

## PHYSICAL CHEMISTRY OF SOLUTIONS

# Dependences of the Osmotic Coefficients of Aqueous Calcium Chloride Solutions on Concentration at Different Temperatures

A. M. Rudakov, V. V. Sergievskii\*, and O. A. Nagovitsyna

National Research Nuclear University, Moscow Engineering Physics Institute (MEPhI), Moscow, 115409 Russia

\*e-mail: vsereg@mail333.com

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**Abstract**—A model that considers the contributions from hydration, ion association, and electrostatic interactions to the nonideality of 2–1 electrolyte solutions is substantiated. The parameters of the model's equations are the mean ion hydration number, the spread of the distribution of hydrated ion stoichiometric coefficients in the standard state, and the number of association. The model is successfully used to describe literature experimental data on the concentration dependence of osmotic coefficients of aqueous  $\text{CaCl}_2$  solutions at temperatures ranging from 0 to 100°C. The modeling of the above systems shows that as the temperature rises, the hydration number falls slightly, the distribution of the hydration number broadens, and the ion pairing of the salt rises by the first degree.

**Keywords:** aqueous solutions, calcium chloride, modeling, ion hydration, osmotic coefficient, activity coefficient

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## INTRODUCTION

Nonideality in aqueous electrolyte solutions results from Coulombic interactions, ion association, and solvation. A number of physical models of electrolyte solutions have been proposed whose equations of state allow us to describe the dependences of the thermodynamic properties of solutions (osmotic coefficients ( $\phi$ ), the activity of water ( $a_w$ ), and the mean coefficients of ionic activity ( $\gamma_{\pm}$ )) [1–4]. The Robinson–Stokes model considers electrostatic interactions through the Debye–Hückel equation, and electrolyte solvation is described by hydration number  $h$ . It is assumed that the value of  $h$  does not depend on the concentration of the electrolyte solution [1]. The Robinson–Stokes equation agrees with experimental data on  $\phi$  and  $\gamma_{\pm}$  in a limited range of solution concentrations [1–4].

Researchers have recently shown much interest in the Zavitsas model, in which the activity of water is determined by the mole fraction of unbound water, which is calculated by considering the electrolyte hydration number [5]. In his theory, Zavitsas also assumed the complete dissociation of the electrolyte, and that the electrolyte hydration number does not change along with concentration.

In concentrated solutions, deviations from Raoult's law are negative; i.e., they are chiefly due to the hydration of ions. This is the reason for the satisfactory agreement between the experimental data and predictions based on the Zavitsas model for saturated

vapor pressure over concentrated solutions [6]. Nevertheless, the values for  $\gamma_{\pm}$  calculated using the Zavitsas model and considering only hydration's contribution to complete nonideality were found to exceed unity in every considered case [7].

In our earlier works, we focused on solvation's contribution to the deviation of the thermodynamic properties of electrolyte and nonelectrolyte solutions from ideal behavior [4]. Using the example of systems containing alkali metal nitrites, the concept of a mean ionic hydration number enabled us to describe the thermodynamic properties of 1–1 electrolyte solutions over the range of concentrations from diluted to saturated solutions (e.g., up to a molal concentration of 36 mol/kg of water for cesium nitrate).

The aim of this work is to develop a model that can predict the thermodynamic properties of concentrated aqueous solutions of 2–1 electrolytes, in which ion association and ion hydration contribute to their nonideality. The model is applied to literature data on aqueous calcium chloride solutions characterized by a broad range of temperatures and concentrations (up to that of saturation) [1, 6–10].

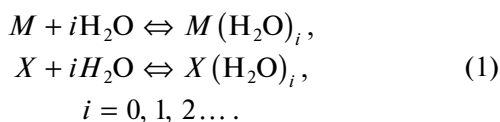
## THEORY

In the proposed model, the nonideality of electrolyte solutions is attributed to ion hydration, association, and electrostatic interactions between ions—fac-

tors that are assumed to operate independently of each other.

### Mean Ion Hydration

Let us consider a solution containing  $n$  moles of electrolyte  $M_{v_+}X_{v_-}$ . At infinite dilution, the solution contains  $(v_+ + v_-)n = \nu n$  moles of ions, where  $\nu$  is the stoichiometric total number of ions into which the electrolyte dissociates. Upon interaction with water, a series of stoichiometric hydrated ions emerges:



The presumed formation of hydrated ions with variable hydration stoichiometry implies that the hydration numbers must follow some (statistical) distribution. We define mean hydration number  $h$  of the electrolyte as its mathematical expectation:

$$h = \frac{v_+ \sum_i i n_{+,i} + v_- \sum_i i n_{-,i}}{\nu n}, \quad (2)$$

where  $n_{+,i}$  and  $n_{-,i}$  are the number of moles of cations and anions, respectively, with hydration number  $i$ . Equation (2) implies that the mean hydration number depends on the solution's composition. The concentration dependence of the mean hydration number is given by [4]

$$h = h_1 x_s^{r_1}. \quad (3)$$

Here,  $r_1 = D_1/h_1$  is the mathematical expectation of the hydrated ion distribution in which  $h_1 = h(x_s = 1)$ ;  $D_1 = D(x_s = 1)$  is the variance of this distribution at water mole fraction  $x_s = 1$ ; and  $h_1$  is the mean ion hydration number at an activity of water equal to unity.

Considering Eq. (3), the equation for the activity of water  $a_s$  is

$$a_s = \frac{n_s^0 - \nu h_1 x_s^{r_1} m}{n_s^0 - \nu h_1 x_s^{r_1} m + \nu m}. \quad (4)$$

Here,  $n_s^0 = 55.508$  mol/kg is the number of moles of water in one kilogram of water and  $m$  is the molal concentration of the electrolyte. From the definition of rational activity coefficient  $f_s$  of water according to equation  $a_s = f_s x_s$  for hydration's contribution to activity coefficient  $f_{s,h}$  of water, it follows from Eq. (4) that

$$\ln f_{s,h} = \ln \left( 1 - \frac{h_1 x_s^{r_1-1} x^2}{1 - h_1 x_s^{r_1} x} \right), \quad (5)$$

where  $x$  is the electrolyte mole fraction. Noting that the expression under the logarithm is considerably less than unity, Eq. (5) can be simplified by developing the

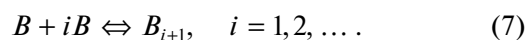
right-hand side into a power series. Limiting ourselves to the first member of the series, we obtain

$$\ln f_{s,h} = - \frac{h_1 x_s^{r_1-1} x^2}{1 - h_1 x_s^{r_1} x}. \quad (6)$$

Equation (6) defines the contribution from the mean ion hydration to the activity coefficient of water as a function of solution concentration and model parameters  $h_1$  and  $r_1$ .

### Ion Association

A rise in the concentration of electrolytes in solutions leads to the formation of ion associates. In simplified form, this process can be presented as association in a solution containing  $N = \nu n$  identical particles of solute  $B$ :



The existence of ion associates with different numbers of association  $i$  implies there is a distribution of forming compounds that follows the numbers of association.

The form of the concentration dependence of the mean number of association in solutions of unlimitedly soluble nonelectrolytes was established in [4]:

$A = A_1 x^{t_1}$ , where  $t_1 = D_{A_1}/A_1$ ;  $A_1 = A(x = 1)$  is the mean number of association or the mathematical expectation; and  $D_{A_1} = D_A(x = 1)$  is the variance of the distribution of associates at electrolyte mole fraction  $x = 1$ . As with systems that have limited solubility of components, we shall use this equation in a simpler form for solutions of electrolytes:

$$A = A_1 x. \quad (8)$$

In light of Eq. (8), the equation for the activity of water can be written as

$$a_s = \frac{n_s^0}{n_s^0 + \nu m / (1 + A_1 x)}. \quad (9)$$

From Eq. (9), we obtain the contribution from association to activity coefficient  $f_{s,a}$  of water:

$$\ln f_{s,a} = \ln \left( 1 + \frac{A_1 x^2}{1 + A_1 x x_s} \right). \quad (10)$$

Since inequalities  $A_1 x^2 \ll 1$  and  $A_1 x_s x \ll 1$  are always true for the investigated system, expression (10) can be written in the form

$$\ln f_{s,a} = A_1 x^2. \quad (11)$$

From Eqs. (11) and the Gibbs–Duhem equations, it follows that the contribution from ion association to the coefficient of electrolyte activity is described by the equation

$$\ln f_{\pm,a} = -A_1 x(1 + x_s). \quad (12)$$

**Table 1.** Results from modeling the concentration dependence of the osmotic coefficient and calculating the mean ionic activity coefficient of  $\text{CaCl}_2$  in aqueous solutions at 25°C

$h_1$	$r_1$	$A_1$	$A_{\max}$	$B_D$	$\sigma_\phi \times 10^3$	$\Delta_\phi, \%$	$\sigma_\gamma$	$\Delta_\gamma, \%$	Ref.
5.45	2.24	1.71	0.49	1.53	5.0	0.24	0.08	0.9	[1]
5.40	2.22	1.55	0.45	1.52	3.1	0.15	0.08	0.9	[10]
5.48	2.25	1.78	0.51	1.53	2.6	0.15	0.06	0.5	[9]
5.50	2.26	1.85	0.53	1.53	2.9	0.15	0.06	0.4	[11]

### Electrostatic Interaction

Electrostatic interactions are considered using an extended Debye–Hückel equation. The expression for the osmotic coefficient then takes the form

$$\phi = 1 + \phi_D, \quad (13)$$

where

$$\phi_D = -\frac{A_D |z_1 z_2| \sqrt{I}}{(B_D \sqrt{I})^3} \times \left( \frac{(1 + B_D \sqrt{I})^2 - 2 \ln(1 + B_D \sqrt{I}) - 1}{1 + B_D \sqrt{I}} \right), \quad (14)$$

while the formula for the mean ionic activity coefficient is

$$\ln \gamma_{\pm, D} = -\frac{A_D |z_1 z_2| \sqrt{I}}{1 + B_D \sqrt{I}}, \quad (15)$$

where  $A_D$  and  $B_D$  are parameters from the Debye–Hückel theory,  $I$  is the ionic strength of the solution, and  $z_1$  and  $z_2$  are the charges of ions.

### Equations for the Osmotic Coefficient and the Coefficient of Electrolyte Activity

Summing the contributions from the above factors to nonideality yields the equations

$$\phi = -\frac{A_D |z_1 z_2| \sqrt{I}}{(B_D \sqrt{I})^3} \times \left( \frac{(1 + B_D \sqrt{I})^2 - 2 \ln(1 + B_D \sqrt{I}) - 1}{1 + B_D \sqrt{I}} \right) - \frac{n_s^0}{vm} \left( -\frac{h_1 x_s^{r_1-1} x^2}{1 - h_1 x_s^{r_1} x} + A_1 x^2 + \ln x_s \right) \quad (16)$$

for the osmotic coefficient, and

$$\ln \gamma_{\pm} = -\frac{A_D |z_1 z_2| \sqrt{I}}{1 + B_D \sqrt{I}} + \int_{x=0}^x \frac{x-1}{x} d \ln f_{s,h} - A_1 x(1 + x_s) + \ln x_s \quad (17)$$

for the mean ionic coefficient of electrolyte activity.

The parametric identification of the model was done by modeling the experimental data according to the concentration dependence of the osmotic coefficient of aqueous calcium chloride solutions, both at room temperature and in the extended temperature range of 0 to 100°C.

## RESULTS AND DISCUSSION

As our criterion of optimization, we chose the value of standard deviation

$$\sigma = \sqrt{\frac{\sum_{j=1}^v (Y_{j,\text{exp}} - Y(\theta)_{j,\text{mod}})^2}{N - b - 1}}, \quad (18)$$

where  $Y_{j,\text{exp}}$  and  $Y(\theta)_{j,\text{mod}}$  are the experimental and calculated values of the thermodynamic property of the solution at the  $j$ th point, respectively;  $b$  is the number of empirical parameters  $\theta$  in the model's equation; and  $N$  is the number of experimental points. In using the obtained estimates of the parameters, we also calculated the values of the average relative errors in percents, according to the formula

$$\Delta = \frac{1}{N} \sum_{j=1}^v \frac{|Y_{j,\text{exp}} - Y(\theta)_{j,\text{mod}}|}{Y_{j,\text{exp}}} \times 100\%. \quad (19)$$

The literature data on  $\phi$  for  $\text{CaCl}_2$  solutions cover concentrations up to  $m = 11$  mol/kg. As was noted in [9], however, the solution reaches saturation at 25°C when  $m = 7.46$  mol/kg. Since the investigated model did not consider the effect solid phase hydration has on the activity of a solution's components, all estimates and calculations were performed up to its saturation point only: concentration  $m = 7.5$  mol/kg. Table 1 shows the results from describing the concentration dependences of the osmotic coefficient and calculations using the parameters of the error in calculating the mean ionic activity coefficients of aqueous  $\text{CaCl}_2$  solutions at 25°C according to data from [1, 9–11].

The results obtained with the data in [10] were used to determine the confidence intervals of the model parameters. At the  $\Delta_\phi$  and  $\sigma_\phi$  values presented in Table 1, the confidence interval for  $h_1$  was  $\pm 0.09$ ; for  $r_1$ , it was  $\pm 0.04$ ; for  $A_1$ , it was  $\pm 0.28$ ; and for  $B_D$ , it was  $\pm 0.06$ . In analyzing the accuracy of determining the osmotic

**Table 2.** Results from describing the concentration dependence of the osmotic coefficient and calculating the mean ionic activity coefficient of  $\text{CaCl}_2$  in aqueous solutions in the temperature interval of 0 to 100°C

$t, ^\circ\text{C}$	$h_1$	$r_1$	$A_1$	$A_{\max}$	$B_D$	$\sigma_\phi \times 10^3$	$\Delta_\phi, \%$	$\sigma_\gamma$	$\Delta_\gamma, \%$
0*	5.53	2.19	1.86	0.51	1.52	10.0	0.32	0.24	1.2
10	5.45	2.18	1.65	0.47	1.51	8.8	0.31	0.22	1.3
20	5.46	2.22	1.71	0.49	1.52	5.1	0.23	0.09	0.6
25	5.45	2.24	1.74	0.50	1.53	4.3	0.21	0.06	0.5
30	5.44	2.25	1.77	0.51	1.53	3.6	0.19	0.06	0.5
40	5.41	2.27	1.84	0.53	1.54	3.1	0.18	0.05	0.8
50	5.38	2.29	1.93	0.56	1.55	2.9	0.17	0.02	0.4
60	5.34	2.30	2.01	0.58	1.56	2.8	0.18	0.02	0.4
70	5.30	2.31	2.09	0.60	1.56	2.9	0.18	0.01	0.4
80	5.27	2.32	2.18	0.63	1.56	3.0	0.2	0.01	0.5
90	5.22	2.34	2.24	0.65	1.56	3.2	0.22	0.01	0.6
100	5.18	2.35	2.31	0.67	1.56	3.7	0.25	0.02	1.1

\* At this temperature, the data provided in [13] go up to  $m = 7.0$  mol/kg.

coefficient from the data of an isopiestic experiment, the author of [12] concluded that when  $m > 2$  mol/kg, the value of  $\phi$  can be known with a precision of  $\pm 0.01$ . When we consider these estimates, the intervals of the model's parameters grow correspondingly to  $\pm 0.2$  for  $h_1$ ,  $\pm 0.09$  for  $r_1$ ,  $\pm 0.8$  for  $A_1$ , and  $\pm 0.2$  for  $B_D$ . Considering both the wider and the narrower estimate intervals, the parameters of the model that were determined according to the data from different authors virtually coincide. The values of  $\sigma_\phi$  and  $\Delta_\phi$  (Table 1) allow us to say that the model's equations satisfactorily describe the experimental data mathematically.

The numerical values of  $r_1$  suggest that the mean hydration number diminishes as the electrolyte concentration increases. It coincides with  $h_1$  in an infinitely diluted solution, while near the saturation concentration it drops to 2.5. The variance of stoichiometric coefficients of hydrated ions is a measure of the spread of this quantity around its mean. According to our findings, an infinitely diluted solution (of  $\text{CaCl}_2$ ) is more likely to consist of ions with hydration numbers from 2 to 9, while the hydration number varies from 0 to 5 for the ions in a nearly saturated solution.

In the literature, it was noted that the contribution from ion association to nonideality in a given system is relatively unimportant. This finding is confirmed by the value of  $A_1$  (Table 1) attributed to a hypothetical state of a system with electrolyte mole fraction  $x = 1$ . The values of mean numbers of association  $A_{\max}$  in saturated solutions, which are close to 0.5, show that at 25°C and concentrations close to the saturation limit, ion association proceeds mainly according to the reaction  $\text{Ca}^{2+} + \text{Cl}^- \rightleftharpoons \text{CaCl}^+$ , and most of the ions are not associated; i.e., they exist as free ions  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ .

Table 2 gives the results from describing the concentration dependence of the osmotic coefficient and

calculations using the obtained estimates of the parameters of the mean ionic coefficient of the activity of  $\text{CaCl}_2$  in aqueous solutions at temperatures ranging from 0 to 100°C [10]. For the reasons stated above, modeling was also done for the range of concentrations up to 7.5 mol/kg. The values of the standard deviations and the relative errors of fitting show that our work provides an mathematically accurate description of the data. The hydration numbers fall slightly as the temperature rises. Since parameter  $r_1$  grows along with temperature, we observe the expected broadening of distribution of the hydration numbers. Ion association grows somewhat as the temperature rises. We may assume this is due to the destruction of ion hydration shells resulting in the emergence of vacancies for ion association.

The formalism of our model is substantiated by Prigogine's hypothesis that considering all interactions in an ideal associated solution is equivalent to equating the activity of water to the mole fraction of free water. The results of this work show that considering the contribution to nonideality from hydration by using variable hydration numbers, electrostatic interactions, and ionic associates in actual solutions of  $\text{CaCl}_2$  fits in well with Prigogine's hypothesis. At the same time, considering the contribution from hydration by using constant hydration numbers leads to notable deviations between the activity and mole fraction of free water.

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