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Description of the Thermodynamic Properties of Aqueous Ionic Solutions within the Mean Spherical Approximation

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Résumé — Description des propriétés thermodynamiques de solutions aqueuses ioniques dans l'approximation sphérique moyenne — Les propriétés thermodynamiques de solutions aqueuses ioniques sont décrites dans l'approximation sphérique moyenne (MSA). Le modèle MSA original et celui avec association (BiMSA) ont été complétés de façon à inclure les effets de la solvatation. On montre que le modèle est capable de représenter la thermodynamique des solutions ioniques dans un large domaine de concentration, généralement jusqu'à la saturation, dans le cas des électrolytes forts et associés. Ce modèle constitue une alternative intéressante au modèle de Pitzer.

Abstract — Description of the Thermodynamic Properties of Aqueous Ionic Solutions within the Mean Spherical Approximation — *The thermodynamic properties of ionic solutions are described within the mean spherical approximation (MSA). The original MSA and binding MSA (BiMSA) have been supplemented so as to include solvation effects. The model is shown to be capable of representing ionic solution thermodynamics in a wide range of concentration, generally up to saturation, in the case of strong and associating electrolytes. It constitutes an interesting alternative to the Pitzer model.*

INTRODUCTION

The modeling of the thermodynamic properties of ionic solutions is of interest in many areas, such as solution chemistry, chemical engineering, atmospheric chemistry and geochemistry. Besides the celebrated Debye-Hückel (DH) theory, the Pitzer model has been widely used in these areas because of its relative simplicity and flexibility, and for its accuracy up to the typical concentration of 6 mol/kg for a 1-1 electrolyte. However, this semi-empirical model, consisting of a modification of the DH theory by adding a virial type series correction, involves parameters that do not have a direct physical meaning. Moreover, ionic association is not accounted for, which may be expected to give rise to inaccuracies in the case of mixtures of electrolytes.

In this paper, we give an outline of the main results obtained in our group by using the mean spherical approximation (MSA), derived from statistical mechanics. Here, we will restrict ourselves to the so-called "primitive" model (Blum, 1980) in which the solvent is regarded as a dielectric continuum (in contrast with the "non-primitive" model in which the solvent is modeled as a hard sphere with embedded point dipole).

1 THE MSA MODEL

In the DH theory, the linearized Poisson Boltzmann equation is solved for a central ion surrounded by a neutralizing ionic cloud. The main simplifying assumption is that the ions in the cloud are point ions.

The primitive MSA is also connected to the DH theory. It is the linearized solution of statistical mechanical equations (Blum, 1980), with finite size for all ions (ions are regarded as charged hard spheres), in particular for ions in the cloud (see *Fig. 1*). A direct consequence of this feature is that the MSA screening distance is larger than the DH one. It turns out that the MSA shares with the DH theory the remarkable simplicity of being a function of a single screening parameter Γ for an arbitrary neutral mixture of ions. The expressions of the thermodynamic excess functions are formally very similar to those of the DH theory (Blum and Høye, 1977).

Association (including ion paring and chemical association) can be described within the binding MSA (BiMSA) (Bernard and Blum, 1996), derived from the Wertheim theory (Wertheim, 1984), in which two ions can bind on sticky sites at the surface of the ions. Unlike the classic chemical model for the ion pair, the effect of the pairing process is included in the computation of the MSA screening parameter Γ. Moreover, the model provides a better representation of the pair (see *Fig. 2*), in which the electrostatic and excluded volume interactions are well accounted for.

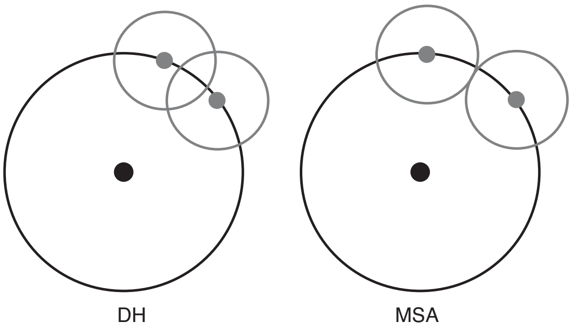

Figure 1

DH *vs.* MSA conditions for ions in the cloud: in the MSA, ions experience volume exclusion while they do not in the DH theory.

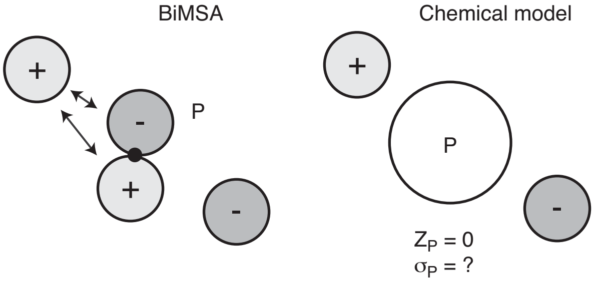

Figure 2

Comparison of BiMSA and chemical models. BiMSA provides a molecular representation of the pair. The red arrows indicate electrostatic interactions between the pair and the surrounding ions. In the chemical model, the pair is uncharged (for a monovalent electrolyte) and its size is arbitrary.

Simple formulas for the thermodynamic excess properties in the BiMSA have been obtained in terms of this parameter when a new exponential approximation is used. This exponential closure is reminiscent of Bjerrum's approximation for the contact pair distribution function. It results in simple analytic expressions for the excess thermodynamic quantities.

2 APPLICATION TO REAL ELECTROLYTES

2.1 Basic Assumptions

For a representation of departures from ideality in real ionic solutions within the MSA, the following assumptions were made.

First, as had been done similarly in previous works (Triolo *et al.*, 1978; Sun *et al.*, 1994), solvation effects were accounted for by taking concentration-dependent cation size, σ_+, and relative permittivity, ε, as (Simonin *et al.*, 1996)

$$\sigma_+ = \sigma_+^{(0)} + \sigma_S^{(1)} C_S \tag{1}$$

$$\varepsilon^{-1} = \varepsilon_w^{-1}\left(1+\alpha_S\, C_S\right) \tag{2}$$

in which C_S is the molar concentration of the electrolyte and $\sigma_+^{(0)}$, $\sigma_+^{(1)}$ and α_S are model parameters. The first one, $\sigma_+^{(0)}$, is the diameter of cation at infinite dilution. Contrary to the latter, the other two parameters reflect the influence of both ions and are characteristic of the nature of salt *S*. Besides, the anion diameter was kept constant, equal to its Pauling crystallographic value for simple anions. It was refined for complex anions such as NO_3^-.

These relationships are justified by the fact that the cation diameter is expected not to vary much with salt concentration and that measured macroscopic solution permittivities are well described by this representation.

It must be underlined that the *experimental* relative solution permittivity, ε_{sol}, is not the relevant quantity to be used in the MSA relations because it is a macroscopic quantity describing the interaction of ions at large separation. In contrast, the permittivity used here, ε in Equation 2, is meant to describe electrostatic interactions between ions in solution, for microscopic ion-ion separations. As has been found in application to real systems (Simonin, 1997), the value of ε is expected to be greater than that of ε_{sol}. This may be justified by the fact that two strongly interacting ions, at short distance, are mainly separated by water molecules. Therefore, considering the water molecules as dipoles shows that the polarization of the medium surrounding the two ions, and consequently the reaction field, is comparatively larger than for distant ions. The value of ε does not however coincide with that of pure water because of the presence of other ions (non polar species producing low polarization) in the surrounding of the two neighboring ions.

Besides the electrostatic interaction, volume exclusion is taken into account by using the Carnahan-Starling expressions for hard spheres (HS) (Carnahan and Starling, 1969). Then, the osmotic coefficient formally reads:

$$\phi = 1 + \Delta\phi^{HS} + \Delta\phi^{MSA} \tag{3}$$

in which Δ denotes an excess quantity. Similarly, for the activity coefficient of an ion *i*,

$$\ln\gamma_i = \ln\gamma_i^{HS} + \ln\gamma_i^{MSA} \tag{4}$$

Another basic ingredient is the conversion of these excess quantities from the McMillan-Mayer level of description (the natural level of the primitive MSA) to the experimental (Lewis-Randall) level. This can be done easily by using formulas requiring the knowledge of solution densities *vs.* salt concentration (Simonin, 1996, 1997).

2.2 Application to Strong Electrolytes

For strong aqueous binary electrolytes at 25°C, good fits have been obtained, not only to 6 mol/kg, but to very high concentrations, generally to saturation (Simonin, 1997). The fits involve only 3 parameters for these adjustments: $\sigma_+^{(0)}$, $\sigma_+^{(1)}$ and α_S. Actually, on average, there are less than 3 parameters because solutions containing a given cation were adjusted at the same time. Thus it was possible to determine a common cation diameter value for H^+ (5.04 Å), Li^+ (5.43 Å), Na^+ (3.87 Å), K^+ (3.45 Å), *etc*. It is interesting to note that these values were used subsequently for associating electrolytes containing these cations.

Figure 3 shows the results of fits of osmotic coefficients for a few lithium salts. The results are compared with those obtained using the Pitzer model with 3 adjustable parameters.

In Figure 4 the adjusted values of $\sigma_+^{(0)}$ are plotted for the series of alkali cations Li^+, Na^+ and K^+ and compared with the Pauling, and Shannon and Prewitt, crystallographic values. It is observed that the adjusted values are above the crystallographic diameters. The difference between the two values represents the contribution from hydration. As expected, this hydration layer thickness decreases in the series Li^+, Na^+, K^+. Comparison is also made in Figure 4 with "experimental" estimates of hydrated cation sizes, as represented by the hydrodynamic Stokes diameter values, obtained with slipping (coefficient 4π) and non-slipping (coefficient 6π) conditions. It is observed that the values of $\sigma_+^{(0)}$ lie between these two sets, wich is a satisfying result.

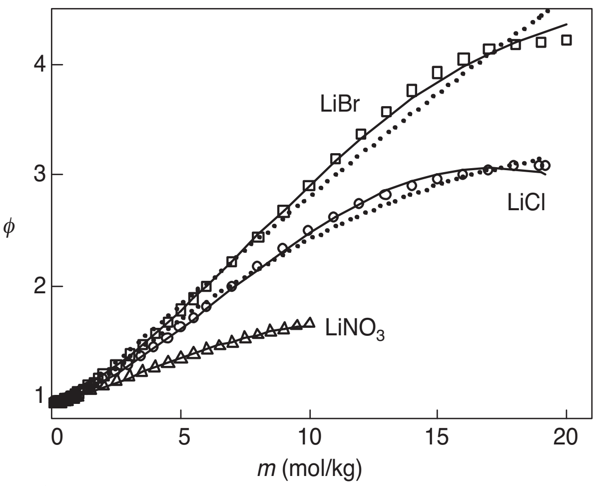

Figure 3

Experimental and calculated osmotic coefficients for Li salts in water at 25°C as a function of molality. Symbols: experimental data; solid lines: MSA fits; dotted lines: results of fits using the Pitzer model with 3 adjustable parameters.

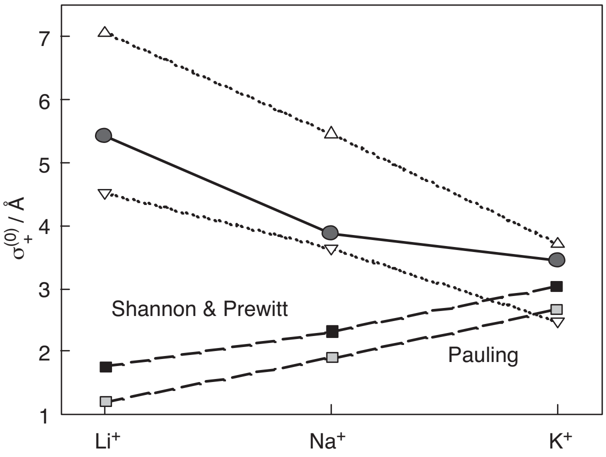

Figure 4

Fitted cation diameter (circles) at infinite dilution compared with crystallographic values (of Shannon and Prewitt, and Pauling) and hydrodynamic Stokes diameters: for slipping (△) and non-slipping (▽) conditions.

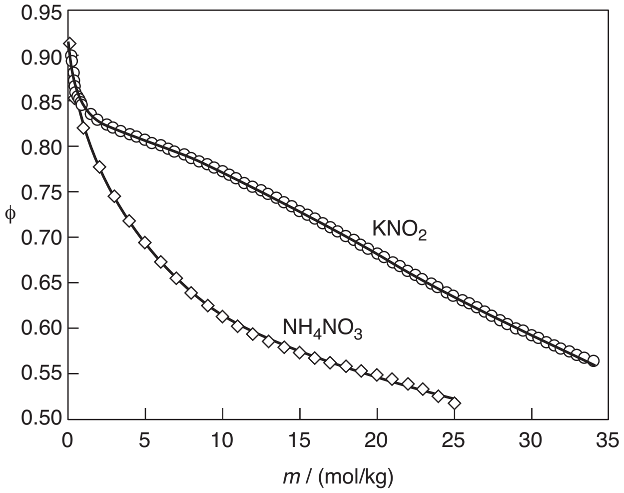

Figure 5

Osmotic coefficient of KNO_2 and NH_4NO_3 solutions. Symbols: experimental values; solid lines: results of fits using BiMSA.

It is worth noting that, in these representations, the dominant contribution at high salt concentration is the effect of short range forces, described here by the hard sphere interaction potential. So, in the case of LiCl above 6 mol/kg, the $\Delta\phi^{HS}/\Delta\phi^{MSA}$ ratio has a value of the order of 2.

2.3 Application to Associating Electrolytes

The BiMSA model (Bernard and Blum, 1996) has been applied in a first study (Simonin *et al.*, 1998) to represent departures from ideality for associating ionic solutions to very high concentrations. A typical example is presented in Figure 5, in the case of KNO_2 and NH_4NO_3 solutions to 34 mol/kg and 25 mol/kg, respectively. For these systems, the diameters of K^+ and NH_4^+ were taken from fits for strong electrolytes.

Worth of note is the fact that the adjusted thermodynamic association constant values were within experimental range.

This model has been applied recently to the case of lanthanide and actinide ions in solution (Ruas *et al.*, 2005a, b, 2006a, b).

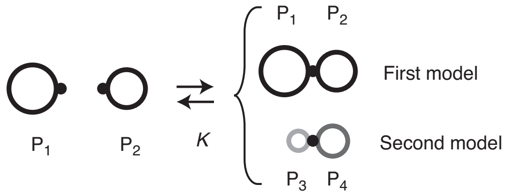

Figure 6

Sketch of the new BiMSA model. A property P (size or charge) for an ion may change when it associates (*e.g.*, $\sigma_3 \neq \sigma_1$, $z_3 \neq z_1$).

For the case of electrolytes in which the dehydration of the cation or anion in the pairing process is significant, a new version of the BiMSA has been developed. The model is depicted in Figure 6, in which P stands for a property being either the diameter of the ion or its charge. The model allows either of these properties to be different for an ion in the pair as compared to the free ion.

This new model was applied to solutions of acids and one base up to very high concentration (Vilariño *et al.*, 2004) and to the modeling of the speciation in solutions of NaOH containing small amounts of hydrogen peroxide H_2O_2 which produces HO_2^- in that medium (Chlistunoff and Simonin, 2006).

Figures 7 and 8 show the results for HCl (to 45 mol/kg) and H_2SO_4 (to 28 mol/kg) aqueous solutions, respectively. For sulfuric acid, the following equilibrium was taken into account: $H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$. It is noted that, at the concentration of 28 mol/kg (which corresponds to ca. 12.2 mol L^{-1}), it is believed (Hood and Reilly, 1957) that no molecular species H_2SO_4 is present in solution (complete first dissociation of H_2SO_4).

For these two solutions, the fitted association constants values were $K = 0.002$ L mol^{-1} and $K = 86.9$ L mol^{-1}, respectively. Surprisingly, in the case of HCl the introduction of a low degree of association permits the description to very high concentration (instead of the order of 16 mol/kg without association (Simonin, 1997)). In the case of sulfuric acid, the value of K is consistent with experimental values.

The result in the case of the H_2SO_4 solution is particularly satisfying because it is quite difficult to obtain such a representation with a molecular model for the solute.

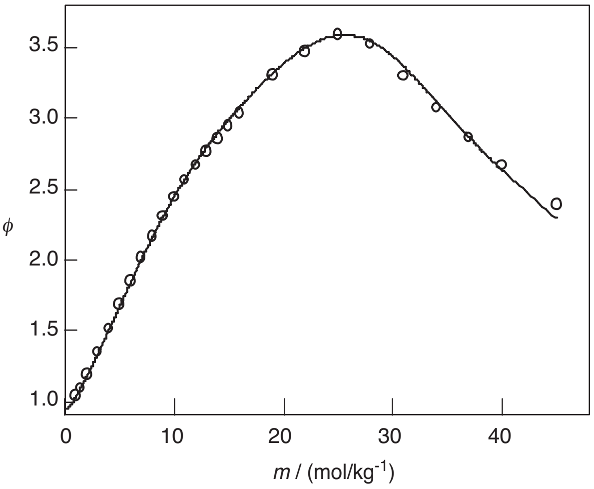

Figure 7

Osmotic coefficient of HCl solution. Symbols: experimental values; solid line: result of fit using BiMSA.

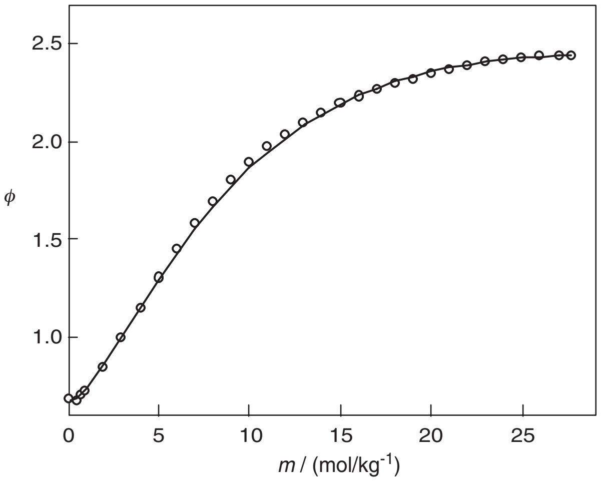

Figure 8

Osmotic coefficient of H_2SO_4 solution. Symbols: experimental values; solid line: result of fit using BiMSA.

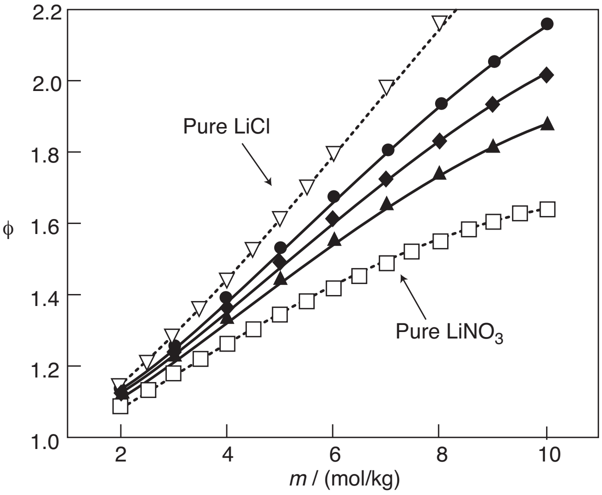

Figure 9

Osmotic coefficient of LiCl+$LiNO_3$ mixture solution for various LiCl mole fractions. Symbols: experimental values; solid lines: results of calculations (without adjustable parameter).

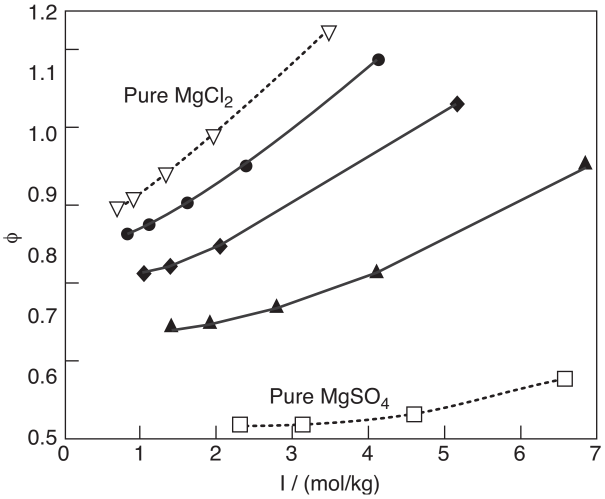

Figure 10

Osmotic coefficient of $MgCl_2$+$MgSO_4$ mixture solution for various $MgCl_2$ mole fractions. Symbols: experimental values; solid lines: results of calculation (without adjustable parameter).

2.4 Application to Electrolyte Mixtures

The model has been applied to electrolyte mixtures (Simonin, 1997; Simonin *et al.*, 1999).

For a mixture of two salts A and B with *common cation* in water, the assumed form of Equations 1 and 2 suggests the following extension

$$\sigma_+ = \sigma_+^{(0)} + \sigma_A^{(1)} C_A + \sigma_B^{(1)} C_B \tag{5}$$

$$\varepsilon^{-1} = \varepsilon_w^{-1} \left(1 + \alpha_A\, C_A + \alpha_B\, C_B\right) \tag{6}$$

Hence, in this particular case, there is no new parameter and osmotic coefficients can be predicted from the results for the pure solutions.

Actually, this simple scheme was found to give good results for three ternary mixtures of strong electrolytes (Simonin, 1997) and nine mixtures giving rise to association (Simonin *et al.*, 1999). Examples are shown in Figures 9 (two strong electrolytes) and 10 (mixture of a strong electrolyte, $MgCl_2$, with an associating electrolyte, $MgSO_4$).

For other types of mixtures, the introduction of additional cross terms in Equation 5 is required (Simonin, 1997; Simonin *et al.*, 1999).

2.5 Application to the VLE of CO_2 Over Ionic Solutions

The vapor-liquid equilibria of carbon dioxide over aqueous solutions containing an electrolyte have been described with a reduced number of parameters as compared to previous models (Papaiconomou *et al.*, 2003).

Three different types of solutions were investigated: aqueous solutions of carbon dioxide with acetic acid, NaOH and NaCl. The results for 4 mol/kg NaCl aqueous solution are presented in Figure 11.

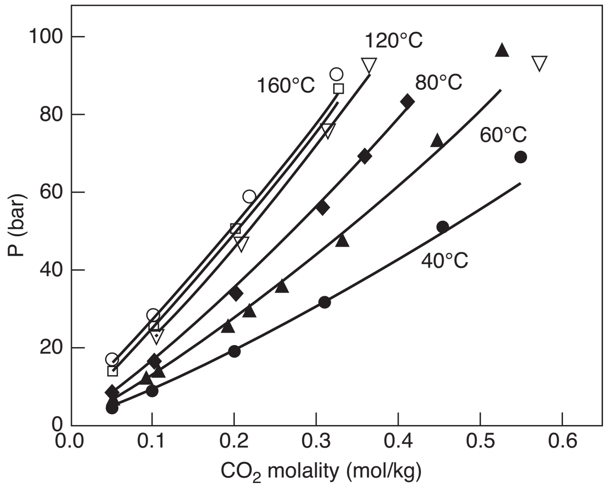

Figure 11

Pressure over solution for 4 mol/kg NaCl aqueous solution containing CO_2 at various temperatures. Symbols: experimental values; solid lines: results of MSA fits.

An important feature of this work is that the CO_2 was represented by a simple hard sphere whose fitted diameter was 3.41×10^{-10} m at 25°C.

CONCLUSION

The MSA model constitutes an interesting alternative to the Pitzer model. It involves a smaller number of parameters that moreover have some physical meaning. It is applicable to very high concentrations, generally to saturation. It is capable of accounting for association effects (it can accommodate ion pairing and chemical association). Therefore, it may be used to describe speciation in ionic solutions.

In this work, the model has been parameterized for a great number of electrolytes: 168 binary and 65 ternary ionic solutions.

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