
PHYSICAL CHEMISTRY
OF SOLUTIONS

Temperature and Concentration Dependences of the Activity Coefficients of Electrolytes

N. A. Tikhonov* and G. B. Sidel'nikov

Faculty of Physics, Moscow State University, Moscow, 119991 Russia

*e-mail: niktandr@yandex.ru

Received October 21, 2016

Abstract—A model has been suggested that describes the interaction of hydrated ions in electrolytes and allows the calculation of the main physical effects. The model explains the character of the curves of the activity coefficients. Binary solutions of uni-univalent electrolytes at concentrations from zero to several moles per liter and at temperatures from zero to a few dozens of degrees were studied. The results of simulation were verified by comparing them with many literature data.

Keywords: activities, strong electrolytes, binary solutions

DOI: 10.1134/S0036024417100387

The activity coefficients in solutions were studied by many researchers. For low concentrations, there are well-developed theories that describe the dependence of the activity coefficients on the solution concentration (e.g., Debye–Hückel theory subsequently refined by other authors). For high concentrations, Pitzer [1], Robinson and Stokes [2], Bahe [3], Kuznetsova [4], and others developed approaches to calculation of the activity coefficients in reasonably wide ranges for many electrolytes.

These studies have two aspects. The values of the coefficients at different solution concentrations are required for calculating the equilibrium between the components. For this purpose, we can use the equations and summarized parameters obtained by different authors. At the same time, the tables of coefficients present a substantial material that can be used for mathematical simulation to analyze and study the physics of processes in electrolytes. Apart from the values of the coefficients, it is also of interest to examine how they are formed. In this aspect, the above (certainly useful) approaches have certain disadvantages.

The Debye–Hückel theory describes the process in electrolyte at very low concentrations. Pitzer used direct selection of many parameters of the model for constructing the curves of the activity coefficients, up to eight parameters for a mixture of two electrolytes. Kuznetsova obtained the formulas that allow the calculation of the activity coefficients in a very wide range of concentrations. The formulas adequately describe the final result, but arouse doubts from the viewpoint of physical substantiation. The main doubt is that the energy calculation neglects the considerable contribu-

tion of the interaction of the hydration shells of ions. It seems that the concept on the reasons and mechanism of changes in the activity coefficients at concentrations from ~0.1 to a few mol/L needs further development and study.

The role of modeling based on a study of the physics of the process increases if we consider the activity coefficients at different temperatures. The literature data are much more scarce in this case. Therefore, the creation of a model that makes it possible to construct the activity coefficients for different temperatures is not only of theoretical interest, but also of practical importance. This issue was studied in the present work for varying the concentrations of uni-univalent electrolytes from zero to several moles per liter and the temperatures from 0 to 70–80°C. It was important to use the minimum experimental data to determine the parameters of the model designed to calculate the activity coefficients for the variable temperature. The suggested approach helps to solve this problem. The obtained results were compared with the published data, and the regularities were substantiated in all the cases under study.

Model for the Uni-Univalent Strong Electrolyte at a Constant Temperature

Let the volume of the solution V contain M moles of a substance AD (molar concentration $C = M/V$). An equilibrium $A^+ + D^- \rightleftharpoons AD$ sets in the solution. Here A^+ and D^- are the nonbonded ions, and AD is the interacting pair. AD may differ in nature, which depends on the interaction energy. Namely, when the ions A^+ and D^- approach each other, the energy of the

system decreases due to the Coulomb attraction of ions. However, their unification into a molecule requires overcoming the energy of hydration of these ions. If the latter is larger, then the ions cannot throw off their hydration shells, remaining a loosely coupled pair. This situation is typical for strong electrolytes considered in this paper.

Let us denote the number of A^+ ions (in moles) in solution by the symbol $[A]$; accordingly $[D]$ is the number of D^- ions. The process will be analyzed based on the following model approximation. For the A^+ ions, the volume of the solution is divided into two energy bands. The first zone (conventionally called the "attraction" zone) is a set of small volumes with the D^- ions lying at their centers in a free state or in a state bonded with A^+ . Let us have the sum of these volumes around N (the Avogadro number) ions be denoted as v . The rest of the solution will be conventionally called the "free" zone. The average energy of the A^+ ion in the attraction zone is smaller than in the free zone by a certain quantity $\langle\phi\rangle$. Let us denote $\langle\phi\rangle/kT$ as U ($U < 0$). The size of the attraction zone is assumed to be such that the U value is minimum. In other words, the size is such that the difference between the average energies in the attraction and free zones is the largest.

The concentration of A^+ ions in the free zone is designated as θ . According to the Boltzmann law, the average concentration of these ions in the attraction zone is θe^{-U} . Since the volume of the free zone is $(V - vM)$ and that of the attraction zone is vM , we have

$$\begin{aligned} [A] &= \theta(V - vM), & [AD] &= \theta e^{-U} vM, \\ M &= [A] + [AD], & [D] &= [A]. \end{aligned} \quad (1)$$

Let us denote that

$$\lim_{C \rightarrow 0} U = U_0, \text{ and } \lim_{C \rightarrow 0} v = v_0.$$

Taking into account the association equation

$$\frac{[AD]}{[A][D]\gamma_{\pm}^2} = \text{const} = \lim_{C \rightarrow 0} \frac{[AD]}{[A][D]},$$

from this equation and (1) we obtain

$$\gamma_{\pm}^2 = \frac{e^{U_0 - U} (1 - Cv + Cve^{-U}) v}{(1 - Cv)^2 v_0}. \quad (2)$$

The v_0 value is determined by the choice of electrolyte and is a characteristic of the latter. Equations (2) describe the dependence of the activity coefficient γ on C for the electrolyte that has a certain value of v_0 if the functions $U(v_0, C, T)$ and $v(v_0, C, T)$ are known. Now let us consider the construction of these functions.

Following the Debye–Hückel idea, we consider the situation in a statistic aspect, introducing some

additions that are significant at high solution concentrations. To be more specific, let us choose negative ions. Around each ion (as a center) we record the particle distribution patterns. Let us superpose and "sum" these patterns and divide the result by their number. The distance from the center to the observation point is denoted by r . Each ion in solution is surrounded by a hydration shell. Some water molecules most closely lying to the ion form a stable structure [2]. At longer distances from the ion, the shell is diffuse. Since in strong electrolytes the ion energy is insufficient to destroy the stable parts of the shells, there will be a certain closest approach distance of ions. The result of the statistical averaging is obtained in the form of a negative "central" ion with a stable hydration shell with a radius a around it and a continuous distribution of the low density of the hydrated ions with an opposite sign at $r > a$. Below the a value acts as a parameter determined by the choice of solution. For this "object" that describes the statistically averaged characteristics of ion interactions, we will calculate the potential.

Let ψ be the electrostatic potential at a certain point of the space; $u = \frac{q\psi}{kT} < 0$, q is the electron charge; $w = \frac{W}{kT}$, W is the correction for the potential energy due to the change in the energy of the hydration shell during the motion of the positive ion from infinity to the space point in question. Hence the total energy Φ normalized to kT equals the sum of u and w .

The dependence $u(a, r, C)$ in the range $a < r < \infty$ is described by the Poisson equation, the right side of which contains the density of charges determined by the Boltzmann distribution:

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \epsilon \frac{\partial u}{\partial r} \right) &= \chi_1 C (e^{\Phi} - e^{-\Phi}), \\ \chi_1 &= \frac{4\pi q^2 N}{kT \times 10^3}, \end{aligned} \quad (3)$$

$$\frac{\partial u}{\partial r} \Big|_{r=a} = \frac{\chi_2}{\epsilon a^2}, \quad u \Big|_{r \rightarrow \infty} \rightarrow 0, \quad \chi_2 = \frac{q^2 \times 10^8}{kT}, \quad (4)$$

$$\Phi = u + w, \quad (5)$$

where ϵ is the local dielectric permeability.

Let us consider the case of fixed room temperature (25°C). The dielectric permeability of pure water is denoted as ϵ_w ; the dipole moment of the water molecule as d ; and the concentration of water molecules as n ($[n] = \text{\AA}^{-3}$). In the equations given below, all the distances are given in angstroms, and solution concentrations in mol/L.

The literature data on the dependence of ϵ on r was analyzed in [5], and the change in the energy of hydra-

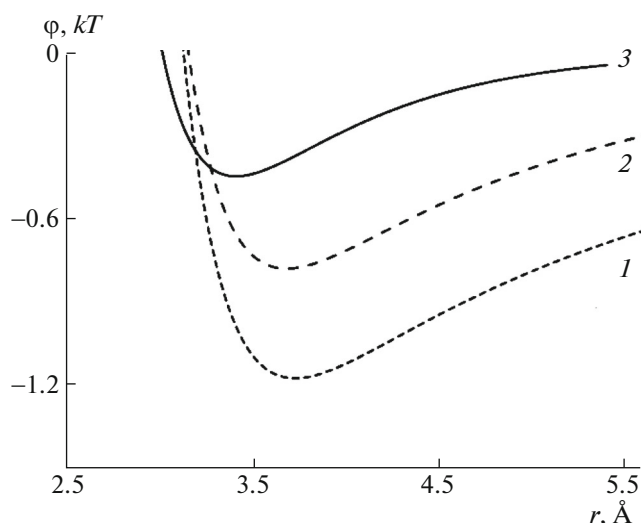


Fig. 1. Dependences of the total energy $\phi = q\psi + W$ on r for different C : (1) 0.2, (2) 1, and (3) 6.

tion shells $w(a, r, C)$ after the approach of ions was studied theoretically to obtain

$$\varepsilon(a, r, C) = \frac{\varepsilon_w}{1 + 1.7e^{2(a-r)} + 0.013Ca^2}, \quad (6)$$

$$\delta E(a, r, C) = -\frac{d}{kT} \left(\frac{q}{r^2} + \frac{9d}{d_w^3} \right) (1/\varepsilon - 1/\varepsilon_a), \quad (7)$$

$$\varepsilon_a = \lim_{r \rightarrow \infty} \varepsilon,$$

$$w_0(a, r, C) = 4\pi n \int_r^\infty \delta E(a, x, C) (e^{-\delta E(a, x, C)} - 1) x^2 dx, \quad (8)$$

$$w(a, r, C) = \frac{w_0}{1 + k_1 Ca^6}, \quad k_1 = 2.7 \times 10^{-4}. \quad (9)$$

Equations (3)–(9) form the model used to calculate the function $u(a, r, C)$.

Figure 1 shows the typical form of the calculated dependence of the total potential energy $\phi = q\psi + W$ on r for the “external” positive ion.

According to the Boltzmann law, the probability of finding the ion at a certain point is $Ce^{-\phi}$. At $r < a$, the energy W is high; hence $e^{-\phi} \approx 0$. If we take this into account, the average energy in a sphere of radius R with a negative ion at the center of the sphere including the probability of occurrence of the positive ion there is recorded as

$$\langle \Phi(a, R, C) \rangle = \frac{\int_a^R \Phi(a, r, C) e^{-\Phi(a, r, C)} r^2 dr}{\int_a^R e^{-\Phi(a, r, C)} r^2 dr}. \quad (10)$$

Let us denote the R minimum in (10) at certain values of C and a as $\Phi_v(a, C)$ and the R value at which this minimum is reached as $R_v(a, C)$. The volume v_0 that appears in (2) is related to a by the one-to-one dependence: $v_0(a) = \frac{4\pi}{3} R_v^3(a, 0) N 10^{-27}$. The desired dependences of (2) are recorded as

$$U(v_0(a), C) = \Phi_v(a, C)$$

$$\text{and } v(v_0(a), C) = \left(\frac{R_v(a, C)}{7.34} \right)^3. \quad (11)$$

Comparison of the Results of Simulation with the Literature Data

Equation (2), where the values of the functions $U(v_0, C)$ and $v(v_0, C)$ are determined by using the model (3)–(11), allows us to calculate the activity coefficient of electrolyte $\gamma(v_0, C)$. The v_0 value depends on the choice of electrolyte and its characteristic value. We compared the tabulated data of [6, 7] for various uni-univalent electrolytes in 30 instances with the results of numerical calculations using the described model. The model approximates well the experimental data in all instances without exception. Figure 2 shows the typical cases. By way of illustration, we chose electrolytes for which the curves $\gamma(C)$ differ significantly.

The given approach naturally explains the initial drop and further growth of the $\gamma(C)$ curves. As follows from (2), these curves form under the action of two main factors. The U value is negative and decreases in magnitude as C increases. This can be seen in Fig. 1. For free ions, it becomes increasingly less favorable to unite. This factor is reflected by the form of the e^{-U} factor in (2). As a consequence, the $\gamma(C)$ curves at first decrease. The second main factor that forms the increase in the $\gamma(C)$ curves is the decrease in the “vacant” zone ($V - vM$) at increasing solution concentration (the first Eq. (1)). Indeed, any observed process in solution (in this case, the intensity of formation of bonded AB pairs) is determined by the ion concentration in the free zone. This concentration is

$\theta = \frac{[A]}{V - vM}$, while the average concentration of free ions throughout the solution is $[A]/V$. Therefore, the effect is stronger than it would be at a medium concentration. This corresponds to the $(1 - vC)^2$ factor in the denominator of (2). Therefore, as C increases further, the $\gamma(C)$ curve starts to increase ($\gamma \sim (1 - vC)^{-1}$). The electrolytes with small v do not go to the increase stage in the range $0 < C < 6$. For all other electrolytes, $\gamma(C)$ has the form of initially decreasing and then increasing curve.

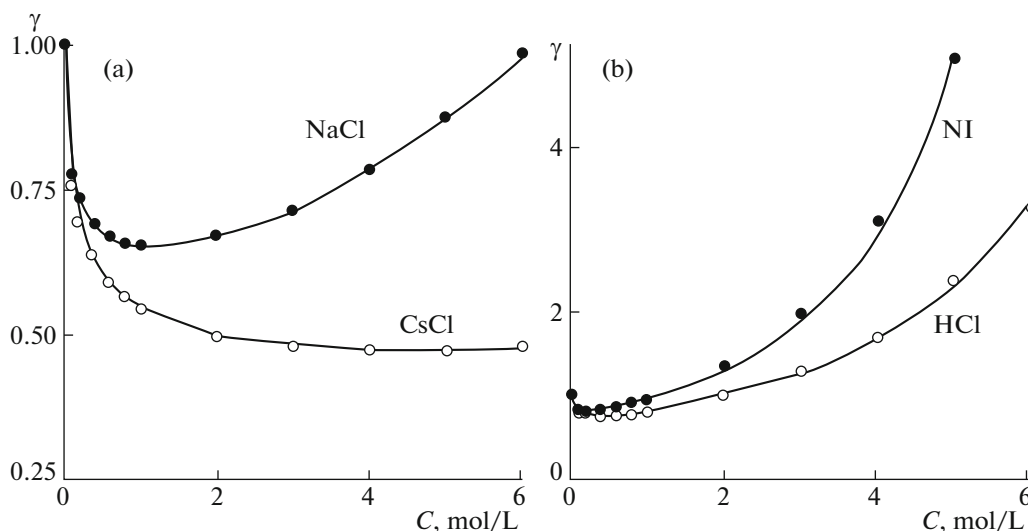


Fig. 2. Dependences $\gamma(C)$; dots: tabulated data; curves: calculated data.

Modification of the Model and Results of Simulation for Different Temperatures

Equations (3), (4), and (7) contain the temperature T in explicit form. In addition, ε and k_1 change with the temperature. For the sake of simplicity, the temperature expressed in degrees centigrade is denoted as \bar{T} , and 25°C as \bar{T}_0 . Let us consider the temperature range $0 \leq \bar{T} < 100$.

The changes in ε and k_1 were evaluated in [8]. Namely, for ε it was obtained that

$$\varepsilon(a, r, C, T) = \frac{\varepsilon_w(\bar{T}_0)e^{4(a-r)} + \varepsilon_w(\bar{T})(1 - e^{4(a-r)})}{1 + 1.7e^{2(a-r)} + 0.012Ca^2}. \quad (12)$$

For k_1 it was found that

$$k_1 = k_1(T) = 0.0003 \left(1 - e^{-3(1-\bar{T}/100)} \right). \quad (13)$$

As a result, we have model (2)–(11), in which the equation for ε in (6) is replaced by (12), and k_1 in (9) is defined in (13).

Let us consider the results of simulation. At a fixed temperature, the dependence $\gamma(C)$ obtained in the simulation is completely determined by a (or v_0 explicitly related to it). For variable temperature, judging from the arrangement of the experimental (literature) data shown in Fig. 3, it is expected that $a = a(T)$. In addition, the data prompt that this function may be decreasing or increasing.

Within the framework of the given model we constructed the curves $\gamma(a(T), C, T)$, compared them with the known tabulated values, and constructed the dependences $a(T)$ for various electrolytes. This comparison was performed for all uni-univalent electrolytes for which comprehensive experimental data are

available [6] for concentrations from zero to 3–4 mol/L and temperatures from zero to several dozen degrees. These data were found for six electrolytes. The calculated γ curves correspond to the tabulated values in all instances. The mean square normalized deviation from the tabulated values was 1.5%.

The left part of Fig. 3 contains the γ curves constructed using the model and the tabulated data; the right part contains the corresponding $a(T)$ dependences.

For concentrations of up to 4 mol/L, the handbooks contain the data only for temperatures of up to 60–80°C. Therefore, it was impossible to check the reliability of the data calculated using the model by comparing them with the literature data for temperatures higher than 80°C.

The $a(T)$ function was obtained in the form of a square parabola in all cases (Fig. 3). A more comprehensive description of the effect may contain deviations from this functional form. In the given approach, however, the approximation had a square form with high accuracy.

At fixed $C \approx 3$ –4 mol/L and fixed temperature, the γ value calculated by simulation monotonically changes with a . Therefore, a is readily determined only from γ . The square parabola is given by three coefficients. Consequently, to construct the $a(T)$ function for a certain electrolyte, it suffices to have the results of three experimental measurements at markedly different temperatures. For example, for the solution at a concentration $C = 3$, it suffices to experimentally determine γ at $T = 0, 25$, and 70°C. Given the $a(T)$ dependence, we can calculate the activity coefficient

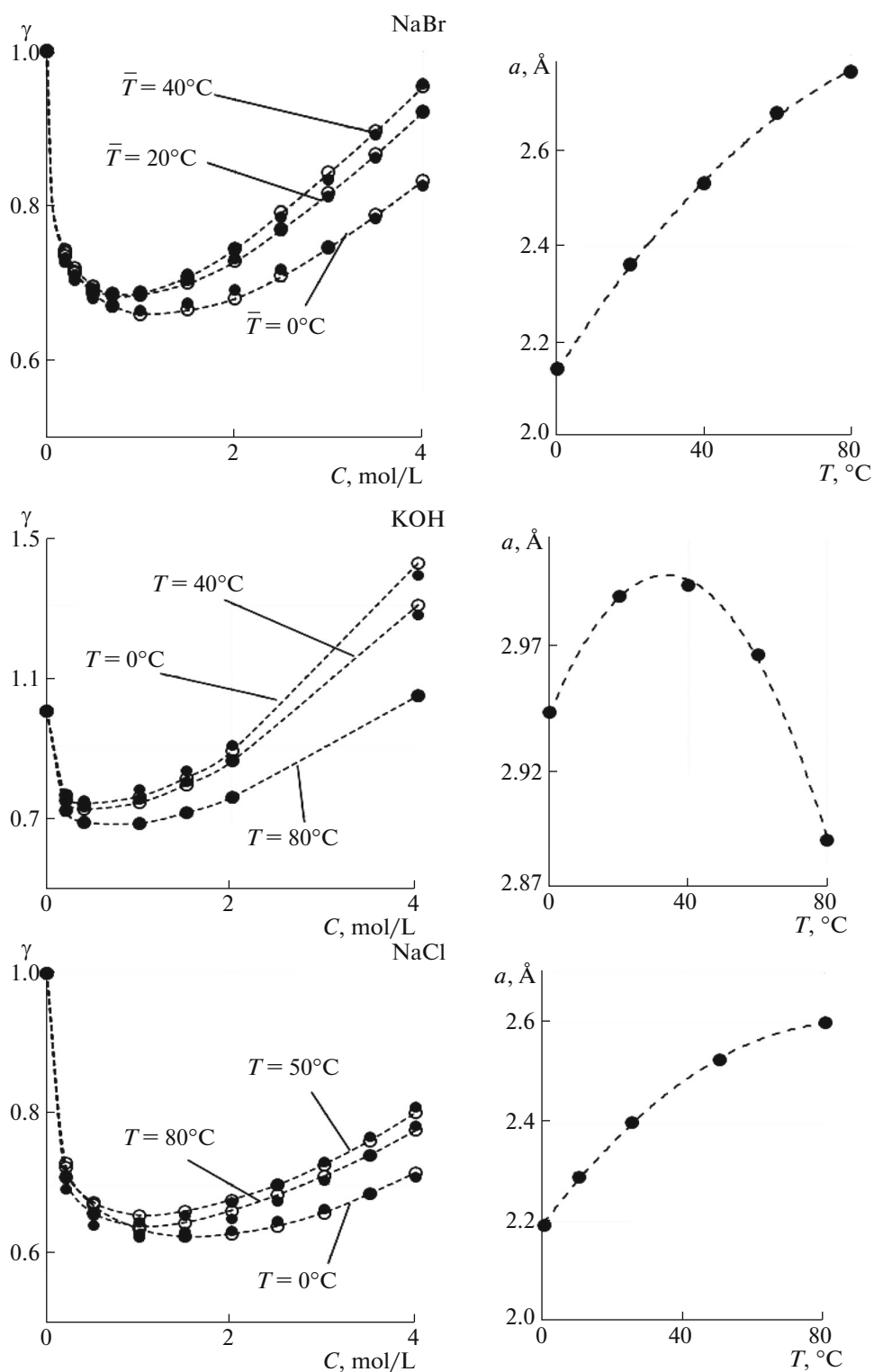


Fig. 3. Temperature and concentration dependences of a and γ . Left part: dots: tabulated values, curves: calculation by the model. Right part: dots: calculated values; curves: interpolation with quadratic parabolas.

cient γ in the range in which the reliability of the results of simulation was verified for any C from 0 to 4 mol/L and any temperatures from 0 to 80°C.

The difference between the $a(T)$ curves (they may be increasing or decreasing) for different electrolytes may be explained as follows. The energy of the hydra-

tion shell is largely determined by the local dependence of ϵ on r , which changes with temperature. The model under study is based on the concept that the hydration shell of an ion consists of two parts. One part is the central stable part, whose radius is set equal to a . At $r < a$, the water molecules are fixed with a field; the local dielectric permeability ϵ is small as a consequence of polarization saturation of molecules [2]. In the “surface” part at $r > a$, the saturation effect is weakened, and ϵ tends to the value in water outside the shell as r increases.

In the outer part of the shell, as well as outside it, the ordering of the arrangement of water dipoles in the electric field, which determines the polarization P , decreases as T increases. Consequently, at fixed r in the induction field D , $\epsilon = D/(D - 4\pi P)$ also decreases. This determines the decrease in the $\epsilon_w(T)$ function.

The opposite situation should take place in the peripheral zone of the stable part of the shell. Here an increase in T leads to a loosening of the molecular structure and a decrease in the polarization saturation. The dipoles now can react to the field of external ions. Hence ϵ increases. The interaction of these opposite effects determines the change in the size of the stable part of the shell, i.e., of the radius a , with temperature. Which tendency will prevail depends on the shell structure. The tabulated data given in Fig. 3 show that the change may be bidirectional.

Thus the suggested physical model describes the interaction of hydrated ions in electrolytes. Its use allows us to quantitatively study the main physical

effects and analyze on this basis the behavior of the activity coefficients of electrolytes at concentrations from 0 to several moles per liter and at temperatures from 0 to 70–80°C. Determination of the parameters of the model that characterize the electrolyte requires the minimum experimental data. The given approach was validated by comparing the results of calculations with the literature data.

REFERENCES

1. K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.* **96**, 5701 (1974).
2. R. Robinson and R. Stokes, *Electrolyte Solutions* (Butterworth, London, 1959).
3. L. W. Bahe, *J. Phys. Chem.* **72**, 1608 (1972).
4. E. M. Kuznetsova, *Russ. J. Phys. Chem. A* **76**, 866 (2002).
5. N. A. Tikhonov and G. B. Sidelnikov, *J. Math. Chem.* **51**, 2746 (2013).
6. *The Chemist's Handbook*, Vol. 3: *Chemical Equilibrium and Kinetics, Solution Properties, Electrode Processes*, Ed. by B. P. Nikol'skii (Khimiya, Moscow, 1965) [in Russian].
7. A. I. Efimov, L. P. Belorukova, I. V. Vasil'kova, and V. P. Chechev, *Properties of Inorganic Compounds, The Handbook* (Khimiya, Leningrad, 1983) [in Russian].
8. N. A. Tikhonov and G. B. Sidelnikov, *J. Math. Chem.* **53**, 163 (2014).

Translated by L. Smolina