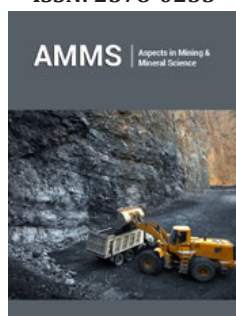# Thermodynamics of the Electrolyte Solutions

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Abstract

The article considers a statistical model of binary solutions of electrolytes to describe the concentration dependence of the thermodynamics properties of solution in the entire area of their existence, including separated solutions.

Keywords: Solvent activity; Osmotic coefficient; Hydration of electrolyte

Introduction

The coincidence of the formulations of Van Hoff 's law for dilute solutions and the equation of state for ideal gases reflects the general statistical regularities that determine the properties of these systems [1]. Moreover, the ideal gas itself is quite similar to a system consisting of particles of solute occupying a volume equal to the volume of the solution [2]. This analogy is also evident in systems with the interaction of components, for example, the Debye-Huckel theory is applicable for both electrolyte solutions and classical plasma in the state of a fully ionized gas. These facts characterizing the observed generality in the behavior of these systems can be taken as a basis for statistical description of the properties of electrolyte solution where the simplest formulations for the ideal gas are used as starting points.

Theory

According to Landau LD et al. [1], the Helmholtz free energy of an ideal gas containing N molecules in volume V can be represent as

$$A_{id} = N\chi - kTN \ln \frac{eV}{N} \quad (1)$$

where k is Boltzmann constant, T is temperature, χ is a certain function that depends only on temperature. In a solution that contains interacting components, free energy can be represented as [3]

$$A = A_w + N\chi - kTN \ln \frac{eV}{N} - NkT \ln Z \quad (2)$$

where A_w is free energy of solvent, Z is partition function. Eq.(2) can be generalized for solution containing particles of different grades. So, for a binary electrolyte solution containing N_p cations and N_n anions ($N=N_p+N_n$), we can write

$$A_s = A_w + \sum N_i \chi_i - kT \sum N_i \ln \frac{eV}{N_i} - kT \sum N_i \ln Z_i \quad (3)$$

where Z_i is the ionic constituent of the partition function. Differentiating Eq.(3) it is possible to determine the pressure in the system

$$P_s = -\left(\frac{\partial A_s}{\partial V}\right)_T = P_w + kT \frac{\sum N_i}{V} + kT \sum N_i \frac{\partial \ln Z_i}{\partial V} \quad (4)$$

where P_w refers to the pure solvent. Osmotic pressure is defined as

$$P = P_s - P_w \quad (5)$$

If there are no interactions in the solution and each value $Z_i=1$, the osmotic pressure of the ideal solution can be defined as

$$P_{id} = kT \frac{N}{V} \quad (6)$$

It's the Van Hoff equation. It bears a close resemblance to the equation of state of an ideal

gas and is applicable to ideal solutions regardless of the nature of both the solute and the solvent. Here instead of the pressure of gas there is osmotic pressure, instead of the volume of gas there is volume of solution, instead of the number of particles in the gas there is the number of particles of the dissolved substance.

The degree of deviation from the ideal solution is defined as $\varphi = \dfrac{P}{P_{id}}$, where ϕ is the osmotic coefficient, determined according to Eq. (4) and (6) as

$$\varphi = 1 + \frac{V}{N} \sum N_i \frac{\partial \ln Z_i}{\partial V} \quad (7)$$

In dilute solutions we can put $N \ll N_w$ and $V = N_w v_w$, where N_w is the number of solvent molecules and v_w is the molecular volume of the solvent. Then Eq.(7) can be represent as [3]

$$\varphi = \frac{P}{P_{id}} = 1 + \frac{N_w}{N} \sum N_i \frac{\partial \ln Z_i}{\partial N_w} \quad (8)$$

and Eq.(3) as

$$A_S = A_w + \sum N_i \chi_i - kT \sum N_i \ln \frac{e N_w v_w}{N_i} - kT \sum N_i \ln Z_i \quad (9)$$

Differentiating Eq.(9), we can determine the chemical potential of solvent in the electrolyte solution

$$\mu_w = \left(\frac{\partial A_S}{\partial N_w} \right)_{T,V,N_i} = \mu_w^0 - kT \left(\frac{\sum N_i}{N_w} + \sum N_i \frac{\partial \ln Z_i}{\partial N_w} \right) \quad (10)$$

where μ_w^0 is the chemical potential of a pure solvent. Using Eq.(8), Eq.(10) can be transformed to

$$\mu_w = \mu_w^0 - kT \varphi \frac{N}{N_w} \quad (11)$$

On the other hand, the chemical potential of the solvent can be determined as

$$\mu_w = \mu_w^0 + kT \ln a_w \quad (12)$$

where a_w is the solvent activity. Comparing Eq.(11) and Eq.(12), we have

$$\varphi = -\frac{N_w}{N} \ln a_w \quad (13)$$

Eq.(13) extends to the entire field of existence of electrolyte solution and is the basis for calculation the osmotic coefficient from experimental data. In aqueous electrolyte solutions, the solvent activity can be defined as $a_w = \dfrac{P_S'}{P_W'}$ and Eq.(13) can be represented in the form

$$\frac{P_S'}{P_W'} = e^{-\frac{N}{N_w} \varphi} \quad (14)$$

By limiting the exponential expansion to a linear term for dilute solutions, where one can put $\phi=1$, Eq.(14) can be represented as

$$\frac{P_w' - P_s'}{P_w'} = \frac{N}{N_w} \quad (15)$$

Thus, the relative decrease in vapor pressure during dissolution is equal to the concentration of the solution (Raoul's law). Eq.(15) contains the relative concentration of the solute $x=N/N_w$. This value is related to the molality (m) ratio

$$x = \frac{vm}{m_w} \quad (16)$$

where m_w is the number of moles of the solvent in 1kg (for water m_w=55.51), v is stoichiometric coefficient ($v = v_p + v_n$). Assuming the statistical independence of the ionic constituent of the partition function can determine the chemical potential of each ion

$$\mu_i = \left(\frac{\partial A_S}{\partial N_i} \right)_{T,N_w} = \chi_i - kT \ln v_w^0 + kT \ln \frac{N_i}{N_w} + kT \ln \gamma_i \quad (17)$$

where γ_i is the ion activity coefficient

$$\ln \gamma_i = -\ln Z_i - N_i \frac{\partial \ln Z_i}{\partial N_i} \quad (18)$$

The mean chemical potential can be defined as

$$\mu = \sum q_i \mu_i \quad (19)$$

where q_i is molar fraction of each ion

$$q_p = \frac{N_p}{N} = \frac{v_p}{v} \; ; \; q_n = \frac{N_n}{N} = \frac{v_n}{v} \quad (20)$$

Then using Eq.(18) and (19) we have

$$\mu = \sum q_i \chi_i - kT \ln v_w^0 + kT \ln \left(q_p^{q_p} q_n^{q_n} x \right) + kT \ln \gamma \quad (21)$$

where γ is the mean ionic activity coefficient.

$$\ln \gamma = \ln \left(\gamma_p^{q_p} \gamma_n^{q_n} \right) = -\ln Z - N \frac{\partial \ln Z}{\partial N} \quad (22)$$

Using Eq.(22) this value can be represented in the equivalent form (since m_w is a constant)

$$\ln \gamma = -\ln Z - x \frac{d \ln Z}{dx} \quad (23)$$

where the partition function of the solution is determined as

$$Z = Z_p^{q_p} Z_n^{q_n} \quad (24)$$

The chemical potentials of the solvent and the solute are related by the Gibss-Duhem equation, which, under the condition of constant temperature and pressure, takes the form

$$Nd\mu + N_w d\mu_w = 0 \quad (25)$$

Substituting here the values of chemical potentials, we have

$$d(\varphi x) = xd \ln (x\gamma) = x + xd \ln \gamma \quad (26)$$

Than using Eq.(23) and integrating Eq.(26) we obtain

$$\varphi = 1 - x \frac{d \ln Z}{dx} \quad (27)$$

Comparing Eq.(23) and Eq.(27) we also obtain equations

$$\ln \gamma = \varphi - 1 - \ln Z \quad (28)$$

$$\ln Z = -\int_0^x (\varphi - 1) d \ln x \quad (29)$$

Thus, the partition function of the solution can be determined experimentally. Turning to the theoretical estimation of the partition function of the solution, we assume that the various processes in the solution are independent. Then this value can be represented in form [4]

$$Z = Z_h Z_a Z_e \quad (30)$$

where Z_h, Z_a, Z_e are the partition functions corresponding to the processes of hydration, association and electrostatic interaction of ions, respectively. In this case, the osmotic coefficient of the solution

can be represented as separate components

$$\varphi = 1 + \varphi_h + \varphi_a + \varphi_e = 1 + \sum \varphi_i \quad (31)$$

the meaning of which clear from comparing the last equality with Eq.(27) and Eq.(31)

$$\varphi_i = -x \frac{d \ln Z_i}{dx} \quad (32)$$

Consider the process of hydration of ions, for example, an anion coordinating n water molecules around itself. The equilibrium constant of this process can be expressed as

$$K_n = \frac{N_n^*}{N_0^*} a_w^{-n} \quad (33)$$

where N_0^*, N_n^* is the number of free and hydrated ions (hydrate complex), respectively. In the formation of various forms of hydrated ions, we can write the equation of material balance

$$N_n = N_0^* + \sum_n N_n^* = N_0^* \sum_0^n K_n a_w^n \quad (34)$$

where, according Eq.(33), $K_0 = 1$.

The distribution function for a hydrated ion can be expressed as [3]

$$w_n = \frac{N_n^*}{N_n} = \frac{e^{-\varepsilon_n/kT}}{Z_n} \quad (35)$$

where ε_n is the difference of the energy between the standard states of the hydrate complex and its constituent components. For a free ion w_n makes the form

$$\frac{N_0^*}{N_n} = \frac{e^{-\varepsilon_0/kT}}{Z_n} = \frac{1}{Z_n} \quad (36)$$

where $\varepsilon_0 = 0$ is assumed, since this energy level is taken as the reference point. Comparing equations (34) and (36), the partition function of the ion hydration process can be determined as

$$Z_n = \sum_0^n K_n a_w^n \quad (37)$$

To determine the activity coefficient, the partition function mast be normalized. In an infinitely dilute solution, Z_n takes value

$$Z_{n0} = \sum_0^n K_n \quad (38)$$

and normalized partition function can be represented as

$$Z_n^* = \frac{Z_n}{Z_{n0}} = \frac{\sum_0^n K_n a_w^n}{\sum_0^n K_n} \quad (39)$$

This normalization condition is obviously not essential for determining the osmotic coefficient, since constant Z_{n0} disappears when function $\ln Z_n^*$ is differentiated.

The mean hydration number an ion is determined as

$$h_n = \frac{\sum_0^n n N_n^*}{N_n} \quad (40)$$

or using Eq.(35) in the form

$$h_n = \sum_0^n n w_n \quad (41)$$

where

$$w_n = \frac{N_n^*}{N_n} = \frac{K_n a_w^n}{\sum_0^n K_n a_w^n} \quad (42)$$

Function $\ln w_n$ can be expanded into Taylor series

$$\ln w_n = \ln w_n^0 + \left(\frac{d \ln w_n}{dx} \right)_0 x + \ldots \quad (43)$$

In an infinitely dilute solution $a_w = 1$ and $\phi = 1$, then using Eq.(42) we obtain

$$w_n^0 = \frac{K_n}{\sum_0^n K_n} \quad (44)$$

Limiting to the linear term in the Eq.(43) we have

$$w_n = w_n^0 e^{-B_n x} \quad (45)$$

where according Eq.(13)

$$B_n = \left(\frac{d \ln w_n}{dx} \right)_0 = \lim_{x \to 0} \frac{d \ln w_n}{d \ln a_w} \frac{d \ln a_w}{dx} = n - \frac{\sum_0^n n K_n}{\sum_0^n K_n} \quad (46)$$

Substitution Eq.(46) into eq.(41) we obtain

$$h_n = \sum h_n^0 e^{-B_n x} \quad (47)$$

where h_n^0 is the hydration number in an infinitely dilute solution

$$h_n^0 = n w_n^0 = \frac{n K_n}{\sum_0^n K_n} \quad (48)$$

Thus, the mean hydration number of each ion can be represented as the sum of the components containing a various number of water molecules. By combining Eq.(41) and (42), this value can be defined as

$$h_n = \frac{\sum_0^n n K_n a_w^n}{\sum_0^n K_n a_w^n} \quad (49)$$

This formula also can be obtained by differentiating Eq.(37)

$$h_n = \frac{d \ln Z_n}{d \ln a_w} \quad (50)$$

For another ion, we can write similar equations with a complete replacement of subscripts.

The mean hydration number of the electrolyte can be defined as

$$h = \sum q_i h_i = \frac{v_p}{v} \sum h_p^0 e^{-B_p x} + \frac{v_n}{v} \sum h_n^0 e^{-B_n x} \quad (51)$$

and also by an equation similar Eq.(50)

$$h = \frac{d \ln Z_h}{d \ln a_w} \quad (52)$$

where Z_h is the partition function of the process of hydration of the electrolyte, determined by Eq.(24).

Consider the hydration process in the absence of other interactions in solution. In this case, we can put $\phi_h = \phi - 1$. Using Eq.(32), this value can be defined as

$$\varphi_h = -x \frac{d \ln Z_h}{d \ln a_w} \frac{d \ln a_w}{dx} \quad (53)$$

where according Eq.(13)

$$\frac{d \ln a_w}{dx} = -\varphi - x \frac{d\varphi}{dx} \quad (54)$$

Substitution Eq.(52) and (54) into Eq.(53), we have

$$\varphi_h - (\varphi_h + 1)hx - \frac{d\varphi_h}{dx}hx^2 = 0 \quad (55)$$

Solving differential Eq.(55), limiting to a quadratic term, imagine as [4]

$$\varphi_h = hx + 2(hx)^2 \quad (56)$$

Eq.(56) shows the dependence of the hydration constituent of the osmotic coefficient on the solution concentration.

Turning to the description of the process of ion association in a solution, we restrict ourselves to considering the formation of molecular complexes with ratio of unlike ions 1:1, which is typical for most electrolyte solutions. The equilibrium constant of this process can by determined in the form

$$K_a = \frac{N_w N_a^*}{N_p^* N_n^*} \quad (57)$$

where N_a^*, N_p^*, N_n^* are the number of associates and free cations and anions, respectively. For each ion species, for example cation, the equation of material balance can be written down

$$N_p = N_p^* + N_a^* \quad (58)$$

Then from Eq.(57) and (58) we can determine the distribution function of free ions

$$\frac{N_p^*}{N_p} = \left(1 + \frac{K_a N_n^*}{N_w}\right)^{-1} \approx \left(1 + \frac{K_a N_n}{N_w}\right)^{-1} \quad (59)$$

where, when writing the last equality, the approximation is accepted $N_n^* \approx N_n$. Using an equation similar Eq.(36) we have

$$Z_p = 1 + q_n K_a x \quad (60)$$

For symmetric I-I and II-II valence electrolytes $q_p = q_p$ and $Z_p = Z_n = Z_a$, where Z_a is the partition function of the process of ion association. Hence according Eq.(32) we obtain

$$\varphi_a = -x \frac{d \ln Z_a}{dx} = -\frac{K_a x / 2}{1 + K_a x / 2} \quad (61)$$

In general case, for electrolytes of various types, in a good approximation, we can use equation

$$\varphi_a = -\frac{2q_p q_n K_a x}{1 + K_a x / 2} \quad (62)$$

As is known from electrostatics, the energy of the electrical interaction of a system of charged particles can be defined as

$$U_e = \frac{1}{2} \sum_i N_i z_i e_0 \psi_i \quad (63)$$

where e_0 is the elementary charge numerically equal to the charge of the electron, z_i are positive and negative numbers expressing the ion charge in units of elementary charge and ψ_i is the potential of the electric field acting on the ion from the side of the other charges at the point of location of the selected ion. The Debye-Huckel theory defines the potential of the electric field as [5,6]

$$\psi = z_i e_0 \frac{e^{-\chi r}}{Dr} \quad (64)$$

where D=4πε (ε is the dielectric constant of the medium) and χ has a dimension of inverse length

$$\chi = \left(\frac{4\pi e_0^2}{DkT} \sum_i \frac{N_i}{V} z_i^2\right)^{1/2} \quad (65)$$

and $1/\chi$ is called the Debye radius. This value can be considered as determining the size of the ionic atmosphere since the field becomes negligible at distances large compared to $1/\chi$. Based on the principle of additivity of electric fields, the potential ψ_i can be defined as the Debye potential ψ minus own potential to the selected ion equal $(z_i e_0)/Dr$ it follow

$$\psi_i = \frac{z_i e_0}{Dr}\left(e^{-\chi r} - 1\right) \quad (66)$$

From this expression we can determine the potential at the location of the selected ion using the expansion of the exponential in a Taylor series

$$\frac{e^{-\chi r} - 1}{r} = -\chi + \cdots \quad (67)$$

The omitted terms at r=0 turn to zero. Then, the potential ψ_i can be represented as

$$\psi_i = -\frac{z_i e_0}{D}\chi \quad (68)$$

Substitution this expression into Eq.(63) we have

$$U_e = -\frac{1}{2}\frac{e_0^2}{D}\chi \sum_i N_i z_i^2 \quad (69)$$

Eq.(69) is the basic equation of Debye-Huckel theory, which represents an amendment to the energy due the interaction of ions [6]. However, this correction is found in the variables T,V,N, which does not correspond to the proper variables of the potential U_e. For these variables the thermodynamics potential is the Helmholtz free energy. Therefore, using the well-known thermodynamics equation

$$\frac{\partial(A/T)}{\partial T} = -\frac{U_e}{T^2} \quad (70)$$

and Eq.(69) one can obtain a relation linking the potentials A_e and U_e for the Coulomb interaction

$$A_e = \frac{2}{3}U_e \quad (71)$$

The scope of Eq.(69) is limited to dilute solutions. In this approximation $N \ll N_w$ ions can be considered as point charge. However, at high concentrations, the physical size of the ions plays an important role; therefore, the electric field is bounded by a spherical surface at some distance r_0 from the center of symmetry where the selected ion is located. In this case, determining ψ_i for $r = r_0$ and substituting the result in Eq.(63), the energy of the Coulomb interaction can be determined as [7]

$$U_e = \frac{1}{2} \frac{e_0^2}{D} \frac{e^{-\chi r_0} - 1}{r_0} \sum_i N_i z_i^2 \quad (72)$$

Further, using Eq.(71) we have finally

$$A_e = \frac{1}{3} \frac{e_0^2}{D} \frac{e^{-\chi r_0} - 1}{r_0} \sum_i N_i z_i^2 \quad (73)$$

The contribution of the Coulomb interaction to the osmotic pressure of the solution can be determined by differentiating Eq.(73)

$$P_e = -\left(\frac{\partial A_e}{\partial V}\right)_T = -\frac{1}{6} \frac{e_0^2}{DV} \chi e^{-\chi r_0} \sum_i N_i z_i^2 \quad (74)$$

and further determine corresponding value

$$\varphi_e = \frac{P_e}{P_{id}} = -\frac{1}{6} \frac{e_0^2}{DkT} \frac{\sum N_i z_i^2}{\sum N_i} \chi e^{-\chi r_0} \quad (75)$$

Using definition $z_p N_p = -z_n N_n$ from which equality $\sum N_i z_i^2 = |z_p z_n| \sum N_i$ follows, Eq.(75) can be represented in a compact form

$$\varphi_e = -\frac{1}{6} |z_p z_n| L \chi e^{-\chi r_0} \quad (76)$$

where $L = \frac{e_0^2}{DkT}$. Similarly, Eq.(65) can be transformed as

$$\chi = \left(4\pi |z_p z_n| L \frac{N}{V}\right)^{1/2} \quad (77)$$

In an infinitely dilute solution assuming as before $V = N_w v_w$, the Eq.(77) can be represented as

$$\chi = Q |z_p z_n|^{1/2} x^{1/2} \quad (78)$$

where $Q = \left(\frac{4\pi L N_A}{v_w}\right)^{1/2}$, N_A is Avogadro number, and

then present Eq.(76) in a convenient form for calculation

$$\varphi_e = -\frac{1}{6} L Q |z_p z_n|^{3/2} x^{1/2} \exp\left(-Q r_0 |z_p z_n|^{1/2} x^{1/2}\right) \quad (79)$$

where $L = 7.156 * 10^{-8}$ cm and $Q = 1.735 * 10^8$ cm^{-1} for aqueous solution at 298K.

Discussion

From Eq.(76) it follows that the osmotic coefficient in case of Coulomb interaction ($\phi = 1 + \phi_e$) tends to the ideal value both with dilution of the solution and with increase in its concentration (Figure 1). Such a change in the osmotic coefficient corresponds to the physical meaning of the model under discussion. If the ions were uniformly distributed in the solution independently of each other, then the mean value of the Coulomb interaction energy would vanish, since the solution as a whole is electrical neutral. Therefore, corrections in the thermodynamics values of the solution arise only when the correlation between the positions of various particles is taken into account. Comparing the average distance between particles $r_m \sim c^{-1/3}$, where c=N/V, and the Debye radius $r_D \sim c^{-1/2}$, which determines the correlation scope, it can be notes that with a decreases in the concentration of the solution (c<1), the ratio r_D/r_m increases, so that the correlation captures an increasing number of particles, but the solution becomes ideal because c→0. In the opposite case, with an increase in the concentration of the solution (c>1), the ratio r_D/r_m decreases and a smaller number of particles appear in the correlation sphere, and despite the increase in the solution concentration, the osmotic pressure tends to the ideal value. To confirm this reasoning, we will give some examples. In dilute solutions, when using approximation $e^{-\chi r_0} \approx \frac{1}{(1 + x r_0)}$, Eq.(76) take the form

$$\varphi_e = -\frac{1}{6} |z_p z_n| L \frac{\chi}{1 + \chi r_0} \quad (80)$$
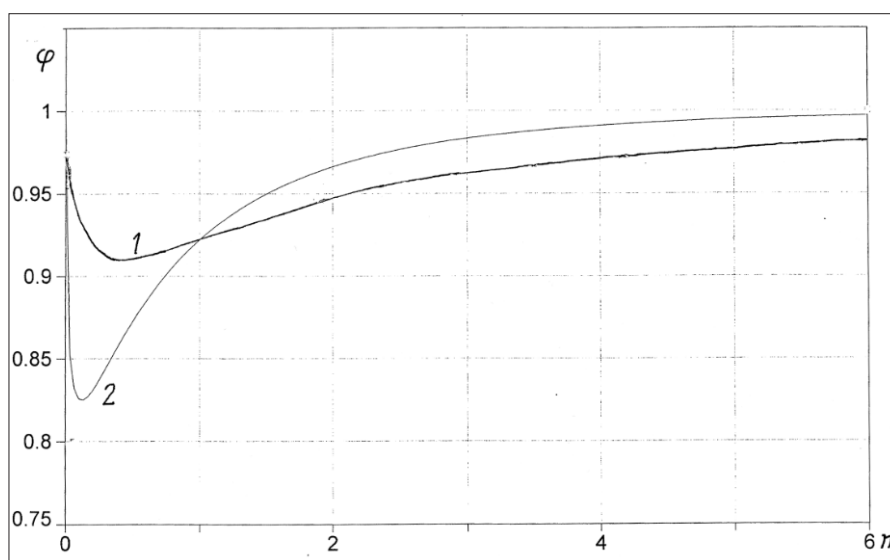
Figure 1: Coulomb component of the osmotic coefficient of aqueous solutions at $r_0 = 0.5$nm and 298K. 1: I-I valence electrolyte, 2: II-I valence electrolyte.

This formula differs from the result of the Debye-Huckel theory, but fully corresponds to the second virial coefficient in the Pitzer theory [8]. Using Eq.(32), we can determine the partition function corresponding to Coulomb interaction as

$$\ln Z_e = \frac{1}{3} L |z_p z_n| \frac{1 - e^{-\chi r_0}}{r_0} \quad (81)$$

and then obtain the conductivity equation of electrolyte solutions

$$\Lambda = \Lambda_0 \exp\left(-\frac{1}{3} \beta L |z_p z_n| \frac{1 - e^{-\chi r_0}}{r_0} - 2 \frac{v_p v_n}{v} K_a c \right) \quad (82)$$

where Λ_0 is equivalent electric conductivity in an infinitely dilute solution, c is molarity. This equation described well the experimental data in both dilute and highly concentrated solution, and parameter β is completely consistent with the result of calculation according the Onsager theory [9]. In other cases, when, on the contrary, the Coulomb interaction can be neglected, can be found equation for describing the density of electrolyte solutions [10] and describing thermodynamics characteristics of binary solution of nonelectrolytes [11], and also calculating the separated factor of inorganic substances during crystallization from solutions [12]. However, when calculating the osmotic coefficient of electrolyte solutions, all interaction processes must be taken into account.

Let's imagine Eq.(13) in a more convenient form for analysis,

$$a_w = e^{-\varphi x} \quad (83)$$

from which it is clear that at a given concentration the osmotic coefficient reflects the total interaction of the dissolved substance with the solvent, so the higher its value, the lower the activity of the solvent. Thus, comparing the solvent activity in solutions of various salts at the same concentration, their relative degree of hydration can be estimated, since ions hydration leads to an increase in the osmotic coefficient, and other interaction act in the opposite direction. For example, aqueous solution of alkaline halides can see the growth of the osmotic coefficient in the series of compounds with a common ion (Figure 2): for Cs^+ is I<Br<Cl<F, for Rb^+ is Br<I<Cl<F , for K^+ is Cl<Br<I<F , for Na^+ is F<Cl<Br<I , for Li^+ is Cl<Br<I. Using a similar construction for cations, all ions can be arranged in order to increase hydration: I≤Cs<Rb<Br<Cl<K<F≤Na<Li. Location in this series of both cations and anions corresponds to a change in the surface density of their charge, so ions of the same species having a smaller size distinguish a greater degree of hydration. From this point of view, the inversion of the osmotic coefficient in a series of anions from F^- to I^- can be explained when cesium ion is replaced by a sodium ion. Large cesium ion are slightly hydrated; therefore, when replaced with a smaller sodium ion, an increase in the osmotic coefficient is observed. On the contrary, in the series from I^- to F^-, when anions are replaced in solutions containing sodium ions, hydration is weakened due to more powerful counteraction from the side of a smaller ion. In the series of alkali metal compounds, when passing from chlorides to hydroxides, hydration is more pronounced, the greater the difference in the sizes of the ions forming this compound (Figure 3). Otherwise, hydration is weakened up to its complete disappearance in solution LiOH, where it is possible to put $\phi=1+\phi_e$ (Table 1). Thus, we can formulate a model of competitive hydration, where only one is hydrated, creating a more powerful electric field.
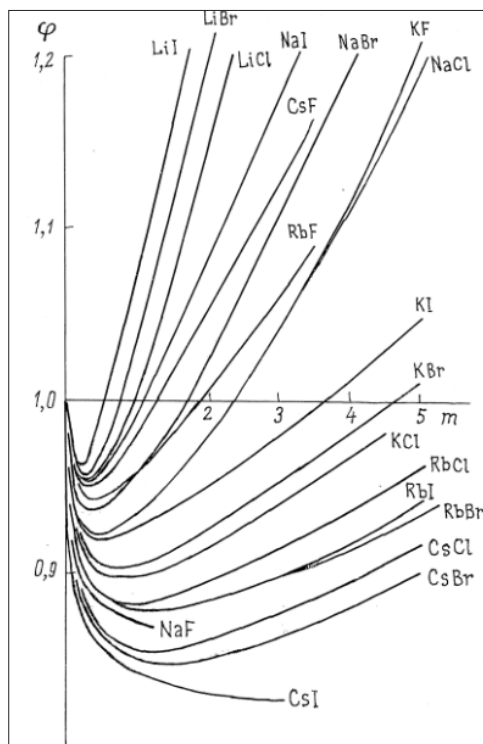
Figure 2: Osmotic coefficients of aqueous solutions of alkali halides at 298K.
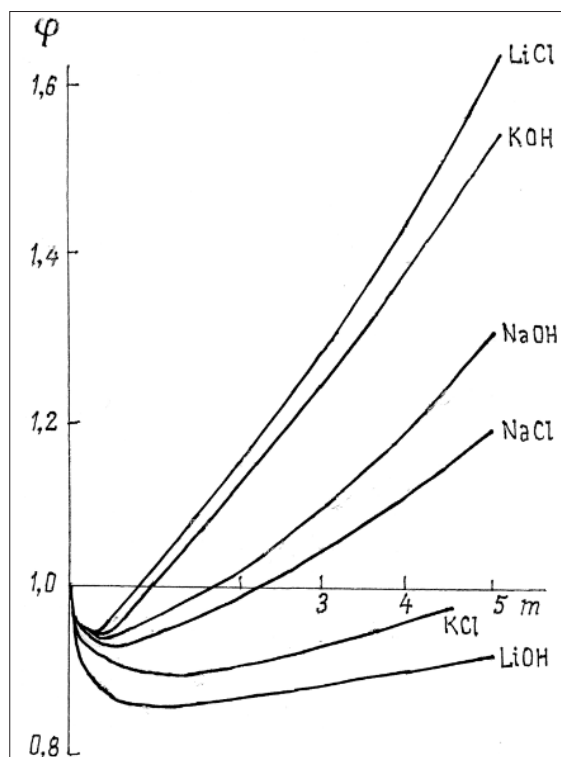
Figure 3: Osmotic coefficients of aqueous solutions of hydroxides and chlorides of an alkaline elements at 298K.

Table 1: The parameters for calculating osmotic coefficient of aqueous solutions of electrolytes at 298K.

Electrolyte	r_0, nm	K_a	h*	B	m, mol/kg	δ, %
HCl	5.297	0.267	2.751	1.182	19.0	0.3
HBr	6.634	4.10^{-4}	3.006	1.007	16.0	1.0
HI	7.974	1.10^{-4}	3.233	0.474	3.0	0.3
HClO₄	6.091	2.725	3.365	0.841	16.0	0.3
HNO₃	4.948	0.173	1.448	1.512	30.0	0.5
H₂SO₄	2.269	1.377	0.625	0.333	76.0	1.0
			1.129	1.476		
H₃PO₄	16.134	2711.61	0.329	0.481	30.0	0.6
AgNO₃	4.692	12.294	0.195	0.083	15.12*)	0.2
LiCl	8.036	6.923	3.586	1.379	19.93*)	0.5
LiI	8.576	2.149	3.163	2.10^{-4}	12.19*)	0.1
LiOH	3.138	1.10^{-5}	0	0	5.39*)	0.5
NaF	5.228	3.507	0	0	0.99*)	0.2
NaCl	6.143	7.201	2.564	1.536	6.15*)	0.1
NaI	5.641	2.289	2.348	1.414	12.28*)	0.3
NaClO₃	5.967	9.483	2.195	2.746	9.44*)	0.2
NaClO₄	4.8	3.08	1.259	0.974	17.14*)	0.5
NaBrO₃	5.561	10.015	1.249	0.029	2.61*)	0.1
NaH₂PO₄	5.874	15.868	1.561	1.61	7.9*)	0.1
NaNO₃	4.939	6.859	1.067	1.407	10.8*)	0.2
Na(CH₃COO)	6.549	4.781	3.186	2.486	3.50	0.1

NaNCS	6.686	5.032	2.387	1.502	17.12*)	0.3
Na_2CO_3	4.73	16.654	2.218	2.216	4.82*)	0.3
Na_2SO_4	5.58	28.105	1.346	0.377	3.63*)	0.3
KF	5.439	5.882	2.331	1.213	16.68*)	0.5
KCl	6.043	9.878	2.651	2.668	4.83*)	0.1
KOH	5.171	1.692	2.542	0.997	21.0*)	0.2
NH_4Cl	5.508	7.62	2.189	2.461	7.39	0.1
NH_4NO_3	4.252	6.056	0.473	0.93	27.0	0.2
RbCl	5.195	7.943	2.141	2.124	7.78*)	0.1
RbBr	5.132	7.682	1.994	2.152	6.89*)	0.1
CsCl	4.093	6.593	1.753	1.713	11.37*)	0.2
CsI	3.608	1.884	0	0	3.33*)	0.2
$CsNO_3$	3.994	10.41	0.239	2.10^{-3}	1.4*)	0.2
$BeSO_4$	5.363	66.781	4.766	1.527	4.83*)	0.5
$Mg(CH_3COO)_2$	4.621	13.193	3.121	2.313	4.62*)	0.3
$Mg(NO_3)_2$	5.602	7.865	4.082	1.482	5.06*)	0.3
$MgSO_4$	6.393	95.41	4.642	1.939	3.68*)	0.6
$CaCl_2$	6.649	18.335	4.968	1.794	7.41*)	0.6
$FeCl_2$	5.721	14.99	5.324	2.901	5.09*)	0.7
$NiCl_2$	6.362	18.439	5.708	2.598	5.06*)	0.3
$NiSO_4$	6.121	100	3.56	1.10^{-4}	2.66*)	0.7
$MnSO_4$	5.997	90.395	3.562	0.602	3.84*)	0.3
$CoCl_2$	6.622	20.89	6.027	3.171	4.33*)	0.2
$Cu(NO_3)_2$	5.257	8.995	3.621	1.611	8.04*)	0.5
$CuSO_4$	5.428	80.267	3.195	1.10^{-3}	1.4*)	0.3
$CdSO_4$	5.606	87.04	3.269	0.494	3.7*)	0.5
$Pb(NO_3)_2$	4.138	23.56	0.187	0.002	1.8*)	0.5
$Pb(ClO_4)_2$	4.579	2.637	3.449	1.322	10.83*)	1
$ZnCl_2$	7.026	25.729	2.007	0.924	22.0	0.5
			3.473	26.17		
$ZnBr_2$	7.439	36.632	2.318	1.03	20.9*)	0.5
			9.006	17.503		
ZnI_2	9.421	54.7	2.5	1.104	12.0	0.5
			12.256	15.598		
$Zn(ClO_4)_2$	6.535	8.967	6.54	1.668	4.3*)	0.5
$Zn(NO_3)_2$	5.588	7.829	4.04	1.616	6.72*)	0.7
$ZnSO_4$	6.099	95.867	3.632	3.10^{-4}	3.59*)	0.6
$UO_2(ClO_4)_2$	7.431	6.753	7.701	1.908	5.50	0.2
$AlCl_3$	6.67	33.579	6.828	1.798	3.46*)	0.5
$Al_2(SO_4)_3$	8.928	293.961	4.943	0.312	1.12*)	0.5
$Cr(NO_3)_3$	6.813	44.619	7.166	3.791	1.4	0.3
$LaCl_3$	6.454	38.048	5.841	2.434	3.97*)	0.5
$Th(NO_3)_4$	8.923	259.12	3.525	2.384	4.0*)	0.5

) saturated solution; m is upper limit of concentration, lower limit 0.1m for all electrolytes; δ is average approximation error; bottom line is the second pair of values h and B.

To calculate the hydrate constituent of the osmotic coefficient we restrict ourselves to a maximum of two form of hydrate complexes and present Eq.(51) in the form

$$h = h_1^* e^{-B_1 x} + h_2^* e^{-B_2 x} \quad (84)$$

where h_1^* and h_2^* can belong to one of the ions or to both ions. These values include stoichiometric coefficients, so hydration number of the select ion is determined as $h_i^0 = \nu/\nu_i h_i^*$. For example, for an aqueous solution of sulfuric acid, the most stable form corresponds to hydration of the proton and the hydration number in infinitely diluted solution is determined as $h_p^0 = \nu/\nu_p h_1^* = 3/2 h_1^* \approx 1$. This value corresponds to formula H_3O^+, and even with solution concentration 76m fourth hydrogen ion is in this form, while the probability of existence of the second form is less than 1/400. This form should also be attributed to the hydrogen ion because of the ion radii $r(H_3O^+)=0,113nm$ and $r(SO_4^{2-})=0.24nm$ [13] it follows that the surface charge density of the ion H_3O^+ more than twice as high. A similar pattern can be observed in aqueous solution ZnI_2. (Figure 4) shows the contribution of two hydrated forms, from which it can be seen that at high concentration only the most stable form exist. In the series of zinc halides, there is an increase in hydration during the transition from chloride to zinc iodide due to the weakening of the competitive ability of anions in this series, therefore, the second hydration number in (Table 1) should also be attributed to zinc ion.
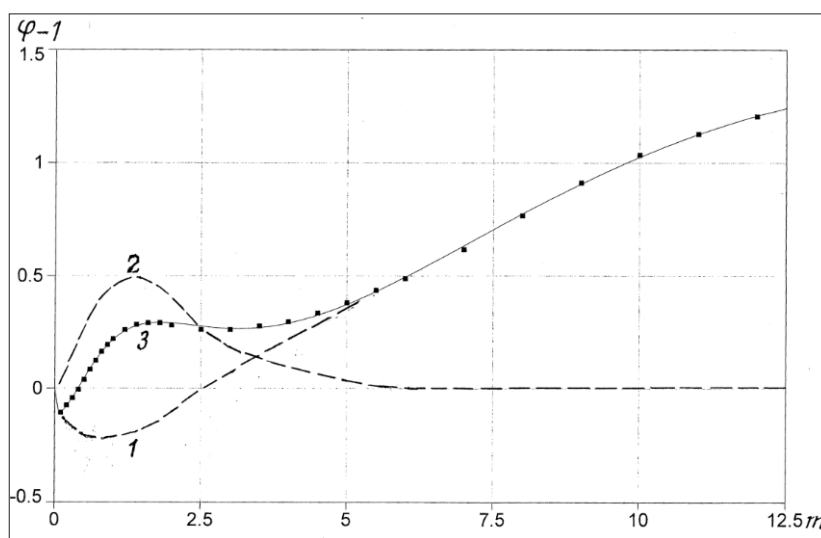
Figure 4: Osmotic coefficients of aqueous solutions ZnI_2 at 298K. 1: $h_1^*=2.5$; $B_1=1.1$; 2: $h_1^*=12.3$; $B_1=15.6$; 3: calculated curve and experimental points.

As shown in (Table 1) the above statistical model of binary solution of electrolytes describes well the known experimental data [14,15], with the exception of cadmium halide solutions, where it is possible to form a number of associates, for example, CdI^+, CdI_2, CdI_3^-, CdI_4^{2-}, that requires the use of supplementary parameters. In addition, this model allows us to calculate the osmotic coefficient of dilute solutions based on data from concentrated solution (Table 2), and thus covers the entire area of existence of solution.

Table 2: Osmotic coefficient of dilute electrolyte solutions at 298K.

m	Cacl$_2$		KCl		NaCl	
	(calc)	(meas)	(calc)	(meas)	(calc)	(meas)
0.0016	0.954	0.953	-	-	-	-
0.0064	0.920	0.919	0.973	0.973	0.974	0.973
0.0144	0.894	0.894	-	-	-	-
0.0256	0.879	0.877	0.953	0.952	0.955	0.954
0.0400	0.867	0.867	-	-	-	-
0.0576	0.859	0.860	0.938	0.937	0.941	0.940
0.0784	0.855	0.857	-	-	-	-
0.1024	-	-	0.926	0.926	0.932	0.931

Conclusion

The statistical model of solution includes the main factors of the deviation of the thermodynamics functions of binary solution of electrolytes from the ideal values–Coulomb interaction, hydration and ion association, and allows us to calculate the osmotic coefficient of solution in the entire area of the existence of solution. This model provides the basis for calculation the separation factor of inorganic substances during crystallization from solution, as well as for calculation the density and conductivity of solutions required for the control of mineral processing technology.

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