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Fluid Phase Equilibria

Development of a rationale for decoupling osmotic coefficient of electrolytes into electrostatic and nonelectrostatic contributions

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A B S T R A C T

In this work, a method has been developed to decouple the electrostatic and the nonelectrostatic contributions to the osmotic coefficient. The observation, that the osmotic coefficient-molality plot exhibits a linear region over a significant range of concentration, allows estimation of the primary hydration number of electrolytes and also to hypothesize that the primary hydration number does not depend on electrolyte concentration. The estimated value of the primary hydration number agrees well with that obtained using NMR spectroscopy and exhibits correct dependence on temperature. It is also shown that in a mixture of electrolytes, each electrolyte retains its own primary hydration number irrespective of the presence of the other electrolytes. The estimate of the primary hydration number allows us to determine the nonelectrostatic contribution to the osmotic coefficient for the single and the mixed electrolytes over the entire range of electrolyte concentration. Subtraction of this contribution from the osmotic coefficient yields the electrostatic contribution. The secondary hydration number, which is responsible for modulating electrostatic interaction, attains a constant value beyond the electrostatic screening limit and at a fixed temperature, this value is found to be independent of the type of electrolyte. The sum of the primary hydration number and the limiting secondary hydration number agrees well with the hydration number estimated using the extended X-ray absorption fine structure spectroscopy. The most important contribution of this work is the isolation of the electrostatic contribution to the osmotic coefficient of solutions of single and mixed electrolytes. The electrostatic interaction is shown to much stronger than that predicted by the extended Debye-Hückel theory, which points to a need for revision of the existing theories for electrostatics of concentrated electrolytes. The electrostatic contribution estimated using the present method, for both single as well as mixed electrolytes, would provide the basis for validation of the revised theories.

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1. Introduction

Electrolytes, on dissolution, reduce the activity of water. This fact is utilized in many applications such as food preservation [1], chelation therapy [2], urinary kidney-stone drug design [3,4], separation of biomolecules [5], folding/unfolding of proteins [6,7], solvent extraction [8], leaching of minerals [9—11], ocean acidification and its effects [12—14], heavy metal pollution [15—21] etc. Therefore, prediction of the activity of water in electrolyte solutions has been a subject of continued active research over the past several decades [22,23]. It is convenient to express water activity in terms of its osmotic coefficient, defined as the ratio of the actual

chemical potential of water to that in the absence of interactions among the constituent ions of the electrolyte. The classical model for prediction of the osmotic coefficient is the Extended Debye-Hückel equation [24] in which the effective ionic size 'a' is the only fitted parameter.

However, the Extended Debye-Hückel equation is not accurate in concentrated solutions due to two important reasons. First, it ignores the non-electrostatic interactions (especially the hydration interactions) which become important in concentrated electrolytes. Second, it uses bulk dielectric constant of water for computing the electrostatic interaction. However, there exists a region surrounding the ion where the water molecules are highly oriented (due to the extremely high electric field generated by the ion around it) and therefore exhibit lower dielectric constant. Within this region, the electrostatic interaction between the central ion and the surrounding counterions is significantly stronger than the region

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outside where the bulk dielectric constant of water prevails. As the electrolyte concentration increases, the probability of finding the counterion in the low dielectric constant region in the vicinity of the central ion progressively increases. This causes deviation of the electrostatic interaction from that based on the Extended Debye-Hückel equation. So, an improved theory should not only correctly account for the nonelectrostatic interaction, but also appropriately modify the electrostatic interaction. The major impediment in this endeavor is that there is no rationale to correctly partition the osmotic coefficient into electrostatic and non-electrostatic contributions in concentrated solutions. Hence, there is a certain degree of arbitrariness in extrapolating electrostatic contribution to osmotic coefficient beyond the dilute region.

Earlier theories (Guggenheim [25], Bromley [26], and Zemaitis et al., [27,28]) have extended Debye-Hückel equation by adding concentration-dependent semi-empirical terms. In addition to having greater number of fitted parameters, these models are applicable only over a limited range of the electrolyte concentration (approximately 2m) [28]. A fundamental refinement in the extended Debye-Hückel theory was made by Frank [29] using the two-region model for the counterion cloud, with low dielectric constant in the inner region and the bulk dielectric constant in the outer region. This model can extend the applicability of the Extended Debye-Hückel equation up to electrolyte concentration of 1m.

The aforementioned models assume the interactions to be purely electrostatic. The models developed later are the composite models which account for both electrostatic and nonelectrostatic interactions. Practically all composite models use the Extended Debye-Hückel equation to estimate the electrostatic interactions over the entire range of electrolyte concentration. They differ from each other in the methods used for estimating nonelectrostatic interactions. The most popular model among these is the Pitzer model [30–34] in which the binary and ternary short-range interactions have been incorporated using the virial equation [33]. Although the popularity of the Pitzer model stems from the availability of extensive databank encompassing a large number of electrolyte species, the model has a large number of empirical parameters, many of which are devoid of any physical significance as pointed out by several workers [35–37]. There are also models, which are based on local composition theory [38]. These take into account the fact that the local composition of the solution around a molecule is different from the bulk composition. The models in this category include specific-ion interaction model by Brønsted [39,40], the nonrandom two-liquid (NRTL) models [41–47], and the extended universal quasi-chemical (EUNIQUAC) models [48–51]. There are also models based on the hydration theory (reviewed by Balomenos et al., and Marcus [22,52]) and the models based on molecular dynamic simulation (reviewed by Loehe and Donohue [23]). In all these composite models, the electrostatic interaction is incorporated using the Extended Debye-Hückel equation over the entire range of electrolyte concentration. However, since the Extended Debye-Hückel equation is not accurate at high electrolyte concentrations, the error associated with estimation of the electrostatic contribution is counted as a part of the nonelectrostatic contribution in these composite theories. This procedure can introduce inaccuracies of unspecified magnitude in the models which are used to estimate the non-electrostatic interactions. Therefore, there is a need to develop a rationale, which will allow us to correctly segregate electrostatic and nonelectrostatic interactions. This step will provide the impetus to develop more accurate predictive models for both electrostatics and nonelectrostatic interactions.

In the present paper, we have suggested a possible way to decouple electrostatic and nonelectrostatic contributions to the osmotic coefficient. Our method is based on the hydration theory,

first developed by Robinson and Stokes [53], and later modified by Glueckauf [54]. It permits decoupling of the electrostatic contribution from the nonelectrostatic contribution to the osmotic coefficient of single as well as mixed electrolytes in an unambiguous manner. The electrostatic interaction, decoupled by our technique, is shown to be much stronger than that estimated using the extended Debye-Hückel theory, which points to the fact that a significant revision of the theory for electrostatics in concentrated electrolytes is needed. The electrostatic contribution estimated using the present method, for both single as well as mixed electrolytes, would provide the basis for validation of the revised theory.

2. Development of the basis for decoupling of interactions

The osmotic coefficient, φ, of an aqueous electrolyte is related to the chemical potential of water, μ_w, as follows

$$\varphi = -\frac{\mu_w - \mu_w^0}{M_w RT \nu m} \tag{1}$$

where, μ_w^0 is the chemical potenitial of water in its standard state, M_w is the molecular mass of water, ν is the number of ions produced on dissociation of one molecule of the electrolyte and m is the molality of the electrolyte solution, R is the gas constant and T, the absolute temperature.

Osmotic coefficient can be split into its electrostatic and non-electrostatic contributions as follows

$$\varphi = 1 + \varphi_e^E + \varphi_e^{NE} \tag{2}$$

Here the first term on the right ($= 1$) is the osmotic coefficient of the solution in the absence of ionic interaction (i.e. osmotic coefficient of the ideal solution). The terms φ_e^E, and φ_e^{NE}, are respectively, the electrostatic (superscript E) and nonelectrostatic (superscript NE) contributions to the nonideal part of the osmotic coefficient. They are the excess quantities and hence denoted by subscript e.

In most models reported in the literature, the Extended Debye-Hückel theory is used to estimate the electrostatic contribution. According to this theory, the excess electrostatic contribution of the osmotic coefficient is given by the following equation [55].

$$\varphi_e^E = \frac{1}{3} z_+ z_- A_\varphi \sqrt{I} \sigma(\kappa a) \tag{3}$$

where

$$\sigma(x) = \frac{3}{x^3}\left[1 + x - \frac{1}{1+x} - 2\ln(1+x)\right] \tag{4}$$

and

$$A_\varphi = \frac{F^2 e \sqrt{2}}{8\pi(\varepsilon\varepsilon_0 RT)^{3/2}} \tag{5}$$

In these equations, I is ionic strength of the solution, κ is the inverse Debye length $\left(\kappa = \frac{F\sqrt{I}}{\sqrt{2\varepsilon\varepsilon_0 RT}}\right)$, a is the ionic size parameter, e is the electronic charge, F is the Faraday constant, ε is the dielectric constant of water and ε_0 is the permittivity of free space. One of the objectives of our work is to test the applicability of this equation to concentrated solutions.

The development of the methodology for segregating electrostatic and nonelectrostatic contributions is illustrated here using the example of NaCl. Fig. 1 shows variation of the osmotic