

401. *Acidity Functions. Part I. Dissociation of Hydrogen Chloride in, and Proton Affinities of, Some Oxygen-containing Solvents.*

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The nature of solutions of "strong" acids in non-aqueous solvents can be investigated by means of the acidity function H , first introduced by Hammett (cf. *Chem. Reviews*, 1935, **16**, 67). *p*-Nitroaniline being used as proton acceptor, H has been determined spectrometrically for 0.2—1M-solutions of hydrogen chloride in water and three organic oxygen-containing solvents. The variation of H with the acid concentration (c_A) can be represented by $H = m + n \log c_A$, where n has values close to unity in water, ethanol, and acetone, and a value of 0.5 in dioxan. These results indicate that in the range of acid concentrations studied, the dissociation of hydrogen chloride is large or complete in the first three solvents, but only small in dioxan, in agreement with evidence derived from conductivity measurements as far as these are available.

The equilibrium constants (K_B^S) of the proton-transfer reactions $SH^+ + B \rightleftharpoons BH^+ + S$, where SH^+ represents the solvated proton and B the proton-accepting indicator, can be calculated from H and are found to increase in the sequence water < dioxan < ethanol < acetone. Since K_B^S is an inverse measure of the proton-affinity of the solvent S , this is the sequence to be expected from simple considerations of decreasing electron-availability at the oxygen atom in the series ether > alcohol > water > ketone, except that the position of water is anomalous. The exceptionally high proton-affinity of water is further discussed in the following paper.

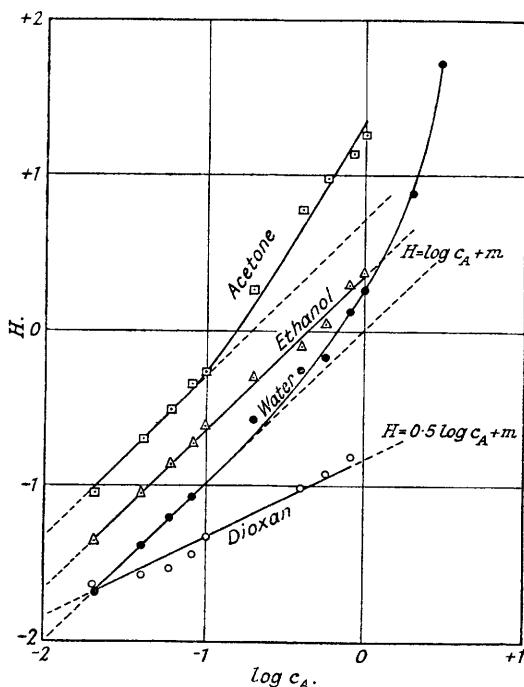
THE question of the nature of solutions of the so-called "strong" acids in solvents other than water has received much attention. Considerable information is now available regarding a number of individual solvent systems, but comparatively little progress has been made in establishing quantitative scales of comparison of such properties as proton-availability in different solvents. Apart from its intrinsic interest, this subject is of obvious importance to the interpretation of acid catalysis in non-aqueous solutions.

A quantity suitable for comparison of proton-availabilities is represented by the acidity function H , first introduced by Hammett (*loc. cit.*; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827; Hammett, "Physical Aspects of Organic Chemistry," McGraw Hill, New York, 1940; cf. Lewis and Biegeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1144; Schwarzenbach and Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 348) to deal with concentrated aqueous solutions of strong acids. The acidity function is an extension of the familiar indicator method of determining hydrogen-ion concentration in dilute aqueous solution, which depends on the colorimetric or spectrometric determination of the indicator ratio I , defined by $I = [BH^+]/[B]$, where B represents the indicator and BH^+ its conjugate acid. In dilute solution, the reaction $B + H^+ \rightleftharpoons BH^+$ obeys the mass law $K_B = [BH^+]/[B][H^+]$

where K_B is the indicator constant,* and $[H^+]$ is then directly proportional to I . In more concentrated acid solution, the classical mass law no longer applies, but I still represents a quantitative measure of the tendency of the solution to donate a proton to a neutral base. In order to provide a common basis for the use of different indicators, dilute aqueous solution is chosen as a reference state and H is defined by

$$H = \log ([BH^+]/[B]) - \log K_B^{H_0} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $K_B^{H_0}$ is the indicator constant in dilute aqueous solution. (The acidity function H as defined here is the negative value of Hammett's acidity function H_0 . The present definition is preferred because H , unlike H_0 , increases with increasing proton-availability.) The only assumption involved is that the ratio of different indicator constants is independent of the medium, and this is likely to be true for indicators of similar type. If only one indicator is employed, this question does not arise, and H , like I , is a direct experimental quantity.



The dependence of acidity function on hydrogen chloride concentration in water, dioxan, ethanol, and acetone.

In the present work, the acidity functions of solutions of hydrogen chloride in water and three other oxygen-containing solvents have been determined over a wide range of acid concentration, *p*-nitroaniline being used as indicator. The indicator ratios I were determined spectrophotometrically. If Beer's law is obeyed, and if ϵ_N and ϵ_S are the extinction coefficients at a chosen wave-length of the indicator B and its conjugate acid BH^+ in neutral solution, then $I = (\epsilon_N - \epsilon_A)/(\epsilon_A - \epsilon_S)$, where ϵ_A is the extinction coefficient in a given acid solution. Since the ultra-violet and the visible light absorption of an aromatic amine $R \cdot NH_2$ become identical, or nearly so, with that of the parent compound RH in sufficiently strong acid solution, ϵ_S can be derived from the light absorption of nitrobenzene. The location of the absorption band associated with the $R \cdot NH_2$ system is usually somewhat displaced in acid solution, and in order to minimise these medium effects, ϵ_N is determined at the wave-length position (λ_N) of the maximum in neutral solution, while ϵ_A and ϵ_S are determined at the wave-length position (λ_A) of the maximum in the acid solution. The spectrometric method of determining I is thus much to be preferred to the colorimetric one (cf. Flexser, Hammett, and Dingwall, *J. Amer. Chem.*

* The indicator constant K_B as defined here is the reciprocal of the indicator constant K_a employed by Hammett (*loc. cit.*).

Soc., 1935, 57, 2103), not merely because it allows of a higher accuracy in the estimation of absorption intensities, but also because spectral resolution makes it possible largely to eliminate the effects of a change in medium on the light absorption. This is of especial importance in non-aqueous media where these effects tend to be larger than in aqueous solution. A further advantage of the spectrometric method is that the choice of indicator is not limited to those showing selective light absorption in the visible range of the spectrum. The band maximum of *p*-nitroaniline does, in fact, lie in the near ultra-violet region, though it has been employed by Hammett and Paul (*loc. cit.*) in their colorimetric determinations of H_0 .

The choice of indicators is governed by two main considerations: the light-absorption properties, which should be such that ϵ_N is as large and ϵ_S as small as possible, and the base strength, which must be such that the ratio $[BH^+]/[B]$ has a suitable value in the acid solutions concerned. It can readily be shown (see Experimental) that the error in I consequent upon a given error in ϵ_A is least if ϵ_A has a value close to $\sqrt{\epsilon_N \epsilon_S}$, when the accuracy in I is about equal to that in ϵ_A , *i.e.*, *ca.* 2% in the present spectrometric work. For *p*-nitroaniline, the outer limits of I for an error in I not exceeding 10% are *ca.* 0.2 and 20. The range of solutions studied could be covered within these limits of I by using a single indicator.

The results of the measurements are collected in Table I. For water, the plot of I against c_A is linear up to $c_A = 0.1M$, and $K_B^{H^+}$, the limiting slope, has the value 9.0. The acidity functions are therefore given by $H = \log I - 0.954$, and the values thus obtained are set out in Table II. For acid concentrations up to about 0.1M in water and acetone, and up to about 1M in ethanol and dioxan, the plots of H against c_A are linear (see Fig.), *i.e.*, H can be expressed in the form $H = n \log c_A + m$. The values of the slopes n are 1.00, 1.05, and 1.05 in water, ethanol, and acetone, respectively, and 0.50 in dioxan. At higher acid concentrations n increases with c_A . The relative magnitudes of H in the different solvents at one acid concentration are somewhat dependent on the latter, but mostly increase in the order dioxan < water < ethanol < acetone.

TABLE I.

Indicator ratios for *p*-nitroaniline in solutions of hydrogen chloride: c_A = acid concentration (mol./l.); λ_N , ϵ_N refer to the wave-lengths ($m\mu$) and molecular extinction coefficients of the maxima in neutral solution; λ_A , ϵ_A refer to the acid solutions; ϵ_S is the extinction coefficient of nitrobenzene at λ_A in the same solvent; $I = (\epsilon_N - \epsilon_A)/(\epsilon_A - \epsilon_S)$.

Water.					Dioxan.				
$\lambda_N = 378, \epsilon_N = 12,800.$					$\lambda_N = 353, \epsilon_N = 15,400.$				
c_A .	λ_A^*	ϵ_A .	ϵ_S .	I .	λ_A .	ϵ_A .	ϵ_S .	I .	
0.02	378	10,800	50	0.18	353	12,900	150	0.20	
0.04	378	9,400	50	0.36	353	12,500	150	0.23	
0.06	378	8,300	60	0.55	353	12,200	150	0.26	
0.08	376	7,400	60	0.73	353	11,700	150	0.32	
0.10	373	6,800	80	0.89	353	11,000	150	0.40	
0.20	373	3,800	80	2.42	353	9,500	150	0.63	
0.40	373	2,200	80	4.91	353	8,400	150	0.84	
0.60	373	1,400	80	8.63	353	6,900	150	1.26	
0.80	371	980	90	13.2	351	6,500	160	1.40	
1.00	371	715	90	19.3	340	3,500	180	3.60	
2.00	360	320	150	69	—	—	—	—	
3.00	360	175	150	500	—	—	—	—	
4.00	360	150	150	—	—	—	—	—	

Ethanol.					Acetone.				
$\lambda_N = 374, \epsilon_N = 15,200.$					$\lambda_N = 366, \epsilon_N = 15,800.$				
c_A .	λ_A .	ϵ_A .	ϵ_S .	I .	λ_A^*	ϵ_A .	ϵ_S .	I .	
0.02	373	11,000	60	0.39	366	8400	85	0.89	
0.04	373	8,400	60	0.81	366	5500	85	1.89	
0.06	373	6,900	60	1.21	366	4200	85	2.82	
0.08	373	5,700	60	1.68	366	3100	85	4.23	
0.10	373	4,800	60	2.19	365	2800	85	4.80	
0.20	373	2,800	60	4.52	365	950	85	17.1	
0.40	372	2,000	60	6.80	362	310	100	74	
0.60	372	1,500	60	9.50	351	330	150	86	
0.80	371	860	65	17.9	350	290	160	120	
1.00	368	720	70	22.3	350	260	160	155	

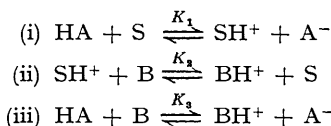
* Figures in italics signify that there is no clearly discernible maximum, but only an inflection or "bend" at this wave-length.

TABLE II.

Acidity functions for hydrogen chloride derived from indicator ratios of *p*-nitroaniline:
 $H = \log I - 0.954$.

c_A .	Water.	Dioxan.	Ethanol.	Acetone.	c_A .	Water.	Dioxan.	Ethanol.	Acetone.
0.02	-1.70	-1.65	-1.36	-1.05	0.40	-0.26	-1.03	-0.12	+0.92
0.04	-1.40	-1.59	-1.04	-0.68	0.60	-0.18	-0.94	-0.02	+0.98
0.06	-1.21	-1.54	-0.87	-0.50	0.80	+0.17	-0.81	+0.30	+1.13
0.08	-1.09	-1.45	-0.73	-0.33	1.00	+0.33	-0.40	+0.39	+1.24
0.10	-1.01	-1.35	-0.62	-0.27	2.00	+0.89	—	—	—
0.20	-0.57	-1.15	-0.30	+0.28	3.00	+1.75	—	—	—

The indicator ratio is governed by the three equilibria



where HA represents the undissociated acid and SH^+ the solvated proton. When the indicator concentration is small compared with the acid concentration, equilibrium (iii) may be neglected in comparison with (i) and (ii), hence

$$I = [\text{BH}^+]/[\text{B}] = K_2[\text{SH}^+]f_{\text{SH}^+}f_{\text{B}}/[\text{S}]f_{\text{BH}^+}f_{\text{S}} \dots \dots \dots (2)$$

where f 's represent activity coefficients; the factors containing these are completely symmetrical and may be assumed to be unity, hence

$$I = K_2[\text{SH}^+]/[\text{S}] = K_{\text{B}}^{\text{S}}[\text{SH}^+] = K_{\text{B}}^{\text{S}}\alpha c_A \dots \dots \dots (3)$$

and

$$H = \log (K_{\text{B}}^{\text{S}}/K_{\text{B}}^{\text{H}_2\text{O}}) + \log \alpha c_A$$

where K_{B}^{S} is the indicator constant * for the solvent S, and α the degree of dissociation of the acid. If α is large, $[\text{SH}^+] \sim c_A$ and $H = (K_{\text{B}}^{\text{S}}/K_{\text{B}}^{\text{H}_2\text{O}}) + \log c_A$. If α is small, $[\text{SH}^+] \sim \sqrt{K_{\text{A}}c_A}$ and $H = \log (K_{\text{B}}^{\text{S}}/K_{\text{B}}^{\text{H}_2\text{O}}) + 0.5 \log K_{\text{A}}c_A$, where K_{A} is the dissociation constant of the acid. The fact that the slopes of the H - c_A plots have values close to unity in water, ethanol, and acetone, and a value of 0.5 in dioxan, therefore indicates that the dissociation of hydrogen chloride is large or complete in the first three solvents, but only small in dioxan at concentrations above 0.02M.

These findings are in agreement with evidence derived from conductivity measurements. The complete or nearly complete dissociation of hydrogen chloride in water is generally accepted. Data for ethanol (Goldschmidt, *Z. physikal. Chem.*, 1915, **89**, 129; 1916, **91**, 46; 1927, **108**, 121; Murray-Rust and Hartley, *Proc. Roy. Soc.*, 1929, *A*, **126**, 84; Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330) lead to a value of 0.011 for the thermodynamic dissociation constant of hydrogen chloride in this solvent. Taking the mean activity coefficient as 0.24 for $c_A = 0.1\text{M}$ (Butler and Robertson, *Proc. Roy. Soc.*, 1929, *A*, **125**, 694), a value of 0.7 is obtained for α . The only data available for acetone appear to be those of Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, **3**, 12) and Sackur (*Ber.*, 1902, **35**, 1248). (Details of more recent measurements cited by Murray-Rust, Hartley *et al.*, *Ann. Reports*, 1930, **27**, 326, have not been published.) On plotting Sackur's values of Λ against $\sqrt{c_A}$, and extrapolating to $c_A = 0$, a value of 12.7 is obtained for Λ_0 , the equivalent conductivity at infinite dilution. The value of the initial slope of the Λ - $\sqrt{c_A}$ curve is 90, which is very much lower than the theoretical one of 350 calculated by Onsager's equation (cf. Davies, "The Conductivity of Solutions," Chapman and Hall, London, 1930), and thus does not readily permit the calculation of the true degree of dissociation. An approximate measure of α should be given by $\Lambda/\Lambda_0 - k\sqrt{\alpha c_A}$, where k is the observed slope; this leads to $\alpha > 1$, indicating large or complete dissociation. No measurements at all appear to have been made in dioxan, but solutions of hydrogen chloride in the related solvent ethyl ether have been examined by Kablukoff (*Z. physikal. Chem.*, 1899, **4**, 429) and by Mounajed (*Compt. rend.*, 1933, **197**, 44). Extrapolation of Mounajed's results gives values of 0.016 for Λ_0 and of 0.07 for the limiting slope of the Λ - $\sqrt{c_A}$ curve. The latter is again lower than that required by Onsager's equation. Calculation of α as above gives the value 0.2 when $c_A = 0.1\text{M}$, thus indicating only about 20% dissociation at this acid concentration. The

* In this and the following two papers K_{X}^{Y} represents the equilibrium constant of the reaction $\text{XH}^+ + \text{Y} \rightleftharpoons \text{YH}^+ + \text{X}$ in the solvent X, i.e., $K_{\text{X}}^{\text{Y}} = [\text{YH}^+]/[\text{XH}^+][\text{Y}]$.

value for dioxan is likely to be of the same order (cf. Gordy and Martin, *J. Chem. Physics*, 1939, 7, 99).

The differences in the acidity functions for the four solvents may now be considered. These will be due to differences in both the equilibria (i) and (ii). Since $I = K_B^0 \alpha c_A$, K_B^0 can be calculated from I by using the values of α deduced from conductivity measurements. For $c_A = 0.1M$, the values of I for water, dioxan, ethanol, and acetone are 0.9, 0.4, 2.2, and 4.8 (Table I), and α being taken as 1.0, 0.2, 0.7, and 0.9, the values of K_B^0 are 9, 20, 31, and 53. (The accuracy of the values for acetone and dioxan are dependent on the uncertainty in α , but this is unlikely to affect the sequence of magnitudes.) Since K_B^0 is an inverse measure of the proton-affinity or basicity of the solvent relative to the indicator, these values indicate basicities decreasing in the order water > dioxan > ethanol > acetone. The order of basicity expected from simple considerations of electron-availability at the oxygen atom for the formation of proton-solvates of the oxonium type, e.g., R_2OH^+ , ROH_2^+ , H_3O^+ , R_2C^+OH is ether > alcohol > water > ketone, since alkyl groups are electron-repelling relative to hydrogen, and since a double-bonded oxygen atom in a carbonyl compound is very electron-deficient compared with that in water. The sequence of basicities determined by the indicator constants is thus the expected one, except that the position of water is anomalous. The conclusion that water is a stronger base than ethanol is in agreement with evidence derived from the thermodynamic activity of hydrogen chloride in these two solvents (Heston and Hall, *J. Amer. Chem. Soc.*, 1934, 56, 1462) and from the effects of small concentrations of water on the catalytic properties (Goldschmidt, *Z. physikal. Chem.*, 1907, 60, 728; *Z. Elektrochem.*, 1914, 20, 473; Braude, *J.*, 1944, 443), electrical conductivity (Goldschmidt, *Z. physikal. Chem.*, 1914, 89, 129; Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, 67, 1330), and indicator ratios (Lapworth and Partington, *J.*, 1910, 97, 19; Braude and Stern, following paper) of ethanolic solutions. The fact, indicated by the present results, that water also appears to be a stronger base than the ether dioxan is even more remarkable. The exceptionally high proton-affinity of water is further discussed in the following paper.

EXPERIMENTAL.

Materials.—Dioxan was purified by treatment with sodium (Hess and Frahm, *Ber.*, 1938, 71, 2629), b. p. 101°/760 mm., m. p. 12°. Ethanol ("Burnett absolute alcohol") was dehydrated with magnesium ethoxide (Lund and Bjerrum, *Ber.*, 1931, 64, 210) until ϵ_A was constant. Acetone ("AnalaR") was treated with potassium permanganate and distilled from potassium carbonate (Scheibe, May, and Fischer, *Ber.*, 1924, 57, 1330). *p*-Nitroaniline was crystallised from ethanol, m. p. 149°. Nitrobenzene was distilled in nitrogen, b. p. 93°/18 mm., n_D^{20} 1.5518. Acid solutions were prepared by passing hydrogen chloride, obtained by dropping concentrated hydrochloric acid ("AnalaR") on concentrated sulphuric acid and dried over phosphoric oxide, into the solvent, and then diluting as required. Hydrogen chloride concentrations were determined by titration with sodium borate. All non-aqueous solutions were made up immediately before use and carefully protected from moisture.

Determination of the Indicator Ratio I.—For the technique of spectrometric measurements, see Braude, *J.*, 1945, 490. The indicator concentration varied from 0.002 to 0.02%. ϵ 's were independent of the indicator concentration within the experimental error ($\pm 2\%$). The data for the neutral solutions agree closely with those of Morton and McGookin (*J.*, 1934, 901) for ethanol, and of Dede and Rosenberg (*Ber.*, 1934, 67, 147) for water and dioxan. The error in I relative to the error in ϵ_A is given by

$$Z = (dI/I)/(d\epsilon_A/\epsilon_A) = \epsilon_A(\epsilon_S - \epsilon_N)/(\epsilon_N - \epsilon_A)(\epsilon_A - \epsilon_S) \dots \dots \dots (4)$$

Z has a minimum value when $\epsilon_A = \sqrt{\epsilon_S \epsilon_N}$. If ϵ_S is small compared with ϵ_N , as in the case of *p*-nitroaniline, $Z_{\text{min.}} \sim 1$, i.e., the errors in ϵ_A and I are nearly equal when ϵ_A has a value of the order of $\sqrt{\epsilon_S \epsilon_N}$, and (4) reduces to $Z \sim (I + 1)/I$, from which the lower limit of I for a given limit of error in I can readily be calculated. Thus, if the error in ϵ_A is 2% and the error in I is not to exceed 10%, then $Z = 5$ and the lower limit of I is 0.25. The upper limit of I for a given limit of error in I can be calculated by (4) using the constants for the indicator, but owing to the intrinsic uncertainty in ϵ_S and owing to the fact that the absorption band becomes ill-defined as ϵ_A approaches ϵ_S , this limit is somewhat lower than indicated by equation (4). In the present case, it is estimated that the error in I does not exceed 10% for the values of I up to about 20. As would be expected, the present values of I for the aqueous solutions differ somewhat from those previously obtained colorimetrically by Hammett and Paul (*loc. cit.*).