The M_C Activity Coefficient Function for Acid–Base Equilibria. Part 2.[1] A Critical Analysis of Acidity Functions and the Incompatibility amongst Proposed Empirical Correlations

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Protonation equilibria of two weak bases X and Y in sulphuric acid are discussed and experimental linear relationships between their log [BH$^+$]/[B] (log I) and between their log [BH$^+$][B][H$^+$] (log Q) values are analysed. The validity of the relationships has been tested either by using acidity functions or by comparisons with experimental data. It is shown that the utilization of acidity functions leads to different empirical correlations which are incompatible. Approximations involved in the evaluation of acidity functions and acidity ranges where experimental data have been tested were recognized to give rise to apparent compatibility, till now accepted, amongst the relationships. Evidence of the validity of log Q_Y *versus* log Q_X relationships, through experimental data, is given in the range 0—98% sulphuric acid, whilst log I_Y *versus* log I_X relationships are only apparently verified. The reasons why relationships involving log Q and log I can appear to be verified simultaneously are discussed.

THE measurement of acidity in aqueous acid where pH is inappropriate was first realised by Hammett and Deyrup, using an acidity function.[2] The subject has been extensively developed, and different aspects of it have been analysed.[3-5] The original idea has undergone modification since it has been shown that Hammett's acidity function is not applicable generally to the protonation equilibria of all basic indicators.[3-5]

There are, specifically, three approaches to the treatment of the problems involved: (i) the procedure of Yates[6,7] which is used to correlate various acidity functions with the same basic groups; (ii) the procedure of Bunnett and Olsen,[8] involving a linear free energy relationship; and, more recently, (iii) a procedure involving an activity coefficient relationship M_C.[1]

The difference between the last method and the other two lies in the basic idea of stressing the individuality of each indicator as regards the behaviour of the activity coefficients of the species involved, rather than the similar trends of activity coefficients of many indicators within a series of compounds with the same basic groups.

Our present objective is to test the validity of the assumptions involved in the different approaches. In discussing equilibria involving weak bases in moderately concentrated aqueous solutions of strong acids, as represented by equation (1), it is important to analyse the empirical relationships which have been used for obtaining the thermodynamic parameters of equation (1). In this paper we are concerned with equilibria in aqueous sulphuric acid.

$$\mathrm{p}K_{\mathrm{BH^+}} = \log\frac{[\mathrm{BH^+}]}{[\mathrm{B}]} - \log\,[\mathrm{H^+}] + \log\frac{f_{\mathrm{BH^+}}}{f_{\mathrm{B}}f_{\mathrm{H^+}}} \quad (1)$$

Analysis of Empirical Relationships and their Validity.—A general analysis of empirical data for two weak bases X and Y, protonated in overlapping acidity ranges, shows that the linear relationships (2) and (3) seem to be satisfactorily verified in the range 10—80% sulphuric acid.

In (2), I (= [BH$^+$]/[B]) is the measured ionization ratio and Q (= [BH$^+$]/[B][H$^+$]) in (3) involves a knowledge of [H$^+$].† Equations (2) and (3), taking into

$$\log I_{\mathrm{X}} = m\log I_{\mathrm{Y}} + C \quad (2)$$

$$\log Q_{\mathrm{X}} = n\log Q_{\mathrm{Y}} + D \quad (3)$$

account (1), can be rewritten as (4) and (5) respectively, where m and n are of great importance in characterising the different behaviour of the indicators being compared.

$$\log\frac{f_{\mathrm{XH^+}}}{f_{\mathrm{X}}f_{\mathrm{H^+}}} = m\log\frac{f_{\mathrm{YH^+}}}{f_{\mathrm{Y}}f_{\mathrm{H^+}}} + (1-m)\log[\mathrm{H^+}] + \mathrm{p}K_{\mathrm{XH^+}} - m\mathrm{p}K_{\mathrm{YH^+}} - C \quad (4)$$

$$\log\frac{f_{\mathrm{XH^+}}}{f_{\mathrm{X}}f_{\mathrm{H^+}}} = n\log\frac{f_{\mathrm{YH^+}}}{f_{\mathrm{Y}}f_{\mathrm{H^+}}} + \mathrm{p}K_{\mathrm{XH^+}} - n\mathrm{p}K_{\mathrm{YH^+}} - D \quad (5)$$

Values m and $n \simeq 1$ have been often observed for series of compounds of closely similar structures.[3-5] Hence the idea of classifying the weak bases in 'series' and of determining the corresponding acidity functions (H_{X}).[3-5] In the latter case equations (4) and (5) become (6) which justifies the existence of H_{X}. However the

$$\log\frac{f_{\mathrm{XH^+}}}{f_{\mathrm{X}}f_{\mathrm{H^+}}} = \log\frac{f_{\mathrm{YH^+}}}{f_{\mathrm{Y}}f_{\mathrm{H^+}}} + \mathrm{p}K_{\mathrm{XH^+}} - \mathrm{p}K_{\mathrm{YH^+}} - \text{constant} \quad (6)$$

simple relation between a 'series' and its H_{X} function fails as soon as significant deviations of m and n from unity are observed for structurally similar compounds. Moreover, for m and $n \neq 1$, equations (4) and (5) represent

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† [H$^+$] = molar concentration of H$^+$ ions and C_{A} = molar concentration of H_2SO_4. [H$^+$] values from ref. 9 have been used for the calculation of log Q values. Also for the experimental verification of relationships, unless otherwise designated, log [BH$^+$]/[B] values reported in the literature have been utilized.

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[7] K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, 1973, **95**, 418.

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

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

two different descriptions of the behaviour of indicators, whether pairs of weak bases with the same or different structure are considered. The necessity arises of testing which of them is the more closely verified.

First, analysis by using the empirical correlations till now proposed, involving acidity functions, is attempted. From equation (4), Yates' relationship (7) is obtained.[6] Yates' plots suggest that equation (7) is satisfied in the range 10—80% sulphuric acid [6,7] so that these results give a test of validity of equation (4).

$$H_X = mH_Y + pK_{XH^+} - mpK_{YH^+} - C \qquad (7)$$

An analogous treatment of equation (5) leads to equation (8), the latter largely verified by Bunnett and Olsen [8] through equation (9) assuming the approximation $[H^+] \equiv C_A \equiv [H_2SO_4]$. However equations (7) and (8), as pointed out by Greig,[10] are mutually incompatible, in contrast with their accepted verification.

$$H_X = nH_Y + (n - 1)\log[H^+] + pK_{XH^+} - npK_{YH^+} - D \qquad (8)$$

$$\log I_X + H_0 = \phi(H_0 + \log[H^+]) + pK_{XH^+} \qquad (9)$$

Also equation (10), proposed first by Arnett [11] and examined by him and by Yates [7] seems to be well verified and yet neither $(H_0 + \log[H^+])$ nor H_0 are linearly related to $C_A \equiv [H_2SO_4]$. That they should be can be seen by rewriting (7) and (8) as (7′) and (8′) respectively.

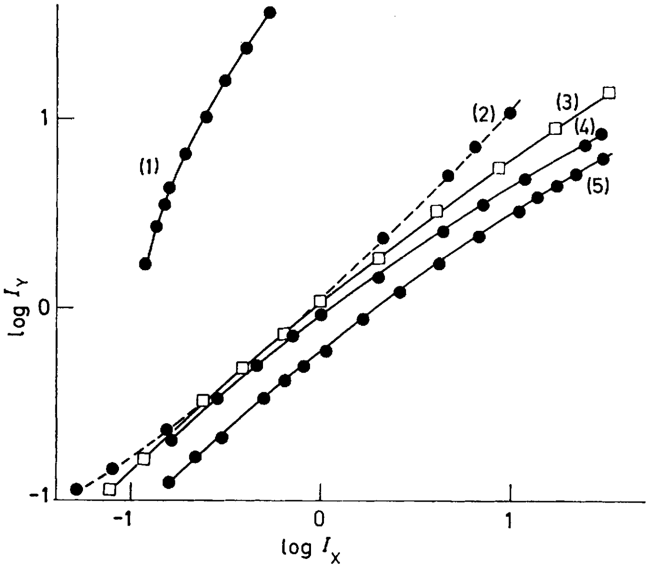

FIGURE 1 Plots of log I_Y *versus* log I_X for the following pairs of indicators: (1) X = 4-methyl-3,5-dinitrobenzamide, Y = *NN*-dimethyl-2,4-dinitro-1-naphthylamine; (2) X = *NN*-dimethyl-2,6-dinitro-4-methylaniline, Y = 2,3-dimethylindole; (3) X = *NN*-dimethyl-2,4-dinitro-1-naphthylamine, Y = 2,5-dichloro-4-nitroaniline; (4) X = *N*-(2,4-dinitrophenyl)piperidine; Y = 2-nitroaniline; (5) X = 4-chloro-2-nitroaniline; Y = pyrrole-2-carboxamide. * All points obtained by interpolating experimental data

It follows that previous experimental evidence in support of the relationships discussed must be examined more critically, since they lead to incompatible correlations without any possibility of choosing among them.

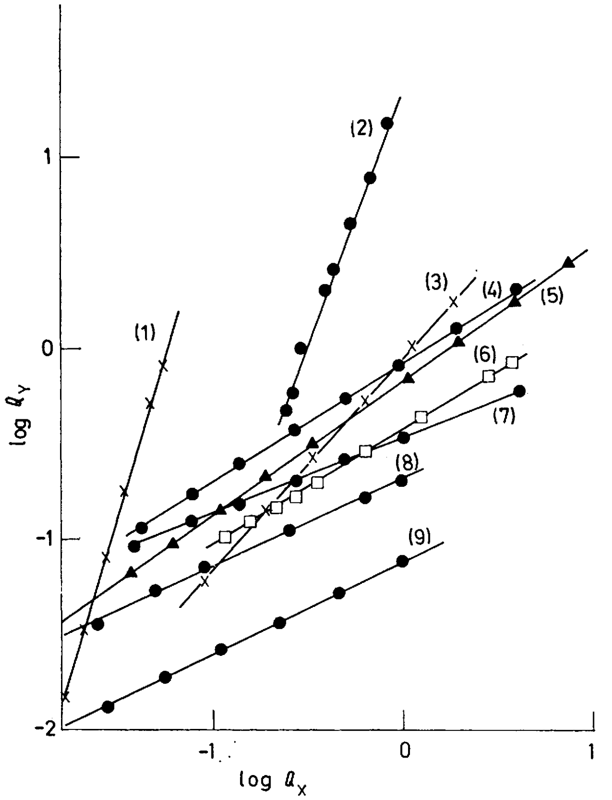

FIGURE 2 Plots of log Q_Y *versus* log Q_X for the following pairs of indicators: (1) X = 2,4-dichloro-3,5-dinitrobenzamide, Y = 5-nitroindole; (2) X = 4-methyl-3,5-dinitrobenzamide, Y = *NN*-dimethyl-2,4-dinitro-1-naphthylamine; (3) X = 2,3-dimethylindole, Y = 4,*NN*-trimethyl-2,6-dinitroaniline; (4) X = 4,*NN*-trimethyl-2,6-dinitroaniline, Y = 4-chloro-2-nitroaniline; (5) X = *NN*-dimethyl-2,4-dinitro-1-naphthylamine, Y = 2,5-dichloro-4-nitroaniline; (6) X = 4-chloro-2-nitroaniline, Y = pyrrole-2-carboxamide; (7) X = 4,*NN*-trimethyl-2,6-dinitroaniline, Y = pyrrole-2-carboxamide; (8) X = *x*′,4′-dibromo-*N*-methyl-2,4-dinitrodiphenylamine, Y = 2,4,6-trinitrobenzamide; (9) X = 2,6-dinitroaniline; Y = 2,4,6-trinitrobenzamide. * As Figure 1

$$(H_X - H_0) = m'C_A = \log\frac{f_{XH^+}f_B}{f_{BH^+}f_X} \qquad (10)$$

$$(H_X - H_0) = (m - 1)H_0 + pK_{XH^+} - mpK_{YH^+} - C \qquad (7')$$

$$(H_X - H_0) = (n - 1)(H_0 + \log[H^+]) + pK_{XH^+} - npK_{YH^+} - D \qquad (8')$$

Particularly we need to establish whether acidity functions are too broad approximations for the treatment of activity coefficient behaviour, or whether the empirical relationships (2), (3) and (10) are only apparently verified.

Many experimental data can be found in the literature to support the first possibility.[3-5,8,12]

It is thus important to test equations (2), (3), and (10)

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

[11] E. M. Arnett and G. W. March, *J. Amer. Chem. Soc.*, 1966, **88**, 1177.

[12] T. A. Modro, K. Yates, and J. Janata, *J. Amer. Chem. Soc.*, 1975, **97**, 1942.

by using experimental values of log I and log Q, instead of acidity functions.

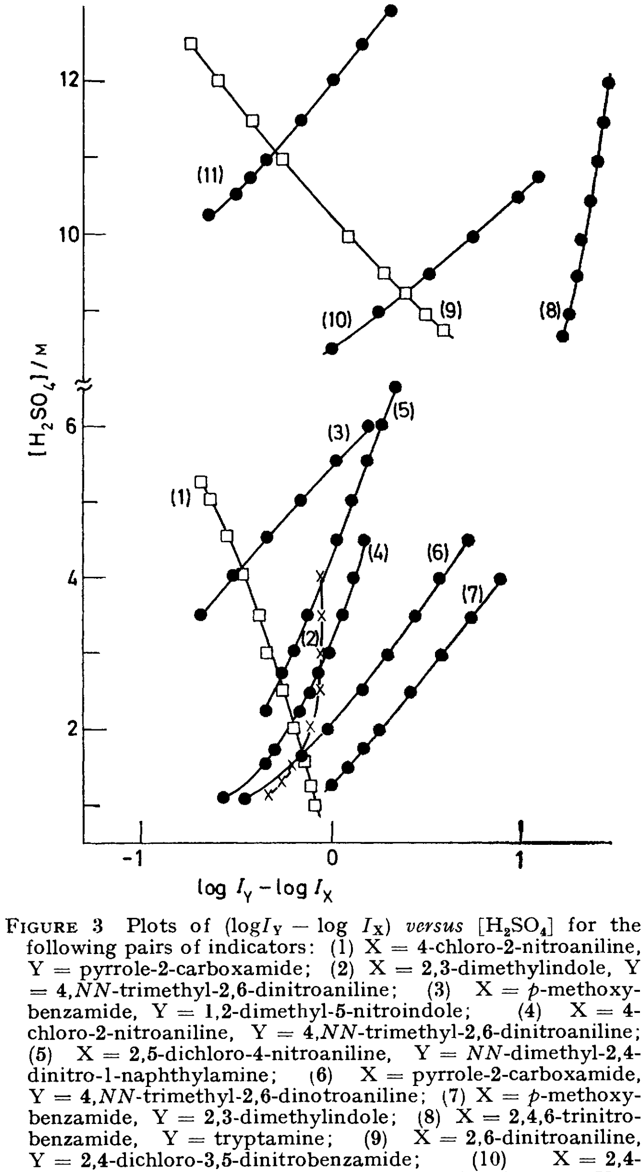

FIGURE 3 Plots of ($\log I_Y$ − log I_X) *versus* [H_2SO_4] for the following pairs of indicators: (1) X = 4-chloro-2-nitroaniline, Y = pyrrole-2-carboxamide; (2) X = 2,3-dimethylindole, Y = 4,*NN*-trimethyl-2,6-dinitroaniline; (3) X = *p*-methoxybenzamide, Y = 1,2-dimethyl-5-nitroindole; (4) X = 4-chloro-2-nitroaniline, Y = 4,*NN*-trimethyl-2,6-dinitroaniline; (5) X = 2,5-dichloro-4-nitroaniline, Y = *NN*-dimethyl-2,4-dinitro-1-naphthylamine; (6) X = pyrrole-2-carboxamide, Y = 4,*NN*-trimethyl-2,6-dinotroaniline; (7) X = *p*-methoxybenzamide, Y = 2,3-dimethylindole; (8) X = 2,4,6-trinitrobenzamide, Y = tryptamine; (9) X = 2,6-dinitroaniline, Y = 2,4-dichloro-3,5-dinitrobenzamide; (10) X = 2,4-dichloro-3,5-dinitrobenzamide, Y = 5-nitroindole; (11) X = 2,4,6-trinitrobenzamide, Y = *x*,4′-dibromo-*N*-methyl-2,4-dinitrodiphenylamine. * As Figure 1

Accordingly, we have plotted log I_Y *versus* log I_X and log Q_Y *versus* log Q_X for a large number of indicators, with the same or different basic groups, in the acidity range 0—98% sulphuric acid. Some results are illustrated in Figures 1 and 2, which show that equation (3) always gives linear relationships over the whole acidity range, whilst there are exceptions, expecially at very low acidity, in the case of (2). The reverse situation was never observed.

Moreover, equation (10), re-written as (10′) has been tested by using experimental data. Plots (log I_Y − log I_X) *versus* molar concentration of sulphuric acid reported in Figure 3 show that (10), also, is apparently verified.

$$\log I_Y - \log I_X = m'C_A \qquad (10')$$

The observed behaviour of log I and log Q plots is of considerable significance since, from the results obtained, it appears that only equation (3) seems to be always true.

Analysis of experimental data has been also extended in order to show under which experimental conditions equations (2) and (3) can both appear to be verified. It has been done by plotting log Q *versus* log [H^+], as relation (11) would be required to be satisfied for both (2) and (3) to be verified.

$$\log Q = A \log [H^+] + \text{constant} \qquad (11)$$

The results obtained, reported in Figure 4, show the impossibility of choosing between (2) and (3) in the range 8M < [H_2SO_4] < 13M, where relation (11) is verified, but not elsewhere. It thus follows that very low and high acidities rather neglected until now, are the most significant ranges which allow the validity of equations examined to be established. Examples of plots of indicators, mainly protonated in the low acidity ranges are in Figures 1 and 2. The fundamental difference

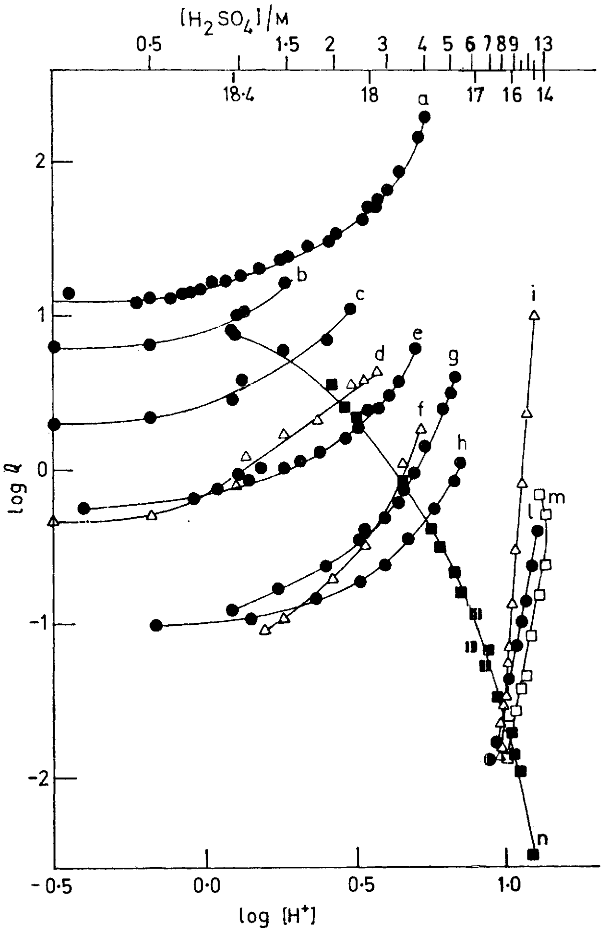

FIGURE 4 Plots of log Q *versus* log [H^+] for the following indicators: a, 4-nitroaniline; b, *NN*-dimethyl-4-nitroaniline; c, *NN*-diethyl-2,4-dinitroaniline; d, *N*-(2,4-dinitrophenyl) piperidine; e, 2-nitroaniline; f, 2,3-dimethylindole; g, 4-chloro-2-nitroaniline; h, pyrrole-2-carboxamide; i, *NN*-diethyl-2,4,6-trinitroaniline; l, 2,3,6-trichlorobenzamide; m, 2,4-dichloro-3,5-dinitrobenzamide; n, 3-bromo-2,4,6-trinitroaniline

between (2) and (3) can be understood as in this range only the latter seems to be always experimentally verified. It can be observed that apparent linearity of log I_Y *versus* log I_X and log Q_Y *versus* log Q_X plots can arise everywhere, when short overlapping ranges between pairs of indicators are considered.

It follows from the above analysis that the supposed validity of many empirical relationships herein examined, at one and the same time, is only apparent, depending mainly on the use of particular acidity ranges and approximations hitherto accepted, than on compatibility amongst the relationships.

The validity of equations (3) and (5) over the whole acidity range is evident, so that relationship (12)[1] between activity coefficients of any *j* and *i* indicators can be obtained.

$$\log \frac{f_{B_j} f_{H^+}}{f_{B_jH^+}} = n_{ji} \log \frac{f_{B_i} f_{H^+}}{f_{B_iH^+}} \qquad (12)$$

It is important to test the validity of (12) using a method far more rigorous than the stepwise one already applied.[1] We deal with this problem in Part **3**.

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