The M_C Activity Coefficient Function for Acid–Base Equilibria. Part I. New Methods for Estimating pK_a Values for Weak Bases

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An experimental linear relation in strong aqueous acids between overlapping indicators, available for the whole acidity range, allows the determination of the pK_a values of weak bases by a new method of approximation. A new activity coefficient function (M_C) in aqueous sulphuric and perchloric acid is also proposed. The thermodynamic equilibrium constants of various groups of compounds including primary nitroanilines, tertiary amines, amides, indoles, alkoxy- and hydroxy-benzenes, triphenylmethyl alcohols, and sulphoxides, have been reinvestigated and the results compared with those reported in the literature. The solvation effects of the medium on the M_C function are also discussed.

It is well known that H_0 [1] cannot be used as an acidity function for all bases [2,3] and several attempts have been made to relate the new functions which have arisen.[4-6] In attempting to overcome some uncertainties intrinsic in the Hammett method for determining the relative strength of weak bases, we propose in this paper a new approach using a different criterion of analysis than usually adopted. This is based on the linear plots observed over the whole acidity range, between the logarithms of the [BH$^+$]/[B][H$^+$] values of two overlapping indicators at the same acid concentration. Also the activity coefficient ratios for different indicators are found to be proportional to one another.

The M_C Function.—For indicators whose protonation equilibrium can be measured up to a concentration of 2M, extrapolation to infinite dilution of a plot of function (1) against acid concentration (C_A) leads to the thermodynamic pK_{BH^+} values. This method is related to the

$$\log \frac{[XH^+]}{[X]} - \log [H^+] = -\log K_{app} \qquad (1)$$

linear plots obtained from equation (2) and to the linear variation of the activity coefficients [equation (3)] when the acid concentration is not too high. Then, for two

$$\log K_{app} = -pK_{XH^+} + b[C_A] \qquad (2)$$

$$-\log \frac{f_X f_{H^+}}{f_{XH^+}} = b[C_A] \qquad (3)$$

bases A and B, protonated in this range of acidity, equation (4) can be derived for the same acid concentration.

$$\log \frac{f_B f_{H^+}}{f_{BH^+}} = n_B \log \frac{f_A f_{H^+}}{f_{AH^+}} \qquad (4)$$

This equation shows that the log of the ratio of the activity coefficients of base B are multiples of those of base A, the latter being taken as the standard indicator; hence the validity of the equation (5). If

$$\log K_{app}^{B} = n_B(\log K_{app}^{A} + pK_{AH^+}) - pK_{BH^+} \qquad (5)$$

the parameters for the standard indicator A are known and $\log K_{app}^{B}$ of base B is measured in the overlap range, a plot of $\log K_{app}^{B}$ against $\log K_{app}^{A}$ leads by equation (5) to the thermodynamic pK_{BH^+} value. This is an alternative to the method of extrapolation to infinite dilution of the log K_{app} against acid concentration [equation (2)].

For weaker bases for which the protonation equilibrium must be studied at higher acid concentrations than 2M, the log K_{app} function ceases to vary linearly with acidity and calculation of thermodynamic pK_{BH^+} values by equation (2) is unreliable. However, with acidity $>$2M, for two bases, C and D, with an overlapping range of protonation, it has been observed that a plot of the log K_{app} of base C *vs.* log K_{app} of base D, at the same acidity, is linear. This experimental behaviour for different series of basic indicators has been tested over the whole range of acidity. By extrapolation of the plots of log K_{app}^{D} against log K_{app}^{C} to pure solvent as the standard state, the thermodynamic equilibrium constants of an indicator can be calculated by an equation such as (5). The stepwise method allows the estimation of the equilibrium constant for a series of bases of decreasing strength.

Moreover the extension of equation (4) to the whole

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[1] For extensive reviews of the H_0 acidity function see (*a*) M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1; (*b*) E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 1.

[2] C. H. Rochester, 'Acidity function,' Academic Press, London, 1970, vol. 17.

[3] E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Amer. Chem. Soc.*, 1970, **92**, 1260.

[4] K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, 1967, **89**, 2686.

[5] C. C. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 6453.

[6] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

acidity range for any two overlapping weak bases leads to relation (6) which connects all the indicators. This

$$\log \frac{f_A f_{H^+}}{f_{AH^+}} = \frac{1}{n_B} \log \frac{f_B f_{H^+}}{f_{BH^+}} = \frac{1}{n_B n_C} \log \frac{f_C f_{H^+}}{f_{CH^+}}$$

$$= \frac{1}{n_B n_C n_D} \log \frac{f_D f_{H^+}}{f_{DH^+}}$$

$$= \ldots \frac{1}{n_B n_C n_D \ldots n_Z} \log \frac{f_Z f_{H^+}}{f_{ZH^+}}$$

$$= \frac{1}{n_{Z^*}} \log \frac{f_Z f_{H^+}}{f_{ZH^+}} \qquad (6)$$

equation relates the ratio of the activity coefficients of the weaker base Z to that of the first base taken as standard by the corresponding n_{Z^*} values.

Relation (6) allows the calculation of a new function M_C [equation (7)] for the whole range of acidity by use

$$M_C = -\log \frac{f_A f_{H^+}}{f_{AH^+}} \qquad (7)$$

of a set of indicators chosen independently of the conditions formulated for the H_0 function. In this method it is only necessary to select the first indicator and to calculate the *n* values of each base used. Then the unknown pK_{XH^+} of base X can be calculated by the M_C function by use of equation (8).

$$\log \frac{[X][H^+]}{[XH^+]} = -pK_{XH^+} - \log \frac{f_X f_{H^+}}{f_{XH^+}}$$

$$= -pK_{XH^+} - n_X \frac{f_A f_{H^+}}{f_{AH^+}} = -pK_{XH^+} n_X M_C \qquad (8)$$

TABLE 1

pK_a Values for the ionization of primary nitroanilines in aqueous sulphuric acid at 25 °C

	Aniline	pK_a [a]	pK_a [b,c]	*n* [b,c]	σ_y [b,c]	pK_a [d]
1	4-Nitro	1·00	1·00	—	—	
2	2-Nitro	−0·30	−0·34	1·090 ± 0·071	0·008	−0·30
3	4-Chloro-2-nitro	−1·06	−1·14	1·060 ± 0·017	0·006	−1·09
4	2,5-Dichloro-4-nitro	−1·75	−1·72	0·864 ± 0·035	0·014	−1·68
5	2-Chloro-6-nitro	−2·38	−2·49	1·104 ± 0·011	0·006	−2·45
6	2,6-Dichloro-4-nitro	−3·27	−2·98	0·798 ± 0·025	0·008	−2·94
7	2,4-Dinitro	−4·27	−4·09	1·050 ± 0·033	0·015	−4·05
8	2,6-Dinitro	−5·39	−4·97	0·941 ± 0·045	0·012	−4·94
9	2-Bromo-4,6-dinitro	−6·69	−6·20	0·984 ± 0·043	0·014	−6·17
10	3-Methyl-2,4,6-trinitro	−8·33	−8·09	1·042 ± 0·029	0·004	−8·05
11	3-Bromo-2,4,6-trinitro	−9·34	−9·18	1·007 ± 0·180	0·018	−9·15
12	2,4,6-Trinitro	−10·03	−8·15	0·800 ± 0·041	0·012	−8·12

[a] Values of C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654. [b] Calc. by equation (5) using 4-nitroaniline ($pK_{BH^+} = 1·00$) as the standard indicator. [c] pK_a Is the intercept of the plot; *n* is the slope ±95% confidence limit; σ_y is the standard deviation of points from the linear regression line in the *y* direction. [d] Calc. by equation (5) using]2-nitroaniline ($pK_{BH^+} = -0·30$) as the standard indicator.

The experimental linear relation between $\log K_{app}^D$ and $\log K_{app}^C$ for two overlapping indicators has also been observed by Bunnett and Olsen;[6] however the theoretical treatment proposed here for the calculation of pK_a values differs from that suggested for the linear free energy relationship. Our approach, in fact, is independent of the factors limiting the H_0 function such as the parallelism and structure of indicators[2,3] since the relation between the activity coefficient of related bases gives pK_{BH^+} values not affected by variations of the slopes of the successive indicators.

RESULTS

Thermodynamic dissociation constants in perchloric and sulphuric acid of several indicators of various classes of weak bases have been reinvestigated by use of equation (5). The pK_a obtained and the *n* values of slopes of two successive indicators are listed in Tables 1—6 together with results reported in the literature.

In order to account for the ionization equilibrium of triarylmethyl alcohols in sulphuric acid,[7] their pK_a values (Table 6) have been determined by equation (9). The

$$\log K_{R'}{}^* = n_{R'} (\log K_R{}^* + pK_R) - pK_{R'} \qquad (9)$$

expression was derived, as was equation (5), by a plot of $\log K_{R'}{}^*$ against $\log K_R{}^*$ where $\log K_R{}^* = \log([ROH]/[R^+]) + \log[H^+] - \log a_{H_2O}$ and $\log K_{R'}{}^*$ is a similar relation for the weaker overlapping alcohol R′. In the calculations using equation (5), a few results have been omitted due to the lack of an overlap range for successive indicators with the same structure; for analogous reasons some results for triarylmethyl alcohols have been calculated using nitroanilines as the overlapping indicators.

The M_C function has been determined by equation (10)

$$M_C = \log \frac{f_A f_{H^+}}{f_{AH^+}} = \frac{1}{n_B} (\log \frac{[B]}{[BH]} + \log[H^+] + pK_{BH^+})$$

$$= \frac{1}{n_B n_C} (\log \frac{[C]}{[CH^+]} + \log[H^+] + pK_{CH^+})$$

$$\ldots = \frac{1}{n_B n_C \ldots n_Z} (\log \frac{[Z]}{[ZH^+]} + \log[H^+] + pK_{ZH^+}) \qquad (10)$$

given the values of pK_{XH^+}, $\log([X]/[XH^+])$, n_X for various indicators, and of $\log[H^+]$ of the acid solutions.[8,9] All

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[7] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

[8] E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, 1964, **86**, 5080.

[9] K. E. Heinzinger and R. E. Weston, *J. Chem. Phys.*, 1965, **42**, 272.

TABLE 2

pK_a Values for the ionization of primary nitroanilines in perchloric acid at 25 °C

	Aniline	pK_a [a]	pK_a [b,c]	n [b,c]	σ_y [b,c]	pK_a [d]
1	2-Nitro	−0·29	−0·30	—	—	−0·30
2	4-Chloro-2-nitro	−1·07	−1·097	1·049 ± 0·162	0·010	−1·09
3	2,5-Dichloro-4-nitro	−1·79	−1·77	0·951 ± 0·036	0·011	−1·68
4	2-Chloro-6-nitro	−2·49	−2·41	1·016 ± 0·040	0·018	−2·45
5	2,6-Dichloro-4-nitro	−3·20	−2·82	0·813 ± 0·028	0·012	−2·94
6	2,4-Dinitro	−4·26	−3·90	1·008 ± 0·113	0·015	−4·05
7	2,6-Dinitro	−5·25	−4·82	0·986 ± 0·053	0·011	−4·94
8	4-Chloro-2,6-dinitro	−6·12	−5·60	0·984 ± 0·044	0·002	—
9	2-Bromo-4,6-dinitro	−6·69	−6·22	1·008 ± 0·056	0·014	−6·17
10	3-Methyl-2,4,6-trinitro	−8·56	—	—	—	−8·05
11	3-Bromo-2,4,6-trinitro	−9·77	—	—	—	−9·15

[a] Values of K. Yates and H. Wai, *J. Amer. Chem. Soc.*, 1964, **86**, 5408. [b] Calc. by equation (5) using 2-nitroaniline (pK_{BH^+} = −0·30) as the standard indicator. [c] See footnote *c* of Table 1. [d] Values calc. by equation (5) for sulphuric acid.

TABLE 3

pK_a Values for the ionization of amides in aqueous sulphuric acid at 25 °C

	Amide	pK_a [a]	pK_a [b,c]	n [b,c]	σ_y [b,c]	pK_a [c,d]	n [c,d]	σ_y [c,d]
1	Pyrrole-2-carboxamide	−1·23	−1·15	0·750 ± 0·022	0·011	−1·11	0·676 ± 0·042	0·013
2	4-Methoxybenzamide	−1·44	−1·22	0·604 ± 0·023	0·019	−1·29	0·920 ± 0·044	0·007
3	3,4,5-Trimethoxybenzamide	−1·82	−1·62	0·609 ± 0·012	0·010	−1·63	0·954 ± 0·019	0·007
4	3-Nitrobenzamide	−2·42	−2·05	0·500 ± 0·012	0·010	−2·07	0·819 ± 0·030	0·006
5	3,5-Dinitro-4-methylbenzamide	−2·69	−2·27	0·486 ± 0·014	0·015	−2·25	0·906 ± 0·022	0·006
6	2,3,6-Trichlorobenzamide	−3·30	−2·59	0·396 ± 0·008	0·008	−2·54	0·790 ± 0·023	0·002
7	2,4-Dichloro-3,5-dinitrobenzamide	−3·73	−2·98	0·394 ± 0·009	0·013	−2·94	0·978 ± 0·020	0·005
8	2,4,6-Trinitrobenzamide	−4·08	−3·55	0·432 ± 0·026	0·019	−3·50	1·103 ± 0·037	0·0012

[a] Values of K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957. [b] Calc. by a plot log K_{app} against M_C. [c] See footnote *c* of Table 1. [d] Calc. by equation (5), using 2-nitroaniline (pK_{BH^+} = −0·30) as the standard indicator.

TABLE 4

pK_a Values for the ionization of tertiary amines in aqueous sulphuric acid at 25 °C

	Amine	pK_a [a]	pK_a [b,c]	n [b,c]	σ_y [b,c]	pK_a [c,d]	n [c,d]	σ_y [c,d]
1	*NN*-Dimethyl-4-nitroaniline	+0·66	+0·65	1·585 ± 0·119	0·009			
2	*NN*-Diethyl-2,4-dinitroaniline	+0·21	+0·23	1·394 ± 0·214	0·031	+0·21		
3	*N*-(2,4-Dinitrophenyl)piperidine	−0·38	−0·46	1·909 ± 0·140	0·040	−0·52	1·307 ± 0·013	0·04
4	*NN*,4-Trimethyl-2,6-dinitroaniline	−1·66	−1·94	2·344 ± 0·244	0·030	−1·89	1·086 ± 0·021	0·003
5	*NN*-Dimethyl-1-naphthyl-2,4-dinitroaniline	−2·59	−2·40	1·582 ± 0·135	0·039	−2·42	0·759 ± 0·039	0·009
6	4-Chloro-*NN*-dimethyl-2,6-dinitroaniline	−3·12	−2·80	1·474 ± 0·087	0·026	−2·93	1·025 ± 0·021	0·007
7	*N*-Methyl-4-nitrodiphenylamine	−3·42	−2·98	1·440 ± 0·072	0·022	−2·97	0·902 ± 0·029	0·013
8	4-Bromo-*N*-methyl-4′-nitrodiphenylamine	−4·21	−3·06	1·024 ± 0·056	0·020	−3·10	0·764 ± 0·034	0·006
9	*NN*-Diethyl-2,4,6-trinitroaniline	−5·71	−4·66	1·108 ± 0·066	0·070	−4·70	1·067 ± 0·079	0·009
10	*N*-Methyl-2,4-dinitrodiphenylamine	−6·19	−5·12	1·118 ± 0·104	0·043	−5·10	0·976 ± 0·049	0·017
11	*NN*-Dimethyl-2,4,6-trinitroaniline	−6·55	−5·46	1·103 ± 0·087	0·022	−5·51	1·003 ± 0·062	0·016
12	4-Bromo-*N*-methyl-2′,4′-dinitrodiphenylamine	−6·93	−5·85	1·105 ± 0·014	0·011	−5·77	0·974 ± 0·050	0·017
13	X,4-Dibromo-*N*-methyl-2′,4′-dinitrodiphenylamine	−8·17	−6·13	0·907 ± 0·093	0·046	−6·23	0·852 ± 0·099	0·015
14	*N*-Methyl-2,2′,4,4′-tetranitrodiphenylamine	−10·56	−9·52	1·048 ± 0·032	0·023			

[a] Values of E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671. [b] Calc. by a plot of log K_{app} against M_C. [c] See footnote *c* of Table 1. [d] Calc. by equation (15) using *NN*-diethyl-2,4-dinitroaniline (pK_{BH^+} = 0·21) as the standard indicator.

TABLE 5

pK_a Values for the ionization of indoles in aqueous sulphuric acid at 25 °C

	Indole	$\frac{d \log I}{d(C_{H_2SO_4})}$ [a]	pK_a [b]	pK_a [b,c]	n [b,c]	σ_y [b,c]	pK_a [c,d]	n [c,d]	σ_y [c,d]
A	1,2-Dimethyl	0·77	+0·30	+0·25	1·861 ± 0·375	0·019			
B	2-Methyl	0·73	−0·28	−0·27	1·615 ± 0·189	0·014	−0·28		
C	1,2,3-Trimethyl	0·68	−0·66	−0·62	1·592 ± 0·172	0·008	−0·64	1·016 ± 0·064	0·008
D	2,3-Dimethyl	0·67	−1·49	−1·48	1·705 ± 0·089	0·016	−1·45	0·967 ± 0·081	0·009
F	1-Methyl	0·68	−2·32	−2·38	1·737 ± 0·243	0·042	−2·48	1·131 ± 0·030	0·005
G	1,2-Dimethyl-5-nitro	0·68	−2·94	−2·77	1·557 ± 0·092	0·024	−2·71	0·804 ± 0·047	0·008
L	3-Methyl	0·71	−4·55	−4·03	1·361 ± 0·056	0·026	−3·87	1·210 ± 0·043	0·008
H	1,3-Dimethyl	0·78	(−3·30)	−3·59	1·861 ± 0·063	0·029	−3·53	1·204 ± 0·053	0·012
J	Indole	0·46	(−3·50)	−2·78	1·152 ± 0·151	0·049	−2·63	0·575 ± 0·024	0·004
N	3-CH_2CO_2H	0·70	−6·13	−4·92	1·102 ± 0·170	0·039			
O	Tryptamine	0·77	−6·31	−5·54	1·226 ± 0·055	0·020			
P	5-Nitro	0·47	(−7·40)	−4·25	0·690 ± 0·041	0·033			

[a] Values of R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796. Values in parentheses calc. by H_I function. [b] Calc. by a plot of log K_{app} against M_C. [c] See footnote *c* of Table 1. [d] Calc. by equation (5) using 2-methylindole (pK_{BH^+} = −0·28) as the standard indicator.

calculations were performed using the log I values reported in the literature; molar concentration for medium acidity as for $[H^+]$ in K_{app} have been utilized.

The M_C values for structurally similar bases in perchloric and sulphuric acids are reported in Table 9, and the dissociation constants of indicators evaluated by the M_C function [equation (8)] in Tables 3—8 and compared with others obtained by different approximations. In this method the n values are the slopes of indicators X referred to 4-nitroaniline as the standard indicator for the M_C function. Each set of data has been subjected to standard linear regression analysis by use of a computer program and the results are collected in Tables 1—8. The experimental errors in both methods of calculation are of the same order of magnitude as the uncertainties usually accepted for linear relations. The limits of these approaches are, however, the estimation of the slopes and intercepts as the bases studied become weaker. Decreasing accuracy is expected with increasing extrapolation. Moreover our results suffer the same approximations intrinsic in the experimental measurements of the reported log I and $[H^+]$ values.

TABLE 6

pK_a Values for the ionization of triphenylmethyl alcohols and related compounds in aqueous sulphuric acid at 25 °C

	Triphenylmethyl alcohol (unless otherwise stated)	pK_a [a]	pK_a [b,c]	n [b,c]	σ_y [b,c]	pK_a [c,d]	n [c,d]	σ_y [c,d]
1	4,4′,4″-Trimethoxy	+0·82	+0·67	3·213 ± 0·423	0·016	+0·67		
2	4,4′-Dimethoxy	−1·24	−1·20	2·322 ± 0·141	0·023	−1·14	2·174 ± 0·078	0·022
3	4-Methoxy	−3·40	−3·22	2·304 ± 0·073	0·015	−3·13	1·895 ± 0·149	0·028
4	2,2′,2″-Trimethyl	−3·40	−2·84	2·006 ± 0·121	0·025	−2·76	0·868 ± 0·024	0·006
5	4,4′,4″-Trimethyl	−3·56	−3·31	2·262 ± 0·086	0·013	−3·22	0·978 ± 0·076	0·056
6	4-Methyl	−5·24	−4·34	1·880 ± 0·054	0·004	−4·34	1·046 ± 0·040	0·011
7	Bis-(4-methoxyphenyl)methanol	−5·71	−4·73	1·816 ± 0·035	0·005	−4·69	1·734 ± 0·134	0·032
8	3,3′3″-Trimethyl	−6·35	−5·95	2·097 ± 0·325	0·028	−5·97	1·174 ± 0·670	0·021
9	4,4′,4″-Tri-isopropyl	−6·54	−5·87	1·964 ± 0·095	0·008	−5·87	0·931 ± 0·090	0·013
10	Unsubstituted	−6·63	−5·96	1·963 ± 0·761	0·014	−5·98	0·938 ± 0·032	0·004
11	4,4′,4″-Trichloro	−7·74	−6·32	1·659 ± 0·119	0·012	−6·54	1·880 ± 0·121	0·006
12	4-Nitro	−9·15	−7·37	1·551 ± 0·092	0·022	−7·37	1·105 ± 0·042	0·010
13	2-Phenylborneol	−9·75	−7·45	1·415 ± 0·042	0·018	−7·41	1·531 ± 0·058	0·019
14	3,3′,3″-Trichloro	−11·03	−8·85	1·450 ± 0·062	0·020	−8·98	1·727 ± 0·211	0·007
15	Chloro-bis-(4-nitrophenyl)-phenylmethane	−12·90	−10·33	1·383 ± 0·056	0·011	−10·43	1·634 ± 0·122	0·028
16	4,4′,4″-Trinitro	−16·27	−10·87	0·893 ± 0·114	0·004			
17	9-Methyl-fluoren-9-ol	−16·60	−10·19	0·772 ± 0·313	0·024	−10·39	0·882 ± 0·281	0·016
18	2,4,6-Trimethylbenzyl alcohol	−17·38	−10·53	0·715 ± 0·067	0·027	−10·68	0·926 ± 0·071	0·010
19	Chloro(diphenyl)-4-t-butylphenylmethane	−6·10	−4·72	1·619 ± 0·052	0·013			
20	Chloro(phenyl)bis-4-(t-butylphenyl-methane	−6·6	−4·27	1·224 ± 0·148	0·037			
21	4,4′,4″-Tri-t-butyl	−6·5	−4·35	1·333 ± 0·158	0·023			
22	Dimesitylmethanol	−6·6	−4·77	1·462 ± 0·108	0·027			
23	Bis-(4-methylphenyl)methanol	−10·4	−7·89	1·381 ± 0·0812	0·011			
24	Bis-(2-methyldiphenyl)methanol	−12·45	−9·47	1·309 ± 0·062	0·022			
25	Bis-(4-t-butylphenyl)methanol	−13·2	−10·72	1·387 ± 0·455	0·071			
26	Diphenylmethanol	−13·3						
27	Bis-(4-chlorophenyl)methanol	−13·96	−8·89	0·959 ± 0·171	0·033			
28	Fluoren-9-ol	−14·0	−6·07	0·559 ± 0·736	0·018			

[a] Values of N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044. [b] Calc. by a plot of log k_{app}* against M_C. [c] See footnote *c* of Table 1. [d] Calc by equation (9) using 2-nitroaniline ($pK_{BH^+} = -0{\cdot}30$) as the standard indicator.

TABLE 7

pK_a Values for the ionization of hydroxy- and alkoxy-benzenes in aqueous sulphuric acid at 25 °C

	Benzene	pK_a [a]	pK_a [b,c]	n [b,c]	σ_y [b,c]
1	1,3,5-Trihydroxy	−3·37	−3·69	1·036 ± 0·021	0·023
2	1,3,5-Trimethoxy	−5·46	−4·95	1·458 ± 0·032	0·019
3	1,3-Dihydroxy	−8·05	−6·79	0·897 ± 0·010	0·009
4	1,3-Dihydroxy-2-methyl	−8·24	−6·40	0·943 ± 0·054	0·025
5	1-Hydroxy-3-methoxy	−9·54	−7·65	1·096 ± 0·035	0·025
6	1,3-Dimethoxy-2-methyl	−9·66	−7·68	1·085 ± 0·033	0·020
7	1,3-Dimethoxy	−9·75	−7·97	1·162 ± 0·045	0·026

[a] Values of A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *J. Amer. Chem. Soc.*, 1971, **93**, 6174. [b] Calc. by a plot of log K_{app} against M_C. [c] See footnote *c* of Table 1.

DISCUSSION

In order to test the validity of the M_C function it is useful first to examine the dissociation constant values obtained by the methods reported above [equations (5) and (8)]; within the set a comparison can be made with the values calculated by the Hammett procedure.

The general behaviour observed can be summarized as follows. Both calculation methods usually give very similar pK_{BH^+} values and in reasonable agreement, at low acidity range, with pK_{BH^+} values reported in literature. Deviations are observed for progressively

TABLE 8

pK_a Values for the ionization of sulphoxides in aqueous sulphuric acid at 25 °C

	Sulphoxide	pK_a [a]	pK_a [b]	pK_a [c,d]	n [c,d]	σ_y [c,d]
1	4-Methylphenyl methyl	−2·08	−1·72	−1·99	0·485 ± 0·023	0·026
2	Phenyl methyl	−2·26	−1·92	−2·13	0·450 ± 0·017	0·014
3	3-Nitrophenyl methyl	−3·07	−2·71	−2·62	0·598 ± 0·039	0·012
4	4-Nitrophenyl methyl	−3·20	−2·80	−2·66	0·410 ± 0·012	0·022
5	4-Methylphenyl phenyl	−2·72	−2·23	−2·49	0·408 ± 0·019	0·025
6	Diphenyl	−2·85	−2·39	−2·60	0·354 ± 0·017	0·019
7	3-Nitrophenyl phenyl	−3·41	−2·97	−3·06	0·422 ± 0·017	0·017
8	4-Nitrophenyl phenyl	−3·50	−3·05	−3·10	0·392 ± 0·010	0·022

[a] Values of N. C. Marziano, G. Cimino, U. Romano, and R. Passerini, *Tetrahedron Letters*, 1969, 2833; ref. 12. Calc. by the method of Bunnett. [b] Values from *a* calc. by the method of Yates. [c] Calc. by a plot of log K_{app} against M_C. [d] See footnote *c* of Table 1.

TABLE 9

The activity coefficient functions (M_C) of aqueous perchloric and sulphuric acid at 25 °C

	$HClO_4$	H_2SO_4				
Acid (%)	$M_C (H_0)$ [a]	$M_C (H_0)$ [b]	$M_C (H_0)$ [c]	$M_C (H_A)$ [d]	$M_C (H_0''')$ [e]	$M_C (H_I)$ [f]
2				−0·01	−0·08	
4		−0·08		−0·04	−0·15	
6		−0·12	−0·09	−0·09	−0·23	−0·18
8	−0·30	−0·18	−0·14	−0·15	−0·32	−0·27
10	−0·33	−0·23	−0·21	−0·21	−0·41	−0·36
12	−0·37	−0·29	−0·27	−0·27	−0·49	−0·46
14	−0·43	−0·35	−0·34	−0·33	−0·58	−0·55
16	−0·49	−0·41	−0·41	−0·40	−0·68	−0·65
18	−0·55	−0·48	−0·49	−0·48	−0·78	−0·76
20	−0·62	−0·56	−0·57	−0·56	−0·88	−0·88
22	−0·69	−0·63	−0·65	−0·64	−0·98	−1·01
24	−0·76	−0·71	−0·74	−0·73	−1·08	−1·15
26	−0·84	−0·80	−0·83	−0·83	−1·18	−1·29
28	−0·93	−0·89	−0·93	−0·92	−1·30	−1·45
30	−1·02	−0·98	−1·03	−1·02	−1·43	−1·61
32	−1·11	−1·08	−1·14	−1·13	−1·57	−1·78
34	−1·22	−1·19	−1·25	−1·23	−1·71	−1·95
36	−1·34	−1·29	−1·37	−1·34	−1·85	−2·14
38	−1·47	−1·41	−1·49	−1·47	−2·01	−2·34
40	−1·62	−1·53	−1·62	−1·60	−2·19	−2·58
42	−1·78	−1·66	−1·77	−1·74	−2·36	−2·80
44	−1·96	−1·80	−1·93	−1·89	−2·56	−3·06
46	−2·15	−1·97	−2·11	−2·06	−2·77	−3·34
48	−2·37	−2·14	−2·30	−2·24	−3·00	−3·66
50	−2·63	−2·32	−2·49	−2·43	−3·24	
52	−2·96	−2·52	−2·70	−2·64	−3·49	
54	−3·32	−2·73	−2·93	−2·89	−3·76	
56	−3·74	−2·95	−3·18	−3·14	−4·05	
58	−4·18	−3·17	−3·43	−3·41	−4·38	
60	−4·65	−3·41	−3·70	−3·70	−4·75	
62	−5·19	−3·67	−3·98	−3·99	−5·16	
64	−5·77	−3·95	−4·28	−4·31	−5·59	
66	−6·36	−4·28	−4·61	−4·67	−6·07	
68	−7·00	−4·63	−5·00	−5·04	−6·55	
70	−7·68	−4·99	−5·39	−5·41	−7·01	
72		−5·35	−5·79	−5·79	−7·50	
74		−5·70	−6·19	−6·18	−7·98	
76		−6·06	−6·61		−8·52	
78		−6·45	−7·03		−9·11	
80		−6·84	−7·44			
82		−7·25	−7·86			
84		−7·69	−8·28			
86		−8·02	−8·69			
88		−8·39	−9·10			
90		−8·77	−9·51			
92		−9·23	−10·02			
94		−9·77	−10·61			
95		−10·11				
96		−10·54				
97		−11·05				
98		−11·90				

[a] Calc. for primary nitroanilines (Table 2) using 2-nitroaniline as the standard indicator. [b] Calc. for primary nitroanilines (Table 1) using 4-nitroaniline as the standard indicator. [c] Calc. for primary nitroanilines (Table 1) using 2-nitroaniline as the standard indicator. [d] Calc. for amides (Table 3) using 2-nitroaniline as the standard indicator. [e] Calc. for tertiary amines (Table 4) using *NN*-diethyl-2,4-dinitroaniline as the standard indicator. [f] Calc. for indoles (Table 5) using 2-methylindole as the standard indicator. H_X = Original function in the literature.

weaker bases, and the dissociation constants obtained from equations (5) and (8) are smaller compared with those calculated by the usual stepwise method. The order of basicity parallels that previously observed for the ionization of amides[10] (Table 3), tertiary amines[11] (Table 4), and sulphoxides[12,13] (Table 8); some deviations occur for other classes of indicators.

TABLE 10

Comparison between M_C activity coefficient functions for sulphuric and perchloric acids

[Acid]/M	H_2SO_4			$HClO_4$		
	a_w[a]	M_C[b]	H_0	a_w[c,d]	M_C[b]	H_0
0·0	1·00			1·00		
0·8	0·969	−0·234	−0·17	0·970	−0·30	−0·17
1·6	0·928	−0·452	−0·67	0·928	−0·455	−0·64
2·4	0·872	−0·681	−1·13	0·877	−0·665	−1·06
3·2	0·804	−0·954	−1·52	0·815	−0·90	−1·41
4·0	0·720	−1·237	−1·86	0·735	−1·15	−1·77
4·8	0·628	−1·521	−2·18	0·638	−1·46	−2·18
5·6	0·529	−1·859	−2·59	0·520	−1·84	−2·63
6·4	0·430	−2·219	−2·99	0·400	−2·29	−3·15
7·2	0·339	−2·644	−3·36	0·295	−2·84	−3·64
8·0	0·259	−3·091	−3·75	0·197	−3·55	−4·24
8·8	0·188	−3·571	−4·18	0·120	−4·32	−4·95
9·6	0·131	−4·077	−4·64	0·066	−5·20	−5·74
10·4	0·086	−4·640	−5·14	0·033	−6·16	−6·55
11·2	0·053	−5·262	−5·65	0·015	−7·17	−7·34
12·0	0·031	−5·873	−6·15			

[a] E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, 1964, **86**, 5080. [b] Referred to 2-nitroaniline as the standard indicator. [c] H. Wai and K. Yates, *Canad. J. Chem.*, 1969, **47**, 2326. [d] J. N. Pearce and A. F. Nelson, *J. Amer. Chem. Soc.*, 1933, **55**, 3075.

Thus, on ionization of primary nitroanilines[14] (Table 1) the figure of −8·15 for the pK_{BH^+} of substituted 2,4,6-trinitroaniline, calculated by a plot of log $k_{app}{}^D$ against log $K_{app}{}^C$ give for indicators 10—12 the sequence: 3-Me > H > 3-Br. This order is more reliable than that calculated by the H_0 function and accounts for the effect of bromine in decreasing the basic strength of 2,4-dinitroaniline (Table 1, indicators 7 and 9).

Analysis of the ionization of indoles[15] (Table 5) shows the following order of basicity with the indicator F as standard: H $\simeq$ 1,2-Me_2-5-NO_2 > 1,3-Me_2 > 3-Me > 5-NO_2 > 3-CH_2CO_2H > tryptamine.

The divergence observed in this range of acidity can be related to the different slopes of indicators when the Hammett method is used; as reported, indicators H, J, and P (Table 5) do not follow the original H_I function. For the basicity order of triarylmethyl alcohols[7] (Table 6) the new pK_{BH^+} values shows that the tris-2-methylphenylmethyl alcohol is stronger than 4-methoxytriphenylmethyl alcohol, similarly the tris-4-isopropyl derivative is stronger than the tris-3-methyl analogue. Variations in the basicity order of alcohols are also observed at higher acidity for indicators 15—18 of Table 6 of which the tris-4-nitro-derivative is the least basic compound. It is interesting also to compare the results in Table 7 on the dissociation constants of the hydroxy- and alkoxy-benzenes. For the alkoxy-compounds the sequence obtained by equation (8), 1,3,5-$(MeO)_3$ > 1,3-$(MeO)_2$-2-Me > 1,3-$(MeO)_2$ parallels the basicity order of Kresge *et al.*[16] For the hydroxy-derivatives the observed trend, 1,3,5-$(OH)_3$ > 1,3-$(OH)_2$-2,Me > 1,3-$(OH)_2$ analogous to that given for the alkoxybenzenes, shows some discrepancy on comparison with the literature data.[16] These results involve the similar influence of the methyl group on the basicity constants of the methoxy- and hydroxy-benzenes.

One observes that the pK_{BH^+} values for the ionization of primary nitroanilines in perchloric acids, are very similar to those obtained in sulphuric acid using equation (5) (Table 2).

The results discussed up to now indicate that the revised values of the dissociation constants can be considered to be more reliable than those calculated by the Hammett procedure. Other examples support this statement. A better linear relation is observed when the new dissociation constants are used to plot pK_a against partial molar heats of transfer of primary nitroanilines.[3] Equations, obtained by the least-square method, using the pK_a values reported here and in the literature, respectively, are as follows: $\Delta\bar{H}$/kcal mol^{-1} (nitroanilines, 96·48% H_2SO_4) = 1·873 pK_a + 18·03 (r 0·999, σ_y 0·276, σ_{slope} 0·088); $\Delta\bar{H}$/kcal $mole^{-1}$ (nitroanilines, 96·48% H_2SO_4) = 1·536 pK_a + 17·696 (r 0·994, σ_y 0·626, σ_{slope} 0·163).

Recently the linear relationship (r 0·998) between the dissociation constants of a series of substituted anilines and the corresponding 2-nitroanilines[17] was given as evidence for the reliability of the Hammett overlap method. For the same example, using the new pK_a values for the 2-nitroanilines, some scatter for bases of decreasing strength is observed. However, more accurate analysis of the results shows that for the literature values of aniline derivatives two different linear plots can be obtained. *p*-Hydroxy, *p*-methoxy, *p*-methyl, *m*-methyl, and unsubstituted compounds fit a linear plot with slope 1·47; all other derivatives fit a linear plot with slope 1·10. The break-down of correlation is near for 3-substituted anilines and is more evident when the dissociation constants calculated here are used. This behaviour should be expected on account of the variable base-weakening effect of the 2-nitro-group on the 2-nitroanilines.

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[10] K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

[11] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671.

[12] N. C. Marziano, G. Cimino, R. Passerini, and P. Fiandaca, *Boll. Acc. Gioenia Sci. Nat. Catania*, 1969, IV, IX, 589.

[13] N. C. Marziano, G. Cimino, U. Romano, and R. Passerini, *Tetrahedron Letters*, 1969, 2833.

[14] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.

[15] R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796.

[16] A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *J. Amer. Chem. Soc.*, 1971, **93**, 6174.

[17] M. J. Kamlet and R. R. Minesinger, *J. Org. Chem.*, 1971, **36**, 610.

The M_C activity coefficient functions of primary nitroanilines in sulphuric and perchloric acids are in Table 9 together with the respective H_0 acidity functions. A comparison between M_C and H_0 in sulphuric acid is shown in Figure 1.

Linear relations are found for the whole acidity range when every M_C, calculated for structurally similar bases and with a different standard indicator, is plotted against any other taken as reference.

The behaviour of M_C in different acids (Table 9), as observed for H_0, suggest a more rapid increase of the $f_B f_{H^+}/f_{BH^+}$ ratio in perchloric compared with sulphuric acid. Also it was found that a plot of $M_C(HClO_4)$ against $M_C(H_2SO_4)$ at the same molarity, as opposed to the behaviour of H_0, is linear at concentrations >8M (Figure 2).

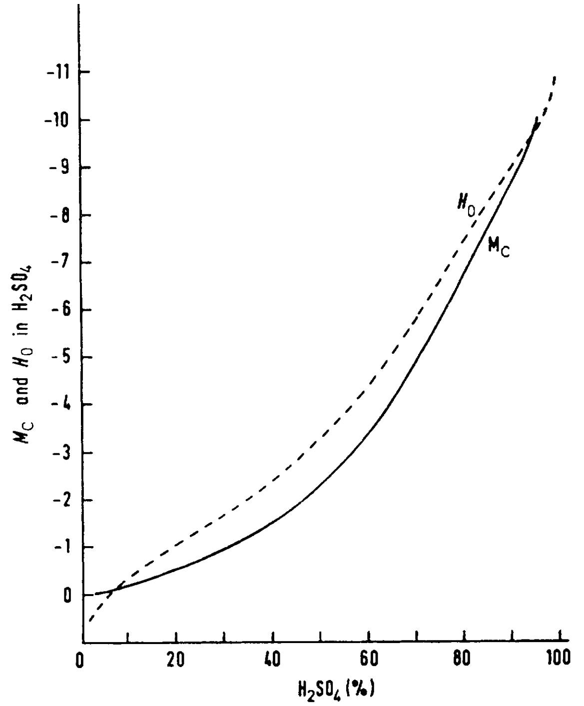

FIGURE 1 Plot of M_C and H_0 functions against % sulphuric acid

Several approaches have been developed in order to study the principal factors determining this behaviour. The approximation of Bascombe and Bell[18] and Wyatt,[19] correlating the solvation effects of the medium on the Hammett acidity function, have been adapted to the M_C scale. The identity of the plot of H_0 against a_w up to 9M[20] for the H_0 function in sulphuric and perchloric acids has been tested for the corresponding M_C functions, using the same range of acid concentration (Table 10), and verified up to 8M (Figure 3). The analysis of these results suggest that M_C is a unique function of the water activity of the acid at low acidity (see Figure 3) and of the acid concentration at high acidity (see Figure 2).

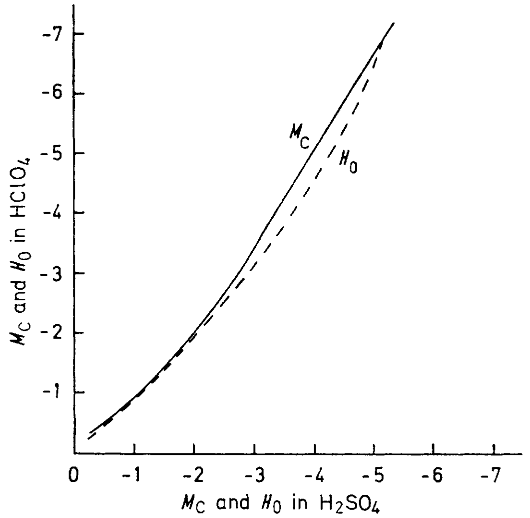

FIGURE 2 Plot of M_C and H_0 functions in $HClO_4$ against those in H_2SO_4 at the same molarity

All these factors provide evidence for the reliability of our theoretical treatment and also that the pK_a values and the M_C function are actually related to medium acidity. In this approach, in fact, the variation of the $f_B f_{H^+}/f_{BH^+}$ ratio with acid concentration is the only

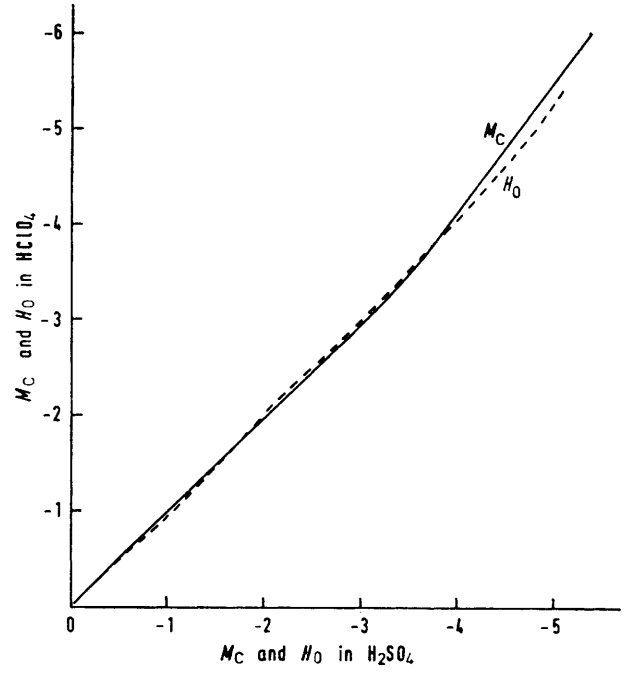

FIGURE 3 Plot of M_C and H_0 functions in $HClO_4$ against those in H_2SO_4 at the same water activity

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[18] K. N. Bascombe and R. P. Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[19] P. A. H. Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162.

[20] K. Yates and H. Wai, *J. Amer. Chem. Soc.*, 1964, **86**, 5408.

factor affecting the protonation equilibrium; the dissociation constant obtained for each base, when related to that of the indicator taken as standard, gives an activity coefficient function independent of the structure of the indicators used, as required from equation (7). Evidence for this statement is given by the identity of the M_C functions calculated by amides and nitroanilines using in both cases 2-nitroaniline as the standard. (Table 9).

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