

The M_C Activity Coefficient Function for Acid-Base Equilibria. Part 3.¹ Improvement on the M_C Function by Mathematical Treatment

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The empirical relationship $\log f_{B_j/H^+}/f_{B_jH^+} = n_{ji} \log f_{B_i/H^+}/f_{B_iH^+}$ for protonation equilibria in aqueous sulphuric acid, between any two weak bases i and j has been tested. The weak bases examined are primary nitroanilines, amides, tertiary amines, indoles, benzophenones, sulphoxides, and hydroxy- and alkoxy-benzenes. A mathematical treatment which accounts for all the indicators, independently of their structure or acidity range, has been used. The results obtained show in all cases the validity of the relationship examined. Activity coefficient functions have been calculated by using both structurally similar indicators and all the compounds. The results show the identity between the particular functions and the general one. A single function [$M_C f(x)$ 'generatrix function'] able to give the dependence on acid concentration of $\{\log \{[BH^+]/[B]\} - \log [H^+]\}$ of any indicator is obtained. The analysis of relative n_{ji} values for different or structurally similar indicators show the limitation of classing indicators by series.

Our previous analysis¹ of empirical relationships for equilibria of weak bases in aqueous sulphuric acid is here extended to provide evidence for the validity of relation (1) using a mathematical treatment different from the stepwise method.² The meaning of the M_C

$$\log \frac{f_{B_j/H^+}}{f_{B_jH^+}} = n_{ji} \log \frac{f_{B_i/H^+}}{f_{B_iH^+}} \quad (1)$$

activity coefficient function² in terms of a 'generatrix function' [$M_C f(x)$] is also given.

The $M_C f(x)$ Function.—Relation (1) can be verified through the experimental relation (2) where $Y_j =$

$$Y_j(x) = n_{ji} Y_i(x) + r_{ji} \quad (2)$$

$\log(B_jH^+/B_j) - \log [H^+]$; † n_{ji} , r_{ji} are constants and suffixes i and j identify the indicators. (x) Is the molar acid concentration.

Since relation (2) is valid for any indicators, i and j , one can write (2') so that (2'') is obtained, which shows

$$Y_i = n_{ik} Y_k + r_{ik} \quad (2')$$

the interplay of the coefficients. It is clear that all the

$$Y_j = n_{ji}(n_{ik} Y_k + r_{ik}) + r_{ji} = (n_{ji} n_{ik}) Y_k + (n_{ji} r_{ik} + r_{ji}) \quad (2'')$$

† $[H^+]$ = Molar concentration of H^+ ions.³

‡ The suffix $f(x)$ in the M_C activity coefficient function is here adopted in order to distinguish the present method of analysis from the stepwise one.²

indicators Y_i , can be referred to a specific, fixed Y_k , as in (2'). Then we can define Y_k as $f(x)$ and write equation (3) where $N_i = n_{ik}$ and $C_i = r_{ik}$ in (2').

$$Y_i = N_i f(x) + C_i \quad (3)$$

Relation (3) guarantees that any Y_i indicator can be expressed through a single $f(x)$ function, a 'generatrix function', and two appropriate constants. It appears, also, that any $f^*(x)$ function, related to $f(x)$ by (4) is a generatrix function as is $f(x)$ itself. Any $f(x)$ function,

$$f^*(x) = a f(x) + b \quad (4)$$

relative to the standard aqueous state where $f(x) \equiv 0$, gives the dependence on acid concentration of any $Y_i(x)$ function [$M_C f(x)$ activity coefficient function ‡].

Concerning the criterion of estimating a particular $f(x)$, one has to consider that practically the $Y_i(x)$ functions are taken from only a few experimental points, so that any coefficient deduced is affected by an error in the estimation. To replace $f(x)$ in (3) with $Y_i(x)$ would give $N_i = 1$ and $C_i = 0$ and clearly the error for these coefficients is zero; but the error on the other coefficients N_k and C_k with k other than i , is rather large. The

¹ Part 2, N. C. Marziano, P. G. Traverso, and R. C. Passerini, preceding paper.

² N. C. Marziano, G. M. Cimino, and R. C. Passerini, *J.C.S. Perkin II*, 1973, 1915.

³ E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, 1964, **86**, 5080.

obvious aim is to give no emphasis to a particular Y_i , but to share the errors among the various functions. This can be easily done by using the least-squares technique by which the whole set of experimental data is used simultaneously. To this end, the polynomial form (5) has been utilized where the unknowns are the A_k

$$f(x) = \sum_k A_k x^k \quad (5)$$

coefficients of the polynomial. The global error to be minimized is given by (5'), which comes from (3) and (5). The values of x to be considered in the summation are peculiar for each indicator, so that they will be different, in general, for the i th and the j th, depending on the

$$\sum_i \sum_x [Y_i(x) - (\sum_k A_k x^k) N_i - C_i] \quad (5')$$

available experimental data. Formula (5') is not the familiar quantity to be minimized by least-squares, since certain unknowns appear multiplied by each other. Calculations are obviously more difficult, but any suitable numerical technique gives the optimal values.

The purpose of numerical work is to obtain the best possible consistency of the experimental values with the calculated functions. The goodness of fit of the results has been evaluated by σ^2 values, so that their magnitude is the parameter able to verify the validity of the model expressed by relation (1). It follows that the new criterion of analysis realises a significant improvement over the stepwise method, used in the first attempt in this field.² This is because it allows indicators to be compared independently from the extension and the range of the overlap. Since all the relations are computed at the same time, it thus avoids possible biases of step-by-step coupling of indicators. However the new results suffer from the approximations intrinsic in the experimental measurements of the reported $\log I$ and $[H^+]$ values and also from the limitation that a discrete set of points are experimentally available for any indicator. Utilization of experimental points has been preferred, because, in this way, any artificial use of interpolated data is avoided.

The latter procedure was followed in a preliminary paper,⁴ since this allows a constant ratio between the number of experimental points and the interval of acid concentration to be used. Utilization of random Y_i values, however, shows no significant differences in the results.

RESULTS AND DISCUSSION

Using relation (3) the mathematical treatment already discussed has been applied to primary nitroanilines, amides, tertiary amines, indoles, benzophenones, sulphoxides, and hydroxy- and alkoxy-benzenes. Using simultaneously all the experimental data the $f(x)$ generatrix function, representing the acidity dependence of any Y_i function, has been obtained. The graph of chosen $f(x)$, relative to the standard aqueous state ' $M_C f(x)$ activity coefficient function' is shown in

⁴ R. C. Passerini, N. C. Marziano, and P. G. Traverso, *Gazzetta*, 1975, **105**, 901.

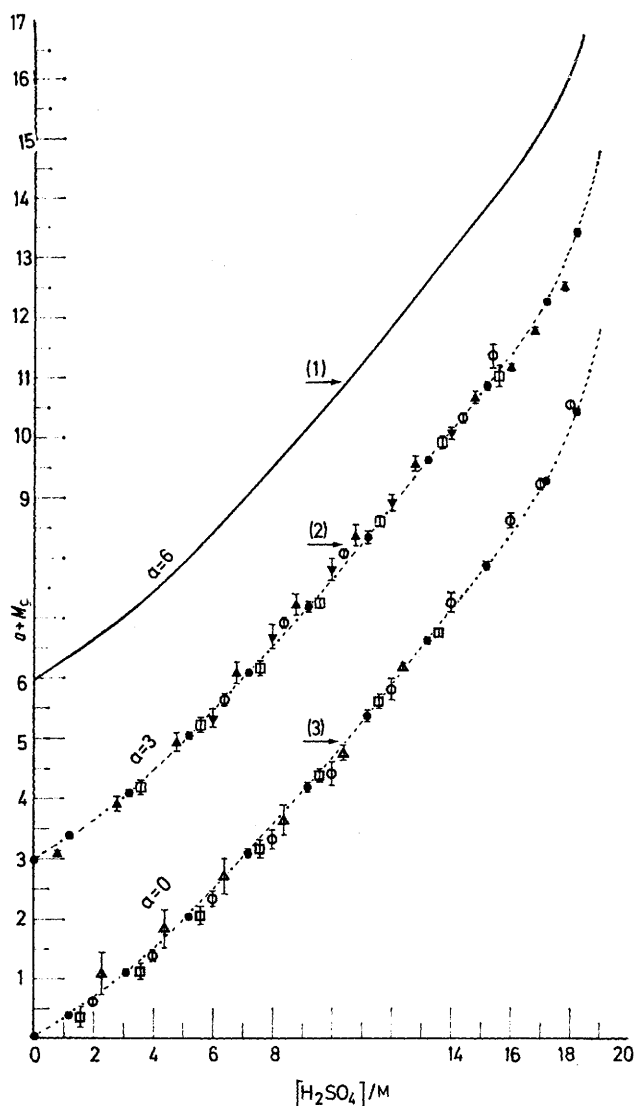


FIGURE 1 (1) The activity coefficient function $M_C f(x)$ versus concentration of sulphuric acid at 25 °C; (2) $f_i(x)$ functions and estimated errors for tertiary amines (\blacktriangle), sulphoxides (\square), benzophenones (\blacktriangledown), M_C (\bullet and dotted line); (3) $f_i(x)$ functions and estimated errors for amides (\square), primary nitroanilines (\circ), indoles (\triangle), M_C (\bullet and dotted line)

TABLE I

The new activity coefficient function M_C and estimated errors in aqueous sulphuric acid at 25 °C^a

$[H_2SO_4]/M$	$-M_C$
0.2	0.006 66 ± 0.000 99
0.4	0.013 19 ± 0.001 76
0.6	0.019 65 ± 0.002 36
0.8	0.026 10 ± 0.002 83
1.0	0.032 59 ± 0.003 19
1.2	0.039 15 ± 0.003 48
1.4	0.045 83 ± 0.003 71
1.6	0.052 65 ± 0.003 91
1.8	0.059 62 ± 0.004 09
2.0	0.066 76 ± 0.004 25
2.2	0.074 09 ± 0.004 41
2.4	0.081 61 ± 0.004 58
2.6	0.089 32 ± 0.004 74
2.8	0.097 22 ± 0.004 90
3.0	0.105 31 ± 0.005 07
3.2	0.113 59 ± 0.005 24

TABLE 1 (Continued)

$[\text{H}_2\text{SO}_4]/\text{M}$	$-M_G$
3.4	0.122 05 \pm 0.005 42
3.6	0.130 67 \pm 0.005 59
3.8	0.139 47 \pm 0.005 76
4.0	0.148 41 \pm 0.005 94
4.2	0.157 50 \pm 0.006 11
4.4	0.166 73 \pm 0.006 29
4.6	0.176 08 \pm 0.006 46
4.8	0.185 55 \pm 0.006 63
5.0	0.195 13 \pm 0.006 79
5.2	0.204 80 \pm 0.006 96
5.4	0.214 57 \pm 0.007 12
5.6	0.224 41 \pm 0.007 28
5.8	0.234 33 \pm 0.007 44
6.0	0.244 32 \pm 0.007 59
6.2	0.254 38 \pm 0.007 74
6.4	0.264 49 \pm 0.007 88
6.6	0.274 65 \pm 0.008 01
6.8	0.284 87 \pm 0.008 14
7.0	0.295 13 \pm 0.008 27
7.2	0.305 43 \pm 0.008 39
7.4	0.315 78 \pm 0.008 50
7.6	0.326 17 \pm 0.008 61
7.8	0.336 60 \pm 0.008 71
8.0	0.347 07 \pm 0.008 81
8.2	0.357 57 \pm 0.008 89
8.4	0.368 12 \pm 0.008 97
8.6	0.378 70 \pm 0.009 04
8.8	0.389 32 \pm 0.009 11
9.0	0.399 97 \pm 0.009 17
9.2	0.410 66 \pm 0.009 23
9.4	0.421 39 \pm 0.009 27
9.6	0.432 16 \pm 0.009 31
9.8	0.442 96 \pm 0.009 34
10.0	0.453 79 \pm 0.009 36
10.2	0.464 65 \pm 0.009 37
10.4	0.475 55 \pm 0.009 37
10.6	0.486 48 \pm 0.009 36
10.8	0.497 43 \pm 0.009 34
11.0	0.508 40 \pm 0.009 31
11.2	0.519 40 \pm 0.009 26
11.4	0.530 42 \pm 0.009 21
11.6	0.541 46 \pm 0.009 15
11.8	0.552 52 \pm 0.009 07
12.0	0.563 60 \pm 0.008 98
12.2	0.574 69 \pm 0.008 89
12.4	0.585 79 \pm 0.008 78
12.6	0.596 92 \pm 0.008 67
12.8	0.608 07 \pm 0.008 54
13.0	0.619 24 \pm 0.008 40
13.2	0.630 45 \pm 0.008 26
13.4	0.641 71 \pm 0.008 11
13.6	0.653 02 \pm 0.007 95
13.8	0.664 41 \pm 0.007 78
14.0	0.675 90 \pm 0.007 61
14.2	0.687 50 \pm 0.007 42
14.4	0.699 26 \pm 0.007 23
14.6	0.711 20 \pm 0.007 02
14.8	0.723 37 \pm 0.006 81
15.0	0.735 83 \pm 0.006 59
15.2	0.748 62 \pm 0.006 36
15.4	0.761 83 \pm 0.006 11
15.6	0.775 51 \pm 0.005 86
15.8	0.789 77 \pm 0.005 60
16.0	0.804 70 \pm 0.005 32
16.2	0.820 41 \pm 0.005 30
16.4	0.837 04 \pm 0.004 73
16.6	0.854 72 \pm 0.004 41
16.8	0.873 61 \pm 0.004 08
17.0	0.893 90 \pm 0.003 72
17.2	0.915 77 \pm 0.003 34
17.4	0.939 44 \pm 0.002 96
17.6	0.965 15 \pm 0.002 63
17.8	0.993 17 \pm 0.002 48
18.0	1.023 78 \pm 0.002 72
18.2	1.057 29 \pm 0.003 47
18.4	1.094 06 \pm 0.004 72

^a $M_{cf}(x)$ Function calculated by equation (3) using all 64 indicators (Tables 2—6).

Figure 1. The corresponding values and their confidence intervals are reported in Table 1.

It can be seen that estimated errors in M_G (Table 1) give evidence of the validity of relation (1), as the small uncertainties observed over the whole acidity range can be reasonably ascribed to the experimental errors only.

The goodness of fit and the same curvature observed on comparison between theoretical and experimental Y_i plots gives a further test of validity (Figure 2). Further

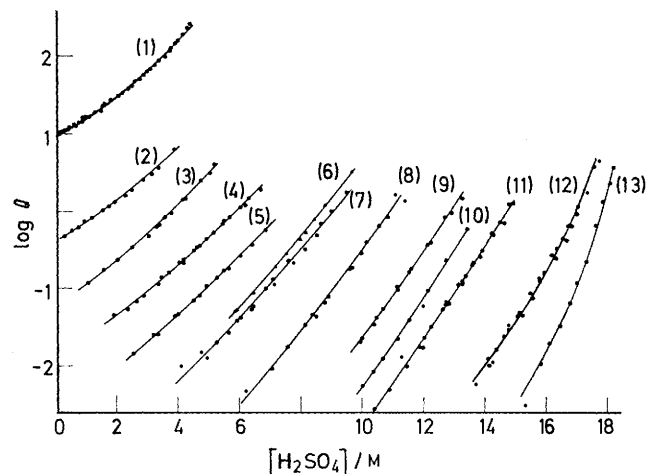


FIGURE 2 Calculated curves and experimental points of $\log Q \equiv Y_i$ versus concentration of sulphuric acid for primary nitroanilines (for indicator numbers see Table 2)

evidence in this case is also suggested from the σ^2 value of each indicator (Tables 2—6), the values of which can arise only from the spread of the experimental points.

An $M_{cf}(x)$ function, by using indicators with the same basic group, has been separately calculated and the

TABLE 2

Relative n_{ji} coefficients and mean square roots of deviations for primary nitroanilines in aqueous sulphuric acid at 25 °C.

Aniline ^a	σ^2 ^b	σ^2 ^c	n_{ji} ^d
4-Nitro (1)	0.030	0.023	1.00
2-Nitro (2)	0.009	0.015	1.052 \pm 0.047
4-Chloro-2-nitro (3)	0.016	0.017	0.976 \pm 0.039
2,5-Dichloro-4-nitro (4)	0.025	0.024	1.100 \pm 0.043
2-Chloro-6-nitro (5)	0.018	0.019	1.081 \pm 0.049
2,6-Dichloro-4-nitro (6)	0.064	0.065	0.996 \pm 0.048
2,4-Dichloro-6-nitro (7)	0.018		0.939 \pm 0.053
2,4-Dinitro (8)	0.062	0.060	0.890 \pm 0.047
2,6-Dinitro (9)	0.025		0.842 \pm 0.051
4-Chloro-2,6-dinitro (10)	0.043		0.796 \pm 0.051
2-Bromo-4,6-dinitro (11)	0.048	0.058	
3-Methyl-2,4,6-trinitro (12)	0.067	0.044	0.942 \pm 0.058
3-Bromo-2,4,6-trinitro (13)	0.080		0.913 \pm 0.058

^a $\log I$ values from C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **61**, 6654; P. Tickle, A. G. Briggs, and J. M. Wilson, *J. Chem. Soc. (B)*, 1970, 65; M. I. Vinnik and N. B. Librovich, *Tetrahedron*, 1966, **22**, 2945; M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878. ^b Mean square roots of deviations between experimental points and theoretical lines by equation (3) using all indicators. ^c Mean square roots of deviations between experimental points and theoretical lines by equation (3) using only indicators with the same basic group. ^d Relative n_{ji} coefficients [see equation (2)] and estimated errors by equation (3) using all indicators.

TABLE 3

Relative n_{ji} coefficients and mean square roots of deviations for amides in aqueous sulphuric acid at 25 °C

Amide ^a	σ^2 ^b	σ^2 ^c	n_{ji} ^d
Pyrrole-2-carboxamide (1)	0.021	0.015	0.862 ± 0.039
4-Methoxybenzamide (2)	0.020	0.021	0.962 ± 0.036
3,4,5-Trimethoxybenzamide (3)	0.019	0.011	0.954 ± 0.033
3-Nitrobenzamide (4)	0.020	0.017	1.00
3,5-Dinitro-4-methylbenzamide (5)	0.030	0.027	0.969 ± 0.029
2,3,6-Trichlorobenzamide (6)	0.022	0.023	0.915 ± 0.035
2,4-Dichloro-3,5-dinitrobenzamide (7)	0.037	0.031	0.941 ± 0.038
2,4,6-Trinitrobenzamide (8)	0.035	0.027	0.818 ± 0.036

^a log *I* Values from K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957. ^{b-d} As Table 2.

TABLE 4

Relative n_{ji} coefficients and mean square roots of deviations for tertiary amines in aqueous sulphuric acid at 25 °C

Tertiary amines ^a	σ^2 ^b	σ^2 ^c	n_{ji} ^d
<i>NN</i> -Diethyl-2,4-dinitroaniline (1)	0.038	0.038	0.944 ± 0.086
<i>N</i> -(2,4-Dinitrophenyl)piperidine (2)	0.032	0.032	0.955 ± 0.076
<i>NN</i> ,4-Trimethyl-2,6-dinitroaniline (3)	0.019	0.022	1.089 ± 0.083
<i>NN</i> -Dimethyl-2,4-dinitro-1-naphthylamine (4)	0.037		1.174 ± 0.058
4-Chloro- <i>NN</i> -dimethyl-2,6-dinitroaniline (5)	0.026	0.027	1.100 ± 0.064
<i>N</i> -Methyl-4-nitrodiphenylamine (6)	0.027	0.029	1.177 ± 0.065
4-Bromo- <i>N</i> -methyl-4'-nitrodiphenylamine (7)	0.200	0.180	1.278 ± 0.067
<i>NN</i> -Diethyl-2,4,6-trinitroaniline (8)	0.038	0.039	1.029 ± 0.041
<i>N</i> -Methyl-2,4-dinitrodiphenylamine (9)	0.040	0.040	1.00 ± 0.968
<i>NN</i> -Dimethyl-2,4,6-trinitroaniline (10)	0.021	0.021	0.959 ± 0.055
4-Bromo- <i>N</i> -methyl-2',4'-dinitrodiphenylamine (11)	0.015	0.015	0.959 ± 0.048
α ,4-Dibromo- <i>N</i> -methyl-2',4'-dinitrodiphenylamine (12)	0.062	0.066	1.075 ± 0.052
<i>N</i> -Methyl-2,2',4,4'-tetranitrodiphenylamine (13)	0.148	0.074	1.272 ± 0.064

^a log *I* Values from E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671. ^{b-d} As Table 2.

TABLE 5

Relative n_{ji} coefficients and mean square roots of deviations for indoles in aqueous sulphuric acid at 25 °C

Indole ^a	σ^2 ^b	σ^2 ^c	n_{ji} ^d
1,2-Dimethyl (1)	0.007	0.011	1.095 ± 0.286
2-Methyl (2)	0.009	0.006	1.254 ± 0.231
1,2,3-Trimethyl (3)	0.025	0.027	1.098 ± 0.165
2,3-Dimethyl (4)	0.036	0.049	1.188 ± 0.096
1-Methyl (5)	0.040	0.042	1.107 ± 0.101
1,2-Dimethyl-5-nitro (6)	0.078	0.077	1.140 ± 0.089
1,3-Dimethyl (7)	0.036	0.038	1.00
3-Methyl (8)	0.030	0.026	1.090 ± 0.078
Tryptamine (9)	0.026	0.050	1.066 ± 0.086
5-Nitro (10)	0.066	0.050	1.636 ± 0.117
Indole (11)	0.092		1.714 ± 0.110

^a log *I* Values from R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796. ^{b-d} As Table 2.

observed trend compared with that of the general $M_{cf}(x)$. This comparison is a matter of interest, since it might be expected that the $M_{cf_i}(x)$ functions obtained for each series of indicators are different, so that the

general $M_{cf}(x)$ is only their average. Two arguments show that it is not the case. The acidity dependence and estimated errors of any $M_{cf_i}(x)$ function (Figure 1) gives evidence of identity between the individual functions and the general one. Comparison between the

TABLE 6

Relative n_{ji} coefficients and mean square roots of deviations for benzophenones in aqueous sulphuric acid at 25 °C

Benzophenone ^a	σ^2 ^b	σ^2 ^c	n_{ji} ^d
2,4,4'-Trimethoxy (1)	0.049	0.040	0.756 ± 0.031
4,4'-Dimethoxy (2)	0.066	0.081	1.00
4-Hydroxy-3,3',4'-trimethoxy (3)	0.025	0.029	1.068 ± 0.044
4-Methoxy (4)	0.021	0.017	1.046 ± 0.038
3-Chloro-4-methoxy (5)	0.009	0.020	1.115 ± 0.055
Unsubstituted (6)	0.088	0.076	1.343 ± 0.056
4-Chloro (7)	0.026	0.039	1.130 ± 0.052
3-Chloro (8)	0.014	0.027	1.023 ± 0.050
4,4'-Dichloro (9)	0.062	0.061	1.146 ± 0.025

^a log *I* Values from T. G. Bonner and J. Philips, *J. Chem. Soc. (B)*, 1966, 650. ^{b-d} As Table 2.

corresponding σ^2 values also demonstrates consistency (Tables 2—6). No significant improvement is observed when the $M_{cf_i}(x)$ functions are used instead of $M_{cf}(x)$.

It appears from the results, mainly from the small σ^2 values observed in all cases, that the validity of relation (1) is established both within each series, and between any two indicators.* The validity of the numerical treatment is also confirmed. This evidence allows an explanation of the relative n_{ji} values obtained for indicators with the same (Tables 2—6) or with different basic groups (Table 7). The results show that significantly

TABLE 7

Relative n_{ji} coefficients for indicators with different basic groups

Compounds	n_{ji} ^a	Compounds	n_{ji} ^b
4-Nitroaniline	1.00	Primary nitroanilines	1.00
3-Nitrobenzamide	1.843 ± 0.088	Amides	1.632
<i>N</i> -Methyl-2,4-dinitro-diphenylamine	0.648 ± 0.038	Tertiary amines	0.666
1,3-Dimethylindole	0.594 ± 0.038	Indoles	0.690
4,4'-Dimethoxy-benzophenone	1.087 ± 0.060	Benzophenones	1.248

^a Relative n_{ji} coefficients [see equation (2)] calculated by using the values of proper indicators. ^b n_{ji} Coefficients relative to 'primary nitroanilines' by using the average of values inside any series.

different and closely similar n_{ji} values can be observed among members of the same series and among structurally different indicators. The breakdown of the assumption $n_{ji} \approx$ constant inside any series,^{4,5} follows so that any

* The confidence that n_{ji} values for any indicator remain constant over the whole acidity range, where experimental log *I* values are not available, can be discussed in terms of probability. Since no exception has been observed for a very large number of indicators, in the range where experimental data are available, we consider relation (1) valid. We believe that some guarantee of its validity can be derived from the consequences of its applications.

⁵ T. A. Moodie, K. Yates, and J. Janata, *J. Amer. Chem. Soc.*, 1975, **97**, 1942.

subdivision of indicators in series 6-8 seems to be unnecessary. It appears unlikely, then, to relate a basic site to

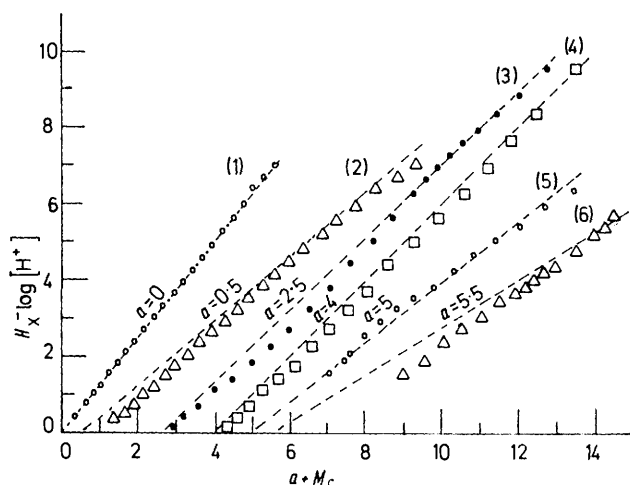


FIGURE 3 Plots of $(H_X - \log[H^+])$ versus $M_C(x)$ (odd numbers) and versus $M_{Cf_i}(x)$ (even numbers) for indoles (1), (2), primary nitroanilines (3), (4), and benzophenones (5), (6)

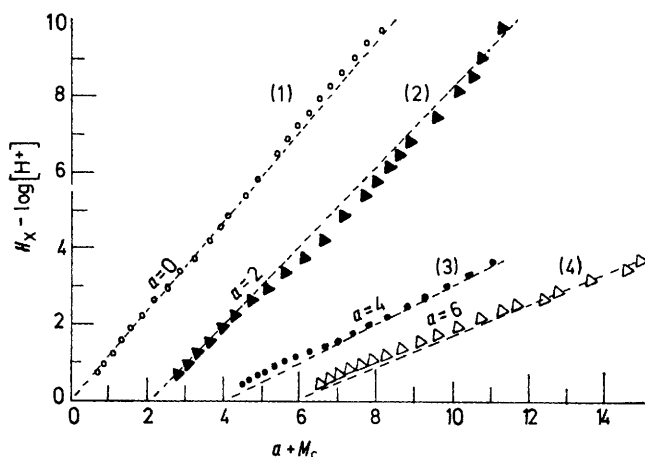


FIGURE 4 Plots of $(H_X - \log[H^+])$ versus $M_{Cf}(x)$ (odd numbers) and versus $M_{Cf_i}(x)$ (even numbers) for tertiary amines (1), (2), and amides (3), (4)

$n_{ji} \pm \delta$ values. On the other hand, by relation (1), it is possible to account for the behaviour of indicators through similarities in n_{ji} values, as the nature of basic site, by

⁶ L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970, 2nd edn.

itself, does not appear to be a valid method of discriminating among indicators.

Figures 3-5 report a comparison among the activity coefficient functions obtained by different approaches. Plots of $(H_X - \log[H^+])$ versus $M_{Cf}(x)$ or versus $M_{Cf_i}(x)$ show different deviations from linearity, although not very large, depending on the series of indicators examined. (Figures 3 and 4). This behaviour can be understood in terms of internal compensation of errors which can occur in H_X upon using the stepwise method and the assumption $n_{ji} \approx \text{constant}$. The importance of such errors differs from series to series, depending on the extent of

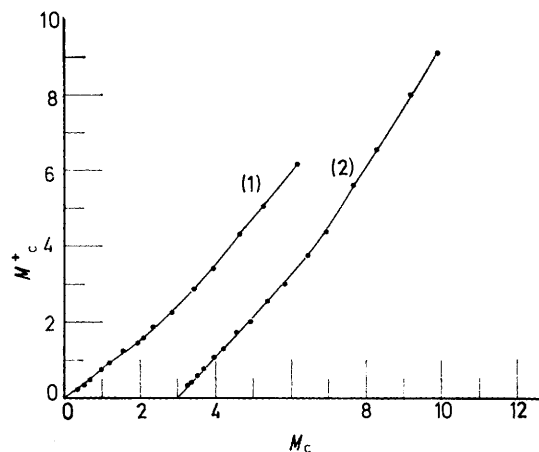


FIGURE 5 Plots of M_C^+ (stepwise method of ref. 2) versus the new $M_{Cf}(x)$ for amides (1) and tertiary amines (2)

the deviation of n_{ji} values from the average. The uncertainties which arise from the stepwise method appear in Figure 5 where a comparison between M_C functions, calculated by different method of analysis, is reported. N_i and C_i (pK_a) values of indicators will be discussed in later papers.

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⁷ C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

⁸ M. Liler, 'Reaction Mechanism in Sulphuric Acid,' Academic Press, London, 1971.