

Scientific paper

Ion Association Phenomena and Static Dielectric Properties in Electrolyte Solutions: Application of the Effective Mean Spherical Approximation – Mass Action Law Approach

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Received: 25-11-2008

Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

Mean spherical approximation – mass action law approach is developed to describe the influence of ion association on solvent and solution dielectric constants in electrolyte solutions. The dependences of the dielectric constants on electrolyte concentration, ionic sizes, and the degree of ion association are analyzed. The results are compared with recent experimental data for aqueous solutions of nitrate and formate salts and a fair agreement is obtained.

Keywords: Electrolyte solutions, ion association, dielectric properties, mean spherical approximation.

1. Introduction

It is a great pleasure for us to dedicate this paper to Professor Josef Barthel, one of the true leaders in Physical Chemistry of electrolyte solutions. Our collaboration with Professors Josef Barthel and Hartmut Krienke gave us an opportunity for better understanding of the role of ion association in shaping of the physico-chemical properties of electrolytes. This paper is partly based on our discussions with them.

According to the concept of ion association, an electrolyte solution is a mixture of solvent molecules, free ions and ionic clusters (usually ion pairs and sometimes also trimers, or higher clusters). These “species” are assumed to be in chemical equilibrium described by the corresponding mass action law (MAL).¹ It is known that the phenomenon of ion association manifests itself differently in thermodynamic and electrical properties of electrolyte solutions, and accordingly these properties require different theoretical treatments.² Thermodynamic properties, such as osmotic and activity coefficients, are influenced by both free ions and ionic clusters. These properties have

been described correctly in framework of the associative mean spherical approximation (AMSA),^{3–7} which is based on the modern theory of associating fluids.^{8–10} The AMSA theory was also generalized for ion–dipole fluids,^{11–13} what made possible to describe solvation effects, together with the association phenomena. Since the ion pairs have no free electric charges, they give polarization effects only for such electrical properties as are the ionic conductivity⁴ or capacitance of the electrical double layer.¹⁴ It was shown² that in order to describe the electrical properties correctly, it is necessary to combine the mean spherical approximation (MSA) with MAL, and to modify MSA–MAL approach by including the ion pairs as separate polar entities.

Free ions and ion pairs play distinct roles in dielectric properties of electrolyte solutions. Due to the saturation of the dipole orientation near free ions, the dielectric constant of the electrolyte decreases with an increase of the concentration of free ions. Ion pairs possess the dipole moments and produce an additional contribution to the dielectric properties. Due to the polarization effect, the dielectric constant of the entire system increases with an increase of the ion pair concentration. It is generally ac-

cepted to distinguish between the solvent dielectric constant, ϵ_s , and the solution dielectric constant, ϵ .¹ The dielectric constant of solvent reflects the polarization effect of solvent molecules in presence of ions; ϵ_s decreases with an increase of ionic concentration. The dielectric constant of a solution in addition includes the polarization effects from ionic pairs, that can increase or decrease with an increase of electrolyte concentration. Accordingly, $\epsilon > \epsilon_s$, and only for a completely dissociated electrolyte, $\epsilon = \epsilon_s$.

In this paper we study the influence of the ion-ion association on the dielectric properties of electrolyte solution. For this purpose, we develop the mean spherical approximation – mass action law approach for description of the solvent dielectric constant, ϵ_s . The theory is based on the MSA solution for the ion–dipole mixture.^{15–18} In addition we improved the MSA–MAL theory for dielectric constant of solution, ϵ , by including the relevant contribution from ion pairs. Finally, the theory is tested against the experimental data.

2. Theory

One of the simplest models of electrolyte solution can be represented as a mixture of charged hard spheres and hard spheres with embedded dipoles. This is the, so-called, ion–dipole model. For simplicity we consider that both ionic species have equal diameters $\sigma_+ = \sigma_- = \sigma_p$, while the solvent molecules have diameter σ_s . We also assume for cations and anions to be charge symmetric, having charges of the same magnitude. The process of ionic pair formation is characterized by the equilibrium constant K_{as} . According to MAL, the formation of ion pairs determines the concentration of free ions $c_+ = c_- = \alpha c$.^{1,2}

$$\frac{1-\alpha}{\alpha^2} = cK_{as}g_{+-}^{00}(\sigma_i)\exp(-b_i), \quad (1)$$

where α is the degree of dissociation, $c = \rho_i/2N_A$ is the analytical electrolyte concentration, N_A is the Avagadro number, $\rho_i = \rho_+ + \rho_-$ is the total number density of ions, $b = e^2/(\epsilon_0 kT\sigma_i)$ is the Bjerrum parameter characterizing the Coulomb interactions between cations and anions at contact distance. Further, e is the elementary charge, ϵ_0 the solvent dielectric constant at the infinite dilution of ions, T the absolute temperature, k Boltzmann's constant, and $g_{+-}^{00}(\sigma_i)$ the contact value of the non-associative part of cation–anion distribution function.

In view of the fact that ion pairs do not contribute to the dielectric constant of solvent, we can only consider free ions and dipolar solvent molecules to describe ϵ_s . As a result, the MSA–MAL description of such a system is similar to the usual MSA theory for the ion-dipole mixture [15–18], and can be described in terms of the energy parameters (b_0 , b_1 and b_2) for the ion-ion, ion-dipole, and the dipole-dipole interactions, correspondingly. The para-

meters b_0 , b_1 , b_2 are connected with the usual ion and dipolar parameters

$$\kappa^2\sigma_i^2 = 4\pi e^2 \frac{1}{kT} \rho_i \sigma_i^2, \quad y_s = \frac{4}{9} \pi \rho_s \frac{p_s^2}{kT}, \quad \gamma = \frac{\sigma_s}{\sigma_i} \quad (2)$$

via the system of coupled nonlinear equations

$$\begin{aligned} a_1^2 + a_2^2 &= \alpha \kappa^2 \sigma_i^2, \\ a_1 K_{10} + a_2 (K_{11} - 1) &= \kappa \sqrt{3y_s \alpha}, \\ K_{10}^2 + (K_{11} - 1)^2 &= \frac{\beta_6^2}{\beta_{12}^4} + 3y_s, \end{aligned} \quad (3)$$

where ρ_s is the density of dipolar subsystem, and p_s is dipole moment of dipolar molecules,

$$\begin{aligned} a_1 &= (b_1^2(3 + \gamma\beta_6)/6 - 2b_0\beta_6^2)/D_2, \\ a_2 &= -b_1(\beta_6 + b_1^2/6 + \beta_3(1 + b_0)/\gamma)/D_2, \\ K_{10} &= \gamma b_1(1 + a_1\Lambda)/(2\Delta), \\ K_{11} &= (\beta_3 - \gamma a_2 b_1 \Lambda/2)/\Delta. \end{aligned} \quad (4)$$

$$\begin{aligned} D_2 &= ((1 + b_0)\beta_6 - \gamma b_1^2/12)^2, \\ \Delta &= \beta_6^2 + b_1^2/4, \\ \Lambda &= (1 + \gamma b_0 \beta_6/3)/2, \\ \beta_3 &= 1 + b_2/3, \beta_6 = 1 - b_2/6, \beta_{12} = 1 + b_2/12. \end{aligned} \quad (5)$$

Contact value of the non-associative part of the cation-anion distribution function $g_{+-}^{00}(\sigma_i)$, needed for the calculation of the degree of dissociation α , is given in the form

$$g_{+-}^{00}(\sigma_i) = g_{ii}^{(HS)}(\sigma_i) \exp(-h^{000}(\sigma_i)) \quad (6)$$

where

$$g_{ii}^{(HS)}(\sigma_i) = \frac{1}{1 - \epsilon_3} + \frac{3\epsilon_2}{(1 - \epsilon_3)^2} \sigma_i \quad (7)$$

is the hard sphere contact value, $\epsilon_n = \frac{\pi}{6} [\rho_+ \sigma_i^n + \rho_- \sigma_i^n]$.

$$h^{000}(\sigma_i) = \frac{1}{2\pi\rho_i\sigma_i\Delta} \left[\left(\Delta b_0 - \frac{1}{4} \Lambda b_1 \right) a_0 - \frac{1}{2} b_1^2 \right] \quad (8)$$

Eq. (8) provides the electrostatic part of the contact value of the cation-anion distribution function. The solvent dielectric constant can then be obtained from the Adelman expression¹⁹ in the form:

$$\epsilon_s = 1 + 3y_s \frac{\beta_{12}^4}{\beta_6^2} \quad (9)$$

The ion pairs provide, in contrast to the case (ε_s) described above, a direct contribution to the solution dielectric constant ε . Theoretical description of ε now reduces to the consideration of a four-component system, which includes the free ions, ionic pairs, and dipolar solvent molecules. One of the simplest models for an ion pair can be a hard sphere of diameter σ_{ip} with the dipole moment $p_{ip} = e\sigma_i$. The size of an ion pair $\sigma_{ip} = \sqrt[3]{2}\sigma_i$ can be estimated from the condition that creations of ion pairs should not change the packing fraction of ions in solution.¹ As a result, the ionic pairs are characterized by

$$3y_{ip} = \frac{1}{6}\kappa^2\sigma_i^2(1-\alpha), \quad \gamma_{ip} = \frac{\sigma_{ip}}{\sigma_i} = \sqrt[3]{2} \approx 1.25 \quad (10)$$

If we suppose for simplicity that $\gamma = \gamma_{ip}$, then our system can be described by the formulas (3)–(9), with the replacement of y_s by

$$y = y_s + \frac{1}{18}\kappa^2\sigma_i^2(1-\alpha). \quad (11)$$

3. Discussion

The theory proposed here describes the dependence of the solvent and solution dielectric constants ε_s and ε on the ion concentration, their sizes, and the degree of ion association. To analyze the dependence of ε_s on the size parameter γ and the degree of association α , we consider the dilute concentration regime in which parameters b_0 , b_1 and b_2 can be expressed by $\kappa\sigma_i$.¹⁷ Hence,

$$\varepsilon_s = \varepsilon_0 - a_2\kappa^2\sigma_i^2\alpha, \quad (12)$$

where $\varepsilon_0 = (\beta_3^0)^2(\beta_{12}^0)^4(\beta_6^0)^{-6}$ is the Wertheim expression [20] for the dielectric constant of pure solvent, the set of values $\beta_{3,2}^0$ is given according to (5) with the change of b_2 to b_2^0 , that corresponds to a pure hard-sphere dipolar system and is given by equation,

$$\frac{(\beta_3^0)^2}{(\beta_6^0)^4} - \frac{(\beta_6^0)^2}{(\beta_{12}^0)^4} = 3y_s, \quad (13)$$

$$a_2 = 6y_s^2\gamma(\beta_{12}^0)^8(\beta_6^0)^4\beta_{24}^0$$

$$\left\{ \left[\gamma^2 \frac{(\beta_6^0)^2}{\beta_3^0} \left(\beta_{12}^0 + \frac{1}{4}\beta_3^0 \right) + \left(3\gamma \frac{\beta_6^0}{\beta_3^0} + 1 \right) \beta_{12}^0 \right] + \right. \quad (14)$$

$$\left. + \frac{1}{4} \frac{\beta_6^0}{\beta_3^0} \gamma (1 + b_2^0) + \beta_{12}^0 \right\}$$

Coefficient a_2 describes the behaviour of ε_s as a function of the electrolyte concentration. As we can see, a_2 increases with an increase of γ . As a result, the dielectric constant ε_s , given as a function of ion concentration, decreases faster with the decrease of ion size. From equation (12) we can see that ε_s decreases slower with an increase of the degree of ion association ($1 - \alpha$); for $\alpha = 0$, $\varepsilon_s = \varepsilon_0$. The functional dependence of the solvent dielectric constant ε_s on parameters γ and α is illustrated in Figures 1 and 2. In these figures we present numerical results for a simple model of aqueous solution where water molecules are modeled by hard spheres with the diameter $\sigma_s = 2.76 \text{ \AA}$ and the effective dipole moment $p_s = 2.23 D$. Such a value of the dipole moment of water molecules (at normal conditions) yields $y_s = 1.892$ and by using the Wertheim expression reproduces the experimental value of the water dielectric constant: $\varepsilon_0 = 78.4$. First figure, Figure 1, corresponds to the non-associated case ($\alpha = 1$). In Figure 2 $\gamma = 1/2$ and the constant of the formation ion pairs K_{as} is a parameter. As we can see, an increase of ionic sizes and the ion association constant both yield the same effect.

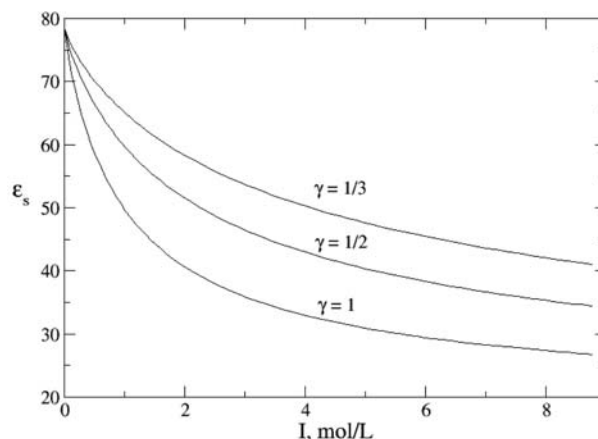


Figure 1. Concentration dependence of the solvent dielectric constant, ε_s , for the non-associative model of aqueous electrolyte solution; the influence of ion size.

The theory, proposed for description of the dielectric constant of solution ε , contains two opposite tendencies. Due to the change of κ to $\kappa\sqrt{\alpha}$, the solution dielectric constant, ε , similarly as ε_s , decreases with an increase of the ionic concentration. On the other hand, due to the replacement of y_s with y , the dielectric constant ε can increase with an increase of the ionic concentration. For low concentrations,

$$\varepsilon = \varepsilon_0 - a_2\kappa^2\sigma_i^2 \cdot \alpha + \frac{1}{2}\kappa^2\sigma_i^2(1-\alpha) \frac{(\beta_{12}^0)^4}{(\beta_6^0)^2}. \quad (15)$$

As we can see, the solution dielectric constant ε , given as the function of ion concentration, decreases in the regime of weak association ($\alpha \rightarrow 1$) and increases in the

regime of strong association ($\alpha \rightarrow 0$). This result is illustrated in Figure 3, which shows the concentration dependence of the dielectric constant of solution, calculated for different values of the association constant K_{as} .

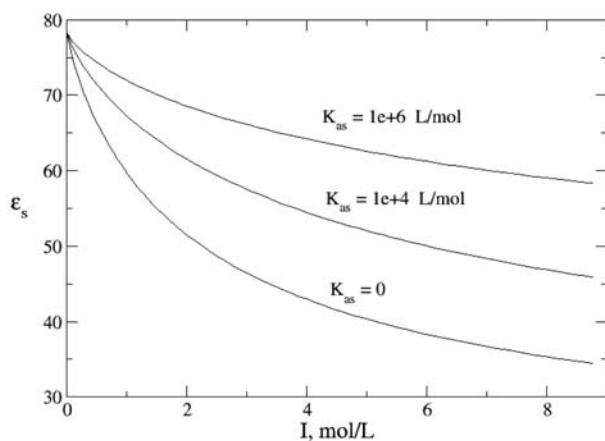


Figure 2. The concentration dependence of solvent dielectric constant, ϵ_s , for the associative model of aqueous electrolyte solution; the influence of the association constant at $\gamma = 1/2$.

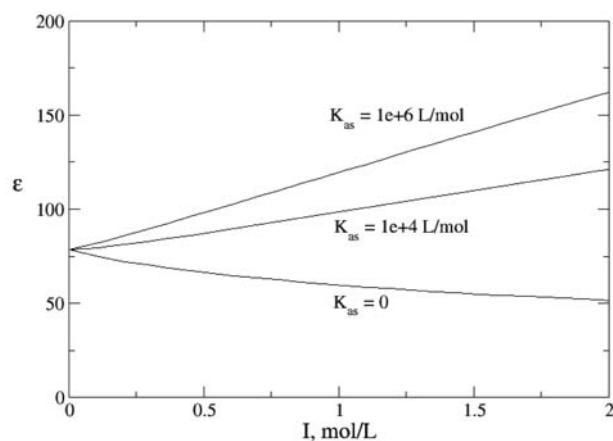


Figure 3. The concentration dependence of the solution dielectric constant, ϵ , for the associative model of aqueous electrolyte solution; the influence of the association constant.

4. Comparison with Experimental Data

Dielectric properties of electrolyte solutions can be measured by a microwave dielectric spectroscopy technique.¹ Due to the high electrical conductivity, the dielectric constants can only be evaluated by an extrapolation of the high-frequency dielectric measurement data. In such experiments the solvent dielectric constant ϵ_s is evaluated from the measurements of the dielectric spectra in 10–100 GHz and the solution dielectric constant ϵ is evaluated from the dielectric spectra in the region around 1 GHz.

The data for the dielectric properties of different aqueous and non-aqueous electrolyte solutions are available in literature.²¹ To compare our theory with the experiment we use recent measurements of the dielectric properties on aqueous solutions of nitrate and formate salts.²² Since the lowest frequency in this experiment is 13 GHz, the obtained results measure the solvent dielectric constant ϵ_s . The theory developed here applies for the charge symmetric electrolytes, while the experimental data apply to the charge asymmetric case. For the sake of comparison we map the asymmetrical case to the symmetrical one by simply replacing the electrolyte concentration c with its ionic strength $I = \frac{1}{2} \sum_i c_i z_i^2$.

Table 1. Ionic parameters.

Electrolyte	$\sigma_i / \text{Å}$	$K_{as}, \text{L/mol}$
Ba(CHOO) ₂	7	2.36×10^5
Y(CHOO) ₃	10	3.49×10^5
Cu(CHOO) ₂	7	1.57×10^6
Y(NO ₃) ₃	10	0
Cu(NO ₃) ₂	7	0

The results of such a comparison are presented in Figure 4. Values of the effective ion parameters used in the theoretical calculations are given in Table 1.

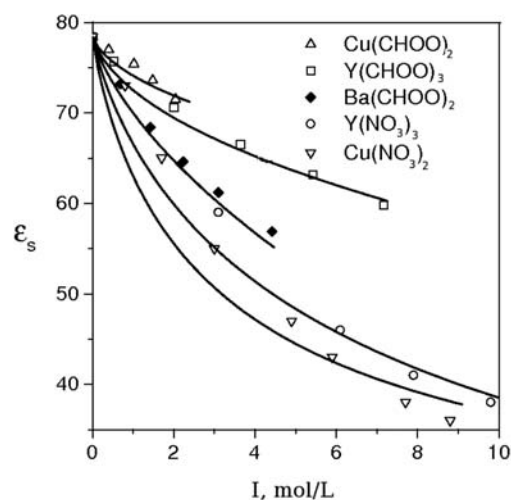


Figure 4. Comparison of the dielectric constant of solvent as the function of ionic strength as predicted from the MSA-MAL theory (lines) with the experimental data²² for aqueous solutions of nitrate and formate salts.

In these calculations we took into account the dependence of solvent density ρ_s from electrolyte concentration.²³ Since anion NO_3^- does not create ion associates with cations Cu^{2+} and Y^{3+} , the order of change of ϵ_s in aqueous solution of nitrate salts is governed by the cation sizes, and is qualitatively similar to that displayed in Fig-

re 1. For the formate salts the cations create ion complexes with anions CHOO^- due to hydrogen bonds between anion and water molecules from the hydration shell of a cation. The degree of association increases with a decrease of the ion size. As a result, we obtain the concentration dependence of ϵ_s that is opposite to that of the nitrate salt. The effect of association is the strongest for Cu^{2+} and the weakest for Ba^{2+} . For formate salts, the order of change of ϵ_s is given by the strength of ionic association, while the concentration dependence of ϵ_s has a shape similar to that shown in Figure 2. In view of the fact that the theory is designed for symmetric electrolytes and the experimental data apply to asymmetrical ones, we can consider the agreement between the theoretical and experimental results to be quite satisfactory.

5. Conclusions

In this paper we develop the MSA-MAL approach for description of the ion-ion association on the solvent and solution dielectric constants, ϵ_s and ϵ , in electrolyte solutions. Our theory combines the analytical solution of the MSA for ion-dipole mixtures with the mass action law approach for the treatment of ionic association. The solvent dielectric constant ϵ_s does not include the contributions from ion pairs, and the description of ϵ_s reduces to the three-component system, consisting of free ions (cations and anions) and dipolar solvent molecules. In this way, the description of ϵ_s reduces to the description of the dielectric constant of the non-associating electrolyte solution with replacement of the ion concentration c with αc , where α is the degree of dissociation. As a result, an increase of the association constant K_{as} always leads to a slow decrease of ϵ_s with the electrolyte concentration.

For calculation of the solution dielectric constant, ϵ , the MSA-MAL approach was modified by including the contribution from ion pairs; the latter were considered as separate polar entities. This description requires consideration of a four-component mixture of free ions (cations and anions), ion pairs and dipolar solvent molecules. Due to reduction of the concentration of free ions, the solution dielectric constant, ϵ , can decrease with an increase of the electrolyte concentration. The contribution from ionic pairs can be significant, and may lead to an increase of the solution dielectric constant. Depending on the extent of the ionic association, both situations (decrease or increase of the solution dielectric constant) can be observed.

6. Acknowledgments

The authors would like to thank J. Barthel, H. Krienke, and A. Lyashchenko for useful discussions on different aspects of this investigation. For M. H. this study was partially supported by the NAS of Ukraine within the frame-

work of the Ukrainian-Russian Scientific collaboration (project No 18).

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Povzetek

Z uporabo MSA-MAL metode smo opisali vpliv asociacije ionov na dielektrično konstanto topila ter raztopine v raztopinah elektrolitov. Raziskovali smo vpliv koncentracije elektrolita, velikosti ionov ter stopnjo asociacije ionov na vrednosti dielektrične konstante. Primerjava dobljenih rezultatov z eksperimentalnimi podatki za vodne raztopine nekaterih soli dušikove (V) ter metanojske kisline kaže razmeroma dobro ujemanje.