Talanta 112 (2013) 49–54

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

On the isohydricity concept—some comments

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

[a] Department of Analytical Chemistry, The University of Seville, 41012 Seville, Spain
[b] Cerko Sp. z o.o. Sp.K., Al. Zwycięstwa, 96/98, 81 451 Gdynia, Poland
[c] Faculty of Engineering and Chemical Technology, Technical University of Cracow, 31-155 Cracow, Poland

ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form
14 March 2013
Accepted 25 March 2013
Available online 31 March 2013

Keywords:
Isohydricity
Acids
Bases
pH titration
Conductometric titration

ABSTRACT

The isohydricity property, referred to systems composed of acids or bases, is presented. The related isohydricity conditions are formulated for different pairs of solutions. The pH titrations in the system of isohydric solutions are put in context with conductometric titrations. The differences between pK_1 values obtained according to both methods are not too significant and the conductometric titration can be perceived, in some instances, as a reasonable alternative to the pH titration.

1. Introduction

Titrimetric methods of analysis are commonly involved with mixing the solutions of two substances endowed with opposite properties, e.g., acid with base, or *vice versa* [1,2]. Mixing two acids or two bases according to this mode is usually not practiced. The special property is attributed to the solutions of two different acids (A_1 and A_2) or two different bases (B_1 and B_2) having equal pH values. Such a pair of solutions is termed as isohydric solutions after Arrhenius.

A constant pH-value appears in a mixture formed of solutions of two acids (A_1 and A_2) or two bases (B_1 and B_2), i.e., the condition pH=const. is valid at any ratio in volumes V_1 and V_2 of the composing solutions only at a proper relation formulated between molar concentrations, C_1 and C_2, of components of the related solutions. In particular, the pH constancy was stated [3] for mixtures of strong monoprotic acid (HB, C_2 mol/L) and a weak monoprotic (HL, C_1 mol/L) or pseudo-monoprotic (H_nL, C_1 mol/L) acid, $n \geq 2$, when mixed according to titrimetric mode. Two cases of pseudo-monoprotic acids were considered [3]. The case 1° refers to the acid H_nL whose second dissociation constants K_2 is much smaller than the first dissociation constant, K_1. The case 2° refers e.g. to $MHSO_4$ (C_1) (see Table 1) or to H_2LB (C1) when titrated with strong acid HB (C_2), at $C_2 \gg 2K_2$, where $[H^+][L^-]=K_2[HL]$. For such solutions, when mixed according to titrimetric mode, the Michałowski formula [3–5]

$$C_1 = C_2 + {C_2}^2 \cdot 10^{pK} \tag{1}$$

expressing the isohydricity condition is applied, where $pK = -\log K$, $K=K_1$ for the case 1°, and H_2LB, and $K=K_2$ for $NaHSO_4$.

Despite some appearances arising from the wording, the isohydricity concept introduced by Arrhenius in 1889 was not involved with hydrogen ions, but with conductivity that was the main area of his scientific activity that time. In [6] it were literally stated that “the author has applied the term “isohydric” to two solutions the conductivities of which are not altered when they are mixed (Wied. Ann., vol. XXX, p. 51, 1887). According to the author views, what is called the electrolytic dissociation (into ions) of the two electrolytes is unaltered in these circumstances when they are mixed”. It contradicts the statement “Arrhenius proved that when solutions of two acids have the same concentration of hydrogen as ion, these solutions could be mixed in any proportion without changing the degrees of dissociation of either acid” expressed by Bancroft [7], the chemist contemporary to Arrhenius, and in Encyclopedia.com note devoted to Arrhenius [8]. According to de Levie [9], it was “the first quantitative paper on pH, long before pH was defined”; note that the term pH was introduced by Sørensen later, in 1909 [10]. Similar statement, referred to any pair of solutions having the same concentration of hydrogen ions, is not true [3–5,11].

One can read that “among Arrhenius' most important contributions to this theory are his publications on isohydric solutions; solutions of two acids that can be mixed without any change in the degree of dissociation (1888)”. Both statements/opinions are

---

* Correspondence to: Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland.
E-mail addresses: michalot@o2.pl, michalot@chemia.pk.edu.pl (T. Michałowski).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.03.067

repeated and mixed in contemporary media; e.g., in [12], it were stated that the term "isohydric" refers to "solutions that have the same pH and conductivity", and that "these values remain constant upon mixing the solutions".

Mixing the solutions can be carried out according to titrimetric mode, in *quasistatic* manner, under isothermal conditions; it enables some changes in equilibrium constants, affected by thermal effects, to be avoided. The ionic strength (I_0) 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. The system composed of solutions of a weak monoprotic acid (HL, C_1 mol/L) and a strong monoprotic acid (HB, C_2 mol/L) will be considered below as the simplest case of isohydric solutions.

In experimental part of this paper, the curves obtained according to the isohydric method from results of pH titrations will be compared with results of conductometric titrations.

In the present article, the formulation of isohydricity condition is applied to some other acid–base systems, not included in earlier issues [3–5] devoted to isohydric solutions. In all the formulae derived below, concentrations are expressed in mol/L, and volumes in millilitre.

2. Some pairs of isohydric solutions

The isohydricity concept was extended by Michałowski also on more complex acid–base systems [3]. Another mixtures formed by acid–base systems are specified in Table 1. The formulae referred to the systems specified in it are derived in Appendix A. In nos. 1–4, solution I refers to buffering systems composed of a weak acid or base and its salt; e.g., LHB is exemplified by $C_6H_5NH_3Cl$ (in acidic media), or NH_4Cl (in basic media); B^- is an anion of strong acid, HB (e.g., HCl), M^+ is a cation of strong base, MOH (e.g., NaOH); for H_2SO_4 (no. 5) and $NaHSO_4$ (no. 6) we have $K_2=[H^+][SO_4{}^{2-}]/[HSO_4{}^-]$. In no. 7, Ba^{2+} ions form only mono-hydroxo-complex $BaOH^+$, $[BaOH^+]=K_1{}^{OH}[Ba^{2+}][OH^-]$. Solid **$Zn(OH)_2$** in no. 8 forms with an excess of MOH (C_1) a homogeneous mixture, with hydroxo-complexes $Zn(OH)_i{}^{+2-i}$ ($i=1,\ldots,4$); $[Zn(OH)_i{}^{+2-i}]=K_i{}^{OH}[Zn^{2+}][OH^-]^i$, and

$$\overline{n}^* = \frac{\sum_{i=1}^{4} iK_i{}^{OH}C_2{}^i}{1+\sum_{i=1}^{4} K_i{}^{OH}C_2{}^i} \tag{2}$$

The relationships between concentrations indicated in Table 1 fulfil the condition pH=const., valid under assumption of additivity in volumes of the solutions (I and II) when mixed. Independent of the system considered, the isohydricity condition is valid at any volume ratio of the solutions mixed according to titrimetric mode [1,2]. Eq. (1) is a particular case ($C_0=0$) of equation no. 1 in Table 1. Particularly, after mixing isohydric solutions of weak (HL) and strong (HB) acids at any proportion, the degree of HL dissociation

$$\alpha = \frac{[L^-]}{[HL]+[L^-]} = (10^{pK_1-pH}+1)^{-1} \tag{3}$$

is not changed.

The isohydric system is characterized by extremely high buffer capacity $\beta=|dc/dpH|$ [1]. Referring to addition of V mL C_1 mol/L HL into V_0 mL of C_2 mol/L HB, we apply $c=C_1V/(V_0+V)$; in ideal case $\beta\to\infty$.

It can also be noticed that ionic strength (I_0) of the solution remains constant. Particularly, at $[H^+]\gg[OH^-]$, from the balances: $[H^+]=[B^-]+[L^-]$ and $[H^+]=C_2$, referred to the system (HL (C_1), HB (C_2)) we have [3]

$$I_0 = \tfrac{1}{2}\left((H^+)+[B^-]+[L^-]\right) = C_2 \tag{4}$$

In the light of the Debye–Hückel law, the constancy in ionic strength (I_0) is, apart from constancy in temperature T and dielectric permittivity ε, one of the properties securing constancy in K_1 and K_W values. It is a unique property of isohydric solutions. In this case, addition of basal electrolytes to both solutions mixed is not required. However, when a basal electrolyte MB (C_{MB} mol/L) is present at equal concentrations in the titrand and titrant, then $I=C_2+C_{MB}$.

In [3–5] it was stated that the isohydricity condition is referred to the systems where only acid–base equilibria are involved. On this basis, a very sensitive, isohydric method of dissociation constants determination, based on Eq. (1), has been proposed [3,4], also for mixed-solvent media.

The isohydric method involves preparation of a series of solutions of both acids: weak acid HL (C_{1i} mol/L) and strong acid HB (C_2 mol/L), whose concentrations (C_{1i}, C_2) are interrelated in the equality [3,4]

$$C_{1i} = C_2 + C_2{}^2\cdot 10^{pK_{1i}} \quad (i=1,\ldots,n) \tag{5}$$

where pK_{1i} are the pre-assumed numbers, not far from true pK_1 value. For this purpose, n pairs $(HL, HB)_i$ of the solutions (i=1,…,n) are mixed according to a common pH-metric titration procedure, where V_1 mL of C_2 mol/L HB is added (as titrant T), in portions, into V_2 mL of C_{1i} mol/L HL (considered as titrand, D) or *vice versa*. It is advisable to choose the pre-assumed pK_{1i} values smaller and higher than the pK_1 value; in this case, the true pK_1 value can be found by interpolation that seems to be more advantageous than extrapolation.

To formulate the related procedure, let us consider titration of: (a) V_2 mL C_1 mol/L HL with V_1 mL C_2 mol/L HB, and (b) V_2 mL C_2 mol/L HB with V_1 mL C_1 mol/L HL, $K_1=[H^+][L^-]/[HL]$. The pH=pH(V) relationships are obtained on the basis of charge balance $[H^+]-[OH^-]-[B^-]-[L^-]=0$ and concentration balances: (a) $[B^-]=C_2V_1/(V_1+V_2)$, $[HL]+[L^-]=C_1V_2//(V_1+V_2)$; and (b) $[B^-]=C_2V_2/(V_1+V_2)$, $[HL]+[L^-]=C_1V_1/(V_1+V_2)$; in both instances, V_1 is ascribed

Table 1
The formulae for isohydricity conditions in indicated acid–base systems.

No.	Medium	Solution I	Solution II	Isohydricity condition
1	$[H^+]\gg[OH^-]$	HL (C_1)+ML (C_0)	HB (C_2)	$C_1=C_2+C_2(C_2+C_0)/K_1$
2		LHB (C_1)+L (C_0)	HB (C_2)	
3	$[H^+]\ll[OH^-]$	HL (C_1)+ML (C_0)	MOH (C_2)	$C_0=C_2+C_2(C_1+C_2)(K/K_W)$
4		LHB (C_1)+L (C_0)	MOH (C_2)	
5	$[H^+]\gg[OH^-]$	H_2SO_4 (C_1)	HB (C_2)	$C_1=C_2(C_2+K_2)/(C_2+2K_2)$
6		$MHSO_4$ (C_1)	HB (C_2)	$C_1=C_2+C_2{}^2/K_2$
7	$[H^+]\ll[OH^-]$	$Ba(OH)_2$ (C_1)	MOH (C_2)	$C_1=C_2(C_2+1/K_1{}^{OH})/(C_2+2/K_1{}^{OH})$
8		**$Zn(OH)_2$** (C_0)+MOH (C_1)	MOH (C_2)	$C_1=C_2-(2-\overline{n}^*)C_0$

to T, and V_2 to D. Assuming $[H^+] \gg [OH^-]$, on the basis of Eq. (5) and

$$x=K_1-\frac{C_2V_1}{V_1+V_2} \quad \text{and} \quad y_i=C_2\cdot K_1\cdot\left(1+\frac{1}{K_{1i}}\cdot\frac{C_2V_2}{V_1+V_2}\right) \quad \text{for } (a), \quad \text{or} \tag{6}$$

$$x=K_1-\frac{C_2V_2}{V_1+V_2} \quad \text{and} \quad y_i=C_2\cdot K_1\cdot\left(1+\frac{1}{K_{1i}}\cdot\frac{C_2V_1}{V_1+V_2}\right) \quad \text{for } (b) \tag{7}$$

we formulate the relationship

$$\mathrm{pH}=\mathrm{pH}(i)=-\log\left(\frac{(x^2+4y_i)^{1/2}-x}{2}\right) \tag{8}$$

Let us assume: $V_2=3$ mL, $C_2=0.002$ mol/L and $pK_1=-\log K_1=3.0$ for true dissociation constant K_1 value of an acid HL. Taking pK_{1i} values from the vicinity of pK_1, we plot the related pH(i) vs. V relationships (Eq. 8) for the cases (a) and (b), see Fig. 1a and b. As we see, in both cases, pH(i)=const. for $pK_{1i}=pK_1=3.0$, i.e., for the pair of isohydric solutions; pH=const. only for C_1 and C_2 values that fulfil the relation (1), at $pK_{1i}=pK_1$, see Eq. (1) for $pK=pK_1$.

3. Isohydricity in terms of conductometric and pH titrations

The diversity in meaning the isohydricity term made an inevitable inconsistency/controversy between different terms, e.g., one referred to pH and conductivities. Conductivity $\kappa=1/\rho$ (ρ—resistivity) of a solution depends on properties of the solution, not on dimensions of the conductometric cell. The conductivity of the solution is a sum of terms involved with all cationic and anionic species that contribute the current passing through the solution. The conductivity of an ionic solution is [13]

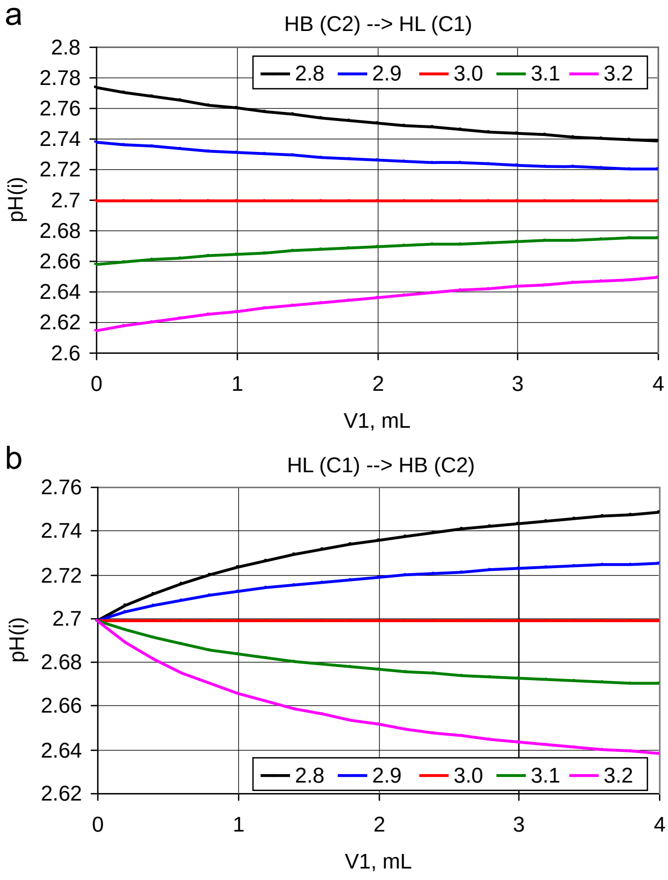

Fig. 1. The pH changes (Eq. (8)) resulting from addition of (a) V_1 mL of HB (C_2 mol/L) into V_2 mL of HL (C_1 mol/L); (b) V_1 mL of HL (C_1 mol/L) into V_2 mL HB (C_2 mol/L); $pK_1=3.0$ for HL; $C_2=0.002$ mol/L, $V_2=3$ mL; pK_{1i} values (Eq. (5)) are indicated in legends.

$$\kappa=F\sum_i |z_i|u_i[X_i^{z_i}] \tag{9}$$

where z_i—charge (in elementary charge units), and u_i—ionic mobility for i-th ionic species, $X_i^{z_i}$, F—Faraday constant; each ion contributes a term proportional to its concentration $[X_i^{z_i}]$. The property (9) is valid at low concentrations, where interactions between ions can be neglected. Ionic interactions can alter the linear relationship between conductivity and concentration in more concentrated solutions. Denoting $|z_i|u_iF=a_i$, for the solution composed of a weak acid HL and a strong acid HB we have the formula

$$\kappa=a_1[H^+]+a_2[B^-]+a_3[L^-] \tag{10}$$

From the simplified charge balance $[H^+]=[L^-]+[B^-]$, valid at $[H^+] \gg [OH^-]$, from (10) it results that

$$\kappa=(a_1+a_2)[B^-]+(a_1+a_3)[L^-] \tag{11}$$

Assuming, for a moment that $a_2=a_3$, we have

$$\kappa=(a_1+a_3)[B^-]+(a_1+a_3)[L^-]=(a_1+a_3)([B^-]+[L^-])=(a_1+a_3)[H^+]$$
$$=(a_1+a_3)10^{-\mathrm{pH}}=\mathrm{const} \tag{12}$$

at pH=const. At constant ionic strength (this property is immanent in such isohydric system [3]), 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. Experimental part

In order to compare the results of conductometric and pH titrations performed according to the isohydric method, the comparative titrations were made with use of chloroacetic acid ($ClCH_2COOH$, abbr. CA), and mandelic acid ($C_6H_5CH(OH)COOH$, abbr. MA); MA is considered there as pseudo-monoprotic acid. Chloroacetic acid (CA) was purchased from Fluka (p.a. > 99%, m.p. 61–62 °C), and mandelic acid (MA)—from Alfa Aesar GmbH & Co. (pure > 99%). Redistilled water was used for preparation of stock and working solutions. The pH titrations were made with combined pH electrode (Hydromet ERH-13-6 type), and conductometric titrations—with conductometric sensor (Hydromet, CD-201 type), at temperature 23.0 ± 0.2 °C. The pH electrode was calibrated as indicated in [3], and the conductometric electrode was standardized with conductivity standards (aqueous KCl solutions) of conductivity 84 μS/cm and 1413 μS/cm, purchased from Hamilton Company. The pH and conductometric titrations of $V_0=3$ mL of C_{1i} mol/L chloroacetic acid (CA) were made with $C_2=0.00965$ mol/L HCl, and the related titrations of $V_0=3$ mL of C_{1i} mol/L mandelic (MA) acid were made with $C_2=0.00472$ mol/L HCl. The titrants were added in increments 0.02 mL. In all instances, the appropriate C_{1i} values for CA and MA were calculated from Eq. (5), at pK_{1i} values indicated in legends for the corresponding Figs. 2a,b and 3a,b.

Comparing the curves plotted in Figs. 2a,b and 3a,b, one can state that the conductomeric titration curves are arranged in the reverse order than pH titration curves. The conductometric curves have more regular course than pH titration curves. At $pK_{1i}=pK_1=2.87$, the pH titration curve for CA is nearly parallel to V-axis (Fig. 2a), 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. 3b), whereas from results of pH titrations the value $pK_1=3.481$ was obtained [3]; the pH titration curve for MA at $pK_{1i}=3.55$ is not parallel to V-axis (Fig. 3a). This means that a_2

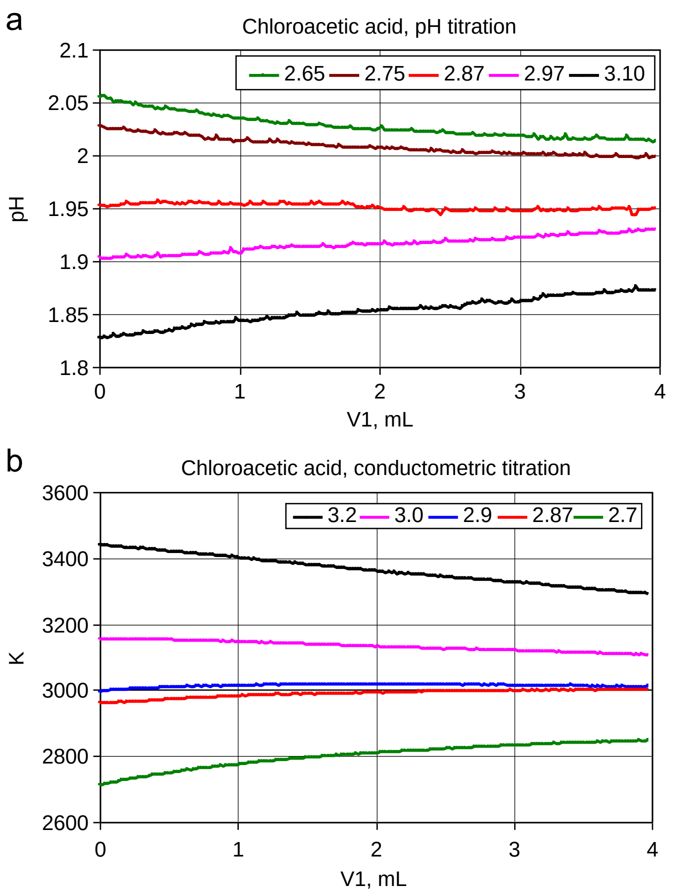

Fig. 2. The curves of (a) potentiometric, and (b) conductometric titration of $V_0=3$ mL of C_1 mol/L chloroacetic acid (CA) with $C_2=0.00965$ mol/L HCl. For more details see text.

for Cl$^-$ (see Eq. 11) differs from a_3 for anions related to CA and MA. 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.

5. Further remarks

From simple calculations made with use of Eq. (1) at $C_2=0.01$ mol/L, one can calculate: $C_1=0.01+(0.01)^2\cdot 10^{2.87}=0.0841$ mol/L for chloroacetic acid and $C_1=0.01+(0.01)^2\cdot 10^{4.76}=5.76$ mol/L for acetic acid. The latter concentration, although realizable in the experiment, will not be applied, owing to undesirable effect of non-additivity in volumes of D and T during the titration occurred when diluted and concentrated solutions are mixed together. To lower the C_2 value, smaller concentrations C_1 of HB should be used. Applying $C_2=0.002$ mol/L HB, we get $C_1=0.002+(0.002)^2 10^{4.76}=0.232$ mol/L acetic acid.

The pK$_1$ value for a weak acid of HL type is usually registered from titration curve referred to titration of V_2 mL of C_2 mol/L HL with V_1 mL of C_1 mol/L MOH. We have

$$V_1=V_1(pH)=V_2\frac{(1-\bar{n})C_2-10^{-\mathrm{pH}}+10^{\mathrm{pH}-\mathrm{pK_w}}}{C_1+10^{-\mathrm{pH}}-10^{\mathrm{pH}-\mathrm{pK_w}}} \qquad (13)$$

where $\bar{n}$ is identical with (A1) in Appendix A. The functions $V_1=V_1(\mathrm{pH})$ and its inverse form $\mathrm{pH}=\mathrm{pH}(V_1)$ are bijective, owing to their monotonicity, i.e., one-to-one correspondence between the variables: V_1 and pH. Then the (simpler in notation) functions $V_1=V_1(\mathrm{pH})$ are usually considered as ones particularly useful for

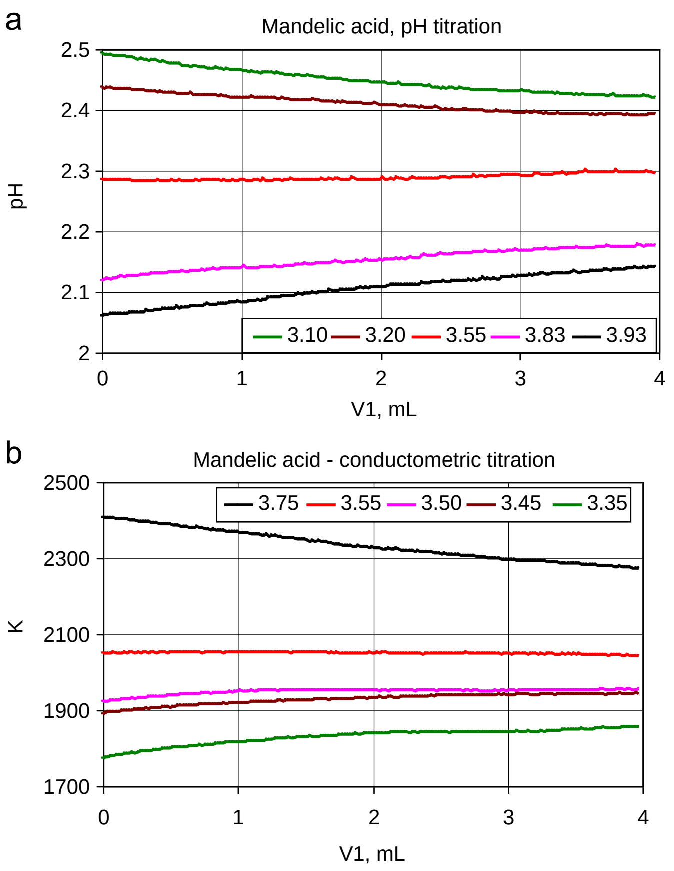

Fig. 3. The curves of (a) potentiometric and (b) conductometric titration of $V_0=3$ mL of C_1 mol/L mandelic acid (MA) solution with $C_2=0.00472$ mol/L HCl. For more details see text.

Table 2
The $V_1=V_1(\mathrm{pH}=\mathrm{pK}_1)$ values found at $V_2=100$ mL, $C_2=0.01$ mol/L and $C_1=0.1$ mol/L, at $\bar{n}=0.5$ in Eq. (13).

No.	Acid	pK$_1$	V(pH=pK$_1$)
1	Dichloroacetic	1.48	none
2	Cyanoacetic	2.45	1.40
3	Chloroacetic	2.85	3.60
4	Formic	3.75	4.81
5	Acetic	4.76	4.98
6	HCN	9.21	5.02
7	o-Cresol	10.26	5.19

acid–base systems of higher degree of complexity [14,15] than one presented above.

The common method of pK$_1$ determination is based on the assumption that $\mathrm{pK}_1=\mathrm{pH}(V_{eq}/2)$ on the $\mathrm{pH}=\mathrm{pH}(V_1)$ titration curve. However, this assumption fails, particularly at lower pK$_1$ values [16], see also Table 2, where $V_{eq}/2=5.00$ mL. In this context, the method suggested below, based on the isohydricity principle, seems to be noteworthy.

6. Final comments

In addition to cognitive values, the isohydric method, formulated by Michałowski on the basis of isohydricity property, is also a sensitive tool applicable for the determination of dissociation constants of weak acids, especially ones for which the standard method of pK$_1$ determination based on the first inflection point on the related titration curve is not applicable [1]. And last but not least, the isohydric systems consisting of weak and strong acids (HL and HB) have valuable and unique property; a constant ionic strength, not stated in other acid–base systems, is maintained in such systems. From the viewpoint of pK_1 determination, the conductometric titration method can be perceived as an alternative for pH titration.

Appendix

Derivation of formulae referred to the systems indicated in Table 1 (numbers 1–8). In all instances, V_1 mL of titrant T is added into V_2 mL of titrand D. Notations as in [1].

Ad. 1.

$$\alpha = [H^+] - [OH^-]$$

$$\overline{n} = \frac{[HL]}{[HL] + [L^-]} \qquad (A-1)$$

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

$\alpha + [M^+] - [B^-] = [L^-]$

$\alpha + \frac{C_0V_1}{V_1+V_2} - \frac{C_2V_2}{V_1+V_2} = (1-\overline{n})\frac{C_1V_1+C_0V_1}{V_1+V_2}$

At $V_1 = 0$

$\alpha = C_2$

$C_2 + \frac{C_0V_1}{V_1+V_2} - \frac{C_2V_2}{V_1+V_2} = (1-\overline{n})\cdot\frac{C_1V_1+C_0V_1}{V_1+V_2}$

$C_2V_1 + C_2V_2 + C_0V_1 - C_2V_2 = (1-\overline{n})(C_1V_1 + C_0V_1)$

$\frac{K_1}{[H^+]+K_1} = \frac{C_2+C_0}{C_1+C_0}$

$[H^+] = K_1\frac{C_1-C_2}{C_0+C_2}$

$[OH^-] = \frac{K_W}{[H^+]} \rightarrow [OH^-] = \frac{K_W}{K_1}\cdot\frac{C_0+C_2}{C_1-C_2}$

$C_2 = [H^+] - [OH^-]$

$C_2 = K_1\frac{C_1-C_2}{C_0+C_2} - \frac{K_W}{K_1}\cdot\frac{C_0+C_2}{C_1-C_2}$

$C_2(C_0 + C_2)(C_1 - C_2) = K_1(C_1 - C_2)^2 - (K_W/K_1)(C_0 + C_2)^2$

$$1-\overline{n} = \frac{C_2 + C_0}{C_1 + C_0} \qquad (A-2)$$

If $[H^{+1}] \gg [OH^{-1}]$, the last term in (A-2) can be neglected, and we get

$$C_1 = C_2 + C_2\cdot(C_2 + C_0)\cdot 10^{pK_1} \qquad (A-3)$$

At $C_0=0$, (A-3) is transformed into (1).

Ad. 2.

$\overline{n} = \frac{[LH^+]}{[LH^+]+[L]};\quad K_1 = \frac{[H^+][L]}{[LH^+]}$

$\alpha + [LH^+] - [B^-] = 0$

$[LH^+] + [L] = (C_1 + C_0)V_1/(V_1 + V_2)$

$[B^-] = (C_1V_1 + C_2V_2)/(V_1 + V_2)$

$[LH^+] = \overline{n}(C_1 + C_0)V_1/(V_1 + V_2)$

$\alpha + \overline{n}\,(C_1 + C_0)V_1/(V_1 + V_2) = (C_1V_1 + C_2V_2)/(V_1 + V_2)$

At $V_1 = 0:$

$\alpha = C_2$

$\overline{n} = \frac{[H^+]}{[H^+]+K_1}$

$C_2 + \overline{n}(C_1 + C_0)V_1/(V_1 + V_2) = (C_1V_1 + C_2V_2)/(V_1 + V_2)$

$\overline{n} = \frac{C_1-C_2}{C_1+C_0}$

$\frac{[H^+]}{[H^+]+K_1} = \frac{C_1-C_2}{C_1+C_0}$

$[H^+] = K_1\frac{C_1-C_2}{C_0+C_2}$

At $[H^+] \gg [OH^-], \quad \alpha = [H^+] = C_2$

$C_2 = K_1\frac{C_1-C_2}{C_0+C_2}$

$C_1 = C_2 + C_2(C_2 + C_0)10^{pK_1}$

Ad. 3.

$\alpha + [M^+] = [L^-]$

$\alpha + \frac{C_0V_1+C_2V_2}{V_1+V_2} = (1-\overline{n})\frac{C_1V_1+C_0V_1}{V_1+V_2}$

At $V_1 = 0$

$\alpha + C_2 = 0 \rightarrow \alpha = -C_2$

$-C_2 + \frac{C_0V_1+C_2V_2}{V_1+V_2} = (1-\overline{n})\frac{C_1V_1+C_0V_1}{V_1+V_2}$

$[H^+] = K_1\frac{C_1+C_2}{C_0-C_2}$

At $[OH^-] \gg [H^+] \rightarrow \alpha = -[OH^-] = -C_2 \rightarrow [OH^-] = C_2 \rightarrow \frac{K_W}{[H^+]}$

$$= C_2 \rightarrow \frac{K_W}{K_{1i}}\cdot\frac{C_0-C_2}{C_1 + C_2} = C_2$$

$C_0 = C_2 + C_2(C_1 + C_2)(K_1/K_W)$

Ad. 4.

$\alpha + [M^+] + [LH^+] - [B^-] = 0$

$\alpha + \frac{C_2V_2}{V_1+V_2} + \overline{n}\frac{C_1V_1+C_0V_1}{V_1+V_2} - \frac{C_1V_1}{V_1+V_2} = 0$

At $V_1 = 0, \quad \alpha + C_2 = 0 \rightarrow \alpha = -C_2$ and then

$-C_2 + \frac{C_2V_2}{V_1+V_2} + \overline{n}\frac{C_1V_1+C_0V_1}{V_1+V_2} - \frac{C_1V_1}{V_1+V_2} = 0$

$\overline{n} = \frac{C_1+C_2}{C_1+C_0}$

$$\frac{[H^+]}{[H^+] + K_1} = \frac{C_1 + C_2}{C_1 + C_0}$$

$$[H^+] = K_1\frac{C_1 + C_2}{C_0 - C_2}$$

At $[OH^-] \gg [H^+] \rightarrow \alpha = -[OH^{-1}] = -C_2 \rightarrow [OH^-]$

$$= C_2 \rightarrow \frac{K_W}{[H^+]} = C_2 \rightarrow \frac{K_W}{K_1}\frac{C_0-C_2}{C_1 + C_2} = C_2$$

$$C_0 = C_2 + C_2(C_1 + C_2)\cdot\frac{K_1}{K_W}$$

Ad. 5.

$$\alpha = [HSO_4^-] + 2[SO_4^{2-}] + [B^-]$$

$$\alpha = (2-\overline{n})\frac{C_1V_1}{V_1 + V_2} + \frac{C_2V_2}{V_1 + V_2}$$

where:

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

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

at $V_1 = 0 \rightarrow \alpha = C_2$

$(2-\overline{n})\frac{C_1V_1}{V_1+V_2} + \frac{C_2V_2}{V_1+V_2} = C_2$

$\overline{n} = 2 - \frac{C_2}{C_1}$

$\frac{[H^+]}{[H^+]+K_2} = 2 - \frac{C_2}{C_1}$

$[H^+] = K_2\cdot\frac{2C_1-C_2}{C_2-C_1}$

At $[H^+] \gg [OH^-]$ we have $[H^+] = C_2$. Then

$C_1 = C_2\frac{C_2+K_2}{C_2+2K_2}$

Ad. 6.

From analogous calculations, at $\alpha = [H^+] = C_2$ we get the relation

$$C_1 = C_2 + C_2^2/K_2$$

similar to (1).

Ad. 7.

$$\alpha + 2[Ba^{2+}] + [BaOH^+] + [M^+] = 0$$

$$[Ba^{2+}] + [BaOH^+] = \frac{C_1V_1}{V_1 + V_2};\quad [M^+] = \frac{C_2V_2}{V_1 + V_2}$$

Applying the stability constant K_1^{OH} for $BaOH^+$

$$K_1^{OH} = \frac{[BaOH^+]}{[Ba^{2+}][OH^-]}$$

(log $K_1^{OH}=0.7$), we get the relation

$$\alpha + (2-\overline{n})\frac{C_1V_1}{V_1+V_2} + \frac{C_2V_2}{V_1+V_2} = 0$$

where

$$\overline{n} = \frac{[BaOH^+]}{[Ba^{2+}]+[BaOH^+]} = \frac{K_1^{OH}[OH^-]}{1+K_1^{OH}[OH^-]}$$

At $V_1=0$, $\alpha=-C_2$, then

$$\overline{n}=2-\frac{C_2}{C_1}$$

$$[OH^-]=\frac{1}{K_1^{OH}}\frac{2C_1-C_2}{C_2-C_1}$$

At $[OH^-]\gg[H^+]$ we have $[OH^-]=C_2$ and

$$C_1=C_2\frac{C_2+1/K_1^{OH}}{C_2+2/K_1^{OH}}$$

Ad. 8.

$$\alpha+\sum_{i=0}^{4}(2-i)[Zn(OH)_i^{+2-i}]+[M^+]=0$$

$$\sum_{i=0}^{4}[Zn(OH)_i^{+2-i}]=\frac{C_0V_1}{V_1+V_2}$$

$$[M^+]=\frac{C_1V_1+C_2V_2}{V_1+V_2}$$

Applying the notation

$$\overline{n}=\frac{\sum_{i=1}^{4} i[Zn(OH)_i^{+2-i}]}{\sum_{i=0}^{4}[Zn(OH)_i^{+2-i}]}=\frac{\sum_{i=1}^{4} iK_i^{OH}[OH^-]^i}{1+\sum_{i=1}^{4}K_i^{OH}[OH^-]^i}$$

we get

$$\alpha+(2-\overline{n})\frac{C_0V_1}{V_1+V_2}+\frac{C_1V_1+C_2V_2}{V_1+V_2}=0$$

At $[OH^-]\gg[H^+]$, at $V_1=0$, $\alpha=-[OH^-]=-C_2$ and then

$$C_1=C_2-(2-\overline{n}^*)C_0$$

where $\overline{n}^*$ is expressed by Eq. (2).

References

[1] A.G. Asuero, T. Michałowski, Crit. Rev. Anal. Chem. 41 (2011) 151.
[2] T. Michałowski, A.G. Asuero, Crit. Rev. Anal. Chem. 42 (2012) 220.
[3] T. Michałowski, B. Pilarski, A.G. Asuero, A. Dobkowska, Talanta 82 (5) (2010) 1965.
[4] T. Michałowski, B. Pilarski, A.G. Asuero, A. Dobkowska, S. Wybraniec, Talanta 86 (2011) 447.
[5] T. Michałowski, A.G. Asuero, J. Anal. Sci., Methods Instrum. 2 (1) (2012) 1.
[6] S. Arrhenius, Philos. Mag. Ser. 5 27 (166) (1889) 287.
[7] W.D. Bancroft, J. Phys. Chem. 4 (1900) 274.
[8] 〈http://www.encyclopedia.com/topic/Svante_August_Arrhenius.aspx〉.
[9] R. de Levie, J. Electroanal. Chem. 582 (2005) 21.
[10] S.P.L. Sørensen, Biochem. Z. 21 (1909) 131.
[11] T. Michałowski, M. Rymanowski, A. Pietrzyk, J. Chem. Educ. 82 (2005) 470.
[12] 〈http://en.wiktionary.org/wiki/isohydric〉.
[13] J. Janata, Principles of Chemical Sensors, 2nd ed., Springer126 〈http://www.clubedequimica.com.br/PGQ-UFC/mestrado/ref36.PDF〉.
[14] T. Michałowski, Talanta 39 (1992) 1127.
[15] T. Michałowski, E. Gibas, Talanta 41 (1994) 1311.
[16] T. Michałowski, M. Toporek, M. Rymanowski, Talanta 65 (2005) 1241.