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Study of Acid-Base Properties of Weak Electrolytes by Conductometric Titration

A. V. Selitrenikov[a] **and Yu. E. Zevatskii**[a–c]

[a] *Novbytkhim, ul. Zheleznodorozhnaya 45, Gatchina, 188300 Russia*
e-mail: selitrenikov@newchem.ru
[b] *St. Petersburg State University of Technology and Design, St. Petersburg, Russia*
[c] *St. Petersburg State Electrotechnical University, St. Petersburg, Russia*

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Abstract—Processing of nonlinear conductometric titration curves of aqueous solutions of weak electrolytes ($\sim 10^{-4}$ mol/L) has been developed, accounting for dissociation of water and describing the established protolytic equilibriums involving dissolved carbon dioxide. By the nonlinear regression analysis dissociation constants of phenol, aniline, and other weak acids and bases were obtained.

Keywords: conductometric titration, weak acid, weak base, dissociation constant

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Conductometry is a well-recognized method to accurately determine dissociation constants of weak electrolytes in aqueous medium [1]; it has been most often used in a direct conductometry version, measurement of specific conductance of a series of binary aqueous solutions of an acid or a base [2].

Application of this method is seriously limited in the case of weak ($pK_a > 7$) acids, their dissociation degree being too low to be accurately measured and being additionally suppressed by inescapable presence of traces of the stronger carbonic acid in the solution. Therefore, accurate measurements are only possible at quite high concentration of the analyte (>0.01 mol/L) [3], but this is not always possible due to the limited solubility of weak electrolytes; additional measurements are often required to account for the changed viscosity of the solution [4]. Similar reasons limit the application of direct conductometry to study weak bases.

Determination of the weak electrolyte dissociation constant from the data on hydrolysis of its salt has been considered more convenient. For instance, the study of a series of weak acid solutions in the presence of strong base allows adjustment of the weak electrolyte dissociation degree. The studied solutions can be either prepared independently or produced in the course of conductometric titration [3, 5]. The method was described in [4, 6, 7]; however it has not been widely accepted due to the sensitivity to the presence of traces of carbon dioxide and strong electrolytes.

Another drawback of direct conductometry arises from the complexity of the experimental data processing. In particular, specific conductance L (μS/cm) is represented as a sum of the contributions from individual ions [Eq. (1)].

$$L = 1000\Lambda c = \sum_{i=1}^{n} |z_i| c_i \lambda_i, \qquad (1)$$

where Λ (S cm^2 mol^{-1}) being observed molar conductance of the electrolyte; c (mol/L) being its concentration; z_i, c_i, and λ_i being charge, concentration, and ionic conductance (mobility) of the i type of the ions present in the solution, respectively; the summation runs over all the charged species types. The ions concentrations c_i are expressed via the electrolyte concentration and the corresponding dissociation constants using the equations of material balance and electric neutrality. The ions mobility λ_i at the modern level of theory of solutions conductance is represented via a power series of ionic strength I [Eq. (2)].

$$\lambda_i = \lambda_i^0 - S_i\sqrt{I} + E_i I \ln I + J_{1i} I - J_{2i} I^{3/2}, \; I = \sum_{i=1}^{n} z_i^2 c_i. \qquad (2)$$

The S_i, E_i, J_{1i}, and J_{2i} parameters are sophisticated functions of many parameters; they can be calculated according to the Quint–Viallard, Lee–Wheaton, and other approximations [8]. Description of experimental curves of conductometric titration leads to a substantial complication of the above-given equations when considering an asymmetric electrolyte instead of a symmetric one [9], a multi-base acid instead of a single-base one [10], and a mixture of electrolytes instead an individual substance [11, 12]. Dissociation constants of the studied electrolytes are determined via joint solution of material balance equations and Eqs. (2) by means of nonlinear regression, using experimental data for solutions of varied concentration. Complexity of the data processing requires additional measurements to be done; for example, the limiting ionic conductance λ_i^0 of the weak acid anion is often determined using conductometric data for the corresponding salts [2].

Direct conductometric measurements are usually performed for the solutions containing 5×10^{-5} to 10^{-1} mol/L of the studied compound, free of any buffer additives [2, 8]; therefore, ionic strength of the sample varies in several orders of magnitude along the experimental series. Hence, dissociation constants should be expressed in terms of activities in the material balance equations, further complicating the data processing [3].

Conductometric titration is routinely used in analytical applications, and the equivalence point is found as intersection of the linear parts of the titration curves [13]. It was noted that the shape of nonlinear parts of the curve obtained during titration of a weak acid with alkali depends, among other factors, on the titrated acid strength [14]; however, the nonlinear parts of the curves have been regarded as practically not important so far, due to the complexity of the data analysis. Rare examples of application of conductometric titration to determine the ionization constants are based on empirical and semi-empirical functions [15–17]. Thus, conventional conductometric analysis of weak electrolytes is possible at their concentration of at least $\sim 10^{-3}$ mol/L; the titration curves become nonlinear in more diluted solutions due to hydrolysis.

At the same time, the conductometric titration at low ($<10^{-4}$ mol/L) concentration of the reactants has several advantages:

(1) conductance Eqs. (2) show that at sufficiently low ionic strength I the contribution of all the terms but the first one into the ionic conductivity λ_i drops below the experimental error, and they can be hence neglected; in this case Eqs. (2) are transformed into Eqs. (3) in accordance with the Arrhenius hypothesis of independent mobility of the ions that significantly simplifies the data processing;

$$\lambda_i = \lambda_i^0 \equiv \mathrm{const}I. \quad (3)$$

(2) ionic strength of the studied solutions is low and does not change much during the titration; therefore, the activity coefficients can be neglected, and the material balance equations can be written using the concentration constants;

(3) application of weakly alkaline medium in the case of weak acids ($\mathrm{p}K_\mathrm{a} > 6$) and weakly acidic medium in the case of weak bases ($\mathrm{p}K_\mathrm{b} > 6$) allows adjustment of their dissociation degree;

(4) in the cases of acids and bases of intermediate strength the conductometric titration allows for direct conductometry of the acid (base) and the corresponding salt in a single experiment; of course, in the cases of stronger acids and bases ($\mathrm{p}K_\mathrm{a} < 3$ or $\mathrm{p}K_\mathrm{b} < 3$) that dissociate almost completely, the dissociation constant is determined with worse accuracy;

(5) at a low concentration of the studied compounds the contribution of various side processes (neutral molecules dimerization or ionic association) is suppressed, especially in nonaqueous media [18];

(6) the contribution of inactive ions in the specific conductance of the solution does not exceed 50%, that means that differential methods of conductivity measurements are not required, in contrast to the case of large excess of background electrolytes [19].

One of the variations of the above-described method is a recently developed procedure to analyze acidic admixtures in rainwater at $\sim 10^{-5}$ mol/L [20]; according to the procedure, the nonlinear conductometric titration curves are processed by means of nonlinear regression.

This work aimed to develop a convenient method to investigate acid-base properties of weak electrolytes via conductometric titration at low concentration of the reactants. As conductometric measurements are sensitive to the presence of carbon dioxide in water, the data processing should account for the corresponding protolytic equilibria. To do so, carbon dioxide concentration was maintained constant during the experiment; it was then determined among other unknown parameters as described elsewhere [21].

Weak monobase acids. To investigate dissociation of weak acids, we used the data of titration of dilute solution of sodium carbonate with a solution of the studied acid (HA). Sodium carbonate is a convenient weakly basic agent as its composition is constant, and it can be stored for a long time without decomposition under dry atmosphere, whereas sodium hydroxide inevitably contains unknown amounts of other carbonates and moisture. At concentration of ~10^{-5} mol/L sodium carbonate is hydrolyzed to more than 90%, and its aqueous solutions have pH of about 9. That allows significant enhancement of the dissociation degree of acids weaker than carbonic acid as compared to their solution in deionized water frequently used for conductometric measurements ($L \approx 0.2$ μS/cm, pH ≈ 6.3 due to dissolved CO_2 at ~10^{-6} mol/L).

The titration resulted in N pairs of experimental values of specific conductance (L_j) and the corresponding concentration of the added acid (c_j). Then the dissociation constant K_a of the HA acid and its anion mobility λ_{A^-} was found assuming validity of the Arrhenius approximation [Eq. (3)].

The following equilibria were accounted for in the material balance Eqs. (4).

$$\begin{gathered} HA \rightleftarrows H^+ + A^- \quad K_a = [H^+]\frac{\alpha}{1-\alpha}, \\ H_2CO_3 \rightleftarrows HCO_3^- + H^+ \rightleftarrows H_2CO_3 + 2H^+, \\ K_{c1} = [H^+]\frac{\beta_1}{1-\beta_1-\beta_2}, \quad K_{c2} = [H^+]\frac{\beta_2}{\beta_1}, \\ H_2O \rightleftarrows H^+ + OH^-, \quad K_w = [H^+][OH^-]. \end{gathered} \tag{4}$$

Here α is the degree of dissociation of the studied acid; β_1 and β_2 are degrees of dissociation of carbonic acid (the first and the second steps, respectively); K_{c1} and K_{c2} are dissociation constants of carbonic acid, and K_w is the constant of water autoprotolysis. The electric neutrality of the solution was written as follows.

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [A^-], \tag{5}$$

where x is the unknown concentration of carbon dioxide in water used for solutions preparation; y is the concentration of Na_2CO_3 by weight; and c is the concentration of the weak acid HA. Accounting for expressions (6), Eqs. (4) and (5) could be re-written in the form (7).

$$\begin{gathered} [H^+] = K_{c2}\frac{\beta_1}{\beta_2}, \quad [Na^+] = 2y, \quad [OH^-] = \frac{K_w}{[H^+]}, \\ [HCO_3^-] = \beta_1(x+y), \quad [CO_3^{2-}] = \beta_2(x+y), \quad [A^-] = \alpha c, \end{gathered} \tag{6}$$

$$\frac{K_w}{K_{c2}}\frac{\beta_2}{\beta_1} + (\beta_1 + 2\beta_2)(x+y) + \alpha c - 2y = K_{c2}\frac{\beta_1}{\beta_2}, \tag{7}$$

$$\beta_1 = \frac{K_{c1}}{2K_{c2}}\left[\sqrt{\beta_2^2 + 4\frac{K_{c2}\beta_2(1-\beta_2)}{K_{c1}}} - \beta_2\right], \quad \alpha = \left(\frac{K_{c2}\beta_1}{K_a\beta_2} + 1\right)^{-1}.$$

Numerical solution of Eqs. (7) by iterations method gave the expression of equilibrium constants of all ions in the solution via the K_w, K_{c1}, K_{c2}, and K_a constants and analytical concentrations c, x, and y. Accounting for Eq. (1), specific conductance L [μS/cm] could be written in the form (8)

$$L(c_j) = 10^3\{[H^+]\lambda_{H^+} + [OH^-]\lambda_{OH^-} + (x+y)[\beta_1\lambda(HCO_3) + 2\beta_2\lambda(CO_3)] + \alpha c_j\lambda_{A^-} + 2y\lambda_{Na^+}\}, \tag{8}$$

where unknown values of K_w, K_{c1}, K_{c2}, and λ_i (except for λ_{A^-}) were found via joint processing of seven series of conductometric measurements during titration of sodium carbonate, sodium hydroxide, hydrochloric acid, triethylamine, and acetic acid in aqueous solutions. The procedure of the data processing is described below.

Further, the desired values of λ_{A^-}, K_a and x were calculated via minimization of sum of squares of relative deviations of the experimental values L_j obtained during the titrations from the computed values $L(c_j)$.

$$S(K_a, \lambda_{A^-}, x) = \sum_j^N \frac{[L(c_j) - L_j]^2}{L_j^2}. \tag{9}$$

Minimization of the S function was performed using the conjugated gradient method implemented in MATCAD 14 software package (*minimize*). Equation (7) was solved using the Mueller or the secant methods (*root* function in the same software package).

Weak monoacid bases. Conductometric titration of a weak base B was reduced to the determination of dissociation constant of the conjugated acid BH^+ and its mobility λ_{BH^+} under conditions of the Arrhenius approximation (3) validity. The unknown values were determined using the results of titration of hydrochloric acid solution with solution of the weak base [N pairs of experimental values of specific conductance (L_j) as function of concentration of the added base (c_j)]. Initial HCl concentration was selected in the range of (1–3) × 10^{-5} mol/L (pH ≈ 5), so that the fraction of protonated forms of the studied bases (aniline and quinoline) was higher than in their solutions in deionized water.

HCl solution was prepared via dilution of the weighed portion of 0.1 mol/L solution prepared in turn from the standard sample; hydrochloric acid concentration y was not known with the required accuracy (0.01%). Therefore this value was regarded as unknown and was determined along with other parameters: K_{BH^+}, λ_{BH^+}, and x.

To do so, the equilibria system (4) was used, with the weak acid HA dissociation substituted with that of the conjugated acid BH^+ of the studied base.

$$BH^+ \rightleftarrows H^+ + B,\quad K_{BH^+} = [H^+]\frac{\alpha}{1-\alpha}. \tag{10}$$

The α value was defined as the dissociation degree of BH^+ or as a fraction of the neutral base form B ($\alpha = [B]/c$). The electric neutrality of the solution required that Eq. (11)

$$[H^+] + [BH^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [Cl^-]. \tag{11}$$

After denoting the unknown concentration of CO_2 in water used for the solutions preparation as x, that of HCl as y, and that of the weak base as c and accounting for Eq. (12), Eq. (13) was obtained.

$$[H^+] = K_{c2}\frac{\beta_1}{\beta_2}[BH^+] = (1-\alpha)c[OH^-] = \frac{K_w}{[H^+]}, \tag{12}$$

$$[HCO_3^-] = \beta_1 x[CO_3^{2-}] = \beta_2 x[Cl^-] = y,$$

$$\frac{K_w}{K_{c2}}\frac{\beta_2}{\beta_1} = (\beta_1 + 2\beta_2)x + y + (\alpha - 1)c = K_{c1}\frac{\beta_1}{\beta_2}. \tag{13}$$

The β_1 and α were expressed similar to the case of Eq. (7). Numerical solution of Eq. (13) using the iterations method gave equilibrium concentration of all ions via K_w, K_{c1}, K_{c2}, K_{BH^+}, c, x, and y. Specific conductance L [μS/cm] during the titration was found using Eq. (14).

$$L(c_j) = 10^3\{[H^+]\lambda_{H^+} + (\alpha - 1)c_j\lambda_{BH^+} + [OH^-]\lambda_{OH^-} \\ + x[\beta_1\lambda(HCO_3) + 2\beta_2\lambda(CO_3)] + y\lambda_{Cl^-}\}. \tag{14}$$

All λ_i values except for λ_{BH^+} (3) as well as the K_w, K_{c1}, and K_{c2} values were found via joint processing of seven series of conductometric measurements during titration of sodium hydrocarbonate, sodium hydroxide, hydrochloric acid, triethanolamine, and acetic acid in aqueous solutions.

Unknown values of K_{BH^+}, λ_{BH^+}, y, and x were determined by minimization of the sum of squares of relative deviations $S(K_{BH^+}, \lambda_{BH^+}, y, x)$ as described above for the case of weak acid [Eq. (9)].

Joint processing of the conductometric titrations data was performed for seven series listed below in the following format: titrated compound (concentration, mol/L) + titrant (concentration at the titration end point, mol/L).

NaOH (4.8 × 10^{-5}), Na_2CO_3 (2.6 × 10^{-5}) + HCl (1.64 × 10^{-4});
Na_2CO_3 (5.0 × 10^{-5}) + HCl (1.63 × 10^{-4});
NaOH (1.10 × 10^{-4}) + HCl (1.68 × 10^{-4});
NaOH (9.4 × 10^{-5}) + HCl (1.58 × 10^{-4});
Na_2CO_3 (4.8 × 10^{-5}) + CH_3COOH (2.76 × 10^{-4});
Et_3N (1.02 × 10^{-4}) + HCl (1.68 × 10^{-4});
Et_3N (9.7 × 10^{-5}) + CH_3COOH (2.65 × 10^{-4}).

For all seven series, the calculated ionic strength of the studied solutions was of (8.6–17) × 10^{-5} mol/L; CO_2 concentration in water used for titration was of (1.5–2.5) × 10^{-6} mol/L. The measured pH values were of 4–10, and specific conductance ranged 7–40 μS/cm. In total, the seven series contained N 768 experimental pairs of the values. Mean values of $<Z_i>$ listed in Table 1 were found by minimization of sum of relative deviations $S(K_i, \lambda_i, x)$ using an expression similar to Eq. (9), via the conjugated gradient method.

Mean-square deviations σ_Z of parameters Z were determined as follows. Z_j was calculated to satisfy the $L_j = L(c_j)$ condition for all N of the processed points, when other parameters Z_i equaled their mean values $<Z_i>$. From all the existing solutions, a subset of n ($n \le N$) was chosen so that $Z \in [0.5<Z>; 1.5<Z>]$. Such selection was necessary to remove the values with low statistical weight. Further, σ_Z was calculated according to Eq. (15).

$$\sigma_Z = \sqrt{\frac{\sum_j^n (<Z> - Z_j)^2}{n-1}}. \tag{15}$$

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Overall mean-square deviation σ of the computed conductance values $L(c_j)$ from the experimental ones L_j for all the experimental series was 7.57 × 10^{-4}.

$$\sigma = \frac{\sqrt{\sum_j^N [L(c_j) - L_j]^2}}{(N-1)L_j^2}. \tag{16}$$

Table 1. Dissociation constants and ion mobilities determined by joint processing of conductometric titration runs

Z	$<Z>$, $(\mathrm{p}<Z>)$	$\frac{100\sigma Z}{<Z>}$, %	n/N	$(\lambda_{0+}+\lambda_{0-})$ and $\mathrm{p}K^{\mathrm{T}}$
$(\lambda_{H^+}+\lambda_{OH^-})$	545.5	9.7	0.46	547.65 [23], 548.1 [22]
K_w	9.08×10^{-15} (14.04)	17	0.37	13.995 [23], 13.995 [22]
$(\lambda_{H^+}+\lambda_{Cl^-})$	421.7	0.57	1.00	425.96 [23], 426.41 [22]
$(\lambda_{Na^+}+\lambda_{Cl^-})$	126.3	0.13	0.72	126.39 [23], 126.42 [22]
$(\lambda_{H^+}-\lambda_{Na^+})$	295.4	–	–	–
$[\lambda_{H^+}+\lambda(HCO_3)]$	389.3	10	0.65	394.2 [23], 394.6 [22]
K_{c1}	3.76×10^{-7} (6.42)	17	0.43	6.35 [23] ,6.352 [22]
$[\lambda_{H^+}+\lambda(CO_3)]$	437.5	8.4	0.41	419.0 [23], 419.4 [22]
K_{c2}	1.03×10^{-10} (9.99)	21	0.29	10.33 [23], 10.329 [22]
$(\lambda_{H^+}+\lambda_{Ac^-})$	385.5	0.36	0.18	390.6 [23], 391.1 [22]
K_{AcOH}	1.81×10^{-5} (4.74)	8.8	0.11	4.756 [23], 4.756 [22]
$[\lambda(Et_3N^{++})\lambda_{Cl^-}]$	108.5	0.18	0.11	110.6 [23]
$K(Et_3N^+)$	1.64×10^{-11} (10.8)	7.4	0.06	10.75 [23], 10.72 [22]

First moment (m_1) of the deviations was 6.80×10^{-6}.

$$m_1 = \frac{1}{N^j}\Sigma\frac{N[L(c_j)-L_j]}{L_j}. \tag{17}$$

The values of the mean-square deviation and its first moment obtained via joint processing of the conductometric titration runs evidenced a perfect description of the experimental results with the suggested model. This result was of primary importance, as the parameters listed in Table 1 were then used as known (predefined) values. Even small errors in their determination would result in significant inaccuracy in determination of limiting conductance λ and the dissociation constants at the nonlinear regression step (Table 2). The low errors (<4%) of the K_a and λ of anions determination for the studied acids and ampholytes resulted from the accuracy of the values obtained during joint processing of the titration data. Hence, the joint processing of the results should be included into analysis of any titration data for the sake of calibration.

The higher errors of determination of K_{BH^+} and λ of cations of the studied bases and ampholytes were due to inaccurate determination of the dissolved carbon dioxide. Nevertheless, the mean values of K_{BH^+} were well in line with the reference data [22, 23]. We failed to find any data on limiting mobility of ions of the compounds studied in the second stage (Table 2). The mean-square deviations and first moments of distribution of the calculated conductance values $L(c_j)$ with respect to the experimental data L_j calculated in the second titration stage (Table 2) were of the order magnitude of the corresponding values obtained in the first stage. That additionally confirmed the validity of the developed model.

To conclude, the two-stage procedure of conductometric titration of very weak electrolytes and ampholytes for determination of their dissociation constants and limiting mobility was proved to be simple and reliable.

EXPERIMENTAL

Water used for conductometric measurements was prepared from bidistilled water using a Vodolei-M (Khimelektronika, Moscow) deionizer. Specific conductance of water used for solutions preparation was below 0.063 μS/cm at 25°C).

Air bubbled through the measuring cell was obtained from the atmosphere using an R-200 compressor (excessive pressure 0.05 at, gas consumption up to 300 mL/min). The air was passed through concentrated sulfuric acid, the column (diameter 30 mm, height 250 mm) filled with 1–1.5 mm solid sodium hydroxide, saturated sodium hydroxide solution, and water, and then filtered through porous glass.

Table 2. Dissociation constants of weak electrolytes and ion mobilities determined by joint processing of conductometric titration runs[a]

Titrate (c, mol/L)	Titrant (c, mol/L)	Number of points in a run N	Ionic strength I, mol/L	Z	Mean values and accuracy $\langle Z\rangle + \frac{100\sigma Z}{\langle Z\rangle}$ (p$\langle Z\rangle$)	n/N	$\sigma \times 10^3$ $m_1 \times 10^6$	$(\lambda_{0+}+\lambda_{0-})$ and pK^{T}
Na_2CO_3 (4.5×10^{-6})	Phenol (9.3×10^{-5})	29	9.1×10^{-6}	$(\lambda_{\mathrm{H}^+}+\lambda_{\mathrm{PhO}^-})$, K_{PhOH}	368.3±0.43% 1.15×10^{-10}±1.1% (9.94)	0.89 0.89	0.59 0.46	– 9.99 [23] 9.99 [22]
Na_2CO_3 (5.9×10^{-6})	3-Nitrophenol (2.8×10^{-5})	23	1.2×10^{-5}	$(\lambda_{\mathrm{H}^+}+\lambda_{\mathrm{PhO}^-})$, $K_3(\mathrm{NO_3PhOH})$	379.0±0.15% 4.85×10^{-9}±1.2% (8.31)	1.00 1.00	0.67 0.43	– 8.36 [23] 8.36 [22]
HCl (1.6×10^{-5})	Aniline (1.5×10^{-4})	47	1.6×10^{-5}	$(\lambda_{\mathrm{An}^+}+\lambda_{\mathrm{Cl}^-})$, K_{An^+}	111.3±4.0% 2.54×10^{-5}±2.4% (4.60)	0.98 0.98	0.69 0.26	– 4.87 [23] 4.60 [22]
HCl (1.7×10^{-5})	Quinoline (3.2×10^{-4})	65	1.7×10^{-5}	$(\lambda_{\mathrm{Qn}^+}+\lambda_{\mathrm{Cl}^-})$, K_{Qn^+}	109.5±2.0% 1.29×10^{-5}±1.6% (4.89)	0.99 0.99	0.87 3.2	– 4.90(20°C) [23] 4.80 [22]
NaOH (1.0×10^{-4}), glycine (4.4×10^{-5})	HCl (1.7×10^{-4})	83	(1.0–1.7) × 10^{-5}	$(\lambda_{\mathrm{Gly}^+}+\lambda_{\mathrm{Cl}^-})$, K_{Gly^+}, $(\lambda_{\mathrm{H}^+}+\lambda_{\mathrm{Gly}^-})$, K_{Gly}	85±27% 3.4×10^{-3}±18% (2.47) 392.4±3.8% 1.97×10^{-10}±2.8% (9.71)	0.17 0.35 0.61 0.60	0.59 0.35	– 2.34, 2.35 [23] 2.341 [22] – 9.58, 9.78 [23] 9.60 [22]
NaOH (9.7×10^{-5}), L-tryptophan (4.5×10^{-5})	HCl (1.6×10^{-4})	74	(0.9–1.6) × 10^{-5}	$(\lambda_{\mathrm{Trp}^+}+\lambda_{\mathrm{Cl}^-})$ K_{Trp^+}, $(\lambda_{\mathrm{H}^+}+\lambda_{\mathrm{Trp}^-})$, K_{Trp}	94±30% 3.3×10^{-3}±16% (2.48) 361.5±0.26% 2.89×10^{-10}±1.6% (9.54)	0.22 0.32 0.64 0.64	0.57 0.34	– 2.38, 2.46 [23] 2.38 [22] – 9.34, 9.41 [23] 9.39 [22]
NaOH (1.0×10^{-4}), 4-aminobenzoic acid (5.1×10^{-5})	HCl (1.6×10^{-4})	82	(1.0–1.6) × 10^{-5}	$(\lambda_{\mathrm{Aba}^+}+\lambda_{\mathrm{Cl}^-})$, K_{Aba^+}, $(\lambda_{\mathrm{H}^+}+\lambda_{\mathrm{Aba}^-})$, K_{Aba}	111±28% 4.5×10^{-3}±21% (2.35) 374.9±0.35% 1.41×10^{-5}±1.3% (4.85)	0.26 0.46 1.00 0.68	0.63 0.39	– 2.50 [23] 2.41 [22] – 4.87 [23] 4.85 [22]

[a] CO_2 concentration in water used for titration (x) was (0.7–4.5) × 10^{-6} mol/L.

Potassium chloride (“chemically pure” grade), phenol, aniline, glycine, L-tryptophan, and 4-aminobenzoic acid (all of “analytically pure” grade) were used as received. *m*-Nitrophenol (“pure” grade) was crystallized from water and ethanol and sublimated in a vacuum. Quinoline and triethanolamine (both of “pure” grade) were distilled at 5 mmHg and at atmospheric pressure, respectively. Acetic acid (“chemically pure” grade) was purified by freezing off at 14–15°C.

Diluted solutions were prepared in tightly closed vials made of polypropylene and polyethylene (VITLAB GmbH). Fluoropolymeric tubes (inner diameter 3 mm) equipped with polypropylene joints were used to operate with the solutions and to pass the purified air. Glassware (PYREX) was used exclusively for preparation of stock solutions (>0.01 mol/L), the glass leaching effects were negligible. The solutions were never stored for longer than 24 h after preparation.

The solutions were prepared by weighing the specimens of up to 80 g with a САРТОГОСМ МВ-210-А balance (accuracy of 0.01 mg), the specimens of up to 1100 g were weighed with an AND GX-1000 balance (accuracy of 1 mg).

Solutions density was measured with an automated ultrasound device DA-500 (Japan), absolute accuracy of ±0.1 g/L.

Titration procedure. Sufficient amount of purified water (250 mL) was first prepared and put in contact with a submersible conductometric cell. The CO_2-free air was slowly bubbled through the water until its specific conductance L_s was constant, 0.1–0.3 μS/cm (25°C), the allowed drift being of <0.002 μS/cm in 30 min. The weighed portion of titrated substance was added to the prepared water sample.

Then, the titrant solution was added by portions. Other conditions (temperature, aerating rate) being the same and the measurement being relatively fast (1.5–2 min per point), the L_s changes due to diffusion of carbon dioxide from outside were negligibly low.

Specific conductance of the solutions was measured with an InoLab Cond 740 conductometer (WTW GmbH) equipped with a LR 325/001 submersible two-electrode cell (built-in temperature sensor, coaxial electrodes of stainless steel, the cell constant 0.0100 cm^{-1} ±2%). The titrant solution was dosed with an automated device ATP-02 (Akvilon, Russia). Temperature was kept constant at 25.00±0.05°C during the measurement using an UTU ZN-68 ultrathermostat (Poland).

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