OPEN ACCESS
Freely Available Online

JOURNAL OF NEW DEVELOPMENTS IN CHEMISTRY
ISSN NO: 2377-2549

Review Article

DOI: 10.14302/issn.2377-2549.jndc-20-3219

Formulation of Isohydricity Conditions in Acid-Base systems - A Review

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Abstract

The isohydricity conditions are formulated for D+T systems composed of titrand D and titrant T, mixed according to titrimetric mode; only acid-base equilibria are involved there. The original method of dissociation constants determination, based on the isohydricity principle, is presented and confirmed experimentally. The pH titrations in the system of isohydric solutions are also put in context with conductometric titrations.

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Citation: Anna M. Michałowska-Kaczmarczyk, Tadeusz Michałowski (2020) Formulation of Isohydricity Conditions in Acid-Base systems - A Review. Journal of New Developments in Chemistry - 2(4):1-19. https://doi.org/10.14302/issn.2377-2549.jndc-20-3219

Keywords: Isohydricity; acids; bases; pH titration; conductometric titration.

Received: Feb 18, 2020 **Accepted:** Mar 16, 2020 **Published:** Mar 28, 2020

Editor: Zhe-Sheng Chenz, Professor, Department of Pharmaceutical Sciences, College of Pharmacy and Allied Health Professions, St. John's University, United States.

Introduction

Titrimetric methods of analysis are commonly involved with mixing the solutions of two substances endowed with opposite properties, e.g., acid with base (B ⇨ A), or *vice versa* (A ⇨ B) [1,2]. Mixing two different acids (A_1 ⇨ A_2) or two bases (B_1 ⇨ B_2) according to titrimetric mode is usually not practiced. However, the special, isohydricity property is attributed here to solutions of two different acids, A_1 and A_2, or two different bases, B_1 and B_2, having equal pH values, i.e., the term "isohydric" refers to solutions of the same hydrogen-ion concentration, $[H^{+1}]$. After Arrhenius, such a pair of solutions is termed as isohydric solutions [3,4].

However, the Arrhenius' statement [5], expressed in more contemporary terms, as "if two solutions of the same pH are mixed, pH of the mixture is unchanged, regardless the composition of the solutions" [6], is not true, when referred to any pair of electrolytic systems.

As an example [7], let us take the pair of solutions: $C_1 = 10^{-2.5} \approx 0.003$ mol/L HCN and $C_2 = 1$ mol/L $AgNO_3$. From the approximate formulae: $[H^{+1}] = (C_1 \cdot K_1)^{1/2}$ for HCN (C_1) and $[H^{+1}] = (C_1 \cdot K_1^{OH} \cdot K_W)^{1/2}$ for $AgNO_3$ (C_2) we get pH=5.85, for both solutions; $[AgOH] = K_1^{OH} [Ag^{+1}][OH^{-1}]$), $\log K_1^{OH} = 2.3$; $[H^{+1}][CN^{-1}] = K_1[HCN]$, $pK_1 = 9.2$; $K_W=[H^{+1}][OH^{-1}]$, $pK_W = 14$. However, as were stated in [8], Ag^{+1} ions when added into HCN solution act as a strong acid generating protons, mainly in the complexation reaction $Ag^{+1} + 2HCN = Ag(CN)_2^{-1} + 2H^{+1}$, and pH of the mixture drops abruptly. The degrees of dissociation of HCN is then changed, contrary to Arrhenius' statement [6]. So, the isohydricity property is limited to the systems where only acid-base equilibria are involved.

Despite some appearances arising from the wording, the isohydricity concept introduced by Arrhenius was not involved with hydrogen ions, but with conductivity, K [9]; it was the main area of his scientific activity that time. In [10] it were explicitly stated that "the term *isohydric* is applied to two solutions, the conductivities of which are not altered when they are mixed". Both statements/remarks were repeated and mixed in contemporary media, see e.g. [11]; we will refer to this matter too. The term pH was introduced by Sørensen later, in 1909 [12,13]. The preliminary assumptions in isohydrocity formulation made by Carpéni [14] and then modified by McBryde [15] are unacceptable. In turn, de Levie introduced for this purpose the so-named proton condition, but the results of his clumsy trials, presented in [16], can be passed over in silence.

Correct equations, expressing the isohydricity property, were formulated by Michałowski and presented, for different systems, in a series of papers [3,4,7,17]. This was the basis of precise determination of dissociation constant values in pH-metric titrations, made both in aqueous [3] and binary-solvent [4,18] media.

Preliminary Information

The pH change resulting from addition of a strong acid HB (C) into a weak acid HL (C_0), is characterized by equation for titration curve

$$V = V_0 \cdot (\alpha - \delta \cdot C_0)/(C - \alpha) \quad ....(1)$$

where:

$$\alpha = [H^{+1}] - [OH^{-1}] = [H^{+1}] - K_W/[H^{+1}] = 10^{-pH} - 10^{pH-14},\ \delta = [L^{-1}]/([HL] + [L^{-1}]) = K_1/(K_1 + [H^{+1}]),\ K_W = [H^{+1}][OH^{-1}],$$
$$\text{and } K_1 = [H^{+1}]\,[L^{-1}]/[HL] \quad .....(2)$$

As results from Fig. 1, the decrease of pH value (dpH/dV < 0) occurs at higher C values, whereas the dilution effect, expressed by dpH/dV > 0, predominates at low C-values. Generalizing, the related effect depends on the dissociation constant K_1 value and on the relative concentrations (C_0, C) of both acids: HL and HB. Under special conditions, expressed by the set of (C_0, C, pK_1) values [7], we have pH = const (i.e., dpH/dV = 0) when mixing the solutions in different proportions C_0/C; it is just the subject of the next section.

Generalizing, the D+T mixture may appear pH = const. during the titration T(V) ⇨ D(V_0) only at defined

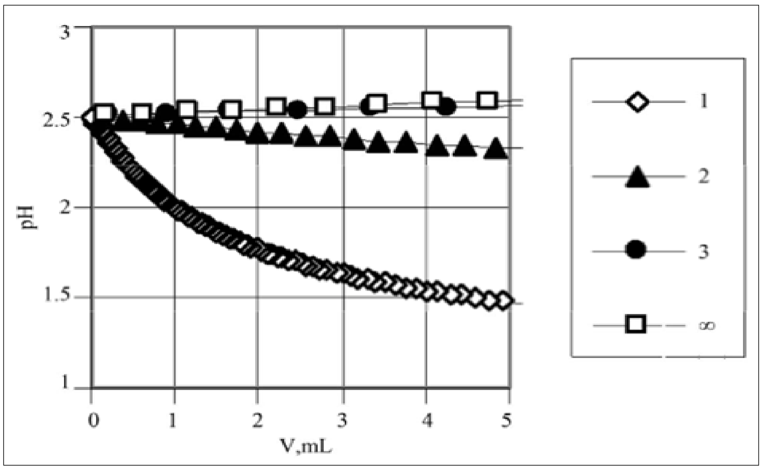

Figure 1. The pH-effect of addition of V mL of strong acid HB (C) into V_0 = 10 mL of C_0 = 0.1 mol/L HL (pK_1 = 4.0). The titration curves are plotted here for indicated pC = – logC values, pC = 1, 2, 3, ∞ [7].

relation between molar concentrations of components in D and T, as presented below.

Formulation of the Isohydricity Conditions – Examples

Example 1. HB (C) ⇨ HL (C_0) and HL (C_0) ⇨ HB (C)

The simplest isohydric system is composed of a strong monoprotic acid HB and a weak monoprotic acid HL with K_1 expressed by Eq. 2. We derive first the isohydricity relation for the titration HB (C,V) ⇨ HL (C_0,V_0), where V_0 of C_0 mol/L HL is titrated with V mL of C mol/L HB; V is the total volume of HB (C) added up to a defined point of the titration. From charge and concentration balances

$[H^{+1}] - [OH^{-1}] = [B^{-1}] + [L^{-1}]$ ....(3)

$[B^{-1}] = CV/(V_0+V)$ ....(4)

$[HL] + [L^{-1}] = C_0V_0/(V_0+V)$ ....(5)

we get

$$[H^{+1}] - [OH^{-1}] = \frac{CV}{V_0+V} + (1-\bar{n})\cdot\frac{C_0V_0}{V_0+V} \quad ....(6)$$

where

$$\bar{n} = \frac{[HL]}{[HL]+[L^{-1}]} \quad ....(7)$$

i.e.,

$$1-\bar{n} = \frac{[L^{-1}]}{[HL]+[L^{-1}]} = \frac{K_1}{[H^{+1}]+K_1} \quad ....(8)$$

(see Eq. 2).

Mixing the solutions according to titrimetric mode can be made 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 (Eq. 2) and $K_W = [H^{+1}][OH^{-1}]$ values. This way, the terms: $[H^{+1}] - [OH^{-1}] = [H^{+1}] - K_W/[H^{+1}]$ and $1-\bar{n}$ (Eq. 8) in Eq. 5 are constant at any V- value. In particular, at the start for the titration, V = 0, from Eq. 6 we have

$[H^{+1}] - [OH^{-1}] = (1-\bar{n})\cdot C_0$ ……(9)

Comparing the right sides of Equations 6 and 9, we get, by turns:

$$(1-\bar{n})\cdot C_0 = \frac{CV}{V_0+V} + (1-\bar{n})\cdot\frac{C_0V_0}{V_0+V} \Rightarrow$$
$$(1-\bar{n})\cdot C_0V_0 + (1-\bar{n})\cdot C_0V = CV + (1-\bar{n})\cdot C_0V_0 \Rightarrow$$
$$(1-\bar{n})\cdot C_0 = C \Rightarrow 1-\bar{n} = \frac{C}{C_0} \quad …….(10)$$

From Equations 9, 10

$[H^{+1}] - [OH^{-1}] = C$ ….(11)

From Equations 8, 10

$K_1/[H^{+1}] + K_1 = C/C_0 \Rightarrow [H^{+1}] = K_1\cdot(C_0/C-1)$ …..(12)

$[OH^{-1}] = K_W/K_1\cdot(C_0/C-1)^{-1}$ ….(13)

Assuming $[H^{+1}] >> [OH^{-1}]$ in Eq. 11, from $[H^{+1}] = C$, and Eq. 12 we get

$K_1\cdot(C_0/C-1) = C \Rightarrow C_0 = C+C^2/K_1 \Rightarrow C_0 = C+C^2\cdot 10^{pk_1}$ ……(14)

Alternately, after insertion of Equations 12 and 13 in Eq. 11 we have

$K_1\cdot(C_0/C-1) - K_W/K_1\cdot(C_0/C-1) = C$

Denoting $K_1\cdot(C_0/C-1) = y$, we have: $y - K_W/y - C = 0 \Rightarrow y^2 - C\cdot y - K_W = 0 \Rightarrow y = C/2\cdot(1+(1+4K_W/C^2)^{1/2})$ ...(15)

as the positive root. At $4K_W/C^2 << 1$, from Eq. 15 we get y = C, i.e.

$K_1\cdot(C_0/C-1) = C$ …..(16)

and then we obtain Eq. 14 again.

After mixing isohydric solutions of HL and HB at any proportion, the degree of HL dissociation (see Eq. 8)

$$\delta = 1-\bar{n} = \frac{[L^{-1}]}{[HL]+[L^{-1}]} = (10^{pK_1-pH}+1)^{-1}$$

(see Eq. 1) is not changed.

The property, expressed by Eq. 14, was formulated first by Michałowski for different pairs of acid-base systems [3,4], then generalized on more complex mixtures, and extended on mixtures containing basal salts and binary-solvent media [4,17]. Moreover, the isohydricity concept was the basis for a very sensitive method of determination of dissociation constants values [3,4].

Identical formula is obtained for reverse titration, HL (C_0,V) ⇨ HB (C,V_0), where V_0 of C mol/L HB is titrated with V mL of C_0 mol/L HL. From Eq, 2 and $[B^{-1}] = CV_0/(V_0+V)$, $[HL] + [L^{-1}] = C_0V/(V_0+V)$, we get, by turns,

$[H^{+1}] - [OH^{-1}] = \frac{CV_0}{V_0+V} + (1-\bar{n})\cdot\frac{C_0V}{V_0+V} \Rightarrow [H^{+1}] - [OH^{-1}] = C$ at V=0 $\Rightarrow \frac{CV_0}{V_0+V} + (1-\bar{n})\cdot\frac{C_0V}{V_0+V} = C$

at $[H^{+1}] >> [OH^{-1}]$. Then we have Eq. 10, and then Eq. 14. It means that the isohydricity condition is fulfilled for the set (C_0, C, pK_1), where Eq. 14 is valid, independently on the volume V of T added; it is identical for titrations: HB (C,V) ⇨ HL (C_0,V_0) and HL (C_0,V) ⇨ HB (C,V_0).

The related curves expressed by Eq. 14 are plotted in Fig. 2, for different pK_1 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 Eq. 14 transformed as follows:

$C_0 = C_2/K_1 \cdot (1+K_1/C)$ ⇨

$pC_0 = 2 \cdot pC - pK_1 - \log (1+10^{pC-pK_1})$ ....(17)

and valid for $K_1/C << 1$.

It can also be noticed that ionic strength (I) in the isohydric system (HB, HL) remains constant during the titration, i.e., it is independent on the volume V of the titrant T added. Namely, at $[H^{+1}] >> [OH^{-1}]$, from Equations 3, 11 we get [7]

$I = 0.5\times([H^{+1}] + [B^{-1}] + [L^{-1}]) = C$ .....(18)

It is the unique property in titrimetric analyses, exploited in the new method of pK_1 determination, suggested in [3,4]. According to Debye–Hückel theory, the constancy in ionic strength (I) is, apart from constancy in temperature T and dielectric permeability Ɛ, one of the properties securing constancy of K_1 and K_W values. The systems of isohydric solutions (HL, HB) have then 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 [19-24].

Other Pairs of Isohydric Solutions

The isohydricity concept can be extended on other T (V) ⇨ D (V_0) systems, exemplified below.

Example 2. H_2SO_4 (C) ⇨ HCl (C_0)

From the balances:

$\alpha - [HSO_4^{-1}] - 2[SO_4^{-2}] - [Cl^{-1}] = 0;$

$[HSO_4^{-1}] + [SO_4^{-2}] = cv/(V_0+V); [Cl^{-1}] = C_0V_0/(V_0+V)$

we get the relation

$$(2-\bar{n}) \cdot \frac{CV}{V_0+V} + \frac{C_0V_0}{V_0+V} = [H^{+1}] - [OH^{-1}] \quad ....(19)$$

where $\bar{n}$ is the mean number of protons H^{+1} attached to SO_4^{-2}

$$\bar{n} = \frac{[HSO_4^{-1}]}{[HSO_4^{-1}]+[SO_4^{-2}]} = \frac{[H^{+1}]}{[H^{+1}]+K_2} ;$$

$$K_2 = \frac{[H^{+1}][SO_4^{-2}]}{[HSO_4^{-1}]} \quad (pK_2 = 1.8) \quad ......(20)$$

At V = 0, from Eq. 19 we have $C_0 = [H^{+1}]$ at $H^{+1}] >> [OH^{-1}]$. Then we obtain, by turns,

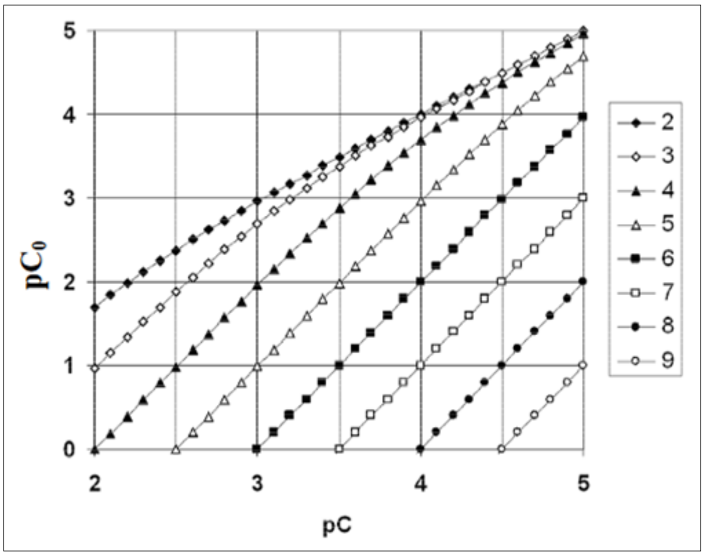

Figure 2. The plots of $pC_0 = -\log C_0$ vs. $pC = -\log C$ relationships obtained on the basis of Eq. 14, for different pK_1 values indicated at the corresponding lines [3].

$$(2-\bar{n})\cdot\frac{CV}{V_0+V}+\frac{C_0V_0}{V_0+V}=C_0 \Rightarrow (2-\bar{n})\cdot CV + C_0V_0 = C_0(V_0+V) \Rightarrow$$

$$\bar{n}=2-\frac{C_0}{C} \Rightarrow \frac{[H^{+1}]}{[H^{+1}]+K_2}=2-\frac{C_0}{C} \Rightarrow C_0=\frac{2C-C_0}{C_0-C}\cdot K_2 \Rightarrow$$

$$C=\frac{C_0(C_0+K_2)}{C_0+2K_2} \qquad ....(21)$$

Example 3. $NaHSO_4$ (C) ⇨ HCl (C_0)

From the balances:

$$[H^{+1}]-[OH^{-1}]+[Na^{+1}]-[HSO_4^{-1}]-2[SO_4^{-2}]-[Cl^{-1}]=0\ ;$$

$$[HSO_4^{-1}]+[SO_4^{-2}]=\frac{CV}{V_0+V}\ ;\quad [Na^{+1}]=\frac{CV}{V_0+V}\ ;\quad [B^{-1}]=\frac{C_0V_0}{V_0+V}$$

We get the relation

$$(1-\bar{n})\cdot\frac{CV}{V_0+V}+\frac{C_0V_0}{V_0+V}=[H^{+1}]-[OH^{-1}] \qquad ......(22)$$

At V = 0, from Eq. 22 we have $C_0 = [H^{+1}]$ at $[H^{+1}] >> [OH^{-1}]$. Then we obtain, by turns,

$$(1-\bar{n})\cdot\frac{CV}{V_0+V}+\frac{C_0V_0}{V_0+V}=C_0 \Rightarrow (1-\bar{n})\cdot CV + C_0V_0 = C_0(V_0+V) \Rightarrow$$

$$\bar{n}=1-\frac{C_0}{C} \Rightarrow C_0=\frac{C-C_0}{C_0}\cdot K_2 \Rightarrow$$

$$C=C_0+\frac{C_0^{\,2}}{K_2} \qquad ......(23)$$

Example 4. $Ba(OH)_2$ (C) ⇨ NaOH (C_0)

From the balances:

$$[H^{+1}] - [OH^{-1}] + 2[Ba^{+2}] + [BaOH^{+1}] + [Na^{+1}] = 0 \ ;$$

$$[Ba^{+2}] + [BaOH^{+1}] = \frac{CV}{V_0+V} \ ; \quad [Na^{+1}] = \frac{C_0V_0}{V_0+V}$$

We get the relation

$$(2 - \bar{n}) \cdot \frac{CV}{V_0+V} + \frac{C_0V_0}{V_0+V} = [OH^{-1}] - [H^{+1}] \qquad .....(24)$$

where

$$\bar{n} = \frac{[BaOH^{+1}]}{[Ba^{+2}]+[BaOH^{+1}]} = \frac{K_1{}^{OH}[OH^{-1}]}{1+K_1{}^{OH}[OH^{-1}]} \ ; \ K_1{}^{OH} = \frac{[BaOH^{+1}]}{[Ba^{+2}][OH^{-1}]} \ (\log K_1{}^{OH} = 0.85);$$

At V = 0, from Eq. 24 we have $C_0 = [OH^{-1}]$ at $[H^{+1}] << [OH^{-1}]$. Then we obtain, by turns,

$$(2 - \bar{n}) \cdot CV + C_0V_0 = C_0(V_0 + V) ⇨ (2 - \bar{n}) \cdot C = C_0 ⇨ \bar{n} = 2 - \frac{C_0}{C} ⇨$$

$$\frac{K_1{}^{OH}[OH^{-1}]}{1+K_1{}^{OH}[OH^{-1}]} = 2 - \frac{C_0}{C} ⇨ \frac{K_1{}^{OH}C_0}{1+K_1{}^{OH}C_0} = 2 - \frac{C_0}{C} ⇨ \frac{C_0}{C} = 2 - \frac{K_1{}^{OH}C_0}{1+K_1{}^{OH}C_0} ⇨$$

$$\frac{C_0}{C} = \frac{2+K_1{}^{OH}C_0}{1+K_1{}^{OH}C_0} ⇨ C = C_0 \cdot \frac{C_0+2/K_1{}^{OH}}{C_0+1/K_1{}^{OH}} \qquad ......(25)$$

Example 5. Na_2CO_3 (C) ⇨ NaOH (C_0)

From the balances:

$$\alpha + [Na^{+1}] = [HCO_3{}^{-1}] + 2[CO_3{}^{-2}]$$

$$[Na^{+1}] = \frac{C_0V_0+2CV}{V_0+V} \ ; \quad [H_2CO_3] + [HCO_3{}^{-1}] + [CO_3{}^{-2}] = \frac{CV}{V_0+V}$$

we get the relation

$$[H^{+1}] - [OH^{-1}] + \frac{C_0V_0+2CV}{V_0+V} = (2 - \bar{n}) \cdot \frac{CV}{V_0+V} \qquad .....(26)$$

where :

$$\bar{n} = \frac{2[H_2CO_3]+[HCO_3^{-1}]}{[H_2CO_3]+[HCO_3^{-1}]+[CO_3^{-2}]} = \frac{2[H^{+1}]^2+K_1[H^{+1}]}{[H^{+1}]^2+K_1[H^{+1}]+K_1K_2}$$

$K_1 = [H^{+1}][HCO_3{}^{-1}]/[H_2CO_3]$, $K_2 = [H^{+1}][CO_3{}^{-2}]/[HCO_3{}^{-1}]$

At V = 0, from Eq. 26 we have $C_0 = -\alpha = [OH^{-1}]$ at $[H^{+1}] << [OH^{-1}]$. Then we get, by turns,

$$\frac{C_0V_0+2CV}{V_0+V} = (2-\bar{n})\cdot\frac{CV}{V_0+V} + C_0 \Rightarrow C_0V_0 + 2CV = (2-\bar{n})\cdot CV + C_0(V_0+V) \Rightarrow$$

$$\bar{n}\cdot C = C_0 \Rightarrow C = \frac{C_0}{K_W}\cdot\frac{{K_W}^2+K_1K_WC_0+K_1K_2C_0^2}{2K_W+K_1C_0} \qquad ......(27)$$

Example 6. $CClH_2COOH$ (C_1) + $CClH_2COONa$ (C_2) ⇨ HCl (C_0)

From the relations:

$$\alpha + [Na^{+1}] = [Cl^{-1}] + [CClH_2COO^{-1}]$$

$$[Na^{+1}] = \frac{C_2V}{V_0+V}\ ;\ [Cl^{-1}] = \frac{C_0V_0}{V_0+V}\ ;\ [CClH_2COOH] + [CClH_2COO^{-1}] = \frac{(C_1+C_2)V}{V_0+V};$$

$$K_1 = \frac{[H^{+1}][CClH_2COO^{-1}]}{[CClH_2COOH]}\ (pK_1 = 2.68);\ 1-\bar{n} = \frac{K_1}{[H^{+1}]+K_1}$$

we have, by turns:

$$\alpha + \frac{C_2V}{V_0+V} = \frac{C_0V_0}{V_0+V} + \frac{K_1}{[H^{+1}]+K_1}\cdot\frac{(C_1+C_2)V}{V_0+V} \qquad \Rightarrow \qquad ....(28)$$

At V = 0, from Eq. 28 we have $C_0 = \alpha = [H^{+1}]$ at $[H^{+1}] >> [OH^{-1}]$. Then we get, by turns,

$$C_0 + \frac{C_2V}{V_0+V} - \frac{C_0V_0}{V_0+V} = \frac{K_1}{C_0+K_1}\cdot\frac{(C_1+C_2)V}{V_0+V} \qquad \Rightarrow$$
$$C_0 + C_2 = \frac{K_1}{C_0+K_1}(C_1+C_2) \qquad \Rightarrow$$
$$C_1 = C_0 + C_0(C_0+C_2)/K_1 \qquad \Rightarrow \qquad ....(29)$$

$$C_0 = \frac{1}{2}\cdot\left(((C_2+K_1)^2 + 4\,C_1K_1)^{\frac{1}{2}} - (C_2+K_1)\right) \qquad ......(30)$$

For example, at $pK_1 = 2.87$, $C_1 = 0.1$, $C_2 = 0.05$, from Eq. 30 we get $C_0 = 0.002505$. For $pK_1 = 2.87$, $C_0 = 0.025$, $C_2 = 0.05$, from Eq. 29 we get $C_1 = 0.0998$.

In further examples: 7 – 10 we apply the notation

$$\bar{n}_i = \frac{[HL_{(i)}]}{[HL_{(i)}]+[L_{(i)}{}^{-1}]} = \frac{[H^{+1}]}{[H^{+1}]+K_{1i}} \quad (i=1,2)\ ;\quad \bar{n}_3 = \frac{[L_{(3)}H^{+1}]}{[L_{(3)}H^{+1}]+[L_{(3)}]} = \frac{[H^{+1}]}{[H^{+1}]+K_{13}}$$

where

$[H^{+1}][L_{(i)}{}^{-1}] = K_{1i}[HL_{(i)}]$ (i=1,2) ; $[H^{+1}][L_{(3)}] = K_{13}[L_{(3)}H^{+1}]$

Example 7: $HL_{(2)}$ (C) ⇨ $HL_{(1)}$ (C_0)

From the balances:

$$[H^{+1}] - [OH^{-1}] = [L_{(1)}{}^{-1}] + [L_{(2)}{}^{-1}]$$
$$[HL_{(1)}] + [L_{(1)}{}^{-1}] = \frac{C_0V_0}{V_0+V}\ ;\quad [HL_{(2)}] + [L_{(2)}{}^{-1}] = \frac{CV}{V_0+V}$$

we get

$$[H^{+1}] - [OH^{-1}] = (1-\bar{n}_1)\,\frac{C_0V_0}{V_0+V} + (1-\bar{n}_2)\,\frac{CV}{V_0+V} \qquad ......(31)$$

For V = 0, at $[H^{+1}] >> [OH^{-1}]$, from Eq. 31 we have $[H^{+1}] = (1-\bar{n}_1)\cdot C_0$ and then, by turns,

$$(1-\bar{n}_1)\cdot C_0 = (1-\bar{n}_1)\cdot\frac{C_0V_0}{V_0+V} + (1-\bar{n}_2)\cdot\frac{CV}{V_0+V} \quad \Rightarrow$$

$$(1-\bar{n}_1)\cdot C_0 = (1-\bar{n}_2)\cdot C \quad \Rightarrow \quad \frac{K_{11}}{[H^{+1}]+K_{11}}\cdot C_0 = \frac{K_{12}}{[H^{+1}]+K_{12}}\cdot C \quad \Rightarrow$$

$$[H^{+1}] = \frac{K_{11}K_{12}(C-C_0)}{K_{11}C_0-K_{12}C}$$

$$\frac{K_{11}K_{12}(C-C_0)}{K_{11}C_0-K_{12}C} = \frac{K_{11}C_0}{[H^{+1}]+K_{11}}$$

$$\frac{K_{11}K_{12}(C-C_0)}{K_{11}C_0-K_{12}C} = \frac{K_{11}C_0-K_{12}C}{K_{11}-K_{12}}$$

$$(K_{11}C_0 - K_{12}C)^2 = K_{11}K_{12}(K_{11}-K_{12})(C-C_0) \qquad ......(32)$$

Example 8: $L_{(3)}HB$ (C) ⇨ $HL_{(1)}$ (C_0)

From the balances:

$$[H^{+1}] - [OH^{-1}] - [B^{-1}] - [L_{(1)}^{-1}] + [L_{(3)}H^{+1}] = 0$$

$$[HL_{(1)}] + [L_{(1)}^{-1}] = \frac{C_0V_0}{V_0+V} \quad ; \quad [L_{(3)}H^{+1}] + [L_{(3)}] = \frac{CV}{V_0+V} = [B^{-1}]$$

we get

$$[H^{+1}] - [OH^{-1}] - \frac{CV}{V_0+V} - (1-\bar{n}_1)\,\frac{C_0V_0}{V_0+V} + \bar{n}_3\,\frac{CV}{V_0+V} = 0$$

$$[H^{+1}] - [OH^{-1}] = (1-\bar{n}_1)\,\frac{C_0V_0}{V_0+V}\,(1-\bar{n}_3)\,\frac{CV}{V_0+V} \qquad .....(33)$$

For V = 0, at $[H^{+1}] >> [OH^{-1}]$, from Eq. 33 we have $[H^{+1}] = (1-\bar{n}_1)\cdot C_0$ and then, by turns,

$$(1-\bar{n}_1)\cdot C_0 = (1-\bar{n}_1)\,\frac{C_0V_0}{V_0+V} + (1-\bar{n}_3)\,\frac{CV}{V_0+V}$$

$$(1-\bar{n}_1)\cdot C_0 = (1-\bar{n}_3)\cdot C$$

$$\frac{K_{11}}{[H^{+1}]+K_{11}}\cdot C_0 = \frac{K_{13}}{[H^{+1}]+K_{13}}\cdot C$$

$$(K_{11}C_0 - K_{13}C)^2 = K_{11}K_{13}(K_{11}-K_{13})(C-C_0) \qquad .....(34)$$

Example 9: $ML_{(2)}$ (C) ⇨ $ML_{(1)}$ (C_0)

From the balances:

$$[H^{+1}] - [OH^{-1}] + [M^{+1}] = [L_{(1)}^{-1}] + [L_{(2)}^{-1}]\ ;[HL_{(1)}] + [L_{(1)}^{-1}] = \frac{C_0V_0}{V_0+V}\ ;$$

$$[HL_{(2)}] + [L_{(2)}^{-1}] = \frac{CV}{V_0+V}\ ;\ \ [M^{+1}] = \frac{C_0V_0+CV}{V_0+V}$$

we get

$$[H^{+1}] - [OH^{-1}] + \frac{C_0V_0+CV}{V_0+V} = (1-\bar{n}_1)\frac{C_0V_0}{V_0+V} + (1-\bar{n}_2)\frac{CV}{V_0+V}$$

$$\bar{n}_1 \cdot \frac{C_0V_0}{V_0+V} + \bar{n}_2 \cdot \frac{CV}{V_0+V} = [OH^{-1}] - [H^{+1}] \qquad \text{........(35)}$$

For V = 0, at $[OH^{-1}] >> [H^{+1}]$, from Eq. 35 we have $[OH^{-1}] = \bar{n}_1 \cdot C_0$ and then, by turns,

$$\bar{n}_1 \cdot \frac{C_0V_0}{V_0+V} + \bar{n}_2 \cdot \frac{CV}{V_0+V} = \bar{n}_1 \cdot C_0 \Rightarrow \bar{n}_1 \cdot C_0 = \bar{n}_2 \cdot C \ \Rightarrow$$

$$\frac{C_0}{[H^{+1}]+K_{11}} = \frac{C}{[H^{+1}]+K_{12}} \Rightarrow [H^{+1}] = \frac{K_{11}C-K_{12}C_0}{C_0-C} \ \Rightarrow$$

$$\frac{K_W}{[OH^{-1}]} = \frac{K_{11}C-K_{12}C_0}{C_0-C} \Rightarrow [OH^{-1}] = K_W \cdot \frac{C_0-C}{K_{11}C-K_{12}C_0} \ \Rightarrow$$

$$\frac{1}{1+\frac{K_{11}}{[H^{+1}]}} \cdot C_0 = K_W \cdot \frac{C_0-C}{K_{11}C-K_{12}C_0} \Rightarrow \frac{K_{11}C-K_{12}C_0}{K_{11}-K_{12}} = K_W \cdot \frac{C_0-C}{K_{11}C-K_{12}C_0} \ \Rightarrow$$

$$(K_{11}C - K_{12}C_0)^2 = K_W(K_{11} - K_{12})(C_0 - C) \qquad \text{......(36)}$$

Example 10: $L_{(3)}$ (C) ⇨ $ML_{(1)}$ (C_0)

From the balances:

$$[H^{+1}] - [OH^{-1}] + [M^{+1}] - [X_{(1)}^{-1}] + [X_{(3)}H^{+1}] = 0$$

$$[HL_{(1)}] + [L_{(1)}^{-1}] = \frac{C_0V_0}{V_0+V} = [M^{+1}]\ ; \qquad [L_{(3)}H^{+1}] + [L_{(3)}] = \frac{CV}{V_0+V}$$

we get

$$[H^{+1}] - [OH^{-1}] + \frac{C_0V_0}{V_0+V} - (1-\bar{n}_1) \cdot \frac{C_0V_0}{V_0+V} + \bar{n}_3 \cdot \frac{CV}{V_0+V} = 0 \qquad \text{......(37)}$$

$$\bar{n}_1 \frac{C_0V_0}{V_0+V} + \bar{n}_3 \frac{CV}{V_0+V} = [OH^{-1}] - [H^{+1}]$$

For V = 0, at $[OH^{-1}] >> [H^{+1}]$, from Eq. 37 we have $[OH^{-1}] = \bar{n}_1 \cdot C_0$ and then, by turns:

$$\bar{n}_1 \cdot \frac{C_0V_0}{V_0+V} + \bar{n}_3 \cdot \frac{CV}{V_0+V} = \bar{n}_1 \cdot C_0 \qquad \Rightarrow$$

$$\bar{n}_1 \cdot C_0 = \bar{n}_3 \cdot C \quad \Rightarrow \quad \frac{C_0}{K_{11}+[H^{+1}]} = \frac{C}{K_{13}+[H^{+1}]} \qquad \Rightarrow$$

$$[H^{+1}] = \frac{K_{11}\cdot C - K_{13}\cdot C_0}{C_0 - C} \qquad \Rightarrow$$

$$[OH^{-1}] = \frac{[H^{+1}]}{[H^{+1}]+K_{11}} \cdot C_0 = K_W \cdot \frac{C_0 - C}{K_{11}\cdot C - K_{13}\cdot C_0} \qquad \Rightarrow$$

$$\frac{1}{1+\frac{K_{11}}{[H^{+1}]}} \cdot C_0 = K_W \cdot \frac{C_0 - C}{K_{11}\cdot C - K_{13}\cdot C_0} \qquad \Rightarrow$$

$$\frac{K_{11}\cdot C - K_{13}\cdot C_0}{K_{11} - K_{13}} = K_W \cdot \frac{C_0 - C}{K_{11}\cdot C - K_{13}\cdot C_0} \qquad \Rightarrow$$

$$(K_{11} \cdot C - K_{13} \cdot C_0)^2 = K_W \cdot (K_{11} - K_{13}) \cdot (C_0 - C) \qquad \text{......(38)}$$

Example 11: (a) HB (C) ⇨ H_nL (C_0) and (b) H_nL (C_0) ⇨ HB (C)

Assuming that the acid H_nL forms the species H_iL^{+i-n} (i = 0, 1, … , q), we get the charge and concentration balances:

$$[H^{+1}] - [OH^{-1}] = [B^{-1}] + \sum_{i=0}^{q}(n-i)[H_iX^{+i-n}] \qquad \text{....(39)}$$

$$\sum_{i=0}^{q}[H_iL^{+i-n}] = \frac{C_0V_0}{V_0+V}\ ; \quad [B^{-1}] = \frac{CV}{V_0+V}$$

Applying the function

$$\bar{n} = \frac{\sum_{i=1}^{q} i\cdot[H_iX^{+i-n}]}{\sum_{j=0}^{q}[H_jX^{+j-n}]} = \frac{\sum_{i=1}^{q} i\cdot K_i^H[H^{+1}]^i}{\sum_{j=0}^{q} K_j^H[H^{+1}]^j} \qquad \text{.....(40)}$$

expressing the mean number of protons attached to the basic form L^{-n}, where

$$[H_jL^{+j-n}] = K_j^H \cdot [H^{+1}]^j[L^{-n}]$$

from Eq. 39 we get , by turns :

$$[H^{+1}] - [OH^{-1}] = \frac{CV}{V_0+V} + (n - \bar{n}) \cdot \frac{C_0V_0}{V_0+V}$$

$$[H^{+1}] - [OH^{-1}] = (n - \bar{n}) \cdot C_0 \quad \text{(for V = 0)}$$

$$n - \bar{n} = \frac{C}{C_0} \qquad \text{.......(41)}$$

Eq. 41 is also obtained for the reverse titration (b), where we get, by turns:

$$[H^{+1}]-[OH^{-1}]=\frac{CV_0}{V_0+V}+(n-\bar{n})\cdot\frac{C_0V}{V_0+V}$$

$$[H^{+1}]-[OH^{-1}]=C \quad (\text{for } V=0) \Rightarrow [H^{+1}]=C \text{ at } [H^{+1}]\gg[OH^{-1}] \Rightarrow \quad .....(42)$$

$$\frac{CV_0}{V_0+V}+(n-\bar{n})\cdot\frac{C_0V}{V_0+V}=C$$

Assuming $[H^{+1}] >> [OH^{-1}]$, from Eq. 42 we get $[H^{+1}] = C$. Putting it into (3), from (7) we get

$$\frac{\sum_{i=1}^{q} i\cdot K_i^H\cdot C^i}{\sum_{j=0}^{q} K_j^H\cdot C^j}=n-\frac{C}{C_0} \quad .....(43)$$

In particular, for $q = n = 1$, $K_1 = 1/K_1^H$, from Eq. 43 we get the relation

$$\frac{K_1^H\cdot C}{1+K_1^H\cdot C}=1-\frac{C}{C_0} \quad \Rightarrow \frac{C}{K_1+C}=1-\frac{C}{C_0}$$

transformed into Eq. 14.

Isohydricity in Terms of Conductometric and pH Titrations

The diversity in meaning the isohydricity term, referred to pH and conductivities, made an inevitable inconsistency/controversy, indicated above. Conductivity $\kappa = 1/\rho$ (ρ – resistivity) of a solution is a sum of terms involved with all cationic and anionic species contributing the current passing through the solution [25]

$$\kappa = F\cdot\sum_i |z_i|\cdot u_i\cdot[X_i^{z_i}] \quad ......(44)$$

where z_i – charge (in elementary charge units), and u_i – ionic mobility for i-th ionic species, X_j^{zi}, F – Faraday constant; each ion contributes a term proportional to its concentration $[X_j^{zi}]$. The property (44) is valid at low concentrations, where interactions between ions can be neglected. Ionic interactions in more concentrated solutions can alter the linear relationship between conductivity and concentrations. Denoting $|z_i|\cdot u_i\cdot F = a_i$, for ionic species composing the HB + HL mixture considered in Example 1, we have the formula [4]

$$k = a_1\cdot[H^{+1}] + a_2\cdot[B^{-1}] + a_3\cdot[L^{-1}] \quad .....(45)$$

From the simplified charge balance $[H^{+1}] = [L^{-1}] + [B^{-1}]$, valid at $[H^{+1}] >> [OH^{-1}]$, from Eq. 45 it results that

$$k = (a_1+a_2)\cdot[B^{-1}] + (a_1+a_3)\cdot[L^{-1}] \quad .....(46)$$

Assuming, for a moment, that $a_2 = a_3$, from Eq. 46 we have

$$K = (a_1+a_3)\cdot[B^{-1}] + [L^{-1}]) = (a_1+a_3)\cdot[H^{+1}] = (a_1+a_3)\cdot 10^{-pH} = const \quad .....(47)$$

at pH = const. At constant ionic strength I (this property is immanent in such isohydric system, see Eq. 18), a_1 and a_3 are not changed during the titration/mixing. However, the assumption $a_2 = a_3$ is not valid, in general [4].

In experimental part of the paper, the results from pH titrations (in aqueous and mixed-solvent media) will be compared with results from conductometric titrations.

The Isohydric Method of Acidity Constant Determination

The conjunction of properties: pH = const, I = const, together with constancy of temperature (T = const), as stated above, provided a useful tool for a sensitive method of determination of pK_1 values for weak acids HL, as indicated and applied in [3,4]. This method is illustrated with some examples taken from [4].

The isohydricity property can be perceived as a valuable tool applicable for determination/validation [3,4] of pK_1 for a weak acid HL. For this purpose, a series of pairs of solutions {HB (C), HL (C_{0i}^*)} (i=1,…,n) is prepared, where C and C_{0i}^* are interrelated in the formula

$C_{0i}^* = C + C^2 \cdot 10^{pK_{1i}^*}$ .....(48)

where pk_{1i}^* (i = 1,…, n) are the numbers chosen from the vicinity of the true (expected, correct) pK_1 value for HL (compare with Eq. 14). From Equations 14 and 48 we have the relation

$C_{0i}^* = C_0 + (C_0 - C) \cdot (10^{\Delta pK_{1i}} - 1)$ ....(49)

The principle of the method is illustrated in Fig. 3, where simulated titration curves pH = pH(V) are obtained for titrations HB (C) ⇨ HL (C_{0i}^*) related to different C_{0i}^* values at constant C value. As we see, a misfit $DpK_i = pK_{1i}^* - pK_1$ between real (pK_1) and pre-assumed (pK_{1i}^*) values for acidity constant causes a non-parallel, to V-axis, course of the related curve pH = pH(V); the curve/line is parallel to the V-axis only for $pK_1^* = pK_1$, at $C_0^* = C_0 = C + C^2 \cdot 10^{pk}{}_1$.

Experimental Data

pH-Metric Titrations

The validity of some models presented above were verified and confirmed by results of pH-metric and conductometric titrations T (V) ⇨ D (V_0), presented in [4]. In the present article, we refer to the results of titrations of (1) chloroacetic acid (HL = $CH_2ClCOOH$) and (2) mandelic acid (HL = $C_6H_5CH(OH)COOH$) solutions as titrands with HB = HCl (C) as the titrant. All technical details of these titrations are specified therein [4]. The pH titrations considered here are as follows.

(1) pH titration HCl (C) ⇨ $CH_2ClCOOH$ (C_{0i}^*)

(2) pH titration HCl (C) ⇨ $C_6H_5CH(OH)COOH$ (C_{0i}^*)

The C and C_{0i}^* (i=1,…,5) values are collected in Tables 1 and 2. For example, at C = 0,00965 and pK_{11}^* = 2,65, we have C_{01}^* = 0,051246; at C = 0.00472, pK_{11}^* = 3.10 we get C_{01}^* = 0.032767. The C_{0i}^* values were calculated from Eq. 48 for pK_1^* values taken from the vicinity of the related pK_1 value known from the literature data.

The pH titrations HB (C) ⇨ HL (C_{0i}^*) were made at V_0 = 3 mL of D and T added up to V = 4 mL. The exact pK_1^o value was searched here according to interpolation procedure. The results of titrations (Figures 4a, 4b) are approximated by straight lines pH = a + b·V (see Figures 5a, 5b), where $b=b_i$ is the slope of the related line (i=1, …,5). The coefficients a and b are calculated according to least squares method from the formulae:

$$a = \frac{\Sigma V_j^2 \cdot \Sigma pH_j - \Sigma V_j \cdot \Sigma V_j pH_j}{N \cdot \Sigma V_j^2 - (\Sigma V_j)^2}$$ ……(50)

$$b = \frac{N \cdot \Sigma V_j \cdot pH_j - \Sigma V_j \cdot \Sigma pH_j}{N \cdot \Sigma V_j^2 - (\Sigma V_j)^2}$$ …….(51)

where

$\Sigma = \sum_{j=1}^N$

For example, linear approximation of the curve in Fig. 4b obtained at pK_{11}^* = 3.10 (see Table 2) gives the line pH = 2.48438 – 0.01766·V, The value s = 0.0036 obtained for this approximation from the formula

$s=(s^2)^{1/2}$,where $s^2 = (N-2)^{-1} \cdot \sum_{j=1}^N (pH_j - pH(V_j))^2$

(where N=200 – number of experimental points (V_j, pH_j)) from the V-interval < 0, 4 > is comparable with precision of pH-measurements. Note that the curve at pK_{11}^* = 3.10 (Fig. 4b) has relatively great curvature.

The slopes b, obtained from the series of n = 5 titrations were applied for evaluation of the true $pK_1 = pK_1^o$ value. Assuming the linear relation between b = b_i and $pK_1^* = pK_{1i}^*$, we apply the regression equation

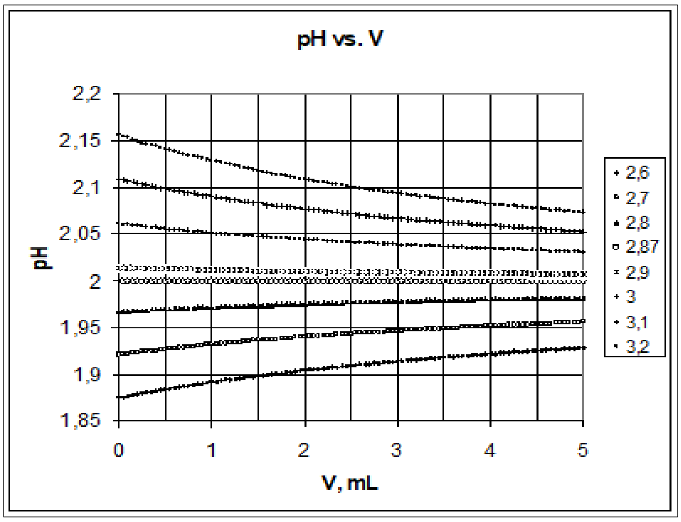

Figure 3. The pH vs. V relationships plotted for the titration HB (C) ⇨ HL (C_{0i}^*) at pK_1 = 2.87 for HL; V_0 = 3, C = 0.01, C_{0i}^* calculated from Eq. 48 at indicated pK_{1i}^* values.

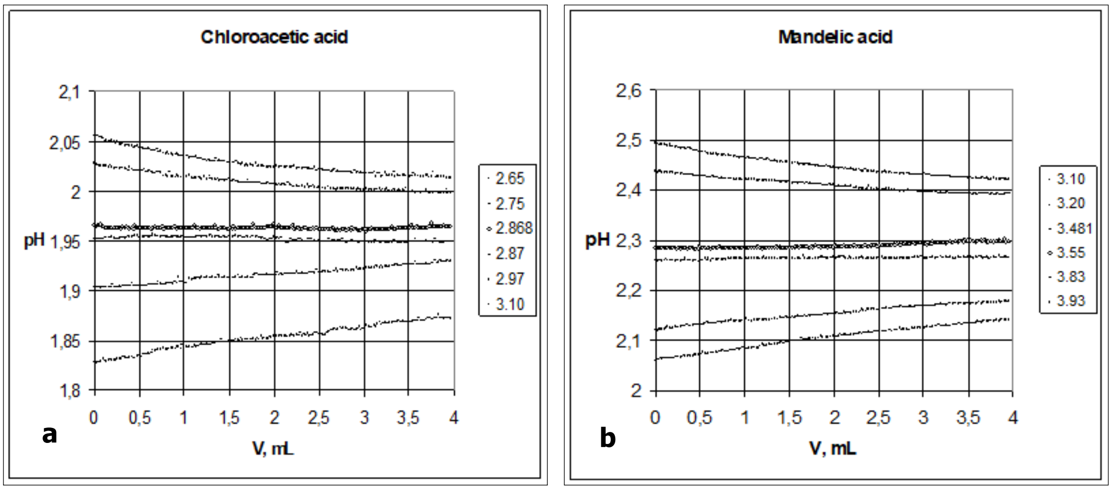

Figure 4. The pH vs. V relationships for (5a) HL = chloroacetic acid and (5b) HL = mandelic acid, plotted for indicated pK_1^* = pK_{1i}^* (i = 1,...,6) values. For further details see Tables 1 and 2 [4].

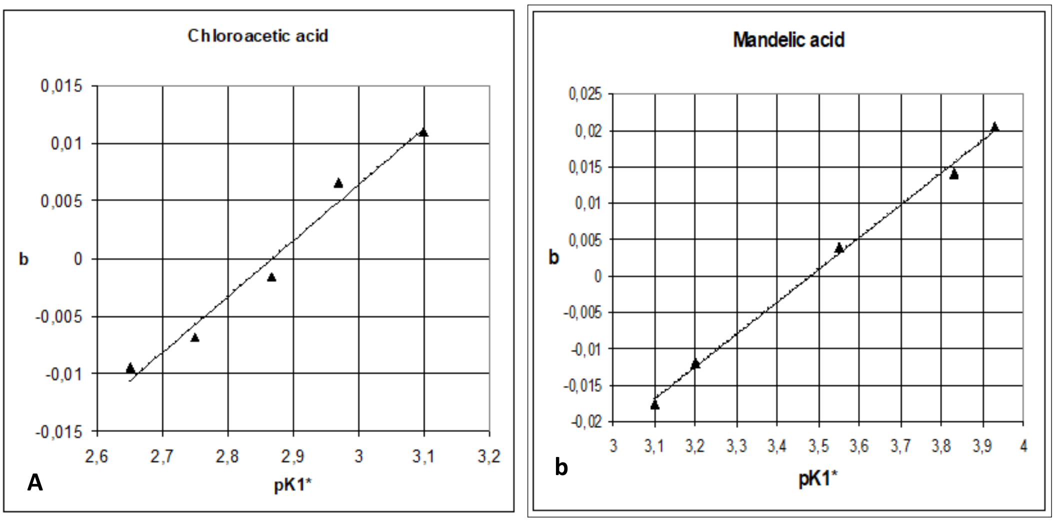

Figure 5. The b vs. pK_1^* relationships (Eq. 52) found for (5a) chloroacetic and (5b) mandelic acids, see Tables 1, 2.

Table 1. The data related to pH-titrations with chloroacetic acid (C_{0i}^*) in D.

HL = chloroacetic acid				
pK_{1i}^*	C	C_{0i}^*	a	b
2,65	0.00965	0.05125	2.04646	-0.00942
2,75	0.00965	0.06202	2.02252	-0.00692
2.87	0.00965	0.07868	1.95490	-0.00162
2.97	0.00965	0.09643	1.90275	0.00664
3.10	0.00965	0.1269	1.83071	0.01105

$b = -0.13954 + 0.048647 \cdot pK_1^*$; $pK_1^o = 2.868$

Table 2. The data related to pH-titrations with mandelic acid (C_{0i}^*) in D.

HL = mandelic acid				
pK_{1i}^*	C	C_{0i}^*	a	b
3.10	0.00472	0.03277	2.48438	- 0.01766
3.20	0.00472	0.04003	2.43421	- 0.01197
3.55	0.00472	0.08377	2.28123	0.00393
3.83	0.00472	0.15534	2.12521	0.01417
3.93	0.00472	0.19434	2.06462	0.02054

$b = -0.1547 + 0.04442 \cdot pK_1^*$; $pK_1^o = 3.481$

$$b_i = \alpha + \beta \cdot pK_{1i}^* + \varepsilon_i \text{ .....(52)}$$

where i = 1,…,n; n = 5. Then we have:

$$\alpha = \frac{\sum(pK_{1i}^*)^2 \cdot \sum b_i - \sum pK_{1i}^* \cdot \sum pK_{1i}^* \cdot b_i}{n \cdot \sum(pK_{1i}^*)^2 - \left(\sum pK_{1i}^*\right)^2} \quad \text{...(53)}$$

$$\beta = \frac{n \cdot \sum pK_{1i}^* \cdot b_i - \sum pK_{1i}^* \cdot \sum b_i}{n \cdot \sum(pK_{1i}^*)^2 - \left(\sum pK_{1i}^*\right)^2} \quad \text{.......(54)}$$

where $\Sigma = \Sigma_{i=1}^{n}$ For example, α = − 0.13954, β = 0.048647 in the relation specified at the bottom of Table 1; then we have $pK_1^* = pK_1^o$ = 0.13954/0.048647 = 2.868 at b = 0.

The pK_1^o values are related to b = 0. In both cases, an additional, 6th titration made for $pK_{16}^* = pK_1^o$, obtained by interpolation, confirmed the adequacy of this evaluation (see Figures 4a, 4b).

The experimental value for pK_1^o = 2.868 referred to chloroacetic acid agrees with the one cited in literature: 2.87 [26,27], 2.82 [28], 2.85 [29,30], 2.86 [31]. For mandelic acid, pK_1^o = 3.481 lies within the wide interval: from 3.41[32] to 3.85 [29,33].

Comparison of Results Obtained from Conductometric and pH Titrations

The results of pH titrations presented in Figures 4a and 4b can be compared with results of conductometric titrations specified in [4] for the (HCl, HL) systems with (a) HL = chloroacetic acid (CA), (b) HL = mandelic acid (MA). First, one can state that the conductomeric titration curves are arranged in the reverse order than pH titration curves, from the viewpoint of changes in C_{0i}^* values; this is understandable because higher pH values correspond to lower $[H^{+1}]$ values. Moreover, the conductometric titration curves have more regular course than pH titration curves. At pK_{1i}^* = 2.87, the pH titration curve for CA is nearly parallel to V-axis (Fig. 4a), whereas for conductometric titration the parallel course can be ascribed to the line obtained at pK_{1i}^* ca. 2.90. For MA, the parallel course of conductometric titration occurs at pK_{1i}^* = 3.55 (Fig. 4b), whereas from results of pH titrations the value pK_1^* = 3.481 was obtained (Table 2); the pH titration curve for MA at pK_{1i} = 3.55 is not parallel to V-axis (Fig. 3a). This means that a_2 for Cl^{-1} (see Eq. 47) differs from a_3 for anions L^{-1} related to CA and MA, respectively. However, the differences are not too large and the conductometric titration, offering more regular course of the respective curves, can be considered as a reasonable alternative to the pH titration made within the isohydric method of pK_1 determination.

Different Aspects and Meanings of Isohydricity

Constancy of pH during addition of one of the solutions forming the isohydric system into another one recalls the concepts of buffering action and the dynamic buffer capacity β_V = |dc/dpH| [1,2,34-36]. Isohydric systems are characterized by extremely high β_V value. Referring e.g. to addition of V mL of titrant T mol/L HL (C) into V_0 mL of C_0 mol/L HB, we apply $c = CV/(V_0+V)$; in ideal case $\beta_V \rightarrow \infty$. The isohydricity is not directly relevant to buffering action; nevertheless, it is *on–line* with a general property desired from buffering systems. The isohydricity concept is also in some relevance with pH-static titration [37,38] principle. Moreover, the isohydricity concept is referred to acid-base homeostasis in living organisms [39,40]. In biology, it is used for describing plants that limit transpiration in order to maintain a constant amount of water in the leaves [41-44]. The isohydric principle has special relevance to *in vivo* biochemistry, where multiple acid-base pairs are in solution.

Some acids involved in redox (e.g. HClO, HBrO) and complexation equilibria do not meet the conditions imposed by the isohydricity property, see e.g. [45-48], and other authors' references cited therein.

Final Comments

The formulation referred to the isohydric D+T acid-base systems formed from D and T of different complexity was presented. Particularly, the titration in (HL, HB) system may occur at constant ionic strength (*I*) value, not resulting from presence of a basal electrolyte. This very advantageous conjunction of the properties provides, among others, a new, very sensitive method for verification of pK_1 value for HL. The method was tested experimentally on (HL, HCl) systems in aqueous and mixed-solvent media, and compared with the literature data. Some useful (linear and hyperbolic) correlations were applied for pK_1 validation purposes.

The isohydric method, formulated on the basis of isohydricity property, is also a proposal for use in physicochemical laboratories, as a sensitive tool for the determination of dissociation constants of weak acids HL, especially ones with small pK_1 values, for which the standard method of pK_1 determination based on inflection point location on the related titration curve obtained for (HL, MOH) system is not applicable [4]. The reference of isohydricity to conductometric titrations was also discussed in context to the pH-metric titration.

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