Acidity function of methanesulfonic acid solutions in DMF

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The acidity function of solutions of methanesulfonic acid (MSA) in DMF and H_2O were measured by the indicator method at 25 °C in the 0—100% concentration range. A higher ionizing activity of HCl complexes with DMF as compared to that of similar MSA complexes was established. The relative ionizing activity of MSA molecules, $H_5O_2^+$ ions, and ion pairs between MSA and DMF was determined.

Key words: solutions, acid-base interaction, acidity function, methanesulfonic acid, *N,N*-dimethylformamide.

The replacement of water by an organic solvent substantially changes catalytic activity of acids in solutions.[1] However, this fact remains to be explained. Acid-base interactions result in aqueous solutions of strong acids (HA) forming ions, whose composition and structure are well studied.[2,3] In nonaqueous solutions of acid, the formation of an HA—solvent complex is often reduced to the formation of ion pairs with a partial transfer of a proton (DMF,[4—6] *N*-methylpyrrolidone[7]) or molecular complexes (ethyl acetate, propylene carbonate[8]). On going from water to aprotic solvents, the mechanism of ionization of standard indicators used to determine the acidity function changes.[9] Protonation in aqueous solutions[2,10] gives way to the formation of ion pairs in nonaqueous solutions of acids.[11] In addition, different solvations of weak organic bases (indicators and reagents) by water and organic solvents change their basicities. All these facts complicate comparison of the catalytic activities of solutions of acids in water and organic solvents.

The purpose of this work is to obtain data on the relative ionizing power of solutions of methanesulfonic acid (MSA) and HCl in DMF and solutions of MSA in water and DMF. For this purpose, the acidity functions of the MSA—H_2O and MSA—DMF systems were measured by the indicator method for concentrations of HA ranging from 0 to 100%. Data on the acidity of the HCl—DMF system are presented in the previous work.[11]

Experimental

Reagent grade DMF and MSA (Fluka) and indicators of the nitroaniline series with different basicities purified by recrystallization (Table 1) were used.

Table 1. p*K* values of indicators used for determination of acidity functions of MSA—H_2O and MSA—DMF systems at 25 °C

No.	Indicator	MSA—DMF		MSA—H_2O	
		pK^a	pK'^b	pK^b	pK^c
1	3-Nitroaniline	0.56	2.82	—	2.50
2	4-Nitroaniline	−1.09	1.17	1.00	0.99
3	2-Nitroaniline	−2.27	−0.01	−0.28	−0.29
4	4-Chloro-2-nitroaniline	−3.03	−0.77	—	−1.03
5	2,5-Dichloro-4-nitroaniline	—	—	−1.85	−1.82
6	6-Chloro-2-nitroaniline	−4.75	−2.49	—	−2.46
7	2,4-Dichloro-6-nitroaniline	−5.53	−3.27	—	−3.29
8	2,6-Dichloro-4-nitroaniline	—	—	−3.47	−3.24
9	2,4-Dinitroaniline	—	—	−4.12	−4.48
10	2,6-Dinitroaniline	−7.23	−4.97	−5.00	−5.48
11	6-Bromo-2,4-dinitroaniline	−8.66	−6.40	−6.40	−6.71

[a] Standardized to an infinitely dilute solution of MSA in DMF.
[b] Standardized to an infinitely dilute solution of MSA in H_2O.
[c] According to the data in Ref. 9.

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Measurement procedure. Degrees of ionization of indicators at 25 °C were determined on a Specord UV-VIS spectrophotometer using positions of the maximum on the absorption bands of their nonionized forms. The acidity functions H_0 of the MSA—H_2O system and H_s of the MSA—DMF system were calculated by the equation:

$$H_0(H_s) = pK + \log I, \qquad (1)$$

where I are the ratios of concentrations of nonionized and ionized forms of indicators, and K are their basicity constants. Solutions with desired composition were prepared by the gravimetric method. The densities of the MSA—H_2O[12] and MSA—DMF[5] systems were used for the calculation of molar concentrations.

Acidity function of the MSA—H_2O system. The acidity function H_0 of the MSA—H_2O system at 25 °C was obtained by the indicator method for compositions with the MSA concentration varying from 0.1 to 100%. Seven indicators of the nitroaniline series were used (see Table 1). An infinitely dilute solution of MSA in H_2O was chosen as the standard state for H_0. At acid concentrations lower than ~1% (~0.1 mol L^{-1}), a linear dependence between I and C_{HA} is observed for 4-nitroaniline, yielding $pK = 1$. Then $H_0 = -\log C_{HA}$. The value $pK = 1$ coincides with the data reported for other strong acids in aqueous solutions (see Table 1). The pK values of other indicators necessary for calculation of H_0 were obtained by the overlapping method.[11] For all pairs of indicators with similar pK values, the curves describing $\log I$ as a function of the content of MSA are parallel. The I values from 0.1 to 10 were used for calculation of H_0 by Eq. (1). The H_0 values characterizing the concentration range of 0.2—15.41 mol L^{-1} are presented in Table 2.

Acidity function of the MSA—DMF system. The acidity function H_s for the MSA—DMF system at 25 °C (see Table 2) was obtained similarly to H_0 for aqueous solutions of MSA. Eight indicators of the nitroaniline series were used (see Table 1). The H_s scale was standardized to an infinitely dilute solution of the acid in DMF. The equation $H_s = -\log C_{HA}$ is fulfilled at concentrations below ~2.8% (~0.28 mol L^{-1}). This range of concentrations of the acid corresponds to the region of ionization of 3-nitroaniline.

Table 2. Acidity functions H_0 of aqueous solutions of MSA and H_s for the MSA—DMF system at 25 °C

MSA (%)	MSA—H_2O		MSA—DMF	
	MSA/mol L^{-1}	H_0	MSA/mol L^{-1}	H_s
2	0.21	0.62	0.20	0.68
5	0.53	0.19	0.51	0.24
10	1.09	−0.20	1.04	−0.11
15	1.67	−0.47	1.61	−0.35
20	2.28	−0.70	2.20	−0.52
25	2.91	−0.90	2.82	−0.66
30	3.57	−1.10	3.47	−0.80
35	4.25	−1.28	4.16	−0.96
40	4.97	−1.48	4.86	−1.11
45	5.70	−1.70	5.60	−1.32
50	6.47	−1.95	6.36	−1.56
55	7.25	−2.23	7.15	−1.96
60	8.08	−2.58	7.97	−2.51
65	8.96	−2.97	8.82	−3.17
70	9.85	−3.40	9.70	−3.95
75	10.76	−3.91	10.59	−4.86
80	11.69	−4.45	11.47	−6.02
85	12.65	−5.01	12.46	−7.14
90	13.63	−5.77	13.42	−8.23
95	14.58	−6.70	12.40	−9.20
100	15.41	−7.74	15.41	−10.00

Results and Discussion

Comparison of ionizing power of solutions of MSA and HCl in DMF. Acid-base interactions in solutions of MSA and HCl in DMF accompanied by the formation of ion pairs K_1 and K_2 follow the same scheme.

$$\begin{gathered} HA + S \rightleftharpoons S...H...A\ (K_1), \\ S...H...A + HA \rightleftharpoons SH^+ \cdot (A...H...A)^-\ (K_2), \end{gathered} \qquad (1)$$

where S is a DMF molecule. Complexes K_1 are formed by a strong quasi-symmetrical H bond with a partial proton transfer[6] to the O atom of the DMF molecule. Complexes K_2 are contact ion pairs consisting of the protonated DMF molecule and the $(A...H...A)^-$ anion with a strong symmetrical H bond. Subsequent solvation of K_1 and K_2 in an excess of one of the components does not affect the structures of H bonds in these complexes. In the MSA—DMF and HCl—DMF systems, ionization of indicators (In) involves the addition of an acid molecule to the indicator. Therefore, the pK values of the same indicator in two systems are different. For example, for 3-nitroaniline in solutions of MSA and HCl, they attain the values of 0.56 and 0.91, respectively.

$$In + HA \overset{pK}{\rightleftharpoons} InHA \qquad (2)$$

The position of equilibrium (2) is determined by the acidity functions H_s. Complexes K_1 and K_2 donate an acid molecule in this process. The central H bonds in K_1 and K_2 with MSA and HCl differ in their atomic composition

	K_1	K_2
MSA	O...H...O	$(O...H...O)^-$
HCl	O...H...Cl	$(Cl...H...Cl)^-$

Therefore, the ionizing abilities of structurally similar complexes with MSA and HCl can differ.

The H_s values of the MSA—DMF and HCl—DMF systems for mixtures containing up to 65 mol.% HA are compared in Fig. 1. In an excess of DMF, both acids are bound in complexes K_1. In solutions with higher concentrations of acids, both complexes K_1 and K_2 are simultaneously present (Scheme 1, $C_{K_1} + C_{K_2} = C_{DMF}$). For compositions close to the equimolar ratio, equilibrium (3) is incompletely shifted to the left[4,5]:

$$2K_1 \rightleftharpoons K_2 + DMF. \qquad (3)$$

The MSA—DMF system, like solutions of HCl, contains complexes K_2 with ionizing power higher than that

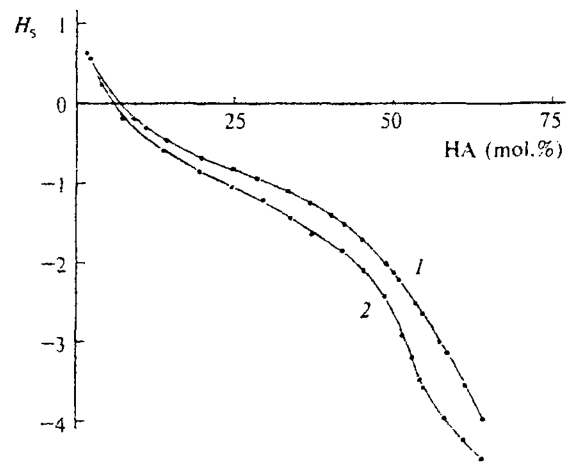

Fig. 1. Acidity functions H_s of MSA—DMF (*1*) and HCl—DMF (*2*) systems at 25 °C.

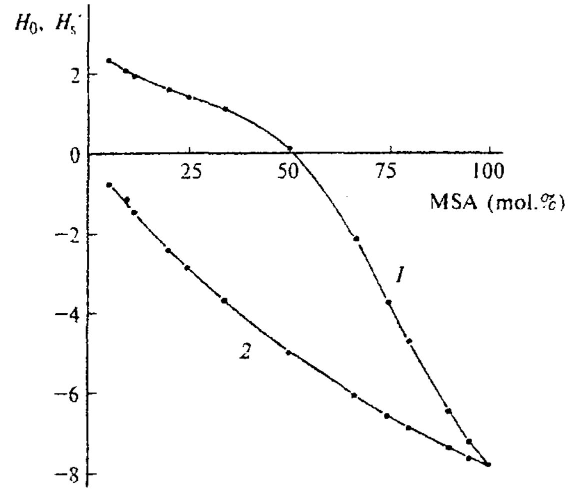

Fig. 2. Dependences of H_s' of the MSA—DMF system (*1*) and H_0 of aqueous solutions of MSA (*2*) on the molar concentration of MSA at 25 °C.

of K_1. In the range of 50—65 mol.% MSA, the acidity of the solution h_s ($H_s = -\log h_s$) continues to increase (see Fig. 1) as the concentration of K_2 increases and the total concentration of complexes increases. Figure 1 presents the acidity functions H_s of two systems at equal ratios of concentrations of ion pairs K_1 and K_2 characterized by different ionizing powers.

Standardization conditions imply that in the most dilute solutions of HCl and MSA, the acidity functions H_s of two systems are equal. As the acid concentration increases, the response of the H_s value for solutions of HCl is more pronounced. The difference $\Delta H_s = H_s(\text{MSA}) - H_s(\text{HCl})$ reaches 0.35 and 0.75 at concentrations of HA of 40 and 60 mol.% respectively. The acidity function in a solution is determined by concentrations and activity coefficients of different equilibrium forms of acid. For the same ratios of HA and DMF, the molar concentrations of the complexes in the system with HCl are higher than those in solutions of MSA. The differences in the concentration of complexes makes up ~25% of the ΔH_s value outlined above. Thus, the analysis of the data presented in Fig. 1 indicates a higher ionizing power of complexes K_1 and K_2 formed by HCl and DMF, as compared to similar complexes of MSA.

Comparison of acidity functions of solutions of MSA in water and DMF. Numerical values of acidity functions of different homogeneous systems with different acid-base properties are often used for correlating the catalytic activity and acidity. The conclusions obtained are seldom appropriate, because any scale of acidity is relative, and absolute values depend on the chosen standard state. This is clearly illustrated by the values of H_0 of the MSA—H_2O system and H_s of the MSA—DMF system presented in Table 2. The H_0 and H_s values are standardized in different manners: to infinitely dilute solutions of MSA in water and DMF, respectively. For 100% MSA, two values of the acidity function were obtained: −7.74 from the H_0 scale and −10 from the H_s scale. Both values were calculated with the same accuracy. Quantitative comparison of the catalytic properties of different acid-base systems necessitates that the acidity functions and basicity constants used for this purpose were standardized in the same way.

For solutions of MSA in DMF, the data in Table 2 make it possible to obtain the acidity scale standardized to an infinitely dilute solution of MSA in water. In this case, $H_0 = -7.74$ for 100% MSA, and the values of the acidity function at all MSA concentrations in DMF are 2.26 units more positive than H_s. Let us designate the obtained acidity scale as H_s'. The corresponding pK' of indicators (see Eq. (*1*)) are also 2.26 units more positive than those for the H_s scale (see Table 1). Figure 2 shows the H_0 values for aqueous solutions of MSA and H_s' of solutions of MSA in DMF for compositions containing from 5 to 100 mol.% of the acid. Solutions of MSA in DMF contain, along with acid molecules (>66.7 mol.% HA), only ion pairs K_1 and K_2 (see Scheme 1), whereas aqueous solutions of MSA contain the ions[3]: $(\text{MeSO}_3...\text{H}...\text{O}_3\text{SMe})^-$, $H_5O_2^+$, and $MeSO_3^-$. Figure 2 illustrates the relative ionizing power of MSA molecules as well as ions and ion pairs indicated above. Comparison of the acidity functions in the molar scale does not give valid conclusions, because the equilibrium composition of the catalyst is determined by the ratio of components rather than their concentration.

Ionization of indicators of the nitroaniline series in aqueous solutions of MSA leads to their protonation, while in the MSA—DMF system, the addition of an acid molecule is observed. A change in the ionization mechanism is possible in concentrated solutions of MSA in DMF. This conclusion follows from the pK′ values of indicators *6*, *7*, *10*, and *11* (see Table 1), which almost coincide with pK values of these indicators obtained in aqueous solutions of acids. The ionization region of indicators *6*, *7*, *10*, and *11* corresponds to concentrated solutions of MSA in DMF (>66.7 mol.% HA), in which the acid is not completely bound in complexes K_2. It appears that it is the intersection with MSA that leads to protonation of the indicators molecules. In an excess of the acid[5] in the MSA—DMF system partial dissociation of ion pairs K_2 is possible.

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References

1. E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, **11**, 1976.
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. 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.)].
5. 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.)].
6. I. S. Kislina, S. G. Sysoeva, N. B. Librovich, O. N. Temkin, I. L. Eremenko, and S. E. Nefedov, *Dokl. Akad. Nauk*, 1998, **360**, 649 [*Dokl. Chem.*, 1998 (Engl. Transl.)].
7. 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.)].
8. V. D. Maiorov, G. I. Voloshenko, A. P. Kirilova, and N. B. Librovich, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 312 [*Russ. Chem. Bull.*, 1999, **48**, 313 (Engl. Transl.)].
9. C. H. Rochester, *Acidity Functions*, Academic Press, London—New York, 1970, Ch. 6.
10. M. I. Vinnik, I. S. Kislina, and N. B. Librovich, *Dokl. Akad. Nauk SSSR*, 1980, **251** [*Dokl. Chem.*, 1980 (Engl. Transl.)].
11. I. S. Kislina, S. G. Sysoeva, and O. N. Temkin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1025 [*Russ. Chem. Bull.*, 1994, **43**, 960 (Engl. Transl.)].
12. L. N. Bascome and R. P. Bell, *J. Chem. Soc.*, 1959, 1096.

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