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Inflection Points on Some S-Shaped Curves

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Abstract

This paper refers to inflection point—the fundamental property of S-shaped curves. In this paper, the inflection points are related to pH titration curve pH = pH(V), and to the curve $\sigma = \sigma$(pH) involved with surface tension, σ.

Keywords

pH Titration; Surface Tension

1. Introduction

This paper recalls the well-known property of different functions represented by the curves with sigmoidal shape (S-shape) [1], involved with inflection (inf) point. An inflection point is the point on 2D plane where the curvature of the curve changes direction. The S-shape is characteristic, among others, for potentiometric titration curves [2]. Different methods of equivalence (eq) point determination are based on location of the inflection point on the curves pH = pH(V) or $E = E(V)$, where E—potential, V—volume of titrant added. The inflection points are registered also in different physicochemical studies.

Generalizing, we refer to a monotonic function y = $y(x)$. The inflection point (x_{inf}, y_{inf}) corresponds to maximal slope $|\eta|$, where

$$\eta = \frac{\mathrm{d}y}{\mathrm{d}x} = \frac{1}{\mathrm{d}x/\mathrm{d}y} \tag{1}$$

Applying the relation

$$\frac{\mathrm{d}^2x}{\mathrm{d}y^2} \cdot \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^3 + \frac{\mathrm{d}^2y}{\mathrm{d}x^2} = 0 \tag{2}$$

at the inflection point on the curve $y = y(x)$ we have

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$$\frac{d^2y}{dx^2}=0 \tag{3}$$

and then at $dy/dx \neq 0$ we get

$$\frac{d^2x}{dy^2}=0 \tag{4}$$

It means that the maximal slope is equivalent with the relation (4) valid for the inverse function $x = x(y)$. This property is important for pH titration curves; namely, the functions $V = V(\text{pH})$ assume relatively simple form [3].

In this paper, we refer to a simple acid-base titration (y = pH, $x = V$), and to the relationship $\sigma = \sigma(\text{pH})$ for surface tension ($y = \sigma$, x = pH).

2. Relation between Equivalence and Inflection Points in pH Titration

The main task of titration made for analytical purposes is the estimation of the equivalence volume (V_{eq}). Let us consider the simplest case of titration of V_0 mL of C_0 mol/L HCl as titrand (D) with V mL of C mol/L NaOH as titrant (T). At $V = V_{eq}$, the fraction titrated

$$\Phi_{eq}=\frac{C\cdot V_{eq}}{C_0\cdot V_0}=1 \tag{5}$$

i.e., $CV_{eq} = C_0V_0$. In this D+T system, the titration curve $V = V(\text{pH})$ has the form

$$V=V_0\cdot\frac{C_0-\alpha}{C+\alpha} \tag{6}$$

where

$$\alpha=\left[\text{H}^+\right]-\left[\text{OH}^-\right]=10^{-\text{pH}}-10^{\text{pH}-pK_W},\quad pK_W=-\log K_W,\ K_W=\left[\text{H}^+\right]\left[\text{OH}^-\right] \tag{7}$$

To facilitate the calculations, it is advisable to rewrite (6) into the form

$$V_0+V=V_0\cdot\left(C_0+C\right)\cdot\frac{1}{C+\alpha} \tag{8}$$

From (5) and (6) we get

$$\alpha=C\cdot\frac{V_{eq}-V}{V_0+V}=C\cdot z,\ \text{ where } z=\frac{V_{eq}-V}{V_0+V} \tag{9}$$

From (8)

$$u=\frac{d\left(V_0+V\right)}{\text{dpH}}=\ln10\cdot V_0\left(C_0+C\right)\cdot\left(C+\alpha\right)^{-2}\cdot\left(\left[\text{H}^+\right]+\left[\text{OH}^-\right]\right)$$

$$\frac{du}{\text{dpH}}=\frac{d^2V}{\text{dpH}^2}=-\left(\ln10\right)^2\cdot V_0\left(C_0+C\right)\left(\alpha\cdot\left(C+\alpha\right)^{-2}-2\cdot\left(\left[\text{H}^+\right]+\left[\text{OH}^-\right]\right)^2\cdot\left(C+\alpha\right)^{-3}\right) \tag{10}$$

Setting $d^2V/\text{dpH}^2 = 0$ and writing $\left(\left[\text{H}^+\right]+\left[\text{OH}^-\right]\right)^2=\alpha^2+4K_W$, from (10) we get, by turns,

$$\begin{aligned}&\alpha\left(C+\alpha\right)-2\left(\alpha^2+4K_W\right)=0\\&\alpha^2-C\cdot\alpha+8K_W=0\\&z^2-z+8K_W/C^2=0\end{aligned} \tag{11}$$

From (11) we obtain for $z = z_{inf}$

$$z_{inf}=\frac{1}{2}\cdot\left(1-\sqrt{1-32\cdot K_W/C^2}\right)=8K_W/C^2+\left(8K_W/C^2\right)^2+\cdots \tag{12}$$

and then for $V = V_{\text{inf}}$ [3] [4]

$$V_{eq} - V_{inf} = z_{inf} \cdot V_0 \cdot \frac{1 + C_0/C}{1 + z_{inf}} \tag{13}$$

Analogous result can be obtained for titration of V_0 mL of C_0 mol/L NaCl with V mL $AgNO_3$ [5]. Denoting $[Ag^+][Cl^-] = K_{so}$ we get (13), where [5]

$$z_{inf} = \frac{1}{2} \cdot \left(1 - \sqrt{1 - 32 \cdot K_{so}/C^2}\right) \tag{14}$$

At $pK_{so} = 9.75$ for AgCl, $V_0 = 100$ mL, $C_0 = 10^{-4}$ and $C = 10^{-3}$, we get $V_{eq} - V_{inf} = 0.16$ mL.

3. A Comment to Szyszkowski Formula

Many physicochemical processes are graphically represented by the curves with the sigmoidal shape. In this section, we refer to the function $\sigma = \sigma(\text{pH})$ obtained on the basis of Szyszkowski's empirical formula [6]

$$\sigma = \sigma_0 - a \cdot \ln\left(1 + b \cdot [\text{HL}]\right) \tag{15}$$

expressing the relationship between surface tension σ and concentration [HL] of uncharged form HL of an aliphatic fatty acid as a surfactant in aqueous media; σ_0—surface tension of pure water, a, b—constants.
Denoting $[\text{HL}] + [\text{L}^-] = C$ and

$$K_1 = \frac{[\text{H}^+][\text{L}^-]}{[\text{HL}]}$$

we get, by turns:

$$[\text{HL}] = C \cdot \frac{[\text{H}^+]}{[\text{H}^+] + K_1}$$

$$1 + b \cdot [\text{HL}] = \frac{(1 + b \cdot C) \cdot [\text{H}^+] + K_1}{[\text{H}^+] + K_1}$$

$$\sigma = \sigma_0 - a \cdot \ln\left((1 + b \cdot C) \cdot [\text{H}^+] + K_1\right) + a \cdot \ln\left([\text{H}^+] + K_1\right) \quad \frac{d\sigma}{d[\text{H}^+]} = -a \cdot \left(\frac{(1 + b \cdot C)}{(1 + b \cdot C) \cdot [\text{H}^+] + K_1} - \frac{1}{[\text{H}^+] + K_1}\right)$$

$$\begin{aligned} u = \frac{d\sigma}{d\text{pH}} &= \left(\frac{d\sigma}{d[\text{H}^+]}\right) \cdot \left(\frac{d[\text{H}^+]}{d\text{pH}}\right) = -\ln 10 \cdot [\text{H}^+] \cdot \frac{d\sigma}{d[\text{H}^+]} \\ &= -\ln 10 \cdot a \cdot \left(\frac{(1 + b \cdot C) \cdot [\text{H}^+]}{(1 + b \cdot C) \cdot [\text{H}^+] + K_1} - \frac{[\text{H}^+]}{[\text{H}^+] + K_1}\right) \end{aligned}$$

$$\begin{aligned} \frac{d^2\sigma}{d\text{pH}^2} &= -\ln 10 \cdot [\text{H}^+] \cdot \frac{du}{d[\text{H}^+]} \\ &= (\ln 10)^2 \cdot a \cdot K_1 \cdot [\text{H}^+] \cdot \left(\frac{1 + b \cdot C}{\left((1 + b \cdot C) \cdot [\text{H}^+] + K_1\right)^2} - \frac{1}{\left([\text{H}^+] + K_1\right)^2}\right) \end{aligned} \tag{16}$$

Putting $d^2\sigma/d\text{pH}^2 = 0$, from Equation (16) we get $[\text{H}^+] \cdot (1 + b \cdot C)^{1/2} = K_1$, and then

$$\text{pH} = \text{pH}_{inf} = pK_1 + \frac{1}{2} \cdot \log\left(1 + b \cdot C\right) \tag{17}$$

From Equation (17) it results that the abscissa (pH_{inf}) corresponding to inflection point does not overlap with pK_1 value for HL.

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