A Discussion of the pK_{BH^+} Values of Weak Bases as Derived by Different Calculation Methods

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The Hammett acidity function method (HAFM), the excess acidity function method (EAM), and the Bunnett–Olsen method (BOM) have been compared in order to rationalize the differences observed between pK_{BH^+} values estimated by each classical method. The results point out that on the basis of (i) the strength and kind of bases analysed and (ii) the aqueous acid solution used to determine the ionization ratios $C_{BH^+}/C_B = I$, it is possible to predict when the three methods give similar results and when they give different pK_{BH^+} values.

The dissociation constants of conjugate acids of very weak bases are usually determined spectrophotometrically by measuring, in concentrated aqueous acid solution, the ionization ratios, $C_{BH^+}/C_B = I$ where C_B and C_{BH^+} are the molar concentrations of the base and the conjugate acid, respectively. The pK_{BH^+} values are usually estimated by means of three different methods: the Hammett acidity function method[1] [HAFM, eqn. (1)], the excess acidity function method[2] [EAM, eqn. (2)] and the Bunnett–Olsen method[3] [BOM, eqn. (3)].

$$\log I = -H_0 + pK_{BH^+} \qquad (1)\dagger$$

$$\log I - \log C_{H^+} = m^*X + pK_{BH^+} \qquad (2)$$

$$\log I - \log C_{H^+} = (\varphi - 1)(H_0 + \log C_{H^+}) + pK_{BH^+} \qquad (3)$$

Theoretical[5] and practical[5a,6] aspects of the above methods have been treated extensively and will not constitute the subject of this paper, the aim of which is instead to compare the pK_{BH^+} values obtained by the three methods.

Recently Johnson and Stratton[7] have reported results obtained by using eqns. (1)–(3). They showed that large differences are frequently observed between the pK_{BH^+} values derived from eqns. (1)–(3) and only in a few cases do the different approaches give pK_{BH^+} values in good agreement (differences up to ±0.2 pK units). The conclusion[7] was that HAFM works as well as EAM or BOM and, in some cases, somewhat better. In fact, in some cases, the pK_{BH^+} values obtained by HAFM correlate with other physicocochemical properties of substrates, such as substituent constants, better than the pK_{BH^+} values estimated by EAM and BOM.

However, pK_{BH^+} data reported by Johnson and Stratton and other literature data show a general pattern of behaviour. In order to illustrate the differences between the pK_{BH^+} values obtained by the three methods and in the two acids (sulphuric and perchloric acid), we have collected (Table 1) some data for a number of bases of different strengths. Indeed, the range of acid concentrations used can significantly affect the pK_{BH^+} values calculated. For bases which are not too weak (pK_{BH^+} values up to *ca.* −3) the three different methods give pK_{BH^+} values which agree closely with each other and the differences observed are random (Table 1, lines 1–5). Mononitroanilines,[7] 5-substituted thiophene-2-carboxamides,[8] 5-substituted 3-nitro- and 3-substituted 5-nitro-2-(dimethylamino or piperidino)thiophenes,[9] and 5-substituted 2-acetylthiophenes[10] constitute examples of the above behaviour. For weaker bases HAFM, EAM and BOM often give quite different pK_{BH^+} values. Moreover, the pK_{BH^+} values (Table 1, lines 6–12) do not appear to be independent of the nature of the acid used to measure ionization ratios although this is required by the definition of pK_{BH^+}. Thus, for example, for 2-bromo-4,6-dinitroaniline the following pK_{BH^+} values have been reported:[7] −6.69, −6.68, −5.88 and −7.52 (Table 1, line 8); the first two values have been estimated by HAFM, the next two by EAM; in both pairs the first value has been determined in sulphuric acid, the other one in perchloric acid. The above data show that the ionization ratios measured either in sulphuric or in perchloric acid when analysed by HAFM give the same pK_{BH^+} value; in contrast the EAM method furnishes two different pK_{BH^+} values for the data in sulphuric and in perchloric acid solutions.

Furthermore, it must be noticed that the pK_{BH^+} values calculated by the two methods are quite different from each other and while in sulphuric acid 2-bromo-4,6-dinitroaniline is estimated to be a stronger base by EAM than by HAFM ($\Delta pK_{BH^+} = 0.81$), the opposite occurs in perchloric acid ($\Delta pK_{BH^+} = -0.84$). Other polynitroanilines show a parallel behaviour.[7a] In contrast, in the case of 3-bromo-2,4,6-trinitroaniline (Table 1, line 12), the pK_{BH^+} values estimated by EAM are always lower than those estimated by HAFM, irrespective of the acid used. However, in the cases where the three methods used to analyse the protonation data obtained in sulphuric acid produce different pK_{BH^+} values (*i.e.*, at high acid concentrations), the pK_{BH^+} values estimated by EAM are always higher than those estimated by HAFM or BOM.

Dramatic differences in the pK_{BH^+} values estimated by the three different methods, for example, have been found for very weak bases (p$K_{BH^+} < -9$) such as thiobenzoates[11] (Table 1, lines 10 and 11) and triarylmethanols.[7a,12] Moreover, significant differences in the pK_{BH^+} values have been found for other weak bases.[7]

For the reasons given above it seems to us that the problem of estimating pK_{BH^+} values of conjugate acids of very weak

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† If the base analysed does not follow a known acidity function, *i.e.* when the slope of eqn. (1) differs from unity, pK_{BH^+} may be estimated[4] by the equation:

$$pK_{BH^+} = mH_0(1/2)$$

where $H_0(1/2)$ is the value of the H_0 acidity function at half-protonation of the base.

Table 1. pK_{BH^+} values for some bases calculated by different methods (HAFM, BOM and EAM).

		Sulphuric acid				Perchloric acid			
Line	Base	Acidity range	HAFM	BOM	EAM	Acidity range	HAFM	BOM	EAM
1	3-NO$_2$-2-PipTh[a]	4–25	−1.07	−1.07	−1.06	5–25	−1.00	−1.00	−0.90
2	5-NO$_2$-2-PipTh[a]	9–40	−1.92	−1.93	−1.87	10–30	−1.75	−1.73	−1.75
3	2-Cl-6-NO$_2$An[b]	21–50	−2.38[c]	−2.30	−2.40	25–50	−2.43	−2.35[d]	−2.45
4	5-NO$_2$-2-ThCONH$_2$[e]	20–80	−2.66	−2.46	−2.54				
5	5-OMe-2-ThCOMe[f]	25–57	−2.67	−2.68	−2.79	29–60	−2.70	−2.72	−2.80
6	2,4-(NO$_2$)$_2$-An[b]	45–68	−4.27	−4.30[c]	−4.53	49–61	−4.53	−4.42[d]	−4.98
7	5-Br-2-ThCOMe[f]	59–80	−5.05	−5.10	−5.19	54–66	−5.58	−5.55	−6.21
8	2-Br-4,6-(NO$_2$)$_2$-An[b]	65–85	−6.69	−6.29[c]	−5.88	60–70	−6.68	−6.88[d]	−7.52
9	3-Me-2,4,6-(NO$_2$)$_3$-An[b]	79–94	−8.33	−8.30[c]	−7.64	69–76	−8.56	−8.15[d]	−11.20
10	5-Br-BCOSEt[g]	74–82	−9.63	−9.49	−7.99[h]				
11	5-NO$_2$-BCOSEt[g]	79–89	−10.55	−10.07	−8.60[h]				
12	3-Br-2,4,6-(NO$_2$)$_3$-An[b]	85–98	−9.34	−9.92[c]	−10.49	73–79	−9.46	−9.06[d]	−12.55

[a] PipTh = piperidinothiophene, ref. 9. [b] An = aniline, ref. 7. [c] Values calculated by using ionization ratios from C. D. Johnson, A. R. Katritzky and S. A. Shapiro, *J. Am. Chem. Soc.*, 1969, **91**, 6654. [d] Values calculated by using ionization ratios from K. Yates and H. Wai, *J. Am. Chem. Soc.*, 1964, **86**, 5408. [e] ThCONH$_2$ = thiophenecarboxamide, ref. 8. [f] ThCOMe = acetylthiophene, unpublished results, ref. 10. [g] BCOSEt = thiobenzoate, ref. 11(*a*). [h] Values evaluated from Fig. 2 of ref. 7(*a*).

Table 2. Statistical results[a] for the correlations between $-(H_X + \log C_{H^+})$ and X in aqueous sulphuric acid.

Line	Range	$s \pm s_s$	$i \pm s_i$	n	r	H_X
1	5–94[c]	1.02 ± 0.01	0.01 ± 0.03	19	0.9996	H_0[b]
2	5–65[c]	1.03 ± 0.01	−0.01 ± 0.02	13	0.9991	
3	70–94[c]	0.96 ± 0.02	0.46 ± 0.13	6	0.9992	
4	86–96[c]	1.08 ± 0.02	−0.62 ± 0.19	6	0.9991	
5	5–99.5[d]	1.03 ± 0.01	−0.01 ± 0.02	20	0.9999	
6	70–96[d]	1.00 ± 0.01	0.21 ± 0.09	10	0.9994	
7	74–86[d]	0.95 ± 0.01	0.52 ± 0.05	5	0.9999	
8	86–96[d]	1.08 ± 0.02	−0.46 ± 0.17	6	0.9991	
9	2.5–90[c]	0.53 ± 0.01	−0.06 ± 0.02	18	0.9989	H_A[e]
10	2.5–65[c]	0.57 ± 0.01	−0.10 ± 0.01	13	0.9997	
11	65–85[c]	0.47 ± 0.01	0.23 ± 0.05	5	0.9995	
12	2.5–90[d]	0.52 ± 0.01	0.01 ± 0.02	18	0.9988	
13	2.5–65[d]	0.56 ± 0.01	−0.06 ± 0.01	13	0.9992	
14	65–85[d]	0.46 ± 0.01	0.26 ± 0.05	5	0.9995	
15	1–90[c]	1.28 ± 0.03	0.42 ± 0.10	18	0.9963	H_0'''[f]
16	1–65[c]	1.46 ± 0.02	0.16 ± 0.03	13	0.9992	
17	65–90[c]	1.04 ± 0.03	1.82 ± 0.16	6	0.9987	
18	1–90[d]	1.29 ± 0.03	0.38 ± 0.10	18	0.9964	
19	1–65[d]	1.47 ± 0.02	0.12 ± 0.03	13	0.9993	
20	65–90[d]	1.05 ± 0.03	1.05 ± 0.16	6	0.9987	
21	10–90[c]	1.41 ± 0.01	0.19 ± 0.05	17	0.9993	H_T[g]
22	70–90[c]	1.30 ± 0.01	0.88 ± 0.09	5	0.9998	
23	10–90[d]	1.43 ± 0.01	0.13 ± 0.05	17	0.9993	
24	70–90[d]	1.28 ± 0.03	1.05 ± 0.17	5	0.9993	

[a] s, slope of the regression line; i, intercept; s_s and s_i, standard deviations; n, number of points; r, correlation coefficient. [b] C. D. Johnson, A. R. Katritzky and S. A. Shapiro, *J. Am. Chem. Soc.*, 1969, **91**, 6654. [c] $\log C_{H^+}$ and X values from ref. 2(*b*). [d] $\log C_{H^+}$ and X values from ref. 5(*c*). [e] J. T. Edward and S. C. Wong, *Can. J. Chem.*, 1977, **55**, 2492. [f] Ref. 14. [g] Ref. 10(*a*).

bases is still an open question. In order to contribute to the solution of this problem we report here some considerations about the data analysis by means of eqns. (1)–(3).

By comparing eqn. (2) with eqn. (3) it can be easily seen that both EAM and BOM give the same pK_{BH^+} value when, in the acidity range over which the ionization ratios are determined, the condition $(\varphi - 1)(H_0 + \log C_{H^+}) = m^*X$ is verified. Because $(\varphi - 1)$ and m^* are constants which depend on the degree of solvation[3,5c] of the conjugate acid-base pair (BH$^+$–B) it should be possible to test whether the above condition is valid by plotting $-(H_0 + \log C_{H^+})$ *vs.* X. Which values of $\log C_{H^+}$ in sulphuric acid should be used is still an open question.[7b] However, both the values reported by Cox and Yates[2b] and those more recently published by Bagno, Scorrano and More

Table 3. Statistical results[a] for the correlations between $-(H_X + \log C_{H^+})$ and X[b] in aqueous pechloric acid.

Line	Range	$s \pm s_s$	$i \pm s_i$	n	r	H_X
1	5–79	1.10 ± 0.02	−0.27 ± 0.10	19	0.9962	H_0[c]
2	5–45	0.80 ± 0.02	0.08 ± 0.02	9	0.9983	
3	50–70	1.12 ± 0.02	−0.71 ± 0.08	5	0.9996	
4	70–79	1.40 ± 0.03	−2.27 ± 0.24	7	0.9985	
5	5.5–70	0.51 ± 0.01	0.31 ± 0.03	13	0.9973	H_A[d]
6	50–70	0.44 ± 0.02	0.64 ± 0.09	5	0.9972	
7	5.5–70	1.45 ± 0.02	0.13 ± 0.07	13	0.9986	H_0'''[e]
8	5.5–50	1.32 ± 0.02	0.29 ± 0.04	9	0.9986	
9	20–50	1.26 ± 0.01	0.41 ± 0.02	7	0.9999	
10	50–70	1.61 ± 0.01	−0.61 ± 0.07	5	0.9999	
11	5–45	1.46 ± 0.02	0.34 ± 0.03	12	0.9987	H_I[f]
12	5–35	1.68 ± 0.08	0.25 ± 0.04	6	0.9960	
13	35–45	1.38 ± 0.01	0.47 ± 0.01	7	0.9999	

[a] s, slope of the regression line; i, intercept; s_s and s_i, standard deviations; n, number of points; r, correlation coefficient. [b] Ref. 2(*b*). [c] R. A Cox and K. Yates, *Can. J. Chem.*, 1981, **59**, 2116. [d] K. Yates and H. Wai, *J. Am. Chem. Soc.*, 1964, **86**, 5408. [e] K. Yates, H. Wai, G. Welch and R. A. McClelland, *J. Am. Chem. Soc.*, 1973, **95**, 418. [f] Ref. 16.

O'Ferrall[5c] arrive at essentially the same conclusions (Table 2). When non-linear plots or intercept values which differ from zero (within experimental uncertainty) are observed, the two methods must give rather different pK_{BH^+} values.

The data relative to the above correlations are reported in Tables 2 and 3; if we consider the complete range of acidity (5–94% or 5–99.5% for sulphuric acid or 5–79% for perchloric acid) the two functions X and $-(H_0 + \log C_{H^+})$ are linearly correlated to each other, the slope and the intercept values of these correlations being almost one and zero, respectively, for sulphuric acid and not very different from these values for perchloric acid. Indeed, BOM and EAM methods have to be considered essentially as equivalent methods[13] and consequently X corresponds to $-(H_0 + \log C_{H^+})$ and m^* to $(1 - \varphi)$. However, when a narrow operational range of acid concentrations is examined, in some cases the linear correlation between the two functions gives intercept values significantly different from zero. The intercept value in the above correlation corresponds to the ratio $\Delta pK_{BH^+}/(1 - \varphi)$ where ΔpK_{BH^+} is the difference between the pK_{BH^+} values estimated by the two methods. For those classes of organic weak bases (sulphides,[14] thiocarbonyl derivatives,[11] tertiary amines,[3,9,15] indoles[3,16] and triarylmethanols[3,17]) characterized by negative φ values, the intercept values reported (Table 2, lines 1–8, and Tables 3, lines 1–4) represent an underestimate of the difference in pK_{BH^+} values obtained by EAM and BOM approaches. In contrast, for bases (alcohols,[18] ethers,[19] amides,[3,8,20] sulphoxides[21] and phosphine oxides[22]) characterized by positive φ values, the intercept values reported (Table 2, lines 1–8, and Table 3, lines 1–4) represent an overestimate of the difference of pK_{BH^+} values obtained by EAM and BOM approaches.

The slope of the above correlation corresponds to the ratio $m^*/(1 - \varphi)$. Thus the slopes (1.00 ± 0.08) found (Table 2, lines 1–8) for sulphuric acid solutions confirm that m^* corresponds to $(1 - \varphi)$.[5c] This correspondence seems less operative in perchloric acid solutions.

The condition necessary for both HAFM and EAM to give the same pK_{BH^+} value for a general base is: $-(H_X + \log C_{H^+}) = m^*X$; where H_X is the acidity function obeyed by the base B. Of course this condition for primary aromatic amines is the same as that seen above. In the case of other specific bases it is sufficient to substitute the appropriate function. The results of the tests of linearity between $-(H_X + \log C_{H^+})$ and X for the acidity functions H_A, H_0''', H_T and H_I related to amides, tertiary aromatic amines, thiocompounds and indoles, respectively, are reported in Tables 2 and 3.

The correlation data reported in Tables 2 and 3 allow one to foresee for any family of bases when the three methods give similar results and when they would give different pK_{BH^+} values.

In the case of mononitroanilines the pK_{BH^+} values are independent both of the method and of the strong acid solution used, in accord with the condition $-(H_0 + \log C_{H^+}) = m^*X$ which is verified for acid solution concentrations up to 70% or 45% of sulphuric or perchloric acid, respectively. Out of these ranges of concentrations significant differences must be observed in the pK_{BH^+} values estimated by means of EAM, HAFM or BOM. In fact, for example, 2-bromo-4,6-dinitroaniline (which undergoes protonation in the range 65–85% of sulphuric acid or 60–70% of perchloric acid) shows different pK_{BH^+} values (see Table 1, line 8); however, the differences between the pK_{BH^+} values estimated by EAM and HAFM, $\Delta pK_{BH^+} = 0.81$ in sulphuric acid solutions and $\Delta pK_{BH^+} = -0.84$ in perchloric acid solutions, are in line with the intercept values of lines 3 of Tables 2 and 3. It must be noticed that for sulphuric acid solutions the correlation between $-(H_0 + \log C_{H^+})$ and X gives positive intercept values up to 86% of sulphuric acid and negative intercept values in the range 86–96%. In contrast, for a concentration of perchloric acid higher than 45% only negative intercept values are obtained. Consequently, for very weak nitroanilines which are protonated in the range 86–96% of sulphuric acid and in the range 50–79% of perchloric acid, the EAM estimates these bases to be weaker than do the other two methods. For nitroanilines which undergo protonation in less concentrated acid solutions the pK_{BH^+} values calculated by EAM are higher than those calculated by HAFM for sulphuric acid solutions and the contrary occurs for perchloric acid solutions.

The intercept values shown in Tables 2 and 3 confirm the data reported in the literature and mentioned above. Thus the considerable differences found between the pK_{BH^+} values of conjugate acids of some thiobenzoates[11] estimated by HAFM and EAM (Table 1, lines 10 and 11) reflect the high intercept value (0.88) of the plot $-(H_T + \log C_{H^+})$ *vs.* X in the concentration range 70–90% of sulphuric acid where the above pK_{BH^+} values have been measured. In contrast, the pK_{BH^+} values of conjugate acids of thiobenzamides[11b] do not show particular differences when estimated by HAFM or EAM and this agrees with an intercept value near to zero. Other examples of acids which give similar pK_{BH^+} values using the two different approaches are, as previously pointed out, the conjugate acids of 5-substituted thiophene-2-carboxamides,[8] together with the 5-substituted-3-nitro- and 3-substituted-5-nitro-2-(dimethylamino or piperidino)thiophenes[9] and 5-substituted 2-acetylthiophenes.[10] The protonation behaviour of the above carboxamido derivatives has been investigated in aqueous sulphuric acid, where $-(H_A + \log C_{H^+}) \approx 0.5X$ over the whole range of sulphuric acid concentrations. The protonation of the tertiary thiopheneamines has been studied in both aqueous sulphuric and perchloric acids in a concentration range where the intercept values of the plots $-(H_0''' + \log C_{H^+})$ are < 0.3.

From the values reported in Tables 2 and 3 it appears that for very weak tertiary aromatic amines the two different approaches (HAFM and EAM) should give quite significant differences. Furthermore it is interesting to notice that the pK_{BH^+} values of very weak amides should be insensitive to the approach used for sulphuric acid solution but if the ionization ratios are determined in perchloric acid solution, then HAFM and EAM should furnish different values.

In less concentrated acid solutions, as has been pointed out, the pK_{BH^+} values estimated are independent both of the method used in the calculation and of the nature of the acid solution in which the ionization ratios have been measured. Thus the practical and theoretical advantages of the EAM should render this method the most suitable in less concentrated acid solutions. But in the case of very weak bases for which more concentrated acid solutions are necessary, the validity of the results obtained by EAM is questionable. In Cox's opinion[23] the drawback arises from the extrapolative nature of the EAM. But this is not the only problem: in fact, the evaluation of pK_{BH^+} values by the other two methods also occurs *via* extrapolation,* nevertheless, both HAFM and BOM are sometimes more satisfactory. Probably, as suggested by Johnson and Stratton,[7] the X scales in the higher region of the acidity must be perfected again in order to constitute the desirable universal acidity function.

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* When the applicability of eqn. (1) is firmly established, pK_{BH^+} may be calculated from either (*i*) the intercept of the plot of log I *vs.* H_X or (*ii*) the average pK_{BH^+} values obtained by application of eqn. (1) to log I data at various acid concentrations.[11b]

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