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The theoretical calculation of activity coefficients in the use of baromembrane methods for water treatment

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SUMMARY

Baromembrane methods are a modern tool for implementing a number of priority areas of science, technology and engineering. One of the main problems in the use of baromembrane methods in water treatment processes is the problem of calculating one of the main parameters of these processes - osmotic pressure. For medium and high values of concentration, due to deviations of thermodynamic equations from ideality due to electrostatic forces and forces of intermolecular interaction, in the formula for calculating osmotic pressure it is necessary to enter values of activity coefficients. The existing methods of calculation of activity coefficients are analysed in the article and the method of theoretical calculation of activity coefficients in the process of using baromembrane methods for water treatment is offered.

Keywords: osmotic pressure, baromembrane methods, aqueous solution, activity coefficient, ion, thermodynamic processes

Introduction

Baromembrane methods are a modern tool for implementing a number of priority areas of science, technology and engineering. Their practical significance is taken into account, first of all, with the solution of important problems posed to humanity in the XXI century. Among them are the creation of highly efficient technologies for the preparation of quality drinking water, environmentally friendly food and the formation of the necessary balance between solving socio-economic problems and preserving the environment. One of the main problems in the use of baromembrane methods in water treatment processes is the problem of calculating one of the main parameters of these processes - osmotic pressure. For high concentrations of dilute aqueous solutions, which can be sources of water supply, there is a need to calculate the activity, which is expressed in relation to the concentration in the form:

$$a = \gamma \cdot c \quad (1)$$

where a – activity, c – concentration of aqueous solution, γ – activity coefficient.

Osmotic pressure in the general case is determined (Dytnersky, 1978) by the Vant-Goff equation:

$$\pi = iRT \frac{x}{M} \quad (2)$$

where x – the concentration of solute; M – mass of 1 mole of solute, g / mol; R – universal gas constant; T – absolute temperature, K ; i - Vant-Goff coefficient, that is, a value is introduced into the equation that takes into account the number of particles.

However, the presented formula is valid for aqueous solutions of low concentrations. For medium and high values of concentration, due to deviations of thermodynamic equations from ideality due to electrostatic forces and forces of intermolecular interaction, in the formula for calculating osmotic pressure it is necessary to enter values of activity coefficients, which are given in reference books only for some aqueous solutions, however, they do not have their unambiguity.

Methods of investigation

The study (Dytnersky, 1978) lacks generalized data from the theory of osmotic pressure calculation, and the values of osmotic pressure or osmotic coefficients given in the reference books are unsystematized. All this complicates the calculation of the membrane devices parameters for the processes of reverse osmosis, ultrafiltration and nanofiltration. To ensure the integrity of solving their use problem in the system "membrane - dilute aqueous solution" on the basis of the continuous theory of electricity a series of works electrolytes theory creation was performed, and, in particular, solving the problem of theoretical calculation of the aqueous solutions components activity taking into account the concentration (Simonov and Zahrai, 1992; Kravchenko, 2012). The problems of activity coefficients determination are mainly related to the idea of the charged particles interaction with each other in complex dilute aqueous solutions, which are, in most cases, cluster systems.

The difficulty in the activity calculating is that it is not possible to obtain an available explanation of the activity coefficients dependence on the aqueous solution concentration. Known theories based on the use of statistical physics methods are either very simplified and allow to describe experimental data in a narrow range of concentrations, or so cumbersome that do not allow their use in the high concentrations field (Simonov and Zahrai, 1994; 2001). The solute activity is associated with the chemical potential of charged particles in solution. In essence, the chemical potential of a charged particle is the Gibbs thermodynamic potential that falls on it in solution (Simonov and Zahrai, 1994).

Considering charged particle systems, even today, use methods developed by Debye and Huckel (Debye and Huckel, 1923), which give values of activity coefficients that are less consistent with their

experimentally determined values based on the continuous electricity theory. The efficiency and economic feasibility of baromembrane processes and their widespread use requires solving one of the main problems in substantiating and calculating these processes, the theoretical determination of the essence and content of activity coefficient γ in a wide range of concentrations for the whole range of components that are present in the water supply sources. From the works (Simonov and Zahrai, 1992; 1994) there is a known method of determining the energy of ions in solution - the Debye method or the process of ion charging. According to it, the distribution of the field around an ion with an ionic atmosphere can, at low interaction energies, be described by the equation:

$$\Delta U = \kappa^2 \cdot U \quad (3)$$

where U – distribution of the electric field potential around the central ion; κ – shielding radius by Debye.

For a binary electrolyte, the equation takes the form:

$$d^2 = \frac{F^2 z^+ z^- (z^+ + z^-) c_0}{\varepsilon \varepsilon_0 R T}, \kappa = \frac{1}{d} \quad (4)$$

where F – Faraday constant; z^+, z^- - valences; c_0 – electrolyte concentration; ε_0 – dielectric constant; ε – permittivity; R – universal gas constant; T – absolute temperature.

The potential around the ion is determined by solving the equation (3):

$$U = A \frac{e^{-\kappa r}}{r} \quad (5)$$

where the constant A can be determined from the boundary conditions, in particular, from the condition that at $r \rightarrow 0$ the potential must pass into the Coulomb field potential of the point charge $z_i e$, is:

$$\lim_{\kappa \rightarrow 0} U_{\kappa \rightarrow 0} = \frac{z_i e}{4\pi \varepsilon \varepsilon_0 r} \quad (6)$$

For the constant A is obtained equation:

$$U = \frac{z_i e e^{-\kappa r}}{4\pi \varepsilon \varepsilon_0 r}; A = \frac{e^{-\kappa r}}{r} \quad (7)$$

In an aqueous solution, at least, there is a pair of ions of opposite sign and such a system can be considered electroneutral in the first approximation. When concentrating the solution, the number of such pairs will increase. Along with this, the average distance between ion pairs decreases and the energy of interaction between ions in the pair and other pairs increases. Appears an effect of collective interaction. It should be noted that the ion pair, although electroneutral, creates a dipole-type field around it, in there is no shielding effect. Ions in aqueous solution are part of the clusters structure in general, and of the giant heterogeneous clusters in particular, forming electroneutral pairs not only between specifically isolated ions, but also with any other ion of the opposite sign with a cluster corresponding to the structure. In this case, the ion can approach from any direction due to the chaotic motion of particles. The average distance between a pair of ions, which is formed in such structures, when using statistical calculations, corresponds to the Debye distance (Simonov, 2001). The distance between the charges is determined by the structure of the dynamic equilibrium cluster system and the dipole can be considered as spherically symmetric (Simonov and Zagray, 1992; 2001). The countercharge of such a system is not formed by a single ion, which is limited by the cluster structure, and is a collective effect of ion penetration into the field of central charge and dipole formation for two ions or more complex spatial structures to which cluster systems belong. Therefore, the charge system is difficult to consider as a spatial capacity, even on the basis of cluster systems that can be charged or discharged, and the distance between the ions is determined by the structure of the cluster

system and at the same time the average ion potential is determined (Simonov and Zahrai, 1994; 2001). Thus, the process of ion and ion atmosphere charging can be studied only hypothetically. The calculation of thermodynamic quantities within the charging process cannot earn unambiguous character. Based on the theory of the Debye atmosphere, the paper (Simonov, 2001) shows the charging process that determines the energy costs associated with the charging of the central ion and the Debye atmosphere, which are part of the cluster structure. If N_i particles are dissolved in the volume under consideration, in there are N_i pairs of systems "central ion + ionic atmosphere", the energy spent on their charging will be equal to:

$$W_N = N_i \cdot W = -\frac{N_i z_i^2 e^2}{12\pi\epsilon\epsilon_0} \kappa \quad (8)$$

where W_N – energy of N particles spent on their charge; N_i - the number of dissolved particles that are identical to N_i pairs.

That is,

$$W_N = -\frac{N_i z_i^2 e^2}{12\pi\epsilon\epsilon_0} \cdot \sqrt{\frac{F^2 z^+ z^- (z^+ + z^-) c_0}{\epsilon\epsilon_0 RT}} \quad (9)$$

Taking into account that $N_i = V \cdot N_A \cdot C_0$, the last expression can be written as:

$$W_N = -f(V, T) \cdot c_0^{\frac{3}{2}} \quad (10)$$

The derivative by the number of particles in the system from the dependence (10) will lead to the expression for the chemical potential, is:

$$\mu_i = \mu_{i0} - \frac{3}{2V} f(V, T) \cdot c_0^{\frac{1}{2}} = \mu_{i0} - N_A \cdot \frac{z_i^2 e^2}{8\pi\epsilon\epsilon_0} \kappa \quad (11)$$

Thus, for the ions activity in solution due to the contribution of the Debye atmosphere (11) follows an expression with a known ratio:

$$\mu_i = \mu_{i0} + RT \ln a_i = \mu_{i0} - \frac{z_i^2 e^2}{8\pi\epsilon\epsilon_0} \kappa \quad (12)$$

from which follows:

$$\mu_i = \mu_{i0} + RT \ln a_i = \mu_{i0} + RT \ln c_i + RT \ln \gamma_i; \gamma_i = \exp\left(-\frac{z_i^2 e^2}{8\pi\epsilon\epsilon_0 kT} \kappa\right) \quad (13)$$

where k – Boltzmann constant equal to $(1,38054 \pm 0,00018) \cdot 10^{-23}$ J/K.

Osmotic coefficients of solution components are directly related to their activity and are important thermodynamic parameters of baromembrane processes. Thus, the considered methods (Simonov, 2001) of ion charging do not allow to obtain a consistent description of the activity in solution, but the continuous theory of electricity uses a different approach to solving the problem of activity in solution. In works (Simonov and Zahrai, 1994; 2001), taking into account the basic equation (3), the methods of continuous electrodynamics were applied to the problem of determining the activity of ions. The energy of ions with charge $z_i^2 e$ will differ from the energy of the ion in the extremely dilute solution by the value:

$$\Delta W_i = -\frac{z_i^2 e^2 \kappa a_i}{8\pi\epsilon\epsilon_0 (1+\kappa a_i)^2} \quad (14)$$

Based on expression (14), the calculation of the activity coefficient is obtained:

$$\gamma = \exp\left(-\frac{1}{kT} \cdot \frac{z_i^2 e^2 \kappa a_i}{8\pi\epsilon\epsilon_0 a_i (1+\kappa a_i)^2} \cdot \frac{n_i}{n_i+n_j} - \frac{1}{kT} \cdot \frac{z_j^2 e^2 \kappa a_j}{8\pi\epsilon\epsilon_0 a_j (1+\kappa a_j)^2} \cdot \frac{n_j}{n_i+n_j}\right) \quad (15)$$

where z_i – valences; ε_0 – dielectric constant; ε – permittivity; R – universal gas constant; T – absolute temperature; κ – Debye shielding radius; a_i – radius of the i -th ion; $z_i e$ – the potential of the point charge Coulomb field, k – Boltzmann constant.

The average values of the ions activity coefficients are often used, in this regard it is necessary to take into account the influence of ions of another grade. The calculation in this case does not differ from the above and it allows formally for ions of grade j to use this ratio with the index j .

The average activity coefficient is determined using ratios:

$$\ln \gamma_{ij} = \frac{n_i \ln \gamma_i + n_j \ln \gamma_j}{n_i + n_j} = \frac{1}{n} \sum_i n_i \ln \gamma_i \quad (16)$$

where n_i – the number of ions of grade "i", into which the electrolyte molecule breaks down; n – the number of ions in the molecule.

The regard effect of ion hydration on the formation of activity coefficients values is determined by the ratio:

$$\ln \lambda_{ci} = \frac{1}{kT} \cdot \frac{z_i^2 e^2}{8\pi \varepsilon \varepsilon_0} \cdot \frac{a_i - b_i}{a_i \cdot b_i} \quad (17)$$

where a_i, b_i – accordingly the outer and inner radii of the ion hydrate shell.

Taking into account the hydration of ions as the radius of the ion, it is necessary to consider the outer radius of the shell a_i , which allows more accurately describe the experimental data and calculate the necessary parameters in the design and construction of membrane devices.

Conclusions

Theoretical calculation of activity coefficients opens up fundamentally new, efficient and economically justified, possibilities in the field of installation parameters calculation and use of baromembrane methods in the process of adjusting the composition of dilute aqueous solutions in a wide concentration range and especially in high concentrations. Such areas of application of the proposed technique can be pharmaceutical, nuclear, food industry, medicine, water treatment with different purposes, especially demineralization of sea water.

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