Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State

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A new equation of state for electrolyte solutions has been developed from an expression of the Helmholtz free energy containing a nonelectrolyte part and a part relative to ions. The nonelectrolyte part is taken from the equations of state (EOS) of Schwartzentruber et al. (1989). The ionic part is composed of an MSA long-range term to account for electrostatic interactions and a short-range interaction term specific to ions. Using correlations between parameters and experimental ionic diameters, the model reduces to a one-parameter model. It has been applied to numerous strong electrolyte systems and extended to ternary systems to test its predictability without mixing parameters for ions. Its results compare well to the results reported for other one-parameter models (electrolyte EOS). Furthermore, it was found that the cation-anion interaction parameter could also be correlated to experimental ionic diameters. Then, the osmotic coefficients of 28 alkaline and alkaline-earth halide systems may be represented with a root mean square relative deviation of 2.9% using only six correlation parameters. This result has been extended to other systems, with the conclusion that the model with all parameters correlated may also be applied to systems other than halide solutions. The resulting model is predictive. The quality of the prediction was tested by determining osmotic coefficients relative to six systems without any parameter adjustment. The deviations of the predicted values range from 2.0 to 5.4%. The quality of the representation of mixed salts systems without mixing parameters was evaluated using experimental osmotic coefficients of 30 ternary systems.

Introduction

Most models for the representation of nonideality in electrolyte solutions use the formalism of the excess Gibbs energy. Few attempts to use Helmholtz free energy expressions and derived equations of state have been published. This contrasts with the noticeable development of the equation of state (EOS) approach in the representation of equilibria involving nonelectrolyte solutions. As new precise equations of state of nonelectrolyte are now available for the representation of equilibrium properties of mixtures of nonelectrolytes, including polar compounds, it becomes useful to develop methods extending the application of those EOS to the representation of the thermodynamic properties of nonelectrolyte solutions where electrolytes are dissolved. One of the first attempts to develop an equation of state for electrolyte solutions was that of Planche (Planche and Renon, 1981). Planche used the mean spherical approximation (MSA) approximation to derive an expression of the Helmholtz free energy from a nonprimitive model. It contains a hard sphere Percus-Yevick term, a long-range interaction term derived from the one developed by Blum and Hoye (1977) and an original attractive term for the interactions between all type of compounds. The model was then modified by Ball et al. (1985) and applied to a large number of strong electrolyte solutions. Using correlations between parameters, the number of parameters to be adjusted using equilibrium data is limited to one per anion-cation pair.

From the few other published electrolyte EOS, one has to mention the models of Raatschen et al. (1987), Harvey and Prausnitz (1989), Copeman and Stein (1987), Jin and Donohue (1988, 1991), Aasberg-Petersen et al. (1991) and Simon et al. (1991). Raatschen's model, applied to the representation of

the excess properties of the ternary LiBr-Methanol-Water system, is based on an expression of the Helmholtz free energy including six contributions. Three of these are specifically related to the presence of ions. The model has three binary (cation-anion) adjustable parameters per electrolyte. Furthermore, two ionic parameters are associated to the individual ions (ionic diameter and an energy parameter). The model developed later by Harvey and Prausnitz (1989) to represent the solubility of various compounds in aqueous electrolyte solutions at high pressure has only three terms including a Born-type contribution and a long-range interaction term derived from the application of MSA approximation to the primitive model. In the model of Copeman and Stein (1987), the contributions to the expression of the Helmholtz free energy are a repulsive term, a long-range interaction term, and an attractive term. It should be noticed that this last term is used for interactions involving ions as well as molecules as in Planche and Ball's model (Planche and Renon, 1981; Ball et al., 1985). The model has been applied to various systems and especially to the representation of the mean activity coefficients of 13 strong electrolyte systems. Mainly one ionic binary parameter is sufficient to represent the excess properties of these strong electrolyte solutions but for highly concentrated systems a second parameter is needed. Jin and Donohue (1988) expression of the Helmholtz free energy contains up to ten terms. The model contains one adjustable parameter per anion-cation pair. Moreover, the ionic radii included in his expressions were taken from various references: most of the used values were Pauling radii (for cations as well as anions), but some values also refer to hydrated radii. In a second version of his model, Jin and Donohue (1991) used the ionic radii as the adjusted parameters instead of the preceding binary cation-anion parameter. Unfortunately the reported results were less extensive and, for instance, no deviations were given in the case of the most hydrated cations (Li^+ and Mg^{++}). The Electrolyte EOS of Aasberg-Petersen et al. (1991) is specific in that sense that, as the aim of the work was to express the influence of salts on the fugacities of molecular compounds, the author did not consider ions but only salts. Furthermore, he developed his model on the base of an expression of the fugacity coefficients instead of an expression of the Helmholtz free Energy. Simon et al. (1991) have recently developed an Electrolyte EOS combining the Redlich-Kwong-Soave EOS and two ionic terms which are a Debye-Hückel type term derived from Pitzer's expression (Pitzer, 1979) and a Born type term. The two preceding models are unfortunately not extensively applied to strong electrolyte systems and then it is very difficult to compare the results to those presented in the present work. Other equations of state have been published and applied to weak electrolyte solutions but often ignoring the presence of ions.

The new equation of state resulting from this work is based on an expression of the Helmholtz energy including a nonelectrolyte part and two terms devoted to the representation of interactions specific to the ions. The originality of the present approach is the use for the nonelectrolyte part (solvent) of a Redlich-Kwong-Soave type EOS previously developed for the modeling of nonelectrolyte systems by Schwartzentruber et al. (1989). It is precise, especially in the representation of equilibrium properties of polar compounds, and this is crucial for the present purpose. Moreover an important characteristic of this nonelectrolyte EOS is that its mixing parameters can be deduced from UNIFAC group parameters (Schwartzentruber et al., 1989). Another important feature of the new electrolyte EOS is the use of two short-range terms. The first short-range term is the usual term of the Redlich-Kwong type EOS and is for interactions between molecular compounds. The second one is an original expression for short-range interactions involving ions. The aim of the article is to test the application of this approach to strong aqueous electrolyte systems with a minimum number of adjusted parameters and to develop correlations of the parameters with experimental data representative of the solvation of ions.

Molecular Interaction Terms in the Expression of the Helmholtz Energy

The model is based on an expression of the molar Helmholtz energy $a(T,V,x_i)$. The advantage of such an approach is that all thermodynamic functions can be derived from that expression. The molar Helmholtz energy is developed as the sum of four contributions:

$$\left(\frac{a-a^0}{RT}\right) = \left(\frac{a-a^0}{RT}\right)_{RF} + \left(\frac{a-a^0}{RT}\right)_{SR1} + \left(\frac{a-a^0}{RT}\right)_{SR2} + \left(\frac{a-a^0}{RT}\right)_{LR} \quad (1)$$

The term of repulsive forces (RF), as well as the first attractive short-range forces term (SR1), are similar to those of Schwartzentruber et al. (1989):

$$\left(\frac{a-a^0}{RT}\right)_{RF} = \Sigma_k x_k \ln \frac{x_k RT}{P_0(v-b)} \quad (2)$$

where the summation is over ions as well as molecular species (the meaning of subscripts is given in the Notation section) and

$$\left(\frac{a-a^0}{RT}\right)_{SR1} = \frac{a^{SR}}{RT(b+c)} \ln \frac{v+c}{v+b+2c} \quad (3)$$

where v is the molar volume of the electrolyte solution and b is defined by:

$$b = \Sigma_s x_s b_s + \Sigma_i x_i b_i \quad (4)$$

where s corresponds to molecular species and i to ions. For molecular species b_s is expressed in the usual way as a function of the critical properties:

$$b_s = \frac{2^{1/3}-1}{3} \frac{RT_c}{P_c} \quad (5)$$

The parameters a^{SR} and c are the same as in the original EOS, but, as we are dealing in this article with aqueous strong electrolyte solutions, the only molecular species is water (denoted as w). Therefore, the nonelectrolyte parameters are expressed as:

$$c = x_w c_w \tag{6}$$

and

$$a^{SR} = x_w^2 a_w^{SR} \tag{7}$$

with

$$a_w^{SR} = \frac{1}{9(2^{1/3}-1)} \frac{(RT_c)^2}{P_c} \alpha(T_r) \tag{8}$$

$$\sqrt{\alpha(T_r)} = 1 + m(\omega)(1-\sqrt{T_r}) - p_1(1-T_r)(1+p_2T_r+p_3T_r^2) \tag{9}$$

and

$$m(\omega) = 0.48508 + 1.55191\omega - 0.15613\omega^2 \tag{10}$$

The third term is a short-range term specific to interactions involving ionic species.

$$\left(\frac{a-a^0}{RT}\right)_{SR2} = -\Sigma_k \Sigma_l \frac{x_k x_l W_{kl}}{v(1-\xi_3)} \tag{11}$$

where at least one of k and 1 is an ion.

ξ_3 is defined as:

$$\xi_3 = \frac{N\pi}{6} \Sigma_k \frac{x_k \sigma_k^3}{v} \tag{12}$$

where k is over all species.

It may be considered as a simplified form of the corresponding term in Planche and Ball's MSA model (Planche and Renon, 1981; Ball et al., 1985). The fact that a short-range interaction term specific to ionic species is added to the equivalent term of Schwartzentruber's model is justified by the fact that short-range interactions between ions and polar molecular species are very different from the corresponding interactions in nonelectrolyte solutions. Two types of parameters appear in Eqs. 11 and 12. They are interaction parameters W_{kl} and the diameters σ_k.

The last term is the long-range interaction term in the form used by Ball:

$$\left(\frac{a-a^0}{RT}\right)_{LR} = -\frac{\alpha_{LR}^2}{4\pi} \Sigma_i \frac{x_i Z_i^2 \Gamma}{1+\Gamma\sigma_i} + \frac{\Gamma^3 v}{3\pi N} \tag{13}$$

where the shielding parameter Γ is obtained from:

$$4\Gamma^2 = \alpha_{LR}^2 N \Sigma_i \frac{x_i}{v} \left(\frac{Z_i}{1+\Gamma\sigma_i}\right)^2 \tag{14}$$

and

$$\alpha_{LR}^2 = \frac{e^2 N}{\epsilon_0 DRT} \tag{15}$$

The dielectric constant of the solution is expressed as:

$$D = 1 + (D_w - 1)\left(\frac{1-\xi_3''}{1+\frac{\xi_3''}{2}}\right) \tag{16}$$

In this equation ξ_3'' is similar to ξ_3 defined in Eq. 12 but the sum is only over ions. The expression of Pottel has been used instead of the more complicated expression of Planche's model, because it is a better compromise between representation of the initial decrease of D as a function of the ionic concentration and the values at high ionic strengths. From the preceding equations, it is possible to derive the other thermodynamic functions; some are reported in the appendix.

Representation of the Osmotic Coefficients of Halide (Cl^-, Br^- and I^-) Solutions

The first step of the study was to test the model on the experimental osmotic coefficients of alkaline and alkaline-earth halide solutions (Robinson and Stokes, 1970). The parameters for water appearing in RF and SR1 terms are those of Schwartzentruber et al. (1989); they were fitted to vapor pressure data and experimental densities of boiling water. The water diameter σ_w used in the SR2 term was assumed to have the same value as in the MSA model (Planche and Renon, 1981; Ball et al., 1985), which is 2.52 Å. Three types of ionic parameters appear in the equations of the model. They are the ionic covolumes b_i, ionic diameters σ_i and the interaction parameters W_{ik}. As in Ball's model, the parameters $W_{aa'}$ and $W_{cc'}$ were ignored because of the charge repulsion effect and parameter W_{aw} because of the generally accepted lower solvation of the anions. Then the model has six adjustable parameters involving ions per binary system (one salt solution). They are the cationic and anionic diameters σ_c and σ_a, the ionic covolumes b_c and b_a and the interaction parameters between cation and solvent W_{cw} and between cation and anion W_{ca}.

To reduce the number of parameters the following relation between b_i and σ_i was used for all ions:

$$\sigma_i = \sqrt[3]{\frac{6b_i}{N\pi}} \tag{17}$$

In a preliminary simultaneous determination of b_i, W_{ca}, and W_{cw} parameters by treatment of experimental osmotic coefficients (Robinson and Stokes, 1970), the parameters appeared to be strongly correlated. Adjusted cationic covolumes b_c can be related to the Stokes cationic diameters σ_c^S by a linear correlation:

$$b_c = \lambda_1 (\sigma_c^S)^3 + \lambda_2 \tag{18}$$

As the solvation of anions is lower than the solvation of cations, Pauling diameters may be used as the characteristic anionic diameters σ_a, at least for halides, and the preceding relation can be extended to anions, Pauling diameters being used instead of Stokes diameters.

$$b_a = \lambda_1 (\sigma_a^P)^3 + \lambda_2 \tag{19}$$

The second step of the optimization was to determine si-

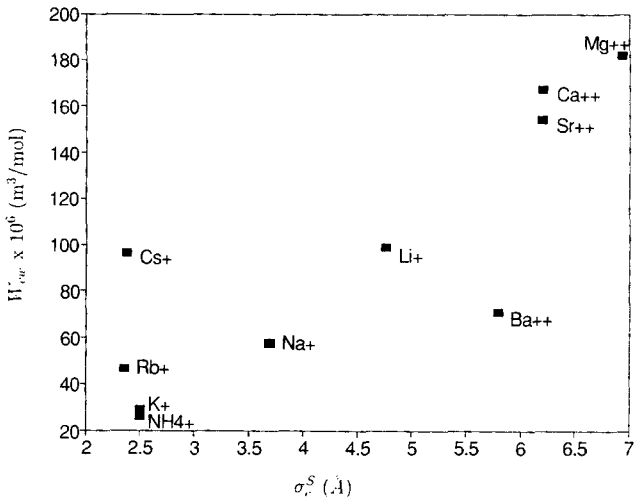

Figure 1. Correlation between W_{cw} parameters and Stokes cationic diameters.

multaneously λ_1 and λ_2 and the parameters W_{ca} and W_{cw} using the same data set. The obtained root mean square relative deviation in osmotic coefficients ($\delta\Phi$) is practically unchanged (0.94% instead of 0.87%) by use of correlations. Figure 1 illustrates the relation between adjusted W_{cw} values and the Stokes diameters. It appears that W_{cw} is linearly correlated to σ_c^S.

$$W_{cw} = \lambda_3 \sigma_c^S + \lambda_4 \tag{20}$$

except for the largest cation in both series (Cs^+ and Ba^{++}), but the strong correlation between adjusted W_{cw} and W_{ca} parameters, especially in the case of cesium where the correlation coefficient is greater than 0.999, results in a unsignificant loss of precision in the representation of experimental osmotic coefficients when the correlation is used.

The third step of the optimization is the determination of W_{ca} parameters, when correlations 18, 19, and 20 are used. $\delta\Phi$ is still not significantly different from the preceding ones (1.1% for the 28 systems).

The results for each system are given in Table 2 and compared to Ball's results. The average of $\delta\Phi$ is not significantly different for the two models which have the same number of adjusted parameters (one per electrolyte system). The comparison with the results of Copeman and Stein (1987) is not easy, because he did not use the same database. A real comparison is only possible for the solutions of KBr, NaCl, and KCl, the rms being 2.5, 2.4 and 2.4% on the mean activity coefficients (with his one parameter model) instead of 1.4, 1.5 and 1.3 in present work (obtained by a data treatment of the experimental (Robinson and Stokes, 1970) mean activity coefficients). The comparison is easier with the one binary parameter model of Jin and Donohue (1988). The representation of the mean activity coefficients, using the new EOS in the same concentration range as Jin, gives an average error of 1.85% over all the systems instead of 3.54% for Jin's model. For comparison, for the same data set the average rms obtained using Pitzer's model (Pitzer, 1979) limited to parameters β^0_{ac} and β^1_{ac} is 0.4% instead of 1% with the new model but with two adjusted parameters instead of only one.

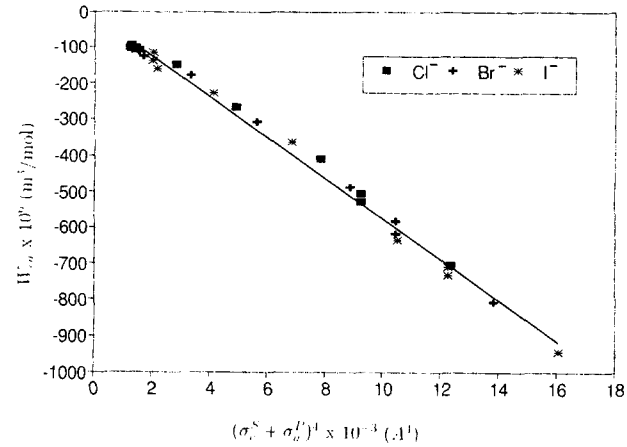

Figure 2. Correlation between W_{ca} parameters and $(\sigma_c^S + \sigma_a^P)^4$.

Therefore a one-parameter model is obtained which represents the excess properties of 28 halide systems with a precision which compares well with the precision obtained using other one parameter models. But here the adjustable parameter is related to the most important solvation interactions, mainly with cations. In addition an attempt to correlate the W_{ca} parameters to experimental values related to solvation has been made. It was observed that the anion-cation interaction parameter could be related to the sum of the Stokes cationic diameter and the Pauling anionic diameter. A very suitable linear correlation valid for all halides with the same values of λ_5 and λ_6 is:

$$W_{ca} = \lambda_5 (\sigma_c^S + \sigma_a^P)^4 + \lambda_6 \tag{21}$$

Figure 2 illustrates this result.

The last step of the optimization work on halide systems was to determine the best values of the correlation coefficients for the 28 data sets. The obtained $\delta\Phi$ is 2.9 with the parameter values given in Table 1. The detailed results for each system

Table 1. Values of the Fitted λ_5 and λ_6 Correlation Parameters, the Other Parameters being $\lambda_1 = 0.10688$; $\lambda_2 = 6.5665$; $\lambda_3 = 35.09$; $\lambda_4 = 6.004$*

	$10^6\lambda_5$	$10^6\lambda_6$	Dia. (Å)
Cl^-	−0.04304	−27.51	3.6**
Br^-	−0.04304	−27.51	3.9**
I^-	−0.04304	−27.51	4.32**
F^-	0.01823	−123.36	2.72**
OH^-	0.007448	−178.22	3.52**
BrO_3^-	−0.02197	−39.86	6.16**
ClO_3^-	−0.0274	−3.88	5.76**
ClO_4^-	−0.04298	119.59	5.84**
ClO_4^-	−0.04583	77.21	4.83
Ac^-	−0.02801	−132.38	2.35
NO_3^-	−0.02886	8.54	4.01
CrO_4^{2-}	−0.01828	−108.97	6.0**
SO_3^{2-}	−0.03208	18.93	5.8**
SO_4^{2-}	−0.05465	−31.33	3.32
PO_4^{3-}	0.001873	−1280.04	10.55
AsO_4^{3-}	0.005893	−409.77	9.36

*All Parameters are Relative to SI Units for W_{ik} or b_i and Å for Diameters.
**Pauling Diameters and the Other are Fitted.

Table 2. Comparison Between Ball's Model and the New Equation of State for the Representation of Osmotic Coefficients of Halide Solutions

Electrolyte	Molality Range	rms Rel. Dev. in Osmotic Coeff. $\delta\Phi$ (%)		
		Model of Ball et al. (1985)	New Model	
			Adjusted W_{ca} Para.	W_{ca} Para. Correlated by Eq. 21
NH_4Cl	0.1-6	0.6	1.2	2.1
LiCl	0.1-6	0.7	0.7	1.6
LiBr	0.1-6	1.3	0.6	0.7
LiI	0.1-3	0.8	1.6	2.1
NaCl	0.1-6	0.9	0.7	2.7
NaBr	0.1-4	0.2	0.7	1.4
NaI	0.1-3.5	0.5	1.0	1.5
KCl	0.1-4.5	0.4	0.7	2.9
KBr	0.1-5.5	0.3	0.8	2.7
KI	0.1-4.5	1.0	1.3	3.3
RbCl	0.1-5	0.5	0.3	2.8
RbBr	0.1-5	0.5	0.2	0.5
RbI	0.1-5	1.1	0.4	1.8
CsCl	0.1-6	2.0	1.4	1.1
CsBr	0.1-5	2.3	1.5	3.3
CsI	0.1-3	1.5	0.6	5.8
$MgCl_2$	0.1-3	1.5	1.0	2.8
$MgBr_2$	0.1-3	3.6	1.1	1.4
MgI_2	0.1-3	5.3	1.0	1.7
$CaCl_2$	0.1-3	2.0	1.2	2.3
$CaBr_2$	0.1-3	0.9	1.3	4.4
CaI_2	0.1-2	0.7	1.3	4.2
$SrCl_2$	0.1-4	2.0	1.1	3.4
$SrBr_2$	0.1-2	1.2	1.1	1.7
SrI_2	0.1-2	0.5	1.4	2.0
$BaCl_2$	0.1-1.8	0.9	1.8	4.7
$BaBr_2$	0.1-2	0.8	1.7	2.6
BaI_2	0.1-2	0.6	1.7	6.0
Average		1.2	1.0	2.6

are reported on Table 2. The precision of the representation is significantly worse than in the case of the use of adjusted W_{ca}, especially in the case of the iodide of the largest cation of each series, but is satisfactory if it is considered that all parameters are correlated to experimental ionic properties.

Extension of the Model to Systems with other Anions

Using the osmotic data reported by Robinson and Stokes (1970), the W_{ca} values corresponding to the one parameter model have been determined for F^- and nonhalide systems assuming Pauling value for the anionic diameters. The results are given in Table 3 and compared to Ball's results. It has to be pointed out that, for all the data treatments relative to nonhalide systems, the parameters $\lambda_{i,i=1,4}$ are set to the values reported in Table 1 and obtained by a simultaneous determination of $\lambda_{i,i=1,6}$ in the case of halide systems. It appears that the new results are better than Ball's excepted if anion is

Table 3. Representation of Osmotic Coefficients of Binary Systems Using Pauling Radii for the Anion

Electrolyte	Molality Range	rms Rel. Dev. in Osmotic Coeff. $\delta\Phi$ (%)		
		Model of Ball et al. (1985)	New Model	
			Adjusted W_{ca} Parameters	W_{ca} Parameters Correlated by Eq. 21
NaF	0.1-1	0.1	0.3	-
KF	0.1-4	0.5	0.6	-
LiOH	0.1-4	5.9	1.3	1.5
NaOH	0.1-6	1.0	1.2	1.6
KOH	0.1-6	2.3	0.5	0.8
CsOH	0.1-1	2.1	2.1	2.5
$NaBrO_3$	0.1-2.5	-	0.6	-
$KBrO_3$	0.1-0.5	-	0.2	-
$NaClO_3$	0.1-3.5	-	1.7	-
$KClO_3$	0.1-0.7	-	0.2	-
Na_2CrO_4	0.1-3.5	-	2.0	-
K_2CrO_4	0.1-3.5	-	1.6	-
$LiClO_4$	0.1-4	1.4*	3.3	3.6
$NaClO_4$	0.1-6	1.0*	4.7	4.7
$Mg(ClO_4)_2$	0.1-2	1.4*	3.2	4.8
$Ca(ClO_4)_2$	0.1-3	1.4*	3.4	7.4
$Sr(ClO_4)_2$	0.1-3	1.4*	4.4	4.5
$Ba(ClO_4)_2$	0.1-3.5	1.4*	8.2	8.7
$(NH_4)_2SO_4$	0.1-4	-	4.3	4.5
Li_2SO_4	0.1-2	1.9*	1.1	5.2
Na_2SO_4	0.1-4	6.8*	4.0	25.3
K_2SO_4	0.1-0.7	1.0*	0.7	2.5
Rb_2SO_4	0.1-1.8	2.2*	1.0	4.8
Cs_2SO_4	0.1-1.8	2.7*	0.5	7.8
$MgSO_4$	0.1-2	7.9*	1.3	4.4

*Means that the Corresponding Results Reported by Ball are Obtained with Anionic Diameter Adjustment.

perchlorate but, in that case, as in the case of sulfate systems, the anionic diameter was simultaneously adjusted by Ball.

Figure 3 shows that for nonhalide systems, W_{ca} parameters are also related to $\sigma_c^S + \sigma_a^P$. However, the correlation is obviously less unambiguous than in the case of halide systems. This is of great importance because W_{ca} is the unique adjustable parameter and then a very sensitive one. To illustrate this point, the range of W_{ca} corresponding to a variation of $\delta\Phi$ of one percent centered at the optimum value is shown on Figure 3 by vertical bars. It follows that the use of a unique correlation for all systems results in a significant loss of precision in the representation of excess properties. Therefore, it was decided to define a correlation between W_{ca} and $\sigma_c^S + \sigma_a^P$ for each anionic system.

W_{ca} parameters are related through Eq. 21 to $(\sigma_c^S + \sigma_a^P)^4$ for ClO_4^-, SO_4^{--}, and OH^-, with values of R^2 0.992 and 0.988, respectively, for the first two systems but only 0.83 for OH^-. However, if λ_5 and λ_6 are determined by a data treatment, systems with OH^- give better results than ClO_4^- and SO_4^{--}, as reported in last column of Table 3. Only the system Na_2SO_4 is very poorly represented.

As pointed out by various authors, oxyanions have specific interactions with the solvent. For instance, the anions may be classified in various groups (Harned and Owen, 1958) such as

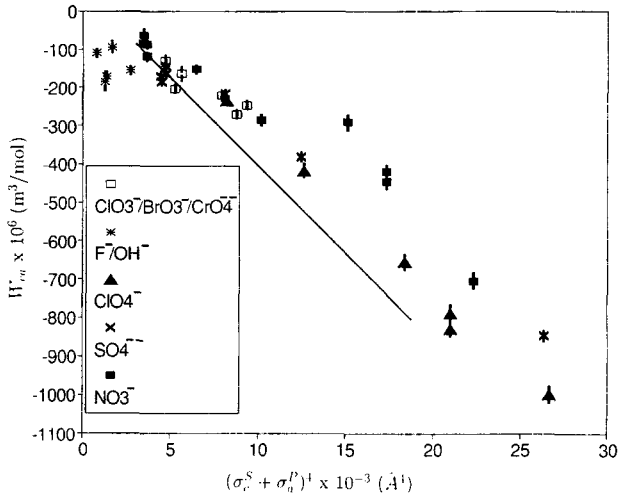

Figure 3. Correlation between W_{ca} parameters and $(\sigma_c^S + \sigma_a^P)^4$ in the case of nonhalide systems.

halide, proton acceptors of small size (F^-, OH^-, . . .), unsymmetrical proton acceptors (such as Acetate) and polyatomic anions (NO_3^-, ClO_4^-, . . .). Therefore, the use of adjusted diameters instead of Pauling ones, as in the case of halide, is justified as the ionic diameters used in the various correlations were supposed to be representative, in some way, of solvent ions interactions. The results of the simultaneous fitting of anionic diameters and W_{ca} parameters are in Table 4. The systems with anions ClO_4^- and SO_4^{--} which were previously modeled using Pauling diameters have been also modeled using fitted anionic diameters. The results corresponding to these systems are obviously improved, giving precisions for the one parameter model which compares well with Ball's model, as in the case of systems with anions acetate (Ac^-) and NO_3^-. It has also to be noticed that a good precision is also obtained in the case of 1-3 systems containing PO_4^{3-} or AsO_4^{3-} as the anion. Table 4 gives the detailed $\delta\Phi$ deviations. The average rms compares well with the results using Ball's models (2.1% instead of 2.6%). For all the 35 systems reported in Table 4, the average rms is 2.2% using the new electrolyte EOS instead of 1.1% using Pitzer's model (Pitzer, 1979) limited to parameters β^0_{ac} and β^1_{ac}, but in this case also the model has one adjusted parameter and Pitzer's model two.

As previously, the osmotic coefficients are poorly represented if a unique correlation is used for all systems even if λ_5, λ_6, and anionic diameters are optimized simultaneously. Therefore, λ_5 and λ_6 values specific to each anionic systems have been determined using osmotic coefficient data. The obtained values are in Table 1 and the rms relative deviations in Table 4. The model using a correlation similar to Eq. 21 is inefficient only in the simultaneous representation of all nitrate systems. There is a specific difficulty in the case of nitrate solutions of the smaller cation of each series. This is why it was decided to make the data treatment without the data sets corresponding to Li^+ and Mg^{++}, but the obtained correlation parameters were applied afterwards to these systems to give an idea of the representation.

Predictions for Ternary Systems

To complete the study, the extension to ternary two salts aqueous solutions systems without additional parameters was made to test the predictivity of the model for the representation of mixed electrolyte systems. The model containing no mixing parameters, the extrapolation has been made using the parameters deduced from the work on binary systems. The detailed results are reported in Table 5.

The results show that the one parameter model is well adapted to the representation of mixed electrolyte solutions, except in the case of sulfate solutions when lithium salts are mixed with salt of the larger alkali cations Rb^+ and Cs^+. But it is noticeable that the model using only $\lambda_{i,i=1,6}$ parameters (the SO_4^{--} diameter being set to the value deduced from the parameters fitting on binary data) represents these systems with an acceptable $\delta\Phi$ value. The model with correlated parameters only fails in the representation of $LiNO_3$-$NaNO_3$ mixed solutions. This is related to the poor representation of osmotic coefficients of $LiNO_3$ solutions which was mentioned above.

Table 4. Representation of Osmotic Coefficients of Binary Systems with Adjusted Anionic Diameters

Electrolyte	Molality Range	rms Rel. Dev. in Osmotic Coeff. $\delta\Phi$ (%)		
		Model of Ball et al. (1985)	New Model	
			Adjusted W_{ca} Para.	W_{ca} Para. Correlated by Eq. 21
LiAc	0.1-4	1.3	2.1	6.5
NaAc	0.1-3.5	1.7	2.2	2.7
KAc	0.1-3.5	2.3	2.1	2.7
RbAc	0.1-3.5	2.4	2.0	3.4
CsAc	0.1-3.5	2.7	2.2	3.7
$Mg(Ac)_2$	0.1-3	4.0	2.5	2.6
$Ba(Ac)_2$	0.1-1.4	2.1	2.7	3.4
NH_4NO_3	0.1-6	2.3	0.3	9.1*
$LiNO_3$	0.1-6	0.3	3.8	18.6*
$NaNO_3$	0.1-6	3.9	0.6	1.6*
KNO_3	0.1-3.5	2.9	1.9	6.9*
$RbNO_3$	0.1-4.5	4.6	3.3	7.9*
$CsNO_3$	0.1-1.4	1.0	1.0	6.5*
$Mg(NO_3)_2$	0.1-3	1.5	3.1	25.5*
$Ca(NO_3)_2$	0.1-6	2.4	6.5	10.6*
$Sr(NO_3)_2$	0.1-4	3.6	3.7	9.7*
$Ba(NO_3)_2$	0.1-0.4	1.0	0.4	9.1*
Na_3AsO_4	0.1-0.7	-	0.9	-
K_3AsO_4	0.1-0.7	-	1.8	-
Na_3PO_4	0.1-0.7	-	1.6	-
K_3PO_4	0.1-0.7	-	6.2	-
$LiClO_4$	0.1-4	1.4	2.1	4.0
$NaClO_4$	0.1-6	1.0	1.8	2.6
$Mg(ClO_4)_2$	0.1-2	1.4	1.8	2.7
$Ca(ClO_4)_2$	0.1-3	1.4	2.1	6.3
$Sr(ClO_4)_2$	0.1-3	1.4	2.1	2.7
$Ba(ClO_4)_2$	0.1-3.5	1.4	4.8	7.8
$(NH_4)_2SO_4$	0.1-4	-	3.1	2.2
Li_2SO_4	0.1-2	1.9	1.9	9.7
Na_2SO_4	0.1-4	6.8	1.5	8.7
K_2SO_4	0.1-0.7	1.0	1.3	1.1
Rb_2SO_4	0.1-1.8	2.2	1.0	5.0
Cs_2SO_4	0.1-1.8	2.7	0.4	8.2
$MgSO_4$	0.1-2	7.9	1.9	2.2

*Correlation was Obtained Ignoring the Data Relative to Li^+ and Mg^{++}; Ac is for Acetate Anion.

Table 5. Prediction of Osmotic Coefficients of Ternary Systems

Systems	Max. Ionic Strength	rms Rel. Dev. in Osmotic Coeff. $\delta\Phi$ (%)		Ref.
		Model with One Para. per Salt	All Para. Correlated	
LiCl-NaCl	5.84	0.8	2.2	a
LiCl-$BaCl_2$	4.32	0.8	1.6	b
NaCl-$CaCl_2$	6.86	1.3	2.0	c
NaCl-CsCl	7	3.9	6.3	d,e
NaCl-$BaCl_2$	4.82	1.0	3.7	f
CsCl-$BaCl_2$	4.08	7.3	7.4	b
KCl-$CaCl_2$	6.26	4.9	1.5	g
KCl-$BaCl_2$	4.72	3.2	4.8	h
NaCl-KCl	6.6	2.2	3.8	i
KCl-$SrCl_2$	7.76	6.5	5.6	j
$MgCl_2$-$CaCl_2$	9.49	1.1	1.7	k
NaCl-$SrCl_2$	5.94	0.9	2.8	l
NaCl-$MgCl_2$	8.0	1.6	3.3	m,n
NaCl-NaBr	3.5	0.4	3.3	o
KCl-CsCl	5	0.8	1.9	p
NaBr-KBr	4.32	1.9	1.9	o
KCl-$MgCl_2$	5.64	5.8	3.4	q
KCl-KBr	3.56	0.8	3.6	o
NaCl-$NaNO_3$	5.73	2.5	2.1	r
KCl-KNO_3	3.77	1.7	3.9	r
$NaNO_3$-KNO_3	3.71	1.2	5.3	r
$LiNO_3$-$NaNO_3$	8.31	6.7	14.5	a
Na_2SO_4-$MgSO_4$	14.18	3.2	8.8	s
Li_2SO_4-Cs_2SO_4	8.13	15.9	5.2	t
Na_2SO_4-Cs_2SO_4	10.43	4.8	8.9	t
K_2SO_4-Cs_2SO_4	8.78	7.5	5.2	t
Na_2SO_4-Rb_2SO_4	12.72	4.1	6.1	u
Li_2SO_4-Rb_2SO_4	7.7	15.3	5.6	u
Li_2SO_4-Na_2SO_4	9.6	5.9	6.4	u
Li_2SO_4-K_2SO_4	9.5	7.8	7.1	u

(a) Robinson et al. (1971); (b) Lindenbaum et al. (1972); (c) Robinson and Bower (1966a); (d) Robinson (1952); (e) Rard and Miller (1982); (f) Robinson and Bower (1965); (g) Robinson and Covington (1968); (h) Reilly et al. (1971); (i) Robinson (1961); (j) Downes (1974); (k) Robinson and Bower (1966b); (l) Macaskill et al. (1978); (m) Platford (1968); (n) Rard and Miller (1987); (o) Covington et al. (1968); (p) Robinson (1953); (q) Padova and Saad (1977); (r) Bezboruah et al. (1970); (s) Rard and Miller (1981); (t) Filipov et al. (1987); (u) Filipov et al. (1989).

Discussion

The model has two original features. The first is that it extends a precise EOS of the classical Redlich-Kwong-Soave type to electrolyte solutions. It has been demonstrated that the chosen supplementary term allows a representation of the excess properties of an extensive number of ionic solutions with a precision of the same order or better than the precisions reported for other electrolyte EOS.

The second is that it has the lowest possible number of parameters for the representation of strong electrolyte systems. Using correlation involving Stokes or Pauling diameters, the model requires only one binary parameter per electrolyte system. The precision of this new electrolyte EOS compares well with the precision obtained using other models with the same number of parameters (for example, Ball et al., 1985; Jin and Donohue, 1988; Lu et al., 1988).

To reduce further the number of parameters to less than one, it is possible to use ionic instead of electrolyte parameters as in the second version of the model of Jin and Donohue (1991) or in the model of Xu and Hu (1986). An alternative method is to correlate the binary electrolyte parameters to ionic properties as in present work or in the model of Lu et al. (1988) who correlated the binary parameters of his model to $Z_a/(\sigma_a^P)^2$ and $Z_c/(\sigma_c^P)^2$. Both methods lead to predictive models which can be applied to unknown systems without fitting parameters. Unfortunately, no real attempts to test the predictivity of such models is to be found in literature.

Table 6. Prediction of Osmotic Coefficients without any Regression of Parameters Except H_3O^+ Solvated Diameter Estimated from Data on HCl, HBr, and HI Systems*

Electrolyte	Molality Range	New Model with All Para. Correlated
HCl	0.1-6	2.4
HBr	0.1-3	2.1
HI	0.1-3	2.0
$BeCl_2$	0.2-1.24	5.4
$HClO_4$	0.1-6	5.3
$Pb(ClO_4)_2$	0.1-4	4.9
$Zn(ClO_4)_2$	0.1-4	2.4
$La(ClO_4)_3$	0.1-1.91	3.1
$Ga(ClO_4)_3$	0.1-2	3.4

*All the Data are from Robinson and Stokes (1970) except for $BeCl_2$ (Vasilev et al., 1973) and for $La(ClO_4)_3$ (Rard et al., 1977).

The new model was tested for the prediction of excess properties of new systems without any parameter adjustments by comparison of calculated osmotic coefficients to experimental values. The representation of $BeCl_2$ osmotic coefficients was compared to the values reported by Vasilev et al. (1973) who estimated the activity of water in $BeCl_2$ solutions using a correlation involving the heat capacity of the solution. The obtained rms relative deviation (Table 6) shows that Vasilev's values are consistent with the values obtained by the new EOS. Adjusting H_3O^+ diameter, a good representation of the osmotic coefficients relative to the solutions of HCl, HBr, and HI was obtained. Using the resulting value of H_3O^+ diameter (5.06 Å), it was possible to predict the osmotic coefficients of $HClO_4$ solutions without parameter adjustment. Table 6 gives the result as well as results relative to other perchlorate solutions including 1-3 systems. These results confirm the predictivity of the new EOS.

Two versions of the new model can therefore be used. If a very good precision is needed in the representation of excess properties, the model with one interaction parameter per binary electrolyte system is recommended. Sometimes, however, a predictive model may be very useful, even if less precise. For instance, this is the case when the solution contain many ionic species related by chemical equilibria. In this case, the predictive version of the model, with all parameters related to ionic diameters, is more appropriate. It has to be pointed out that both versions can be extended to mixed salt systems without mixing parameters. The model is therefore well adapted to the representation of the excess properties of the various kinds of electrolyte solutions.

The predictive version of the model has some characteristics of a group contribution model. Considering the nonelectrolyte part of the model, it has to be pointed out that Schwartzentruber's EOS binary parameters can be evaluated from UNIFAC group contribution parameters (Schwartzentruber and Renon, 1989). The ionic terms also involve "group" contributions, because it requires only ionic diameters. However, it

has to be noted that, at least for cations, the diameters corresponding to solvated diameters depend of the solvent.

Notation

a = molar Helmholtz free energy
a^{SR} = short-range parameter defined in Eq. 3
a_w^{SR} = attraction parameter in the SR1 part of the EOS
b = covolume
c = volume translation factor
D = dielectric constant of the solution
e = protonic charge
$m(\omega)$ = parameter defined in Eq. 10
n = number of moles
N = Avogadro number
p_1, p_2, p_3 = parameters defined in Eq. 9
P = pressure
R = gas constant
T = absolute temperature
V = volume of the solution
v = molar volume of the solution
W = interaction parameter defined in Eq. 11
x = mole fraction
Z = ionic charge

Greek letters

α_{LR} = defined in Eq. 15
$\beta^0_{ac}, \beta^1_{ac}$ = Pitzer's binary interaction parameters
Γ = defined in Eq. 14
$\delta\Phi$ = root mean square relative deviation in the representation of osmotic coefficients
ϵ_0 = electric permittivity of free space
λ = parameters defined in Eqs. 18, 19, 20, and 21
μ = chemical potential
ξ_3 = defined in Eq. 12
σ = diameter
Φ = osmotic coefficient
ω = Pitzer acentric factor

Superscripts

P = Pauling diameter
S = Stokes diameter
0 = standard properties

Subscripts

LR = long-range term
RF = repulsive forces term
SR1 = nonelectrolyte short-range term
SR2 = ionic short-range term
c = critical property
i, j = ions
k, l = ions and molecular species
s, s' = molecules
r = reduced property
w = water

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Appendix: Expressions of Thermodynamic Properties According to the Model

Pressure

$$\left(\frac{P}{RT}\right) = \left(\frac{P}{RT}\right)_{RF} + \left(\frac{P}{RT}\right)_{SR1} + \left(\frac{P}{RT}\right)_{SR2} + \left(\frac{P}{RT}\right)_{LR} \quad \text{(A1)}$$

with

$$\left(\frac{P}{RT}\right)_{RF} = \frac{1}{v-b} \quad \text{(A2)}$$

$$\left(\frac{P}{RT}\right)_{SR1} = -\frac{a^{SR}}{RT(v+c)(v+b+2c)} \quad \text{(A3)}$$

$$\left(\frac{P}{RT}\right)_{SR2} = -\Sigma_k\Sigma_l \frac{x_k x_l W_{kl}}{v^2(1-\zeta_3)^2} \quad \text{(A4)}$$

$$\left(\frac{P}{RT}\right)_{LR} = -\frac{\alpha_{LR}^2}{4\pi D}\left(\frac{\partial D}{\partial V}\right)_{T,n_k} \Sigma_j \frac{n_j Z_j^2 \Gamma}{1+\Gamma\sigma_j} - \frac{\Gamma^3}{3\pi N} \quad \text{(A5)}$$

Chemical potential and osmotic coefficient

$$\left(\frac{\mu_k-\mu_k^0}{RT}\right) = \left(\frac{\mu_k-\mu_k^0}{RT}\right)_{RF} + \left(\frac{\mu_k-\mu_k^0}{RT}\right)_{SR1} + \left(\frac{\mu_k-\mu_k^0}{RT}\right)_{SR2} + \left(\frac{\mu_k-\mu_k^0}{RT}\right)_{LR} \quad \text{(A6)}$$

with

$$\left(\frac{\mu_k-\mu_k^0}{RT}\right)_{RF} = 1 + \ln\frac{x_k RT}{P_0(v-b)} + \frac{b_k}{v-b} \quad \text{(A7)}$$

$$\left(\frac{\mu_k-\mu_k^0}{RT}\right)_{SR1} = \frac{2\Sigma_l x_l a_{kl}^{SR}}{RT(b+c)} \ln\frac{v+c}{v+b+2c} - \frac{a^{SR}(b_k+c_k)}{RT(b+c)^2} \ln\frac{v+c}{v+b+2c} - b_k \frac{a^{SR}}{RT(v+c)(v+b+2c)} - \frac{b_k+c_k}{b+c}\frac{a^{SR}(v-b)}{RT(v+c)(v+b+2c)} \quad \text{(A8)}$$

$$\left(\frac{\mu_k-\mu_k^0}{RT}\right)_{SR2} = -2\Sigma_l \frac{x_l W_{kl}}{v(1-\zeta_3)} - \frac{N\pi}{6}\sigma_k^3\Sigma_k\Sigma_l \frac{x_k x_l W_{kl}}{v^2(1-\zeta_3)^2} \quad \text{(A9)}$$

$$\left(\frac{\mu_k-\mu_k^0}{RT}\right)_{LR} = \frac{\alpha_{LR}^2}{4\pi D}\left(\frac{\partial D}{\partial n_k}\right)_{T,V,n_{l\neq k}} \Sigma_j \frac{n_j Z_j^2 \Gamma}{1+\Gamma\sigma_j} - \frac{\alpha^2}{4\pi}\frac{Z_k^2\Gamma}{1+\Gamma\sigma_k} \quad \text{(A10)}$$

The osmotic coefficient is expressed as a function of the chemical potential (in the liquid phase):

$$\Phi = -\left[\left(\frac{\mu_w-\mu_w^0}{RT}\right) - \left(\frac{\mu_w-\mu_w^0}{RT}\right)^{ref}\right]\frac{x_s}{\Sigma_j x_j} \quad \text{(A11)}$$

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