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LETTERS TO THE EDITOR

Limit of Concentration Constant of Protolytic Equilibrium

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Dissociation of a weak acid HA occurs as follows

$$\mathrm{AH} \rightleftarrows \mathrm{A}^- + \mathrm{H}^+,$$

its thermodynamic equilibrium constant being expressed in terms of activities of the reactants:

$$K_a^{\mathrm{T}} = a_{\mathrm{A}^-} a_{\mathrm{H}^+}/a_{\mathrm{HA}}.$$

Generally, experimental methods allow determining either the concentration constant K_a^{C} expressed via the equilibrium concentrations of the reactants or the apparent constant K_a^m expressed via the lyonium ion activity a_{H^+} and equilibrium concentrations of other reactants. In order to recalculate the thermodynamic constant from K_a^{C} or K_a^m, various approximations and corrections related to ionic strength are used (the Debye–Hückel equation, the Davies equation, the Stokes–Robinson equation, etc) [1–3]. The solution is normally considered close to the ideal one at low ionic strength (I < 0.01 mol/L), and the intermolecular interactions are neglected for [1, 4]. In such a case, the activity coefficients of the ionic species are close to unity, and hence $K_a^{\mathrm{C}} = K_a^{\mathrm{T}}$.

Analysis of the referenced values of thermodynamic dissociation constants of weak acids and bases, including biologically important organic compounds, revealed that in some cases significantly different values have been reported as determined independently by different research groups [5, 6].

One of possible sources of the observed deviations is nonzero ionic strength of the studied solutions. Extrapolation of the dissociation constants determined at varied ionic strength to $I = 0$ gives the K_a^{T} values [7, 8]. Herein we report a novel facile route to determine the thermodynamic dissociation constant from spectrophotometric measurements in the binary system (weak electrolyte – solvent) by extrapolating the measured K_a^{C} values to infinite dilution. The experiments were performed at the electrolyte concentration of 10^{-5}–10^{-2} mol/L in order to eliminate the effects caused by presence of carbonic acid in the solution.

We demonstrated that the measured K_a^{C} value was a function of the electrolyte concentration at 10^{-5}–10^{-2} mol/L, and therefore the thermodynamic constant K_a^{T} could be found by extrapolation of $K^{\mathrm{C}} = f(c)$ to $c = 0$ [9]. In particular, we used the parabolic fitting function

$$K^{\mathrm{C}} = K_a^{\mathrm{T}} + bc + qc^2,$$

where K^{C} being the dissociation constant measured at the electrolyte molar concentration of c, parameters; b and q were determined by the least squares method. The experimental value of dissociation constant $K^{\exp}$ was calculated using the general equation

$$K^{\exp} = \alpha^2 c/(1 - \alpha),$$

and the dissociation degree was in turn derived from the spectrophotometric measurements using the Beer–Lambert law:

$$\alpha = (\varepsilon - \varepsilon_{\mathrm{AH}})/(\varepsilon_{\mathrm{A}^-} - \varepsilon_{\mathrm{AH}}),$$

where ε, absorptivity of a studied mixture of the neutral molecule HA and the anion A^-; $\varepsilon_{\mathrm{A}^-}$, the anion absorptivity; and $\varepsilon_{\mathrm{AH}}$, neutral acid molecule absorptivity.

The following acids were studied: benzoic, phenoxyacetic, acetic, propionic, and picric. The acids dissociation was studied in deionized water, aqueous isopropanol, acetone, and ethyl acetate. Absorptivity of the purely neutral and the completely ionized forms of the acids were determined by measurements of the acids solutions in 0.1 mol/L of HCl and in 0.1 mol/L of NaOH, respectively. The absorption spectra were recorded using the UV-1800 spectrophotometer (Shimadzu).

The so determined pK_a^T (water, 25°C) were of 4.18 (4.20 [10]) (benzoic acid), 3.17 (3.17 [10]) (phenoxyacetic acid), 4.63 (4.76 [10]) (acetic acid), and 4.66 (4.87 [10]) (propionic acid). The dissociation constants in binary and nonaqueous solvents could be determined similarly; for example, 5.53 (6.04 [11]) (benzoic acid in 1 : 1 water–isopropanol), 6.11 (6.3, 7.81, and 9.26 [12]) (picric acid in acetone), and 4.79 (picric acid in ethyl acetate).

To conclude, spectrophotometric investigation of solutions of weak acids in water as well as in binary and organic solvents revealed definite concentration dependence of the measured dissociation constant K_a^C at 10^{-5}–10^{-2} mol/L of the electrolyte. The observed dependence allowed extrapolation of the measured values to zero ionic strength and hence determining of the thermodynamic dissociation constant. The proposed method is very simple and fast; moreover, it is applicable in the cases of solutions with undefined activity of the lyonium ion activity.

REFERENCES

1. *Nauchnoe nasledie N.A. Izmailova i aktual'nye problemy fizicheskoi khimii* (The Scientific Legacy of N.A. Izmailov and Current Problems of Physical Chemistry), Lebed', V.I., Mchedlov-Petrosyan, N.O., and Kholin, Yu.V., Eds., Kharkov: Karkov. Nauch. Univ. im. V.N. Karazina, 2007, p. 227.
2. Tanganov, B.B., *Vzaimodeistviya v rastvorakh elektrolitov: modelirovanie sol'vatatsionnykh protsessov, ravnovesij v rastvorakh polielektrolitov i matematicheskoe prognozirovanie svoistv khimicheskih system* (Interaction in Electrolyte Solutions: Modeling Solvation Processes, Equilibria in Solutions of Polyelectrolytes and Mathematical Prediction of the Properties of Chemical Systems), Moscow: Akademiya Estestvoznaniya, 2009.
3. Beits, R., *Opredelenie pH* (pH Determination), Leningrad: Khimiya, 1972.
4. Izmailov, N.A., *Elektrokhimiya rastvorov* (Electrochemistry of Solutions), Kharkov: Karkov. Nauch. Univ. im. V.N. Karazina, 1976.
5. Erdemgil, F.Z., Sanli, S., Sanli, N., Oezkan, G., Barbosa, J., Guiteras, J., Beltran, J.L., *Talanta*, 2007, vol. 72, no. 2, p. 489. DOI: 10.1016/j.talanta.2006.11.007.
6. Babic, S., Horvat Alka, J.M., Pavlovic, D.M., and Kastelan-Macan, M., *Trends Analyt. Chem.*, 2007, vol. 26, no. 11, p. 1043. DOI: 10.1016/j.trac.2007.09.004.
7. Jerez, G., Kaufman, G., Prystai, M., Schenkeveld, S., and Donkor, K.K., *J. Sep. Sci.*, 2009, vol. 32, p. 1087. DOI: 10.1002/jssc.200800482.
8. Meloun, M., Ferencikova, Z., Malkova, H., and Pekarek, T., *Cent. Eur. J. Chem.*, 2012, vol. 10, no. 2, p. 338. DOI: 10.2478/s11532-011-0150-3.
9. Porshnev, S.V. and Belenkova, I.V., *Chislennye metody na baze Mathcad* (Numerical Methods based on the Mathcad), St. Petersburg: BHV-Peterburg, 2005.
10. *Langes Handbook of Chemistry*, Dean, J.A., Ed., New York: McGraw-Hill, 1999. Sect. 8, p. 24.
11. Bosch, E., Rafols, C., and Roses, M., *Analyt. Chim. Acta*, 1995, vol. 302, p. 109. DOI: 10.1016/0003-2670(94)00435-O.
12. Izutsu, K., *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents. IUPAC*, Oxford: Blackwell Scientific Publications, 1990.