718. *The Hammett Acidity Function in Aqueous Nitric Acid.*

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The H_0 scale for nitric acid at 20° is revised and extended up to 65% with the usual accuracy for these measurements ($c \pm 0{\cdot}1$ unit), and beyond to 100% less reliably, the abnormal indicator *NN*-dimethyl-2,4,6-trinitroaniline being used to bridge a gap in the chain of normal indicators. The H_0 values are found to be related to the corresponding values for sulphuric acid at the same water activity by an equation involving the extent of dissociation of nitric acid; and the implications of the value for the pure acid ($-6{\cdot}3$) are discussed.

The existing figures for the Hammett acidity function, H_0, in nitric acid extend only up to 7M (36%) and, though recently corrected to the new scale,[1] are based on the original visual colorimeter measurements by Hammett and Paul.[2] Using a modern ultraviolet spectrophotometer (Unicam S.P. 500), we have now revised the data and extended the concentration range up to 65% (~14M). Estimated H_0 values are also suggested for concentrations between 65% and 100%, but these are less reliable since there is an important gap in the chain of indicators in this region of composition. Difficulties were encountered with many indicators at concentrations above 65%, and amongst those too rapidly attacked by the acid (or found to be unsuitable in other ways) were 2,4-dinitroaniline, *N*-methyl-2,4-dinitroaniline, 4-methyl-2,6-dinitroaniline, 4-chloro-2,6-dinitroaniline, 6-chloro-2,4-dinitroaniline, 4-nitrodiphenylamine, and 2,4-dinitrodiphenylamine. It now appears that perseverance with the diphenylamine indicators, along the lines described by Bascombe and Bell [3] for sulphuric acid, might have been profitable, for we observed similar medium effects (shifting maxima and variable extinction coefficients) at acid concentrations too low for protonation to occur. Further, the indicator used in the 100% region, 4,4′-dinitrodiphenylamine, was of this type and suffered from the same troublesome medium effects to some extent. Acetic acid, with a pK_{BH^+} of $-6{\cdot}2$, was also considered as a possible indicator for the pure acid region, but its absorption spectrum was completely obscured by that of the acid itself.

EXPERIMENTAL

Solutions were stored in a thermostat at 20° before transference to the spectrophotometer cells and, although no temperature regulator was built into the cell-housing in the spectrophotometer, the laboratory temperature rarely fluctuated from 20° by more than a degree.

Solutions were made up by weight in graduated flasks so that both weight and volume compositions could easily be calculated. Indicator solutions were added by pipette or (for the more concentrated solutions) by an " Agla " microsyringe, and optical densities were measured against solutions of the same composition but without the indicator.

Materials.—For the most concentrated solutions pure nitric acid was prepared, by distillation from a mixture of the 70% acid and concentrated sulphuric acid, and then diluted with weighed quantities of water. The 70% analytical-grade acid was, however, satisfactory for preparing more dilute solutions, and its concentration was determined by titration.

The indicators, apart from those specially prepared, were of B.D.H. laboratory-reagent quality; and those which yielded useful results were purified or prepared as follows: *p*- (m. p. 148·5°) and *o*-nitroaniline (m. p. 71°) were recrystallised twice from water, and 4-chloro-2-nitroaniline (m. p. 117°) and 2,6-dichloro-4-nitroaniline (m. p. 190°) from aqueous alcohol.

2,4-Dichloro-6-nitroaniline (m. p. 102°) was prepared by Blanksma's method [4] except that in the last stage dry ammonia was bubbled through an alcoholic solution of dichlorodinitrobenzene instead of the chloro-compound's being heated in a sealed tube with alcoholic ammonia.

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

[2] Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 827.

[3] Bascombe and Bell, *J.*, 1959, 1096.

[4] Blanksma, *Rec. Trav. chim.*, 1908, **27**, 47.

NN-Dimethyl-2,4,6-trinitroaniline (m. p. 137—138°) separated on addition of an excess of alcoholic dimethylamine to a warm alcoholic solution of picryl chloride.[5] It was twice recrystallised from alcohol.

4,4′-Dinitrodiphenylamine (m. p. 213°) was prepared by a standard method [6] from *p*-bromonitrobenzene and *p*-nitroaniline and recrystallised five times from anhydrous alcohol.

Results.—The experimental indicator ratios are recorded in Table 1, where the wavelengths at which the ratios were determined are also given. The position of maximum absorption was independent of concentration except in the case of 4,4′-dinitrodiphenylamine, for which the ratios were calculated from the maximum optical densities in the range quoted. The p*K* value of *p*-nitroaniline was determined by extrapolating a graph of log ([BH$^+$]/[B]) − log [H$^+$] against the acid concentration,[1] and all the remaining p*K* values were then determined in the usual way be measuring the vertical distances between the curves of log ([BH$^+$]/[B]) against

TABLE 1.

(a) p-*Nitroaniline*, p*K* = 1·03 (cf. 0·99 [1])

(at 383 mμ)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
0·019	0·12	0·206	1·72
0·038	0·24	0·417	1·41
0·057	0·36	0·638	1·23
0·094	0·59	1·128	0·98
0·133	0·84	1·743	0·79
0·188	1·18	2·563	0·62
0·189	1·19	2·44	0·64
0·283	1·77	4·32	0·39
0·376	2·35	6·25	0·23
0·492	3·06	9·40	0·06

(b) o-*Nitroaniline*, p*K* = −0·28 (cf. −0·29 [1])

(at 416 mμ)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
0·077	0·49	0·046	1·06
0·192	1·21	0·135	0·59
0·282	1·76	0·211	0·40
0·382	2·38	0·307	0·23
0·562	3·47	0·518	0·01
0·763	4·71	0·733	−0·15
0·963	5·90	0·936	−0·25
1·14	6·94	1·222	−0·37
1·53	9·17	1·906	−0·56
1·89	11·2	2·74	−0·72
2·29	13·4	3·79	−0·86
2·66	15·5	5·16	−0·99
2·87	16·6	5·45	−1·02

(c) 4-*Chloro*-2-*nitroaniline*, p*K* = −1·11 (cf. −1·03 [1])

(at 429 mμ)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
1·02	6·21	0·163	−0·32
1·53	9·22	0·297	−0·58
2·01	11·9	0·464	−0·78
2·47	14·5	0·673	−0·94
2·81	16·3	0·876	−1·05
3·84	21·6	2·03	−1·42
4·75	26·2	3·31	−1·63
4·90	26·8	3·42	−1·64
5·30	28·6	4·75	−1·79
5·93	31·6	6·05	−1·89
6·00	31·9	6·84	−1·95
7·11	36·7	11·4	−2·17
7·39	37·6	14·9	−2·28

(d) 2,6-*Dichloro*-4-*nitroaniline*, p*K* = −2·55

(at 370 mμ)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
5·54	29·7	0·199	−1·85
6·18	32·6	0·243	−1·94
6·34	33·0	0·274	−1·99
7·12	36·4	0·425	−2·18
8·60	43·2	0·959	−2·51
10·30	49·6	2·10	−2·85
11·4	54·0	3·17	−3·05
11·8	55·9	4·59	−3·21
11·9	56·2	4·99	−3·25
12·4	58·4	6·23	−3·34
12·7	58·5	5·71	−3·31

(e) 2,4-*Dichloro*-6-*nitroaniline*, p*K* = −3·30 (cf. −3·32 [1])

(at 425 mμ)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
7·46	38·3	0·092	−2·27
8·80	44·0	0·188	−2·57
9·49	46·8	0·267	−2·73
9·81	48·1	0·302	−2·78
10·8	52·0	0·439	−2·94
11·5	54·9	0·670	−3·13
12·4	58·0	0·831	−3·22 (?)
13·2	61·0	1·58	−3·50
14·2	64·5	2·69	−3·73

(f) NN-*Dimethyl*-2,4,6-*trinitroaniline*

(at 390 mμ) (from H_2SO_4)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
16·0	71·2	0·032	−4·07
17·0	75·0	0·063	−4·24
18·0	78·6	0·178	−4·50
18·8	81·5	1·55	−5·08 (?)
21·7	92·5	6·6	−5·54

(g) 4,4′-*Dinitrodiphenylamine*, p*K* = −6·2

(420—396 mμ)

Molarity	Wt. %	[BH$^+$]/[B]	H_0
19·4	83·7	0·051	−4·91
19·9	85·6	0·048	−4·88
20·5	87·7	0·143	−5·36
21·2	90·5	0·191	−5·48
21·9	93·0	0·216	−5·53
22·3	94·1	0·239	−5·58
22·6	95·4	0·372	−5·77
23·1	97·5	0·573	−5·96
28·8	98·9	0·850	−6·13
24·1	99·4	0·960	−6·18

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[5] Van Romburgh, *Rec. Trav. chim.*, 1883, **2**, 105.

[6] Smiles and Hilditch, *J.*, 1908, 153.

acid concentration for successive indicators in the "chain." Where the indicators have been used previously, the "best" p*K* values of Paul and Long [1] are shown for comparison; and this comparison illustrates once more that the p*K* values of indicators are practically independent of the nature of the acid in which they are measured. The H_0 values in the Table were obtained from pK − $\log_{10}$ ($[BH^+]/[B]$), except for *NN*-dimethyl-2,4,6-trinitroaniline, where they were assigned at each point from the known H_0 value at that concentration of sulphuric acid which gives the same colour ratio for this indicator as the nitric acid solution in question. It is well known that this particular indicator behaves anomalously in both sulphuric acid–water [7] and sulphuric acid–acetic acid,[8] and in nitric acid it shows the same kind of anomaly, the indicator ratio varying much more rapidly with concentration than would be expected. Nevertheless, there is such a serious gap in the normal indicators in this region that the above procedure has been adopted in an attempt to bridge it. The important assumption underlying this procedure, that the changes in colour ratio for this indicator, though anomalous, are still principally determined by H_0, may well be invalid; but it is given some support by the fact that the values of the logarithm of the colour ratio in sulphuric acid–water [7] and sulphuric acid–acetic acid [8] lie almost on a common curve when plotted against H_0 as determined by normal indicators. Further, the data for other acids would not lead us to expect violent changes in the H_0 dependence upon concentration in the 65—85% region of nitric acid; and the H_0 values determined by using *NN*-dimethyl-2,4,6-trinitroaniline (apart from one unexplained value) lie on a smooth extension of the curve for points below 65% and permit an estimate to be made of the relative position of the 84—100% section of the curve.

Up to 5M the new values are about 0·1 unit more negative than the old, but this gap widens to 0·2 unit by 7M. The new scale is summarised in Table 2.

TABLE 2. H_0 *scale for nitric acid* (20°).

Wt. %	Molarity	H_0	Wt. %	Molarity	H_0	Wt. %	Molarity	H_0
2	0·32	+0·33	30	5·62	−1·85	70	15·7	−3·99
4	0·65	−0·08	35	6·75	−2·10	75	17·1	−4·30
6	0·97	−0·29	40	7·92	−2·36	80	18·5	−4·62
8	1·32	−0·46	45	9·13	2·62	85	19·8	−4·96
10	1·68	−0·64	50	10·4	−2·88	90	21·2	−5·31
15	2·58	−0·97	55	11·7	−3·13	95	22·5	−5·75
20	3·55	−1·28	60	13·0	−3·42	100	24·0	−6·3
25	4·56	−1·57	65	14·3	−3·72			

Discussion

Although the Hammett acidity function has mainly been used empirically in kinetic investigations, some attention has been given to the significance of this quantity in the interpretation of the constitution of acid solutions. Two recent papers [9,10] have shown that the large H_0 changes in concentrated solutions of strong acids are consistent with the hypothesis that the H_3O^+ ion is heavily hydrated in aqueous solution; and in one of these [10] it was shown that H_0 is a common function of the water activity for completely dissociated acids, as would be expected from the hydration hypothesis. The difference between H_0 for a weak acid and that for a fully dissociated acid at the same water activity was also deduced [10] to be related to α, the extent of dissociation of the weak acid, by the equation:

$$(H_0)_{\text{weak}} - (H_0)_{\text{strong}} = \log_{10}\{(1+\alpha)/2\alpha\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

but lack of information about the extents of dissociation in concentrated solutions of those weaker acids for which H_0 data were available (hydrofluoric and phosphoric) hampered an attempt to test this relation adequately. Nitric acid is of particular interest in this respect, however, for not only has the constitution of its aqueous solutions been discussed

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[7] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[8] Hall and Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.

[9] Bascombe and Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[10] Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162.

in detail, but also its extent of dissociation has been accurately determined over the whole concentration range by Raman spectroscopy.[11]

The results of calculating H_0 from eqn. (1) are shown in the penultimate column of Table 3. These figures were arrived at by the following steps: (i) the α value at the given concentration of nitric acid was measured off on the graph given by Young, Maranville, and Smith; [11] (ii) the a_{H_2O} at this concentration was calculated from the vapour-pressure data of Vandoni and Laudy; [12] (iii) the sulphuric acid concentration at which a_{H_2O} was the same was interpolated from the data of Glueckauf and Kitt; [13] (iv) H_0 for sulphuric acid at this concentration was found in the table of Paul and Long; [1] (v) H_0 for nitric acid was calculated from eqn. (1). Considering the chain of experimental data, the agreement between the calculated and the observed H_0 values is surprisingly good. The assumptions involved in the derivation of eqn. (1) are that the most important contributions to the deviations from ideality in these solutions can be treated chemically, and that the equilibrium constants for the hydration reactions of H_3O^+ are the same in all acid solutions. Whilst a general drift of activity coefficients in the same direction could introduce compensations so that eqn. (1) may be obeyed rather better than these assumptions justify, there does seem to be some significance in this good agreement obtained for nitric acid.

TABLE 3. *Test of eqn.* (1).

Wt. %	Molarity	α[11]	a_{H_2O} [12]	$H_0(H_2SO_4)$ [13, 1]	H_0 (HNO_3) calc.	H_0 (HNO_3) obs.
30	5·62	0·77	0·724	−1·85	−1·79	−1·85
35	6·75	0·73	0·645	−2·12	−2·05	−2·10
40	7·92	0·62	0·581	−2·35	−2·23	−2·36
45	9·13	0·56	0·485	−2·75	−2·61	−2·62
50	10·4	0·47	0·404	−3·13	−2·93	−2·88
55	11·7	0·39	0·336	−3·46	−3·21	−3·13
60	13·0	0·30	0·265	−3·84	−3·50	−3·42
65	14·3	0·23	0·199	−4·24	−3·81	−3·72
70	15·7	0·16	0·142	−4·62	−4·06	−3·99
75	17·1	0·11	0·0913	−5·09	−4·39	−4·30

Eqn. (1) was actually derived for an acid HA dissociating into the (hydrated) ions H_3O^+ and A^-, whilst many investigators now believe [11,14] that nitric acid exists mainly in hydrated form in concentrated solutions. It is therefore necessary to show that hydration of the undissociated acid has no effect upon the form of eqn. (1). This follows from the fact that q, defined as the total number of moles of all species present per analytical mole of acid in the solution,[10] is effectively calculated from the mole fraction of " free water " in the solution, *viz.*, $(q - 1 - \alpha)/q$, by setting the latter equal to the water activity, a_{H_2O}. The undissociated acid is already counted with the ions in the $(1 + \alpha)$ moles which are not water, and the question whether or not this acid is hydrated does not affect this number: it does of course affect q, but that is automatically allowed for by relating q to a_{H_2O} as above and not trying to calculate it expressly. The argument by which eqn. (1) was derived in ref. 10 therefore remains unaffected.

A slightly different approach from that described here has recently been adopted by Bascombe and Bell,[3] who have been able to calculate H_0 values for nitric acid up to 6·74M from the Raman dissociation data. They adopt the $H^+(H_2O)_4$ model for the proton, and this restricts the treatment to concentrations below about 9 molar (45%) nitric acid, above which there would be insufficient water to form this ion completely. Nevertheless the two treatments are in effect very similar in the region in which they overlap.[15]

[11] Young, Maranville, and Smith, " The Structure of Electrolytic Solutions," ed. Hamer, Wiley, New York, 1959, Chap. 4.

[12] Vandoni and Laudy, *J. Chim. physique*, 1952, **49**, 99.

[13] Glueckauf and Kitt, *Trans. Faraday Soc.*, 1956, **52**, 1074.

[14] Chédin, *J. Chim. physique*, 1952, **49**, 109.

[15] Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 235.

The H_0 value (—6·3) estimated for pure nitric acid shows that this solvent is, as expected, considerably less acidic than sulphuric acid (with H_0 —11·12 [16,1]). Nevertheless it is acidic enough for acetic acid (pK_{BH^+} — 6·2 [1]) to be approximately one-half protonated, and for water also to be protonated to a considerable extent; for the pK_{BH^+} for H_3O^+ has (implicitly) been estimated as —6·78 [17] or as —5·1 [10] (both corrected to the Paul and Long scale [1]), according to the theory adopted to describe the constitution of sulphuric acid solutions. Therefore, notwithstanding the current solvation theories,[11,14] it seems probable that the protonated forms of both water and acetic acid are more important near the composition of pure nitric acid than is sometimes supposed; for the solvates would have to be very stable to compete with protonation of the free bases.

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[16] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[17] Deno and Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244.