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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

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

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

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

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))

$$C^*_{0i} = C + C^2 \times 10^{pK^*_{1i}} \quad (i = 1, \ldots, n) \qquad (3)$$

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,. . ., 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,. . ., 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.

Table 1
The exemplary data referred to the isohydric method of pK_1 determination.

pK^*_{1i}	C^*_{0i}	a_i	b_i	pK^*_{1i}	C^*_{0i}	a_i	b_i
(A) Mandelic acid ($C_{0i}{}^*$ mol/l) + HCl (C = 0.000741 mol/L) + NaCl (C_1 = 0.1 mol/L)				(B) Mandelic acid ($C_{0i}{}^*$ mol/l) + HCl (C = 0.000894 mol/L) + $MgCl_2$ (C1 = 0.05 mol/L)			
3.20	0.00161	3.1409	−0.02651	3.0	0.00169	3.1013	−0.01097
3.45	0.00229	3.0490	−0.00933	3.2	0.00216	3.0393	−0.00077
3.60	0.00293	2.9758	−0.00079	3.4	0.00290	2.9814	0.00308
3.75	0.00383	2.9082	0.00523	3.6	0.00407	2.8711	0.01320
4.00	0.00624	2.7567	0.01692	4.0	0.00888	2.6400	0.03157
3.654	0.00322	2.9344	−0.00058	3.256	0.00234	3.0300	0.00101
$b = -0.19575 + 0.05357$ pK^*_1; pK_1 = 3.654				$b = -0.13371 + 0.04106$ pK^*_1; pK_1 = 3.256			
(C) Salicylic acid ($C_{0i}{}^*$ mol/l) + HCl (C = 0.001025 mol/L) in $H_2O + (CH_3)_2CHOH$ (20%, v/v)				(D) Salicylic acid ($C_{0i}{}^*$ mol/l) + HCl (C = 0.00110 mol/L) in $H_2O + (CH_3)_2CHOH$ (50%, v/v)			
2.8	0.00169	3.0830	−0.02269	3.6	0.00592	3.2954	−0.04081
3.0	0.00208	3.0304	−0.01513	3.84	0.00949	3.1540	−0.02008
3.2	0.00269	2.9684	−0.00049	4.0	0.0132	3.0752	−0.0109
3.4	0.00312	2.9026	0.00598	4.2	0.02028	2.9520	0.00764
3.6	0.00521	2.7798	0.01953	4.5	0.03936	2.8187	0.01759
3.248	0.00289	2.9570	−0.00111	4.168	0.01895	2.9720	0.00142
$b = -0.17142 + 0.05277$ pK^*_1; pK_1 = 3.248				$b = -0.27542 + 0.06607$ pK^*_1; pK_1 = 4.168			

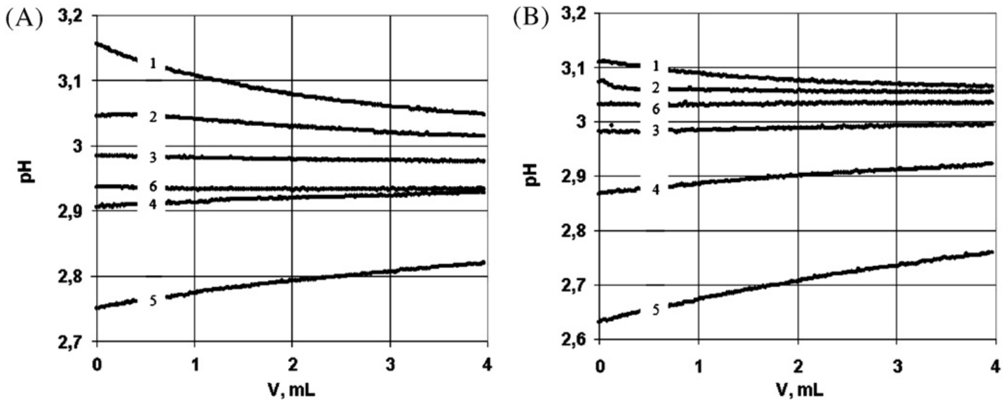

Fig. 1. The points $\{(V_j, \text{pH}_j) \mid j = 1,\ldots, 200\}$ plotted for HL = mandelic acid in presence of (A) C_1 = 0.1 mol/L NaCl; (B) C_1 = 0.05 mol/L $MgCl_2$ in D and T; C, pK^*_1 and C^*_0 values are indicated in Table 1, parts (A) and (B).

Such a procedure was applied for T → D titrations made in the D + T systems of (a) and (b) type, with different MB_r or S.

3. Results and discussion

The principle of the isohydric method [1] is presented in Fig. 1, where the titration curves were plotted at different sets (C, C^*_{0i}) of concentrations for HCl and HL = mandelic acid, respectively. The results (a_i, b_i) obtained from n = 5 titrations (Tables 1 and 2) with use of Eq. (6) gave the set of points (pK_{1i}, b_i) approximated by the straight line (Eq. (7)) and "true" pK_1 value was evaluated on the basis of Eq. (8). For mandelic acid and other acids HL (specified in Tables 1 and 2) as well, the sixth (checking) titration was carried out, at C applied previously in the related series for HCl and C_{06} calculated from Eq. (3) at i = 6 and pK^*_1 = pK_1 obtained from Eq. (8). The plots of the relationships given by Eq. (7) indicated

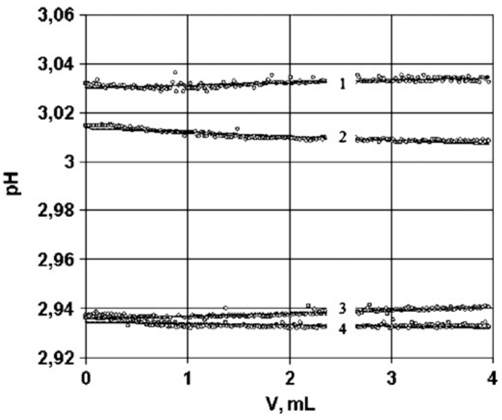

Fig. 2. The points $\{(V_j, \text{pH}_j) \mid j = 1,\ldots, 200\}$ and approximating lines pH = $a_6 + b_6 \cdot V$ plotted at V_0 = 3.000 mL for HL = mandelic acid, in presence of basal electrolyte (Z) in D and T: (1) $MgCl_2$ (C_1 = 0.05); (2) KCl (C_1 = 0.5); (3) KNO_3 (C_1 = 0.1); NaCl (C_1 = 0.1); for further details, see Table 2.

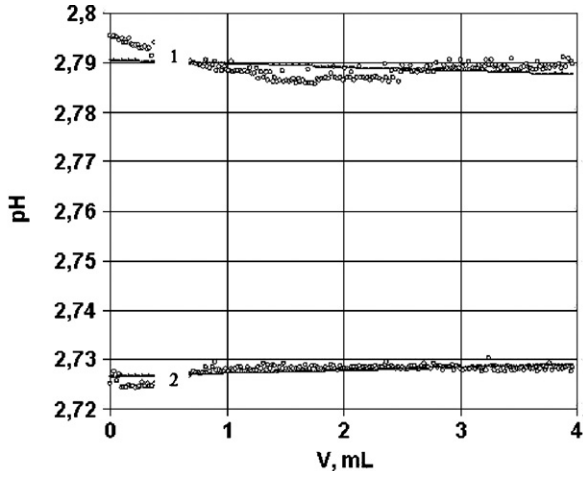

Fig. 3. The points $\{(V_j, \text{pH}_j) \mid j = 1,\ldots, 200\}$ and approximating lines pH = $a_6 + b_6 \cdot V$ plotted HL = mandelic acid in binary-solvent system (H_2O, CH_3OH) in D and T at: (1) 20% (v/v) (x_S = 0.123); (2) 50% (v/v) (x_S = 0.359) CH_3OH. For further details, see Table 2.

Table 2
Collected data for indicated acids in different media and compared with ones found in literature.

1 Acid, HL	2 Z (C_1, mol/L)	3 S (x_{Vs})	4 C (mol/L)	5 C^*_{06} (mol/L)	6 a_6	7 b_6	8 pK_1 [this paper]	9 pK_1 [6]^a	10 pK_1 [literature data]
Mandelic	$MgCl_2$ (0.05)	–	0.000894	0.00234	3.0300	0.0010	3.257 ± 0.002	3.48	3.37 [10], 3.40 [12–14], 3.41 [15,19], 3.85 [20,23]
	KCl (0.5)	–	0.000850	0.00289	3.0135	−0.0017	3.465 ± 0.003		
	KNO_3 (0.1)	–	0.00106	0.00424	2.9356	0.0012	3.457 ± 0.002		
	NaCl (0.1)	–	0.000741	0.00322	2.9344	−0.0006	3.654 ± 0.001		
	–	CH_3OH (0.2)	0.00142	0.01744	2.7905	−0.0007	3.905 ± 0.001	3.79	–
	–	CH_3OH (0.5)	0.00134	0.05774	2.7266	0.00062	4.505 ± 0.001	4.48	5.53 [10]
Salicylic	KCl (0.1)	–	0.000941	0.00175	3.0322	0.00007	2.9699 ± 0.0001	2.97–3.0	2.96 [10,11,25]
	KCl (1.0)	–	0.00114	0.00235	2.8616	0.0018	2.971 ± 0.004		
	KNO_3 (0.1)	–	0.00106	0.00212	2.9475	−0.0016	2.975 ± 0.003		
	–	$(CH_3)_2CHOH$ (0.2)	0.001025	0.00289	2.9570	−0.0011	3.248 ± 0.002	–	–
	–	$(CH_3)_2CHOH$ (0.5)	0.00110	0.01895	2.9720	0.0014	4.168 ± 0.003	–	–
Glycolic	KCl (0.5)	–	0.00085	0.00563	2.9881	0.0014	3.825 ± 0.003	3.815	3.79 [10], 3.83 [20,22], 3.831 [18]
	KCl (1.0)	–	0.00114	0.00961	2.8662	0.00016	3.812 ± 0.003		
Chloroacetic	KCl (0.1)	–	0.00114	0.00208	2.8678	−0.0016	2.861 ± 0.003	2.87	2.82 [21], 2.85 [16,20], 2.86 [17], 2.87 [24], 2.91 [10]
Benzoic	–	$(CH_3)_2SO$ (0.2)	0.00091	0.04270	3.0033	0.0010	4.693 ± 0.002	4.70	–

[a] Unpublished Cerko data, obtained from our previous research; results cited from [10] were computed, not found there in explicit form.

nearly horizontal (parallel to V-axis) course (small b_6 values) for the acids tested – at all concentrations of the basal electrolytes (Z) applied (Fig. 2; Table 2), and for all binary systems considered (Fig. 3; Tables 1 and 2). All these facts testify very well on account of validity of the method proposed. The results obtained for pK_1 are in good accordance with ones found in the literature or in our earlier paper [1], and unpublished data obtained in Cerko laboratory (Table 2). The values in column 9 are related to aqueous solutions, and absence of basal salt (Z).

The slope b_6 of the line obtained in the $n+1=6$th titration, at $C^*_{06} = C + C^2 \cdot 10^{pK_1}$ provides a simple criterion for precision of the pK_1 value calculated from Eq. (8), on the basis of results obtained from $n=5$ titrations. Referring to line pH = pH(V) = $a_6 + b_6 \cdot V$ (Eq. (6)), approximating the results of titrations covering the V-interval $\langle 0, 4 \rangle$ (see Fig. 1), one can write: $\text{pH}(0) = a_6 + b_6 \cdot 0$, $\text{pH}(4) = a_6 + b_6 \cdot 4$, $\delta\text{pH} = |\text{pH}\ (4) - \text{pH}\ (0)| = 4|b_6|$. The indeterminacy δpK_1 in pK_1 value can be assumed (arbitrarily) as $\delta pK_1 = \delta pH/2 = 2|b_6|$. For example, in Table 1 (section D) we have $b_6 = 0.00142$; then $\delta pK_1 = 0.00284 \approx 0.003$, and $pK_1 = 4.168 \pm 0.003$. The $2|b_6|$ values are small (see Tables 1 and 2), i.e. the precision δpK_1 thus calculated is good. However, the difference in the slope (and then in parallelism of the related curve) obtained from titrations made at C^*_{06}, calculated for pK_1 equal 4.168 and 4.171 or 4.165, is practically indistinguishable. Small δpK_1 value testifies in favor of high sensitivity of the method.

4. Final remarks

The isohydricity principle provides a new, sensitive method of pK_1 evaluation. This method, applied previously [1] to mixtures of pure ($C_1 = 0$) solutions of strong (HB) and weak (HL) monoprotic acids, has been extended in this paper on the systems containing a basal electrolyte, present at equal concentration (C_1) in titrand (D) and titrant (T). The second extension is the application of this principle to binary-solvent systems. The results obtained in both kinds of systems confirmed a high sensitivity of this method.

This way, the effect of ionic strength (I) on pK_1 value was stated. The special validity of this method results from the unique property of true (not approximate) ionic strength constancy during the titration; $I = C + C_1$ for D + T systems with MB (e.g. NaCl, KCl, KNO_3), and $I = C + 3 \cdot C_1$ for D + T systems with $MgCl_2$ (C_1 mol/L).

The method proposed can also be applied for preliminary checking the pK_1 value, found in literature for an acid HL. A horizontal course of the line obtained from single pH titration, plotted for the pair of solutions (HB, HL) at concentrations (C, C_0) resulting from Eq. (2), testifies on account of validity of the pK_1 value for this acid. Otherwise, the non-parallel course of the line testifies against this opinion. The degree of parallelism is considered there within the tolerance limits pre-assumed for accuracy of pH-measurements; if pH varies within the limits pH ± 0.01 in the whole V-range covered by titration curve, the opinion on parallelism is admitted. Such experiments can be done at any ionic strength, resulting from presence of a basal electrolyte. This procedure can also be applied in mixed-solvent media. In all instances, the C_1 and then ionic strength (I) values are limited by solubility of the basal electrolyte in the solvent considered.

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