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Formulation of Strong Acid-Strong Base Potentiometric Titration Curve in Terms of Hyperbolic Functions

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The strict relation between pH and the titration fraction, f, representing the strong acid-strong base potentiometric titration curve is formulated, taking the effect of dilution into account, in terms of the inverse hyperbolic sine function. From this, exact expressions for dpH/df and d^2pH/df^2 are derived as a function of f.

In many practical problems, the exponential function does not occur alone, but it appears in the following combinations:

$$\cosh x = \frac{1}{2}(e^x + e^{-x}), \tag{1}$$

$$\sinh x = \frac{1}{2}(e^x - e^{-x}), \tag{2}$$

where x is any real number and e is the base of natural logarithms. While useful therefore in solving a variety of problems, hyperbolic functions[1)] have not yet been applied to describe the titration curves. It is the purpose of the present paper to describe, to begin with, the strong acid-strong base potentiometric titration curve by applying the latter form of the hyperbolic sine function. As an application of the present theory, the exact inflection point of this titration curve is determined, since the problem whether the inflection point and the equivalence point will coincide or not has been paid much attention.[2-4)]

We shall consider the titration of a strong monoprotic acid, e.g., HCl with a strong monoacidic base, e.g., KOH. The activity coefficients and the liquid-junction potential are assumed to remain constant in the course of titration; this assumption may be reasonable if an indifferent electrolyte is present in high concentrations. Thus, we may use pH = $-\log [H^+]$ instead of pH = $-\log a_{H^+}$ as the definition of pH, where $[H^+]$ and a_{H^+} are the concentration and the activity of hydrogen ion, respectively, and log denotes the common logarithm throughout in this paper. Now, let C_a and V_0 be the initial concentration and the initial volume of the acid solution being titrated, respectively, and let C_b and V be the concentration and the added volume of the standard base solution, respectively. We shall describe the course of the titration in terms of the titration fraction defined as

$$f = C_bV/(C_aV_0), \tag{3}$$

so that f = 1 at the equivalence point. In the course of titration, there exist the charge balance and the relation of the ionic product of water:

$$[H^+] + [K^+] = [Cl^-] + [OH^-], \tag{4}$$

$$[OH^-] = K_w/[H^+]. \tag{5}$$

Making use of Eq. 3, $[K^+]$ and $[Cl^-]$ in Eq. 4 can be written as a function of f:

$$[K^+] = C_bV/(V_0+V) = C_b[1-(C_b/C_a)/(f+C_b/C_a)], \tag{6}$$

$$[Cl^-] = C_aV_0/(V_0+V) = C_b/(f+C_b/C_a). \tag{7}$$

Substitution of Eqs. 5-7 in Eq. 4 gives the required equation:

$$C_b[1-(1+C_b/C_a)/(f+C_b/C_a)] = K_w/[H^+] - [H^+]. \tag{8}$$

Let us formulate the right-hand side of Eq. 8 in terms of the hyperbolic sine function of pH. Denoting the common logarithm of x^{-1} by px (p denotes -log), any positive variable x can be transformed according to

$$x = \exp(-px/\log e). \tag{9}$$

By applying Eqs. 2 and 9, the right-hand side of Eq. 8 can then be transformed to

$$\begin{aligned} K_w/[H^+] - [H^+] &= \exp[(pH-pK_w)/\log e] - \exp(-pH/\log e) \\ &= \exp(-\tfrac{1}{2}pK_w/\log e)\ \{\exp[(pH-\tfrac{1}{2}pK_w)/\log e] - \exp[-(pH-\tfrac{1}{2}pK_w)/\log e]\} \\ &= 2\sqrt{K_w}\ \sinh[(pH-\tfrac{1}{2}pK_w)/\log e]. \end{aligned} \tag{10}$$

Substitution of Eq. 10 in Eq. 8 gives the strict relation between pH and f:

$$u(f) = \sinh[(pH-\tfrac{1}{2}pK_w)/\log e], \tag{11}$$

where

$$u(f) \equiv [C_b/(2\sqrt{K_w})]\ [1-(1+C_b/C_a)/(f+C_b/C_a)]. \tag{12}$$

Since f varies from zero to infinity, u(f) should satisfy the inequality

$$-C_a/(2\sqrt{K_w}) \leqq u(f) < C_b/(2\sqrt{K_w}). \tag{13}$$

The exact expression of pH against f can now be obtained from the inverse transformation of Eq. 11:

$$pH = \tfrac{1}{2}pK_w + \log e\ \mathrm{arsinh}\ u(f). \tag{14}$$

A part of the pH-f curve in the vicinity of the equivalence point calculated from Eq. 14 is shown on a greatly enlarged scale in Fig. 1(a). A programmable calculator (Casio FX-801P) is used for all the calculations in the present paper.

We shall calculate the first derivative dpH/df according to

$$dpH/df = (dpH/du)(du/df), \tag{15}$$

u(f) being denoted by u. Differentiation of Eq. 14 with respect to u, using the formula[1] $d(\mathrm{arsinh}\ x)/dx = 1/\sqrt{(x^2+1)}$, gives

$$dpH/du = \log e/\sqrt{(u^2+1)}. \tag{16}$$

Differentiating Eq. 12 with respect to f and substituting

$$(1+C_b/C_a)/(f+C_b/C_a) = 1-(2\sqrt{K_w}/C_b)u \tag{17}$$

in order to express the final result briefly in terms of u(f), we have

$$\frac{du}{df} = \frac{2\sqrt{K_w}}{C_b(1+C_b/C_a)}\left(u - \frac{C_b}{2\sqrt{K_w}}\right)^2. \tag{18}$$

Thus, we have the strict formulation for dpH/df as a function of u(f):

$$\frac{dpH}{df} = \log e \,\frac{2\sqrt{K_w}}{C_b(1+C_b/C_a)}\,(u^2+1)^{-1/2}\left(u - \frac{C_b}{2\sqrt{K_w}}\right)^2. \tag{19}$$

Figure 1(b) shows the dpH/df-f curve calculated from Eq. 19.

We shall calculate the second derivative d^2pH/df^2 according to

$$d^2pH/df^2 = [d(dpH/df)/du](du/df). \tag{20}$$

The derivative d(dpH/df)/du can easily be obtained by differentiating Eq. 19 with respect to u. The derivative du/df has been given by Eq. 18. We have finally the following expression for d^2pH/df^2 as a function of u(f):

$$\frac{d^2pH}{df^2} = \log e \left[\frac{2\sqrt{K_w}}{C_b(1+C_b/C_a)}\right]^2 (u^2+1)^{-3/2}\left(u - \frac{C_b}{2\sqrt{K_w}}\right)^3\left(u^2 + \frac{C_b}{2\sqrt{K_w}}u + 2\right). \tag{21}$$

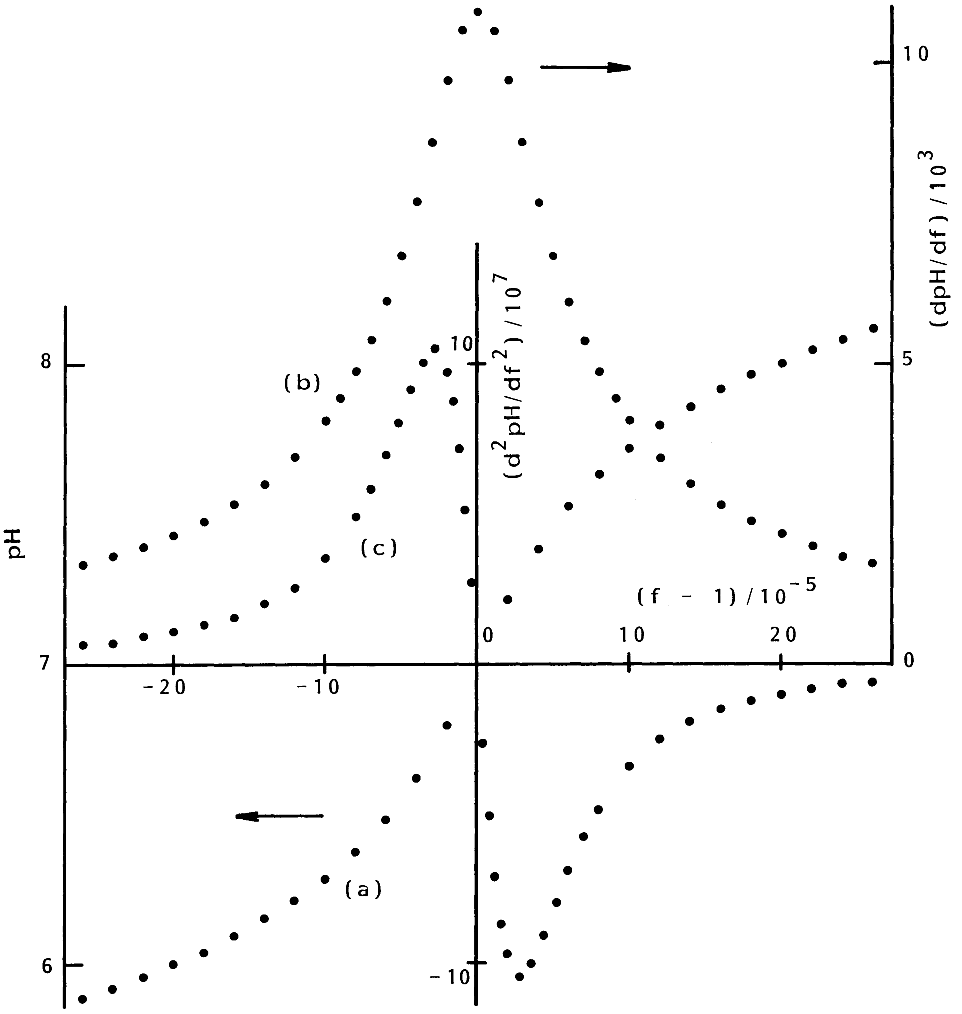

Fig. 1. Plots of (a)pH, (b)dpH/df, and (c)d^2pH/df^2 against f. $C_a = C_b = 0.01$ mol dm^{-3}.

Figure 1(c) shows the d^2pH/df^2-f curve calculated from Eq. 21.

As an application of Eq. 21, we shall determine the inflection point of the pH-f curve from the condition that $d^2pH/df^2 = 0$. Since $u - C_b/(2\sqrt{K_w}) < 0$ always from Eq. 13, this condition is satisfied only when

$$u^2 + [C_b/(2\sqrt{K_w})]u + 2 = 0. \tag{22}$$

If $C_b > \sqrt{(32K_w)}$, then Eq. 22 has two real roots:

$$u = \tfrac{1}{2}\{-C_b/(2\sqrt{K_w}) + \sqrt{[C_b^2/(4K_w) - 8]}\}, \tag{23}$$

$$u = \tfrac{1}{2}\{-C_b/(2\sqrt{K_w}) - \sqrt{[C_b^2/(4K_w) - 8]}\}. \tag{24}$$

Thus, there exist in general two different inflection points in the pH-f curve.

We shall first consider one inflection point derived from Eq. 23. Since u from Eq. 23 should satisfy Eq. 13, so that

$$C_a \geqq \tfrac{1}{2}C_b[1 - \sqrt{(1 - 32K_w/C_b^2)}]. \tag{25}$$

Then, substituting u(f) from Eq. 12 into Eq. 23, solving for f, and denoting this by $f_{inf,max}$, we have

$$f_{inf,max} = 2(1 + C_b/C_a)/[3 - \sqrt{(1 - 32K_w/C_b^2)}] - C_b/C_a. \tag{26}$$

As can be seen by putting numerical values into Eq. 26, $f_{inf,max}$ is extremely close to unity, representing the inflection point having maximum slope nearest to the equivalence point. The curve shown in Fig. 1(c) does not pass through the origin (f = 1), but passes through the point $f_{inf,max}$ given by Eq. 26, though this is hardly distinguishable on the graph.

By the similar method, we can calculate another inflection point, $f_{inf,min}$, from Eq. 24. This inflection point arises only if

$$C_a \geqq \tfrac{1}{2}C_b[1 + \sqrt{(1 - 32K_w/C_b^2)}]. \tag{27}$$

Then, $f_{inf,min}$ is given by

$$f_{inf,min} = 2(1 + C_b/C_a)/[3 + \sqrt{(1 - 32K_w/C_b^2)}] - C_b/C_a, \tag{28}$$

representing the inflection point having minimum slope far before the equivalence point. Under a special condition when $C_b = \sqrt{(32K_w)}$, the pH-f curve shows a single inflection point at $f = (1/3)[2 - \sqrt{(32K_w)}/C_a]$.

Entirely analogous calculations can be carried out for the titration of a strong monoacidic base with a strong monoprotic acid. Expressions 25-28 are mathematically identical, but more straightforward compared with those derived by Meites and Goldman[3,4] through another approach to this problem. Thus, it may be concluded that the method developed in the present paper is a reasonable extension to the prevailing theory of potentiometric titration curve.

References

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