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Modelling of acid–base equilibria in binary-solvent systems: A comparative study

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ABSTRACT

A new approach to modelling of some binary (hydro-organic, $HL/H_2O + B$) acid–base systems with organic co-solvent B fully miscible with water, is suggested and applied for the determination of acidity parameters pK for some weak acids HL. The models are designed to get the $pK = pK(x)$ relationships (x—mole fraction of B in $H_2O + B$) from results of pH titrations made in such systems and for the determination of $pK_B = pK(1)$ for HL in pure B. The Redlich–Kister equation, together with its asymmetric extensions, and the Legendre functions with orthogonal polynomials, appeared to be suitable for such purposes.

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1. Introduction

Composition of mobile phase strongly affects chromatographic retention and electrophoretic migration of substances appearing acid–base behaviour [1]. The satisfactory knowledge of an effect of mobile phase composition on acid–base properties of solutes is therefore essential for analytical procedures applied in optimizing of the separation techniques. It enables to predict and optimize the influence of pH on selectivity and retention in reversed-phase liquid chromatography (RP-HPLC), especially in the gradient elution technique applied for the separation of ionizable compounds.

We focus our attention on binary-solvent hydro-organic systems, whose composition is expressed by the mole fraction $x = x_B$ of organic co-solvent B. Denoting the numbers of moles of $A = H_2O$ and B in a solvent system by n_A and n_B, we have:

$$x = \frac{n_B}{n_A + n_B} \tag{1}$$

Acid–base properties of a weak monoprotic acid HL in aqueous solutions is expressed by its dissociation constant K, usually represented by $pK = -\log K$ value. In binary-solvent media, the pK value depends on x-value, $pK = pK(x)$, and changes when the solvent composition is varied, e.g. during the gradient elution. For this purpose, pK is termed as the acidity parameter [2] or as apparent acid dissociation constant [3] for HL. In further parts of the paper, pK will be referred to K expressed in terms of concentrations, i.e. $K = [H^+][L^-]/[HL] = [H^+]^2/(C-[H^+])$ for C mol L^{-1} HL.

pH measurements made for HL solutions in pure B and in close vicinity of $x = 1$ are not repeatable, and then the $pK = pK_B$ value, calculated from the formula

$$pK = 2pH + \log(C - 10^{-pH}) \tag{2}$$

on the basis of a single pH measurement is doubtful. On the other hand, the results obtained for lower x assume firm values. Application of a regression equation that fits very well within the predominant part of experimental points obtained from pH titration, provides repeatable results for $pK_B = pK(1)$, also when the doubtful points (V_j, pH_j) from the immediate vicinity of $x = 1$ are included in the set of points taken for calculations, realised according to the least squares method. In other words, the approximating function firmly fastened in the predominant part of experimental points withstands the perturbations of the part of doubtful points; this approach has been assumed in this paper. The HL/A+B system, with HL introduced into binary-solvent system A+B, can be obtained by mixing two solutions of HL in pure solvents; the solutions will be denoted later as HL/A and HL/B, respectively. The mixing will be made according to potentiometric titration mode, with pH registration. In order to cover the whole x interval [0, 1], the initial solutions should be titrated mutually: HL/A → HL/B and HL/B → HL/A. The two titrations will be denoted briefly as HL/A ⇔ HL/B titration.

Except potentiometry and absorption spectrophotometry, as the well-established currently applied methods for pK determination

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Nomenclature

Nomenclature

$A = H_2O$, B	organic co-solvent
C	concentration [mol L^{-1}] of HL in T and D
D	titrand (solution titrated)
HL	weak acid (solute)
HL/B	solution of HL in B
HL/A	aqueous solution of HL
LOP	Legendre function with orthogonal polynomials
M–S	Myers–Scott equation
p*K*	–log *K* acidity parameter
R–K	Redlich–Kister equation
T	titrant
V	volume [mL] of T
V_0	volume [mL] of D
x	mole fraction of B in the binary-solvent system A + B

[4–6], other techniques such as cyclic voltammetry [7], coulometry [8], NMR [9], HPLC [10] and capillary electrophoresis [11–13], appeared to be also applicable for such purposes.

For modelling purposes, designed to get the $pK = pK(x)$ relationships and pK_B values ($pK_A = pK(0)$ is determined incidentally), the principle of excess functions is applied.

2. Excess functions and their implications

Non-ideal behaviour of real solutions, formed of two miscible solvents: $A = H_2O$ and organic co-solvent B, whose content is defined by x-value (Eq. (1)), can be expressed in terms of functions $y^E = y^E(x)$, referred to different excess variables [14], of physicochemical or physical nature: excess molar volume ($V^E = V^E(x)$) [15,16], excess molar enthalpy ($\Delta H^E = \Delta H^E(x)$) [17], excess molar free enthalpy ($\Delta G^E = \Delta G^E(x)$) [18] and many other excess properties, referred to surface tension, viscosity, speed of sound, refractive index, etc. The excess molar free enthalpy

$$\Delta G^E = \Delta G - \Delta G_{id} \tag{3}$$

expresses the deviation of the standard (s) free enthalpy (Gibbs function), $\Delta G = \Delta G^s$, from its ideal value:

$$\Delta G_{id} = \Delta G_{id}(x) = (1-x)\Delta G_A + x\Delta G_B \tag{4}$$

In other words, ΔG^E reflects the joint effect of solute–solute, solute–solvent, and solvent–solvent interactions [19–21]. The ΔG interrelates with p*K* in the relation:

$$\Delta G = b\,pK, \text{ i.e. } \quad \Delta G(x) = b\,pK(x) \tag{5}$$

where

$$b = RT \ln 10 \tag{6}$$

Then we get:

$$\begin{aligned} \Delta G(0) &= \Delta G_A = b\,pK(0) = b\,pK_A \text{ and } \Delta G(1) = \Delta G_B \\ &= b\,pK(1) = b\,pK_B \\ \Delta G^E(0) &= \Delta G(0) - \Delta G_{id}(0) = b(pK(0) - pK_{id}(0)) = 0 \\ \Delta G^E(1) &= \Delta G(1) - \Delta G_{id}(1) = b(pK(1) - pK_{id}(1)) = 0 \end{aligned} \tag{7}$$

$$pK(x) = (1-x)pK_A + xpK_B + \frac{1}{b}\,\Delta G^E(x) \tag{8}$$

In this paper, some approximating functions for $\Delta G^E(x)$ are applied for modelling the $pK = pK(x)$ relationships referred to different acid–base HL/A+B systems, tested experimentally according to pH titration, made in thermostated systems (isothermal titration). The functions applied here are as follows: (a) the function derived [22] from the empirical Redlich–Kister (R–K) [23,24] equation, together with its asymmetric versions, suggested by (b) Myers and Scott [25] (M–S) and (c) Michałowski and co-workers [22], where a hyperbolic transformation of x is applied. Moreover, (d) the Legendre function with orthogonal polynomials is applied; the latter function has been used hitherto only for modelling the V^E vs. x relationship, $V^E = V^E(x)$ [26,27]. In this paper, however, a growth in C value during the titration, $C = C(x)$, occurred as a result of contraction of mixed solutions, is neglected when compared with an error resulting from uncertainty $\Delta pH = 0.02$ in common pH titrations [22]. In other words, $C(x) = C = \text{const}$ is assumed in $HL/H_2O + B$ systems thus formed. At $C = 0.01$ mol L^{-1} HL, the inequality $x_{HL} \ll x_{H_2O} + x_B$, referred to mole fractions of HL, H_2O and B respectively, is valid. This way, one can assume that the densities of the solutions HL/A and HL/B are equal to densities ρ_A and ρ_B [g/mL] of the corresponding solvents A and B.

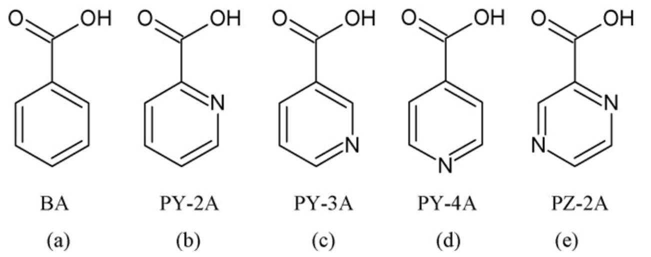

Fig. 1. The acids (HL) tested: (a) BA, (b), PY-2CA, (c) PY-3CA, (d) PY-4CA, and (e) PZ-2CA.

In this paper, the experimental data $\{(V_j, pH_j)\,|\,j = 1, \ldots, N\}$, were obtained from pH titration $HL/B \Leftrightarrow HL/H_2O$, with C mol L^{-1} HL in both solutions: HL/H_2O and HL/B, i.e. $C(0) = C(1) = C$.

Benzoic acid (abbr. BA) and a series of heterocyclic compounds: pyridine-2-carboxylic acid (picolinic acid, PY-2A), pyridine-3-carboxylic acid (nicotinic acid, niacin, vitamin B_3, PY-3A), pyridine-4-carboxylic acid (isonicotinic acid, PY-4A), and pyrazine-2-carboxylic acid (PZ-2A) (Fig. 1) as weak acids (HL) in different hydro-organic media: $H_2O + MeOH$, $H_2O + Me_2SO$ ($Me \equiv CH_3$) are applied in the titration, where V mL of titrant (T) was added dropwise into V_0 mL of titrand (D)

To recalculate V and V_0 on x-values, the formulae:

$$(1^\circ)\; x = \frac{V}{\chi V_0 + V} \text{ valid for titration } HL/B \rightarrow HL/A, \text{ or}$$

$$(2^\circ)\; x = \frac{V_0}{\chi V + V_0} \text{ valid for titration } HL/A \rightarrow HL/B$$

are applied, where $A = H_2O$, $\chi = (\rho_A/\rho_B)\cdot(M_B/M_A)$; M_A, M_B—molar masses [g/mol] of A and B. Particularly, $\chi = 2.2431$ for $H_2O + CH_3OH$ system, and $\chi = 3.9293$ for $H_2O + (CH_3)_2SO$ system of solvents [22].

3. Modelling the functions $pK = pK(x)$

3.1. Some earlier approaches

An effect of the solvent composition on p*K* value was considered in numerous papers issued recently, e.g. [28–31]. In all instances, acid–base titrations in mixed-solvent media were performed in the titrand (D) and titrant (T) systems (D + T systems), containing the same proportion of the solvent components (A and B), sometimes in the presence of a basal (background) salt securing approximately constant ionic strength value [30]. The linear relationship $pK = a_0 + a_1 x$ has been reported in a majority of earlier papers, e.g. [32–34], related to the determination of p*K* in binary-solvent systems. However, some reports [35,36] testify on account of non-linear relationships between the related variables.

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