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Ionizing Properties of Complexes with Strong Symmetrical Hydrogen Bonds in Acid Solutions in Aprotic Solvents

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Abstract—The acidity functions H_0 of solutions of trifluoroacetic acid (TFA) in DMF and methanesulfonic acid (MSA) in 2-pyrrolidone over an acid (HA) concentration range of 0–100% and of H_2SO_4 solutions in 2-pyrrolidone (66.7–100 mol % HA) at 25°C were determined using the indicator method. Data were obtained on the relative ionizing powers of the quasi-ion pairs S···H···A (S is a solvent molecule) formed by DMF with acids (HCl, MSA, and TFA) and by MSA with DMF and 2-pyrrolidone. The effects of the acid anion (with MSA and H_2SO_4 solutions in 2-pyrrolidone acting as examples) and the counterion SH^+ (with MSA solutions in DMF and 2-pyrrolidone acting as examples) on the ionizing power of $(A\cdots H\cdots A)^-$ ions with strong symmetrical H-bonds were studied. It was found that, under comparable conditions, the replacement of a 2-pyrrolidone molecule by a DMF molecule in the SH^+ cation insignificantly decreased the acidity of solution, whereas the $(A\cdots H\cdots A)^-$ ions in H_2SO_4 solutions exhibited a much higher ionizing power than that of structurally similar anions in MSA solutions.

INTRODUCTION

A widespread mechanism of the catalytic effect of acid (HA) solutions consists in the participation of a catalyst in the equilibrium steps of reactant ionization [1]. The acidity function (for example, H_0) can serve as a quantitative characteristic of the ionizing power of a medium. As a rule, the acidity function is determined using the indicator method in studies on the equilibrium steps in the ionization of stable organic compounds (indicators) in acid solutions [2, 3]. Ionized species are formed by the interaction of indicators and reactants (**B**) with various acid–solvent complexes. The structure and concentration of these complexes in the acid–base system depend on the proton-donor and proton-acceptor properties of solution components and on the stoichiometric composition [4–6]. The H-complexes formed in acid solutions are widely different in ionizing power [7]. The higher the ionizing power, the stronger the shift of the ionization equilibrium of base B in solutions with equal concentrations of various forms of catalyst Cat to the right:

$$B + Cat_i \rightleftharpoons BCat_i. \qquad (I)$$

The presence of $H_5O_2^+$ ions with a strong symmetrical H-bond is responsible for the high ionizing power of aqueous solutions of strong acids [1, 3]. Positively charged proton disolvates are practically not formed in aprotic solvents (**S**). In many cases where there is an excess of a base, the acid–base interaction is restricted by incomplete proton transfer in uncharged 1 : 1 complexes with a quasi-ion structure and the formation of quasi-ion pairs (S···H···A) [4, 5, 8]. Thus, acids were completely bound into these complexes in the solutions of HCl in *N*,*N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidone [4] or methanesulfonic acid (MSA) [5] and trifluoroacetic acid (TFA) [8] in DMF at concentrations of 0–50 mol % HA. In the case of an excess of acid, protonation of solvent molecules and formation of the negatively charged proton disolvates $(A\cdots H\cdots A)^-$ occur [5]. In the case of strong bases such as aliphatic amines or isoquinoline, complete proton transfer to the molecule S and the formation of the ion pair $SH^+ A^-$ occur [9]. The dependence of the ionizing power of MSA complexes on the degree of proton transfer in the H-bonds that form these complexes was studied by comparing the acidity functions of MSA in water, DMF, and ethyl acetate [7, 10].

The aim of this work was to study the effects of the proton-donor properties of acids and the base properties of solvents on the ionizing power of the quasi-ion pairs (S···H···A) and the anions $(A\cdots H\cdots A)^-$. For this purpose, the acidity functions H_0 of TFA solutions (3–100 mol %) in DMF and MSA (1–100 mol %) and H_2SO_4 (66.7–100 mol %) solutions in 2-pyrrolidone were determined by the indicator method. In addition, the values of H_0 for the H_2SO_4–2-pyrrolidone–1.5(3.5)% H_2O were found using a kinetic method [11].

EXPERIMENTAL

In this study, the following were used: puriss-grade MSA and DMF ($[H_2O]$ < 0.05 and 0.01%, respectively), purum-grade TFA and 2-pyrrolidone (all from Fluka), reagent-grade HCOOH, and nitroaniline indicators (Table 1) purified by recrystallization. The stock solutions of H_2SO_4 (98.5 (1.5% H_2O) and 100%) were prepared by the distillation of chemically pure sulfuric

Table 1. The values of pK_p for indicators from the nitroaniline series in TFA solutions in DMF and in MSA solutions in 2-pyrrolidone at 25°C

Indicator	pK_p	
	TFA–DMF	MSA–2-pyrrolidone
3-Nitroaniline (**1**)	2.35	3.02
4-Nitroaniline (**2**)	1.17	1.07
2-Nitroaniline (**3**)	−0.23	−0.08
2-Nitro-4-chloroaniline (**4**)	−1.13	−0.96
2,5-Dichloro-4-nitroaniline (**5**)	–	−1.76
2-Nitro-6-chloroaniline (**6**)	−2.66	–
2,4-Dichloro-6-nitroaniline (**7**)	–	−3.33
2,6-Dinitroaniline (**8**)	–	−4.86
2,6-Dinitro-6-bromoaniline (**9**)	–	−6.40

Table 2. Density (ρ) and the stoichiometric composition of the H_2SO_4–2-pyrrolidone system

H_2SO_4, %	ρ, g/cm^3	$[H_2SO_4]_0$, mol/l	[2-Pyrrolidone]$_0$, mol/l
99.96	1.830	18.65	0
97.00	1.813	17.93	0.64
95.14	1.794	17.40	1.08
91.15	1.760	16.36	1.82
86.11	1.718	15.08	2.78
80.98	1.676	13.84	3.75
77.24	1.648	12.98	4.40
70.82	1.602	11.57	5.52

acid followed by saturation with oleum; the concentrations were determined by conductometry.

The degree of ionization of indicators in solutions with different HA concentrations at 25°C was determined by spectrophotometry (Specord UV–VIS) from changes in the molar absorption coefficients (ε) at the absorption band maximums of unionized species B. Acidity function H_0 was calculated from the equation

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

where I is the concentration ratio between the unionized and ionized forms of the indicator, and K_p is the thermodynamic equilibrium constant of ionization of the indicator.

The solutions were prepared by weight. To calculate molar concentrations and ε, the densities (ρ) of H_2SO_4 solutions in 2-pyrrolidone were measured (Table 2) and published values of the densities of TFA solutions in water [12] and DMF [8] and MSA solutions in 2-pyrrolidone [13] were used.

The acidity functions H_0 of TFA solutions in DMF (3–100% HA) or MSA solutions in 2-pyrrolidone (1–100% HA) at 25°C were determined by the indicator method with the use of indicators from the nitroaniline series (**1**–**4** and **6** or **1**–**5** and **7**–**9**, respectively, Table 1). In the calculations of H_0 for concentrated solutions, the following values of pK_p for indicators **6** and **9** obtained by generating H_0 scales for aqueous MSA and TFA solutions were used: $pK_p(\mathbf{9}) = -6.40$ [10] and $pK_p(\mathbf{6}) = -2.66$. The values of pK_p for the other indicators were calculated from the equation

$$pK_p(n-1) = pK_p(n) + \log I(n) - \log I(n-1). \qquad (2)$$

For each pair n, $n-1$ of the test indicators, there is a region of HA concentrations where compound $n-1$ is not yet completely ionized and the less basic indicator n is noticeably ionized. Table 1 summarizes the values of pK_p calculated from Eq. (2). The standard states of the resulting acidity functions H_0 of TFA solutions in DMF and MSA solutions in 2-pyrrolidone (Fig. 1) are 100% acids (TFA and MSA, respectively).

The ionization of 2,4,6-trinitroaniline (**10**) was studied in concentrated H_2SO_4 solutions in 2-pyrrolidone (100–66.7 mol % HA). The absorbance was measured against reference solutions with the same concentrations of 2-pyrrolidone in H_2SO_4 as in a working cell at 25°C. The kinetics of HCOOH decarbonylation were studied in aqueous H_2SO_4 solutions (98.5–85%) and in the H_2SO_4 (1.5% H_2O) + 2-pyrrolidone and H_2SO_4(3.5% H_2O) + 2-pyrrolidone ternary systems at 25°C. Table 3 summarizes the densities and stoichiometric compositions of these systems. The reaction mixtures were stirred using a magnetic stirrer. Pressure changes in the course of kinetic experiments were measured in an automatic mode. The resulting kinetic curves were described by a rate equation for irreversible first-order reactions to deep degrees of conversion of the reagent.

RESULTS AND DISCUSSION

Acidity functions are frequently used for comparing the ionizing properties of various acid–base systems. This leads to correct conclusions only under conditions of equally standardized scales of H_0. This requirement follows from the procedure of determining H_0 through ionization equilibrium (I) and the use of basicity indices pK_p (known to within a constant, which depends on the standard state chosen) in calculations (Eq. (1)). This condition was met for the H_0 of TFA and MSA solutions, which are shown in Fig. 1. In this case, if the numerical values of H_0 are equal, the degrees of ionization of base B (equilibrium (I)) in HA solutions in S are equal for a number of acids and solvents. Taking into account the definition $H_0 = -\log h_0$ (h_0 is the acidity of the medium), the more negative the value of H_0, the higher the ionizing power of solution. For a solution of HA + S with an arbitrary composition, the acidity function depends on the equilibrium concentrations and ionizing properties of various catalyst species Cat_i. The ionizing power of Cat_i can be judged by comparing the numerical values of H_0 for a number of acid–base systems whose components are bound into only one type of H-complex.

In aqueous TFA solutions (Fig. 1a), a minimum of H_0 was reached at an HA : H_2O molar ratio of ~5 : 1 because of a decrease in the ionizing power of TFA molecules upon self-association. Both TFA dimers and higher order associates are formed in 100% acid [15]. The associates undergo decomposition upon dilution with water (which results in an increase in the acidity of solution), and HA complexes with water are formed. The ionizing properties of these complexes are weaker than those of TFA molecules. In aqueous TFA solutions, 1 : 1 complexes (K_h) are formed between the components (hydrates or ion pairs) [12]. The acid is partially or fully bound into these complexes at [TFA] > 8 mol %. In the range [HA] = 100–50 mol %, TFA molecules also occur in solutions, and $H_5O_2^+$ ions occur at [HA] from 8 to 33.7 mol %. In more dilute solutions, TFA is completely dissociated and $[TFA]_0 = [H_5O_2^+]$ [12]. In the TFA–DMF system when there is an excess of the base, the acid is completely bound into the quasi-ion pairs S···H···A (K_1). The K_1 complexes are also formed in more concentrated solutions, whereas the protonation of the DMF molecule and the formation of $(A\cdots H\cdots A)^-$ anions occurs at [TFA] > 90 mol %:

$$S\cdots H\cdots A + HA \rightleftharpoons SH^+(A\cdots H\cdots A)^-. \qquad \text{(II)}$$

The quasi-ion pairs are solvated by DMF or TFA molecules depending on the ratio between components [8].

A comparison between the H_0 of TFA solutions in water and DMF (Fig. 1a) over the HA concentration ranges 5–8 and 35–50 mol % suggests that the ionizing power of K_1 quasi-ion pairs is much lower than that of $H_5O_2^+$ ions or K_h complexes. An analogous conclusion was drawn previously [10] for K_1 formed by a stronger acid (MSA) and DMF (Fig. 1b, curves *2* and *3*). It was also found in [10] that $(A\cdots H\cdots A)^-$ anions are less effective catalysts than $H_5O_2^+$ cations. This also explains the more dramatic change of H_0 in concentrated TFA solutions in DMF, as compared with aqueous TFA solutions.

Unlike the TFA–DMF system, equilibrium (II) is fully shifted to the right in MSA solutions in DMF and 2-pyrrolidone with an excess of acid, and the components are completely bound into $SH^+(A\cdots H\cdots A)^-$ complexes (K_2) at the ratio HA/S = 2 : 1. These complexes are also formed in equimolar solutions in the amount of ~5–7% of component concentrations:

$$2\,S\cdots H\cdots A \rightleftharpoons SH^+(A\cdots H\cdots A)^- + S. \qquad \text{(III)}$$

Figure 1b shows the acidity functions H_0 of MSA solutions in DMF and 2-pyrrolidone (curves *1*, *3*). As in MSA solutions in DMF, the ionizing power of anions that are constituents of K_2 complexes in the MSA–2-pyrrolidone system is much lower than that of acid molecules. Upon diluting 100% MSA with 2-pyrrolidone to [HA] = 66.7 mol %, the acidity function of solution changes from –7.74 to –2.6 ($\Delta H_0 = 5.14$). The difference in the H_0 of MSA solutions in DMF and 2-pyrrolidone of a 2 : 1 composition is equal to 0.5. The H_0 values of equimolar MSA solutions in these solvents are also insignificantly different. In both cases, the acidity is higher in 2-pyrrolidone solutions. When there is an excess of a base, quasi-ion pairs are solvated with one (in DMF solutions [5, 8]) or several (in 2-pyrrolidone [13]) solvent molecules. This leads to a decrease in the ionizing power of K_1 complexes, which is stronger in the MSA–2-pyrrolidone system. As a result, in dilute solutions with the same acid concentrations, the H_0 of MSA solutions in DMF is lower than that in 2-pyrrolidone. When there is an excess of a base, K_1 solvated complexes in TFA solutions in DMF and in MSA solutions in 2-pyrrolidone become practically equal in ion-

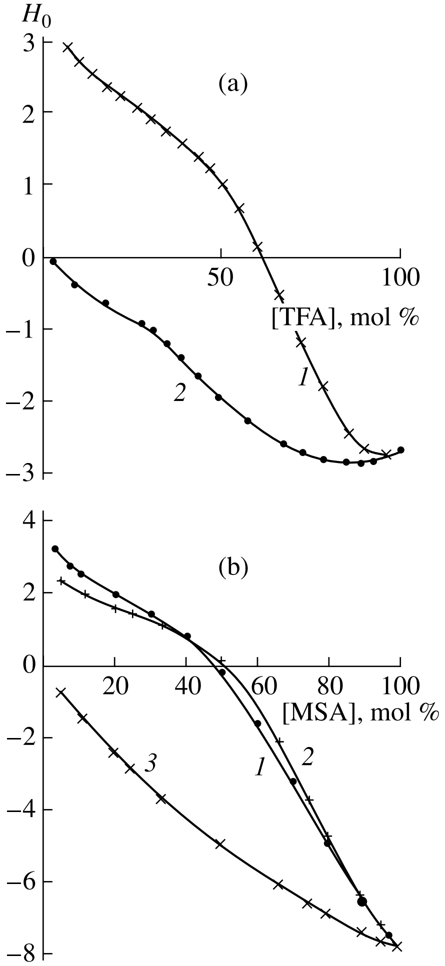

Fig. 1. (a) Dependence of the H_0 of TFA solutions in (*1*) DMF and (*2*) water on the concentration of the acid at 25°C: (*2*) data from [14]. (b) Acidity functions of MSA solutions in (*1*) 2-pyrrolidone, (*2*) DMF, and (*3*) H_2O at 25°C: (*2* and *3*) data from [10].

Table 3. Density (ρ) and the stoichiometric composition of the H_2SO_4 (1.5% H_2O) + 2-pyrrolidone and H_2SO_4 (3.5% H_2O) + 2-pyrrolidone systems at 25°C

H_2SO_4, %	ρ, g/cm^3	$[H_2SO_4]_0$, mol/l	$[H_2O]_0$, mol/l	[2-Pyrrolidone]$_0$, mol/l
98.5	1.833	18.41	1.53	0
91.40	1.774	16.53	1.37	1.50
87.47	1.737	15.49	1.28	2.29
83.12	1.701	14.42	1.20	3.12
78.59	1.665	13.34	1.11	3.95
96.5	1.833	18.03	3.57	0
91.77	1.790	16.75	3.31	1.03
89.84	1.772	16.23	3.21	1.44
86.84	1.743	15.43	3.05	2.05
81.61	1.695	14.10	2.79	3.07

izing power, whereas the acidities of 1 : 1 solutions differ by more than one order of magnitude (Fig. 1, curves *1*).

Figure 2a shows the dependence of $\log I$ on log [HA] plotted for indicator **1** in HCl, MSA, and TFA solutions in DMF. From these data, it follows that at equal acid concentrations the degrees of ionization of **1** are essentially different (by more than one order of magnitude). In our opinion, this suggests that the HA molecule is added to the indicator in the course of ionization. By analogy with aqueous acid solutions [3], if we consider the step of indicator ionization as a substitution reaction with the retention of quasi-ion-type H-bonds in ionized species

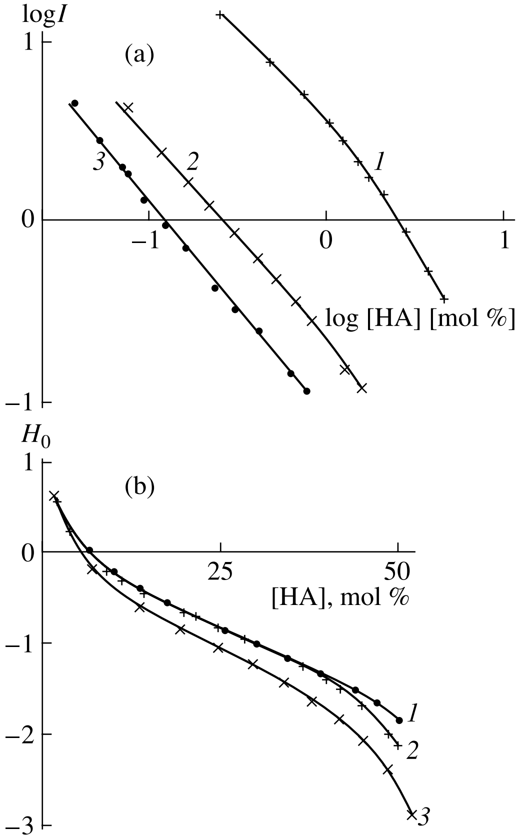

Fig. 2. Dependence of (a) the $\log I$ of 3-nitroaniline on log [HA] and (b) H_0 on [HA] (mol %) in the solutions of (*1*) TFA, (*2*) MSA [10], and (*3*) HCl [16] in DMF at 25°C.

$$B + \underset{K_1}{S\cdots H\cdots A} \rightleftharpoons B\cdots H\cdots A + S, \qquad \text{(IV)}$$

the replacement of the acid anion in K_1 can change both the ionizing power of solution H_0 and the ionization constant K_p of the indicator. The solvation of B, which depends on solvent properties, also affects the position of equilibrium (IV). Under given conditions ([HA], S, and temperature), the numerical values of H_0, pK_p and $\log I$ are related by Eq. (1). Presently, we cannot propose a procedure for determining the contributions of H_0 and pK_p to a change in $\log I$, which is required for the uniform standardization of acidity functions for solutions of the above acids in DMF.

Figure 2b shows the acidity functions H_0 of TFA, MSA, and HCl solutions, which were obtained as described below. In dilute solutions of the above acids, the concentration constants of ionization of indicator **1** are constant: $K_c = I$[HA]. The values of pK_c at 25°C are equal to –0.56 (TFA), 0.56 (MSA), and 0.91 (HCl). They were used for calculating the H_0 of dilute acid solutions and for determining pK_p of less basic indicators from Eq. (2). The H_0 scales thus obtained are standardized in different manners because the acidity functions of TFA, MSA, and HCl solutions in DMF are numerically equal to each other at the same concentrations of K_1 quasi-ion pairs, which are different in terms of ionizing power (Fig. 2a).

The dependence of H_0 on [HA] shown in Fig. 2b can be used for comparing relative changes in H_0 (ΔH_0) in the same ranges of acid concentrations. The values of ΔH_0 are practically equal in TFA, MSA, and HCl solutions in DMF over a wide range of [HA]. Differences in curves *1*–*3* in Fig. 2b are due to higher molar concentrations of K_1 in HCl solutions, as compared with TFA and MSA at equal ratios between components. The divergence of curves *1* and *2* in the range [HA] = 40–50 mol % is explained by the partial formation of K_2 complexes with higher ionizing capabilities in MSA solutions in accordance with equilibrium (III). In an equimolar solution of HCl in DMF, equilibrium (III) is also partially shifted to the right.

Figure 3a demonstrates changes in the ionizing power of concentrated sulfuric acid solutions upon dilution of 100% H_2SO_4 with water and 2-pyrrolidone. The experimental dependence of $\log I$ for 2,4,6-trinitroaniline (**10**) on the ratio between components in the H_2SO_4–2-pyrrolidone system (curve *1*) is compared with data on the ionization of this compound [17–19] in concentrated aqueous H_2SO_4 solutions (curve *2*). We decided on $\log I$ rather than acidity functions for comparing the ionizing properties because the basicity constants of indicator **10** reported in [17–19], which are required for calculating H_0, are somewhat different. The dependence of $\log I$ on $[H_2SO_4]$ can be matched one-to-one with changes in the acidity function (Eq. (1)). Curves *1* and *2* in Fig. 3a coincide in the range $[H_2SO_4]$ = 100–85 mol %; in more dilute solutions, the acidity decreases more rapidly upon dilution of H_2SO_4 with 2-pyrrolidone. At the component ratio H_2SO_4/2-pyrrolidone = 2 : 1, the difference $\Delta \log I$ is equal to ~0.8 (Fig. 3a, curves *1* and *2*). In this case, the change of H_0 in the H_2SO_4–2-pyrrolidone system upon dilution of 100% H_2SO_4 to the above composition is ~2.5. Recall that, in MSA solutions in 2-pyrrolidone, the acidity function of the system changes more dramatically ($\Delta H_0 = 5.14$) over the range [MSA] = 100–66.7 mol %. Consequently, the ionizing power of $(A\cdots H\cdots A)^-$ anions formed by a dibasic acid (H_2SO_4) is higher than that formed by a monobasic acid (MSA). Let us compare the observed changes in the acidity of H_2SO_4 solutions in water and 2-pyrrolidone with ion–molecule compositions. Over the range $[H_2SO_4]$ = 100–66.7 mol % in 2-pyrrolidone, as in the MSA–2-pyrrolidone system, the solvent is completely protonated and $[(A\cdots H\cdots A)^-]$ = [2-pyrrolidone]. The equilibrium ionization of indicator **10** in the H_2SO_4–2-pyrrolidone system can occur by the interaction of this indicator with H_2SO_4 molecules or $(A\cdots H\cdots A)^-$ anions. In concentrated aqueous H_2SO_4 solutions, H_3O^+ ions partially bound into $(H_3O^+ \cdot HSO^-)$ ion pairs at $[H_2SO_4]_0 < 81$ mol % and $(A\cdots H\cdots A)^-$ anions are formed [20]. It is our opinion that the coincidence of curves *1* and *2* in Fig. 3a at $[H_2SO_4] > 85$ mol % suggests that H_3O^+ ions exhibit an extremely low ionizing power, and their contribution to the acidity of solution can be ignored. In divergent curves *1* and *2* in Fig. 3a, the acidity of the H_2SO_4–2-pyrrolidone system decreased strongly with dilution of H_2SO_4. This is most likely due to higher concentrations of undissociated H_2SO_4 molecules in aqueous solutions than in nonaqueous solutions at equal molar concentrations of acid. However, we cannot exclude that the ionizing power of $H_3O^+ \cdot HSO^-$ ion pairs is higher than that of H_3O^+ ions, and the participation of these ion pairs in the step of indicator ionization cannot be ignored. The formation of a hydrogen bond in $H_3O^+ \cdot HSO_4^-$ ion pairs should be accompanied by a decrease in the degree of proton transfer to the H_2O molecule and should increase the ionizing power of these complexes. With the use of MSA solutions in water and aprotic solvents as an example, it was found that, as the degree of proton transfer in the resulting acid–base complexes increased, the ionizing power of these complexes decreased [7, 10]. Aqueous solutions of $(Et)_3NH^+Cl^-$ (complete proton transfer to the amine nitrogen atom) do not exhibit acid properties [21].

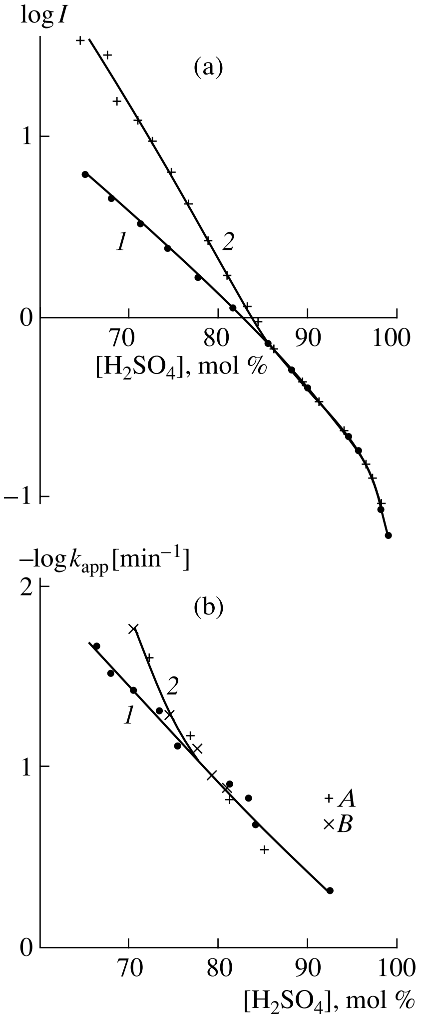

Fig. 3. Dependence of (a) the $\log I$ of 2,4,6-trinitroaniline and (b) the $-\log k_{app}$ of HCOOH decarbonylation on the concentration of H_2SO_4 in (*1*) water and (*2*) 2-pyrrolidone at 25°C: (*A*) H_2SO_4(1.5% H_2O) + 2-pyrrolidone; (*B*) H_2SO_4(3.5% H_2O) + 2-pyrrolidone.

Figure 3b shows the dependence of the apparent reaction rate constant of formic acid decarbonylation k_{app} on the concentration of H_2SO_4 in water and 2-pyrrolidone: H_2SO_4 (1.5% H_2O) + 2-pyrrolidone and H_2SO_4 (3.5% H_2O) + 2-pyrrolidone.

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O. \qquad (V)$$

Popkova *et al.* [11] found that the value of k_{app} of reaction (V) in concentrated aqueous H_2SO_4 solutions changed proportionally to the acidity of the medium and the following relationship was obeyed:

$$H_0 + \log k_{app} = -10.9 \pm 0.05.$$

That is, the curves plotted in Fig. 3b in the $-\log k_{\text{app}}$–$[H_2SO_4]$ coordinates demonstrate changes in the H_0 of the test solutions. As in Fig. 3a, curves *1* and *2* in Fig. 3b coincide in concentrated H_2SO_4 solutions, whereas the k_{app} of reaction (V) in 2-pyrrolidone solutions decreased more sharply at $[H_2SO_4] < 77$ mol %. This means that changes in H_0 in concentrated (>66.7% acid) H_2SO_4 solutions in 2-pyrrolidone obtained by kinetic and indicator methods are analogous. Inconsistency in concentrations below which the divergence of curves *1* and *2* in Figs. 3a and 3b is observed is due to the fact that kinetic experiments were performed in ternary solutions and an increase in the concentration of 2-pyrrolidone in either of the reaction series (H_2SO_4 (1.5% H_2O) + 2-pyrrolidone and H_2SO_4 (3.5% H_2O) + 2-pyrrolidone) was accompanied by a decrease in the concentration of water (Table 3). It was found that the acidity of solutions either remained unchanged or decreased only slightly as [2-pyrrolidone] was increased, whereas a decrease in the concentration of water resulted in an increase in the acidity.

Thus, we obtained data on the relative ionizing powers of complexes with strong symmetrical hydrogen bonds, uncharged S···H···A quasi-ion pairs with incomplete proton transfer to the solvent molecule, and anions as constituents of $SH^+(A\cdots H\cdots A)^-$ ion pairs in acid solutions (TFA, MSA, and HCl in DMF; MSA and H_2SO_4 in 2-pyrrolidone).

These complexes participate in the equilibrium steps of reactant ionization and, in many cases, are responsible for the catalytic activity of acid solutions. The above results were obtained by comparing the acidity functions H_0 of solutions with ion–molecule compositions. This provides an opportunity to study the effects of the proton-donor and proton-acceptor properties of acid–base system components and the solvation of the resulting complexes on catalytic properties. Thus, the basis of a target-oriented search for liquid-phase acid catalysts with specified properties can be expanded. The standardization of H_0 scales for acid solutions in aprotic solvents was considered.

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