223. *Acidity Functions of Some Aqueous Acids.*

By K. N. Bascombe and R. P. Bell.

Measurements have been made of the indicator acidities at 25° of aqueous solutions of sulphuric, phosphorous, methanesulphonic, formic, acetic, monochloroacetic, dichloroacetic, and trichloroacetic acids, several of which were studied over the whole range of compositions. The dissociation constants of several of the indicators were re-determined, and measurements over a range of wavelengths were used to detect effects on the absorption spectra of the indicators due to the medium. Such effects were prominent in the most concentrated solutions of the carboxylic acids, and it is concluded that acidity functions cannot be accurately defined in these solutions. The theoretical treatment previously developed for solutions of strong acids is used to derive an approximate value of 4 for the dissociation constant of methanesulphonic acid.

The Hammett acidity function has been widely used in assessing the mechanistic significance of kinetic measurements in concentrated acid solutions, and recent reviews [1,2] have dealt thoroughly with this subject. There is also a close connection between indicator acidities and the general problem of interpreting the equilibrium properties of concentrated electrolyte solutions.[3,4] Nevertheless, a large proportion of the available experimental data is derived from Hammett's pioneer work, which employed a visual colorimeter without temperature control. The present paper reports measurements at 25°, in which a spectrophotometer was used, and special attention was paid to limitations upon the accuracy with which the acidity function can be defined or measured. In particular, measurements were carried out over a range of wavelengths, so as to detect any effect of changes in the medium on the absorption spectra of the species concerned. Many of the measurements relate to solutions of weak acids which have not previously been fully investigated.

Experimental

Of the acids used, perchloric, hydrochloric, sulphuric, acetic, formic, monochloroacetic trichloroacetic, and iodic were " AnalaR " products. Phosphorous, dichloroacetic, and toluene-*p*-sulphonic acids were of " Laboratory Reagent " grade, the last being recrystallised from alcohol. Methanesulphonic acid was manufactured by Boots Pure Drug Co., Ltd., and its purity checked by titration.

The following indicators were B.D.H. Laboratory Reagents, recrystallised from alcohol, and having m. p. within 2° of the accepted value: *p*-aminoazobenzene, *m*-nitroaniline, phenylazodiphenylamine, *p*-nitroaniline, *o*-nitroaniline, *p*-nitrodiphenylamine, 2 : 4-dinitroaniline, benzylideneacetophenone, and *NN*-dimethyl-*p*-nitroaniline. 4-Chloro-2-nitroaniline was a laboratory specimen recrystallised from alcohol. 4-Methyl-2 : 6-dinitroaniline was prepared as described by Brady, Day, and Rolt [5] (m. p. 165° from alcohol). 6-Bromo-2 : 4-dinitroaniline was prepared by brominating 2 : 4-dinitroaniline in glacial acetic acid at 100° (cf. Elion [6]). The product separated on cooling and was filtered off, washed with water, dried, and twice recrystallised from alcohol (m. p. 151°). *NN*-Dimethyl-2 : 4-dinitroaniline was prepared by adding solid *NN*-dimethyl-*p*-nitroaniline to excess of 1 : 1 aqueous nitric acid. The amine dissolved, but after a few minutes yellow crystals of the nitrate of the required product began to separate. After half an hour the mixture was neutralised with an excess of aqueous sodium hydroxide and the solid product filtered off, washed with water, dried, and recrystallised from alcohol (m. p. 86°).

The acid solutions were standardised by volume either against borax, or (through sodium hydroxide solution) against constant-boiling hydrochloric acid. The weight concentrations

---

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

[2] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

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

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

[5] Brady, Day, and Rolt, *J.*, 1922, 527.

[6] Elion, *Rec. Trav. chim.*, 1923, **42**, 171.

given in the Tables were calculated from published densities, supplemented by our measurements on solutions of phosphorous and methanesulphonic acids. Stock indicator solutions were made up by weight in water or in the acid solution being investigated and the solutions for measurement were made by adding a known weight of indicator solution to a much larger volume of acid solution, giving indicator concentrations of about 10^{-5}M. The same indicator stock solution was used for measuring the absorption of the acidic and the basic form of the indicator and of the solution being investigated, so that it was not necessary to know its concentration accurately.

Optical densities were measured with a Unicam S.P. 500 spectrophotometer with a cell compartment regulated at 25° ± 0·02°. The latter consisted of a metal block resembling that described by Evans, Herington, and Kynaston:[7] the temperature was controlled by a platinum resistance thermometer embedded in the block, which formed one arm of a Wheatstone bridge and actuated a relay. The optical-density scale was tested by making measurements with solutions of potassium chromate which have been shown[8] to obey Beer's law with high accuracy. The apparent extinction coefficient at a given wavelength varied with concentration, decreasing by 2% for each unit increase in optical density. This shows that the scale of the instrument is slightly in error, and the true optical densities (D) were calculated from those read from the scale (D^*) by the relation $D = 50D^*/(50 - D^*)$. Similar difficulties in the accurate use of the Unicam S.P. 500 instrument have been reported by Davies and Prue.[9]

All measurements employed stoppered 10 mm. silica cells which were optically matched. Water was used in the comparison cell, and measurements were made over a range of 1000—1500 Å at intervals of 100 or 200 Å. In any set of measurements the observed optical densities (after application of the correction described above) were converted to a standard indicator concentration, usually that used in measuring the spectrum of the basic form of the indicator: these converted optical densities are represented by D'.

The acidity function H_0, as measured by an uncharged basic indicator B, is defined by

$$H_0 = \mathrm{p}K + \log\,[\mathrm{B}]/[\mathrm{BH}^+] = \mathrm{p}K + \log\,(D' - D'_{\mathrm{BH}^+})/(D'_{\mathrm{B}} - D') \quad . \quad . \quad (1)$$

where pK refers to BH^+, and D'_{BH^+} and D'_{B} are the converted optical densities for solutions in which the indicator is present entirely in the acidic and in the basic form respectively. D'_{BH^+} was usually measured in sulphuric acid of about 50% concentration. It was much smaller than D'_{B} for all the indicators used, with the exception of benzylideneacetophenone, which was used only for a few measurements with methanesulphonic acid: it was therefore not necessary to know D'_{BH^+} accurately. Indicators with p$K > -1$ are appreciably protonated even in dilute acid solution, and for these the value of D'_{B} was measured in 0·1M-aqueous sodium hydroxide. Since these indicators were not used in very concentrated acid solutions it is reasonable to use this value throughout in calculating H_0 from eqn. (1). The validity of this assumption can be tested to some extent by making measurements at different wavelengths, since it is unlikely that a change of medium would change the value of D'_{B} at a given wavelength without also changing the shape of the absorption curve. This test was carried out in most of the measurements, and examples are given under the individual acids. The most weakly basic indicators (pK -3 to -7) were used in very concentrated acid solutions, sometimes up to 100% acid, and it is certainly not appropriate to use the value of D'_{B} measured in water or dilute alkali. In most instances D'_{B} was measured in a solution of the acid being studied just below the concentration range in which protonation begins to become appreciable: this procedure was used by Hammett and Deyrup.[10] However, other procedures are possible and their use does not lead to identical results in concentrated solutions, as illustrated by our measurements with *p*-nitrodiphenylamine in sulphuric acid. The same uncertainty is revealed by the apparent variation of indicator ratio when the same solution is investigated at different wavelengths.

The indicators used, together with the values assumed for pK_a, are listed in Table 1. The pK values for the first three indicators were obtained from measurements in dilute solutions of hydrochloric, perchloric, and toluene-*p*-sulphonic acid, which were assumed to be completely

[7] Evans, Herington, and Kynaston, *Trans. Faraday Soc.*, 1953, **49**, 1284.

[8] Kortüm, *Z. phys. Chem.*, 1936, *B*, **33**, 243.

[9] Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

[10] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 4239.

dissociated. As would be expected in very dilute solution, the observed values of log {[BH+]/[B][H+]} showed no trend with acid concentration, and the values given for p*K* are averages for all measurements. As an example the results for *p*-aminoazobenzene are given in Table 2. The limits of error given for the indicator ratio *I* and the value of log {[BH+]/[B][H+]} calculated from it are based upon the precision and reproducibility of the instrumental readings.

TABLE 1. p*K values of indicators.*

	Indicator	p*K* (i)	Method	p*K* (ii)
I.	*p*-Aminoazobenzene	2·82	(a)	2·76
II.	*m*-Nitroaniline	2·50	(a)	2·50
III.	*p*-Nitroaniline	1·02	(a)	0·99
IV.	*o*-Nitroaniline	−0·29	(c)	−0·29
V.	*NN*-Dimethyl-2 : 4-dinitroaniline	−1·00	(c)	—
VI.	4-Chloro-2-nitroaniline	−1·02	(c)	−1·03
VII.	*p*-Nitrodiphenylamine	−2·4 to −2·9	(c)	−2·50
VIII.	4 : 6-Dichloro-2-nitroaniline	−3·61	(b)	−3·32
IX.	4-Methyl-2 : 6-dinitroaniline	−3·96	(b)	−4·44
X.	6-Bromo-2 : 4-dinitroaniline	−6·64	(b)	−6·71

(i) Present paper.
(ii) " Best value " given by Paul and Long.[1]
(a) Measured directly in dilute solutions of strong acids. (b) From overlap in solutions of methanesulphonic acid. (c) From overlap in solutions of sulphuric acid.

Table 2 shows that the observed indicator ratio is independent of the wavelength, and the same is true for *m*-nitroaniline and *p*-nitroaniline. The values obtained for the p*K* of these indicators agree fairly well with the " best values " of Paul and Long.[1] The values obtained for the remaining seven indicators are discussed in connection with the measurements on solutions of sulphuric and methanesulphonic acids.

Results.—In the Tables the indicators are numbered as in Table 1. Unless otherwise stated, measurements were made at the wavelengths of maximum absorption of the basic form, which were as follows: I 3800 Å, II 3600 Å, III 3800 Å, IV 4100 Å, V 3900 Å, VI 4200 Å, VII 4100 Å, VIII 4200 Å, IX 4500 Å, X 3550 Å. The acid concentration (concn.) is in moles/l. Details follow for the individual acids.

TABLE 2. *Measurement of* p*K for* p-*aminoazobenzene.*

[HCl]	*I*	log {[BH+]/ [B][H+]}	[p-Me·C_6H_4·SO_3H]	*I*	log {[BH+]/ [B][H+]}
0·00358	2·25 ± 0·12	2·80 ± 0·03	0·00171	1·17 ± 0·03	2·83 ± 0·01
0·00366	2·65 ± 0·09	2·86 ± 0·02	0·00435	2·75 ± 0·09	2·80 ± 0·02
	2·60 ± 0·09 *	2·84 ± 0·02		2·79 ± 0·08 *	2·82 ± 0·02
	2·73 ± 0·09 †	2·89 ± 0·02		2·68 ± 0·08 †	2·77 ± 0·02
0·00540	3·66 ± 0·12	2·83 ± 0·02	0·00870	5·73 ± 0·26	2·82 ± 0·02
0·00658	3·87 ± 0·15	2·77 ± 0·03			
0·00715	4·96 ± 0·17	2·84 ± 0·02			
0·00880	5·94 ± 0·18	2·83 ± 0·02			
[$HClO_4$]					
0·00087	0·53 ± 0·02	2·78 ± 0·02			
0·00266	1·72 ± 0·04	2·81 ± 0·01			
0·0455	2·94 ± 0·06	2·81 ± 0·01			
	2·98 ± 0·06 *	2·83 ± 0·01			
	2·95 ± 0·06 †	2·81 ± 0·01			
0·00957	7·10 ± 0·27	2·87 ± 0·02			

I = [BH+]/[B].
Measurements at 3800 Å unless otherwise stated.
* Measurements at 3600 Å.
† Measurements at 4000 Å.

Sulphuric acid. This was studied in order to check the p*K* values for some of the indicators, and also to provide more accurate data for the intermediate range of concentrations. Most of the results are given in Table 3; they are independent of the wavelength within experimental error (2—5% in *I*, or 0·01 to 0·02 in H_0, depending upon the value of *I* and the part of the instrumental scale being used). The values of H_0 derived from indicators I, II, and III are in good mutual agreement, by use of the p*K* values in Table 1, and up to a concentration of c = 0·01 they agree within 0·02 unit with $H_0 = -\log [H^+]$, where $[H^+]$ is calculated from $f_2\,[H^+]([H^+] - c)/(2c - [H^+]) = 0{\cdot}0103$, where f_2 is given in terms of the ionic strength μ by $-\log f_2 = 2\mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}})$. This calculation assumes that $f_{H^+} = f_{HSO_4^-}$, and the ionic strength is obtained by successive approximations, while $K = 0{\cdot}0103$ is the value given by Davies, Jones, and Monk [11] for the second dissociation constant of sulphuric acid.

The pK values for indicators IV, V, and VI have been chosen to give concordant values of H_0 in the region of overlap, as shown in Table 3. pK(IV) and pK(VI) are in good agreement with the best values of Paul and Long [1] (cf. Table 1). Indicator V has not previously been investigated, and is of interest in being a tertiary amine: nevertheless, it gives results closely parallel with those of the primary amine VI of similar pK. The indicator *NN*-dimethyl-2 : 4 : 6-trinitroaniline gives ionisation curves in 65—75% aqueous sulphuric acid and in acetic acid solutions of sulphuric acid which deviate considerably from those given by primary amines,[10, 12] but individual deviations are more prominent in these highly acid solutions.

TABLE 3. *Sulphuric acid.*

Key to wavelengths (λ): *m* maximum absorption, *a* 3400 Å, *b* 3600 Å, *c* 3700 Å, *d* 3800 Å, *e* 3900 Å, *f* 4000 Å, *g* 4400 Å, *h* 4600 Å.

Concn.	Wt. %	Indr.	λ	I	H_0
0·00050	0·0049	I	*m*	0·62	3·03
0·00058	0·0057	I	*m*	0·76	2·94
0·00059	0·0058	I	*b*	0·80	2·92
		I	*m*	0·76	2·94
		I	*f*	0·78	2·93
0·00067	0·0066	I	*b*	1·02	2·81
		I	*m*	0·98	2·83
		I	*f*	1·02	2·81
0·00098	0·0096	I	*m*	1·13	2·77
0·00118	0·0116	I	*m*	1·43	2·67
0·00134	0·0131	I	*m*	2·04	2·51
0·00239	0·0234	I	*m*	2·99	2·35
0·00253	0·0248	I	*m*	3·09	2·33
0·00409	0·0401	I	*m*	4·84	2·14
0·00434	0·0425	I	*m*	5·07	2·12
0·00480	0·0470	I	*m*	5·48	2·08
0·00603	0·0590	I	*m*	6·8	1·99
0·00615	0·0602	II	*m*	3·34	1·98
0·00750	0·0734	I	*m*	8·3	1·90
0·00908	0·0890	I	*m*	9·8	1·83
0·0139	0·136	II	*a*	7·6	1·62
		II	*m*	7·1	1·65
		II	*d*	7·0	1·66
0·0254	0·248	II	*a*	12·4	1·41
		II	*m*	12·1	1·42
		II	*d*	11·3	1·45
0·0333	0·325	II	*m*	15·6	1·32
0·0410	0·400	III	*m*	0·63	1·22
0·0625	0·612	III	*m*	0·91	1·06
0·235	2·26	III	*m*	3·44	0·48
0·278	2·67	III	*m*	4·11	0·41
0·280	2·69	III	*m*	4·14	0·40
0·355	3·39	III	*m*	5·47	0·28
0·540	5·10	III	*m*	8·5	0·09
0·90	8·3	III	m	17·3	−0·22
0·90	8·3	IV	*m*	0·89	−0·24
0·98	9·1	III	*m*	19·5	−0·27
1·18	10·75	III	*m*	27·7	−0·42
1·20	10·9	III	*b*	28·6	−0·44
		III	*c*	28·2	−0·43
		III	*m*	28·7	−0·44
		III	*e*	29·0	−0·44
		III	*f*	29·0	−0·44
1·22	11·1	IV	*d*	1·45	−0·44
		IV	*m*	1·49	−0·46
		IV	*g*	1·47	−0·45
1·49	13·4	IV	*m*	2·13	−0·62
1·54	13·8	VI	*m*	0·415	−0·64
1·56	14·1	IV	*m*	2·43	−0·68
1·57	14·2	III	*m*	48·3	−0·66
1·66	14·75	III	*m*	53·3	−0·71
1·85	16·3	IV	*m*	3·51	−0·83
1·86	16·4	VI	*m*	0·65	−0·83
1·91	16·8	VI	*m*	0·72	−0·88
1·94	17·1	IV	*m*	3·74	−0·86
2·04	17·8	III	*b*	81	−0·89
		III	*m*	83	−0·90
		III	*f*	82	−0·90
2·20	19·1	V	*m*	0·84	−0·93
		VI	*f*	1·57	−1·22
2·61	22·2	VI	*m*	1·55	−1·21
		VI	*g*	1·53	−1·20
2·68	22·6	IV	*m*	9·1	−1·25
2·95	24·6	V	*m*	2·38	−1·38
2·95	24·6	VI	*m*	2·30	−1·38
3·02	25·1	IV	*d*	13·2	−1·40
		IV	*m*	13·6	−1·42
		IV	*g*	13·5	−1·42
3·55	28·7	V	*m*	5·21	−1·72
3·55	28·7	VI	*m*	4·38	−1·66
4·29	33·6	V	*m*	10·8	−2·03
4·33	33·8	IV	*m*	75	−2·16
4·54	35·2	V	*m*	14·1	−2·15
4·61	35·6	VI	*f*	15·9	−2·22
		VI	*m*	15·9	−2·22
		VI	*g*	15·5	−2·21
4·84	37·1	V	*m*	23·7	−2·37
5·08	38·6	VI	*m*	26·7	−2·45

Attempts were made to study sulphuric acid solutions more concentrated than 5M by using indicator VII (*p*-nitrodiphenylamine). Since this will not be appreciably protonated at concentrations less than about 2M, it is possible to investigate the effect of acid concentration upon D'_B, the absorption of the basic form. Table 4 shows the results for three wavelengths in the neighbourhood of the maximum (4100 Å). It is clear that there is a considerable medium effect, which varies with wavelength. Three different assumptions have been made in calculating the indicator ratios in the range 4M—7M-sulphuric acid: (i) D'_B has the same value as in

---

[11] Davies, Jones, and Monk, *Trans. Faraday Soc.*, 1952, **48**, 921.

[12] Hall and Spengemann, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.

neutral aqueous solution. (ii) D'_B has the same value as in 1·8M-sulphuric acid (*i.e.*, just below the protonation range). (iii) D'_B is calculated from Table 4 by linear extrapolation to the relevant acid concentration. Table 5 shows the results of these three assumptions. The values of I differ considerably according to the assumption made about D'_B: with assumptions (i) and (ii) there is also a considerable variation with wavelength, but with assumption (iii) this variation is no greater than the uncertainty in the extrapolation for obtaining D'_B. However, this may be coincidental, since the values of I on assumption (iii) are not consistent with the results of Table 3 obtained with indicators IV, V, and VI. The choice of p$K = -2·4$ for *p*-nitrodiphenylamine gives coincident values of H_0 at 4·4M, but the plots of H_0 against Concn. diverge sharply at higher concentrations. On the other hand, either assumption (i) with p$K = -2·93$ or assumption (ii) with p$K = -2·60$ leads to values of H_0 which are consistent with Table 3. The values of H_0 from measurements at 4100 Å are given in Table 6: as can be seen from Table 5, somewhat different values would be obtained by using other wavelengths.

TABLE 4. *Medium effect on the absorption of* p-*nitrodiphenylamine.*

	$[H_2SO_4]$	0·575	0·98	1·38	1·83
D'_B	3800 Å	2·82	2·87	2·85	2·89
	4100 Å	3·80	3·90	3·94	4·05
	4400 Å	2·50	2·61	2·72	2·76

TABLE 5. *Apparent indicator ratios for* p-*nitrodiphenylamine in sulphuric acid.*

		I		
Concn.	λ (Å)	(i)	(ii)	(iii)
4·38	3800	0·199	0·384	0·465
	4100	0·156	0·323	0·495
	4400	0·130	1·290	1·457
4·87	3800	0·328	0·532	0·665
	4100	0·268	0·457	0·684
	4400	0·226	0·305	0·644
5·68	3800	0·673	1·08	1·25
	4100	0·644	0·89	1·26
	4400	1·516	0·63	1·28
6·36	3800	1·80	2·23	2·54
	4100	1·64	2·03	2·72
	4400	1·33	1·54	2·55
7·04	3800	4·39	5·21	6·3
	4100	4·31	5·09	6·7
	4400	3·80	4·19	6·8

Tables 4—6 illustrate the difficulties which can arise in more concentrated solutions and the consequent uncertainties in H_0. These uncertainties arise partly from effects of the medium upon absorption spectra, and partly from a more fundamental breakdown in the concept of acidity functions, in that H_0 may no longer be independent of the indicator used for its measurement. It is probable that these medium effects are particularly large for *p*-nitrodiphenylamine, since most of the other indicators showed a much smaller dependence of apparent indicator ratio upon wavelength even when no allowance was made for the variation of D'_B with concentration.

TABLE 6. H_0 *from* p-*nitrodiphenylamine in sulphuric acid.*

(All measurements at 4100 Å, maximum.)
pK for indicator: (i) −2·93, (ii) −2·60, (iii) −2·40.

Concn.	Wt. %	Assumption	D'_B	I	H_0
4·38	34·2	i	3·53	0·156	−2·11
		ii	4·05	0·323	−2·11
		iii	4·57	0·495	−2·10
4·87	37·2	i	3·53	0·268	−2·36
		ii	4·05	0·457	−2·26
		iii	4·67	0·68	−2·24
5·68	42·2	i	3·53	0·64	−2·74
		ii	4·05	0·89	−2·55
		iii	4·83	1·26	−2·50
6·36	45·9	i	3·53	1·64	−3·14
		ii	4·05	2·03	−2·91
		iii	4·97	2·72	−2·84
7·04	49·6	i	3·53	4·31	−3·57
		ii	4·05	5·09	−3·31
		iii	5·10	6·70	−3·33

The values of H_0 in Tables 3 and 6 are in general agreement with Hammett and Deyrup's measurements [10] as recalculated by Paul and Long,[1] but show much less scatter.

Methanesulphonic acid. This acid was studied over the whole concentration range 0—100%, partly in order to provide p*K*-values for indicators VIII, IX, and X, and partly because of the interest of an acid slightly weaker than the common mineral acids. Of the eight indicators used two were unsatisfactory. *p*-Nitrodiphenylamine gave inconsistent results, and appeared to react slowly with the acid. With benzylideneacetophenone the basic form has no absorption in the range usually examined, while the protonated form has a peak at 4300 Å in concentrated sulphuric acid. This appears at 4100 Å in 100% methanesulphonic acid; on addition of water the extinction coefficient increases by 30% in 95% acid, and then falls in the range 80—90%, simultaneously shifting to 3900 Å. This behaviour suggests either that several species are present or that the absorption spectra are subject to large medium effects: in either event the indicator is unsuitable for measuring acidities. The results for the remaining indicators are given in Table 7.

TABLE 7. *Methanesulphonic acid.*

Key to wavelengths: *m* maximum absorption, *a* 3300 Å, *b* 3400 Å, *c* 3800 Å, *d* 4200 Å, *e* 4400 Å, *f* 4600 Å, *g* 4800 Å.

Concn.	Wt. %	Indr.	λ	*I*	H_0
0·302	3·0	III	*m*	2·72	0·43
0·749	6·8	III	*b*	11·0	−0·02
		III	*m*	11·3	−0·03
		III	*c*	11·5	−0·04
1·557	13·9	III	*m*	24·7	−0·37
1·925	17·0	IV	*c*	1·78	−0·54
		IV	*m*	1·81	−0·55
		IV	*e*	1·77	−0·54
2·51	21·9	IV	*m*	2·28	−0·65
2·98	25·5	VI	*m*	0·59	−0·79
3·30	28·0	VI	*m*	0·72	−0·88
4·82	39·5	VI	*c*	2·18	−1·36
		VI	*m*	2·27	−1·38
		VI	*f*	2·18	−1·36
6·16	48·3	VI	*m*	7·4	−1·89
6·44	50·2	IV	*m*	56·9	−2·05
7·15	54·5	VI	*m*	19·1	−2·30
8·32	61·5	VIII	*c*	0·165	−2·82
		VIII	*m*	0·151	−2·79
		VIII	*f*	0·170	−2·84
9·38	67·4	VIII	*m*	0·538	−3·34
10·46	73·3	VIII	*m*	1·99	−3·91
10·78	74·9	IX	*d*	1·23	−4·05
		IX	*m*	1·21	−4·04
		IX	*g*	1·20	−4·04
10·85	75·3	VIII	*m*	2·91	−4·07
11·85	80·6	VIII	*m*	9·6	−4·59
12·12	82·1	IX	*m*	7·6	−4·84
12·74	85·2	IX	*m*	26·7	−5·39
13·45	88·9	X	*m*	0·309	−6·12
13·95	91·4	X	*m*	0·94	−6·61
14·77	95·7	X	*a*	6·4	−7·44
		X	*m*	6·1	−7·42
		X	*c*	6·3	−7·43
15·07	100·0	X	*m*	16·7	−7·86

There is no detectable variation of apparent indicator ratio with wavelength for any of the indicators studied, even close to 100% acid. The p*K* values taken for indicators III, IV, and VI are those previously obtained, while those for VIII, IX, and X are chosen so as to give good overlap or alignment in the present set of measurements (cf. Table 1). The values for VIII and IX differ somewhat from Paul and Long's best values, but the latter are based mainly on Hammett's early measurements with sulphuric acid and the differences probably reflect the spread of his experimental data in this region of concentration.

Trichloroacetic acid. An " AnalaR " specimen showed a small absorption in the range 3500—4500 Å, which was increased by vacuum distillation. The unpurified acid was therefor used, and a small correction applied. The results are given in Table 8.

TABLE 8. *Trichloroacetic acid.*

Measurements at peak wavelength, except those marked *a* (3400 Å), *b* (3800 Å), *c* (4200 Å), *d* (4400 Å).

Concn.	Wt. %	Indr.	*I*	H_0
0·221	4·0	IV	0·111	0·67
0·574	9·1	IV	0·306	0·22
0·786	12·5	IV	0·435 (*b*)	0·07
		IV	0·406	1·10
		IV	0·429 (*d*)	0·08
1·07	16·6	IV	0·509	0·00
1·72	25·5	III	10·7	−0·01
2·70	37·0	III	10·8 (*a*)	0·00
		III	10·4	+0·01
		III	10·0 (*c*)	+0·02
3·89	49·5	III	9·5	+0·04
4·99	59·9	III	11·4 (*a*)	−0·03
		III	10·8	−0·01
		III	10·9 (*c*)	−0·01
6·68	74·0	IV	1·12 (*b*)	−0·34
		IV	1·07	−0·32
		IV	1·12 (*d*)	−0·34
7·26	78·6	III	34·3	−0·53

The results are satisfactorily independent of wavelength, and the two indicators give concordant values. If allowance is made for the different p*K* values taken for *p*-nitroaniline, our results agree fairly well with those of Randles and Tedder,[13] who allowed for the absorption of the acid solution, but they are much lower than the three measurements reported by Hammett and Paul,[14] who made no such allowance.

Dichloroacetic acid. Measurements were made over the whole range of composition 0—100% with three indicators, but only the measurements with *p*-nitroaniline are recorded in Table 9. *o*-Nitroaniline and 4-chloro-2-nitroaniline were used in the range 80—100% acid, but the apparent indicator ratios varied greatly with wavelength in the neighbourhood of maximum absorption, and no reliance can be placed on the results.

The values in Table 9 agree fairly well with the less accurate measurements of Bell and Brown [15] when allowance is made for the different p*K* values assumed for the indicator.

Monochloroacetic acid. Measurements were extended up to the saturated solution (82%) and are given in Table 10.

TABLE 9. *Dichloroacetic acid.*

Indicator *p*-nitroaniline. Measurements at peak wavelength, except those marked *a* (3400 Å) or *b* (4200 Å)

Concn.	Wt. %	*I*	H_0	Concn.	Wt. %	*I*	H_0
0·281	3·1	1·18	0·95	5·49	55·5	2·51	0·62
0·558	6·8	1·76	0·77	6·46	63·0	3·03	0·54
1·098	13·1	2·32	0·65	7·28	68·4	3·65	0·46
2·35	26·9	2·34	0·65	8·35	76·4	5·37 (*a*)	0·29
2·93	33·0	2·34 (*a*)	0·66			5·33	0·29
		2·37	0·65			5·68 (*b*)	0·26
		2·15 (*b*)	0·61	9·76	85·5	11·5 (*a*)	−0·05
3·44	37·8	2·28	0·66			15·7	−0·19
5·07	52·0	2·43 (*a*)	0·64			15·9 (*b*)	−0·19
		2·36	0·65				
		2·29 (*b*)	0·66				

TABLE 10. *Monochloroacetic acid.*

All measurements with *p*-nitroaniline, except those marked *, which are with *p*-aminoazobenzene. Measurements at peak wavelength, except those marked *a* (3400 Å) or *b* (4200 Å).

Concn.	Wt. %	*I*	H_0	Concn.	Wt. %	*I*	H_0
0·363	3·38	0·217 (*a*)	1·68	4·90	40·0	0·420 (*a*)	1·39
		0·234	1·65			0·396	1·42
		0·226 (*b*)	1·66			0·432 (*b*)	1·38
0·684	6·30	0·276	1·58	6·67	52·2	0·499 (*a*)	1·32
0·728	6·70	0·277	1·58			0·535	1·29
0·748	6·89	17·7 *	1·57			0·625 (*b*)	1·23
1·357	12·24	0·322	1·51	7·40	56·7	0·624	1·23
1·462	13·12	0·352	1·47	8·06	60·9	0·780 (*a*)	1·13
2·10	18·4	0·361	1·46			0·762	1·14
2·13	18·8	0·360	1·46			1·18 (*b*)	0·94
2·17	19·1	0·366	1·46	9·36	68·8	1·45 (*a*)	0·86
2·19	19·3	0·363	1·46			1·58	0·82
2·40	21·0	22·0 *	1·48			2·11 (*b*)	0·68
2·75	23·8	0·354	1·47	10·86	77·4	2·03 (*a*)	0·72
2·87	24·7	0·364	1·46			2·07	0·70
3·29	28·0	0·362	1·46			2·65 (*b*)	0·60
3·33	28·3	0·346 (*a*)	1·48	11·21	79·3	1·77 (*a*)	0·76
		0·358	1·47			2·06	0·70
		0·347 (*b*)	1·48			2·86 (*b*)	0·57
3·43	29·1	0·362	1·46	11·65	81·6	0·99 (*a*)	1·02
3·56	30·1	0·363	1·46			1·11	0·98
4·59	37·8	22·5 *	1·47			1·40 (*b*)	0·88

The results of measurements with indicators I and III are in good agreement, but for solutions more concentrated than about 50% there is a considerable dependence on wavelength, and in this region the H_0 scale is certainly not defined to better than about $\pm 0{\cdot}1$.

Formic acid. With this acid the observed optical densities changed with time, possibly

---

[13] Randles and Tedder, *J.*, 1955, 1218.

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

[15] Bell and Brown, *J.*, 1954, 774.

because of slow reaction between the acid and the amines (cf. Davis[16]). It was possible to extrapolate back to zero time with fair accuracy, but the results were still unsatisfactory. Measurements with indicator II suggested only small variations of H_0 in the range 1·6—2·0 for 7—80% formic acid solutions. By contrast, the use of indicators III and IV produced H_0 values which decrease continuously by more than 3 units over the same range of concentrations: however, with the p*K* values of Table 1 there is a discrepancy of about 0·25 unit between the values of H_0 derived from these two indicators. It is therefore not possible to define an acidity scale on the basis of these measurements. Because of the variation with time, measurements were carried out at the peak wavelength only.

Acetic acid. Measurements were carried out over the whole range of compositions: there was no change with time during the time necessary for measurement, but it was not found possible to define an acidity scale. Indicator II at its peak wavelength showed very small changes in indicator ratio in the range 5—85% acetic acid, corresponding to H_0 values in the range 2·25—2·45, but the use of different wavelengths introduced discrepancies of up to 0·3 in H_0. In confirmation of this, both nitrobenzene and 2 : 4-dinitroaniline (which are not appreciably protonated in the solutions used) showed considerable changes in absorption spectra when the acetic acid concentration was varied from 5% to 85%. Measurements with indicator I suggested a decrease of H_0 from 2·3 to 1·9 in the range 7—60% acetic acid, but there is no reason to believe that this result is reliable. The most that can be said is that there are no very large changes in indicator acidity in the range 5—85%.

Phosphorous acid. This was investigated up to the limit of solubility (about 50%) with indicators III, IV, and VI, and the results are given in Table 11. There is satisfactory agreement between the different indicators, but the effect of varying the wavelength shows that there are increasing uncertainties in the acidity scale above about 20% acid.

TABLE 11. *Phosphorous acid.*

Key to wavelengths: *m* maximum absorption, *a* 3400 Å, *b* 3800 Å, *c* 4200 Å, *d* 4400 Å, *e* 4600 Å.

Concn.	Wt. %	Indr.	λ	*I*	H_0
0·096	0·436	III	*m*	0·57	1·26
0·235	1·06	III	*m*	1·16	0·96
0·596	2·66	III	*a*	2·31	0·65
		III	*m*	2·23	0·67
		III	*c*	2·17	0·68
0·99	4·36	IV	*b*	0·188	0·43
		IV	*m*	0·208	0·39
		IV	*d*	0·181	0·45
1·18	5·15	III	*a*	4·77	0·34
		III	*m*	5·12	0·31
		III	*c*	4·46	0·36
2·01	8·55	IV	*b*	0·307	0·22
		IV	*m*	0·322	0·20
		IV	*d*	0·288	0·25
4·01	15·6	IV	*b*	0·585	−0·05
		IV	*m*	0·619	−0·08
		IV	*d*	0·627	−0·09
6·04	22·7	IV	*m*	1·22	−0·38
7·46	26·9	IV	*b*	1·36	−0·43
		IV	*m*	1·76	−0·54
		IV	*d*	1·55	−0·48
8·32	29·6	VI	*m*	0·408	−0·63
9·38	32·6	VI	*b*	0·181	−0·28
		VI	*m*	0·449	−0·67
		VI	*e*	0·373	−0·59
10·24	35·8	IV	*m*	3·21	−0·80
10·86	37·2	VI	*m*	0·78	−0·91
12·05	40·8	IV	*m*	4·75	−0·97
12·50	42·2	VI	*m*	1·08	−1·05
13·8	46·1	VI	*b*	0·68	−0·86
		VI	*m*	2·07	−1·34
		VI	*e*	1·71	−1·25

Iodic acid. No satisfactory measurements were obtained with this acid. The " AnalaR " material gave a cloudy solution in water. Clear solutions 0·2—1·6M were obtained after recrystallisation, but their acidity towards *p*-nitroaniline decreased slowly on keeping, without reaching any steady value. This phenomenon may be due to a slow polymerisation or depolymerisation of iodic acid species in solution. The existence of polymerised species has been suggested several times, but the constitution of these solutions is obscure.[17]

DISCUSSION

The above measurements provide revised p*K* values for a number of indicators (including one new one, *NN*-dimethyl-2 : 4-dinitroaniline) and for the acidity functions of solutions of sulphuric, trichloroacetic, and dichloroacetic acids. Solutions of methanesulphonic, monochloroacetic, and phosphorous acid were investigated for the first time, and measurements were also made with solutions of acetic, formic, and iodic acids, though it

---

[16] Davis, *Z. phys. Chem.*, 1912, **78**, 353.

[17] Morgan, *Quart. Rev.*, 1954, **8**, 123.

was not possible to define any reliable acidity functions for the last three. Our measurements show that under favourable conditions it is possible to define H_0 with an accuracy of about 0·02 unit, and it is noteworthy that this is the case for methanesulphonic acid over the whole range of compositions, the pure acid having $H_0 = -7{\cdot}86$. Trichloroacetic acid also gives a satisfactory acidity scale up to the solubility limit of 79% acid, and dichloroacetic acid up to about 80%. However, measurements at different wavelengths show that the spectra of indicators often show considerable changes in concentrated solutions of weak acids, and this was specially marked for acetic, formic, and monochloroacetic acids. Under these conditions the acidity function cannot be accurately defined, and it is dangerous to draw conclusions from measurements at a single wavelength. The indicator *p*-nitrodiphenylamine shows large medium effects even with sulphuric acid solutions, and it is unfortunate that no other indicator has been investigated between pK −1 and pK −3.

Solutions of phosphorous acid show a steady increase of acidity over the concentration range investigated, thus resembling all other inorganic acids which have been studied. In the intermediate range of concentrations the values of H_0 resemble those for orthophosphoric acid and potassium hydrogen sulphate, which have similar dissociation constants.* The three chloroacetic acids (and also trifluoroacetic acid [13]) show quite a different type of behaviour, in that the acidity is almost independent of concentration over the range 1—5M, and is much less than for an inorganic acid of similar dissociation constant. The cause of this behaviour is obscure, but it is possible that, as suggested by Paul and Long,[1] it depends upon the "salting in" effect of the large organic molecules or ions upon the basic form of the indicator.

Methanesulphonic acid behaves as a much stronger acid than any of the others investigated here, though its solutions are less acidic than those of hydrochloric, perchloric, sulphuric, or nitric acids. It has been recently shown [3] that the acidity functions of the strong acids can be accounted for quantitatively up to about 8M by a simple treatment involving the assumption that the hydrogen ion in aqueous solution is firmly associated with four water molecules. If we assume that the same treatment can be applied to methanesulphonic acid, then by inserting the observed values of H_0 in eqn. (5) of ref. 3, it is possible to compute the true hydrogen-ion concentration and hence the degree of dissociation. This gives 89%, 86%, 64%, and 53% dissociation at 0·5, 1·0, 2·0, and 3·0M, corresponding to a concentration dissociation constant of about 4: *i.e.*, methane sulphonic acid is intermediate in strength between trifluoroacetic acid ($K = 0{\cdot}18$) and nitric acid ($K = 23$).[19]

The validity of this procedure can be tested by using it to calculate the acidity functions of aqueous nitric acid, for which the true degrees of dissociation are known with some certainty from measurements of Raman spectra and proton magnetic resonance.[19] The results of such calculations are shown in Table 12: the agreement is as good as could be expected.

TABLE 12. *Observed and calculated acidity functions for aqueous nitric acid.*

Concn.	2·00	3·54	4·55	5·61	6·74
α	0·95	0·89	0·84	0·76	0·71
H_0 calc.	−0·66	−1·21	−1·51	−1·79	−2·10
H_0 obs.	−0·67	−1·18	−1·47	−1·71	−1·94

We thank the Department of Scientific and Industrial Research and Monsanto Chemicals Ltd. for grants to one of us (K. N. B.).

PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, October* 31*st*, 1958.]

---

* The values given by Bell and Brown [15] for potassium hydrogen sulphate indicate a levelling off of the acidity at a relatively low value in the range 1—3M, but recent and more accurate measurements by Satchell [18] show that it does in fact behave like the other inorganic acids.

[18] Satchell, *J.*, 1958, 3904.

[19] Young, Wu, and Krawetz, *Discuss. Faraday Soc.*, 1957, **24**, 37 and personal communication from Professor Young.