Theoretical calculation of the dilute aqueous solutions activity coefficients taking into account factors of electrical nature

M. Kravchenko, *Yu. Bereznytska, L. Vasylenko, S. Fedorenko (*Kyiv National University of Construction and Architecture*)

SUMMARY

The work is devoted to development of the diluted water solutions activity coefficient calculation methodology, using the equalization of the self-agreed systems continuum electrodynamics and allocating processes which are characteristic for the electric system. The dependence of calculated ion activity factors on concentration of diluted water solutions, which are divided into three groups, was obtained. It is justified that for single- and two-valent electrolytes of the first group the influence of the general mechanism of interaction between ions is characteristic, which is determined by the action of ion electric gravity and it`s features. The growth of activity in the area of large concentration values for electrolytes containing hydrogen ion and lithium ion is shown. It has been found that the activity values in the area of electrolytes large concentrations increase is connected with the manifestation of forces of pushing electrical origin in processes, which are accompanied by redistribution of charges. On the basis of equalization for the dielectric component properties of electrolytes water solutions are described. The dependence for calculation of electric field potential, field strength and charge density were obtained. Given the change of diluted water solution internal energy for "i" class ions and free energy is obtained the expression for chemical potential ions. The calculation of the diluted water solutions activity average coefficient is proposed taking into account the nature of electric factors.

Keywords: activity coefficient, activity, electricity factors, diluted water solutions, electrolyte, concentration, electric field potential, charge density, chemical potential, ions

Introduction

Water, as a universal solvent, is part of the environment, and is the main component of any biological and chemical complex. It is necessary to understand that it is a complex system, which includes dissolved electrolytes, various organic and inorganic compounds. Theoretical calculation of the activity coefficient γ in a wide range of concentrations for the whole components present in water range, allows to considerably improve and expand the application of the baromembrane methods, in particular the method of reverse osmosis (Kravchenko et al., 2021), while adjusting the diluted water solutions composition, to which the drinking water belongs. Obtained in work (Kravchenko et al., 2021) expressions for calculation of ions activity factors of electrolytes water diluted solutions allowed to conduct comparison of theoretical and experimental data. However, direct measurement of ion activity is impossible due to the specificity of the research object and introduction of the activity concept, which is thermodynamic value and characterizes degree of properties deviation of real solution from ideal. Thus, the proposed method of activity coefficients calculation (Kravchenko et al., 2021) of diluted water solutions in wide concentration ranges did not take into account the phenomena characteristic of electrical systems. In this paper we will give a consistent theory of activity in solution, using equations of continuous electrodynamics of self-agreed systems and highlighting processes characteristic of electric system. This theory will allow to describe the aggregate of experimental data for both multi-valent diluted water solutions and for single-valent ones, which will reveal essentially new and economically justified possibilities in the field of installations parameters calculation and use of baromembrane methods in the process of adjusting the composition of diluted water solutions.

Methods of investigation

Calculation of the activity coefficient of water solutions components was carried out on the formula (1):

$$\gamma = \exp\left(-\frac{1}{kT} \cdot \frac{z_i^2 e^2 \kappa a_i}{8\pi\varepsilon\varepsilon_0 a_i(1+\kappa a_i)^2} \cdot \frac{n_i}{n_i+n_j} - \frac{1}{kT} \cdot \frac{z_j^2 e^2 \kappa a_j}{8\pi\varepsilon\varepsilon_0 a_j\left(1+\kappa a_j\right)^2} \cdot \frac{n_j}{n_i+n_j}\right), \qquad (1)$$

where: k – Boltzmann constant, J/K; T – absolute temperature, K; z_i – valentness of i-th ion; z_j – valentness of j-th ion; e – elementary charge, Kl; k – Debye screen radius, m; ε_0 – dielectric constant, F/m; ε – water dielectric permeability; a_i – radius of i-th ion, m; a_j – radius of j-th ion, m; n_i, n_j – the number of ions of the variety, respectively, "i-th" and "j-th", on which the molecule of the electrolyte was spread.

Analysis of the obtained results shows that the dependence of calculated ion activity coefficients on the diluted water solutions concentration can be divided into three groups.

The first group includes data whose activity curve smoothly falls from one to a certain minimum value and changes slightly with increasing concentration (Figure 1, a). This group includes diluted water solutions such as, for example, NaCl, KBR, KCl, CuCl2, ZnCl2, Na2SO4, ZnSO4, CuSO4.

The second group includes such dependencies, in which activity coefficientss in the area of small concentrations gradually decrease from one to a certain minimum value, and then with the concentration increase begin to increase to moderate values (Figure 1, b). These group include HBR, HCl, LiCl.

The third group should include dependences, which is characterized by rather large values of activity coefficients in the area of concentration growth, reaching values 5 and more (Figure 1, c). This group includes MgCl2, AlCl3, CrCl3, NiCl2, FeCl3.

Strong growth of activity with solution concentration can be explained by the influence of pushing forces between Debye atmosphere ions (for chlorine ion) and polarity of solution molecules in the field of central multicharge ion. This leads to a change in the values of the dielectric penetration of diluted water solution in the field of the volume charge localization (Simonov, 2008).
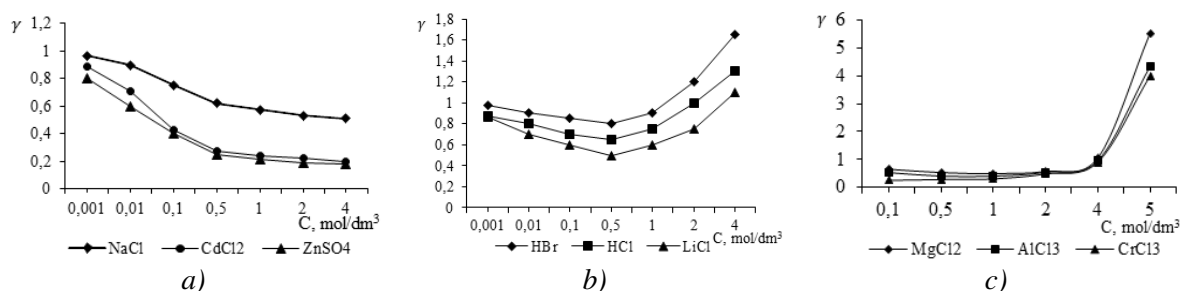
Figure 1 *The calculated curves of ion activity ratio dependence on diluted water solutions concentration are typical for: a) – the first group NaCl, KBr, KCl, CuCl₂, ZnCl₂, Na₂SO₄, ZnSO₄, CuSO₄; b) – second group HBr, HCl, LiCl; c) third group - MgCl₂, AlCl₃, CrCl₃, NiCl₂, FeCl₃.*

It is worth paying attention to a certain uniformity in the behavior of the dependence ions activity curves on concentration, which emphasizes the existence of a general mechanism in the interaction of particles for many diluted water solutions. However, the obtained results of activity cofficients calculations for a number of diluted water solutions allow to conclude that for single and double-valent electrolytes of the first group characteristic influence of the general mechanism of interaction between ions is characteristic. It is determined by the action of electric attraction forces and features of ion, in particular its interaction with molecules of solvent. Especially it is necessary to allocate the second group of dependence, where there is an increase of activity in the area of large concentration values for electrolytes, which contain ion of hydrogen and lithium. The analysis of experimental data for the third group gives an opportunity to conclude that the increase of activity values in the field of large concentrations of electrolytes is connected with the display of electric origin pushing forces (dependence on the valentness) in processes, which are accompanied by redistribution of charges. Water solutions properties of electrolytes can be described on the basis of the equation (2) for the dielectric component:

$$div\varepsilon_0\, E = \delta \cdot \Phi - \tau \cdot E, \qquad (2)$$

where δ and τ are self-concordance functions; E - field tension, Φ - electric field potential.

For the Debye atmosphere, the volumetric distribution of the electric field, whose output data is given by δ, is typical, therefore the following functions are obtained for this occasion (3):

$$\delta = \frac{\varepsilon_0}{r^2},\ \tau = \varepsilon_0 \cdot \frac{r+s}{r^2}. \qquad (3)$$

The expression for calculating the potential Φ has the following form:

$$\Phi = \frac{A}{r} \cdot e^{\frac{s}{r}}. \qquad (4)$$

The potential is related to the field strength by the relation (5):

$$E = -\nabla\Phi = \frac{A}{r^2} \cdot \left(1 + \frac{s}{r}\right) \cdot e^{\frac{s}{r}}. \qquad (5)$$

This distribution characterizes the field of a self-consistent system. Boundary conditions are set on the surface of the central ion for the electric induction vector flow in the following form (6):

$$\oint \varepsilon_0 E\, dS = q. \qquad (6)$$

In this case, for the constant A we have:

$$A = \frac{qa}{4\pi\varepsilon_0(a+s)} \cdot e^{\frac{s}{a}}. \qquad (7)$$

The volumetric charge density can be found from the relationship:

$$div\varepsilon_0\, E = \rho\ \text{або}\ \rho = \delta \cdot \Phi - \tau \cdot E. \qquad (8)$$

The corresponding calculations make it possible to calculate the potential, field and charge density in accordance with (3), (4), (6) and (7):

$$\Phi = \frac{q \cdot a}{4\pi\varepsilon_0(a+s)r} \cdot e^{\frac{s}{r}-\frac{s}{a}},$$
$$E = \frac{q \cdot a}{4\pi\varepsilon_0(a+s)r^2} \cdot \left(1 + \frac{s}{r}\right) \cdot e^{\frac{s}{r}-\frac{s}{a}}, \qquad (9)$$

$$\rho = -\frac{q \cdot a \cdot s}{4\pi \cdot (a+s) \cdot r^4} \cdot \left(\frac{s}{r} + 2\right) \cdot e^{\frac{s}{r} - \frac{s}{a}}.$$

The interaction energy in a self-consistent system with a central ion is determined on the basis of a known expression (Simonov, 2008; 2010):

$$W = \frac{1}{2} \int_V^0 \Phi \cdot \rho \cdot dV. \tag{10}$$

Integrating (10) over the entire volume from the surface of the ion of radius a in the spherical coordinate system, we get W taking into account the dielectric properties of the medium:

$$W = -\frac{q^2}{32\pi\varepsilon\varepsilon_0 \cdot s \cdot (a+s)^2} \cdot \left(a^2 \cdot \exp\left(-\frac{2s}{a}\right) + 2s^2 + 2sa - a^2\right). \tag{11}$$

The central ion induces a potential of the Coulomb type, therefore, for the potential of the ion field of the same sign, we obtain (12):

$$U = \frac{A}{r} \cdot e^{\frac{s}{r}} - \frac{q}{4\pi\varepsilon_0 r}. \tag{12}$$

The value of the potential difference Ψ is determined from the equation (13):

$$\Psi = \frac{q}{4\pi\varepsilon_0 a} - \frac{A}{a} \cdot e^{\frac{s}{a}}. \tag{13}$$

Then for the constant A we find:

$$A = \left(\frac{q}{4\pi\varepsilon_0 a} - \Psi\right) \cdot a \cdot e^{\frac{s}{a}}. \tag{14}$$

And for distribution potential we have:

$$U = \left(\frac{q}{4\pi\varepsilon_0 a} - \Psi\right) \cdot \frac{a}{r} \cdot e^{\frac{s}{r} - \frac{s}{a}} - \frac{q}{4\pi\varepsilon_0 r}. \tag{15}$$

The interaction energy in the ionic atmosphere is found on the basis of equation (16):

$$W_\rho = \frac{1}{2} \int \rho \cdot U dV, \tag{16}$$

where the charge density is determined by relation (8).

For the charge density, we get (17):

$$\rho = -\frac{q \cdot s}{4\pi r^5} \cdot (2r + s) \cdot e^{\frac{s}{r} - \frac{s}{a}}. \tag{17}$$

Using relation (16), taking into account (15), (17) and the influence of the dielectric constant of the medium, we find the interaction energy of ions in the volume region:

$$W_\rho = -\frac{q^2 \cdot (a^2 \cdot e^{-\frac{2s}{a}} - 2s^2 + 2sa - a^2)}{32\pi\varepsilon\varepsilon_0 a^2 s}. \tag{18}$$

Taking into account the influence of valence in equation (18) and obtain:

$$W_\rho = -\frac{z_i^2 e^2 n_i (n_i - 1) \cdot (a^2 \cdot e^{-\frac{2s}{a}} - 2s^2 + 2sa - a^2)}{32\pi\varepsilon\varepsilon_0 a^2 s}, \tag{19}$$

where $q = z_i e$, n_i – the number of ions in the Debye atmosphere.

The contribution of one ion to the interaction will be determined by expression (20):

$$W_{\rho s} = -\frac{z_i^2 e^2 (n_i - 1) \cdot (a^2 \cdot e^{-\frac{2s}{a}} - 2s^2 + 2sa - a^2)}{32\pi\varepsilon\varepsilon_0 a^2 s}, \tag{20}$$

The influence of the dilute aqueous solution concentration on the change in energy, taking into account the processes that occur at a constant charge and potential in the solution, can be found on the basis of the ratio $W + W_{\rho s}$, which determines the internal energy of the ion in the solution due to interaction with other ions. For a totality of ions in a solution, the change in internal energy will be proportional to the

number N_i of ions of this type. Then the change in the internal energy ΔU_i of a dilute aqueous solution for ions of "i" type and the free energy ΔF_i can be determined as:

$$\Delta U_i = N_i \cdot (W + W_{\rho s}), \tag{21}$$

where $N_i = V \cdot C_{0i} \cdot N_A$, C_{0i} – the equilibrium value of the ions concentration of this type in the solution, N_A – Avogadro number.

Taking into account expression (21) and the ratio $\Delta F = \Delta U$, we obtain the expression for the chemical potential of ions (22):

$$\mu_i = -\frac{\partial}{\partial C_{0i}}\left(\frac{C_{0i} z_i^2 e^2}{32\pi\varepsilon\varepsilon_0 \cdot s \cdot (a+s)^2} \cdot \left(a^2 \cdot e^{-\frac{2s}{a}} + 2s^2 + 2sa - a^2\right)\right) -$$

$$-\frac{\partial}{\partial C_{0i}}\left(\frac{C_{0i} z_i^2 e^2 (n_i - 1)}{32\pi\varepsilon\varepsilon_0 \cdot a^2 s} \cdot \left(a^2 \cdot e^{-\frac{2s}{a}} - 2s^2 + 2sa - a^2\right)\right). \tag{22}$$

Knowing the chemical potential, it is possible to determine the contribution of electrical factors that affect the deviation of the ion system from the set of ideal particles (Simonov, 2008; 2010).

The ions activity is found using the known ratio:

$$\mu_i = kT \ln\gamma_i,$$

then the average activity coefficient of diluted aqueous solutions, taking into account the nature of electrical factors, is determined by the expression (23):

$$\gamma_{ij} = e^{\left(\frac{n_i\mu_i + n_j\mu_j}{kT(n_i + n_j)}\right)}. \tag{23}$$

Conclusions

The proposed theory of activity calculation in a dilute aqueous solution based on the equation of continuum electrodynamics of self-consistent systems and processes characteristic of an electrical system will allow describing the set of experimental data for both multivalent dilute aqueous solutions and monovalent ones. The obtained results can be used to compare theoretically calculated and experimentally determined data on the dependence of ion activity coefficients on the concentration of diluted aqueous solutions. The proposed theory of activity calculation in a dilute aqueous solution based on the equation of continuum electrodynamics of self-consistent systems and processes characteristic of an electrical system will allow describing the set of experimental data for both multivalent dilute aqueous solutions and monovalent ones. The obtained results can be used to compare theoretically calculated and experimentally determined data on the dependence of ion activity coefficients on the concentration of diluted aqueous solutions.

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