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A new sensitive method of dissociation constants determination based on the isohydric solutions principle

Tadeusz Michałowski[a,*], Bogusław Pilarski[b], Agustin G. Asuero[c], Agnieszka Dobkowska[b]

[a] *Faculty of Engineering and Chemical Technology, Cracow University of Technology, 31-155 Cracow, Poland*
[b] *P.P.H.U. Cerko s.c., 80 299 Gdańsk, Afrodyty 9, Poland*
[c] *Department of Analytical Chemistry, The University of Seville, 41012 Seville, Spain*

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ABSTRACT

The paper provides a new formulation and analytical proposals based on the isohydric solutions concept. It is particularly stated that a mixture formed, according to titrimetric mode, from a weak acid (HX, C_0 mol/L) and a strong acid (HB, C mol/L) solutions, assumes constant pH, independently on the volumes of the solutions mixed, provided that the relation $C_0 = C + C^2 \cdot 10^{pK_1}$ is valid, where $pK_1 = -\log K_1$, K_1 the dissociation constant for HX. The generalized formulation, referred to the isohydric solutions thus obtained, was extended also to more complex acid–base systems. Particularly in the (HX, HB) system, the titration occurs 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. The new method is particularly useful for weak acids HX characterized by low pK_1 values. The method was tested experimentally on four acid–base systems (HX, HB), in aqueous and mixed-solvent media and compared with the literature data. Some useful (linear and hyperbolic) correlations were stated and applied for validation of pK_1 values. Finally, some practical applications of analytical interest of the isohydricity (pH constancy) principle as one formulated in this paper were enumerated, proving the usefulness of such a property which has its remote roots in the Arrhenius concept.

1. Introduction

Acid–base equilibria and determination of equilibrium constants are among the very important topics in analytical chemistry. In spite on the opinion that the topic may seem to be already exhausted, one can find new analytical resources and possibilities. Such contribution and new possibilities are offered by the isohydricity principle, as one formulated in this paper.

It is commonly stated that addition of a strong acid HB into a weak acid HX decreases pH value of the resulting mixture and, consequently, shifts the HX dissociation according to Le Chatelier–Brown's principle. The related effect depends on the HX strength, expressed by its dissociation constant K_1 value, and on the analytical concentrations of both acids, i.e. HX and HB. Under special conditions, the pH change does not occur at all, i.e. pH remains constant when mixing the solutions in different proportions; it is just the subject of the present article. Apart from (HX, HB) mixture, some other systems will also be considered below.

Mixing the solutions can be made according to titrimetric mode [1], 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 secured; it also acts in favour of constancy in equilibrium constants during the mixing procedure in the system, where constancy in pH is assumed.

Another aspects of pH constancy are involved with pH stat action [2,3] and pH static titration [4,5].

The pH constancy is in close relevance with the concept of isohydric solutions [6–8], introduced by Arrhenius [9,10] who stated (when writing it in more contemporary terms) that "if two isohydric solutions are mixed, pH of the resulting solution is unchanged, regardless the composition of the solutions" [11,12]; the pH concept, introduced by Sørensen in 1909 [13], was unknown at that time. The isohydric solutions concept (isohydricity) should be restricted to the systems where only acid–base equilibria occur. In this respect, two solutions are said to be isohydric, when pH is the same in both solutions and does not change after mixing. Such a topic was also considered by Chatten [14] for a system with two weak acids, but without solving it.

In this paper, the relationships between concentrations of substances composing the isohydric systems will be formulated. On

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* Corresponding author. Tel.: +48 12 628 21 77.
E-mail addresses: michalot@o2.pl, michalot@chemia.pk.edu.pl (T. Michałowski).

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Nomenclature

C, C_0	concentrations (mol/L)
D	titrand (solution titrated)
HB	strong acid
HX, H_nX	weak acids
K_1	dissociation constant for HX
LSM	least squares method
MOH	strong base
pK_1	log K_1
pK_1*	pre-assumed pK_1 value
T	titrant
V	volume (mL) of T
V_0	volume (mL) of D

this basis an original, sensitive method of determination of the dissociation constants values, will be suggested.

2. Formulation of isohydricity conditions

In this paper, some pairs of substances, both having acidic or basic properties, will be considered. On the basis of concentration and charge balances, the relationship between C_0 and C under pH static conditions will be formulated. For all the systems considered below, constancy in pH is tantamount with constancy in $[H^+]$ (on the basis of pH definition) and with constancy of expression $[H^+]–[OH^-]$. Other effects, namely a change in dielectric permittivity (ε) and non-additivity, resulting from mixing different solutions, are not ensured. However, such effects on equilibrium constants values are not significant when diluted solutions are mixed. Anyway, the latter effect is not significant from the viewpoint of constancy in pH value.

In all instances considered below, V_0 mL of titrand D be titrated with V mL of titrant T. Let us start for our consideration from (H_nX, HB) system obtained after addition of V mL of C mol/L HB into V_0 mL of C_0 mol/L H_nX. Assuming that the acid H_nX forms the species H_jX^{+j-n} (j = 0, 1, ..., q), we get the concentration and charge balances:

$$\sum\nolimits_{j=0}^{q}[H_jX^{+j-n}] = \frac{C_0V_0}{V_0+V} \tag{1}$$

$$[B^-] = \frac{CV}{V_0+V}$$

$$[H^+] - [OH^-] = [B^-] + \sum\nolimits_{j=0}^{q}(n-j)[H_jX^{+j-n}] \tag{2}$$

Applying the function

$$\bar{n} = \frac{\sum_{j=1}^{q} j\cdot[H_jX^{+j-n}]}{\sum_{j=0}^{q}[H_jX^{+j-n}]} = \frac{\sum_{j=1}^{q} j\cdot K_j^H[H^+]^j}{\sum_{j=0}^{q}K_j^H[H^+]^j} \tag{3}$$

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

$$[H_jX^{+j-n}] = K_j^H \cdot [H^+]^j[X^{-n}] \tag{4}$$

we get, by turns:

$$[H^+] - [OH^-] = \frac{CV}{V_0+V} + (n-\bar{n})\cdot\frac{C_0V_0}{V_0+V} \tag{5}$$

$$[H^+] - [OH^-] = (n-\bar{n})\cdot C_0 \quad (\text{for} \quad V=0) \tag{6}$$

$$n - \bar{n} = \frac{C}{C_0} \tag{7}$$

On analogous way, from the reverse titration where V mL of C_0 mol/L H_nX is added into V_0 mL of C mol/L HB, we get, by turns:

$$\begin{aligned}&[H^+] - [OH^-] = \frac{CV_0}{V_0+V} + (n-\bar{n})\cdot\frac{C_0V}{V_0+V}\\ &[H^+] - [OH^-] = C \quad (\text{for} \quad V=0)\end{aligned} \tag{8}$$

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

$$n - \bar{n} = \frac{C}{C_0} \tag{7}$$

i.e. identical formula (7) is obtained in both instances. Assuming that $[H^+] \gg [OH^-]$, from (8) we get $[H^+] = C$. Putting it into (3), from (7) we get

$$\frac{\sum_{j=1}^{q} j\cdot K_j^H \cdot C^j}{\sum_{j=0}^{q}K_j^H\cdot C^j} = n - \frac{C}{C_0} \tag{9}$$

One can consider some particular cases. For $q = n = 1$, from (9) we have

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

i.e.

$$\frac{C}{K_1+C} = 1 - \frac{C}{C_0} \tag{10}$$

$$C_0 = C + C^2\cdot 10^{pK_1}$$

where

$$K_1 = [H^+][X^-]/[HX] = 1/K_1^H, \quad pK_1 = -\log K_1. \tag{11}$$

The curves of C_0 vs. C relationships are plotted, in logarithmic scale, in Fig. 1. If HX be replaced by a strong monoprotic acid, HA ($K_1 = K_{1HA} \gg 1$), then $C^2/K_{1HA} \ll 1$, and the trite case, $C_0 = C$, is realised.

For $q = n = 2$, Eq. (9) can be transformed into the form

$$K_2^H\cdot C^3 - K_1^H\cdot C\cdot(C_0 - C) = 2C - C_0 \tag{12}$$

where K_1^H and K_2^H are interrelated with the dissociation constants K_1 and K_2:

$$K_2^H = \frac{1}{K_1K_2} \quad \text{and} \quad K_1^H = \frac{1}{K_2} \tag{13}$$

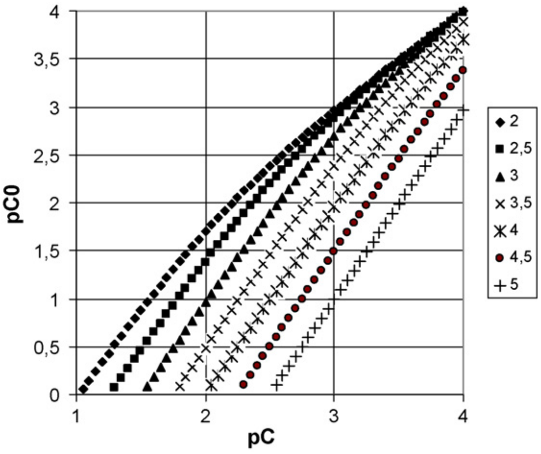

Fig. 1. The $pC_0 = -\log C_0$ vs. $pC = -\log C$ relationships plotted for indicated pK_1 values, on the basis of equation $C_0 = C + C^2/K_1$ (Table 1, no. 1).

For the (HX, HB) system, at $[\mathrm{H^+}] \gg [\mathrm{OH^-}]$, from the charge balance and Eq. (8) we have:

$$[\mathrm{H^+}] = [\mathrm{X^-}] + [\mathrm{B^-}] \quad \text{and} \quad [\mathrm{H^+}] = C$$

Then the ionic strength assumes constant value during the titration, equal to the concentration of HB,

$$I_0 = \frac{1}{2} \cdot ([\mathrm{H^+}] + [\mathrm{X^-}] + [\mathrm{B^-}]) = C \tag{14}$$

i.e. it does not depend on V-value. In the light of the Debye–Hückel law, the constancy in ionic strength is, apart from constancy in temperature T and dielectric permittivity ε, one of the properties securing constancy in K_1 and ionic product of water (K_W) values.

Analogous formulae referred to isohydricity condition can be also derived for other systems. Considering the ($\mathrm{XH}_{n+k}\mathrm{B}_k$, HB) system, where $k = 0, \ldots, q-n$ (at $q > n$), for mutual titrations: HB (C, V) → $\mathrm{XH}_{n+k}\mathrm{B}_k$ (C_0, V_0) and $\mathrm{XH}_{n+k}\mathrm{B}_k$ (C_0, V) → HB (C, V_0) we get the formula

$$n + k - \bar{n} = \frac{C}{C_0} \tag{15}$$

and the relation (8). Assuming again $[\mathrm{H^+}] \gg [\mathrm{OH^-}]$, i.e. $[\mathrm{H^+}] = C$, from (3) and (15) we get

$$\frac{\sum_{j=1}^{q} j \cdot K_j^H \cdot C^j}{\sum_{j=0}^{q} K_j^H \cdot C^j} = n + k - \frac{C}{C_0} \tag{16}$$

At $k = 0$, Eq. (16) becomes identical with (9).

The salts of $\mathrm{M}_k\mathrm{H}_{n-k}\mathrm{X}$ type may appear 1° acid (at low k) or 2° alkaline (at high k) reaction. In the case 1° we consider $\mathrm{M}_k\mathrm{H}_{n-k}\mathrm{X}$ (C_0) in pair with HB (C), and in pair with MOH (C) in the case 2°. The isohydricity condition has the form:

$$\frac{\sum_{j=1}^{q} j \cdot K_j^H \cdot C^j}{\sum_{j=0}^{q} K_j^H \cdot C^j} = n - k - \frac{C}{C_0} \quad \text{for the case } 1^\circ, \quad \text{at } [\mathrm{H^+}] \gg [\mathrm{OH^-}] \tag{17}$$

$$\frac{\sum_{j=1}^{q} j \cdot K_j^H \cdot C^j}{\sum_{j=0}^{q} K_j^H \cdot C^j} = \frac{C}{C_0} + n - k \quad \text{for the case } 2^\circ, \quad \text{at } [\mathrm{H^+}] \ll [\mathrm{OH^-}] \tag{18}$$

The isohydricity condition can easily be extended on mixtures of acid–base systems, in pair with HB or MOH. Assuming V_0 mL of D containing a mixture formed of $\mathrm{M}_{k_i}\mathrm{H}_{n_i-k_i}\mathrm{X}_{(i)}(C_{0i},\quad i = 1, \ldots, r) + \mathrm{H}_{n_i+k_i}\mathrm{X}_{(i)}\mathrm{B}_{k_i}(C_{0i},\quad i = r+1, \ldots, R) + \mathrm{HB}(C_{0a}) + \mathrm{MOH}(C_b)$ titrated with V mL of C mol/L HB, i.e. under assumption that D has an acid reaction. Excluding other (e.g. redox, complexation, and precipitation) equilibria in the system, we have the set of balances:

$$[\mathrm{H^+}] - [\mathrm{OH^-}] + [\mathrm{M^+}] - [\mathrm{B^-}] + \sum_{i=1}^{R} \sum_{s=0}^{q_i} (s - n_i) \cdot [\mathrm{H}_s\mathrm{X}_{(i)}{}^{+s-n_i}] = 0 \tag{19}$$

$$\sum_{s=0}^{q_i} [\mathrm{H}_s\mathrm{X}_{(i)}{}^{+s-n_i}] = C_{0i} \cdot \frac{V_0}{V_0 + V} \quad (i = 1, \ldots, R) \tag{20}$$

$$[\mathrm{M^+}] = \frac{V_0}{V_0 + V} \cdot \left(C_{0b} + \sum_{i=1}^{r} k_i C_{0i} \right);$$

$$[\mathrm{B^-}] = \frac{1}{V_0 + V} \cdot \left(CV + \left(C_{0a} + \sum_{j=r+1}^{R} k_j C_{0j} \right) \cdot V_0 \right) \tag{21}$$

Applying the notation

$$\bar{n}_i = \frac{\sum_{s=1}^{q_i} s \cdot [\mathrm{H}_s\mathrm{X}_{(i)}{}^{+s-n_i}]}{\sum_{s=0}^{q_i} [\mathrm{H}_s\mathrm{X}_{(i)}{}^{+s-n_i}]} = \frac{\sum_{s=1}^{q_i} s \cdot K_{is}^H \cdot [\mathrm{H^+}]^s}{\sum_{s=0}^{q_i} K_{is}^H \cdot [\mathrm{H^+}]^s} \quad (i = 1, \ldots, R) \tag{22}$$

in (19), we have

$$\frac{V_0}{V_0 + V} \cdot \left(C_{0b} - C_{0a} + \sum_{i=1}^{r} (\bar{n}_i - n_i + k_i) \cdot C_{0i} + \sum_{i=r+1}^{R} (\bar{n}_i - n_i - k_i) \cdot C_{0i} \right) - C \cdot \frac{V}{V_0 + V} = [\mathrm{OH^-}] - [\mathrm{H^-}] \tag{23}$$

At $V = 0$, under isohydric conditions,

$$C_{0b} - C_{0a} + \sum_{i=1}^{r} (\bar{n}_i - n_i + k_i) \cdot C_{0i} + \sum_{i=r+1}^{R} (\bar{n}_i - n_i - k_i) \cdot C_{0i} = [\mathrm{OH^-}] - [\mathrm{H^-}] \tag{24}$$

Then from (23) and (24) we get

$$C_{0b} + C - C_{0a} + \sum_{i=1}^{r} (\bar{n}_i - n_i + k_i) \cdot C_{0i} + \sum_{i=r+1}^{R} (\bar{n}_i - n_i - k_i) \cdot C_{0i} = 0 \tag{25}$$

At $[\mathrm{H^+}] \gg [\mathrm{OH^-}]$, we put $[\mathrm{H^+}] = C$, and then (25) assumes the related isohydricity condition

$$\sum_{i=1}^{R} \bar{n}_i \cdot C_{0i} = \sum_{i=1}^{r} (n_i - k_i) \cdot C_{0i} + \sum_{i=r+1}^{R} (n_i + k_i) \cdot C_{0i} - C + C_{0a} - C_{0b} \tag{26}$$

where

$$\bar{n}_i = \frac{\sum_{s=1}^{q_i} s \cdot K_{is}^H \cdot C^s}{\sum_{s=0}^{q_i} K_{is}^H \cdot C^s} \quad (i = 1, \ldots, R) \tag{27}$$

Some simplest formulae related to the systems considered are presented in Table 1. More complex relations between C_0 and C occur for pairs composed of two weak acids or their salts, see Table 2. It was assumed in there that:

$$[\mathrm{HX}_{(i)}] = K_{1i} \cdot [\mathrm{H^+}][\mathrm{X}_{(i)}{}^-]; \quad \bar{n}_i = [\mathrm{HX}_{(i)}]/([\mathrm{HX}_{(i)}] + [\mathrm{X}_{(i)}{}^-]) = [\mathrm{H^+}]/(K_{1i} + [\mathrm{H^+}]) \ (i = 1, 2)$$

$$[\mathrm{X}_{(3)}\mathrm{H^+}] = K_{13} \cdot [\mathrm{H^+}][\mathrm{X}_{(3)}]; \quad \bar{n}_3 = [\mathrm{X}_{(3)}\mathrm{H^+}]/([\mathrm{X}_{(3)}\mathrm{H^+}] + [\mathrm{X}_{(3)}]) = [\mathrm{H^+}]/(K_{13} + [\mathrm{H^+}])$$

Table 1

The C_0 vs. C relationships expressing pH constancy for some pairs of acid–base systems; $\bar{n} = [\mathrm{H^+}]/(K_1 + [\mathrm{H^+}])$; C refers to HB or MOH; C_0 refers to HX, XHB, X or MX.

No.	System	n	q	k	$[\mathrm{H^+}]$	K_1	$\bar{n}$	pH = const at
1	(HB, HX)	1	1	0	C	$[\mathrm{H^+}][\mathrm{X^-}]/[\mathrm{HX}]$	$1 - C/C_0$	$C_0 = C + C^2 \cdot 10^{\mathrm{p}K_1}$
2	(HB, XHB)	0	1	1	C	$[\mathrm{H^+}][\mathrm{X}]/[\mathrm{XH^+}]$	$1 - C/C_0$	$C_0 = C + C^2 \cdot 10^{\mathrm{p}K_1}$
3	(MOH, X)	0	1	0	K_W/C	$[\mathrm{H^+}][\mathrm{X}]/[\mathrm{XH^+}]$	C/C_0	$C_0 = C + C^2 \cdot 10^{\mathrm{p}K_W - \mathrm{p}K_1}$
4	(MOH, MX)	1	1	1	K_W/C	$[\mathrm{H^+}][\mathrm{X^-}]/[\mathrm{HX}]$	C/C_0	$C_0 = C + C^2 \cdot 10^{\mathrm{p}K_W - \mathrm{p}K_1}$

Table 2
The relations expressing pH constancy for some indicated pairs of acid–base systems.

No.	System	pH = const at
1	$(\mathrm{HX}_{(1)}\,(C_0), \mathrm{HX}_{(2)}\,(C))$	$\frac{C_0-C}{K_{12}-K_{11}}+\frac{K_W}{K_{11}\cdot K_{12}}=K_{11}\cdot K_{12}\cdot\left(\frac{C_0-C}{K_{12}\cdot C-K_{11}\cdot C_0}\right)^2$
2	$(\mathrm{HX}_{(1)}\,(C_0), \mathrm{X}_{(3)}\mathrm{HB}\,(C))$	$\frac{C_0-C}{K_{13}-K_{11}}+\frac{K_W}{K_{11}\cdot K_{13}}=K_{11}\cdot K_{13}\cdot\left(\frac{C_0-C}{K_{13}\cdot C-K_{11}\cdot C_0}\right)^2$
3	$(\mathrm{MX}_{(1)}\,(C_0), \mathrm{MX}_{(2)}\,(C))$	$\left(\frac{K_{11}\cdot C-K_{12}\cdot C_0}{C_0-C}\right)^2\cdot\left(1+\frac{C_0-C}{K_{11}-K_{12}}\right)=K_W$
4	$(\mathrm{MX}_{(1)}\,(C_0), \mathrm{X}_{(3)}\,(C))$	$\left(\frac{K_{11}\cdot C-K_{13}\cdot C_0}{C_0-C}\right)^2\cdot\left(1+\frac{C_0-C}{K_{11}-K_{13}}\right)=K_W$

Derivation of the relations is exemplified in Appendices A and B. Similarities within pairs of the relationships are clearly visible.

As were proved in [4,15,16], the common method of pK_1 determination, based on the assumption that pK_1 = pH($V_{\mathrm{eq}}/2$) on the pH = pH(V) titration curve, expressed by equation

$$V=\frac{V_0\cdot(C_0/z-10^{-\mathrm{pH}})}{10^{-\mathrm{pH}}-C},\quad \text{where}\quad z=10^{\mathrm{p}K_1-\mathrm{pH}}+1 \tag{28}$$

fails for low pK_1 values. Such a case occurs, e.g. for the monoprotic (HX, $q = n = 1$) acids, considered in this paper, except acetic acid (see Table 3).

3. A simple method of pK_1 determination

To check the validity of pH constancy principle, the pair of the related solutions should be prepared for this purpose. As an example, let us take the pair of solutions (HX, HB), considered above. Assuming that K_1 is the true value for the reaction HX = H$^+$ + X$^-$ at given temperature (T) and ionic strength (I) values, i.e. the relation (10) is valid at concentrations C_0 and C assumed for HX and HB.

At any pre-assumed K_1* value, for a pre-assumed concentration C of HB we have

$$C_0{}^*=C+C^2\cdot 10^{\mathrm{p}K_1^*} \tag{29}$$

for concentration of HX, as the second component of the pair. For a pre-assumed C-value, C_0* grows with growth of pK_1* value that, in turns, leads to diminution of pH value at the start for titration HB → HX.

From (10) and (29) we have

$$C_0{}^*=C_0+(C_0-C)\cdot(10^{\Delta\mathrm{p}K}-1) \tag{30}$$

where $\Delta\mathrm{p}K=\mathrm{p}K_1^*-\mathrm{p}K_1$. The misfit $\Delta\mathrm{p}K$ makes the non-parallel plot of the pH vs. V relationship. This fact provides a useful method for pK_1 validation. To prove the misfit expressed by Eq. (30), let us assume that pK_1 = 2.87 is a true value for this acid [17]. Then assuming C = 0.01, let us take different presupposed pK_1* values, applied for preparation of some working solutions of HX, with concentrations (C_0*) calculated on the basis of Eq. (29). So, for pK_1* = pK_1 = 2.87, we have C_0* = C_0 = 0.01 + $(0.01)^2 \cdot 10^{2.87}$ = 0.0841, see Eq. (10); its pH value equals exactly 2.000. At pK_1* > pK_1 we take more concentrated HX solution, C_0* > C_0, e.g. for pK_1* = 3.2, we have C_0* = 0.01 + $(0.01)^2 \cdot 10^{3.2}$ = 0.1685 > 0.0841 (Eq. (29)), and then its starting pH value is lower than 2. Otherwise, when applying pK_1* = 2.6 < 2.87, we have C_0* = 0.0498 < 0.0841 and its starting pH value is greater than 2.

Table 3
The V-values corresponding to the point where pH = pK_1, for titration of V_0 = 100 mL of C_0 = 0.01 mol/L HX with V mL of C = 0.1 mol/L HB; $V_{\mathrm{eq}}/2$ = 5.00 mL.

Name of acid	pK_1	V at pH = pK_1
Acetic	4.799	4.99
Chloroacetic	2.87	3.60
Glycolic	3.815	4.84
Mandelic	3.481	4.65

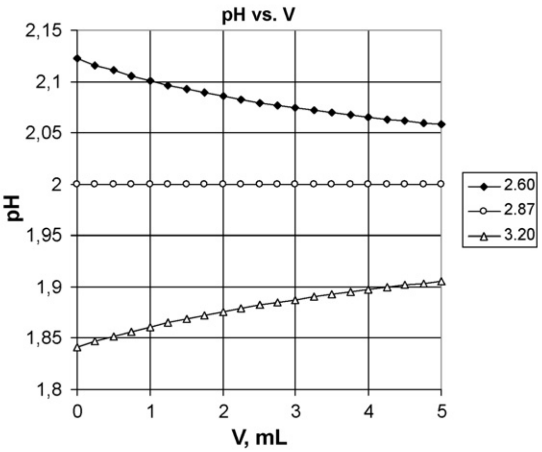

Fig. 2. The pH vs. V relationships plotted for the titration HB → HX, at pK_1 = 2.87, V_0 = 3, C = 0.01, and C_0* calculated from Eq. (28), at different (indicated) pK_1* values.

The related (simulated) curves of pH titrations HB (C, V) → HX (C_0*, V_0), presented in Fig. 2 are obtained after setting C_0* (Eq. (29)) for C_0 in Eq. (28). As we see, a misfit ΔpK = pK_1* − pK_1 between real (pK_1) and pre-assumed (pK_1*) values for acidity constant causes a non-parallel, to V-axis, course of the related curve pH = pH(V); the curve is parallel to the V-axis only for pK_1* = pK_1, at $C_0^*=C_0=C+C_2\cdot 10^{\mathrm{p}K_1}$.

The curves related to pK_1* < pK_1 (i.e. ΔpK < 0), are arranged above the horizontal line referred to pK_1* = pK_1 (ΔpK = 0) and the curves related to ΔpK > 0 are arranged below this line. The distance between the lines considered increases with growth of ΔpK value. The curves are somewhat bended and their curvature grows with growth of $|\Delta\mathrm{p}K|$ value. Because the curves are approximated later by straight lines, it is advised to apply pK_1* not distant from the expected pK_1 values.

A more complex procedure can be applied for simultaneous determination of pK_1 and pK_2 values, on the basis of Eq. (12). Such a procedure appears to be particularly valid for diprotic acids with overlapping pK_i values. The study of the diprotic acids systems will be the subject of a future report.

4. Experimental part

4.1. Apparatus and reagents

The pH titrations were performed with use of Cerko Lab System equipped with combined pH electrode (Hydromet – ERH-13-6 type) and a self-constructed measuring cell (30 mL) with magnetic stirrer. The glass electrode was calibrated with the use of buffer solutions: potassium hydrogen phthalate (pH 4.00), citric acid/Na_2HPO_4 (7.00) and boric acid/KCl/ NaOH (10.00), all purchased from Chempur Company. The calibrations and titrations were performed at 23.0 ± 0.2 °C. The experimental points $\{(V_j, \mathrm{pH}_j)|j=1, \ldots, N\}$, N = 200, were registered in all titrations, made within V-range ⟨0, 4⟩ mL, with titration step 0.02 mL and 8 s pause.

Acetic acid and its three derivatives: chloroacetic ($ClCH_2COOH$), glycolic ($HOCH_2COOH$) and mandelic ($C_6H_5CH(OH)COOH$) acids were used as organic components (HX) in pairs with hydrochloric acid (HB = HCl), considered in context with Eq. (10). All the reagents, of analytical purity grade, were purchased from commercial sources: chloroacetic acid from Fluka (p.a. >99%, m.p. 61–62 °C), glycolic acid manufactured by Fluka (p.a. >99%, m.p. 75–80 °C), D,L-mandelic acid from Alfa Aesar GmbH & Co. (pure >99%), acetic acid purchased from POCh S.A. (extra pure >99.5%). Methanol (MeOH,

Table 4
Collected experimental data for acetic acid and its derivatives.

Acetic acid					Chloroacetic acid				
$pK_1{}^*$	C	$C_0{}^*$	a	b	$pK_1{}^*$	C	$C_0{}^*$	a	b
4.50	0.00227	0.1652	2.76770	−0.01784	2.65	0.00965	0.05125	2.04646	−0.00942
4.66	0.00227	0.2378	2.71756	−0.00651	2.75	0.00965	0.06202	2.02252	−0.00692
4.76	0.00227	0.2988	2.63514	−0.00056	2.87	0.00965	0.07868	1.95490	−0.00162
4.86	0.00227	0.3756	2.58562	0.00354	2.97	0.00965	0.09643	1.90275	0.00664
5.00	0.00227	0.5176	2.47912	0.00959	3.10	0.00965	0.1269	1.83071	0.01105
4.799	0.00227	0.3269	2,60368	−0.00034	2.868	0.00965	0.07836	1.96287	−0.00015
$b = -0.26122 + 0.054429 \cdot pK_1{}^*$; $pK_1 = 4.799$					$b = -0.13954 + 0.048647 \cdot pK_1{}^*$; $pK_1 = 2.868$				

Glycolic acid					Mandelic acid				
$pK_1{}^*$	C	$C_0{}^*$	a	b	$pK_1{}^*$	C	$C_0{}^*$	a	b
3.53	0.00472	0.08021	2.41246	−0.01587	3.10	0.00472	0.03277	2.48438	−0.01766
3.73	0.00472	0.12436	2.32984	−0.00417	3.20	0.00472	0.04003	2.43421	−0.01197
3.83	0.00472	0.15534	2.27824	0.00203	3.55	0.00472	0.08377	2.28123	0.00393
3.93	0.00472	0.19434	2.24026	0.00393	3.83	0.00472	0.15534	2.12521	0.01417
4.13	0.00472	0.30525	2.10145	0.01827	3.93	0.00472	0.19434	2.06462	0.02054
3.815	0.00472	0.15018	2.30922	−0.00182	3.481	0.00472	0.07222	2.26105	0.00161
$b = -0.21080 + 0.05526 \cdot pK_1{}^*$; $pK_1 = 3.815$					$b = -0.1547 + 0.04442 \cdot pK_1{}^*$; $pK_1 = 3.481$				

analytical grade, 99.8%) was supplied by POCH S.A. All chemicals were used without further purification.

Stock solution of hydrochloric acid (HB = HCl) was obtained by dilution of analytical preparation (from Chempur) in redistilled water and standardized against disodium carbonate. Working solutions of HCl, with concentrations C mol/L, were obtained by dilution of the stock solution in redistilled water. Stock solutions of organic acids HX were prepared by dilution of appropriate amounts of the acids in redistilled water and standardized by potentiometric titration, as described for HCl. Working solutions of HX, used for potentiometric titration, with appropriate concentrations $C_0{}^*$, were prepared by dilution of the stock solution.

In all titration series, $V_0 = 3$ mL of $C_0{}^*$ mol/L HX as D was titrated with C mol/L HCl solution as T; concentrations of HCl (C) and HX ($C_0{}^*$) are listed in Table 4. For defined (D, T) = (HX, HCl) pair of the solutions, the $C_0{}^*$ values were calculated from Eq. (29), for $n = 5$ pre-assumed $pK_1{}^*$ values, close to ones found in the literature.

4.2. *Results and discussion*

The experimental data are presented in Tables 4 and 5 and depicted in Figs. 3–6. For clarity of presentation, only essential features are considered.

The pH titration curves plotted in Fig. 3 (compare with Fig. 2) can be approximated by the straight lines

$$\mathrm{pH} = a + b \cdot V \tag{31}$$

The coefficients a and b in (30) are calculated from the formulae:

$$a = \frac{\sum V_j{}^2 \cdot \sum \mathrm{pH}_j - \sum V_j \cdot \sum V_j \mathrm{pH}_j}{N \cdot \sum V_j{}^2 - (\sum V_j)^2} \tag{32}$$

$$b = \frac{N \cdot \sum V_j \cdot \mathrm{pH}_j - \sum V_j \cdot \sum \mathrm{pH}_j}{N \cdot \sum V_j{}^2 - (\sum V_j)^2} \tag{33}$$

where $\sum \equiv \sum_{j=1}^{N}$. The slope b of the line (31) will be the basis for further considerations.

The experimental curve presented in Fig. 4 is identical with the one plotted in Fig. 3d at $pK_1{}^* = 3.10$, chosen here consciously as the most unfavourable from the linearity viewpoint (compare with Fig. 2). As we see, the line expressed by Eq. (31) and formulated according to LSM, fits this curve with the degree of accuracy expressed by

$$s = (s^2)^{1/2}, \quad \text{where} \quad s^2 = (N-2)^{-1} \cdot \sum_{j=1}^{N} (\mathrm{pH}_j - \mathrm{pH}(V_j))^2 \tag{34}$$

The value $s = 0.0036$ found from Eq. (34) is comparable with precision of pH-measurements.

The slopes b, obtained according to interpolative procedure from the series of titrations made at the same C and different $pK_1{}^*$ (and then $C_0{}^*$, Eq. (29)) values, were applied for evaluation of the true pK_1 value (see Table 4 and Fig. 5). The advantageous occurrence in this respect appeared to be the linear correlation [18,19] stated between b and $pK_1{}^*$, expressed by the function

$$b = a_0 + a_1 \cdot pK_1^* \tag{35}$$

where $i = 1, \ldots, n$; $n = 5$. Applying LSM to (35), we have:

$$a_0 = \frac{\sum (pK_{1i}^*)^2 \cdot \sum b_i - \sum pK_{1i}^* \cdot \sum pK_{1i}^* \cdot b_i}{n \cdot \sum (pK_{1i}^*)^2 - (\sum pK_{1i}^*)^2} \tag{36}$$

$$a_1 = \frac{n \cdot \sum pK_{1i}^* \cdot b_i - \sum pK_{1i}^* \cdot \sum b_i}{n \cdot \sum (pK_{1i}^*)^2 - (\sum pK_{1i}^*)^2} \tag{37}$$

where $\sum \equiv \sum_{i=1}^{n}$.

The pK_1 value is related to $b = 0$, and then

$$pK_1 = \frac{-a_0}{a_1} \tag{38}$$

To confirm this evaluation, sixth titration has been made for $pK_1{}^* = pK_1$ value. Moreover, each series of titrations were repeated 2–3 times and very good repeatability of the results for pK_1 values referred to different (HX, HCl) systems has been stated, in all instances. For example, other pK_1 values for acetic acid were: 4.807 and 4.805. The resulting pK_1 values were compared with ones found in the literature.

Table 5
Collected experimental data for (HX, HCl) system with HX = mandelic acid in H_2O + MeOH media, at 23.0 ± 0.2 °C.

$pK_1{}^*$	C	C_0	a	b
3.28	0.002344	0.01280	2.72585	−0.01908
3.481	0.002344	0.01899	2.65431	−0.00616
3.58	0.002344	0.02323	2.59475	−0.00126
3.642	0.002344	0.02642	2.56308	−0.00087
3.68	0.002344	0.02864	2.54176	0.00364
3.88	0.002344	0.04402	2.45330	0.00861

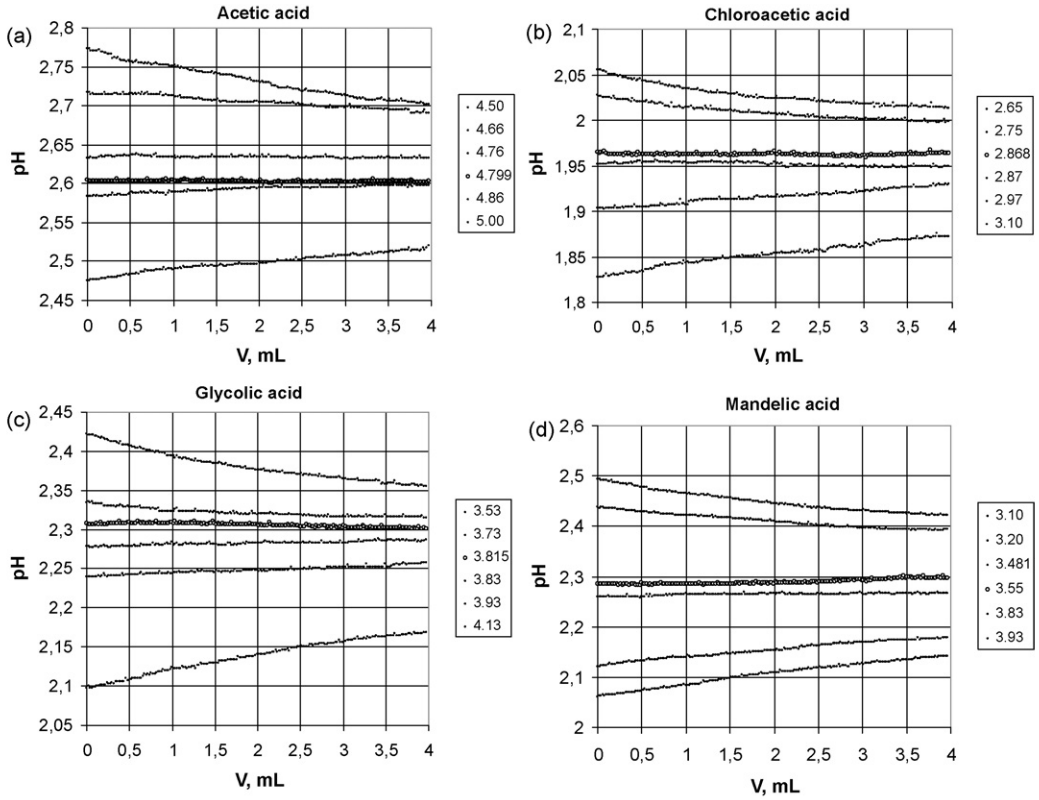

Fig. 3. The pH vs. V relationships for (a) acetic, (b) chloroacetic, (c) glycolic and (d) mandelic acids, plotted for indicated $pK_1{}^* = pK_{1i}{}^*$ ($i = 1, \ldots, n$) values. For further details see Table 4.

The literature data for pK_1s found in Internet and elsewhere, are rarely supplemented by the data referred to temperature and ionic strength values. One can judge that some data were simply copied. The quoted pK_1 values for acetic acid are: 4.65 (25 °C, $I = 0.1$ mol/L in [20] after [21]), 4.74, 4.75, 4.756 [22], 4.76 (most frequently quoted, in [23] for 25 °C, with $dpK_1/dT = -0.0002$), 4.78, 4.79 [24], 4.8 [25].

Other pK_1 values of interest are:

- 2.87 [17,26], 2.82 [27], 2.85 [28,29], 2.86 [30] for chloroacetic acid;
- 3.83 (most frequently quoted) [28,31], 3.831 (25 °C) [32] for glycolic acid;
- 3.85 in [28,33] and 3.41 [34–36] for mandelic acid.

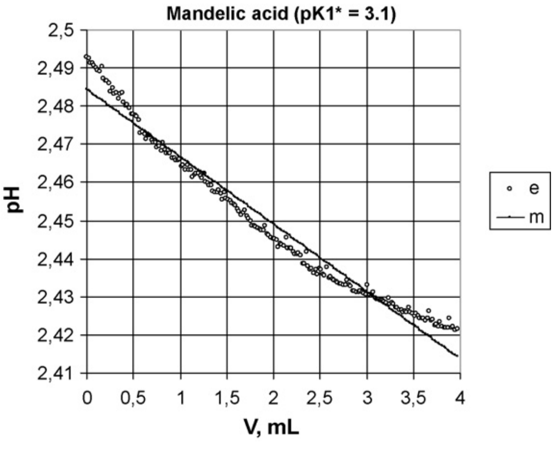

Fig. 4. The juxtaposition of experimental points $\{(V_j, pH_j)|j = 1, \ldots, N\}$ (points e) with the line $pH = 2.48438 - 0.01766 \cdot V$ (line m), obtained at $pK_1{}^* = 3.10$, $C = 0.00472$ mol/L HCl as D, $C_0{}^* = 0.03277$ mol/L mandelic acid as T (see Table 3d).

The experimental value for pK_1 referred to chloroacetic acid agrees with the one cited in [17,26]. The difference $3.83 - 3.815 = 0.015$ is stated for glycolic acid. For acetic acid, the b-value at 4.799 is the closest to zero, although the one found at 4.76 is also very small. For mandelic acid, $pK_1 = 3.481$ lies within the wide interval (3.41, 3.85) spanned by the literature data. The pK_1 values were obtained at ionic strength $I_0 = C$ equal to: 0.00227 for acetic acid, 0.00472 for glycolic and mandelic acid, and 0.00965 for chloroacetic acid. The pK_1 values were confirmed in repeated experiments.

All the above considerations were referred to aqueous media. However, the method can also be extended onto mixed-solvent: aqueous + organic and organic + organic media. In the literature, the effect involved with addition of small amounts of an organic solvent into aqueous media on pK_1 value is frequently neglected [37]. The simple tests, as one presented below, contradict that opinion.

For this purpose, the titrations were made in (H_2O + MeOH) medium, containing 10% (v/v) of methanol and the results are presented in Table 5 and Fig. 6.

From visual inspection of the results obtained in the latter case, it seems to be more advantageous to apply non-linear approximation. The best one seems to be the hyperbolic function $b = (a_0 + a_1 \cdot pK_1{}^*)/(1 + a_2 \cdot pK_1{}^*)$ [38]. After transformation into the form $b = a_0 + a_1 \cdot pK_1{}^* - a_2 \cdot pK_1{}^* \cdot b$, and applying LSM, we get the curve (hyp), where $b = 0$ corresponds to $pK_1{}^* = pK_1 = -a_0/a_1$ (compare with Eq. (38)). The hyperbolic approximation $b = (0.05183 - 0.01439 \cdot pK_1{}^*)/(1 - 0.37686 \cdot pK_1{}^*)$ gives $pK_1 = pK_1{}^*(b = 0) = 3.6008$. For comparison,

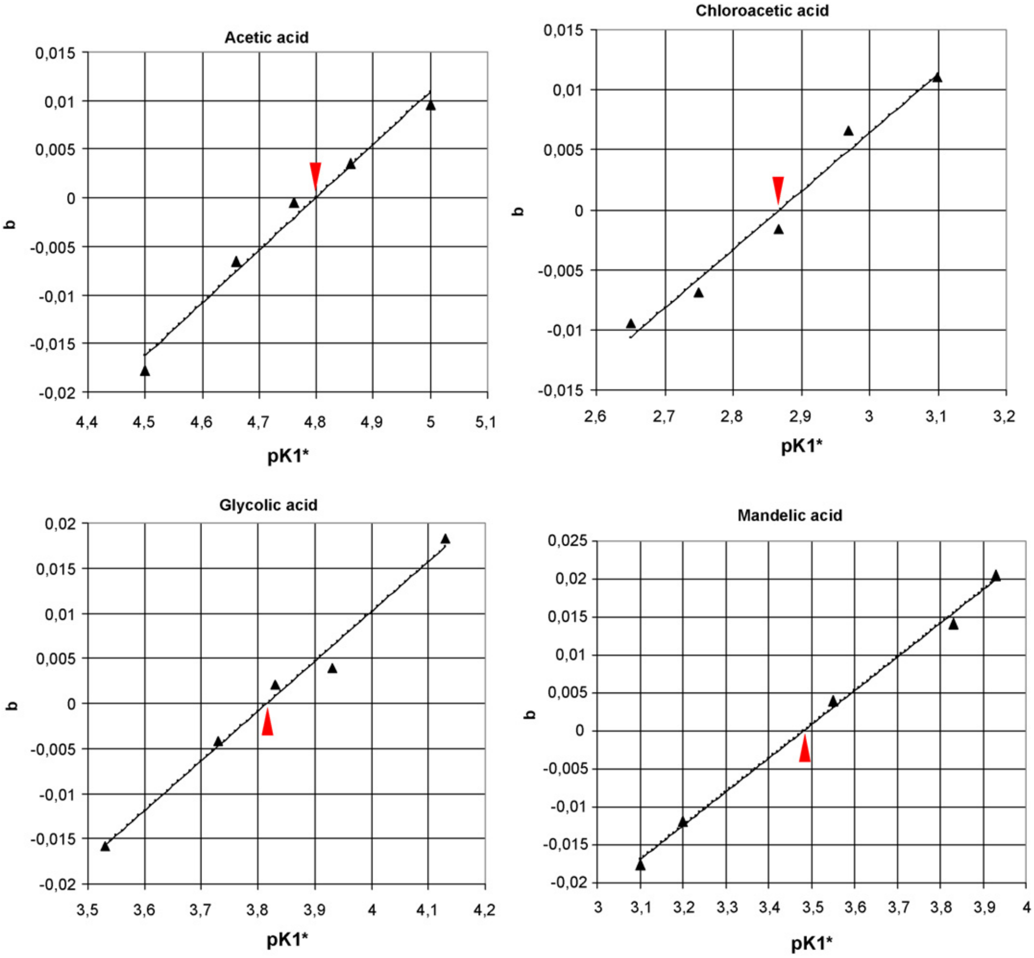

Fig. 5. The b vs. pK_1* relationships (Eq. (35)) found for (a) acetic, (b) chloroacetic, (c) glycolic and (d) mandelic acids. For further details see Table 4.

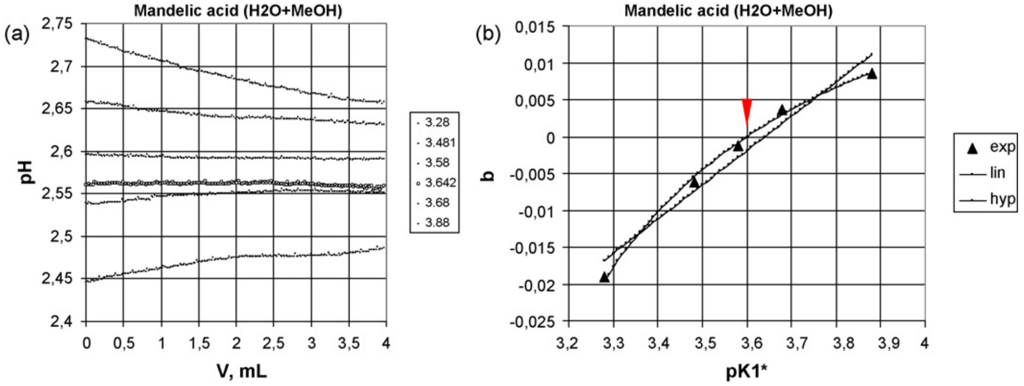

Fig. 6. The data found for HX = mandelic acid in (HX, HCl) system, in the (H_2O + MeOH) medium: (a) pH vs. V relationships plotted for the indicated pK_1* values; (b) the b vs. pK_1* relationship (Eq. (35)) with experimental points (▲), compared with linear (lin) and hyperbolic (hyp) approximations.

the linear approximation $b = -0.16918 + 0.04446 \cdot pK_1{}^*$ gives $pK_1 = pK_1{}^*(b = 0) = 3.6416$ (correlation coefficient $r = 0.979$).

In the latter case, sixth titration has been made at $pK_1 = 3.6416$, evaluated on the basis of linear approximation. The $|b|$ value thus obtained is the smallest among ones registered in the series of titrations (see Table 5). Nonetheless, the $|b|$ value obtained at $pK_1{}^* = 3.58$ is close to that smallest value. Moreover, both b-values are of the same sign; then the next (seventh) titration at $pK_1{}^* = 3.6008$ was unfounded. Nonetheless one can state that this value is far distant from 3.481, related to aqueous media (see Table 4). The non-linearity of b vs. $pK_1{}^*$ relationship in Fig. 6b (hyp) may be perceived in context with non-linearity of pH vs. mole fraction x stated for titrations in binary-solvent systems (H_2O + MeOH), where the function pH = pH(x) referred to monoprotic acids passes usually through maximum [39,40].

5. Final remarks

The isohydricity (pH constancy) is an interesting property of systems composed of solutions of two acids or two bases, when mixed at different proportions. Such a property is not directly relevant to buffering action. Nevertheless, it is on-line with a general property desired from buffering systems.

The problem involved can be perceived not only as an interesting detail, however. It can also find some practical applications, of physicochemical/analytical nature. Namely:

1. The isohydricity principle provides a new sensitive method of pK_1 validation, based on functional relationship between initial concentrations, $C_0{}^*$ and C, of the substances mixed, indicated in Table 1. The sensitivity results from the fact that C and $C_0{}^*$ values are determined with greater accuracy than pH values in pH titrations.
2. Validation of pK_1 for an acid HX is based on preparation of a series of n pairs of solutions; each pair is composed of C mol/L HB and $C_{0i}{}^*$ mol/L HX ($i = 1, \ldots, n$), where $C_{0i}{}^*$ is calculated from the formula (29) for pre-assumed p$K_1{}^*$ values, not far distant from the pK_1 value found in the literature (compare with Fig. 2).
3. One can check the effect of ionic strength value occurred during the titration in a non-buffered system. The special validity of this method results from the unique property of ionic strength constancy during the titration, expressed by Eq. (14).
4. One can check an effect of ionic strength on pK_1 value, when a basal electrolyte, MB (e.g. KCl), be added into the pair of solutions mixed. For this purpose, a series of titrations are made in presence of MB as the basal electrolyte, at equal concentrations (C_{MB} mol/L) in titrand (D) and titrant (T). This way, the constancy in ionic strength value $I = I_0 + C_{MB}$ [mol/L] is assumed (see Eq. (14)) accurately (not approximately) in the D + T systems thus formed. The non-additivity in volume, as an effect involved with mixing different solutions, can be neglected when the systems of diluted solutions are considered.
5. One can test the effect of contamination of a weak acid or its salt by a strong acid or base, or carbonate; for a (very) weak acid, its pH value is distant from the related pK_1, i.e. its buffer capacity is low. In this case, it can be perceived as a sensitive tool for measurement of these contaminations.
6. The method is planned for wider testing binary-solvent systems, as an extension of the approach presented in [39,40].
7. One can also expect an applicability of this approach in separations made according to some LC and CE techniques.
8. The isohydricity principle can be valid only in the systems with acid–base equilibria involved. For example, $AgNO_3$ solution added into HCN solution [41] or dimethylglyoxime added into non-buffered $NiSO_4$ solution [1] act as strong acid, also when pH of the related starting solutions is the same. Similar remarks refer to redox systems [42,43], e.g. ones with multi-hydroxyl bases such as $MnO_4{}^-$ or $Cr_2O_7{}^{2-}$ involved [1,41]. It is thus noteworthy that the generalizing Arrhenius theorem, extending the term of isohydric solutions on other ions [6,11,12] is invalid, in general.

For all these reasons, the isohydric solution principle, which has its remote roots in Arrhenius [9], being recently revised by de Levie [12], which has been exposed here from a different perspective, may be considered as a useful analytical tool to be applied in the study of solution equilibria, as has been shown in this paper, in its application to pK_i's calculation.

Appendix A.

Derivation of formula (2) in Table 2.

From the balances:

$$[HX_{(1)}] + [X_{(1)}{}^-] = C_0V_0/(V_0+V); \quad [X_{(3)}H^+] + [X_{(3)}] = CV/(V_0+V) = [B^-]$$

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

we get:

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

$$[H^+] - [OH^-] = (1-\bar{n}_1)\cdot C_0 \quad (\text{for} \quad V = 0)$$

and then, by turns:

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

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

$$[OH^-] = \frac{K_W}{K_{11}\cdot K_{13}}\cdot\frac{K_{13}\cdot C - K_{11}\cdot C_0}{C_0-C}$$

$$(1-\bar{n}_1)\cdot C_0 = \frac{K_{13}\cdot C - K_{11}\cdot C_0}{K_{13}-K_{11}}$$

$$\frac{C_0-C}{K_{13}-K_{11}} + \frac{K_W}{K_{11}\cdot K_{13}} = K_{11}\cdot K_{13}\cdot\left(\frac{C_0-C}{K_{13}\cdot C - K_{11}\cdot C_0}\right)^2$$

Appendix B.

Derivation of formula (4) in Table 2

From the balances:

$$[HX_{(1)}] + [X_{(1)}{}^-] = C_0V_0/(V_0+V) = [M^+]; \quad [X_{(3)}H^+] + [X_{(3)}] = CV/(V_0+V);$$

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

we get

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

$$[OH^-] - [H^+] = \bar{n}_1\cdot C_0 \quad (\text{for} \quad V = 0)$$

and then, by turns,

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

$$\bar{n}_3\cdot C = \bar{n}_1\cdot C_0$$

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

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

$$[OH^-] = K_W\cdot\frac{C_0-C}{K_{11}\cdot C - K_{13}\cdot C_0}$$

$$\bar{n}_1\cdot C_0 = \frac{1}{K_{11}/[H^+]+1}\cdot C_0 = \frac{K_{11}\cdot C - K_{13}\cdot C_0}{K_{11}-K_{13}}$$

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

$$\left(\frac{K_{11}\cdot C - K_{13}\cdot C_0}{C_0 - C}\right)^2 \cdot \left(1+\frac{C_0 - C}{K_{11}-K_{13}}\right) = K_W$$

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