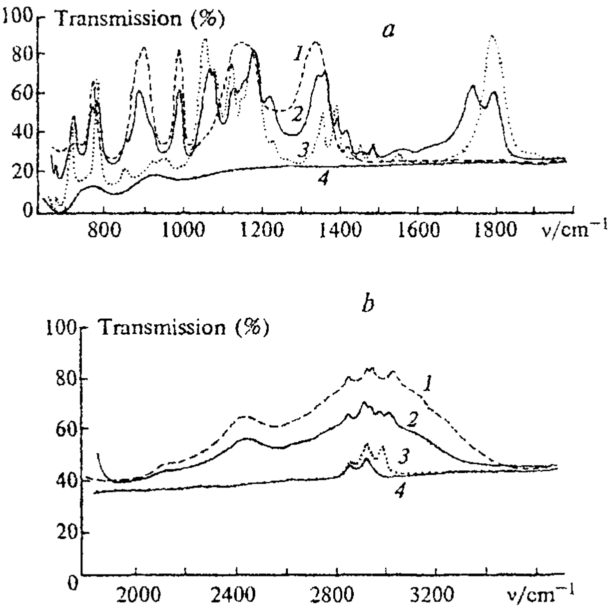


Fig. 1. MATR IR spectra of the MSA—PC system in the frequency range of 700—2000 cm^{-1} (*a*), 2000—3600 cm^{-1} (*b*): 100 mol.% MSA (*1*); 51.0 mol.% MSA (*2*); 100 mol.% PC (*3*); empty cell (*4*).

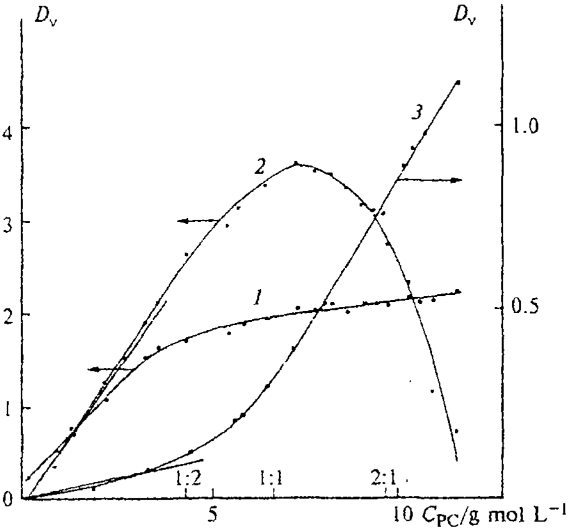


Fig. 2. Optical densities (*D*) of bands as functions of the PC concentration at ν/cm^{-1} = 715 (*1*), 1736 (*2*), 1783 (*3*).

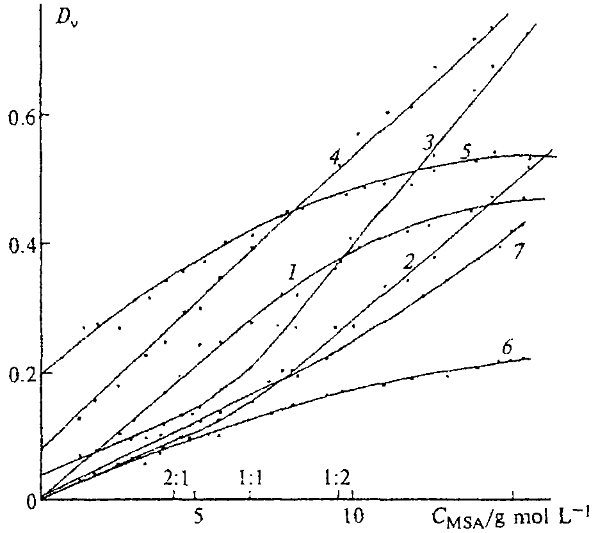
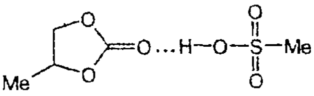


Fig. 3. Optical densities (*D*) of bands as functions of the MSA concentration at ν/cm^{-1} = 880 (*1*), 905 (*2*), 1320 (*3*), 1335 (*4*), 1350 (*5*), 2440 (*6*), 3060 (*7*).

the entire range of system compositions. When MSA [15] (H_0 = −7.86) is replaced by stronger acids, either sulfuric[16] (H_0 = −11.03) or fluorosulfonic[17] (H_0 = −15.09) acid, the ν(C=O) band of PC shifts much more significantly, *viz.*, to 1655 cm^{-1} in H_2SO_4 and to 1650 cm^{-1} in FSO_3H, and in addition, intense continuous absorption (ε = 100 L mol^{-1} cm^{-1} in the PC—FSO_3H system) appears. Thus, unlike the PC—H_2SO_4 and PC—FSO_3H systems in which PC is apparently ionized or quasi ion pairs with a strong quasisymmetrical H-bond are formed, in the PC—MSA system, molecular complexes PSA · PC are produced with participation of the >C=O group of PC and the H—O— group of MSA.



When the content of PC increases, the absorption coefficient of the ν(O—H) band at frequencies of 2800 and 3060 cm^{-1} decreases, while that at 2440 cm^{-1} increases (Fig. 3); this corresponds to a 400—500 cm^{-1} shift of the O—H stretching band to lower frequencies due to the weakening of the O—H bond in MSA upon the formation of the hydrogen bond in MSA · PC (C1). The concentration dependences of the optical densities at frequencies of 2800, 3060, and 2440 cm^{-1} in the composition range of 50—100 mol.% MSA can be interpreted by absorption of MSA and C1:

$$D_\nu = \varepsilon^\nu_{MSA}\cdot l_\nu\cdot C_{MSA} + \varepsilon^\nu_{C1}\cdot l_\nu\cdot C_{C1}. \quad (1)$$

Since each PC molecule binds one MSA molecule, then

$$C_{C1} = C^0_{PC}, \quad C_{MSA} = C^0_{MSA} - C^0_{PC},$$

where C^0_{MSA} and C^0_{PC} are the stoichiometric concentrations of MSA and PC.

From Eq. (1), we obtain

$$D_\nu/(C^0_{MSA} - C^0_{PC}) = \\ = \varepsilon^\nu_{MSA}\cdot l_\nu + \varepsilon^\nu_{C1}\cdot l_\nu\cdot[C^0_{PC}/(C^0_{MSA} - C^0_{PC})]. \quad (2)$$

The linear dependence (2) is valid up to an equimolar ratio of the components for the absorption at 2800 cm^{-1} ($\varepsilon^\nu_{C1}\cdot l_\nu = 2\cdot10^{-2}$, $\varepsilon^\nu_{MSA}\cdot l_\nu = 2.4\cdot10^{-2}$), 3060 ($\varepsilon^\nu_{C1}\cdot l_\nu = 2\cdot10^{-2}$, $\varepsilon^\nu_{MSA}\cdot l_\nu = 5\cdot10^{-2}$), and 2440 cm^{-1} ($\varepsilon^\nu_{C1}\cdot l_\nu = 1.5\cdot10^{-2}$, $\varepsilon^\nu_{MSA}\cdot l_\nu = 1.4\cdot10^{-2}$ L mol^{-1}) (Fig. 4). The resulting $\varepsilon^\nu_{C1}\cdot l_\nu$ values coincide with the corresponding absorption coefficients determined from the linear sections of the concentration plots for dilute (0—50 mol.%) solutions of MSA (see. Fig. 3).

The concentration dependences of the other bands of MSA are also described by Eq. (1). In pure MSA the band at 898 cm^{-1}, assignable[12] to the ν(S—OH) vibrations, consists of two components: 880 and 905 cm^{-1}. When PC is added, the high-frequency component progressively shifts to 920 cm^{-1} (31.4 mol.% MSA) and decays much faster than the low-frequency component, which is proportional to the stoichiometric content of MSA (see Fig. 3). The concentration plot for the optical density of the high-frequency component measured at 905 cm^{-1} is described by relation (1) (see Fig. 4). The absorption coefficients at 905 cm^{-1} were determined from relation (2) to be $\varepsilon^\nu_{C1}\cdot l_\nu = 2\cdot10^{-2}$ and $\varepsilon^\nu_{MSA}\cdot l_\nu = 3.4\cdot10^{-2}$ L mol^{-1}.

The optical densities in the region of the bands at 1350 cm^{-1} and 1332 cm^{-1} ν_s(SO), measured at a frequency of 1320 cm^{-1}, where the overlap of the PC bands at 1340—1350 cm^{-1} is insignificant, also obey Eq. (1): for 1350 cm^{-1}, $\varepsilon^\nu_{C1}\cdot l_\nu = 6.5\cdot10^{-2}$ and $\varepsilon^\nu_{MSA}\cdot l_\nu = 3.6\cdot10^{-2}$; for 1320 cm^{-1}, $\varepsilon^\nu_{C1}\cdot l_\nu = 2.5\cdot10^{-2}$ and $\varepsilon^\nu_{MSA}\cdot l_\nu = 4.9\cdot10^{-2}$ L mol^{-1}. The absorption coefficients of the C1 complexes at 905 and 1320 cm^{-1}

coincide with the coefficients found from the linear sections of the concentration plots of the optical densities at low (<50 mol.%) concentrations of MSA.

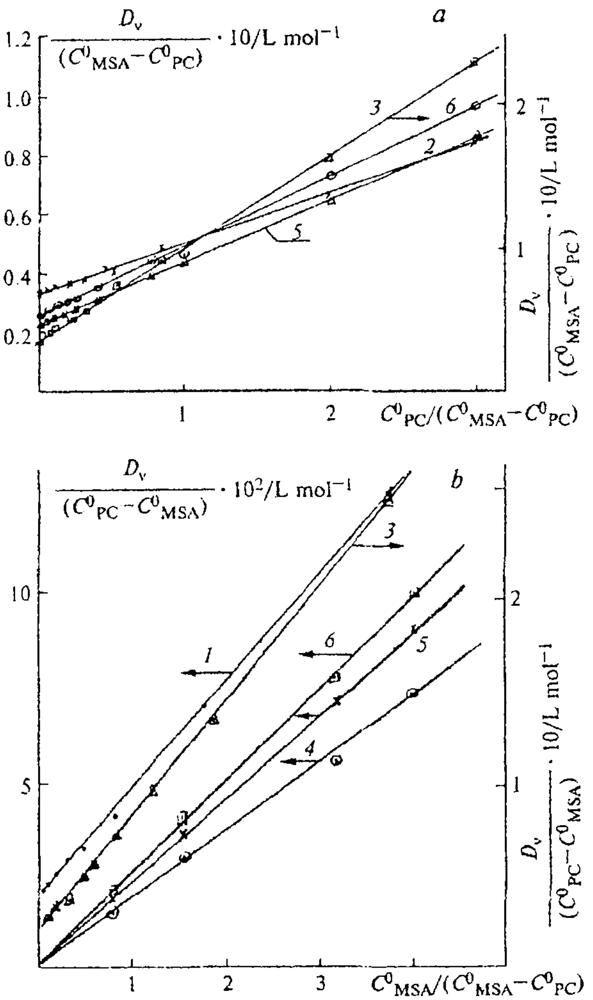


Fig. 4. Graphical solution of Eq. (2) (*a*) for 905 (*2*), 1350 (*3*), 2800 (*5*), 3060 cm^{-1} (*6*) and Eq. (4) (*b*) for 715 (*1*), 1350 (*3*), 2440 (*4*), 2800 (*5*), 3060 cm^{-1} (*6*).

The absorption of PC at low concentrations of the acid is described by a relation similar to (1)

$$D_\nu = \varepsilon^\nu{}_{PC}\cdot l_\nu\cdot C_{PC} + \varepsilon^\nu{}_{C1}\cdot l_\nu\cdot C_{C1}. \quad (3)$$

If we assume that each MSA molecule binds one PC molecule, then

$$C_{C1} = C^0{}_{MSA},\ C_{PC} = C^0{}_{PC} - C^0{}_{MSA}$$

From Eq. (3), we obtain

$$D_\nu/(C^0{}_{PC} - C^0{}_{MSA}) =$$

$$= \varepsilon^\nu_{PC}\cdot l_\nu + \varepsilon^\nu_{C1}\cdot l_\nu\cdot[C^0{}_{MSA}/(C^0{}_{PC} - C^0{}_{MSA})]. \quad (4)$$

The variation of the optical density of the PC band at 1350 cm^{-1} (CH_2 deform.) is described by Eq. (3): $\varepsilon^\nu{}_{C1}\cdot l_\nu = 6.45\cdot10^{-2}$, $\varepsilon^\nu{}_{PC}\cdot l_\nu = 1.7\cdot10^{-2}$ L mol^{-1} (see Figs. 3 and 4). Using relation (2), we obtained $\varepsilon^\nu{}_{C1}\cdot l_\nu = 6.5\cdot10^{-2}$ L mol^{-1} for the region of high (>50 mol.%) concentrations of MSA. The fact that the absorption coefficients obtained for different system compositions coincide confirms the assumed formation of a strong molecular complex C1.

The bands for the C=O stretching vibrations at 1783 and 1736 cm^{-1}, due to free and bound PC, proved to be sensitive not only to the formation of the 1 : 1 complex but also to its solvation by acid or base molecules. It follows from analysis of the concentration dependences of the optical densities of these bands that in the presence of excess acid, the complex (2MSA) · PC (C2) is formed, while in the presence of excess base, the C1 complex is solvated by propylene carbonate molecules.

The entire region of compositions of the system can be divided into four sections. In solutions containing more than two molecules of the acid per PC molecule (section I: 66.7—100 mol.% MSA), absorption is determined by MSA molecules and the C2 complex:

$$D_\nu = \varepsilon^\nu{}_{MSA}\cdot l_\nu\cdot C_{MSA} + \varepsilon^\nu{}_{C2}\cdot l_\nu\cdot C_{C2}, \quad (5)$$

where C_{C2} is the concentration of (2MSA) · PC. Provided that PC is completely bound into the C2 complex, we have

Table 3. Absorption coefficients for the C1, C2, and C3 complexes at various frequencies

ν/cm^{-1}	$\varepsilon^\nu\cdot l_\nu$/L mol^{-1} ($\varepsilon^\nu$/L mol^{-1} cm^{-1})							
	MSA	C2	C2	C1	C1	C3	C3	PC
	I		II		III		IV	
1736	0	$5.6\cdot10^{-2}$	$5.6\cdot10^{-2}$	$5.1\cdot10^{-2}$	$5.3\cdot10^{-2}$	$8.0\cdot10^{-2}$	$8.3\cdot10^{-2}$	$1.1\cdot10^{-2}$
	(0)	(366)	(366)	(333)	(346)	(523)	(542)	(72)
1783	0	$2.2\cdot10^{-2}$	$2.3\cdot10^{-2}$	$4.7\cdot10^{-2}$	$4.8\cdot10^{-2}$	$12.8\cdot10^{-2}$	$13.0\cdot10^{-2}$	$9.2\cdot10^{-2}$
	(0)	(148)	(154)	(315)	(322)	(860)	(870)	(620)
715	$0.15\cdot10^{-2}$	$4.2\cdot10^{-2}$	$4.1\cdot10^{-2}$	$3.0\cdot10^{-2}$	$3.0\cdot10^{-2}$	—	—	$1.85\cdot10^{-2}$
	(4.0)	(113)	(110)	(80)	(80)			(50)

Note. I—IV are ranges of the system composition. The accuracy of the determination of $\varepsilon^\nu\cdot l_\nu$ was 5—7%. The effective thicknesses of the absorbing layer were l_{1736} = 1.53 μm; l_{1783} = 1.49 μm; l_{715} = 3.72 μm.

$$C_{C2} = C^0_{PC}, C_{MSA} = C^0_{MSA} - 2C_{C2} = C^0_{MSA} - 2C^0_{PC}.$$

In section II (50—66.7 mol.% MSA), the solution contains only the C1 and C2 complexes provided that the acid is completely bound

$$D_v = \varepsilon^v_{C2} \cdot l_v \cdot C_{C2} + \varepsilon^v_{C1} \cdot l_v \cdot C_{C1}, \qquad (6)$$

$$C^0_{PC} = C_{C1} + C_{C2}; \quad C^0_{MSA} = C_{C1} + 2C_{C2},$$

$$D_v/(C^0_{MSA} - C^0_{PC}) = \varepsilon^v_{C1} \cdot l_v + \varepsilon^v_{C2} \cdot l_v \cdot \frac{2C^0_{PC} - C^0_{MSA}}{C^0_{MSA} - C^0_{PC}}. \qquad (7)$$

In the range of compositions of 33.3—50 mol.% MSA (section III), the absorption is due to the C1 and MSA · (2PC) (C3) complexes:

$$D_v = \varepsilon^v_{C1} \cdot l_v \cdot C_{C1} + \varepsilon^v_{C3} \cdot l_v \cdot C_{C3}. \qquad (8)$$

If PC is completely bound in the complexes

$C^0_{MSA} = C_{C1} + C_{C3}$; $C^0_{PC} = C_{C1} + 2C_{C3}$ and

$$D_v/(C^0_{PC} - C^0_{MSA}) = \varepsilon^v_{C1} \cdot l_v + \varepsilon^v_{C3} \cdot l_v \cdot \frac{2C^0_{MSA} - C^0_{PC}}{C^0_{PC} - C^0_{MSA}}. \qquad (9)$$

When PC is present in a more than twofold excess (section IV; 0—33.3 mol.% MSA),

$$D_v = \varepsilon^v_{C3} \cdot l_v \cdot C_{C3} + \varepsilon^v_{PC} \cdot l_v \cdot C_{PC}, \qquad (10)$$

$C_{C3} = C^0_{MSA}$ and

$$C_{PC} = C^0_{PC} - 2C_{C3} = C^0_{PC} - 2C^0_{MSA},$$

$$D_v/(C^0_{PC} - 2C^0_{MSA}) = \varepsilon^v_{PC} \cdot l_v + \varepsilon^v_{C3} \cdot l_v \cdot \frac{C^0_{MSA}}{C^0_{PC} - 2C^0_{MSA}}. \qquad (11)$$

The variation of the optical density of bands at 1736 and 1783 cm^{-1} is described by relations (6)—(11) (Fig. 5). The $\varepsilon^v \cdot l_v$ values found for different sections are presented in Table 3.

In addition to the bands due to C=O vibrations, the band at 715 cm^{-1}, relating to the skeletal vibrations of PC, is also sensitive to the solvation of the C1 complex. With excess PC, the optical density of this band varies in conformity with Eq. (4), *i.e.*, it is described by the absorption of PC and C1. However, with an excess of the acid, the optical density is not proportional to the PC concentration, *i.e.*, the concentration dependence of D_{715} cannot be described

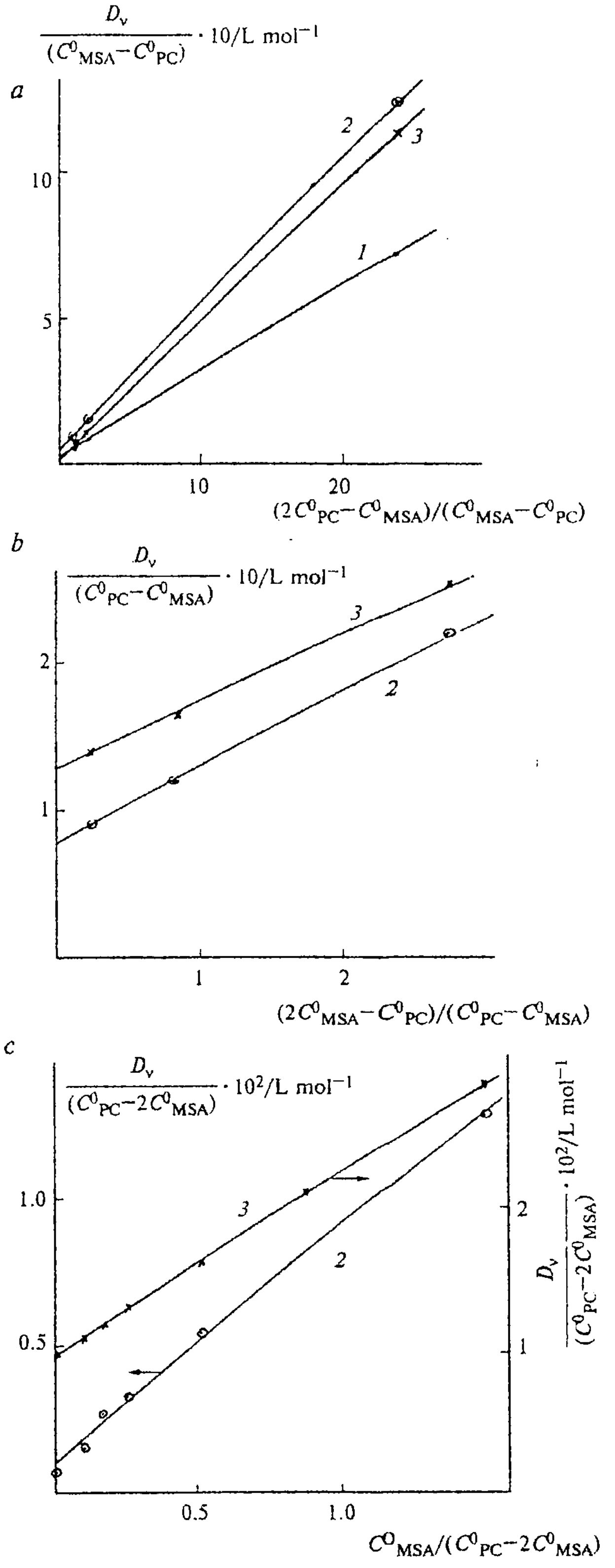


Fig. 5. Graphical solution of Eq. (6) (*a*) for 715 (*1*), 1736 (*2*), 1783 cm^{-1} (*3*) and Eqs. (8) (*b*) and (10) (*c*) for 1736 (*2*) and 1783 (*3*) cm^{-1}.

by the absorption of solely C1 complexes. The variation of D_{715} in sections I and II corresponds to the absorption of the C1 and C2 complexes, *i.e.*, it obeys Eqs. (5) and (6) (see Fig. 5). The absorption coefficients thus obtained are also presented in Table 3; it can be seen that the ε^{v}_{C1}, ε^{v}_{C2}, and ε^{v}_{C3} coefficients are markedly different. This indicates that three different sorts of species are actually present in the system. The slight differences between the coefficients found from the concentration dependences for various sections of the system composition can be explained either by errors in the optical band measurements or by the effects of the change in the solvation, caused by the change in the equilibrium composition of the system, on the absorption coefficients of the complexes.

Since for the majority of bands (including the ν(O—H) bands of MSA), the absorption coefficients of the C1, C2, and C3 complexes do not differ, the C2 and C3 complexes are apparently the C1 complex solvated by an MSA or PC molecule, respectively.

* * *

Unlike the MSA—H_2O, MSA—DMSO, and MSA—DMF systems studied previously,[3,5,9] dissolution of propylene carbonate in MSA is not accompanied by protonation of the base or by the formation of ions or complexes with a strong symmetrical H-bond. This is due to the difference between the electron-donating properties of DMF, DMSO (DN_{SbCl_5} = 29.8), and PC (DN_{SbCl_5} = 15.1). In the MSA—PC system, molecular complexes C1 are formed due to hydrogen bonding between the >C=O group of PC and the H—O— group of MSA. When an excess of the acid or the base is present, complexes C2 or C3 are formed; the latter consist of the C1 complex solvated by an MSA or PC molecule.

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References

1. G. V. Yukhnevich, E. G. Tarakanova, V. D. Maiorov, and N. B. Librovich, *J. Mol. Struct.*, 1992, **265**, 237.
2. G. V. Yukhnevich, E. G. Tarakanova, V. D. Maiorov, and N. B. Librovich, *Usp. Khim.*, 1995, **64**, 963 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].
3. A. P. Kirilova, V. D. Maiorov, A. I. Serebryanskaya, N. B. Librovich, and E. N. Gur'yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1493 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1366 (Engl. Transl.)].
4. A. P. Kirilova, V. D. Maiorov, A. I. Serebryanskaya, N. B. Librovich, and E. N. Gur'yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2724 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 2525 (Engl. Transl.)].
5. A. P. Kirilova, V. D. Maiorov, A. I. Serebryanskaya, N. B. Librovich, and E. N. Gur'yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2435 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2226 (Engl. Transl.)].
6. V. D. Maiorov and I. S. Kislina, *Khim. Fizika*, 1993, **11**, 660 [*Sov. J. Chem. Phys.*, 1993, **11**, 956 (Engl. Transl.)].
7. V. D. Maiorov, S. G. Sysoeva, O. N. Temkin, and I. S. Kislina, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1577 [*Russ. Chem. Bull.*, 1993, **42**, 1511 (Engl. Transl.)].
8. V. D. Maiorov, I. S. Kislina, S. G. Sysoeva, and O. N. Temkin, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1757 [*Russ. Chem. Bull.*, 1995, **44**, 1688 (Engl. Transl.)].
9. V. V. Burdin, I. S. Kislina, V. D. Maiorov, S. G. Sysoeva, and N. B. Librovich, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2484 [*Russ. Chem. Bull.*, 1998, **47**, 2404 (Engl. Transl.)].
10. *Coordination Chemistry in Nonaqueous Solutions*, Ed. V. Gutmann, Springer-Verlag, Wien—New York, 1968.
11. N. J. Harrick, *Internal Reflection Spectroscopy*, Wiley Interscience, New York—London—Sydney, 1967.
12. A. Simon and H. Kriegsmann, *Chem. Ber.*, 1956, **B. 89**, 2384.
13. R. A. Pethrick and A. D. Wilson, *Spectrochim. Acta*, 1974, **30A**, 1073.
14. D. M. Minkin, in *Alkilenkarbonaty* [*Alkylene Carbonates*], Nauka, Leningrad, 1975, 164 (in Russian).
15. W. A. Proele, C. F. Adams, and B. H. Shoemaker, *Industrial and Engineering Chem.*, 1948, **40**, 1129.
16. M. I. Vinnik, *Usp. Khim.*, 1966, **35**, 1922 [*Russ. Chem. Rev.*, 1966, **35** (Engl. Transl.)].
17. S. Nafarajan and A. W. Iache, *The Chemistry of Nonaqueous Solvents*, Ed. J. J. Lagowski, Acad. Press., 1978, p. 54.

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