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Methods of Calculating pK_{BH^+} for Weak Bases

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Methods of calculating pK_{BH^+} for weak bases from spectrometric data are discussed, with special emphasis on methods based on the principle of free energy linearity. It is shown that the ionisation of a weak base in a strongly acid medium is described by two quantities: pK_{BH^+} and the solvation parameter. 77 references.

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I. INTRODUCTION

Over 2000 papers on the basicity of weak bases have been published in the last 20 years[1]. Various aspects of this problem are dealt with in special reviews and monographs[1-10]. The basis of any discussion of the basicity of weak bases is still the Brønsted–Lowry scheme[11,12]

$$BH^+ \rightleftharpoons B + H^+, \quad (1)$$

where B and BH^+ denote the weak base and its conjugate acid respectively. The equilibrium (1) is characterised by the basicity constant of the base[4,5]

$$K_{BH^+} = a_B a_{H^+}/a_{BH^+}. \quad (2)$$

Within the framework of this approach specific solvation phenomena involving both the B and the BH^+ form of the bases are not considered in detail. The influence of these factors on the position of the equilibrium (1) is allowed for by varying the appropriate activity coefficients (f_B and f_{BH^+}).

The basicity of weak bases is usually studied in strongly acid media, where the equilibrium (1) lies very far towards the left. The binary water–sulphuric acid and water–perchloric acid systems are most frequently used, and the indicator ratio[4,5] $I = [B]/[BH^+]$ of the base is determined as a function of the composition of the medium for different concentrations of H_2SO_4 or $HClO_4$.

Up to 1970 the I values were determined mostly by u.v. spectroscopy[4,5]:

$$I = [B]/[BH^+] = (\varepsilon - \varepsilon_{BH^+})/(\varepsilon_B - \varepsilon), \quad (3)$$

where ε_B, ε_{BH^+}, and ε are the molar absorption coefficients of the B form, the BH^+ form, and their mixture respectively. This method can be used to study the basicity of bases whose solubility is very low, because it can handle concentrations as low as 10^{-4}–10^{-5} mole litre^{-1}. However the u.v. spectra are often complicated by the so-called medium effects, resulting in lack of constancy of ε_B and ε_{BH^+} under conditions when the shift of the equilibrium (1) is extreme[13,14]. Various methods have been proposed to overcome this difficulty, but we shall not discuss them here because they are examined in detail in Bernshtein and Kaminskii's book[15].

Following recent developments and improvement in NMR spectroscopy this technique has been widely used since 1970 to determine the indicator ratio of weak bases in water–strong acid systems. Very dilute solutions of the weak bases can be used in the PMR method: in most cases the concentration of the weak base is varied between 0.005 and 0.15 mole litre^{-1}.[16-24] The main disadvantage of the PMR method is that the shift of the signal is very sensitive to specific solvation effects[23,25-28]. Therefore the ^{13}C NMR method is preferable, in principle, because its signal is generated from a nucleus close to the basicity centre[28]. However the signal from the ^{13}C nucleus is ~64 times weaker than the signal from ^1H (assuming equal numbers of carbon and hydrogen atoms in a constant magnetic field)[29], and therefore the ^{13}C NMR method requires a higher concentration of the base B in solution (usually 0.5–1.0 mole litre^{-1}).[29-31]

In both the PMR and the ^{13}C NMR method the indicator ratio is calculated by the equation[30]

$$I = [B]/[BH^+] = (\nu - \nu_{BH^+})/(\nu_B - \nu), \quad (4)$$

where ν_B, ν_{BH^+}, and ν are the characteristic frequencies for the B form, the BH^+ form, and their mixture respectively.

There is still some doubt about the degree of agreement of I values calculated by Eqn.(4) using NMR data for different nuclei (^1H, ^{13}C, and even ^{31}P). Thus some substantial discrepancies between I values obtained from NMR data for different nuclei have been pointed out[23,24].

In spite of these difficulties we shall assume throughout this review that the effect of the composition of the water–strong acid system on the indicator ratio of the weak base is known, either from u.v. spectroscopy or from NMR (^1H or ^{13}C) data.

II. PRESENT STATE OF THE ACIDITY FUNCTION METHOD

Once the I values have been determined from Eqns.(3) or (4) and from experimental data as a function of the concentration of H_2SO_4 or $HClO_4$ we have to choose a method of calculating the basicity constant of the weak base. The classical approach is to use the appropriate acidity function[4]

$$pK_{BH^+} = H_X - \lg I, \quad (5)$$

where H_X is the acidity function, which describes the extent of protonation of the base B. This method of calculating pK_{BH^+} was widely used up to the late 1960's, because it was thought that all electrically neutral bases which are protonated according to Eqn.(1) must follow the Hammett acidity function H_0.[5,32,33] However more than 10 mutually inconsistent acidity functions have now been reported[4,20,32-48]:

$$H_X = -\lg a_{H^+} - \lg \frac{f_X}{f_{XH^+}}, \quad (6)$$

where f_X and f_{XH^+} are the activity coefficients of the indicator X and of its ionised form XH^+. Since the acidity function ceased to be unique, the Hammett postulate[4,5]

$$f_X/f_{XH^+}=f_B/f_{BH^+} \quad (7)$$

became the exception rather than the rule[1,10]. If the condition (7) is not satisfied in the concentration range of the strong acid for which the I values have been calculated by Eqn.(3) it follows that the pK_{BH^+} value given by Eqn.(5) is not a thermodynamic quantity[4,18]. From the practical point of view we have to decide whether the published acidity function describes the protonation of the base under study with sufficient precision (see below)[25]. It is essential to bear in mind that pK_{BH^+} values calculated by using different acidity functions cannot be intercompared directly, in the sense that the most negative values of pK_{BH^+} will not necessarily correspond to the base which is protonated to 50% ("half-protonation") in the most concentrated acid solution.

In recent years pK_{BH^+} values have been calculated from Eqn.(5) only in some special cases, such as studies of the basicity of a series of structurally similar compounds protonated according to some acidity function H_X common to the whole series. Correct application of this method of calculating pK_{BH^+} implies a test of the precision with which the protonation of the base under study is described, in each case, by the given acidity function H_X. For this purpose, Eqn.(5) is conveniently re-written[32]

$$\lg I=aH_X-pK_{BH^+}, \quad (8)$$

where a is the slope of the plot of $\lg I$ against H_X [often referred to as $d(\lg I)/dH_X$].[4,7] Eqn.(8) is solved by least squares, minimising the deviations in $\lg I$.[49] If the protonation of the given base corresponds to the function H_X the regression coefficient of a will be close to unity (as confirmed by considering the width of the confidence interval of the a values)[49]. It is usually assumed that the base B is protonated according to H_X if $a=1\pm0.1$.[14,32]

In addition to the a coefficient, we can calculate pK_{BH^+} and its confidence interval by the least squares method. When applying Eqn.(8) we should remember that the $\lg I$ values are not uniformly precise; the most precise values are those close to zero[15,50,51]. Usually when the modulus of $\lg I$ is greater than unity the value is so inaccurate that its use in Eqn.(8) is not permissible[15]. To allow for the uneven accuracy of $\lg I$ values we can attach to them the weight $w=[s(\lg I)]^{-2}\cdot\text{const}$, where the standard deviation of the determination of $\lg I$ is calculated by the equation[15,32,50-52]

$$s(\lg I)=\pm0.434\,\frac{I+1}{I\Delta R}\sqrt{s_{BH^+}^2+(I+1)^2s^2+I^2s_B^2}, \quad (9)$$

in which $\Delta R=\varepsilon_B-\varepsilon_{BH^+}$ [or $\Delta R=\nu_B-\nu_{BH^+}$, see Eqns.(3) and (4)]; s_{BH^+}, s, and s_B are the standard deviations of the determination of ε_{BH^+} (or ν_{BH^+}), ε (or ν), and ε_B (or ν_B) respectively. If $s_{BH^+}=s=s_B$ we can write[15,32]

$$w=1200\,I^2/(1+I)^2(1+I+I^2). \quad (10)$$

The factor 1200 is introduced into Eqn.(10) in order to make $w=100$ for $I=1$.[15]

The view that each weak base is protonated according to its own acidity function is now widely held[1,7,10,30,39]. Hence the condition $d(\lg I)/dH_X=1$ will apply to a series of bases only if the individual acidity functions (H_B) vary linearly with H_X, with a unit slope. We note from Eqn.(6) that all the acidity functions contain the term $\lg a_{H^+}$, which is a parameter of the medium and is independent of the nature of the weak base X. The dependence of $\lg a_{H^+}$ on the composition of the water–sulphuric acid or water–perchloric acid system is fairly accurately known, though the results of different workers for concentrated solutions show some discrepancies (see Table 1).

Table 1. Values of $\lg a_{H^+}$ for aqueous solutions of sulphuric and perochloric acid at 25 °C.

Acid concn., wt.%	H_2SO_4 solution		$HClO_4$ solution	
	Ref.53	Ref.54	Ref.53	Ref.54
5	0.01	−0.12	−0.02	−0.04
10	0.63	0.49	0.56	0.78
20	1.77	1.58	1.91	2.05
30	2.90	2.70	3.26	3.36
40	4.31	4.10	4.97	4.98
50	6.00	5.72	7.22	7.11
60	7.97	7.44	—	9.41
70	—	9.48	—	—

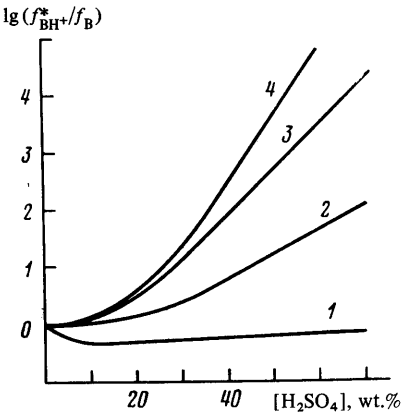


Figure 1. Plots of $\lg(f^*_{BH^+}/f_B)$ against concentration of sulphuric acid in the $H_2O-H_2SO_4$ system: *1*) for olefins, *2*) for *N,N'*-dimethyl substituted aromatic amines (H_0''' indicators[39]), *3*) for substituted aromatic amines (H_0' indicators[32]), *4*) for substituted benzamides (H_A indicators[34]).

It follows from the above that the non-coincidence of different acidity functions is probably due to differences in the dependence of $\lg f_X/f_{XH^+}=\phi$ on the acid concentration for different types of base. The activity coefficient of the non-ionised form f_X can be determined relatively easily either from solubility data or from the distribution coefficient[5,7,10]. It is found that for bases of different structure the variation of f_X with concentration of H_2SO_4 (or $HClO_4$) can be very different: this problem is considered in detail in a special review article[10]. The activity coefficient of the ionised form (f_{XH^+}) is not measurable, and therefore (as suggested by Boyd[6,55]) f_{XH^+} is replaced by the ratio

$$f^*_{XH^+}=f_{XH^+}/f_{Et_4N^+} \quad (11)$$

whose variation with the concentration of H_2SO_4 (or $HClO_4$) can be measured.

The method of determining $f^*_{XH^+}$ is discussed in Refs.6, 55, and 56. It is assumed that the screening of the positive charge on the nitrogen atom by the ethyl groups ensures that the Et_4N^+ ion cannot undergo specific solvation[6,26,57]. Since this type of solvation is the main reason for the deviation of the activity coefficients from unity we can write $f_{Et_4N^+}=1$ for all solutions (from those in pure water to those in concentrated solutions of acids)[6,26,53]. However the ratio $f_X/f^*_{XH^+}$ is found to depend both on the concentration of the strong acid and on the nature of the base X (see Fig.1). We shall not dwell on the reasons for the deviation of f_X and $f^*_{XH^+}$ from unity because they are discussed at length in review articles[1,7,10].

The difference between two arbitrarily chosen acidity functions (H_X and H_Y) at a given concentration of the strong acid is determined by the expression

$$H_X - H_Y = \lg \frac{f_Y f_{XH^+}}{f_{YH^+} f_X}, \qquad (12)$$

from which we can judge the correctness of independently obtained[7,10] values of $f_X/f^*_{XH^+}$ and $f_Y/f^*_{YH^+}$. This type of test has shown that the difference between acidity functions can be calculated from the values of $f_X/f^*_{XH^+}$ and $f_Y/f^*_{YH^+}$.[20,58] Therefore there is no longer any doubt that in general, for any acidity function H_X, the ratio $f_X/f_{XH^+} \neq 1$.[1,10] This is what makes compliance with the Hammett postulate (7) a rare event, and detracts from the value of the classical method of calculating pK_{BH^+}.[58-62]

III. THE YATES–McCLELLAND METHOD

This method was developed[63] because an acidity function H_X for which $d(\lg I)/dH_X = 1.00$ could not be found for many weak bases. According to Yates and McClelland, to a first approximation a simple proportionality always exists between the quantities H_X and H_0:[63]

$$H_X = mH_0. \qquad (13)$$

Inserting (13) into (5) we obtain the Yates equation for calculating pK_{BH^+}:[63]

$$\lg I = mH_0 - pK_{BH^+}. \qquad (14)$$

This equation can be solved by least squares with allowance for the unequal precision of the $\lg I$ values [see Eqns.(9) and (10)].

The pK_{BH^+} value calculated by Eqn.(14) expresses the basicity of the substance B in its own individual acidity scale $H_B = -\lg a_{H^+} f_B/f_{BH^+}$: in other words this value of pK_{BH^+} gives us the H_B value for a solution in which $\lg I = 0$.[14] Often instead of pK_{BH^+} one calculates the H_0 value for a solution in which $\lg I = 0$, i.e. the quantity $H_0^{(1/2)}$. Inserting $\lg I = 0$ into Eqn.(14) we obtain

$$H_0^{(1/2)} = \frac{1}{m} pK_{BH^+}. \qquad (15)$$

The H_0 value at half-protonation of the unknown base ($H_0^{1/2}$) is often identified[32,33] with the pK_{BH^+} value of the base in the H_0 acidity scale[9,17,19,64,65].

The Yates–McClelland method relies on the assumption of a direct proportionality between H_X and H_0 [Eqn.(13)]. This linear variation is obeyed only approximately in practice, with a break near $H_0 = 0$, since in this pH region $m = 1$ for all values of H_X (see Fig.2). As a result, the pK_{BH^+} values calculated by Eqn.(14) lose some of their physical significance, and they cease to be thermodynamic quantities referred to a standard state in water. In the most favourable case these pK_{BH^+} values can be treated as referred to a standard state in an acid solution for which $H_0 = 0$ (i.e. 4.8 wt.% H_2SO_4 or 4.0 wt.% $HClO_4$).

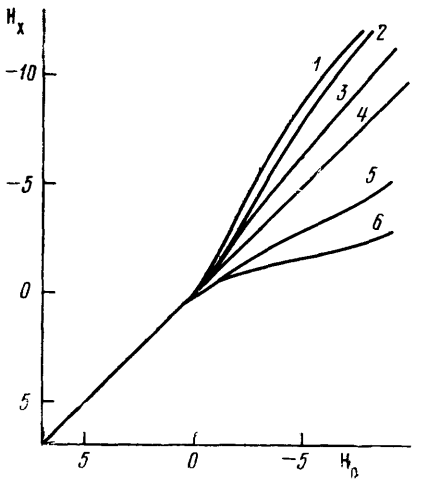


Figure 2. Plots of different acidity functions (H_X) against H_0 [32] in aqueous solutions of sulphuric acid at 25 °C: *1*) $H_{R'}$,[43] *2*) H_C,[35] *3*) H_0''',[39] *4*) H_0,[32] *5*) H_A,[34] *6*) H_{ROH}.[40]

IV. THE BUNNETT–OLSEN METHOD

The Bunnett–Olsen method[66] of calculating pK_{BH^+} is based on the linear expression

$$\lg Q_1 = a \lg Q_2 + b, \qquad (16)$$

where $Q_1 = [B_1][H^+]/[B_1H^+]$; $Q_2 = [B_2][H^+]/[B_2H^+]$; B_1 and B_2 are arbitrarily chosen weak bases; the concentration $[H^+]$ is taken to be numerically equal to the molar concentration of H_2SO_4 or $HClO_4$.[66] The validity of the linear relationship (16) has been tested[58,66,67] for several bases B_1 and B_2: the equation was found to be generally applicable, deviations from it being smaller than experimental error[67].

In order to obtain an equation for calculating pK_{BH^+}, Bunnett and Olsen[66] standardised their reference scale, i.e. the choice of the base B_2. They defined their standard base as a hypothetical primary aromatic amine with $pK_{BH^+} = 0$, for which $\lg [B_2]/[B_2H^+] = H_0$, and

$$\lg Q_2 = H_0 + \lg [H^+]. \qquad (17)$$

We should stress that the choice of the acidity function H_0 as the reference scale has no fundamental significance: in principle H_0 in Eqn.(17) can be replaced by any similar acidity function. The function H_0 is chosen simply because it has been carefully measured and is widely known.

After combining (17) and (16) and simplifying we obtain the expression

$$H_0 - \lg I_1 = \Phi(H_0 + \lg [H^+]) - b, \qquad (18)$$

where $I = [B_1]/[B_1H^+]$ and $\Phi = 1 - a$. If the condition $\Phi = \text{const}$ is obeyed at all concentrations, from the standard state in water (for which $H_0 - \lg [H^+] = 0$) to the acid solutions used for measuring I_1, we can easily see that $-b = pK_{B_1H^+}$ (since

in the standard state $H_0 - \lg I_1 = pK_{BH^+}$). Inserting $-b = pK_{B_1H^+}$ into Eqn.(18) we arrive at the Bunnett–Olsen equation for $pK_{B_1H^+}$:[66]

$$H_0 - \lg I_1 = \Phi(H_0 + \lg [H^+]) + pK_{B_1H^+} . \quad (19)$$

When applying Eqn.(19) we must make allowance for the uneven precision of the $\lg I_1$ values [see (9) and (10)], and treat the H_0 and $[H^+]$ values as exactly known.

By comparing formulae (5) and (19) we can easily show that[1,68]

$$H_X + \lg [H^+] = (1-\Phi)(H_0 + \lg [H^+]). \quad (20)$$

This relationship between the acidity functions H_X and H_0 is free from the shortcomings found in the simpler Yates–McClelland formula (13). It does not show the characteristic break near $H_0 = 0$ given by Eqn.(13) (see Figs.2 and 3), since both $H_X + \lg [H^+]$ and $H_0 + \lg [H^+]$ tend towards zero as we approach the standard state in water. According to the expression (20), plotted in Fig.3, we can judge the constancy of the parameter Φ in all cases from water to concentrated solutions of strong acids. We see from Fig.3 that Φ = const in moderately concentrated solutions of acids. At high concentrations of H_2SO_4 the quantity Φ is often not constant. This effect introduces some uncertainty into the pK_{BH^+} values obtained by Eqn.(19) through a long extrapolation (from concentrated solutions of acids).

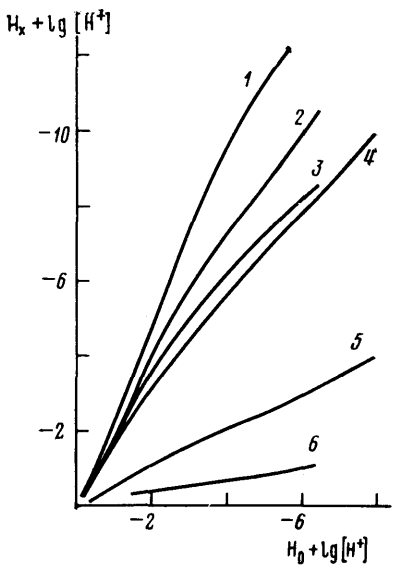


Figure 3. Relationship between the acidity functions according to Bunnett and Olsen[66,68] [see Eqn.(20), aqueous solutions of sulphuric acid at 25 °C]: *1)* $H_X = H_R$,[43] *2)* $H_X = -\lg a_{H^+}$,[54] *3)* $H_X = H_M$,[42] *4)* $H_X = H_0$,[32] *5)* $H_X = H_A$,[34] *6)* $H_X = H_{ROH}$.[40]

The possible error range of the pK_{BH^+} values obtained from Eqn.(19) was evaluated[69,70] by noting that in principle the function H_0 in that equation can be replaced by any analogous acidity scale. The criterion for the validity of such a scale is the linearity of expressions of the type of (20). If the standard base B_2 in Eqn.(16) is taken to be a hypothetical base with $pK_{BH^+} = 0$ which is protonated without specific solvation effects, i.e. according to the $\lg a_{H^+}$ acidity scale, Eqns.(19) and (20) become, respectively,

$$-\lg a_{H^+} - \lg I_1 = \Phi(-\lg a_{H^+} + \lg [H^+]) + pK_{B_1H^+}, \quad (21)$$

$$H_X + \lg [H^+] = (1-\Phi)(-\lg a_{H^+} + \lg [H^+]). \quad (22)$$

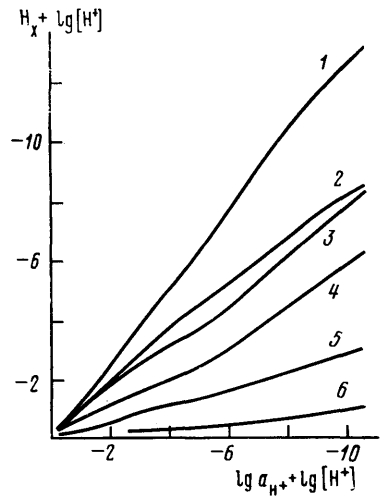


Figure 4. Variation of $H_X + \lg [H^+]$ with $(-\lg a_{H^+} + \lg M)$ for different acidity functions H_X in aqueous solutions of sulphuric acid at 25 °C: *1)* $H_X = H_R$,[43] *2)* $H_X = H_M$,[42] *3)* $H_X = H_0''$,[39] *4)* $H_X = H_0$,[32] *5)* $H_X = H_A$,[34] *6)* $H_X = H_{ROH}$.[40]

We note from Fig.4 that the proportionality (i.e. the condition Φ = const) is more accurately obeyed by Eqn.(22) than by the analogous expression in terms of H_0 [Eqn.(20), see Fig.3].[70] Therefore the $pK_{B_1H^+}$ values calculated by (21) are more nearly equal to the corresponding thermodynamic quantities than those calculated by (19). For $pK_{BH^+} > -3$ the difference between the pK_{BH^+} values given by formulae (19) and (21) is insignificant[69]. However for very weak bases with $pK_{BH^+} < -3$ the discrepancy between the pK_{BH^+} values given by (19) and (21) can be as high as three units of pK_{BH^+}.[69] These discrepancies arise primarily from the loss of linearlity of Eqn.(20) at high concentrations of the strong acid[70].

Because of the wide use made of the Bunnett–Olsen method it is becoming generally assumed that in order to characterise the basicity of a weak base quantitatively we need to know the solvation parameter Φ as well as pK_{BH^+}. This interpretation of the parameter Φ was originally proposed by Hammett[68], and further developed by Modena and Scorrano[1]. The solvation parameter Φ is independent of pK_{BH^+} for a weak base, but is determined by the nature of the base. It is normalised to give $\Phi = 1$ for water[1,20] and $\Phi = 0$ for primary amines[1,66]. Different types of weak bases are assigned the following values of Φ:[1] aryl carbinols from −1.02 to −1.59, azulenes −0.70, tertiary aromatic amines from −0.33 to −0.48, amides from +0.42 to +0.55, alcohols +0.85, etc. The relationship between the value of Φ and the solvation effects during the protonation of weak bases is discussed in Ref.1.

In order to compare Φ with m we note, from Eqn.(14), that at high acid concentrations the quantity $\lg [H^+]$ is small in comparison to the absolute value of H_0. Hence under these conditions Eqn.(19) is equivalent to Eqn.(14) with $m = 1 - \Phi$, which can be confirmed by directly comparing the values of m and $1 - \Phi$.[1]

Both the classical Bunnett–Olsen equation (20) and its modification [Eqn.(22)] are linear free energy functions. Thus from Eqns.(20) and (22) respectively we can obtain[66,69]

$$\lg \frac{f_{H^+} f_X}{f_{XH^+}} = (1 - \Phi) \lg \frac{f_{H^+} f_B}{f_{BH^+}}, \quad (23)$$

$$\lg \frac{f_{XH^+}}{f_X} = \Phi \lg f_{H^+}. \quad (24)$$

These expressions indicate linear relationships between the changes in free energy of the corresponding particles.

V. THE MCP AND COX–YATES METHODS

Bunnett and Olsen's expression (23) was critically examined by an Italian group of workers (Marziano, Cimino, and Passerini, abbreviated to MCP), who concluded[71] that the Hammett acidity function H_0 should not be used to construct a comparative scale of $\lg (f_{H^+} f_B / f_{BH^+})$ [in Eqn.(20)]. Instead, they suggested a description of weak bases involving partially overlapping ionisation regions[71]:

$$\lg \frac{[X]}{[XH^+]} + \lg [H^+] = n_X \left(\lg \frac{[B]}{[BH^+]} + \lg [H^+] + pK_{BH^+} \right) - pK_{XH^+}, \quad (25)$$

where $[H^+]$ is the molar concentration of strong acid, and X is a slightly weaker base than B. The linear relationship (25) allows us to determine pK_{XH^+} for the next indicator X of a given series, and the corresponding slope of the plot of Eqn.(25):

$$n_X = \lg \frac{f_{H^+} f_X}{f_{XH^+}} \Big/ \lg \frac{f_{H^+} f_B}{f_{BH^+}}. \quad (26)$$

Applying Eqn.(25) to the next indicator Y of the series (with $pK_{YH^+} < pK_{XH^+}$) we can evaluate n_Y:

$$n_Y = \lg \frac{f_{H^+} f_Y}{f_{YH^+}} \Big/ \lg \frac{f_{H^+} f_X}{f_{XH^+}}. \quad (27)$$

By stepwise repetition of this procedure we can determine all the slopes n_X, n_Y, ..., n_Z up to that of the weaker base Z. Assuming that n_X, n_Y, ..., n_Z are constant, i.e. that differentials of the type of $d(\lg f_{H^+} f_Y / f_{YH^+}) / d(\lg f_{H^+} f_X / f_{XH^+})$ are independent of the I value [defined by Eqn.(3)] of the base, we can easily relate the first term B of a given series to the subsequent terms X, Y, ..., Z:

$$\lg \frac{f_{H^+} f_B}{f_{BH^+}} = \frac{1}{n_X} \lg \frac{f_{H^+} f_X}{f_{XH^+}} = \frac{1}{n_X n_Y} \lg \frac{f_{H^+} f_Y}{f_{YH^+}} = \ldots = \frac{1}{n_X n_Y \ldots n_Z} \lg \frac{f_{H^+} f_Z}{f_{ZH^+}} = -M_c. \quad (28)$$

Eqn.(28) was used to calculate the "function of the activity coefficients" M_c [71] in terms of n_X, n_Y, ..., n_Z and of the quantity

$$\lg \frac{f_{H^+} f_Z}{f_{ZH^+}} = -pK_{ZH^+} - \lg \frac{[Z][H^+]}{[ZH^+]}. \quad (29)$$

If the function M_c is known the pK_{BH^+} value of an arbitrarily chosen weak base B can be obtained from the linear expression[71]

$$\lg I + \lg [H^+] = n_B M_c - pK_{BH^+} \quad (30)$$

using the method of least squares and allowing for the unequal precision of the I values given by Eqn.(3) [see Eqn.(10)].

Unfortunately the M_c scales calculated from different series of weak bases do not coincide† when the solution contains more than 40 wt.% of H_2SO_4.[71] The authors recommend the use of the M_c scale calculated from the ionisation of Hammett indicators (whose protonation proceeds in the same sense as the acidity function H_0).[71] Therefore the MCP group developed a new method of calculating the M_c scale from all possible values of I for the whole of the ionisation region (usually $0.1 \leq I \leq 1$). However their following paper[72] gives only the new M_c values for aqueous solutions of sulphuric acid (see Table 2) without describing the method of calculating M_c.

Table 2. Values of M_c, X, and $\lg c_{H^+}$ for aqueous solutions of sulphuric and perchloric acid.

Acid concn., wt.%	H_2SO_4 solution			$HClO_4$ solution	
	$-10 \cdot M_c$ (Ref.72)	X (Ref.73)	$\lg c_{H^+}$ (Ref.73)	X (Ref.73	$\lg c_{H^+}$ (Ref.69)
5	0.172	0.103	−0.205	0.091	−0.293
10	0.354	0.231	0.117	0.212	0.018
15	0.555	0.387	0.315	0.371	0.209
20	0.785	0.573	0.461	0.571	0.349
25	1.053	0.790	0.577	0.819	0.459
30	1.358	1.038	0.674	1.116	0.552
35	1.706	1.317	0.757	1.468	0.633
40	2.096	1.628	0.828	1.879	0.705
45	2.526	1.969	0.891	2.354	0.773
50	2.999	2.345	0.945	2.908	0.833
55	3.514	2.763	0.992	3.561	0.891
60	4.075	3.238	1.033	4.337	0.941
65	4.682	3.795	1.069	5.241	0.977
70	5.338	4.459	1.097	6.220	1.022
74	5.896	5.080	1.118	6.983	1.057
80	6.786	6.150	1.143	—	—
84	7.427	6.906	1.133	—	—
90	8.547	7.985	0.996	—	—
95	9.808	8.989	0.654	—	—
99	—	10.754	−0.153	—	—

At approximately the same time (1976–1977) and independently of the MCP group Cox and Yates[73] also worked on this problem. Accepting the universality of Eqn.(23), they wrote it in the form of

$$\lg \frac{f_{H^+} f_B}{f_{BH^+}} = m^* \lg \frac{f_{H^+} f_{B^*}}{f_{B^*H^+}} = m^* X, \quad (31)$$

where B* is a hypothetical standard base. The quantity X is identical to $-M_c$, but Cox and Yates prefer to call it the "excess acidity"[73]. They calculate the pK_{BH^+} value of the weak base B by the equation[73]

$$-\lg I - \lg c_{H^+} = m^* X + pK_{BH^+}, \quad (32)$$

where c_{H^+} is the concentration of hydrated protons in solution (see Table 2). This equation can be solved by least squares allowing for the uneven precision of the I values [see Eqn.(10)].

† The discrepancies between the M_c scales arise from the use of I values [obtained by Eqn.(3)] in the overlap regions of successive indicators where the modulus of $\lg I$ is greater than (0.7–1.1) and the uncertainty in its determination is relatively high [see Eqn.(10)].

Unlike the MCP group[72], Cox and Yates describe in great detail the mathematical procedures adopted in the calculation of X.[73] Without reproducing their algorithm, we shall only point out that the X values are obtained by an iterative method, using the equation

$$X = \frac{1}{m^*}(-\lg I - \lg c_{H^+} - pK_{BH^+}), \qquad (33)$$

in which arbitrary values of pK_{BH^+} and m^* are inserted at first. The first, approximate estimate of the scale is then used to obtain more precise values of pK_{BH^+} and m^* by Eqn. (32), and so on. The procedure is repeated until the values of X become invariant[73]. These workers used I values obtained by Eqn.(3) over the whole ionisation region for 165 bases in solutions containing 0–99.5 wt.% H_2SO_4, and for 76 bases in solutions containing 0–78 wt.% of $HClO_4$.

The X scales for aqueous solutions of sulphuric acid and perchloric acid are given in Table 2. We can see that in general the X values are close to the $-M_c$ values multiplied by 10 (the introduction of this scaling factor affects only the solvation parameter). In spite of this similarity the pK_{BH^+} values calculated by using X and M_c respectively differ by more than 0.3 units of pK_{BH^+}.[73] Of course, this conclusion applies to the pK_{BH^+} values obtained with the original M_c scale[71], to which the authors themselves no longer subscribe, but as yet no pK_{BH^+} values appear to have been obtained from the new M_c scale[72]. Its authors[72] are themselves unwilling to apply the new scale until the method of calculating pK_{BH^+} has been improved so that the quoted uncertainty limits can reflect the uncertainty limits of the M_c scale [see Eqn.(30)].

Extensive comparisons of pK_{BH^+} values obtained by using the X scale [Eqn.(32)], the Bunnett–Olsen method [Eqn.(19)], and the acidity function [Eqn.(5)] are given in the Tables of Ref.73. In most cases the pK_{BH^+} values are not very different (within ±0.2 pK_{BH^+} unit), but differences in excess of 1 pK_{BH^+} unit are occasionally found. We note that Eqns.(5) and (32) will give identical pK_{BH^+} values only if all the indicators used to construct the acidity function H_X have the same m^* value [to within ±0.1,[74] see Eqn.(32)].

VI. CALCULATION OF pK_{BH^+} WITHOUT USING THE INDICATOR RATIO

All the methods of calculating pK_{BH^+} discussed so far use the indicator ratio I, calculated by Eqn.(3) or (4). Recent developments in the application of computers make it possible to calculate pK_{BH^+} (and the solvation parameter) directly from experimental results, i.e. from the ε or ν values, without going through the stage of determining I by Eqns.(3) or (4).[20,75] This approach involves the following steps. From Eqn.(3) we readily obtain

$$\varepsilon = \frac{I\varepsilon_B + \varepsilon_{BH^+}}{1 + I} \qquad (34)$$

and a similar expression is obtained from Eqn.(4). Then, using any of the above methods of calculating pK_{BH^+} [i.e. using Eqn.(8), (14), (19), (21), (30), or (32)], we find the variation of $\lg I$ with pK_{BH^+} for the medium parameter P and the solvation parameter S (relating H_0, H_X, c_{H^+}, X, and M_c to the medium parameters P; and m, Φ, n, and m^* to the solvation parameters S):

$$\lg I = F(pK_{BH^+}, P, S),$$

whence

$$I = 10^{F(pK_{BH^+}, P, S)}. \qquad (35)$$

Inserting (35) into (34) we obtain a system of k transcendental equations ($k \geq 3$) with two unknowns (pK_{BH^+} and S). The problem now reduces to finding values of pK_{BH^+} and S which minimise a function of the difference between calculation and experiment such as

$$\Psi = \sum_{i=1}^{i=k} (\varepsilon_{i,\text{calc}} - \varepsilon_{i,\text{exper}})^2 . \qquad (36)$$

Because of the non-linearity of the system of equations the minimum of the function Ψ cannot be found by the standard methods of regression analysis. The problem must therefore be solved by one of the iteration methods commonly used[76] to solve systems of equations. These include Newton's method and its modifications[76], the method of steepest descent[76], and the coefficient variation method[77]. The best choice of method for solving the system of transcendental equations depends on the type of computer to be used and on the availability of appropriate subprograms.

We note that in principle this method of treating experimental data allows us to determine not only pK_{BH^+} and S, but also one of the parameters of the limiting forms[20] (ε_B or ε_{BH^+}) which appear in Eqn.(34). In this case we evaluate three rather than two unknowns from the system of transcendental equations ($k \geq 4$). However there is a risk of being caught up in the "numbers game": the risk is greatest when the plot of ε against composition of the medium lacks a clear plateau near the limiting form ε_B or ε_{BH^+}.

Thus in recent years the methods of calculating pK_{BH^+} for weak bases have undergone some radical changes. The acidity function method [Eqn.(5)] and the Yates–McClelland method [Eqn.(14)] are no longer at the forefront. The former was abandoned when the limitations of the Hammett postulate (7) (leading to a multiplicity of acidity functions) were realised. The Yates–McClelland method proved too empirical and approximate, as well as relying on the basic acidity function devoid of physical significance (H_0).

These older methods are now being replaced by new methods based on the principle of free energy linearity (FEL) [see Eqn.(23)]. Of these, the Bunnett–Olsen method has proved most popular so far [Eqn.(20)], but since it relies on the acidity function H_0 based on the Hammett postulate (7) its use cannot be recommended. Some of the even newer methods are free from this shortcoming: these include the essentially identical MCP method (based on the M_c function) and Cox–Yates method (based on the X function). The advantages of these methods include: firstly, that the calculation of pK_{BH^+} by using the function X (or M_c) relies on a very simple and clear theoretical foundation (the assumption that the FEL principle (23) applies), and secondly that these methods do not require the use of a multitude of acidity functions. Each strong-acid system is characterised by a single function of the X (or M_c) type, and each weak base has two parameters (pK_{BH^+} and m^*) which describe its ionisation. The parameter m^* can be treated as a measure of the solvation interactions with the medium (thus we note that $m^* \cong 1 - \Phi$ [73]).

However, while stressing these favourable aspects of the new methods, we must repeat that a discrepancy still exists between the X and M_c scales, which points to a need for greater efforts on developing and unifying scales of the type of X.

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