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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 $\text{pH} = \text{pH}(V)$, and to the curve $\sigma = \sigma(\text{pH})$ 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 $\text{pH} = \text{pH}(V)$ 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

$$\eta = \frac{dy}{dx} = \frac{1}{dx/dy} \quad (1)$$

Applying the relation

$$\frac{d^2x}{dy^2} \cdot \left(\frac{dy}{dx}\right)^3 + \frac{d^2y}{dx^2} = 0 \quad (2)$$

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

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$$\frac{d^2 y}{dx^2} = 0 \quad (3)$$

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

$$\frac{d^2 x}{dy^2} = 0 \quad (4)$$

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 ($y = \text{pH}$, $x = V$), and to the relationship $\sigma = \sigma(\text{pH})$ for surface tension ($y = \sigma$, $x = \text{pH}$).

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

$$\Phi_{eq} = \frac{C \cdot V_{eq}}{C_0 \cdot V_0} = 1 \quad (5)$$

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

$$V = V_0 \cdot \frac{C_0 - \alpha}{C + \alpha} \quad (6)$$

where

$$\alpha = [\text{H}^+] - [\text{OH}^-] = 10^{-\text{pH}} - 10^{\text{pH} - \text{p}K_w}, \quad \text{p}K_w = -\log K_w, \quad K_w = [\text{H}^+][\text{OH}^-] \quad (7)$$

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

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

From (5) and (6) we get

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

From (8)

$$u = \frac{d(V_0 + V)}{d\text{pH}} = \ln 10 \cdot V_0 \cdot (C_0 + C) \cdot (C + \alpha)^{-2} \cdot ([\text{H}^+] + [\text{OH}^-])$$

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

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

$$\alpha(C + \alpha) - 2(\alpha^2 + 4K_w) = 0$$

$$\alpha^2 - C \cdot \alpha + 8K_w = 0 \quad (11)$$

$$z^2 - z + 8K_w/C^2 = 0$$

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

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

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

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

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

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

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]

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

expressing the relationship between surface tension σ and concentration $[\text{HL}]$ 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:

$$\begin{aligned} [\text{HL}] &= C \cdot \frac{[\text{H}^+]}{[\text{H}^+] + K_1} \\ 1 + b \cdot [\text{HL}] &= \frac{(1 + b \cdot C) \cdot [\text{H}^+] + K_1}{[\text{H}^+] + K_1} \\ \sigma &= \sigma_0 - a \cdot \ln\left(\frac{(1 + b \cdot C) \cdot [\text{H}^+] + K_1}{[\text{H}^+] + K_1}\right) + a \cdot \ln([\text{H}^+] + K_1) \frac{d\sigma}{d[\text{H}^+]} = -a \cdot \left(\frac{(1 + b \cdot C)}{(1 + b \cdot C) \cdot [\text{H}^+] + K_1} - \frac{1}{[\text{H}^+] + K_1} \right) \\ u &= \frac{d\sigma}{d\text{pH}} = \left(\frac{d\sigma}{d[\text{H}^+]} \right) \cdot \left(\frac{d[\text{H}^+]}{d\text{pH}} \right) = -\ln 10 \cdot [\text{H}^+] \cdot \frac{d\sigma}{d[\text{H}^+]} \\ &= -\ln 10 \cdot a \cdot \left(\frac{(1 + b \cdot C) \cdot [\text{H}^+]}{(1 + b \cdot C) \cdot [\text{H}^+] + K_1} - \frac{[\text{H}^+]}{[\text{H}^+] + K_1} \right) \\ \frac{d^2\sigma}{d\text{pH}^2} &= -\ln 10 \cdot [\text{H}^+] \cdot \frac{du}{d[\text{H}^+]} \\ &= (\ln 10)^2 \cdot a \cdot K_1 \cdot [\text{H}^+] \cdot \left(\frac{1 + b \cdot C}{((1 + b \cdot C) \cdot [\text{H}^+] + K_1)^2} - \frac{1}{([\text{H}^+] + K_1)^2} \right) \end{aligned} \quad (16)$$

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

$$\text{pH} = \text{pH}_{inf} = \text{p}K_1 + \frac{1}{2} \cdot \log(1 + b \cdot C) \quad (17)$$

From Equation (17) it results that the abscissa (pH_{inf}) corresponding to inflection point does not overlap with $\text{p}K_1$ value for HL.

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