THE pK_{BH^+} CALCULATION OF STRONG BASES: A REVISION OF VARIOUS METHODS

Begoña GARCIA and José M. LEAL

Universidad de Valladolid, Departamento de Química Física, Colegio Universitario Integrado, Burgos, Spain

Received January 3rd, 1986

The pK_{BH^+} values have been obtained for seventeen acid-base equilibriums corresponding to thirteen aniline derivatives in dilute perchloric acid media in the pH region at 25°C using the spectrophotometric technique. By revising the method of extrapolation to infinite dilution it was possible to introduce new methods for calculating pK_{BH^+} values of strong bases by means of the functions $\log I = f(\mathrm{pH})$ and $pK_{ap} = f(\mathrm{pH})$. The equation — $\log f_{BH^+}/f_B = f(\mathrm{pH})$ — has been proved to conform to a polynomial function of the third order and is applicable to each compound.

The protonation reaction of a neutral base can be expressed by means of the following general equation

$$B + H^+ \rightleftharpoons BH^+ \qquad (A)$$

which equilibrium constant may be expressed in logarithmic form as

$$pK_{BH^+} = \mathrm{pH} + \log I + \log f_{BH^+}/f_B \qquad (1)$$

when the reaction occurs in the pH acidity region. f_{BH^+} and f_B stand for the acidity coefficients of the protonated base and free base, respectively; I is the ionization ratio and can be calculated by means of Gold–Hawes equation[1]

$$I = \left(\frac{A - A_B}{A_{BH^+} - A}\right)_\lambda, \qquad (2)$$

where A_B, A_{BH^+}, and A are the absorbances of the free base, the totally protonated base, and the base of intermediate acidity, measured at wavelength λ. The procedure for the calculation of I has already been described[2]. Using Eq. (1) as a starting point, the calculation of pK value of the base can be carried out by the following methods:

Graphic method. The plot $A = f(\mathrm{pH})$ leads to sigmoid curves and the abscissa of the inflection point is equal to the pK value and corresponds to 50% ionization[3].

Extrapolation to infinite dilution. Marziano[4,5] defines an apparent constant in the form

$$pK_{ap} = \log I + pH \tag{3}$$

and equation (*1*) can be written:

$$pK_{BH^+} = pK_{ap} - \log f_{BH^+}/f_B \,. \tag{4}$$

Hammett and Paul[6,7] show that the plot $pK_{ap} = f(C_{H^+})$ must lead to straight lines for equilibriums at acid concentrations below 2 mol dm^{-3}. The pK_{BH^+} is obtained by means of extrapolation to infinite dilution.

In the present work thirteen aniline derivatives have been selected and have given rise to seventeen acid–base equilibriums. A detailed spectrophotometric analysis has enabled us to revise the described methods and to introduce other ones which provide more accurate calculations of the pK_{BH^+} values of strong bases. This revision is especially important in the case of weak bases ($pK_{BH^+} < 1$) which need media of higher acidity. The proliferation of acidity functions, H_x, which exist at the present time[8–12], as well as the difficulty in finding that one which satisfies Hammett postulate concerning a particular compound, could be interpreted by means of the said results.

EXPERIMENTAL

For the measurement Bodenseewerk Perkin–Elmer 54 spectrophotometer with double beam and thermostatable cells was used. This permits expansion in absorbances and wavelengths and an accuracy of ±0·001 in the absorbance readings. Both cells contained as a solvent an aqueous perchloric acid solution of the same concentration. Temperature was kept constant at 25 ± 0·01°C by means of a P-Selecta thermostat and pH readings were carried out within ±0·01 units with a Crison pH-meter.

Reactants. *m*-Nitroaniline (MNA) Carlo Erba 99·5%; *m*-aminobenzonitrile (MABN) Aldrich 99·5%; *p*-aminobenzonitrile (PABN) Aldrich 99%; *m*-aminobenzenesulfonamide (MABSA) Carlo Erba 98%; *p*-aminobenzenesulfonamide (PABSA) Fluka 99%; *o*-aminoacetophenone (OAAP) Aldrich 99%; *m*-aminoacetophenone (MAAP) Aldrich 99%; *p*-aminoacetophenone (PAAP) 99%; *o*-methoxyaniline (OMA) Carlo Erba 99%; *m*-methoxyaniline (MMA) Carlo Erba 99%; *p*-methoxyaniline (PMA) Carlo Erba 99%; *o*-aminobenzoic acid (AOAB) Carlo Erba 99%; *p*-aminobenzoic acid (APAB) Carlo Erba 99·5%; perchloric acid Carlo Erba 70%; twice distilled and deionized water was used as a solvent, which was made to bubble by nitrogen current before use. In every case the solutions used had been freshly prepared and kept out of the light.

The UV-VIS spectra of these aniline derivatives are similar to that of PAAP (Fig. 1) which is proposed as an example of the set. These spectra have been obtained at a constant concentration of these compounds, but with changing the acid concentration of the medium by adding the adequate volume of perchloric acid, drop by drop, to a 120 ml volume of the sample. The concentrations in mol dm^{-3} of the aniline derivatives used to obtain the corresponding spectra were: MNA $5{\cdot}067 \,.\, 10^{-5}$; MABN $8{\cdot}446 \,.\, 10^{-5}$; PABN $2{\cdot}409 \,.\, 10^{-5}$; MABSA $8{\cdot}672 \,.\, 10^{-5}$; PABSA

5·386 . 10^{-5}; OAAP 8·068 . 10^{-5}; MAAP 9·104 . 10^{-5}; PAAP 9·467 . 10^{-5}; OMA 9·753 . 10^{-5}; MMA 7·176 . 10^{-5}; PMA 1·997 . 10^{-4}; AOAB 4·375 . 10^{-5}, and APAB 6·806 . 10^{-5}.

RESULTS AND DISCUSSION

Fig. 1 corresponds to the protonation equilibrium of PAAP and shows a type of behaviour common to all the bases under study. The variation in the absorbance with the acidity of the medium is small at the beginning and at the end of the protonation and reaches its highest point when the protonation is in the half-way; pK values obtained by means of the graphic method have already been published and are listed in Table I for comparative purposes[2].

Revision of the extrapolation to infinite dilution method. The variation in the pK_{ap} *vs* pH, defined in Eq. (*3*), is not linear in the case of aromatic amines in a per-

TABLE I

pK_{BH^+} values obtained by different methods (pK > 1)

Indicator	Method				
	a	*b*	*c*	*d*	*e*
MNA	2·45	2·42	2·45	2·45	2·45
MABN	2·79	2·78	2·79	2·79	2·79
PABN	1·83	1·77	1·83	1·84	1·82
MABSA 1°	2·77	2·75	2·77	2·77	2·76
MABSA 2°	9·90	9·90	9·90	9·93	9·92
PABSA 1°	2·10	2·07	2·09	2·10	2·10
PABSA 2°	10·49	10·47	10·48	10·52	10·51
PAAP	2·26	2·25	2·26	2·25	2·26
MAAP	3·57	3·55	3·56	3·56	3·57
OAAP	2·30	2·26	2·30	2·29	2·29
PMA	5·34	5·33	5·34	5·34	5·35
OMA	4·39	4·37	4·39	4·40	4·40
MMA	4·23	4·22	4·23	4·23	4·23
APAB 1°	2·54	2·50	2·52	2·55	2·55
APAB 2°	4·70	4·68	4·77	4·79	4·84
AOAB 1°	2·15	2·14	2·17	2·19	2·19
AOAB 2°	4·95	4·93	4·95	4·94	4·94

[a] According to the graphic method; [b] obtained by extrapolation to infinite dilution; [c] from $\log I = -m\,\mathrm{pH} + n$, $pK_{BH^+} = n/m$; [d] $\log I = A(\mathrm{pH})^3 + B(\mathrm{pH})^2 + C(\mathrm{pH}) + D$ (all margin); [e] as in the preceding case extended only to $\log I$ within ± 1.

chloric acid medium. Fig. 2 shows these results for various compounds which protonation occurs within the same acidity range; in all these cases the behaviour is similar: there is a linear stretch above the 50% limit in the protonation of the base and another, nonlinear one, under this limit. The extrapolation to infinite dilution of the linear stretch leads to values which are close to that of the pK_{BH^+} calculated by other methods (Table I). This behaviour can be accounted for by the fact that the point corresponding to 50% protonation is close to the origin.

Linear variation $\log I\,(\pm 1) = f(\mathrm{pH})$. The study of the $\log I/\mathrm{pH}$ values has enabled to prove that the differences between each two consecutive quotients of the form (5) are constants:

$$\Delta(\Delta \log I/\Delta \mathrm{pH}) = \text{constant}\,, \tag{5}$$

where $\Delta \log I$ and $\Delta\mathrm{pH}$ represent in turn the differences between pairs of consecutive values in the interval of $\log I = +1$ to $\log I = -1$. In this case the relation is deduced as:

$$\log I = -m\,\mathrm{pH} + n\,, \tag{6}$$

where the slope is always negative. Table II sumarizes the values of n, m, and r_{xy}

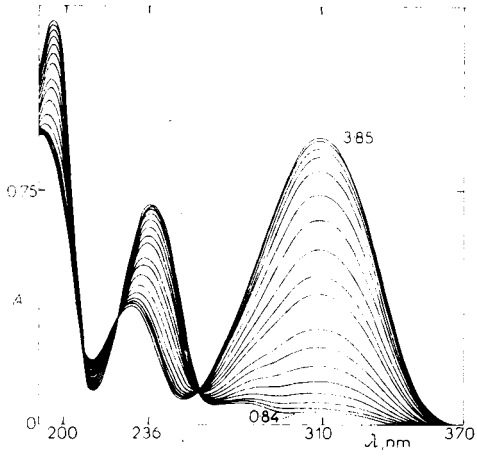

FIG. 1

Absorption UV spectra of the acid-base protonation equilibrium of *p*-aminoacetophenone at pH = 3·85; 3·70; 3·45; 3·26; 3·06; 2·82; 2·62; 2·43; 2·28; 2·17; 1·96; 1·82; 1·67; 1·51; 1·36; 1·20; 1·07; 0·94 and 0·84

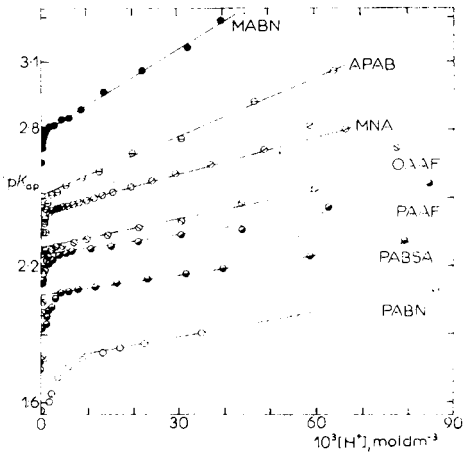

FIG. 2

Plot of the function $pK_{ap} = f(\mathrm{pH})$ for various aniline derivatives. For OAAF read OAAP; for PAAF read PAAP

obtained for each indicator. Beyond the limits of $\log I = \pm 1$, the behaviour is not linear and the function $\log I = f(\mathrm{pH})$ leads to sigmoid curves, so that an interpretation of the parameters in Eq. (*6*) can be made: the graphic method is based on the boundary condition $pK_{BH^+} = \mathrm{pH}$ if $\log I = 0$ and enables to obtain from Eq. (*6*) a new equation for the calculation of constants n, m:

$$pK_{BH^+} = n/m\,. \tag{7}$$

The results obtained in this way are highly satisfactory, as shown in Table I. In so far as m tends towards unity, the system approaches ideal behaviour, since $pK_{ap} = pK_{BH^+}$ and it can be deduced from Eq. (*4*) that $\log f_{BH^+}/f_B = 0$. Eq. (*6*), now written as $\log I = -m\,\mathrm{pH} + m\,pK_{BH^+}$, bears a close relation to Hammett–Deyrup equation: $\log I = -m\,pH_0 + pK_{BH^+}$, where the function H_0 has a similar role to that played by the pH in the case of the weak bases for which $m = 1$. In these conditions, Hammett postulate regarding activity coefficients is satisfied.

Polynominal variation $\log I = f(\mathrm{pH})$ *and* $pK_{ap} = f(\mathrm{pH})$. According to Eq. (*3*) the acceptance of a linear relation $\log I$ *vs* pH implies an analogous relation between

TABLE II

Values of the parameters n, m, and r_{xy} calculated from the equation $\log I = -m\,\mathrm{pH} + n$ (within $\log I = \pm 1$)

Indicator	n	m	r_{xy}
MNA	2·73	1·11	0·9996
MABN	3·14	1·12	0·9997
PABN	2·26	1·23	0·9997
MABSA 1°	3·09	1·11	0·9995
MABSA 2°	12·11	1·22	0·9992
PABSA 1°	2·35	1·12	0·9998
PABSA 2°	12·73	1·21	0·9989
PAAP	2·47	1·09	0·9999
MAAP	4·05	1·13	0·9997
OAAP	2·51	1·09	0·9995
PMA	5·43	1·01	0·9999
OMA	5·43	1·23	0·9997
MMA	4·90	1·16	0·9999
APAB 1°	3·01	1·19	0·9990
APAB 2°	5·65	1·18	0·9996
AOAB 1°	2·79	1·28	0·9988
AOAB 2°	5·73	1·16	0·9999

pK_{BH^+} and pH. By combining Eqs (*6*) and (*3*) we arrive at:

$$pK_{ap} = (1 - m)\,pH + m\,pK_{BH^+} \tag{8}$$

an equation which is valid within the margin $\log I = \pm 1$. However, the graph $pK_{ap} = f(pH)$ is not consistent with Eq. (*8*) and instead displays sigmoid curves. This apparent contradiction between Eqs (*8*) and (*6*) can be explained by allowing a grade three polynomial variation for both $\log I = f(pH)$ and $pK_{ap} = f(pH)$. The proposed equations are:

$$\log I = A(pH)^3 + B(pH)^2 + C(pH) + D \tag{9}$$

$$pK_{ap} = A(pH)^3 + B(pH)^2 + (C(pH) + 1) + D\,. \tag{10}$$

Fitting the data by the least squares method, we obtained values of the coefficients in the $\log I = \pm 1$ interval and also for the whole range of $\log I$ values (Tables III, IV). Another calculation program enabled to obtain the roots of Eq. (*9*). If $\log I = 0$, then we have $pH = pK_{BH^+}$; in all the compounds under study, of the

TABLE III

Roots and coefficients of the polynomial variation $\log I = A(pH)^3 + B(pH)^2 + C(pH) + D$ applied to all margin of $\log I$ values ($S(y)^2$ = variance)

Indicator	D	C	B	A	Roots		$S(y)^2$
MNA	5·49	−4·65	1·46	−0·19	2·52 ± i 2·27	2·45	$1·12\ 10^{-5}$
MABN	7·27	−5·73	1·67	−0·19	2·82 ± i 2·26	2·79	$9·60\ 10^{-6}$
PABN	4·21	−4·77	2·03	−0·37	1·80 ± i 1·69	1·84	$1·07\ 10^{-4}$
MABSA 1°	7·08	−5·54	1·60	−0·18	2·85 ± i 2·32	2·77	$1·00\ 10^{-4}$
MABSA 2°	−220·13	68·06	−6·87	0·22	7·74 ± i 2·24	9·93	$9·28\ 10^{-5}$
PABSA 1°	4·13	−3·87	1·35	−0·21	2·10 ± i 2·17	2·10	$1·38\ 10^{-4}$
PABSA 2°	256·09	−72·28	6·91	−0·22	10·19 ± i 2·25	10·52	$5·40\ 10^{-4}$
MAAP	10·80	−6·89	1·62	−0·15	3·59 ± i 2·69	3·56	$7·33\ 10^{-4}$
OAAP	5·06	−4·55	1·51	−0·21	2·39 ± i 2·15	2·29	$3·00\ 10^{-5}$
PAAP	4·80	−4·36	1·45	−0·20	2·36 ± i 2·15	2·25	$1·83\ 10^{-5}$
PMA	15·76	−6·69	1·03	−0·06	5·86 ± i 3·95	5·34	$2·91\ 10^{-5}$
OMA	13·49	−7·08	1·40	−0·11	4·11 ± i 3·28	4·40	$7·00\ 10^{-7}$
MMA	12·98	−6·94	1·37	−0·10	4·27 ± i 3·22	4·23	$5·14\ 10^{-8}$
APAB 2°	83·80	−46·48	8·68	−0·55	5·50 ± i 1·26	4·79	$1·65\ 10^{-5}$
APAB 1°	6·17	−5·44	1·84	−0·25	2·28 ± i 2·03	2·55	$4·00\ 10^{-6}$
AOAB 2°	53·01	−29·88	5·79	−0·38	4·99 ± i 1·64	4·94	$2·00\ 10^{-6}$
AOAB 1°	6·29	−6·55	2·57	−0·40	2·07 ± i 1·66	2·19	$1·71\ 10^{-4}$

three possible solutions, two were imaginary conjugated values and the third real value coincided with the thermodynamic constant calculated by other methods

TABLE IV

Roots and coefficients of the polynomial variation $\log I = A(\mathrm{pH})^3 + B(\mathrm{pH})^2 + C(\mathrm{pH}) + D$ valid from $\log I = +1$ to $\log I = -1$ ($S(y)^2$ = variance)

Indicator	D	C	B	A	Roots		$S(y)^2$
MNA	4·46	−3·33	0·92	−0·12	2·49 ± i 2·91	2·45	$2·57\ 10^{-7}$
MABN	5·33	−3·62	0·93	−0·11	2·72 ± i 3·07	2·79	$3·14\ 10^{-6}$
PABN	3·60	−3·44	1·15	−0·19	2·03 ± i 2·43	1·82	$8·25\ 10^{-7}$
MABSA 1°	3·80	−1·77	0·18	−0·01	4·44 ± i 8·08	2·76	$8·00\ 10^{-6}$
MABSA 2°	137·97	−40·09	3·99	−0·13	9·67 ± i 2·88	9·92	$1·47\ 10^{-4}$
PABSA 1°	3·34	−2·56	0·71	−0·11	2·17 ± i 3·11	2·10	$1·21\ 10^{-4}$
PABSA 2°	161·34	−44·58	2·13	−0·13	10·21 ± i 2·91	10·51	$3·14\ 10^{-5}$
MAAP	9·28	−5·71	1·31	−0·12	3·49 ± i 2·94	3·57	$1·85\ 10^{-5}$
OAAP	4·38	−3·61	1·09	−0·15	2·40 ± i 2·57	2·29	$1·38\ 10^{-6}$
PAAP	3·24	−2·17	0·48	−0·07	2·29 ± i 3·85	2·26	$3·67\ 10^{-8}$
PMA	7·91	−2·37	0·24	−0·01	5·56 ± i 8·20	5·35	$4·60\ 10^{-6}$
OMA	14·67	−7·91	1·59	−0·12	4·12 ± i 3·06	4·40	$1·58\ 10^{-6}$
MMA	9·16	−4·24	0·73	−0·05	4·22 ± i 4·47	4·23	$4·80\ 10^{-8}$
APAB 2°	81·06	−46·99	9·26	−0·62	5·01 ± i 1·32	4·84	$2·10\ 10^{-7}$
APAB 1°	4·53	−3·39	1·02	−0·15	2·09 ± i 2·71	2·55	$3·67\ 10^{-8}$
AOAB 2°	22·12	−11·20	2·04	−0·13	4·92 ± i 2·84	4·94	$1·10\ 10^{-8}$
AOAB 1°	7·97	−8·88	3·64	−0·57	2·09 ± i 1·40	2·19	$8·80\ 10^{-7}$

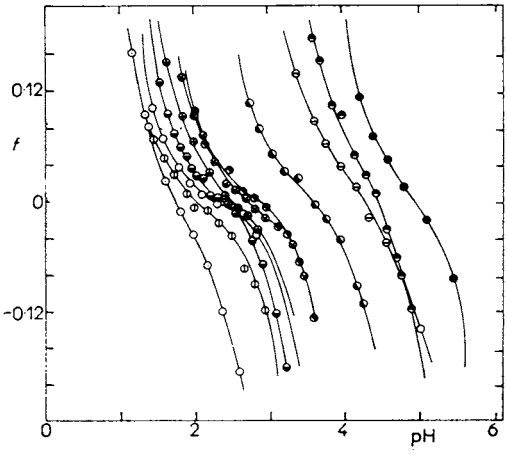

FIG. 3

Plot of the function $-\log f_{BH^+}/f_B = f(\mathrm{pH})$ for various aniline derivatives. ⊙ PABN; ◐ PABSA; ◒ OAAP; ○ MNA; ⊕ APAB; ⊗ MABSA; ◔ MABN; ◐ MAAP; ⊖ MMA; ◓ OMA and ● AOAB

(Tables II, III, IV). Moreover, the pK obtained in this way is close to the value of the inflection point obtained by derivation from Eq. (*9*) or (*10*). In this method, the log I margin is not restricted to ± 1, and the method is more general than the linear variation method but less intuitive, although the results are similar.

By using Eqs (*4*) and (*10*) as a starting point, the variation $\log f_{BH^+}/f_B = f(\mathrm{pH})$ can be obtained, giving in turn a polynomial function of the form:

$$-\log f_{BH^+}/f_B = A(\mathrm{pH})^3 + B(\mathrm{pH})^2 + C(\mathrm{pH}) + D - \mathrm{p}K_{BH^+}\,. \qquad (11)$$

The plots corresponding to each compound are displayed in Fig. 3. The inflection point of each one coincides approximately with $-\log f_{BH^+}/f_B = 0$ and corresponds to 50% ionization of the base. In each case, the f_{BH^+} value is close to unity and oscillates between 0·66 and 1·58 according to the acidity region and the properties of the indicator, $f_B = 1$ having been taken as reference.

CONCLUSIONS

Values of log I have been calculated for thirteen aniline derivatives in perchloric acid media, by means of a thorough analysis of the protonation equilibrium, using the UV-VIS absorption spectroscopy. The function $\mathrm{p}K_{ap} = f(\mathrm{pH})$ has been proved to be linear only when the protonation of the base is above 50%. However, the extrapolation of this linear stretch leads to the $\mathrm{p}K_{BH^+}$ of the base. The revision of this method of extrapolation has enabled us to find more accurate methods, the results being in conformity for most compounds. More accurate results are possible within the $\log I = \pm 1$ interval (polynomial method) but the use of the entire interval should not be discarded, because not all the equilibria take place within $\log I = \pm 1$. Fig. 3 shows that, for the same acidity, the ratio of activity coefficients varies according to the compound. This fact makes it necessary to revise Hammett's cancelation hypothesis[13–15] and those methods which are based on it. This revision is especially important in the case of weak bases ($\mathrm{p}K_{BH^+} < 1$) which need media of higher acidity.

REFERENCES

1. Gold V., Hawes B. W. V.: J. Chem. Soc. *1951*, 2102.
2. Leal J. M., García B., Mata F.: Anal. Quím., in press.
3. Davis C. T., Geissman T. A.: J. Am. Chem. Soc. *76*, 3507 (1954).
4. Marziano N. C., Cimino G. M., Passerini R.: J. Chem. Soc., Perkin Trans 2, *1973*, 1915.
5. Marziano N. C., Traverso P. G., Cimino G. M.: J. Chem. Soc., Perkin Trans 2, *1977*, 306.
6. Paul M. A., Hammett L. P.: J. Am. Chem. Soc. *58*, 2182 (1936).
7. Paul M. A.: J. Am. Chem. Soc. *76*, 3236 (1954).
8. Hammett L. P., Deyrup A. J.: J. Am. Chem. Soc. *54*, 2721 (1932).
9. Edward J. T., Wong S. C.: Can. J. Chem. *55*, 2492 (1977).

10. Traverso P. G.: Can. J. Chem. *62*, 153 (1984).
11. Cox R. A., Yates K.: Can. J. Chem. *61*, 2225 (1983).
12. Geribaldi S., Grec-Luciano A., Maria P. C., Azzaro M.: J. Chim. Phys. *79*, 103 (1982).
13. Yates K., Stevens J. B., Katritzky A. R.: Can. J. Chem. *42*, 1957 (1964).
14. Paul M. A., Long F. A.: Chem. Rev. *57*, 1 (1957).
15. Boyd R. H.: *Solute–Solvent Interactions*, Chapter 3. Marcel Dekker, New York 1964.