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Formulation of the System of Isohydric Solutions

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ABSTRACT

The isohydricity (pH constancy) as the property referred to mixtures of acids or bases, is illustrated on a simple example of the solutions: HL (C_0, mol/L) and HL (C mol/L) mixed according to titrimetric mode (pH titration). A new derivation of the Michałowski formula $C_0 = C + C^2 \cdot 10^{pK_1}$ expressing this property is presented, and its applicability for determination of $pK_1 = -\log K_1$ value is indicated. The principle of the isohydric method of pK_1 determination is also outlined.

Keywords: Isohydric Solutions; pH Titration

1. Introduction

The term "isohydric" refers to solutions of the same hydrogen-ion concentration. According to Arrhenius' statement [1], expressed in more contemporary terms, "if two solutions of the same pH are mixed, pH of the mixture is unchanged, regardless the composition of the solutions". This statement is not valid, however, when referred on any pair of electrolytic systems.

To prove it, let us take, for example, the pair of solutions: $C_1 = 10^{-2.5} \approx 0.003$ mol/L HCN ($pK_1 = 9.2$) and $C_2 = 1$ mol/L AgNO$_3$ ($\log K_1^{OH} = 2.3$ for Ag$^+$ + OH$^-$ = AgOH) [2]. From the approximate formulae: $\left[H^+ \right] = \sqrt{C_1 \cdot K_1}$ and $\left[H^+ \right] = \sqrt{C_2 \cdot K_1^{OH} \cdot K_W}$ we get pH = 5.85, for both solutions. However, as were stated in [3], silver ions when added into HCN solution act as a strong acid, generating protons mainly in the complexation reaction Ag$^+$ + 2HCN = Ag$\left(CN\right)_2^-$ + 2H$^+$, and pH of the mixture drops abruptly. So, the isohydricity property is limited to the systems where only acid-base equilibria are involved. This property was formulated first by Michałowski [4] for different pairs of acid-base systems, then generalized on more complex mixtures of acid-base systems, and extended on mixtures containing basal salts and binary-solvent systems [5]. Moreover, the isohydricity concept was the basis for a very sensitive method of determination of dissociation constants values [4,5].

The present article intends to familiarize the readers with this interesting concept [6] that is in some relevance with buffering action [7,8] and pH-static titration [9,10] principles. Isohydricity concept is also referred to acid-base homeostasis in living organisms [11].

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2. Principle of Isohydricity

It is usually stated that an addition of a strong acid HB (C mol/L) into a weak acid HL (C_0 mol/L) decreases pH value of the resulting solution and, consequently, shifts (retracts) the HL dissociation, according to Le Chatelier's principle. As results from **Figure 1**, the decrease in pH value (dpH/dV < 0) and then retracting the dissociation of HL occurs at higher C values, whereas the dilution effect, expressed by dpH/dV > 0, predominates at lower C-values. The related effect depends, however, on the HL strength, expressed by its dissociation constant K_1 value.
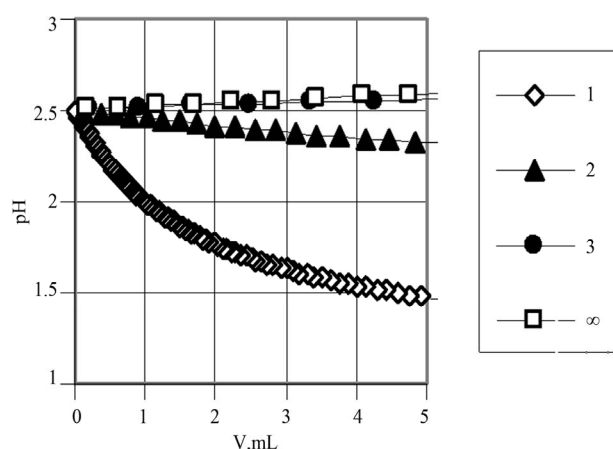

Figure 1. The effect of addition of V mL of $C = 10^{-pC}$ mol/L strong acid HB into $V_0 = 10$ mL of $C_0 = 0.1$ mol/L weak acid ($pK_1 = 4.0$). The titration curves $V = V_0 \cdot (\alpha - C_0/z)/(C - \alpha)$, where $\alpha = 10^{-pH} - 10^{pH-14}$, $z = 10^{pK_1 - pH} + 1$ are plotted for different $pC = -\log C$ values indicated at the corresponding curves; $pC = 1, 2, 3, \infty$.

$$K_1 = \frac{[H^+][L^-]}{[HL]} \qquad (1)$$

and on the relative concentrations (C_0, C) of both acids, *i.e.* HL and HB. Under special conditions, expressed by the set of (C_0, C, pK_1) values [4], pH = const (*i.e.*, dpH/dV = 0) when mixing the solutions in different proportions; it is just the subject of the present note.

3. Formulation of the Isohydricity Concept

The simplest system of isohydric solutions is composed of a strong monoprotic acid HB and a weak monoprotic acid HL, characterized by $pK_1 = -\log K_1$ value, where K_1 is expressed by Equation (1). In order to derive the relation for the isohydricity concept, let us consider the titration of V_0 mL of C_0 mol/L HL with V mL of C mol/L HB. From charge and concentration balances

$$[H^+] - [OH^-] = [B^-] + [L^-] \qquad (2)$$

$$[B^-] = \frac{CV}{V_0 + V} \qquad (3)$$

$$[HL] + [L^-] = \frac{C_0 V_0}{V_0 + V} \qquad (4)$$

we get

$$[H^+] - [OH^-] = \frac{CV}{V_0 + V} + (1 - \bar{n}) \cdot \frac{C_0 V_0}{V_0 + V} \qquad (5)$$

where

$$\bar{n} = \frac{[HL]}{[HL] + [L^-]} \qquad (6)$$

i.e.

$$1 - \bar{n} = \frac{[L^-]}{[HL] + [L^-]} = \frac{K_1}{[H^+] + K_1} \qquad (7)$$

Mixing the solutions can be made according to titrimetric mode, in *quasistatic* manner, under isothermal conditions; it enables some changes in equilibrium constants, affected by thermal effects, to be avoided. As will be seen later, the ionic strength (I) of the related mixture is also secured; it acts in favour of constancy of K_1 and ionic product of water, $K_W = [H^+][OH^-]$ during the titration in the system of isohydric solutions. This way, the terms: $[H^+] - [OH^-] = [H^+] - K_W/[H^+]$ and $1 - n$ (Equation (7)) in Equation (5) are constant at any stage of titration in the isohydric system. In particular, at the start for the titration, *i.e.* for $V = 0$, from (5) we have

$$[H^+] - [OH^-] = (1 - \bar{n}) \cdot C_0 \qquad (8)$$

Comparing the right sides of (5) and (8), we get, by turns:

$$\frac{CV}{V_0 + V} + (1 - \bar{n}) \cdot \frac{C_0 V_0}{V_0 + V} = (1 - \bar{n}) \cdot C_0 \qquad (9)$$

$$1 - \bar{n} = \frac{C}{C_0}$$

$$[H^+] - [OH^-] = C \qquad (10)$$

Then we get, by turns,

$$[H^+] = K_1 \cdot \left(\frac{C_0}{C} - 1 \right) \qquad (11)$$

$$[OH^-] = \frac{K_w}{K_1} \cdot \left(\frac{C_0}{C} - 1 \right)^{-1} \qquad (12)$$

$$K_1 \cdot \left(\frac{C_0}{C} - 1 \right) = \frac{C}{2} \cdot \left(1 + \left(1 + \frac{4K_w}{C^2} \right)^{1/2} \right) \qquad (13)$$

Assuming that $4K_w/C^2 \ll 1$, from (13) we get the formula [4]

$$C_0 = C + C^2 \cdot 10^{pK_1} \qquad (14)$$

Identical formula is obtained for reverse titration, where V_0 mL of C mol/L HB is titrated with V mL of C_0 mol/L HL. It means that the isohydricity condition is fulfilled for the set (C_0, C, pK_1) where the relationship (14) is valid, independently on the volume of titrant added. The related curves expressed by Equation (14) are plotted for different pK_1 in **Figure 2** within (pC, pC_0) coordinates. The curves appear nonlinearity for lower pK_1 values and are linear, with slope 2, for pK_1 greater than ca. 6. This regularity can be stated from the Equation (14) transformed by turns:

$$C_0 = C^2 \cdot 10^{pK_1} \cdot \left(1 + 10^{-pK_1}/C \right)$$
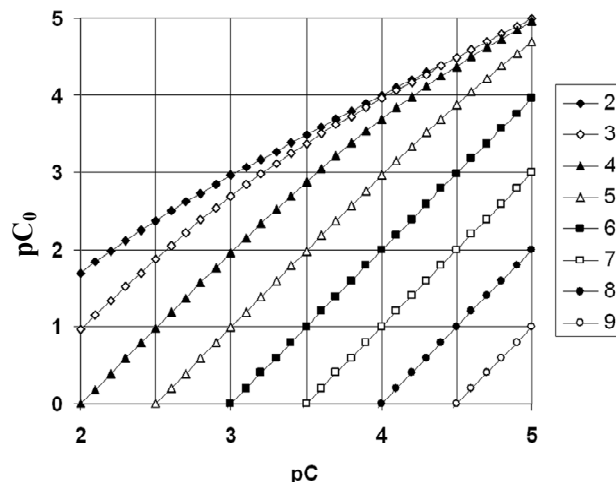$$pC_0 = 2 \cdot pC - pK_1 - \log\left(1 + 10^{pC - pK_1} \right) \qquad (15)$$

Figure 2. The plots of $pC_0 = -\log C_0$ vs. $pC = -\log C$ relationships obtained on the basis of Equation (14), for different pK_1 values indicated at the corresponding lines.

and valid for pC significantly smaller than pK_1.

It can also be noticed that ionic strength (I) of the solution remains constant during the titration, *i.e.* it is independent on the volume V of the titrant added. Namely, from (2), (10)-(12) we get

$$I = 0.5 \times \left(\left[H^+ \right] + \left[OH^- \right] + \left[B^- \right] + \left[L^- \right] \right)$$
$$= 0.5 \times \left(K_1 (C_0/C - 1) + (K_w/K_1)/(C_0/C - 1) + C \right) \quad (16)$$

It is the unique property in titrimetric analyses, exploited in the new method of pK_1 determination, suggested in [4,5]. In the light of the Debye-Hückel theory, the constancy in ionic strength (I) is, apart from constancy in temperature T and dielectric permeability ε, one of the properties securing constancy in K_1 and K_W values. Referring again to **Figure 1**, from Equation (14) we calculate

$$C = 0.5 \cdot 10^{-pK_1} \cdot \left(\sqrt{4 \cdot 10^{pK_1} \cdot C_0 + 1} - 1 \right).$$

For $C_0 = 0.1$, $pK_1 = 4.0$ we have $pC = 2.507$.

4. An Isohydric Method of Acidity Constant Determination

The isohydricity property can be perceived as a valuable tool applicable for determination [4,5] of acidity constant ($pK_1 = -\log K_1$) for a weak acid HL, see Equation 1. For this purpose, a series of pairs of solutions (HB (C), HL (C_{0i}^*)) is prepared, where C and C_{0i}^* are interrelated in the formula

$$C_{0i}^* = C + C^2 \cdot 10^{pK_{1i}^*} \quad (17)$$

where pK_{1i}^* ($i = 1, \cdots, n$) are the numbers chosen from the vicinity of the true pK_1 value for HL. Within each pair (HB (C), HL (C_{0i}^*)), the pH titrations HB (C, V) $\rightarrow$ HL (C_{0i}^*, V_0), are made (see **Figure 3**). In [4,5], at $V_0 = 3$ mL, $n = 5$ titrations were made up to $V = 4$ mL. The results of titrations are approximated by straight lines pH = $a_i + b_i \cdot V$ (see **Figure 4**), where b_i is the slope of the related line. The plots of the slopes vs. pK_{1i}^* values are usually arranged along the straight or hyperbolic line (**Figure 5**). The point of intersection with pK_1^* line, corresponding to the slope $b = 0$ (compare with **Figure 3**) provides an evaluation of the true pK_1 value, $pK_1^* = pK_1$. Additional, $n + 1$ th titration HB (C, V) $\rightarrow$ HL ($C_{0,n+1}^*$, V_0), made at $C_{0,n+1}^* = C + C^2 \cdot 10^{pK_1}$ provides a confirmation of this pK_1 value, if b_{n+1} value obtained in this titration is relatively small.

5. Final Comments

The new derivation of the formula (14) expressing the isohydricity condition for the simplest case of a mixture composed of strong monoprotic (HB, C mol/L) and weak monoprotic (HL, C_0 mol/L), when mixed according to titrimetric mode, is presented. The roles of titrand and
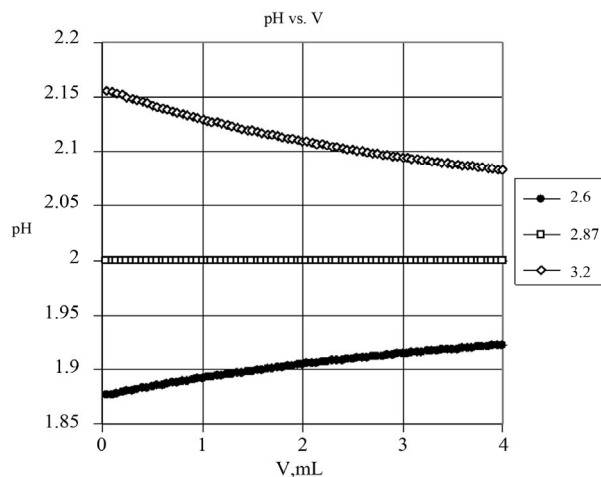

Figure 3. The simulated pH vs. V relationships plotted for the titration HB (C, V) $\rightarrow$ HL (C_{0i}^*, V_0), at $pK_1 = 2.87$, $V_0 = 3$, $C = 0.01$, and C_{0i}^* calculated from Equation (17), at different (indicated) pK_{1i}^* values.
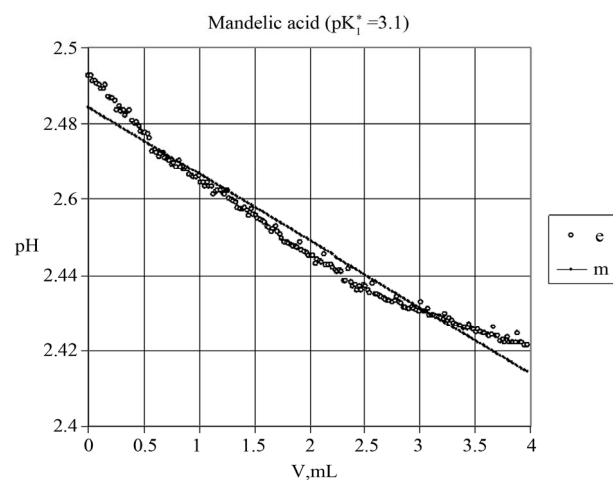

Figure 4. Exemplary approximation of experimental (e) points $\{(V_j, \text{pH}_j) \mid j = 1, \cdots, N\}$ by straight line (m) [4].
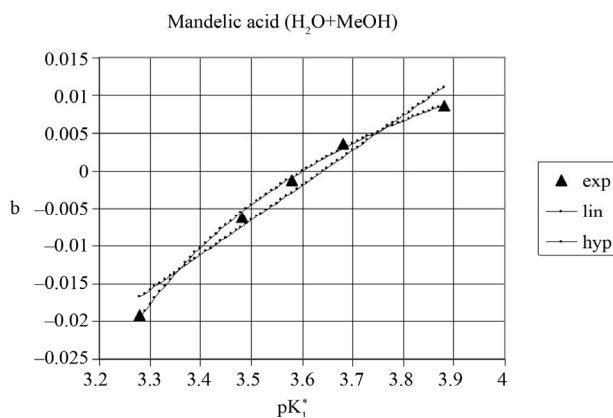

Figure 5. Linear (lin) and hyperbolic (hyp) approximation of experimental (exp, ▲) points in (pK_1^*, b) co-ordinates [4].

titrant in such systems can be reversed. The formulae for more complicated systems are given in [4]. The isohydricity property can be formulated for the systems where only acid-base equilibria occur Equation (14), relates analytical concentrations of strong acid HB and weak acid HL. Such an interesting property is not directly relevant to buffering action. Nevertheless, it is *on-line* with a general property desired from buffering systems.

The systems of isohydric solutions have a unique feature, not stated in other acid-base systems. It is the constancy of ionic strength (I), not caused by presence of a basal electrolyte. The conjunction of properties: pH = const, I = const, together with constancy of temperature (T = const) provided a useful tool for a sensitive method of determination of pK_1 values for weak acids, as indicated and applied in [4,5]. This method is illustrated with some examples taken from [4].

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