The acidity functions $H_0{}^s$ of HCl solutions in EtOH with low water content

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The acidity functions $H_0{}^s$ of HCl solutions in EtOH—H_2O solvents containing 1.09, 3.0, and 5.0 % water have been measured at 25 and 40 °C by the indicator method. The concentration of HCl changes from 10^{-2} to 36 *m*. Nitroanilines, for which a protonation mechanism is realized in the studied systems, were used as indicators.

For each solvent, $H_0{}^s$ is temperature independent at $m_{HCl} < 4$, and acidity at $m_{HCl} > 4$ mol L^{-1} increases more rapidly at 25 °C than at 40 °C. The acidity functions of aqueous and water—ethanol solutions of HCl were compared, and the concentrations of proton solvates of different compositions and their relative protonating ability were evaluated.

Key words: acidity, indicator method, hydrochloric acid, ethanol, water.

The ability of a proton in solution to be included in particles (ions or uncharged complexes) with strong centro-symmetric H-bonds is its fundamental property.[1,2] Changes in the composition, structure, and concentration of these particles to a large degree define the effect of the nature of the solvent and acid concentration on the catalytic activity of a medium. Previously[3] the effect of the solvent composition on $H_0{}^s$ of HCl solutions has been studied for water-ethanol mixtures with an EtOH content from 0 to 73 mol. %. The interrelation between the acidity and the ion-molecular composition of the solutions has been established. A method for the calculation of $H_0{}^s$ in a wide range of HCl and EtOH concentrations has been proposed. The correlations found for the acidities are valid if the protons exist in the solutions in the $H_5O_2{}^+$ form, and they are true for the solutions of acids in different water-organic solvents.[4]

The purpose of this work is to study the effect of low concentrations of water (1—5 %) on the acidity function ($H_0{}^s$) of the HCl—EtOH—H_2O system for a wide range of acid concentrations. Proton disolvates of different compositions can be formed in these solutions.

Experimental

The initial concentrated solution of HCl in EtOH (34 %) was prepared by saturation of dehydrated EtOH (analytically pure, 0.43 % of H_2O) with gaseous HCl (from a cylinder). The acid concentration was determined by alkalimetry, and water content was determined by the Fischer method. Solutions of desired composition were prepared by the gravimetric method. Densities of solutions (ρ) were measured by pycnometry to determine the concentrations on the molar scale.

Indicators (3-nitroaniline (**1**), 4-nitroaniline (**2**), 2-nitroaniline (**3**), 4-Cl-2-nitroaniline (**4**), and 2,5-dichloro-4-nitroaniline (**5**)) were purified by recrystallization.

The values of the acidity functions ($H_0{}^s$) were obtained by the indicator method in a wide range of HCl concentrations in three water-ethanol solvents with a fixed composition and water contents of 1.09, 3.0, and 5.0 % at 25 and 40 °C.

The ratios between the concentrations of the nonionized and ionized forms (*I*) of indicators **1—5** were calculated from the measured optical densities at the absorption maxima of their nonionized forms in the visible spectral range (on a Specord UV-VIS instrument) according to the equation:

$$I = (\varepsilon_T - \varepsilon_{BH^+})/(\varepsilon_B - \varepsilon_T),$$

where ε_B, ε_{BH^+}, and ε_T are the extinction coefficients of the molecular, completely and partially ionized forms of the indicators.

The concentrations of HCl in the studied solutions are expressed in the scale of molar ratios *m* equal to the number of moles of HCl per 55.5 moles of EtOH and H_2O. This expression of HCl concentrations makes it possible to easily obtain the ratio of the concentrations of the components for a solution of any composition. In the studied solvents with water contents of 1.09, 3.0, and 5.0 % from 55.5 moles of EtOH and H_2O, the concentrations of water (m_{H_2O}) are equal to 1.4, 4.07, and 6.58, respectively.

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The error of the obtained values of the acidity functions does not exceed 0.05 for the change in H_0^s by two units and is the same for all of the systems studied.

We believe that, as in aqueous solutions of HCl, the acid is completely dissociated in the water-ethanol solvents studied when the concentration of the solvent (in moles) exceeds the concentration of HCl by 6—8 times.

Results and Discussion

The indicator method was used for constructing the acidity scales.[5] The values of H_0^s were obtained for the three systems studied, whose standard states are infinitely dilute HCl solutions in solvents of fixed composition.

$$H_0^s = pK^s_{BH^+} + \log I$$

The difficulty we met is associated with the justification of the ionization mechanism of the indicators used. The protonation mechanism is realized for these indicators in aqueous solutions of HCl, and the acidity of a solution begins to exceed its concentration at $m_{HCl} > 0.1$. This allows one to use indicators **1** and **2** for standardization of H_0 in aqueous solutions of acids. The concentration protonation constants of indicator **1** are not constant in the studied water-ethanol solutions of HCl in the range of its ionization ($m_{HCl} > 0.01$). The tangents of the slopes of log*I* *vs.* logm_{HCl} significantly differ from one and are equal to ~1.2 when the concentration of water in the solvent is 1—5 %. The same dependence was observed[6] for the ionization of **1** in water-methanol solutions of HCl. Its protonation constants ($K^s_{BH^+}$) are constant only in solvents with a content of MeOH from 0 to 42.6 %, $pK^s_{BH^+} > 1.79$. The ionization mechanism of aniline derivatives in HCl solutions in water-methanol with a low water content and in anhydrous MeOH is justified for the ionization of the more basic indicator, 2-Cl-aniline. For this indicator the concentration protonation constants are unchanged for all concentrations of water in HCl—MeOH—H_2O solutions.[6] Based on the previously obtained results,[6] we believe that the protonation mechanism also occurs when nitroaniline derivatives are ionized in the studied water—ethanol solutions of HCl. The $K^s_{BH^+}$ constants for indicator **1** were obtained by the Paul method[7] by extrapolation of the ($-\log m_{HCl} - \log I$) dependences on m_{HCl} to zero HCl concentration (Table 1). The values of $pK^s_{BH^+}$ for indicators **2—5** at 25 and 40 °C were determined by the method of overlap[5] and used for calculating the H_0^s values of the studied solutions of HCl (Table 2). The H_0^s values are the same in the $-\log m_{HCl}$ range from 2 to 1.2 in solutions with water concentrations of 1.09, 3.0, and 5.0 % at 25 and 40 °C:

$-\log m_{HCl}$	2	1.8	1.6	1.4	1.2
H_0^s	1.97	1.75	1.51	1.28	1.04

The data of Table 2 allow one to follow the effect of temperature on H_0^s of water-ethanol solutions of HCl with low concentrations of water. At $m_{HCl} \le 4$ the acidity functions are almost the same at two temperatures, 25 and 40 °C, for each composition of the solvent. The acidity of a solution at 25 °C is higher than that at 40 °C in more concentrated solutions with the same concentration of HCl in each of the solvents.

Table 1. Values of $pK^s_{BH^+}$ for indicators **1—5** in water-ethanol solutions of HCl with H_2O concentrations of 1.09, 3.0, and 5.0 %

Compound	$pK^s_{BH^+}$					
	1.09 % H_2O		3 % H_2O		5 % H_2O	
	25/°C	40/°C	25/°C	40/°C	25/°C	40/°C
3-nitroaniline	1.35	1.35	0.83	0.83	0.62	0.62
4-nitroaniline	−0.45	−0.45	−0.62	−0.62	−0.88	−0.85
2-nitroaniline	−2.1	−2.1	−2.22	−2.22	−2.54	−2.42
4-Cl-2-nitroaniline	—	−3.01	—	—	−3.57	−3.4
2,5-dichloro-4-nitroaniline	−3.92	−3.81	−3.81	−3.73	−4.14	−3.96

Table 2. H_0^s values for different HCl concentrations in water—ethanol solutions with water contents of 1.09, 3.0, and 5.0 %

m_{HCl}	H_0^s		m_{HCl}	$-H_0^s$	
	1.09 % H_2O	3; 5 % H_2O		1.09 % H_2O	3; 5 % H_2O
0.08	0.85	0.92	0.5	0.33	0.05
0.1	0.71	0.80	0.7	0.57	0.24
0.15	0.44	0.59	1	0.84	0.45
0.2	0.26	0.44	1.5	1.16	0.73
0.3	0.01	0.23	2	1.36	0.96
	3	1.66	1.30		

m_{HCl}	$-H_0^s$					
	1.09 % H_2O		3.0 % H_2O		5.0 % H_2O	
	25/°C	40/°C	25/°C	40/°C	25/°C	40/°C
4	1.84	1.76	1.56	1.49	1.62	1.56
5	1.99	1.89	1.83	1.71	1.89	1.73
6	2.10	1.99	1.99	1.89	2.09	1.91
7	2.19	2.08	2.14	2.01	2.30	2.08
8	2.29	2.17	2.28	2.12	2.47	2.23
9	2.37	2.25	2.40	2.23	2.62	2.36
10	2.46	2.33	2.51	2.33	2.75	2.48
12	2.63	2.48	2.72	2.52	2.99	2.72
14	2.80	2.63	2.90	2.70	3.23	2.93
16	2.98	2.78	3.09	2.88	3.45	3.14
18	3.17	2.93	3.26	3.05	3.66	3.33
20	3.33	3.09	3.43	3.21	3.87	3.53
22	3.50	3.24	3.59	3.36	4.07	3.72
24	3.67	3.39	3.74	3.52	4.25	3.88
26	3.84	3.54	3.89	3.67	4.42	4.04
28	4.00	3.69	4.04	3.81	4.56	4.19
30	4.15	3.84	4.18	3.95	4.69	4.33
32	4.30	3.98	4.32	4.09	4.81	4.46
34	4.44	4.10	4.46	4.22	4.93	4.60
36	4.58	4.13	4.58	4.35	5.04	4.73

Note. H_0^s values are the same at 25 and 40 °C in the range of m_{HCl} from 0.08 to 3.0.

The acidity functions of aqueous solutions of acids are often used to evaluate the effect of organic or water-organic solvents on the acidity function.[7,8] This approach may be effective when several conditions are fulfilled: the ionization mechanism is the same in the compared acid-base systems; acidities are obtained for solutions of acids in solvents with constant compositions;[3,4] the acid concentrations must be expressed in a scale that reflects the ratio of the stoichiometric concentrations of acid and base in solution. The acidity functions of HCl solutions in anhydrous EtOH and EtOH with 6.3 % H_2O $(H_0)_1$, and H_0 in water for the same molar concentrations of HCl have previously been compared.[7] The concentrations of H_2O greatly exceed the concentrations of HCl ($C_{H_2O}/C_{HCl} > 5$) even in concentrated aqueous solutions of HCl, which were used for comparison. The values of $(H_0)_1$ in concentrated solutions of HCl in solvents containing EtOH[7] relate to quite another range of the ratios of concentrations of the components, $(C_{H_2O} + C_{EtOH})/C_{HCl} < 2$. Recall that two solvent molecules are required for the dissociation of one molecule of acid in aqueous and water-alcohol solutions of HCl.[1,9]

The acidity functions ($H_0{}^s$) for the HCl—EtOH—H_2O systems (1.09, 3.0, and 5.0 % H_2O), $(H_0)_1$ of HCl solutions in EtOH and EtOH—6.3 % H_2O (see Ref. 7), and H_0 of aqueous solutions of HCl (see Ref. 10) are compared in Figs. 1 and 2 in the range of HCl concentrations from 10^{-2} *m* to 16 *m*. In order to convert molar concentrations of HCl in EtOH and EtOH—6.3 % H_2O into the scale of molar ratios, the measured values of ρ were used, which allowed us to obtain the dependences of ρ on C_{H_2O} for a wide range of HCl concentrations. The pK_{BH^+} value of indicator **2**, which was obtained for aqueous solutions of HCl and is equal to 0.99 (see Ref. 7), has been previously used in the calculation of $(H_0)_1$. Therefore, the $(H_0)_1$ values may be used only for relative comparisons and not to compare the absolute values of acidity in solvents of different compositions as a function of acid concentration.

As in aqueous solutions of acids, in water-alcohol and alcohol solvents the simplest stable solvates of the proton (when there is sufficient excess solvent) are ions with strong symmetric H-bonds, which are formed as the result of the interaction between a proton and two solvent molecules.[1,9,11,12] In anhydrous EtOH these ions are $(Et(H)O...H...O(H)Et)^+$ ions. In water-ethanol mixtures with a H_2O content of 1—6.3 % at low concentrations of HCl, the protons predominantly exist in the form of $H_5O_2{}^+$ ions (see Refs. 12, 13). The analysis of the dependences presented in Figs. 1 and 2 shows that the acidity increases with increasing m_{HCl} in all of the solvents, including anhydrous EtOH, in the range of the acid concentrations of $0.01 < m_{HCl} \le 0.3$ more rapidly than in aqueous solutions of HCl. This regularity cannot be associated with changes in the composition of the proton solvates (see Table 2). It is likely that there is subsequent solvation of the simplest stable proton solvates of different compositions by water molecules in the HCl—H_2O systems and predominantly by EtOH in the considered water-ethanol solvents.

The dependences of the acidity functions on m_{HCl} are the same for aqueous and water-ethanol solutions at $m_{HCl} \ge 0.3$ in solvents with 3.0, 5.0, and 6.3 % H_2O in a fairly wide range of $(H_0)_{H_2O}$ (from 0.4 to −1.16, and

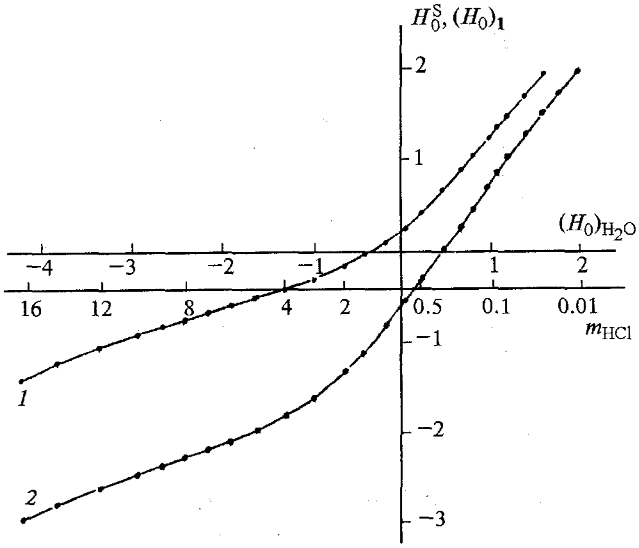

Fig. 1. Comparison of the acidity functions of aqueous $(H_0)_{H_2O}$ and of water-ethanol $(H_0)_1$ (*1*) and $H_0{}^s$ (*2*) solutions of HCl: (*1*), anhydrous EtOH; (*2*), EtOH—1.09 % H_2O, 25 °C. The $(H_0)_1$ values are taken from a previously published work.[7]

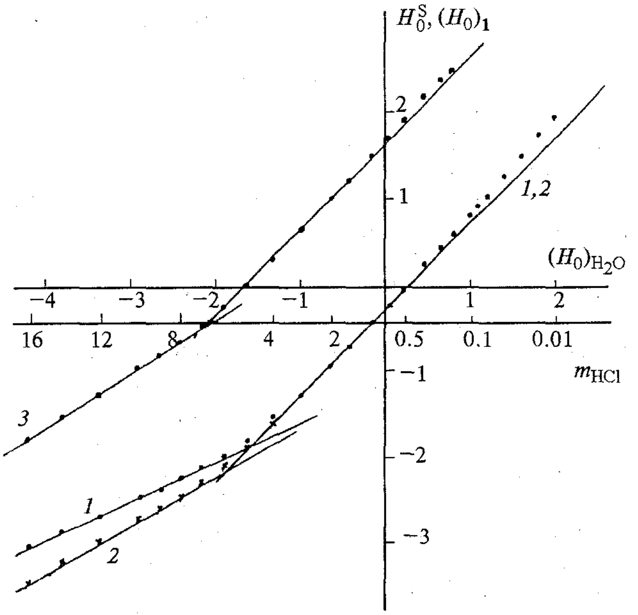

Fig. 2. Comparison of the acidity functions of aqueous $(H_0)_{H_2O}$ and water-ethanol $H_0{}^s$ (*1, 2*) and $(H_0)_1$ (*3*) solutions of HCl with a water content of 3 % (*1*), 5 % (*2*), and 6.3 % (*3*), 25 °C. The values of $(H)_1$ are taken from a previously published work.[7]

−1.75 and −2.16, depending on the concentration of water). This is clearly presented in Fig. 2 in which the tangents of the slopes of the dependences are equal to one in the indicated range of $(H_0)_{H_2O}$. The ranges of $(H_0)_{H_2O}$ presented above correspond to a change in m_{HCl} from 0.3 to ~3.5, ~5.5, and ~7.0 in the solvents with water contents of 3.0, 5.0, and 6.3 % (4.07, 6.58, and 8.1 in the scale of molar ratios), respectively. The relation $m_{H_2O} > m_{HCl}{}^{max} > m_{H_2O}/2$ (where $m_{HCl}{}^{max}$ is the maximum concentration of HCl at which the discussed correlation is fulfilled) is valid for three solvent compositions. This correlation can be explained by assuming that at $m_{HCl} = m_{HCl}{}^{max}$ the protons are in the form of solvates of two types, $H_5O_2{}^+$ and asymmetric solvates, and the protonating ability of these ions is almost the same in aqueous and water-ethanol solvents. In this case, it is necessary to assume that for the solution with $m_{HCl} = m_{H_2O}$ solvates of three types, $H_5O_2{}^+$, $(EtOH)_2H^+$, and $(EtOH \cdot H \cdot H_2O)^+$, coexist, and deviation from the correlation must be related to the lower protonating ability of the $(EtOH)_2H^+$ ions compared with ions that have at least one water molecule in their composition. In our opinion, this agrees well with the concept that the stage of protonation involves the replacement of one of the solvent molecules in a proton solvate by a molecule of an organic indicator or a reagent while the structure of the central H-bond is maintained.[14] In the range of HCl concentrations from 7 *m* to 16 *m*, the acidity functions for the three water-aqueous solvents (see Fig. 2) change more slowly than $(H_0)_{H_2O}$. The lower the concentration of water, the smaller the slope of the corresponding linear dependence. This is in qualitative accordance with the change in the fraction of asymmetric solvates of a proton at m_{HCl} = const as a function of the concentration of water in a solvent.

The stoichiometric compositions of the solutions with m_{HCl} = 18.5 and 27.75 correspond to three- and twofold excesses of base compared to HCl. These are concentrated solutions (m_{HCl} > 18.5) in which a change in the stoichiometric composition of the solution must be accompanied by a change in both the composition of the proton solvates and in their structures and in the degree of dissociation of the acid as well. However, the dependences of $H_0{}^s$ on m_{HCl} remain monotonic in the concentrated solutions of HCl in the solvents considered, and the increment of $H_0{}^s$ is almost independent of the concentration of water (see Table 2).

A comparison of the acidity functions in EtOH—H_2O with a water content lower than 1 % with $(H_0)_{H_2O}$ shows (see Fig. 1) that the whole range of HCl concentrations may be divided into two areas. In dilute solutions, the acidity increases significantly as m_{HCl} increases in solvents with EtOH, while in concentrated solutions this occurs in aqueous solutions of HCl. At $m_{HCl} \geq 3$ the difference in ΔH_0 at the same concentrations of HCl in anhydrous EtOH and in ethanol solutions with 1.09 % H_2O is almost the same.

Thus, the acidity functions $H_0{}^s$ have been measured in a wide range of HCl concentrations in water-ethanol solvents with 1.09, 3.0, and 5.0 % H_2O at 25 and 40 °C. The obtained scales of acidity are a measure of the protonating ability of the solutions studied. The conditions for the correct comparison of the acidity functions of solutions of acids in different solvents have been formulated. The relative protonating ability of proton solvates of different compositions in HCl water-ethanol solutions has been evaluated and compared with that of $H_5O_2{}^+$ ions in aqueous solutions of HCl.

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