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Short communication

Determination of dissociation parameters of weak acids in different media according to the isohydric method

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ABSTRACT

The isohydricity (pH constancy) principle is referred to the pair of solutions: weak acid (HL, C_0 mol/L) and strong acid (HB, C mol/L) when mixed e.g., according to titrimetric mode. Such a case takes place if the relation $C_0 = C + C^2 \times 10^{pK_1}$ is valid, where $pK_1 = -\log K_1$, K_1 – dissociation constant for a weak monoprotic acid HL. This principle, outlined and formulated in earlier paper (Michałowski et al., *Talanta* 82 (2010) 1965), is the basis for a sensitive method of pK_1 determination, confirmed for a series of weak acids in presence of basal electrolytes or in water + organic solvent (dimethyl sulphoxide, methanol, isopropanol) media. The results of titrations were elaborated according to principles of regression analysis, with use of least squares method. A new criterion for precision of the results obtained according to this method is formulated. The pK_1 values obtained are comparable with ones found in literature.

1. Introduction

The term “isohydric” refers to a pair of solutions having the same pH value. The isohydricity concept gained its quantitative utterance in the formulae derived in the paper issued lately [1], where were also stated, that the isohydricity property is limited to the systems where only acid–base equilibria are involved. In other instances, protons are generated/consumed in side (redox, precipitation and/or complexation) reactions. The isohydricity principle can be categorized not only as an interesting curiosity of electrolytic systems, however.

The isohydricity has also some relevance to the buffering action and buffer capacity [2,3], and shows some analogies with pH-stat action and pH-static titration [4,5]. Moreover, it can also be considered as a valuable and sensitive tool for determination/validation/verification of acidity constants ($pK_1 = -\log K_1$) of weak monoprotic acids (HL), where

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

In [1], the isohydricity concept was exemplified by the systems composed of different pairs of mono- or polyprotic acids or their salts. In particular, a weak acid HL (C_0 mol/L) and strong acid HB (C mol/L) form a pair of isohydric solutions, provided that the relation

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

is valid. In this case, pH of the solution obtained after addition of V mL of C mol/L HB (as titrant, T) into V_0 mL of C_0 mol/L HL (as titrand, D) remains constant, irrespectively of V value. Similarly, pH is constant after addition of V mL of C_0 mol/L HL into V_0 mL of C mol/L HB, if C_0 and C are interrelated as in Eq. (2). Moreover, for the pair (HL, HB) of the isohydric solutions, the ionic strength (I_0, mol/L) of the mixture remains unchanged ($I_0 = C$) after mixing the composing solutions at different proportions, particularly when the mixing is carried out according to titrimetric mode, in quasistatic manner, under isothermal conditions; the last requirement is involved with possible changes in K_1 value, resulting from heat effects occurred during the titration. The true (not approximate) constancy inherent in the isohydric systems is a unique property, testifying on account of this method.

The isohydric method is based on preparation of a series of solutions of both acids: weak acid HL (C_{0i}^* mol/L) and strong acid HB (C mol/L), whose concentrations (C_{0i}^*, C) are interrelated in the equality (see Eq. (2))

$$C_{0i}^* = C + C^2 \times 10^{pK_{1i}^*} \quad (i = 1, \ldots, n) \tag{3}$$

where pK_{1i}^* are the pre-assumed numbers, not far from real pK_1 value (Eq. (2)). The n pairs $\{(HL, HB)_i\}$ of the solutions ($i = 1, \ldots, n$) are mixed according to a common pH-metric titration procedure,

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Nomenclature

C	concentration [mol/L] of HB
C_0	concentration [mol/L] of HL
D	titrand (solution titrated)
HB	strong acid
HL	weak acid
K_1	dissociation constant for HL
LS	least squares method
MOH	strong base
$pK_1 = -\log K_1$	acidity parameter
pK_1^*	pre-assumed pK_1-value
S	organic solvent
T	titrant
V	volume [mL] of T
V_0	volume [mL] of D
Z	basal electrolyte

where V mL of C mol/L HB is added (as titrant T), in portions, into V_0 mL of $C_{0i}{}^*$ mol/L HL (considered as titrand, D). 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.

One can also apply another viewpoint, based on simple checking the credibility of pK_1 values, known from literature data. Similarly, one can assume equal concentrations (C_1) of a basal electrolyte MB_r in both solutions mixed: HB (C) + MB_r (C_1) and HL (C_0) + MB_r (C_1); in this case, $I = C + C_1$ for $r = 1$ and $I = C + 3C_1$ for $r = 2$ (e.g., $MgCl_2$). The same procedure can also be applied to the systems with mixed solvents (binary-solvent systems [6]). Both approaches will be applied in the present paper.

As indicated in [6,7], it is advisable to apply to pK_1 the term “acidity parameter” for “acidity constant” when referring to the systems with mixed-solvent media, and binary-solvent media in particular, whose composition can be expressed by mole fraction, x, of the solvent with higher molar mass. Particularly, in binary-solvent media, W + S, composed of water (W = H_2O) and an organic (o) solvent S, we have $x = x_S$ for the mole fraction of S, and $pK_1 = pK_1(x)$. Denoting by $x_{Vo} = V_{(o)}/(V_{(o)} + V)$ the volume fraction of S in binary-solvent medium (W + S) and neglecting the contraction effect, one can calculate

$$x_S = \frac{x_{Vo}}{\chi_{WS} \cdot (1 - x_{Vo}) + x_{Vo}} \tag{4}$$

where [1]

$$\chi_{WS} = \left(\frac{\rho_W}{\rho_S}\right) \cdot \left(\frac{M_S}{M_W}\right) \tag{5}$$

and ρ_X, M_X – density [g/mL] and molar mass [g/mol] of X = W, S.

The pH titrations (T → D) in binary-solvent media were made in D + T systems: HL ($C_{0i}{}^*$, W + S) + HB (C, W + S), where the solvent composition, expressed by x_S value (Eq. (4)), was the same in both solutions mixed. The experiments were made at different x_S values.

2. Experimental

2.1. Apparatus and reagents

The pH titrations were carried out in 30 mL thermostated, self-made measuring cell, fitted with magnetic stirrer and PT 1000 temperature sensor. The temperature was kept at 25.0 ± 0.2 °C by means of the Huber thermostat system. The pH measurements and titrations were performed with Cerko Lab System microtitrator, equipped with syringe pump and pH electrode (Hydromet – ERH-13-6 type and Ionode, IJ44C type). The electrode was standardized with aqueous standard buffers (from Chempur Company). Other preparatory steps were the same as the ones presented in [1]. The experimental points $\{(V_j, pH_j) \mid j = 1,\ldots, N\}$, $N = 200$, were registered in every single titration, made within V-range $\langle 0, 4.0\rangle$ mL; the titrant T was added stepwise, in aliquots of 0.02 mL, with 8 or 10-s pause, into $V_0 = 3.0$ mL of titrand D.

The reagents, of analytical purity grade, were purchased from commercial sources: benzoic acid from Chempur (pure p.a. >99.5%), chloroacetic acid from Fluka (pure p.a. >99%, m.p. 61–62 °C), D,L-mandelic acid from Merck (pure, >99%), salicylic acid from Sigma–Aldrich GmbH (extra pure, 99.5–100.5%). All chemicals were used without further purification. HCl solution was supplied by Chempur.

Background electrolytes were purchased from commercial suppliers and used as received: potassium chloride from POCH S.A. (pure p.a.), sodium chloride from Carl Roth GmbH (≥99.9%), magnesium chloride from Sigma–Aldrich Chemie GmbH (anhydrous, ≥98%, m.p. 714 °C) and potassium nitrate from POCH S.A. (pure p.a.). Sodium carbonate (from Chempur Company) was calcined (220 °C) before standardization of HL and HCl.

Doubly distilled (freshly prepared) water (W), with conductivity not exceeding 0.18 μS/cm, was used. Other solvents (S): methanol (CH_3OH, analytical grade, 99.5%), dimethylsulphoxide ($(CH_3)_2SO$, HPLC grade, 99.5%) were supplied by POCH S.A. 2-Propanol ($(CH_3)_2CHOH$, pure p.a., min. 99,7%) were purchased from Chempur. The mixed solvents, W + S, were prepared by mixing W and S in appropriate proportion, x_{Vo} (% v/v) (Eq. (4)) and cooling in capped flask.

Stock solutions of HL, HCl and other substances were prepared by dissolution of appropriate amounts of the preparations in (a) W or (b) W + S. The HCl and HL stock solutions were standardized by pH titration against Na_2CO_3. The D + T systems:

(a) (HL ($C_{0i}{}^*$) + MB_r (C_1)), (HB (C) + MB_r (C_1)) and
(b) (HL (C_{0i}^*, W + S)), (HB (C, W + S))

were obtained by dilution of the starting reagents in (a) W, or (b) W + S. At given C-value, C_{0i}^* were calculated from Eq. (3).

2.2. Procedures

The procedure applied was similar to one described in [1]. The pH titrations: (a) (HB (C) + MB_r (C_1)) → (HL (C_{0i}^*) + MB_r (C_1)), and (b) (HCl (C, W + S) → HL (C_{0i}^*, W + S)) were made ($i = 1,\ldots, 5$) and the points $\{(V_{ij}, pH_{ij}) \mid j = 1,\ldots, N\}$ ($N = 200$) obtained in i-th titration were approximated by the lines

$$pH = a_i + b_i \cdot V \tag{6}$$

whose parameters: a_i, b_i were determined according to LS method [8,9]. The slopes b_i of the lines (6) are the basis for further considerations. Namely, the collected points (pK_{1i}^*, b_i), $i = 1,\ldots, 5$, are approximated by the straight line

$$b = p + q \cdot pK_1^* \tag{7}$$

whose parameters p, q are determined according to LS method. Then the value

$$pK_1^* = pK_1 = -\frac{p}{q} \tag{8}$$

calculated at the slope $b = 0$, is considered as the evaluation of the true pK_1 value for HL.

In order to confirm this pK_1 value (Eq. (8)), sixth titration was made at $pK_1^* = pK_1$ in Eq. (3). Low (close to zero) value of the slope b, i.e. pH = const within an experimental error, ca. pH ± 0.01, made at $pK_1^* = pK_1$ in pH titration, is the confirmation of the pK_1 value.