

Extension of the Predictive Behaviour of an Electrolyte Equation of State by Incorporating the Temperature Effect on Ionic Solvation

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An electrolyte equation of state that was previously applied to various aqueous and non-aqueous systems has been modified to improve the representation of excess properties in the case of electrolyte aqueous solutions containing non-halide anions. The main modifications are the introduction of interaction parameters between anions and water and the use of a new set of solvated diameters, all interaction parameters being evaluated from these solvated diameters through simple relations. The data treatment considers a database made of 62 systems: salts of alkaline and earth-alkaline cations, the anions being halides, perchlorates, nitrates, hydroxides and sulfates. The second aim of this study was to investigate the possible extension of the model predictive features to the effect of temperature on the excess properties of electrolyte solutions. The new version of the model was then applied to the representation of osmotic coefficients of 12 chloride and bromide salts over the 273.15 – 473.15 K temperature range. To extend the model validity to this large temperature range, it was considered that the cationic solvated diameters were decreasing with temperature through an exponential function that uses only three parameters for all the systems considered.

1. Introduction

Prediction of thermodynamic properties is useful for application when data are lacking, doubtful or even scarce. In the case of non-electrolyte systems, group contribution methods are very popular in industrial applications. However these methods are not adapted to electrolyte solutions because, in many cases, the group is the ion itself. Furthermore excess properties in ionic solutions result from interactions that differ a lot from those relative to non-electrolyte systems.

Some years ago we developed an electrolyte equation of state with predictive features [1]. The prediction was obtained through simple relations between model parameters and experimental solvation diameters of individual ions: Stokes diameters for cations and Pauling diameters for anions. This method proved to be effective, for instance for the calculation of excess properties in methanol ionic solutions without parameter fitting [2].

These results are in favor of some physical significance for the term used to express the solvation characteristics, this term being associated to a MSA term for extending the validity of a non electrolyte cubic EOS to electrolyte solutions.

However the model, in its initial version, ignores anionic solvation and this may explain that the results are not as good for oxyanion and small ions like OH⁻ and F⁻ as for halide systems. Hence the first aim of the present work is to improve the model by taking into account the solvation of anions.

Another important limitation of the model is linked to the validity of the relation between model parameters and solvation diameters. As Stokes diameters are essentially available at 298.15 K, the predictive behavior is valid over a limited temperature range, in the vicinity of ambient temperature. Hence, the purpose of this work is also to investigate the possibility of extending the prediction to the temperature effect on excess properties.

2. Model presentation

Before presenting the model modifications, the initial version of the model will be shortly introduced. It is based on a combination of a non-electrolyte cubic EOS (Redlich Kwong Soave for instance) with terms that are specific to interactions involving ions:

$$\left[\frac{\Delta a}{RT} \right] = \left[\frac{\Delta a}{RT} \right]_{RKS} + \left[\frac{\Delta a}{RT} \right]_{MSA} + \left[\frac{\Delta a}{RT} \right]_{SOLV} \quad (1)$$

where Δa is the difference between the molar Helmholtz energy of the system and its value in the standard state, R being the gas constant and T the temperature in K. The two first contributions appearing in equation (1) are, respectively, the non-electrolyte EOS term, Redlich Kwong Soave in the present case, and a MSA expression for electrostatic interactions between ions:

$$\left[\frac{\Delta a}{RT} \right]_{MSA} = -\frac{e^2 N}{4\pi \varepsilon_0 D} \sum_i \frac{x_i Z_i^2 \Gamma}{1 + \Gamma \sigma_i} + RT \frac{\Gamma^3 v}{3\pi N} \quad (2)$$

where e , N , ε_0 , v , σ_i , D , x_i and Z_i are, respectively, the electronic charge, the Avogadro's number, the electric permittivity of free space, the solution molar volume, the diameter of species i , the dielectric constant, the mole fraction of species i and its number of charge. The Γ parameter is calculated through an implicit equation that is defined elsewhere [1].

The last term in equation (1) is specific to this model and is introduced to take into account the solvation interactions. It involves an adjustable interaction parameter W_{ki} :

$$\left[\frac{\Delta a}{RT} \right]_{SOLV} = -RT \sum_k \sum_l \frac{x_k x_l W_{kl}}{\left(v - \frac{N\pi}{6} \sum_k x_k \sigma_k^3 \right)} \quad (3)$$

The last ionic parameter is b_i , the ionic contribution to the mixture covolume b involved in the RKS term. The calculation of b has to combine a molecular part and an ionic one:

$$b = b_{molecular} + \sum_{ions} x_i b_i \quad (4)$$

But, as the following relation between ionic covolume and diameter is adopted:

$$\sigma_i = \sqrt[3]{\frac{6 b_i}{N \pi}} \quad (5)$$

the model involves two types of ionic parameters: ionic covolumes and W_{ij} interaction parameters. However all these parameters are fixed or related to

solvated diameters (Stokes diameters for cations c and Pauling diameters for anions a , subscript w being for water):

$$b_c = \lambda_1 (\sigma_c^S)^3 + \lambda_2 \quad (6)$$

$$b_a = \lambda_1 (\sigma_a^P)^3 + \lambda_2 \quad (7)$$

$$W_{cw} = \lambda_3 \sigma_c^S + \lambda_4 \quad (8)$$

$$W_{ca} = \lambda_5 (\sigma_c^S + \sigma_a^P)^4 + \lambda_6 \quad (9)$$

$$W_{cc} = W_{ca} = W_{aw} = 0 \quad (10)$$

3. Model modification

Using the preceding assumptions, the model gives a precise representation of the excess properties of electrolyte solutions, at least in the case of halide systems. For systems with other anions, the results are less satisfactory and this is probably due to the fact that neglecting anion – water interactions is only well adapted to the case of halide systems. Hence the assumptions traduced into the relations (6)-(10) have been changed to take into account W_{aw} parameters. Furthermore, as ions have different effects on the solvent structure, various groups of relations have been incorporated to take into account this structure-changing effect. Finally instead of relating model parameters to experimental Stokes or Pauling diameters we decided to consider a new set of solvated diameters σ_c and σ_a that will be determined by a data fitting or estimated. This last modification has been introduced for several reasons, the main one being that for complex systems (weak electrolytes, metallic complexes...) experimental values of ionic solvated diameters are not known or even may not be unambiguously determined because the corresponding ions are always involved in chemical equilibria. Hence the set of correlation allowing calculating model parameters is now:

$$b_i = \frac{N \pi}{6} \sigma_i^3 \quad (11)$$

$$W_{iw} = \lambda_3 \sigma_i + \lambda_4 \quad (12)$$

$$W_{ca} = \lambda_5 (\sigma_c + \sigma_a)^4 + \lambda_6 \quad (13)$$

with different couples of λ_3 - λ_4 parameters for cations, for halides, for small anions (F^- or OH^-), for oxyanions carrying one negative charge and for sulfate.

The improvement of the results is summarized in Table 1.

Table 1. Representation of osmotic coefficients at 298.15 K; comparison between the results of the initial version of the model and of the new one.

Systems	Number of systems	Mean of root mean square relative deviation (in %)	
		Initial version	modified
Halides	28	2.8	1.5
All	62	8.4	3.9

In this table the 28 halide systems correspond to those considered in the initial paper, that means halides of NH_4^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{++} , Ca^{++} , Sr^{++} and Ba^{++} . The systems referenced as "all" include the 28 preceding ones as well as BeCl_2 , ZnClO_4 , acids and salts of alkaline and earth-alkaline cations containing NO_3^- , ClO_4^- , SO_4^{--} , F^- and OH^- . The data are osmotic coefficients covering the 0 – 6 mol Kg^{-1} molality range for 1-1 electrolyte but for 2-1 electrolyte solutions the upper molality limit is 3 or 4 mol Kg^{-1} . The reason of this limitation is that the solvation characteristics change significantly when the ratio of the solvent mole number over the ionic mole number becomes small enough. Hence relating the model parameters to solvation diameters that are determined at infinite dilution becomes ineffective without new assumptions.

Obviously an important difference between the new version of the model and the initial one is that the solvation diameters used to evaluate all model parameters are adjusted parameters instead of experimental ones. However, as it may be seen on Figure 1, these adjusted diameters may be related themselves to experimental diameter allowing to recover the predictive feature of the model. However, as ionic diameters are very sensitive parameters, it was decided to consider them as adjustable parameters in the following.

4. Extension of the model predictivity to the temperature effect

As said in the introduction, the second part of this work is devoted to the study of the temperature effect, the aim being to extend the validity of relations (11)-(13) to a large temperature range.

4.1. Results of the Model Direct Extension. The database used in the calculation are osmotic coefficients over the 273.15 - 473.15 K temperature range. For some systems data have been published

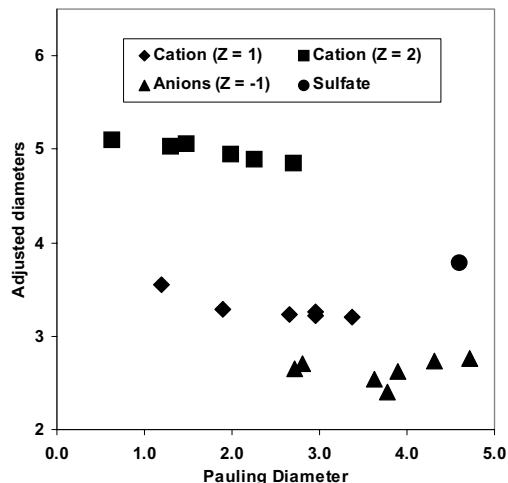


Fig. 1. Relation between adjusted diameters at 298,15 K and Pauling diameters (all values are expressed in 10^{-10} m).

for higher temperatures but these values were not considered in this work because the water dielectric constant is so low that the assumption of entirely dissociated electrolyte will be unreasonable. Even at 473.15 K it may be thought that some association between cations and anions exists, especially for large cations, but it is assumed that this may be neglected. In fact the assumption of total dissociation is necessary, as the aim is to develop a predictive method. For some of the alkaline and alkaline-earth halides no experimental osmotic coefficients are available at high temperatures. This explains, for instance, that Rb^+ salts were not considered. In many cases, also no data have been found at 273.15 K and the lower temperature is, in this case, 298.15 K.

The first step of the study has been to vary the solvated cationic diameters with temperature by making a data treatment at each temperature. The results illustrated in Figure 2.

As expected, the diameters are decreasing with increasing temperature. Very similar results were obtained when bromides are considered. In the case of highly solvated cations, the variation is a regular one. Hence we tried to find an expression to regulate this effect. In Figure 2 it may be observed that the temperature has quite no effect on the Cs^+ diameter. This is linked to the low solvation of this cation.

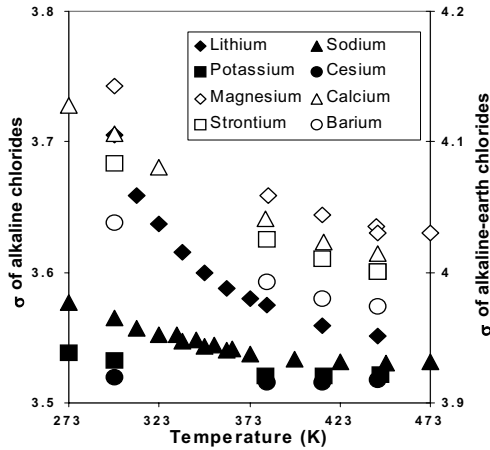


Fig. 2. Variation of adjusted diameters as a function of temperature for various chloride salts (diameter values are in 10^{-10} m).

4.2. Incorporation of an Expression Traducing the Temperature Effect on Ionic Solvation. Several expressions have been tested to represent the influence of temperature on the solvation properties. Finally the following one, involving three kinds of adjustable parameters (A_c , B_c and C_c) have been chosen:

$$\sigma_c = A_c + B_c \left\{ \exp \left[-C_c \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] - 1 \right\} \quad (14)$$

Equation (14) allows identifying A_c parameter to the solvated diameter at 298.15 K. This expression was used for cations, anion diameters being considered as temperature independent.

As the use of as much as 3 parameters per cation seems unreasonable, we have applied eq (14) to the representation of osmotic coefficient over the 273.15 - 473.15 K temperature range, assuming several assumptions that are detailed hereafter: (a) C_c parameter has the same value for all cations, (b) B_c parameter has one value for alkaline cation and another for alkaline-earth cations, and (c) There is one A_c parameter per cation.

With these assumptions we obtained results that are summarized in Table 2. From this table it may be seen that, using only one parameter per ion and 3 more parameters for all systems, a satisfactory result is obtained, especially for the most solvated cations, the global root mean square deviation

being 3.9%. Furthermore as the A_c parameter is the value of the solvated diameter at 298.15 K, this result shows that it is possible to extend the representation of osmotic coefficients at 298.15 K to a large temperature range introducing, in the case of halide systems, only three new parameters (one C_c and two B_c for all cations). Furthermore it was verified that the new values of ionic diameters at 298.15 K may also be related to Pauling diameters as it was done in Figure 1.

Another test has been made with a maximum temperature value of 423.15 K. The aim of this calculation is to try to evaluate the possible effect of ion association for temperature higher than 423.15 K. As we use the same number of adjusted parameters, the results are obviously better than if the 273.15 - 473.15 K range is considered. However the new rms value is 2.9% and the difference between both deviations is not sufficiently large to allow getting unambiguous conclusions about the validity of the complete dissociation assumption.

Table 2. Mean relative deviations obtained using equation 14 for the representation of osmotic coefficients over the 298.15 - 473.15 K temperature range.

Salt	deviation (%) $T_{\max}=473.15$ K	deviation (%) $T_{\max}=423.15$ K
LiCl	3.0	2.5 ^b
^a NaCl	2.4	1.8
^a KCl	1.9	1.1 ^b
CsCl	2.5	1.6 ^b
MgCl ₂	2.0	1.5 ^b
^a CaCl ₂	1.8	1.0 ^b
SrCl ₂	2.3	1.5 ^b
BaCl ₂	6.3	4.9 ^b
LiBr	3.3	2.4 ^b
NaBr	2.7	2.3 ^b
KBr	1.7	1.3 ^b
CsBr	3.7	3.1 ^b
^c MgBr ₂	2.1	1.3
^c CaBr ₂	3.8	3.8
^c SrBr ₂	3.3	3.8

^a System where data at 273.15K are available; $T_{\min}=273.15$ K

^b No data at 423.15K are published; $T_{\max}=413.15$ K)

^c Only values at 298.15K are available

From the preceding results, it may be concluded that the new approach allows representing osmotic coefficient of halide systems over a large range of temperature, using a very low number of new

parameters. Furthermore, as these parameters are valid for all cations, the extrapolation of the model extension to new systems should not involve new parameters. However, we tried to consider non-halide systems but only few data sets at high temperatures may be found in the literature. Among them we have some data for sulfate and hydroxide systems. Hence we were only able to conduct a limited number of tests. The resulting conclusion is that, for these specific systems, the extrapolation of the method applied to halide systems needs to consider specific interactions between anions and water.

5. Conclusions

Numerous methods exist for the calculation of excess properties in electrolyte aqueous solutions. However most of them use a model that combines a Debye-Hückel term with an empirical one. These models need the determination of salt parameters and, to take into account the temperature effect, empirical relations are introduced to express the variation of adjusted parameters with temperature. In the present work we consider a model that uses parameters that may be related to solvated diameters. Several results show that our parameters may be considered as having some physical meaning in relation with solvation interactions. Hence as all the model parameters are related to ionic diameters, extending the validity of the model to a large temperature range means finding an expression that traduces the decrease of solvation with increasing temperature. A simple equation is proposed that involves very few parameters. The resulting model represents experimental osmotic coefficients of chloride and bromide systems over the 273.15 – 473.15 K temperature range with a 3.9% rms.

References and Notes

- [1] W. Fürst and H. Renon, *AIChE J.*, 39, 335 (1993).
- [2] Y. X. Zuo and W. Fürst, *Fluid Phase Equilibria*, **150**, 267 (1998).