

The Acidity Function in Solutions of Hydrogen Chloride in Methanol-Water Mixtures

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Values of Hammett's acidity function H_0 for solutions of hydrogen chloride in water and methanol and in their binary mixtures have been measured spectrophotometrically for the concentration range from 0.08 to 0.8 N. The proton-donating power of the solution decreases at first with increasing methanol content, passes through a minimum when the mole fraction of methanol is approximately 0.5, and then increases as pure methanol is approached. The acidic properties of the solutions are more pronounced in anhydrous methanol than in water, but the addition of even relatively small amounts of water to methanol is able to lower appreciably the proton-availability. The value of the equilibrium constant for the distribution of protons between methanol and water calculated from the values of the acidity function in methanol solutions containing low concentrations of water has been found to be in agreement with the value derived from kinetic data.

The acidity function H_0 introduced by Hammett and co-workers^{1,2} makes possible a comparison of the protolytic properties of a wide range of acid solutions. Values of this quantity have already been determined for aqueous solutions of several inorganic acids¹⁻⁶ and for solutions of hydrogen chloride in dioxan, ethanol and acetone⁷, and in their binary mixtures with water⁸. The values of the acidity function for solutions of hydrogen chloride in water-methanol mixtures presented in this paper have been measured for use in connection with kinetic data⁹.

RESULTS AND DISCUSSION

The measurement of Hammett's acidity function H_0 involves the determination of the ratio of the concentration of a suitably chosen uncharged indicator base to that of its conjugate acid in the acid solution under study. If B denotes the indicator base and BH^+ its conjugate acid, the thermodynamic constant of the equilibrium



is given by the mass-law expression:

$$\frac{[\text{BH}^+] f_{\text{BH}^+}}{[\text{B}] [\text{H}^+] f_{\text{B}} f_{\text{H}^+}} = K_{\text{B}} \quad (1)$$

in which the f 's are the respective activity coefficients. The acidity function H_0 is defined by

$$H_0 = \log K_{\text{B}} - \log \frac{[\text{BH}^+]}{[\text{B}]} = - \log \frac{f_{\text{B}} f_{\text{H}^+}}{f_{\text{BH}^+}} [\text{H}^+] \quad (2)$$

In order to obtain a common basis for the comparison of the proton-availabilities in different solvents, pure water can be taken as the reference solvent, in which case K_{B} is the constant for the indicator equilibrium in dilute aqueous acid.

The acidities of the solutions examined in the present study were such that only one indicator, *p*-nitroaniline, was required, since the ratio of concentrations of the base and conjugate acid forms of the indicator could be spectrophotometrically measured with sufficient accuracy in all cases. Measurements of the equilibrium ratio for *p*-nitroaniline in dilute aqueous hydrochloric acid solutions gave the value 1.02 for $\log K_{\text{B}}$. This value is intermediate between the value 1.11 obtained by Hammett and Paul² and the value 0.95 reported by Braude⁷ for the same indicator. The slight differences between the values for the indicator constant which may be due to differences in apparatus and technique are of no practical significance when the data for a given binary solvent system are compared, as even the selection of the reference solvent is in principle arbitrary.

The recorded values of the indicator ratio in water-methanol mixtures of varying hydrogen chloride content are presented in Table 1. The values λ are the wavelengths of the absorption maxima and ϵ the corresponding molar extinction coefficients. The indicator ratio has been computed by the equation

$$\frac{[\text{BH}^+]}{[\text{B}]} = \frac{\epsilon_{\text{N}} - \epsilon_{\text{A}}}{\epsilon_{\text{A}} - \epsilon_{\text{s}}} \quad (3)$$

where ϵ_{N} and ϵ_{A} are the extinction coefficients of the indicator solutions at the wavelengths of maximum absorption in the neutral solvent and in the acid solution in question, respectively, and ϵ_{s} is a small correction term which denotes the extinction coefficient of the conjugate acid of *p*-nitroaniline in the acid solution. For estimating ϵ_{s} , which cannot be measured directly, Braude and Stern^{7,8} took advantage of the fact that in the near ultraviolet region the absorption of the conjugate acid of an aromatic amine is of the same order of magnitude as that of the corresponding hydrocarbon lacking the amino group, and substituted the extinction coefficients of nitrobenzene for those of the conjugate acid of *p*-nitroaniline. The molar extinction coefficients of nitrobenzene varied from 20 to 90 in ethanol-water mixtures in the wavelength range in question. Since the values of ϵ_{s} are evidently of the same order of magnitude also in methanol-water mixtures, and since the experimental errors when measuring ϵ_{A} were approximately of the same order of magnitude, a

Table 1. Values of the indicator ratio of *p*-nitroaniline and of the acidity function H_0 in solutions of hydrogen chloride in methanol-water mixtures. α is the approximate slope of the plot of H_0 against $\log [\text{HCl}]$.

% MeOH by wt.	[HCl]	λ in $m\mu$	ϵ	$\log \frac{[\text{BH}^+]}{[\text{B}]}$	H_0	α
0	—	378	12 920			
0	0.0792	382	7 100	-0.08	+1.10	
0	0.198	380	4 070	+0.34	+0.68	-1.08
0	0.396	378	2 310	+0.67	+0.35	
0	0.792	379	1 220	+1.00	+0.02	
8.10	—	380	13 830			
8.10	0.0798	384	8 350	-0.18	+1.20	
8.10	0.199	381	4 890	+0.27	+0.75	-1.10
8.10	0.399	381	2 870	+0.59	+0.43	
8.10	0.798	386	1 550	+0.92	+0.10	
16.55	—	380	14 100			
16.55	0.0804	385	9 630	-0.33	+1.35	
16.55	0.201	384	5 700	+0.17	+0.85	-1.12
16.55	0.402	385	3 620	+0.47	+0.55	
16.55	0.804	386	1 950	+0.81	+0.21	
25.37	—	380	14 450			
25.37	0.0811	388	10 700	-0.45	+1.47	
25.37	0.203	387	7 210	+0.01	+1.01	-1.16
25.37	0.406	388	4 520	+0.35	+0.67	
25.37	0.811	388	2 410	+0.71	+0.31	
34.59	—	380	14 880			
34.59	0.0817	385	11 860	-0.59	+1.61	
34.59	0.204	388	8 560	-0.13	+1.15	-1.17
34.59	0.408	390	5 990	+0.18	+0.84	
34.59	0.817	391	3 150	+0.58	+0.44	
44.23	—	381	15 020			
44.23	0.0820	380	12 910	-0.78	+1.80	
44.23	0.205	383	10 590	-0.38	+1.40	-1.14
44.23	0.410	384	7 940	-0.05	+1.07	
44.23	0.820	381	4 580	+0.36	+0.66	
54.33	—	381	15 880			
54.33	0.0821	378	13 920	-0.85	+1.87	
54.33	0.205	382	11 850	-0.47	+1.49	-1.04
54.33	0.411	382	9 430	-0.16	+1.18	
54.33	0.821	380	6 280	+0.19	+0.83	
64.92	—	380	16 270			
64.92	0.0820	381	14 240	-0.84	+1.86	
64.92	0.205	382	12 420	-0.51	+1.53	-1.03
64.92	0.410	382	10 340	-0.24	+1.26	
64.92	0.820	381	6 560	+0.17	+0.85	
76.03	—	379	17 000			
76.03	0.0814	376	14 860	-0.84	+1.86	
76.03	0.204	379	12 900	-0.50	+1.52	-1.04
76.03	0.407	380	10 550	-0.21	+1.23	
76.03	0.814	379	6 880	+0.17	+0.85	
87.71	—	377	17 080			
87.71	0.0805	374	14 640	-0.78	+1.80	
87.71	0.201	376	12 270	-0.40	+1.42	-1.03
87.71	0.403	377	9 420	-0.09	+1.11	
87.71	0.805	377	6 000	+0.27	+0.75	
100	—	365	17 210			
100	0.100	371	3 830	+0.55	+0.47	
100	0.200	375	2 030	+0.89	+0.13	-1.12
100	0.300	379	1 350	+1.09	-0.07	
100	0.400	380	1 040	+1.22	-0.20	

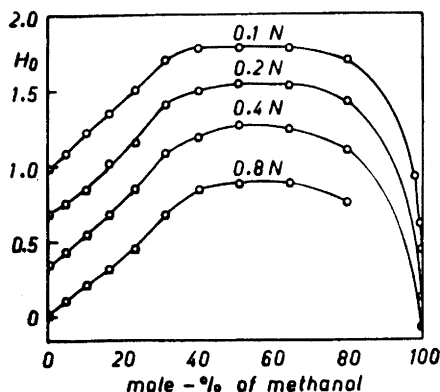


Fig. 1. The variation of H_0 with solvent composition in solutions of hydrogen chloride in methanol-water mixtures.

mean value $\epsilon_s = 60$ was used in all cases to correct for the absorption by the conjugate acid when calculating the indicator ratio by eqn. (3).

The values of the acidity function H_0 calculated by substituting in eqn. (2) the measured values of the indicator ratio and the value 1.02 given above for $\log K_B$ were found to vary approximately linearly with the logarithm of the hydrogen chloride concentration in each solvent mixture. In order to facilitate the calculation of H_0 -values for different acid concentrations by interpolation, the slopes of the plots of H_0 against $\log[\text{HCl}]$ for the different solvents are included in Table 1.

In Fig. 1 H_0 is plotted against the solvent composition in methanol-water mixtures for hydrogen chloride concentrations of 0.1, 0.2, 0.4 and 0.8 N. From the curves it is seen that H_0 increases at first and hence the proton-donating power of the solution decreases when methanol is added to water. The acidity function has its highest values when the mole fraction of methanol is between 0.4—0.7 and remains practically constant over this range. When pure methanol is approached, H_0 decreases rapidly and in anhydrous methanol its values are smaller than in water solution at the same hydrogen chloride concentrations. The variation of H_0 with solvent composition is similar in methanol-water as in ethanol-water mixtures, investigated by Braude and Stern⁸, but is not quite so marked in the former mixtures, which is natural since methanol resembles water more closely in its properties. In the methanol-water mixtures at 0.1 N hydrogen chloride concentration the maximum value of H_0 is by 0.79 unit higher than in water, whereas in the ethanol-water mixtures the corresponding increase is 1.24 units⁸. The value of the acidity function for 0.1 N hydrogen chloride in anhydrous methanol, +0.47, is slightly smaller than the value, +0.61, in anhydrous ethanol. Thus the proton-availability is somewhat higher in methanol than in ethanol solution, which is in accordance with the greater basicity of ethanol as compared with methanol¹⁰.

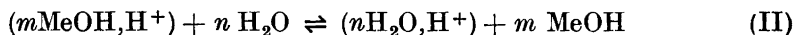
The data in Table 2 illustrate the effect of small additions of water to methanol on the value of H_0 . Owing to the method of preparing the solutions, the hydrogen chloride concentrations varied slightly for different additions of water, and the indicator ratios have been corrected to apply to the same

Table 2. The effect of low concentrations of water on the value of H_0 in methanol and the evaluation of the constant $K_{H_2O}^{MeOH}$ for the equilibrium of proton distribution between methanol and water. In neutral solution, $\epsilon = 17\ 210$.

$[H_2O]_{tot.}$	$[HCl]$	λ	ϵ	$[BH^+]/[B]$	$\{[BH^+]/[B]\}_{0.1}$	$\{H_0\}_{0.1}$	$x_{0.1}$	$K_{H_2O}^{MeOH}$
0.000	0.1000	371	3 830	3.55	3.55	+0.47	—	
0.051	0.0990	372	4 400	2.95	2.98	+0.55	0.20	(5.8)
0.101	0.0980	373	4 720	2.68	2.73	+0.58	0.32	4.2
0.150	0.0971	374	5 120	2.39	2.46	+0.63	0.48	4.1
0.198	0.0962	375	5 550	2.12	2.20	+0.68	0.67	4.2
0.245	0.0952	375	6 030	1.87	1.96	+0.73	0.89	4.5
0.291	0.0943	376	6 500	1.66	1.76	+0.77	1.13	4.7
0.336	0.0935	376	6 740	1.57	1.68	+0.79	1.24	4.4
0.380	0.0926	375	7 220	1.40	1.51	+0.84	1.52	4.8
0.424	0.0917	374	7 610	1.27	1.38	+0.88	1.79	5.0
0.467	0.0909	372	8 580	1.01	1.11	+0.97	2.60	(6.6)

concentration, 0.1 N, of hydrogen chloride that was present in anhydrous methanol by taking into account that the indicator ratio is approximately proportional to the acid concentration, at least in the narrow concentration range in question. The values with subscript 0.1 are the corrected values. The data in Table 2 show that small additions of water to methanol effect a pronounced increase in H_0 , *i.e.* the proton-availability is appreciably reduced by the additions. This result is in accordance with the observations of Goldschmidt and Thuesen¹¹ who found that the equivalent conductance of hydrogen chloride falls rapidly when small quantities of water are added to methanol.

As Braude and Stern⁸ have shown, the values of the indicator ratio determined for acid solutions in alcohol containing small amounts of water can be employed in a study of the alkoxonium-hydroxonium ion equilibrium. If a proton solvated by methanol is denoted by $(mMeOH, H^+)$ (m , the number of methanol molecules in the complex) and a proton solvated by water by (nH_2O, H^+) (n , the number of water molecules in the complex), the following equilibrium may be written:



The equilibrium constant for the reaction is given by

$$K_{H_2O}^{MeOH} = \frac{[nH_2O, H^+]}{[mMeOH, H^+][H_2O]^n} \quad (4)$$

when the methanol concentration is taken to be constant. If hydrogen chloride can be assumed to be completely dissociated in methanol and in methanol-water mixtures, and it is written

$$x = \frac{[nH_2O, H^+]}{[mMeOH, H^+]} \quad (5)$$

eqn. (4) takes the form

$$K_{H_2O}^{MeOH} = \frac{x(1+x)^n}{\{(1+x)[H_2O]_{tot.} - nx[HCl]\}^n} \quad (6)$$

In this equation, $[\text{H}_2\text{O}]_{\text{tot.}}$ denotes the total concentration of water present. The values of x can be computed if it is assumed that the minimum value of the indicator ratio $[\text{BH}^+]/[\text{B}]$ occurs in methanol-water mixtures in a region where the hydrogen ions have been completely transferred from methanol molecules to water molecules. The values of x can then be calculated by the equation

$$x = \frac{I_0 - I}{I - I_{\text{min.}}} \quad (7)$$

where I_0 , I and $I_{\text{min.}}$ are the indicator ratios for the same concentration of acid in pure methanol, in the methanol solution containing a small amount of added water under study, and in the mixture where it has a minimum value, respectively. By interpolation from the data in Table 1, the value of $I_{\text{min.}}$ for 0.1 N hydrogen chloride is found to be 0.17, while the value of I_0 given in Table 2 is 3.55. Using these values, and the indicator ratios for 0.1 N hydrogen chloride solutions in methanol-water mixtures of low water content, the values of x given in Table 2 are obtained by eqn. (7).

The number of water molecules, n , which participate in the solvation of proton (eqn. II) in methanol-water mixtures of low water content can be determined by eqn. (6). For the mixtures studied, it is found that n is equal to unity as the values of the equilibrium constant computed by eqn. (6), by substituting $n = 1$, remain constant within the limits of experimental error, as shown by the figures in the last column of Table 2. The value of n was found to be unity also for ethanol-water mixtures of low water content, investigated by Braude and Stern⁸.

The average value of $K_{\text{H}_2\text{O}}^{\text{MeOH}}$, 4.5 l mole⁻¹, in Table 2 is in excellent agreement with the value 4.8 l mole⁻¹ derived by Goldschmidt and Thuesen¹¹ from their kinetic data on the effect of small water concentrations on the rate of esterification in methanol.

EXPERIMENTAL

Chemicals. Methanol, *pro analysi* from E. Merck, Darmstadt, was dried with magnesium according to Lund and Bjerrum¹², refluxed over anhydrous cupric sulphate, and distilled. The *p*-nitroaniline, of *purum* grade from E. Merck, was crystallised twice from anhydrous ethanol; it melted at 149°C.

Solutions. The solutions, which contained 20 moles per cent or more water were prepared by mixing measured volumes of water, aqueous hydrochloric acid and methanol to which the indicator had been dissolved to give the chosen concentration. When calculating the concentrations of indicator and hydrogen chloride in the mixed solutions, the data for the contraction of methanol-water mixtures given in the International Critical Tables¹³ were employed. In a few cases the hydrogen chloride concentrations were checked also by titration, whereupon values in agreement with those calculated were obtained. The indicator concentration was varied from 1.5×10^{-5} M to 1.5×10^{-4} M depending upon the acidity of the solution. The solutions in pure methanol were prepared by passing carefully dried hydrogen chloride into anhydrous methanol. The methanol-water mixtures of low water content were prepared by mixing anhydrous methanol and methanol containing 5 moles per liter of water. The measurements on the solutions were made immediately after their preparation, in order that the slow reaction between hydrogen chloride and methanol could not influence the results.

Spectrophotometric measurements. The absorptions of the solutions required for the calculation of the indicator ratios were measured at $25 \pm 2^\circ\text{C}$ with a Beckman Model DU

Quartz Spectrophotometer. The solutions containing *p*-nitroaniline exhibited maximum absorptions at wavelengths close to 380 $m\mu$. A slit width of 0.15 mm was employed in the measurements; in the spectral range in question this corresponds to a half-intensity band width of about 1.3 $m\mu$. The absorbance of the indicator solution was in each case measured against the same solution without added indicator because the solvents were found to differ appreciably in their absorption in the wavelength range where the measurements were made.

The value of the indicator constant K_B of *p*-nitroaniline in water which was used for the calculation of the values of the acidity function was determined by measuring the indicator ratio in dilute aqueous hydrochloric acid solutions by the method described above. Table 3 gives the results from which the values of the indicator constants have been calculated according to eqn. (1) by taking into account that the activity coefficient ratio remains practically unity in dilute aqueous solutions.

Table 3. The determination of the indicator constant of *p*-nitroaniline in dilute aqueous hydrochloric acid solutions.

[HCl]	0.0158	0.0317	0.0475	0.0634	0.0792	
$\frac{[BH^+]}{[B]}$	0.170	0.320	0.500	0.680	0.827	
K_B	10.8	10.1	10.5	10.7	10.4	average $K_B = 10.5$

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