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# Quantitative analysis of physical factors that determine the behavior of activity coefficients of electrolytes

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**Abstract** The development of theoretical ideas on the cause and the mechanism of the change of activity coefficients is the main aim of the investigation. The model describing the interaction of hydrated ions in electrolytes is proposed. In the model the electrostatic forces between ions and change of the energy of the hydrate shell in the process of ion convergence determine ions distribution in solution. The significant factor is the dependence of dielectric permittivity on the concentration of the electrolyte and on the distance to ion. The statistical approach developed allows one to calculate the influence of principal physical factors and, on this basis, to explain the nature of curves describing the activity coefficients. The results of simulation have been tested on a large number of experimental data.

## List of Symbols

| | |
|---|---|
| $M$ | The amount of solute (mol) |
| $C = M/V$ | The molar concentration (mol/l) |
| $\theta$ | The concentration of ions in the free zone (mol/l) |
| $\Phi$ | The difference of the average potential energies in the attraction zone and the free zone (J) |

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$U = \Phi/kT,$ $\quad U_0 = \lim_{M \to 0} U$ (dimensionless)

$v$ — The total volume of attraction zones around $N$ negative ions, $v_0 = \lim_{M \to 0} v$ (l/mol)

$\gamma$ — The activity coefficient (dimensionless)

$a$ — The radius of the stable part of the hydrate shell around the "central" ion in the statistical model; approximately corresponds to the distance of the closest approach of ions (Å)

$\psi, u = \frac{q\psi}{kT}$ — The electrostatic potential (J/C)

$W, w = \frac{W}{kT}$ — The correction to the potential energy of the positive ion due to the change of the energy of the hydrate shell (J)

$\phi = q\psi + W$ — The potential energy of a positive ion with hydrate shell (J)

$\langle \Phi \rangle$ — The average value of $\Phi$ in the spherical layer, subject to the probability of finding charges in the layer (dimensionless)

$\varepsilon_w$ — The dielectric permittivity of water (dimensionless)

$\varepsilon$ — The local value of the dielectric permittivity (dimensionless)

$\varepsilon_a$ — The average value of $\varepsilon$ in the solution in the domain $r > a$ (dimensionless)

$d$ — The dipole moment of the molecule of water (C · Å)

## 1 Introduction

The activity coefficients in solutions have been extensively examined in many studies. In the case of small concentrations of solutions, there exist well-developed theories explaining laws of variation of the activity coefficients against the concentration of solutions, namely, the Debye–Hückel theory and subsequent refinements of it proposed by other authors. For large concentrations, several approaches were developed for calculation of the activity coefficients in a fairly wide range for many electrolytes, for example, the approaches of K. Pitzer [1], R. Robinson and R. Stokes [2], L. Bahe [3], E. M. Kuznetsova [4], and others.

The study of the activity coefficients has two aspects. The values of the coefficients for different concentrations of the solution are needed for the calculation of equilibrium between the components. For this purpose, one can use formulas and summaries of the parameters obtained in the works of various authors.

At the same time, tables of the coefficients contain significant and reliable information. Using mathematical modeling, based on this material, one can analyze and study the physical aspects of processes occurring in electrolytes. Not only the activity coefficients themselves are of interest, but also understanding of *how* these values are produced. In this aspect, these approaches, possessing undoubted achievements, are not without drawbacks.

The Debye–Hückel theory describes what happens in electrolytes at very low concentrations. K. Pitzer used a direct selection of a large number of parameters for the curves of the activity coefficients, up to 8 in a mixture of two electrolytes. E. M. Kuznetsova derived formulas for the calculation of the activity coefficients in a wide range of concentrations. These formulas adequately describe the final result but

raise questions regarding the physical justification. Among them, the main problem is as follows: in the calculation of the energy, a significant contribution of the interaction of hydrate shells of ions is not considered. We believe that the development of theoretical ideas on the cause and the mechanism of the change of activity coefficients at concentrations in the range from about 0.1 to several moles per liter, requires further examination.

In this paper, we propose a model in which the choice of functions is determined by the physics of the process. The model allows one to describe the activity coefficients of univalent electrolytes in this range of concentrations. We also compare the results obtained with data published earlier and substantiate principles used in our constructions.

## 2 Model for the case of uni-univalent strong electrolyte

Assume that a solution contains $M$ moles of a chemical substance AB per volume $V$ (i.e., the molar concentration is $C = M/V$). In the solution, an equilibrium $A^+ + B^- \rightleftarrows$ AB is established. Here $A^+$ and $B^-$ are unbound ions and AB is an interacting pair, which can have a different nature depending on the energy of interaction. Namely, if the ions $A^+$ and $B^-$ approach, then the energy of the system decreases due to the Coulomb attraction of the ions, but to join them in a molecule, the energy of hydration of the ions must be overcome. If the energy of hydration is greater, the ions cannot "undress" and remain a weakly coupled pair. This situation is typical for strong electrolytes discussed in this paper.

Denote by $A$ and $B$ the number (in moles) of the ions $A^+$ and $B^-$, respectively. We consider the process based on the following model concept. For the ions $A^+$, we divide the volume of the solution into two energy zones. The first zone, called the *attraction zone*, is a collection of small domains centered at the ions $B^-$, free or bound with $A^+$. We denote by $v$ the sum of the volumes of these domains around $N$ ions $B^-$, where $N$ is the Avogadro constant. The remaining volume 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 certain amount denoted by $\Phi$; we denote $\Phi/kT$ by $U(U < 0)$. We assume that the size of the attraction zone in such that the value of $U$ is minimal. In other words, the size is such that the difference between the energies in the attraction zone and the free zone is most strong.

We denote the concentration of the ions $A^+$ in the free zone by $\theta$. By the Boltzmann law, their average concentration in the attraction zone is $\theta e^{-U}$. Since the volume of the free zone is equal to $(V - \theta M)$ and the volume of the attraction zone is equal to $\theta M$, we have

$$A = \theta(V - vM), \quad AB = \theta e^{-U} vM, \quad M = A + AB, \quad B = A. \qquad (1)$$

Introduce the notation $\lim_{M \to 0} U = U_0$ and $\lim_{M \to 0} v = v_0$. Taking into account the association relation

$$\frac{AB}{A \cdot B \cdot \gamma^2} = \text{const} = \lim_{M \to 0} \frac{AB}{A \cdot B},$$

we obtain

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

where $v_0$ is a characteristic of the chosen electrolyte ($[v] = $ l/mol). Relation (2) determines the dependence of the activity coefficient $\gamma$ on $C$ for an electrolyte with some $v_0$ if the functions $U(v_0, C)$ and $v(v_0, C)$ are known. We now turn to the construction of these functions.

## 3 Potential of ions interaction in electrolyte

Let us consider the Debye–Hückel approach and make some improvements that are essential for high concentrations of solutions.

Each ion in a solution is surrounded by a hydrate shell. An ion together with a shell in this work is called a cluster.

Following the ideas of Debye and Hückel, we study the situation statistically. For definiteness, consider negative ions. Around each of them, we fix the particle distribution and then average these distributions. Denote the distance from the center to the observation point 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 get the result of averaging in the form of a negative ion at the center (we call it the "central" ion) with a stable hydrate shell of radius $a$ around it and a continuous distribution of low-density clusters with ions of various signs for $r > a$. We calculate the potential for such an "object," which statistically describes averaged characteristics of the interaction of ions.

Let $C$ be the concentration of an electrolyte, $\psi$ be the electrostatic potential at a point of the 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 (respectively, $W_-$ is the corresponding correction when moving negative ion). By the Boltzmann equation, the local density of positive ions for $r > a$ is proportional to $C \cdot e^{-(u+w)}$ and the local density of positive ions is proportional to $C \cdot e^{u-w_-}$. Since the normalizing coefficient is equal to 1, the distribution $u(r, C)$ in the domain $a < r < \infty$ is described by the following relations:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \varepsilon \frac{\partial u}{\partial r} \right) = \chi_1 C \left( e^{-(u+w)} - e^{u-w_-} \right),$$

$$\frac{\partial u}{\partial r}_{|r=a} = \frac{\chi_2}{\varepsilon a^2},$$

$$u_{|r \to \infty} \to 0, \tag{3}$$

where $\chi_1$ and $\chi_2$ are known constants: $\chi_1 = \frac{4\pi q^2 N}{kT \cdot 10^3}$, $\chi_2 = \frac{q^2 10^8}{kT}$.

At low concentrations of electrolytes, in the Debye–Hückel theory, the right-hand side of Eq. (3) can be linearized, the constant $\varepsilon$ is set to be equal to the dielectric permittivity $\varepsilon_w$ of water, and the change of the energy of the hydrate shell is neglected. For high concentrations $C$, we (a) leave the equations nonlinear, (b) take into account the dependence of the dielectric permittivity $\varepsilon$ on the concentration of the electrolyte and the value of $r$, and (c) take into account the change of the energy of the hydrate shell.

Since complete experimental data for items (b) and (c) are not available, we specify the necessary relations based on some well-known ideas.

In reality, a hydrate shell is a complex, ill-defined structure. For example, different authors give significantly different estimates of its size and the number of water molecules in it. Therefore, we will use a simple model representation for our statistically defined "object." We assume that the hydrate shell consists of two parts. One of them, the central stable part, has radius $a$. For $r < a$, water molecules are fixed by the field, and the local value of the dielectric permittivity in this region is small due to the saturation of molecule polarization [2]. In the other "surface" part, for $r > a$, the shell is relatively unstable, its energy depends on the proximity of other clusters and the penetration of an "external" ion into this part of the shell.

Consider item (b). It is known that the average dielectric permittivity $\varepsilon_{av}$ substantially depends on the concentration of an electrolyte. Its decrease compared with $\varepsilon_w$ can be explained by the presence of domains near the ions where $\varepsilon$ is small. Experimental data for $\varepsilon_{av}$ (see [6]) are adequately described by the relation

$$\varepsilon_{av} = \frac{\varepsilon_w}{1 + k_{av}C}.$$

The coefficient $k_{av}$ depends on the electrolyte, hence $k_{av} = k_{av}(a)$.

By [2], on the boundary of the stable part of the hydrate shell, the local value of $\varepsilon$ increases up to the average value in the solution out of shells, on the approximate distance 2 Å (in what follows, we measure all distances in Ångströms). Then we assume that the local value of $\varepsilon$ in the domain $r > a$ is equal to

$$\varepsilon = \frac{\varepsilon_w}{1 + 1.7e^{-2(r-a)} + k(a)C} \tag{4}$$

This quantity varies in dilute solutions (for $C = 0$) on the distance 2 Å near the surface $r = a$ within the range approximately from 30 to 80.

In problem (3), the potential is calculated, i.e., the work of the displacement of an ion from infinity to the observation point. Within this displacement, the ion does not falls in $a$-neighborhoods of other ions; therefore, the values of $\varepsilon$ in these neighborhoods are irrelevant. The average value of $\varepsilon$ in the domain $r > a$ is significant; we denote it by $\varepsilon_a$. The deviation of this value from $\varepsilon_w$ is defined by the value of $\varepsilon$ in the surface part of the shell. We have

$$\frac{\varepsilon_w}{\varepsilon_a} - 1 = 2C \cdot N \cdot 10^{-27} \cdot 4\pi \int\limits_{a}^{\infty} 1.7e^{2(a-r)}r^2 dr \approx 0.012a^2C.$$

Therefore, $k(a) = 0.012a^2$.

Now we turn to item (c), the change of the energy $W$ of the hydrate shell of the "central" ion due to the approaching to it of an "external" ion from infinity to the point under consideration at various $C$.

Let $C \neq 0$ and the space contains ions. We choose a sphere around the "central" ion lying outside the shell. In the statistically averaged representation, the charge on it is distributed uniformly over the sphere. As is well known, inside the sphere, such a charge does not change the field $\vec{E}$. Therefore, the energy of the dipole, which is equal to $\vec{E} \cdot \vec{d}$, also remains unchanged. Therefore, the distributed spatial charge located outside the shell does not change the energy of the shell.

The dipoles of neighboring ions change the energy of the shell at the short-range action. In the neighborhood of the negative "central" ion, "external" positive ions predominate. The surface of the shell of the "central" ion contacts, with some probability depending on the concentration $C$, with the surfaces of shells of "external" positive ions with dipoles located on them and directed toward the shell of the "central" ion. These dipoles affect the dipoles of the shell of the "central" ion, pulling them from the "central" ion.

Consider the relationship of the energy of various factors on the boundary of the shell of the "central" ion. Let $C = 0$. We denote the radius of the shell by $r_0$. The energy of the transition of an ion from the shell in a solution is equal to $F_{|r=r_0} \delta r$, where $F$ is the attraction force between the dipole and the shell and $\delta r$ is a small displacement required for the separation from the shell. The condition of the dynamical equilibrium on the boundary of the shell has the form

$$F_{|r=r_0} \delta r = E_{\text{kin}},$$

where $E_{\text{kin}}$ is the average kinetic energy of a molecule of water. Now let $C > 0$. Then, except for the thermal energy, the shell resists the force $F_{\text{d}-\text{d}}$ generated by the dipole–dipole interaction of neighboring shells. The equilibrium condition is as follows:

$$F_{|r=r_c} \delta r = E_{\text{kin}} + F_{\text{d}-\text{d}} \delta r,$$

where $r_c$ is the new radius of the shell of the "central" ion. These equilibrium conditions imply

$$F_{|r=r_c} = F_{|r=r_0} + F_{\text{d}-\text{d}}.$$

Dipole–dipole forces in shells are independent of the radius. Therefore, in expressions for $F_{|r}$, we must consider only the change of the ion–dipole component. We obtain

$$\frac{2q^2 d}{\varepsilon r_c^3} = \frac{2q^2 d}{\varepsilon r_0^3} + \frac{6q^2 d^2}{\varepsilon d_w^4} \cdot n(C),$$

where $d_w$ is the diameter of the molecule of water (the distance between the centers of the neighboring dipoles) and $n(C)$ is the density of distributed dipoles in the statistical models, or, in other words, the probability of finding of "pulling away" dipoles near

a dipole on the surface of the shell of the "central" ion, which is defined by the expression

$$n(C) = \frac{r_c^3}{r_w^3} \frac{CN}{10^{27}} \cdot k_c g,$$

where $r_w$ is the radius of the molecule of water, $k_c$ is a parameter characterizing the increase of the concentration of positive ions near the surface of the negative "central" ion comparing with the average concentration in the solution (in our estimates $k_c = 1.5$), and $g$ is a factor reflecting the fact that a dipole in water interacts with several closest dipoles. By [2], for water $g = 2.5$; this value was obtained experimentally. As was noted above, by [2], the change of $\varepsilon$ up to the value $\varepsilon_w$ (the dielectric permittivity of pure water) occurs at the distance approximately 2 Å from the stable part of the shell. This characterizes the approximate dimensions of the shell since namely the presence of a shell causes the change of $\varepsilon$. Therefore, for estimates we set $r_c = a + 2$.

Using the values of the fundamental constants and parameters specified above, we find

$$\frac{1}{r_c^3} = \frac{1}{r_0^3} + \frac{k_1}{r_c^3} a^6 C,$$

where $k_1 = 3 \cdot 10^{-4}$. If $V_0$ and $V_c$ are the volumes of the shell for $C = 0$ and for $C > 0$, respectively, then we have

$$V_c = \frac{V_0}{1 + k_1 C a^6}.$$

The energy of the dipole–dipole interaction in the shell is approximately proportional to its volume; therefore, it varies similarly as the concentration $C$ increases.

Now we examine the change of the energy of the "surface" part of the shell when an ion of opposite sign (to the sign of the "central" ion) penetrates it. In the outer part of the shell, water molecules are unstable and their dipole moment is unsaturated. If they were located arbitrarily, then $\varepsilon = \varepsilon_a$. If some of them, owing to the short-range interaction, form a certain structure, then $\varepsilon$ changes in accordance with (4). Thus, the dipoles acquire an additional energy. An "external" ion, approached at a distance $r$ to the "central" ion, destroys (in the statistically averaged representation) the dipole structure in the outer part of the shell lying outside the sphere of radius $r$ and deprives it of energy supplements. We calculate it.

The average energy of the dipole of the water molecule in the absence of a structure in the field of the "central" ion is $-qd/r^2\varepsilon_a$; in the presence of a structure it becomes $-qd/r^2\varepsilon$. Moreover, the energy $u_{\text{dip}}$ of the dipole–dipole interaction of neighboring molecules increases. We denote by $r_w$ the radius of the water molecule. The change of $u_{\text{dip}}$ is equal to

$$\frac{2d^2}{r_w^3 \varepsilon_w} \left( \frac{\varepsilon_w}{\varepsilon} - \frac{\varepsilon_w}{\varepsilon_a} \right) \cdot K,$$

where $K$ is the coefficient depending on the order of dipoles in the structure of the shell. Assuming that they are staggered, we obtain $K = 6 - 4 \cdot 2^{-3/2} \approx 4.5$. Thus, the change of the energy of the water molecule is equal to

$$\delta E = -\delta \left(\frac{\varepsilon_w}{\varepsilon}\right) \cdot \frac{d}{\varepsilon_w} \left(\frac{q}{r^2} + \frac{2dK}{r_w^3}\right), \text{ where } \delta \left(\frac{\varepsilon_w}{\varepsilon}\right) = \left(\frac{\varepsilon_w}{\varepsilon(r)} - \frac{\varepsilon_w}{\varepsilon_a}\right) = 1.7e^{2(a-r)}.$$

According to the Boltzmann law, the ratio of the probability of finding a dipole in the structure to the probability of finding it at the same place, but without the inclusion in the structure is equal to $e^{-\delta E/kT}$. Therefore, the probability of transition from the free state to the structure is equal to $e^{-\delta E/kT} - 1$. Find the change of the energy of the part of the shell outside the sphere of radius $r$ when the structure is destroyed:

$$W_{|C=0} = 4\pi n \int\limits_r^\infty \delta E(x, a) \left(e^{-\delta E(x,a)/kT} - 1\right) x^2 dx,$$

where $n$ is the concentration of dipoles in water. Calculating the integral, we obtain $W_{|C=0} \approx k_2 e^{4(a-r)}$, where $k_2 = 1.5 \cdot 10^{-13}$erg. Finally, the expression for the correction $W$ to the potential energy caused by the change of the energy of the hydrate shell has the form

$$W(C, r, a) = \frac{k_2 e^{4(a-r)}}{1 + k_1 C a^6}. \tag{5}$$

Now we consider the value $w_-$ in Eq. (3). As was discussed above, "external" ions lying outside the shell do not change its energy. The change of the energy is determined by the partial destruction of the shell ($w_- > 0$) at the short-range interaction, for $r \approx a$–$2a$. In this region, the electrostatic potential $u$ is a large negative value, which determines a small probability of the convergence of ions of the same charge. Thus, the quantity $e^{-w_-} < 1$ in Eq. (3) is multiplied by $e^u \ll 1$. Therefore, an inaccuracy in determination of $w_-$ is not essential in the calculation of the solution of problem (3). Taking this into account, for examining Eq. (3), we can set $w_- = 0$. The admissibility of this approximation was verified by numerical experiments with different $w_-$ in model (3).

Equations (3)–(5) form a complete model; within the framework of this model, the function $u(C, r, a)$ was calculated ($u$ depends on $a$ as on a parameter). Figure 1 shows a typical dependence of the total potential energy $\phi = q\psi + W$ on $r$ for an "external" positive ion.

Using the function $\phi(C, r, a)$ found by simulation for fixed values $C$ and $a$, one can calculate the average energy of ions in the sphere of radius $R$ centered at the "central" ion. We denote $\frac{\phi}{kT}$ by $\Phi$. By the Boltzmann law, the probability of finding an ion at some point is equal to $Ce^{-\Phi}$. For $r < a$, the energy $W$ has a larger value and hence $e^{-\Phi} \approx 0$. Taking this fact into account, we see that it suffices to calculate the average energy in the spherical layer $a < r < R$; it equals

**Fig. 1** Dependence of the total energy $\phi = q\psi + W$ on $r$ for various $C$
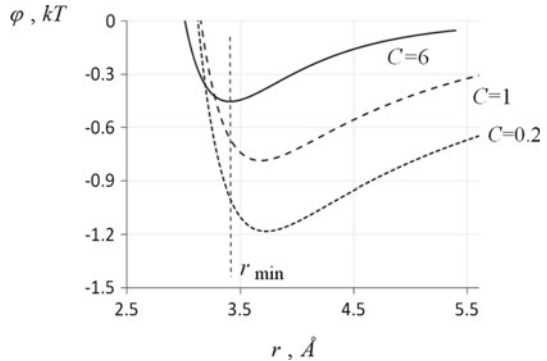
$$\langle \Phi(C, R, a) \rangle = \frac{\int_a^R \Phi(C, r, a) e^{-\Phi(C,r,a)} r^2 dr}{\int_a^R e^{-\Phi(C,r,a)} r^2 dr} \qquad (6)$$

In model (2), the size of the attraction zone was assumed to be such that $\langle \Phi \rangle$ attains the minimum value. Therefore, if we find from (6) the value of $R$ for which $\langle \Phi \rangle$ is minimal, we can obtain the radius $R_v(C, a)$ of the attraction zone and the average value of $\Phi$ in it:

$$\Phi_v(C, a) = \langle \Phi(C, R_v(C, a), a) \rangle.$$

The constructed functions allow us to pass from the characteristic of the electrolyte by specifying a value of $a$ to the characteristic $v_0$ that occurs in model (2). We denote the value of $R_v$ for $C = 0$ by $R_{v_0}$, i.e., $R_{v_0} = R_v(0, a)$. This dependence determines the inverse function $a = a(R_{v_0})$; it has the form similar to a linear function. The volume $v$ of the attraction zone per one mol of the solute is related with $R_v$ by the relation

$$v = \frac{4\pi}{3} R_v^3 \cdot N \cdot 10^{-27} \approx \frac{8\pi}{10^4} R_v^3.$$

We recall that $R_v$ is measured in Ångströms and $v$ in liters per mole. Thus, $R_{v_0} = 7.34 v_0^{1/3}$. Finally, we find the relationship between $a$ and $v_0$ in the form of a single-valued monotonic dependence $a = a(v_0)$. After this, we can construct the functions $U(v_0, C) = \Phi_v(C, a(v_0))$ and $v(v_0, C) = \left( \frac{R_v[C, a(v_0)]}{7.34} \right)^3$.

## 4 Comparison of results of simulation with published data

Model (2), where the values of the functions $U(v_0, C)$ and $v(v_0, C)$ are determined based on the use of model (3)–(6), allows the calculation of the activity coefficient of the electrolyte $\gamma(v_0, C)$. The value of $v_0$ depends on the choice of an electrolyte and
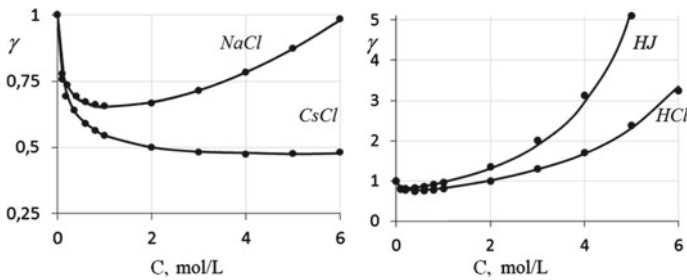
**Fig. 2** Dependence $\gamma(C)$. *Markers* show the table data, *curves* show results of simulation

characterizes it. We compared published data from [5] for various uni-univalent electrolytes in 30 cases with results of numerical simulation by the model described above. In all cases tested, without exclusions, the model adequately describes the experimental data. Figure 2 shows typical situations. For illustration we selected electrolytes whose curves $\gamma(C)$ are substantially different.

This approach naturally explains the initial falling and subsequent rise of the curves $\gamma(C)$. Namely, as (2) shows, these curves are formed under the influence of two major factors. The value $U$ is negative and decreases in absolute value with increasing $C$. From the energetic standpoint, free ions are less profitable to join the association. To this fact, the factor $e^{-U}$ in Eq. (2) corresponds. As a consequence, the curves $\gamma(C)$ initially fall. The second major factor that affects the rise of curves $\gamma(C)$ is the reduction of the free zone $(V - vM)$ as the concentration of the solution increases [the first Eq. (1)]. Indeed, any process observed in the solution (in this case, the intensity of the formation of bound pairs AB) is defined by the concentration of ions in the free zone. This concentration is equal to $\theta = \frac{A}{V - vM}$, whereas the average concentration of free ions in the whole solution is equal to $A/V$. Therefore, the effect produced is stronger than it would be at an average concentration. The apparent concentration—activity— is greater than the actual average concentration. To this fact, the factor $(1 - vC)^2$ in the denominator of expression (2) corresponds. Therefore, the further increase of the concentration $C$ causes the rise of the curve $\gamma(C)$ ($\gamma \sim (1 - vC)^{-1}$). Electrolytes with small values of $v$ ($< 0.05$) do not reach the stage of increasing in the range $0 < C < 6$. For other electrolytes, the curve $\gamma(C)$ initially decreases and then increases.

The value of the activity coefficient $\gamma$ for moderate values of $C$ (for example, $C = 4$ mol/l) monotonically changes with the change of $v_0$. Therefore, for the selection of $v_0$, it suffices to know just one point, for example, the value $\gamma(4)$. Then we can calculate $\gamma(y)$ for all other concentrations. Thus, the proposed model allows one to calculate the activity coefficients in a wide range, from 0 to several moles per liters, using minimum pilot information.

Consider the limits of applicability of expression (2). An obvious constraint is the condition that the total volume of the attraction zones is less than the total volume of the solution. For evaluation, we consider the constraint $C \cdot v(v_0, C) \leq 0.8$. Obviously, the applicability range $C \leq C_{\lim}$ differs for various substances. For example, we present the values of $C_{\lim}$ for electrolytes that are shown in Fig. 2. $C_{\lim} \approx 4$ corresponds to HJ; $C_{\lim} \approx 5$ to HCl; $C_{\lim} \approx 10$ to NaCl; $C_{\lim} \approx 16$ to CsCl.

The distance between ions of opposite sign in the solution is equal to $L(C) = \frac{k_L}{\sqrt[3]{C}}$, where $k_L$ is a constant lying in the range from 7.7 to 9.4, depending on the structure of the package (cubic, tetrahedral, etc.). Let us see in Fig. 1. Let $C$ be such that $L$ is approximately equal to $r_{min}$. Being located at a distance of $r_{min}$, ions of opposite sign occupy a stable position relative to each other. The electrolyte is in a quasi-crystalline state. The values of concentrations at which this occurs exceed the values of $C_{lim}$ specified above.

## 5 Conclusion

In this paper, we propose a physical model describing the interaction of hydrated ions in electrolytes. This model allows one to perform a quantitative examination of the influence of basic physical factors and, based on this, to analyze the behavior of the activity coefficients of electrolytes in the range from 0 to several moles per liter.

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