388. *Indicator Measurements in Solutions of Hydrochloric Acid in Acetic Acid.*

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Data on the ionisation of the indicators *o*-nitroaniline, 4-chloro-2-nitroaniline, *p*-nitrodiphenylamine, and 2 : 4-dinitroaniline, in solutions of hydrogen chloride (up to *ca.* 1·8M) in anhydrous acetic acid are presented. The application of the acidity function H_0 to solvents other than water is discussed.

FOR solutions of sulphuric, phosphoric, and perchloric acid in acetic acid, considerable data on indicator ionisation exist.[1] Solutions of hydrochloric acid have, by comparison, received little attention. Measurements at three acidities around 10^{-3}M have been given by Smith and Elliott,[2] who used two indicators and almost anhydrous acetic acid. The only other study is that of Ogata and Okano,[3] who employed a 10% aqueous solvent, one indicator, and hydrogen chloride concentrations below 1M. Results of measurements with an anhydrous solvent, four indicators, and hydrogen chloride concentrations up to 1·8M are now presented and discussed.

EXPERIMENTAL

Materials.—Anhydrous acetic acid (m. p. >16·6°) was prepared as previously described.[4] The *o*-nitroaniline, 4-chloro-2-nitroaniline, *p*-nitrodiphenylamine,* and 2 : 4-dinitroaniline were recrystallised samples with m. p. 71·6°, 116°, 135°, and 181°, respectively. Hydrogen chloride, prepared by dehydrating a concentrated aqueous solution, was dried by bubbling it through concentrated sulphuric acid. Stock solutions of hydrogen chloride in acetic acid were made by bubbling the dried gas into the solvent. Under ordinary conditions it is difficult to obtain a concentration much above 2·0M. The stock solutions were kept in carefully sealed flasks. Their mineral acid content was found by titration for chloride by Fajans's method.

Measurement of Ionisation Ratios.—The indicator ionisation ratios were found by the standard methods,[5] with a Beckman spectrophotometer. Cells fitted with caps having ground surfaces were used in order to exclude moisture. Measurements were always made at the wavelengths corresponding to the maximum absorption of the basic forms of the indicators, where the ionised forms were shown to have negligible absorption. The four indicators used exist effectively completely in their basic forms in pure acetic acid: the most basic of them, *o*-nitroaniline, is less basic [2] in this solvent than is α-naphtholbenzein, a compound which has been shown to be scarcely ionised.[6] Solutions of known amounts of an indicator and hydrochloric acid were made up by volume from stock solutions, the indicator concentration always being negligible compared with that of the acid. Solutions of the indicators in acetic acid alone, and also in the presence of hydrogen chloride, were sufficiently stable to permit accurate measurements, but, particularly for *o*-nitroaniline and 4-chloro-2-nitroaniline, were not completely stable over long periods.

RESULTS AND DISCUSSION

As Paul and Long [5] conclude, the wide applicability of the acidity function H_0 to solvents other than water has still to be established. For the function to be applied unchanged (*i.e.*, with the aqueous pK_a values) to other solvents, two conditions must be satisfied. First, as in water, analogous trends in ionisation must be shown by different Brønsted bases, and secondly, the relative basicities of the various bases, in these other

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* Kindly supplied by Dr. V. Gold.

[1] (*a*) Paul and Hammett, *J. Amer. Chem. Soc.*, 1936, **58**, 2182; (*b*) Gold and Hawes, *J.*, 1951, 2102; (*c*) Hall and Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487; (*d*) Rocek, *Chem. Listy*, 1956, **50**, 726.

[2] Smith and Elliott, *J. Amer. Chem. Soc.*, 1953, **75**, 3566.

[3] Ogata and Okano, *ibid.*, 1956, **78**, 5423.

[4] Satchell, *J.*, 1956, 3911.

[5] Paul and Long, *Chem. Revs.*, 1957, **57**, 1.

[6] Kolthoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

solvents, must be the same as in water. If the first condition is satisfied in any solvent then obviously an acidity scale *similar* to H_0 may be established. It is the second condition which is critical for the generality of H_0 itself.

It is suggested that the evidence [1d, 7] now clearly indicates that the first condition will prove to be far more widely satisfied than the second. Maintenance of the ideal of wide generality for H_0, in such circumstances, can only hinder the acknowledgment of the dependence of relative basicity on medium [8] as a real phenomenon. When it proves possible to construct acidity scales in solvents other than water, no matter how similar, it seems wisest to treat all such scales as, in principle, independent, though perhaps tying them to the aqueous scale at one point, so that comparisons (more or less rough) of acidity levels may still be made.[1d, 7c]

With such a procedure the pK_a values obtained in building up the various acidity scales will be those appropriate in the particular solvents concerned. Provided the medium is one in which dissociation is complete, they will be values of log $(a_{\mathrm{BH^+}}/a_{\mathrm{B}} \cdot a_{\mathrm{H^+}})$ (with an added constant if the scale is artificially tied to the aqueous scale at some point).

If the principle of the essential independence of different scales is accepted, then, in solvents in which dissociation is incomplete, and ion-pairs are prevalent, difficulties arise concerning the exact meaning of pK_a values determined by the usual step-wise procedure. In such solvents the ionisation ratios measured are of the composite type [6]

$$I_{\mathrm{B}} = (\sum_i c_{\mathrm{BH^+A}_i^-} + c_{\mathrm{BH^+}})/c_{\mathrm{B}}$$

summed over the contributions from all the acidic species, HA$_i$, present. Since the relative amounts of different acidic species in solution will, in general, change with changing acidity, it is clearly difficult, except in the special cases when only one acidic species is active, to give any simple, or useful, meaning to the pK_a's obtained from ionisation data which happen to run reasonably parallel. Nor, in fact, are such data very likely to run particularly parallel in the general case for, ignoring $c_{\mathrm{BH^+}}$, we can write

$$I_{\mathrm{B}} = \sum_i a_{\mathrm{HA}_i} \cdot f_{\mathrm{B}}/K_a^{\mathrm{BH^+A}_i^-} \cdot f_{\mathrm{BH^+A}_i^-}$$

where $K_a^{\mathrm{BH^+A}_i^-} = a_{\mathrm{HA}_i} \cdot a_{\mathrm{B}}/a_{\mathrm{BH^+A}_i^-}$. Therefore, for two indicators, B and C, interacting with two acids, HA$_1$ and HA$_2$,

$$\frac{I_{\mathrm{B}}}{I_{\mathrm{C}}} = \frac{(a_{\mathrm{HA}_1} \cdot f_{\mathrm{B}}/K^{\mathrm{BH^+A^-}{}_1} \cdot f_{\mathrm{BH^+A}_1^-} + a_{\mathrm{HA}_2} \cdot f_{\mathrm{B}}/K_a^{\mathrm{BH^+A}_2^-} \cdot f_{\mathrm{BH^+A}_2^-})}{(a_{\mathrm{HA}_1} \cdot f_{\mathrm{C}}/K_a^{\mathrm{CH^+A^-}{}_1} \cdot f_{\mathrm{CH^+A}_1^-} + a_{\mathrm{HA}_2} \cdot f_{\mathrm{C}}/K_a^{\mathrm{CH^+A}_2^-} \cdot f_{\mathrm{CH^+A}_2^-})}$$

Even assuming that the activity coefficient ratios are compensatory, variations in acid concentration will affect $I_{\mathrm{B}}/I_{\mathrm{C}}$ unless the ratios $K_a^{\mathrm{BH^+A}_1^-}/K_a^{\mathrm{CH^+A}_1^-}$ and $K_a^{\mathrm{BH^+A}_2^-}/K_a^{\mathrm{CH^+A}_2^-}$ are equal. The experimental evidence already mentioned for the specific nature of relative basicity makes this unlikely to be exactly true. Hence the ionisation of different indicators will show somewhat different trends.

When, however, one ionised form of the indicators is dominant ($\mathrm{BH^+Cl^-}$, say, for solutions of hydrogen chloride in acetic acid) then the ionisation data may reasonably be expected to show similar trends, but difficulties still remain about giving a rigorous, yet simple, meaning to the constants, because of the term $\mathrm{BH^+}$ (and possibly terms for larger ion aggregates than pairs [6]) in the expression for I_{B}. In view of the unsatisfactory nature of media permitting ion association, from this theoretical point of view, it is suggested that the construction of acidity scales for them, in only producing ionisation constants of ill-defined meaning, serves little purpose not served by the ionisation data alone. Consequently, an acidity scale is not constructed from the data obtained in the present study.

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[7] (*a*) Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327; (*b*) Kreevoy, *J. Amer. Chem. Soc.*, 1956, **78**, 4237; (*c*) Satchell, *J.*, 1957, 3524.

[8] Gutbezahl and Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559.

These data are given in the Table, from which it can be seen that the values of Δ log I for different acid concentrations, for any given pair of the indicators, stay excellently constant. If the values of Δ log I are taken to represent relative basicities (Δ pK_a's) of some generalised sort, say towards proton acceptance in an all-inclusive sense, then the Δ pK_a's between *o*-nitroaniline and 4-chloro-2-nitroaniline, and between 4-chloro-2-nitroaniline and *p*-nitrodiphenylamine are −0·78 and −1·39, respectively. The corresponding values in water [5] are −0·74 and −1·45. Thus for these three compounds the change in medium, and the proximity of an anion, have little effect on their relative tendencies to accept a proton. For *p*-nitrodiphenylamine and 2 : 4-dinitroaniline the ΔpK_a in acetic acid is −1·80, compared with −2·05 in water.[5] Here there is a discrepancy comparable in magnitude with those recently found in work with other mineral acids.[1d]

Ionisation of (a) o-*nitroaniline,* (b) 4-*chloro*-2-*nitroaniline,* (c) p-*nitrodiphenylamine, and* (d) 2 : 4-*dinitroaniline, in solutions of hydrochloric acid in acetic acid at* 18° ± 2°.

HCl (M)	0·0029	0·0048	0·0096	0·0145	0·0195	0·0290
log I_a	−0·73	−0·39	−0·10	0·06	0·18	0·36
log I_b	—	—	—	−0·71	−0·60	−0·42
log I_b − log I_a	—	—	—	−0·77	−0·78	−0·78

HCl (M)	0·0428	0·058	0·087	0·151	0·213	0·300	0·426
log I_a	0·49	0·67					
log I_b	−0·28	−0·13	0·05	0·27	0·46	0·61	0·81
log I_b − log I_a	−0·77	−0·80					
log I_c	—	—	−1·34	−1·12	−0·94	−0·78	−0·59
log I_c − log I_b	—	—	−1·39	−1·39	−1·40	−1·39	−1·40

HCl (M)	0·592	0·788	1·18	1·40	1·67	1·77
log I_b	0·98	1·17	1·46			
log I_c	−0·41	−0·23	0·07	0·20	0·35	0·42
log I_c − log I_b	−1·39	−1·40	−1·39			
log I_d	—	—	−1·74	−1·61	−1·43	−1·38
log I_d − log I_c	—	—	−1·81	−1·81	−1·78	−1·80

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