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Acidity function of methanesulfonic acid solutions in ethyl acetate

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The acidity function of solutions of methanesulfonic acid (MSA) in ethyl acetate (EA) was measured by the indicator method at 25 °C in the 0.4—100% concentration range. Molecular complexes formed by MSA and EA show a higher ionizing activity than $H_5O_2^+$ ions. The relative ionizing activity of the MSA · EA complexes and ion pairs formed by MSA and DMF was determined.

Key words: solutions, acid-base interactions, acidity function, methanesulfonic acid, ethyl acetate.

Non-dissociated acid molecules and equilibrium HA complexes with a solvent (S) act as catalysts in solutions of acids (HA). According to the scheme of acid-base interactions, molecular complexes, various ion pairs, and dissociated ions can be formed in solutions.[1—5]

$$S + HA \Leftrightarrow S \cdot HA \Leftrightarrow S...H...A \Leftrightarrow$$
$$\Leftrightarrow SH^+ \cdot A^-, SH^+ \cdot (AHA)^- \Leftrightarrow SHS^+ + A^-, (AHA)^-$$

In aqueous and alcoholic solutions acid dissociation gives positively charged proton disolvates[1,2] ($H_5O_2^+$ ions in aqueous solutions) and A^- or $(AHA)^-$ anions in excess of a base or an acid, respectively. Positively charged proton disolvates are not virtually formed in aprotic solvents. With excess base, acid-base interactions result, in many cases, in the formation of quasi-ionic pairs S...H...A,[3,4] and in the case of solvents with a low basicity (for example, ethyl acetate, EA), molecular complexes are formed.[5] Positively and negatively charged proton disolvates SHS^+ and $(AHA)^-$ and uncharged quasi-ionic pairs are formed when strong symmetric or quasi-symmetric H bonds are involved. The continuous absorption (CA) in the ~900—3000 cm^{-1} frequency region is an important feature of IR spectra of species with these H bonds.[1—4] When molecular complexes are formed, the IR spectra of the solutions contain no CA.[5] The CA coefficients at 2000—2200 cm^{-1} are determined by the charge of complexes with strong H bonds, and the CA parameters can be used for the identification of species formed in solutions.[6]

We have previously[7] determined the relative ionizing activity of methanesulfonic acid (MSA) molecules, $H_5O_2^+$ ions, and ion pairs formed by MSA and DMF molecules. This work is aimed at studying the ionizing ability of molecular complexes of MSA with EA. With this purpose, the acidity function H_0 of MSA solutions in EA from 0.4 to 100% was obtained by the indicator method.

Experimental

MSA and EA ("puriss" (H_2O < 0.005), Fluka) and recrystallized indicators of the nitroaniline series (Table 1) were used.

Measurement procedure. The degrees of ionization of indicators **1—7** in solutions of MSA in EA at 25 °C were determined on a Specord UV-VIS spectrophotometer at maxima of absorption bands of their non-ionizing forms. The acidity functions H_0 were calculated by the equation

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

where I is the ratio of concentrations of non-ionized to ionized forms of the indicator, and K_p is the constant of thermodynamic equilibrium. Solutions with a required composition were prepared by weight. Densities of MSA solutions in EA were used for the calculation of molar concentrations.[5]

Acidity function of MSA solutions in EA. The acidity function H_0 of the MSA—EA system at 25 °C was determined

Table 1. pK_p of indicators used for the determination of the acidity function (H_0) of MSA solutions in EA at 25 °C

Indicator	pK_p	
	MSA—EA	MSA—H_2O
4-Nitroaniline (**1**)	2.00	1.00*
2-Nitroaniline (**2**)	0.20	−0.28*
2-Nitro-4-chloroaniline (**3**)	−0.68	−1.03**
2-Nitro-6-chloroaniline (**4**)	−2.53	−2.46**
2,4-Dichloro-6-nitroaniline (**5**)	−3.28	−3.29**
2,6-Dinitroaniline (**6**)	−4.93	−5.00*
2,4-Dinitro-6-bromoaniline (**7**)	−6.40	−6.40*

* Ref. 7. ** Ref. 8.

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Table 2. Acidity functions (H_0) of MSA solutions in EA at 25 °C

MSA (%)	H_0	MSA (%)	H_0	MSA (%)	H_0
0.5	2.61	15	−1.50	60	−4.66
1.0	1.91	20	−1.99	65	−4.97
1.5	1.43	25	−2.43	70	−5.31
2.0	1.10	30	−2.81	75	−5.67
3.0	0.66	35	−3.12	80	−6.07
4.0	0.31	40	−3.43	85	−6.50
5.0	0.01	45	−3.75	90	−6.91
7.5	−0.52	50	−4.06	95	−7.27
10.0	−0.94	55	−4.36	100	−7.74

by the indicator method[8] for compositions with MSA concentrations from 0.4 to 100% (Table 2). Seven indicators of the nitroaniline series with different basicities (see Table 1) were used. To calculate H_0 of concentrated (70—100%) MSA solutions in EA, we used pK_p = −6.4 of indicator **7** obtained[7] in aqueous solutions of MSA by the standardization of the H_0 scale of the MSA—H_2O system to an infinitely dilute solution of the acid. In this case, the acidity function H_0 of MSA solutions in H_2O, DMF,[7] and EA are similarly standardized and H_0(100% MSA) = −7.74. For the calculation of H_0 of more dilute solutions, pK_p of indicators **1**—**6** were obtained by the overlapping method

$$\Delta pK(n,n-1) = pK_p(n) - pK_p(n-1) = \\ = \log I(n-1) - \log I(n).$$

With this purpose, a series of indicators was chosen in such a way that each pair *n*, *n* − 1 was put in correspondence to the region of acid concentrations (overlapping region) where the compound *n* − 1 is not yet ionized completely and the less basic indicator *n* is noticeably ionized. A satisfactory constancy of the Δp*K*(*n*,*n* − 1) values is fulfilled for each pair of indicators at different acid concentrations in the overlapping region. The *I* values from 10 to 0.1 were used for the calculation of H_0 and Δp*K*(*n*,*n* − 1). The obtained pK_p values of indicators **1**—**7** are collected in Table 1, and H_0 are presented in Table 2 and Fig. 1.

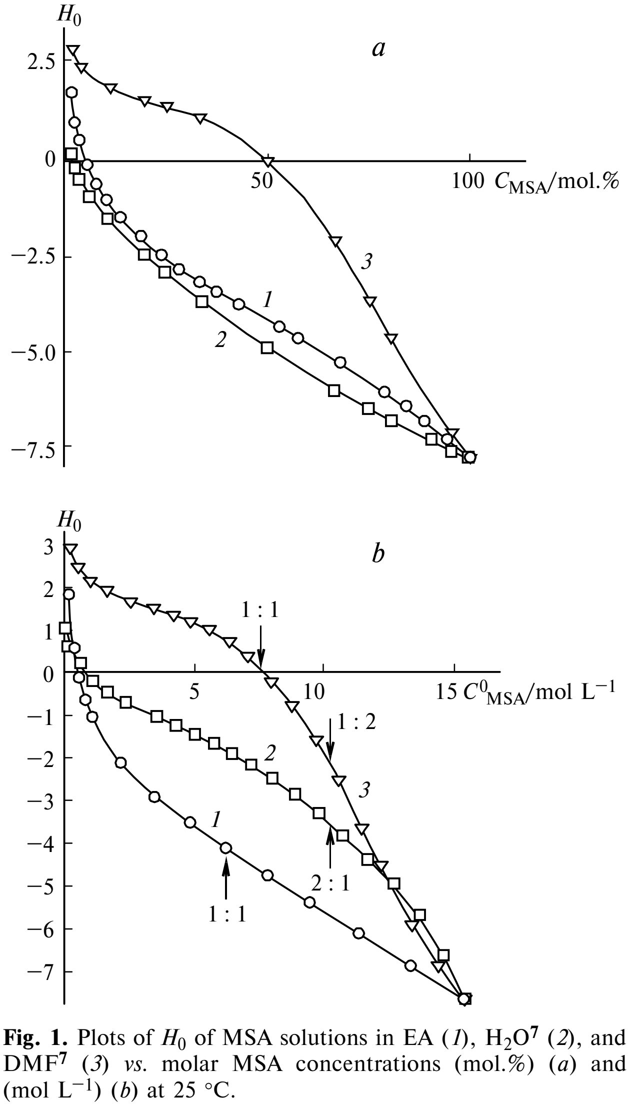

Fig. 1. Plots of H_0 of MSA solutions in EA (*1*), H_2O[7] (*2*), and DMF[7] (*3*) *vs.* molar MSA concentrations (mol.%) (*a*) and (mol L^{-1}) (*b*) at 25 °C.

Results and Discussion

In many cases,[9,10] the catalytic effect of acid solutions lies in the transformation of the reactant (R) into the reactive ionized form (RIF) caused by the interaction with the catalyst (C)

$$R + C \Leftrightarrow RIF.$$

For comparison of the ionizing power of acid solutions in several solvents, the acidity functions H_0 (see Refs. 8 and 11) can be used if they are similarly standardized. This requirement follows from the method of H_0 expression through the thermodynamic equilibrium

$$In + K \Leftrightarrow InK, \qquad (2)$$

$$K_p = a_{In}a_K/a_{InK};\ H_0 = -\log h_0 = -\log(a_K f_{In}/f_{InK}),$$

where In and InK are the non-ionized and ionized forms of the indicator, *a* are the activities, *f* are the activity coefficients, and h_0 is acidity of the solution. In the calculations of H_0 by Eq. (1), we used the thermodynamic constants K_p expressed through the activities known with an accuracy to a constant. Therefore, only if H_0 and K_p values are equally standardized, the numerical equality of the acidity functions in compared acid-base systems implies the same ionizing power of solutions with the same H_0. The acidity function H_0 is a quantitative measure of the ionizing power of an acid solution. Its numerical values determine the overall degree of ionization of the organic base. Ionized forms can be formed at several equilibrium stages of type (2) by the interactions of the indicator or reactant with acid-base complexes, whose ionizing abilities differ.

The values of acidity function of MSA solutions in H_2O, DMF,[7] and EA referred to the same standard state(H_0(100% MSA) = −7.74) are compared in Fig. 1. The dilution of MSA leads to a decrease in the value of acidity h_0 of the solution due to the formation of MSA—solvent complexes with weaker ionizing properties than those of MSA molecules. Schemes (1)—(3) of acid-base equilibria, which determine the equilibrium compositions of MSA solutions in H_2O (3),[2] DMF (4),[3] and EA (5),[5] and material balance equations for some intervals of MSA concentrations are presented below. Proton disolvates $H_5O_2^+$ and anions A^- or $(AHA)^-$ (Scheme 1) are formed[2] in aqueous MSA solutions.

Scheme 1

$$2\ H_2O + 2\ HA \Leftrightarrow H_5O_2^+ + (AHA)^-$$

$$2\ H_2O + HA \Leftrightarrow H_5O_2^+ + A^-$$

for a concentration interval of
70—100 mol.% HA we have

$$[HA]_0 = [HA] + 2\ [AHA^-]$$

33—70 mol.% HA

$$[HA]_0 = [HA] + 2\ [AHA^-] + [A^-]$$

0—33 mol.% HA

$$[HA]_0 = [A^-]$$

In solutions with concentrations between 70 and 100 mol.% HA non-dissociated acid molecules and $(AHA)^-$ anions exist at equilibrium, in less concentrated solutions the A^- anions are present as well, and in dilute solutions only the A^- anions are at equilibrium. The $H_5O_2^+$, $(AHA)^-$ ions and MSA molecules can be involved in the acid-catalyzed reactions at equilibrium stage (2) . In concentrated MSA solutions in DMF[3] (>67 mol.% HA), as in the MSA—H_2O system, the acid is partially bound to the $(AHA)^-$ anions. In more dilute solutions uncharged quasi-ion pairs K_1 with the incomplete proton transfer to the O atom of the DMF molecule are formed[12] (Scheme 2).

Scheme 2

$$\mathrm{DMF} + HA \Leftrightarrow K_1 \text{ (quasi-ion pairs)}$$

$$K_1 + HA \Leftrightarrow \mathrm{DMFH}^+ + (AHA)^-$$

for a concentration interval of
67—100 mol.% HA we have

$$[HA]_0 = [HA] + 2\ [AHA^-]$$

50—67 mol.% HA

$$[HA]_0 = [K_1] + 2\ [AHA^-]$$

0—50 mol.% HA

$$[HA]_0 = [K_1]$$

At concentrations from 67 to 50 mol.% HA, the components of a solution are completely bound to the K_1 complexes, $(AHA)^-$, and DMFH^+. In more dilute solutions, the acid is completely bound to the quasi-ion pairs K_1. In MSA solutions in DMF, the acid molecules, $(AHA)^-$ anions, and K_1 complexes possess the ionizing activity. In the MSA—EA system, the K_1 complexes are partially formed only in concentrated solutions (Scheme 3).

Scheme 3

$$\mathrm{EA} + HA \Leftrightarrow \mathrm{EA \cdot HA} \text{ (molecular complexes)}$$

$$\mathrm{EA} + HA \Leftrightarrow K_1$$

for a concentration interval of
80—100 mol.% HA we have

$$[HA]_0 = [HA] + [\mathrm{EA \cdot HA}] + [K_1]$$

50—80 mol.% HA

$$[HA]_0 = [HA] + [\mathrm{EA \cdot HA}];\ [\mathrm{EA \cdot HA}] = [\mathrm{EA}]_0$$

0—50 mol.% HA

$$[HA]_0 = [\mathrm{EA \cdot HA}]$$

At concentrations from 0 to 50 mol.% HA and from 50 to 80 mol.% HA, the acid and EA, respectively, are completely bound to molecular complexes.[5] Schemes (3)—(5) $[HA]_0$ and $[HA]$ designate the analytical and equilibrium acid concentrations.

The values of the acidity function of solutions in which the components are completely bound to complexes are specified in Fig. 1, *b*: $H_5O_2^+$ in the MSA—H_2O system, K_1 and $(AHA)^-$ in the MSA—DMF system, and $\mathrm{EA \cdot HA}$ molecular complexes in the MSA—EA system. The numerical H_0 values of these solutions change in the series: −4.17 ($\mathrm{EA \cdot HA}$), −3.64 ($H_5O_2^+$), −2.1 ($(AHA)^-$), 0.17 (K_1). The ionizing ability of the indicated non-solvated ions and uncharged complexes decreases in the same order. It follows from this series, in particular, that the quasi-ion pairs possess a very low ionizing ability. However, in many cases,[3,4,13] only these complexes are formed in wide concentration ranges (0—50 mol.% HA) in acid solutions in aprotic solvents, and the solvation of quasi-ion pairs by base molecules weakens their ionizing properties.[14] The non-solvated molecular complexes $\mathrm{MSA \cdot EA}$ have a higher ionizing power compared to the $H_5O_2^+$ ions in aqueous solutions, $\Delta H_0 = H_0(H_2O) - H_0(\mathrm{EA}) = 0.53$. The ionizing activity of the AHA^- anions is lower than that of the $H_5O_2^+$ ions and $\mathrm{MSA \cdot EA}$ complexes. Solvation by base molecules have different effects on the ionizing properties of different acid-base complexes. For example, on diluting MSA solutions in water with the same concentration ratios $[H_5O_2^+] : [H_2O]$ and $[\mathrm{MSA \cdot EA}] : [\mathrm{EA}]$,

Table 3. Acidity functions H_0 of MSA solutions in H_2O and EA and molar concentrations of $H_5O_2^+$ ions and molecular MSA·EA complexes at the same molar concentrations of $H_5O_2^+$ in the MSA—H_2O system and MSA·EA in the MSA—EA system at 25 °C

$H_5O_2^+$, MSA·EA (mol.%)	MSA—EA		MSA—H_2O	
	H_0	[MSA·EA] /mol L^{-1}	H_0	$[H_5O_2^+]$ /mol L^{-1}
100.0	−4.17	6.30	−3.64	10.30
50.0	−3.10	3.90	−2.90	8.85
33.3	−2.55	2.80	−2.45	7.80
12.5	−1.15	1.15	−1.40	4.70
5.6	−0.10	0.50	−0.80	2.55

the difference between the values of the acidity function ΔH_0 first decreases and than changes its sign. In strongly dilute solutions, the ionizing ability of the solvated $H_5O_2^+$ ions is much higher than that of the solvated MSA·EA molecular complexes (Table 3, Fig. 2). In dilute aqueous solutions $H_0 = -\log[\text{MSA}]_0$, and in MSA solutions in EA the acidity function changes more strongly than the squared acid concentration (see Fig. 2).

In concentrated MSA solutions (>50 mol.% HA), the ratio between the ionizing activities obtained for the non-solvated MSA·EA molecular complexes and $H_5O_2^+$ ions remains unchanged (see Fig. 1, *a*). The weak inflection in curve *1* reflects the formation of the K_1 complexes with a low ionizing ability in concentrated MSA solutions in EA. More negative H_0 values of aqueous MSA solutions compared to those of acidity functions of MSA solutions in EA are due to higher equilibrium concentrations of the MSA molecules (Table 4), whose ionizing ability is higher than that of the $H_5O_2^+$ ions and MSA·EA molecular complexes.

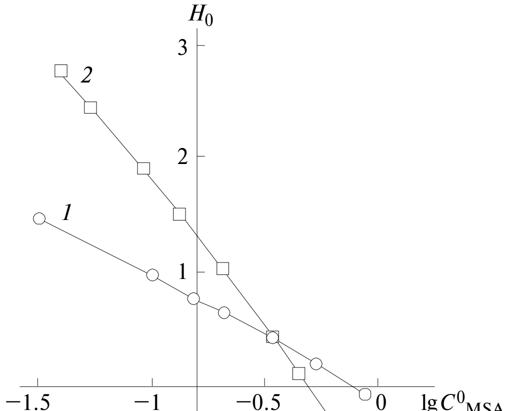

Fig. 2. Plots of H_0 of dilute solutions of MSA in water (*1*) and EA (*2*) *vs.* $\log[\text{MSA}]_0$ at 25 °C.

Table 4. Analytical $[\text{MSA}]_0$ and equilibrium [MSA] concentrations of MSA in concentrated aqueous solutions and EA at the same molar acid : base ratios at 25 °C

MSA (mol.%)	$[\text{MSA}]_0$/mol L^{-1}		[MSA]/mol L^{-1}		H_0	
	H_2O	EA	H_2O	EA	H_2O	EA
80	14.7	11.4	11.0	8.6	−6.8	−6.2
75	14.4	10.5	9.6	7.0	−6.5	−5.8

At MSA concentrations from 67 to 100 mol.%, in DMF solutions each base molecule binds two molecules to form a complex, and in EA solutions it binds one acid molecule to form molecular complexes and quasi-ion pairs (see Scheme (2) and (3)). Therefore, at the same molar concentrations, the equilibrium acid concentrations in MSA solutions in DMF are substantially lower. In addition, complex formation in DMF solutions produces the $(\text{AHA})^-$ anions with a lower ionizing power than that of the molecular complexes. These both reasons determine a sharper (as compared to H_0 in the MSA—EA system) decrease in the acidity in DMF solutions (see Fig. 1, *a*, curves *1* and *3*).

Thus, we studied the ionizing properties of solvated and non-solvated molecular complexes in MSA solutions in EA. The obtained data supplemented the series of relative ionizing power of the ions ($H_5O_2^+$, $(\text{AHA})^-$) and uncharged complexes (quasi-ion pairs K_1, molecular complexes MSA·EA), which are formed in aqueous and non-aqueous solutions of acids. This parameter determines the acidic and catalytic properties of the complexes. The series of ionizing power (MSA > MSA·EA > $H_5O_2^+$ > $(\text{AHA})^-$ > K_1) was established by comparison of the numerical values of acidity function H_0 for MSA solutions in water, DMF, and EA in which MSA is completely bound to but one type of acid-base complexes. The same standardization of acidity function is the necessary condition for the use of the thermodynamic scales of H_0 in comparing catalytic properties of acid solutions. A higher ionizing power of the MSA·EA molecular complexes compared to that of the $H_5O_2^+$ ions was concluded.

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