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ORIGINAL PAPER

Quantitative analysis of physical factors that determine the behavior of activity coefficients of electrolytes. II. Dependence on temperature

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Abstract In the paper we propose the model that describes the interaction energy of the hydrated ions in uni-univalent electrolytes at various concentrations and temperatures. The approach developed allows one to calculate the main effect of various physical factors, and based on this, to determine the activity coefficients in the range of concentrations from zero to several mol/l and the range of temperatures from zero to several tens of degrees. The results of simulation have been tested by comparison with available literature data.

Keywords Activity coefficients · Simulation · Uni-univalent electrolytes

List of symbols

C	The molar concentration of a solution (mol/l)
U	The difference of the average potential energies of an ion in the attraction zone and the free zone divided by kT (dimensionless)
v	The total volume of attraction zones around N negative ions, $v_0 = \lim_{M\to 0} v$(l/mol)
γ	The activity coefficient (dimensionless)
a	The radius of the stable part of the hydrate shell around the "central" ion in the statistical model; it approximately corresponds to the distance of the closest approach of ions(Å)

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u	The electrostatic potential of an ion divided by kT (dimensionless)
w	The correction to the potential energy of a positive ion due to the change of the energy of the hydrate shell divided by kT (dimensionless)
$\Phi = u + w$	The potential energy of a positive ion with hydrate shell divided by kT (dimensionless)
$\langle\Phi\rangle$	The average value of Φ in the spherical layer $a < r < R$ subject to the probability of finding charges in the layer (dimensionless)
ε_w	The dielectric permittivity of water (dimensionless)
ε	The local value of the dielectric permittivity (dimensionless)
d	The dipole moment of the molecule of water (C $\leq\leftarrow$ Å)
d_w	The diameter of a molecule of water (Å)
n	The concentration of molecules of water (Å^{-3})

1 Introduction

In [1], using mathematical modeling, we studied physical factors that determine equilibrium conditions in solutions of uni-univalent electrolytes at the constant temperature (25 °C). It was found that based on the fundamental laws of physics, the Coulomb law and the Boltzmann distribution, using well-known data on the dielectric constant of the solution near ions [2], it is possible to calculate these factors quantitatively and to obtain the dependence of the activity coefficient of the electrolyte on the concentration of the solution. The calculation of the activity coefficients was not an aim in itself since for many electrolytes at a home temperature the coefficients can be found in table references; moreover, there are formulas (see [3,4]) that allow one to calculate these coefficients. The construction of dependences of the activity coefficients on the concentration of a solution based on mathematical modeling and comparison of results obtained with tabular data was needed for verification of the model.

The situation changes if we consider activity coefficients at different temperatures. In this case, there are few available published data. In Fig.1 we present experimental dependences of activity coefficients for some electrolytes [5]. Orderliness in the change of curves with temperature is not detected. Therefore, the creation of a physical and mathematical model that allows one to calculate activity coefficients in the case of different temperatures, acquires practical significance in addition to theoretical interest.

In the present paper we develop the model proposed in [1] to the case, where concentrations of uni-univalent electrolytes change in the range from zero to several mol/l and the temperature changes in the range from 0 to 70–80 °C

2 A model that allows one to calculate activity coefficients for the temperature 25 °C

Consider a solution of a chemical substance AB with molar concentration C. In the solution an equilibrium $A^+ + B^- \rightleftarrows AB$ is established. Here A^+ and B^- are unbound ions and AB is an interacting pair. Ions in the solution are surrounded by hydrate shells. In strong electrolytes, which are discussed in the present paper, the electrostatic energy

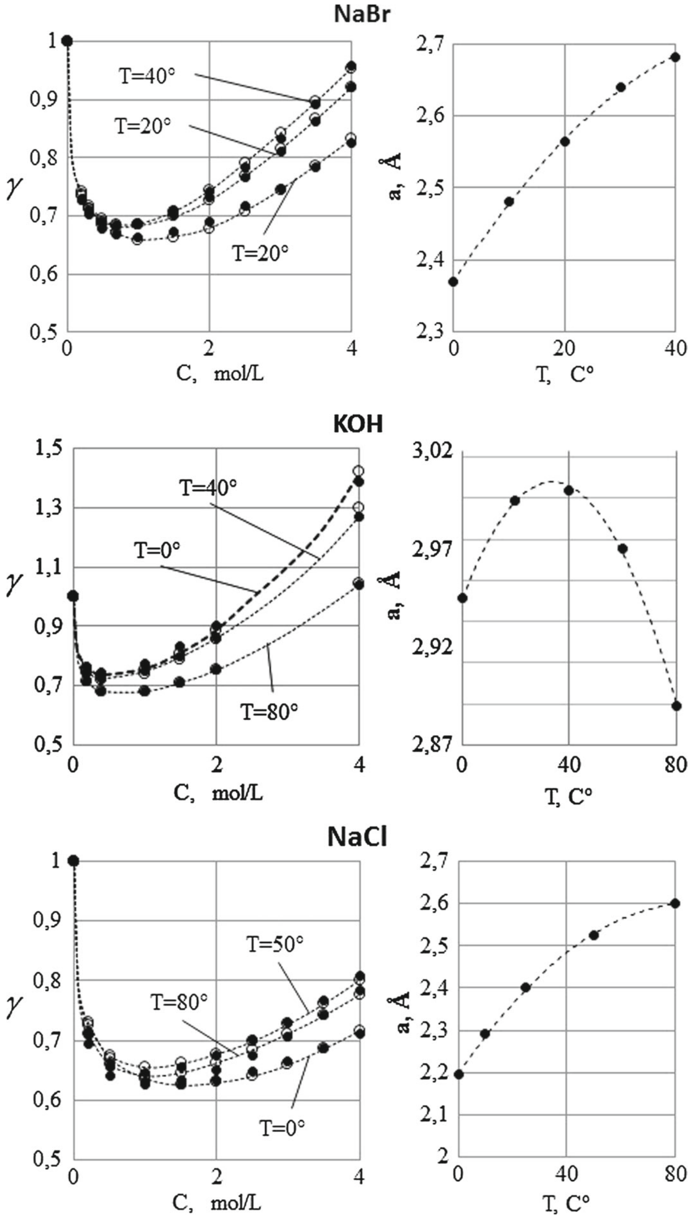

Fig. 1 *Left*: *shaded markers* show the table data, *curves* and *unshaded markers* show results of simulation. *Right*: *markers* show the table data, *curves* show the results of interpolation by quadratic parabolas

of ions is insufficient for destroying the hydrate shell and merging into a molecule, therefore AB is a weakly bound pair.

The aggregate of small volumes centered at ions B^- in the free or bound with A^+form is called the "attraction zone". The rest of the solution is called the "free" zone. The average energy of an ion A^+ in the attraction zone is less than in the free zone by a value φ. We denote φ/kT by $U(U < 0)$ and define size of the "attraction zone" as a volume at which the value of U is minimal. In other words, the size is such that the difference between the energies in the attraction and free zones is the maximal.

We denote by v the sum of the volumes of these domains around N ions B^-, where N is the Avogadro constant. This value may depend on C and T. Let $\lim_{C\to 0} U = U_0(T)$ and $\lim_{C\to 0} v = v_0(T)$. It was shown in [1] that the principle of mass conservation, the Boltzmann law, and the dissociation relation lead to the expression

$$\gamma^2 = \frac{e^{U_0-U} \cdot (1 - Cv + Cve^{-U})}{(1 - Cv)^2} \frac{v}{v_0} \tag{1}$$

where v_0 is a characteristic of the chosen electrolyte. Relation (1) determines the dependence of the activity coefficient γ on C for an electrolyte with some v_0 if the functions $U(v_0, C)$ and $v(v_0, C)$ are known. These functions can be constructed as follows.

Each ion in a solution is surrounded by a hydrate shell. Several water molecules closest to the ion form a stable structure [2]. At a greater distance from the ion, the shell is blurred. Consider the statistically averaged field around a negative ion. The distance from the center to the observation point is denoted by r. Since in strong electrolytes the ion energy is insufficient for destroying the stable parts of the shells, there exists a distance of the closest approach of ions. We obtain the result of averaging in the form of a negative "central" ion with a stable hydrate shell of radius a around it and a low-density continuous distribution of hydrated ions of various signs for $r > a$.

Consider the space occupied by the solution, taking out spheres of radius a surrounding ions. The average value of ε at this part of the solution we denote by ε_a. In equations presented below all distances are measured in Ångströms and concentrations in mol/l.

Let ψ be the electrostatic potential at a point of space, $u = \frac{q\psi}{kT} < 0$, where q is the electron charge; $w = \frac{W}{kT}$, where W is the correction to the potential energy due to the change of the energy of the hydrate shell while moving the positive ion from infinity at the point considered. It was shown in [1] that the distribution of $u(r, C)$ in the domain $a < r < \infty$ can be described by the following relations:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \varepsilon \frac{\partial u}{\partial r}\right) = \chi_1 C\left(e^u - e^{-\Phi}\right), \quad \chi_1 = \frac{4\pi q^2 N}{kT \cdot 10^3}. \tag{2}$$

$$\frac{\partial u}{\partial r}_{|r=a} = \frac{\chi_2}{\varepsilon a^2}, u_{|r\to\infty} \to 0, \quad \chi_2 = \frac{q^2 10^8}{kT}. \tag{3}$$

$$\varepsilon = \frac{\varepsilon_w}{1 + 1.7e^{2(a-r)} + 0.013 \cdot Ca^2}, \quad \varepsilon_a = \lim_{r\to\infty} \varepsilon. \tag{4}$$

$$\delta E = -\frac{d}{kT}\left(\frac{q}{r^2} + \frac{9d}{d_w^3}\right) \cdot \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_a}\right) \tag{5}$$

$$w_0 = 4\pi n \int_r^\infty \delta E(x, a)\left(e^{-\delta E(x,a)} - 1\right)x^2 dx. \tag{6}$$

$$w(C, r, a) = \frac{w_0(r, a)}{1 + k_1 C a^6}, \quad k_1 = 2.7 \cdot 10^{-4}. \tag{7}$$

$$\Phi = u + w. \tag{8}$$

The average energy in a ball of radius R whose center is occupied by a negative ion, with account of the probability of getting a positive ion in it, equals to

$$\langle \Phi(C, R, a) \rangle = \frac{\int_a^R \Phi(C, r, a) e^{-\Phi(C,r,a)} r^2 dr}{\int_a^R e^{-\Phi(C,r,a)} r^2 dr}. \tag{9}$$

Let $R_v(C, a)$ be the value of R for which $\langle \Phi \rangle$ is minimal. Introduce the notations $\Phi_v(C, a) = \langle \Phi(C, R_v(C, a), a) \rangle$ and $R_{v_0} = R_v(0, a)$. The last relation implies the inverse function $a = a(R_{v_0})$, which has the form close to linear. The volume $v$in (1) is related with R_v by the formula $v = \frac{4\pi}{3} R_v^3 \cdot N \cdot 10^{-27}$. Therefore $R_{v_0} = 7.34 v_0^{1/3}$. As a result we find the relation between a and v_0 as a single-valued monotone function $v_0 = v_0(a)$. Now we construct the dependences

$$U(v_0(a), C) = \Phi_v (C, a) \text{ and } v(v_0(a), C) = \left(\frac{R_v [C, a]}{7.34} \right)^3 \tag{10}$$

Relations (1)–(10) form the model that allows one to calculate activity coefficients. Each electrolyte has its own value of a (or v_0). Since γ depends on a monotonically, we can easily pick the value of a if γ is known for certain concentration. For chosen a the model determines $\gamma(a, C)$ for all C from the range considered.

A domain of applicability of the model (1)–(10) is the range of concentrations from zero to several mol/l [1]. In the domain for different uni-univalent electrolytes, in 30 cases, it was verified that results of calculations within the framework of the model are in good agreement with published data [5].

3 Change of the model at different temperatures

Equations (2), (3), and (5) explicitly involve the temperature T. Moreover, ε and k_1 also depend on the temperature. For simplicity we define by $\overline{T}$ the temperature in °C and $\overline{T}_0 = 25\,°C$. Of concern to us is the range of temperatures $0 \le \overline{T} < 100$.

Consider Eq. (4). For pure water $\varepsilon_w(T)$ is a known decreasing function [5]. To specify a functional form of the dependence of ε on the temperature we shall take into account the following reasons.

The value a is the radius of the stable part of the shell, where molecules of water are fixed by the field. The local value of the dielectric permittivity ε for $r < a$ is small and is determined by the saturation of polarization of molecules [2]. It is natural to assume that ε weakly depends on T if r is close to a. We have a value of ε that is approximately equal to that for room temperature: $\varepsilon \approx \frac{\varepsilon_w(\overline{T}_0)}{1+1.7e^{2(a-r)}+0.013 \cdot C a^2}$. As

r increases, ε is affected by the environment, where ε_w depends on the temperature. We assume that the change of influence of these factors occurs approximately in the middle of rapid change of ε. The result will be:

$$\varepsilon = \frac{\varepsilon_w(\overline{T}_0) \cdot e^{4(a-r)} + \varepsilon_w(\overline{T}) \cdot \left(1 - e^{4(a-r)}\right)}{1 + 1.7e^{2(a-r)} + 0.012 \cdot Ca^2}. \tag{11}$$

Consider the dependence of k_1 on T. Molecules of water that occupy the outer part of the hydrate shell of an ion come into dipole interaction with molecules of water in shells of neighboring ions in the case of short-range action [1]. In Eq. (7) the term $k_1 Ca^6$ describes the decrease in energy of the hydrate shell of an ion due to this factor. As temperature increases, the interaction weakens due to the decrease of order of dipole orientation of molecules in the outer part of the shell. We assume that at temperature 100 °C one can neglect the interaction of shells ($k_1 = 0$), whereas at 0–40 °C the value of k_1 can differ from the value (7), which was found by a theoretic way in [1], by no more than 10 %. We obtain

$$k_1 = k_1(T) = 0.0003 \cdot \left(1 - e^{-3(1-\overline{T}/100)}\right). \tag{12}$$

As a result, we have model (1)–(10) in which the expression for ε in (4) is replaced by (11) and the value of k_1 in (7) is defined by (12).

4 Results of simulation

At a fixed temperature the dependence $\gamma(C)$ obtained by modeling is completely defined by the value of a (or by v_0, which is in one-to-one correspondence with a). If the temperature changes, according to the position of curves in Fig. 1, we can expect that $a = a(T)$. Moreover, the experimental data presented in Fig. 1 suggest that this function can either increase or decrease.

In the framework of the model considered curves $\gamma(a(T), C, T)$ were constructed, their behavior were compared with known tabular data, and the dependences $a(T)$ for different electrolytes were obtained. A detailed comparison was performed for six electrolytes, for which sufficiently complete experimental data are available [5] in the range of concentration from zero to 3–4 mol/l and the range of temperatures from zero to several tens of degrees Celsius. In all cases calculated curves γ correspond to the table data; relative standard deviation is 1.3 %.

In the left-hand side of Fig. 1 we present curves γ constructed by using the model and tabular data. In the right-hand side we present the corresponding curves $a(T)$.

Unfortunately, for a concentration range up to 4 mol/l, available for us reference books contained only data up to temperatures 60–80 °C. So we were not able to compare the results of simulation with published data at temperatures greater than 80 °C.

In all cases the function $a(T)$ has the form of a quadratic parabola (see Fig. 1). Possibly, in a more complete description of this phenomenon, deviations from such a functional form can arise. However in the framework of the approach considered the quadratic approximation was observed with high accuracy.

As was noted above, at fixed concentration $C \approx 3$–4 mol/l and fixed temperature, the value of γ calculated by the model monotonically changes against a. Therefore the value of $a$can be easily found by a sole value of γ. A quadratic parabola is determined by three coefficients. Therefore to construct the function $a(T)$ for certain electrolyte it is sufficent to have three experimental data for substantially different temperatures. For example, to find γ at $\mathrm{T} = 0, 25, and 70\,^{\circ}\mathrm{C}$ for the solution of concentration $C = 3$. If we know the function $a(T)$, then we can calculate the activity coefficient γ in a range for which the reliability of the model has been verified, i.e., for any concentration from zero to 4 mol/l and any temperatures from 0 to 80 °C.

The fact that curves $a(T)$ for different electrolytes have different behavior (can be increasing or decreasing) can be explained as follows. By (5) and (6) the energy of the hydrate shell of an ion is substantially determined by the dependence of ε on r, which varies with temperature. The model (2)–(8) is based on the idea that the hydrate shell of an ion consists of two parts. One of them - the central stable part - has radius a. Near an ion ε is small due to the saturation of polarization [2]. The saturation weakens near the border of the stable zone. In the "surface" part, for $r > a$, the saturation effect is negligible and the value of ε tends to its value in water outside the shell as r increases.

Let $C = 0$. In Eqs. (4) and (11) a is the radius, where $\varepsilon \approx 30$. With this choice of a in the model the total energy (8) is positive at $r \leq a$. Therefore ions do not penetrate into this area. So the area is the stable part of hydrate shell. In this sense a is the distance of closest approach of ions.

The value of ε characterizes the modification of molecules polarization when an electric field changes. It is easy to see that dependence of ε on T should be different near or far from an ion. In the last case molecules freely rotated in the direction of the field. The greater is T, the stronger is variation of molecules orientation. Hence $\varepsilon(T)$ is a decreasing function.

The opposite situation should occur in the peripheral zone of the stable part of the shell. Here the increase in temperature leads to a "loosening" of the structure of molecules and reduction of saturation of polarization. Dipoles get the opportunity to respond on the field of external ions. Therefore ε increases. The interaction of these opposing factors determines the change of r, where $\varepsilon \approx 30$. This means the change of the radius a with temperature. Which of these tendencies will prevail depends on the structure of the shell. Table data presented in Fig. 1 show that opposite changes are possible.

The question on the limits of applicability of the model was discussed in [1]. In the case of various temperatures it is solved similarly.

5 Conclusions

The model that describes the interaction of hydrated ions in uni-univalent electrolytes is proposed. The approach allows one to calculate activity coefficients of electrolytes in a wide range of concentrations and temperatures using minimal experimental data.

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