Basis of Hydrogen Ion Binding Curves Deduced from Differences in Solution and Solvent Titrations

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A hydrogen ion binding curve may be constructed by plotting the difference in titers of samples and blanks against pH. The theoretical bases for the determination of pKa and stoichiometry for weak acids and bases by such curves is investigated. The assumptions and limitations of such methods are specified. The nature and degree of the difference in the titration curve and the hydrogen ion binding curve is shown for changes in pK and concentration of solute.

IN A PAPER discussing the use of apparent dissociation constants (Ka') in qualitative organic analysis, Parke and Davis (1) had proposed the use of hydrogen ion binding curves for estimation of pKa'. Their procedures involved the titration of two solutions, one including and one omitting the sample, with titrant of the same high normality. The amount of titer necessary to achieve a given pH for the blank is subtracted from the amount necessary to achieve the same pH for the solution. These titer differences may be calculated in an acidic or basic direction using the amount of titrant at pH 7 as zero for blank and solution. For example, a method would be to subtract the volume of standard acid necessary to bring the blank solution (initially at pH 7) to a given pH, e.g., pH₁, which is less than 7, from the volume of standard acid necessary to change the pH of the sample solution from 7 to that same pH₁. Similarly, the volume of standard alkali necessary to bring the blank solution to a given pH, e.g., pH₂, which is greater than 7, would be subtracted from the volume of standard alkali necessary to change the pH of the sample solution from 7 to that same pH₂.

The titer differences when divided by the total stoichiometric titer for a single titratable function (α) were plotted against the pH and are presumably related to the expression

$$pH = pKa' + \log [\alpha/(1 - \alpha)] \qquad (Eq. 1)$$

where α is the degree of dissociation. The pKa' was estimated from the pH value at $\alpha = 0.5$ (2).

It should be informative to investigate the basic principles validating this technique and to evaluate its limitations.

The general equation for equilibria during titration of a weak acid (HA) by a base (MOH) on the Parke-Davis assumptions of concentrations equal to activities [or for neutralization of a salt (MA) by a strong acid (HX)] (2) is

$$[H^+] = Ka' \frac{[HA]}{[A^-]} =$$
$$Ka' \frac{(a - b) - [H^+] + [OH^-]}{b + [H^+] - [OH^-]} \qquad (Eq. 2)$$

where the total concentrations of weak acid and weak acid anion is

$$a = [HA] + [A^-] \qquad (Eq. 3)$$

where the concentration of the anion given as the salt is

$$b = [M^+] \qquad (Eq. 4)$$

and since the solution is electrically neutral

$$[M^+] + [H^+] = [A^-] + [OH^-] \qquad (Eq. 5)$$

Titration of a Salt of a Weak Acid in Acid Region With a Strong Acid.—When pH < 7, $[H^+] \gg [OH^-]$ so that Eq. 2 reduces to

$$[H^+] = Ka' \frac{(a - b) - [H^+]}{b + [H^+]} \qquad (Eq. 6)$$

If x is the number of milliequivalents of MA before titration in L ml. of solution titrated with M ml. of strong acid of y normality, and if M_x is the stoichiometric acid titer for x meq. of MA, then

$$a = x/(L + M) = M_x y/(L + M) \quad (Eq. 7)$$

and $$b = (M_x - M)y/(L + M) \qquad (Eq. 8)$$

If M' is the ml. of strong acid titer necessary to achieve the same pH or $[H^+]$ with the same equipment for L' ml. of a blank as M ml. does for L ml. of sample solution, then

$$[H^+] = M' y/(L' + M') \qquad (Eq. 9)$$

Equations 7, 8, and 9 may be substituted into Eq. 6, and since the y values cancel

$$[H^+] = Ka' \frac{\alpha'}{(1 - \alpha')} \qquad (Eq. 10)$$

where $\alpha' = \left\{ M - M' \left(\frac{L + M}{L' + M'} \right) \right\} \Big/ M_x$

$$(Eq. 11)$$

The logarithmic form of Eq. 10 is the same as Eq. 1 except for the sign of the log term. The α' values may be calculated for a given pH from knowledge of the ml. of titer (M and M') necessary to achieve that pH in L ml. of sample and L' ml. of the blank.

If the initial volumes of sample and blank solutions are the same ($L = L'$) and the concentration of the acid titer is great with respect to that of the sample solution ($L \gg M > M'$) then the logarithmic form of the simplified expression is

$$pH = pKa' - \log \frac{(M - M')/M_x}{1 - (M - M')/M_x} =$$
$$pKa' - \log \frac{\alpha''}{1 - \alpha''} \qquad (Eq. 12)$$

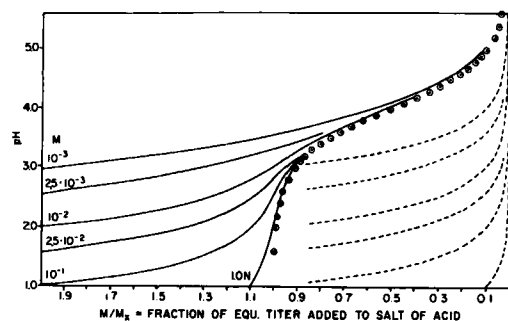**Addition of a Strong Acid to a Weak Acid in Acid**

Fig. 1.—Titration and hydrogen ion binding curves for various concentrations of an acid of pKa 4.0; ———, acid titration curves for the weak acid salt on the assumption of no change in concentration of the solution during the titration; – – –, comparable titrations of blank of the same volume; ⊙⊙⊙, difference in titer at any pH for the titration of a sample and blank. It should be noted that the circles give the same S-shaped curve for any concentration of the acid when the titrations are thus corrected for the titration of the blank.
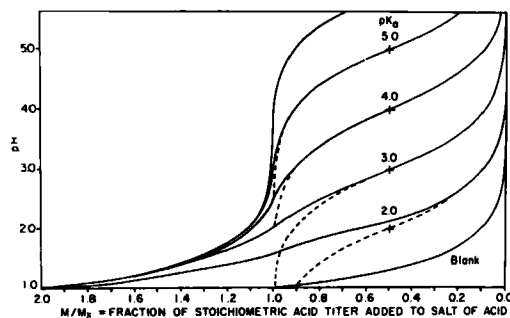

Fig. 2.—Titration and hydrogen ion binding curves for 0.1 M solutions of acids of various pKa; ———, acid titration curves for the weak acid salt on the assumption of no change in concentration of the solution during the titration; – – –, difference in titer at any pH for the titrations of sample and blank. The blank is of the same volume as the sample.

Region.—At any time during the addition of a strong acid (HX) to a weak acid (HA), the hydrogen ion concentration [H$^+$] should be equal to the sum of those ions from the completely dissociated strong acid [H$_s^+$] and the incompletely dissociated weak acid [H$_w^+$]

$$[H^+] = [H_w^+] + [H_s^+] \qquad (Eq. 13)$$

However, the acid anion concentration is

$$[A^-] = [H_w^+] = [H^+] - [H_s^+] \qquad (Eq. 14)$$

and thus,

$$[HA] = a - [H_w^+] = a - [H^+] + [H_s^+] \qquad (Eq. 15)$$

$$[H^+] = Ka \frac{a - [H^+] + [H_s^+]}{[H^+] - [H_s^+]} \qquad (Eq. 16)$$

Substitution of Eqs. 7, 9 and

$$[H_s^+] = (M - M_x)y/(L + M) \qquad (Eq. 17)$$

into Eq. 16 results in Eq. 10, 11, and on simplification. to Eq. 12.

Similar equations result for the same assumptions although the sign of the log term in Eqs. 10 and 12 would differ, if the titrations of both blank and sample were carried out in the alkaline range where [OH$^-$] ≫ [H$^+$], where the undissociated weak acid of the sample is neutralized by strong base and where the pH of the blank is increased by strong base and from Eq. 2

$$[H^+] = Ka' \frac{[HA]}{[A^-]} = Ka' \frac{(a - b) + [OH^-]}{b - [OH^-]} \qquad (Eq. 18)$$

Applications of the Derived Equation.—The simplified expression (Eq. 12) states that a difference in titer necessary to achieve the same pH for a sample and a blank solution when divided by the total ml. of stoichiometric titer may be plotted against pH to give an S-shaped curve that is always of the same form.

A series of curves are given in Fig. 1 for the strong acid titrations of various concentrations of a weak acid salt (pKa = 4.0) and their corresponding blanks. The circles represent the ideal S shape calculated for all concentrations on the basis of the assumptions of Eq. 12. The solid lines represent the titration curves of the sample, and the dashed lines the titration curves of the blanks. The estimates of pKa' at α″ = 0.5 are practical in a manner equivalent to the use of the pH at half-neutralization as the pKa' (2). This presupposes that the purity and stoichiometry are known for all concentrations of the anion of the acid of pKa 4.0. It must be realized, however, that the assumptions of M ≪ L, and activity equal to concentration will not hold for very concentrated solutions of the sample.

At low sample concentrations, the error in calculated titer differences will be large.

A series of theoretical curves are also given in Fig. 2 for the strong acid titrations of 0.1 M solutions of weak acid salts of various pKa's and a corresponding blank. The dashed lines represent the ideal S shapes calculated on the basis of the assumptions of 12 from the differences in titer of sample and blank solutions where the abscissa for the dashed lines now becomes $(M - M'/M_x)$. The method has no advantage over the traditional techniques of determining pKa' at half neutralization for pKa's generally in the range 4–10, unless solubilities of material are low and the inflections are not sharp. The pKa's of material with 2 < pKa <4 may be estimated but the error in subtraction of volumes and in pH readings at pH <2.0, and the failure of the assumptions underlying Eq. 12 invalidate the techniques in those regions, especially for estimates of stoichiometry.

The above discussion considers aqueous solutions. Titrations in nonaqueous solvents are special cases and must be considered separately. For example, a pKa' calculated from the apparent pH at half neutralization in nonaqueous solvent is highly concentration dependent (3).

REFERENCES

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