

## A Semi-empirical Equation for Activity Coefficients of Ions with One Parameter

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Received August 6, 2013, Accepted September 22, 2013

Based on the Debye-Hückel equation, a semi-empirical equation for activity coefficients was derived through empirical and theoretical trial and error efforts. The obtained equation included two parameters: the proportional factor and the effective radius of an ionic sphere. These parameters were used in the empirical and regression parameter fitting of the calculated values to the experimental results. The activity coefficients calculated from the equation agreed with the data. Transforming to a semi-empirical form, the equation was expressed with one parameter, the ion radius. The ion radius,  $\alpha$ , was divided into three parameters,  $\alpha_{cation}$ ,  $\alpha_{anion}$  and  $\delta_{cation}$ , representing parameters for the cation, anion and combination, respectively. The advantage of this equation is the ability to propose a semi-empirical equation that can easily determine the activity coefficient with just one parameter, so the equation is expected to be used more widely in actual industry applications.

**Key Words** : Debye-Hückel equation, Activity coefficient, Semi-empirical equation

### Introduction

The Debye-Hückel equation<sup>1</sup> is widely used to estimate the activity coefficient in a dilute ion solution. In the equation, the activity coefficient decreases when the molality increases. However, in practice, the activity coefficient increases in concentrations with a molality greater than 1. This is caused by the presence of the short-range interaction, or the ion-molecule interaction, which was not considered in the original Debye-Hückel equation.<sup>2</sup>

To correct for this increase, several empirical parameters have been proposed and implemented: the Guggenheim equation,<sup>3</sup> specific interaction theory (SIT),<sup>4</sup> modified SIT,<sup>5</sup> Bromley equation<sup>6</sup> and modified Bromley's methodology.<sup>7</sup> Hydration corrections have also been adapted to improve the prediction of the original equation: Stokes and Robinson's first<sup>8</sup> and second models,<sup>9</sup> Glueckauf's model,<sup>10</sup> Nesbitt's model<sup>11</sup> and Schönert's model.<sup>12</sup>

Lin *et al.*<sup>13</sup> and Pitzer *et al.*<sup>14,15</sup> made attempts to theoretically improve the Debye-Hückel equation. Lin *et al.* em-

ployed the concept of solvation to account for ion-molecule interactions. Pitzer *et al.* modified the equation by including the third term of the Maclaurin expansion, which was neglected in the Debye-Hückel theory. Pitzer also proposed a model with expanded virial parameters to account for the short-range interactions.

Local composition theory gives more detailed information about the electrolyte system as it considers the relationship between the macroscopic composition of a bulk liquid and the composition of lattices using interaction parameters. Based on this model, various other models were developed: Wilson's model,<sup>16</sup> non-random two liquid (NRTL)<sup>17,18</sup> theory, the universal quasi-chemical (UNIQUAC)<sup>19</sup> theory model and the self-consistent local composition (SCLC)<sup>20,21</sup> model.

Recently, using computational simulation, there have been many attempts to precisely calculate thermodynamic factors, such as the activity coefficient.<sup>22,23</sup>

**A Semi-empirical Equation.** Through trial and error, we extended the original equation and found that the following equation was in good agreement with the observed data for calculating activity coefficients. The equation can be applied over a broad concentration range and is especially useful at higher concentrations.

$$\ln \gamma_{\pm} = -\frac{\beta}{\alpha} \cdot I^{1/2} \left( \frac{1 - \kappa\alpha}{1 + \kappa\alpha} \right) \quad (1)$$

The parameters  $\alpha$  and  $\beta$  are, respectively, the proportional factor and the effective radius of an ionic sphere. These parameters are used in the empirical and regression parameter fitting of the calculated values with the experimental results. Table 1 lists the constants for the two parameters using the best fit values for each ion in Eq. (1). The values calculated from the equation agree with the experimental results from Stokes and Robinson.<sup>8</sup> The average values are  $1.375 \times 10^{-10}$  and  $1.884 \times 10^{-10}$  for  $\alpha$  and  $\beta$ , respectively. A

### Notations

- $\alpha$  = radius of the ionic sphere, m
- $h$  = the proportionality factor
- $r$  = radial distance from the center of the spherical unit, m
- $e$  = elementary charge,  $1.602 \times 10^{-19}$  F·V
- $I^{1/2}$  = ionic strength, molality
- $k$  = Boltzmann's constant,  $1.381 \times 10^{-23}$  C·V/K
- $T$  = temperature of the solution, 298.15 K
- $z_{i,j}$  = charge number of ion species  $i, j$
- $\epsilon$  = the permittivity of water at 25 °C,  $6.957 \times 10^{-10}$  F/m
- $\kappa^{-1}$  = the Debye screening length,  $(3.0434 \text{ \AA}) \cdot I^{-1/2}$  m
- $\lambda$  = coupling parameter
- $\mu$  = electric dipole moment
- $\nu$  = stoichiometric coefficient
- $\rho_i$  = the number density of charges of species  $i$
- $\phi_i$  = the potential on the inside of the sphere
- $\psi_j$  = the potential on the outside of the sphere



**Table 3.** Comparison of experimental activity coefficients with calculated values for 2:1 ions

m	MgCl <sub>2</sub>		MgBr <sub>2</sub>		MgI <sub>2</sub>		CaCl <sub>2</sub>		CaBr <sub>2</sub>		CaI <sub>2</sub>		SrCl <sub>2</sub>		SrBr <sub>2</sub>	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
0.1	0.540	0.529	0.551	0.550	0.583	0.580	0.531	0.518	0.541	0.532	0.563	0.560	0.532	0.511	0.540	0.526
0.2	0.489	0.489	0.514	0.518	0.558	0.558	0.472	0.472	0.492	0.492	0.528	0.531	0.467	0.462	0.484	0.483
0.3	0.474	0.477	0.512	0.517	0.566	0.567	0.450	0.455	0.478	0.482	0.526	0.531	0.440	0.442	0.464	0.468
0.5	0.481	0.481	0.545	0.545	0.619	0.614	0.443	0.448	0.489	0.491	0.561	0.561	0.425	0.430	0.463	0.467
0.7	0.511	0.506	0.604	0.599	0.698	0.698	0.460	0.460	0.522	0.522	0.621	0.614	0.432	0.434	0.484	0.484
1	0.581	0.570	0.723	0.723			0.506	0.500	0.597	0.597	0.741	0.741	0.463	0.461	0.538	0.535
1.4	0.709	0.709					0.595	0.587					0.528	0.524	0.640	0.643
1.8							0.712	0.712					0.614	0.614		
2.5																
3																
4																
5																

m	SrI <sub>2</sub>		BaCl <sub>2</sub>		BaBr <sub>2</sub>		BaI <sub>2</sub>		MnCl <sub>2</sub>		FeCl <sub>2</sub>		CoCl <sub>2</sub>		NiCl <sub>2</sub>	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
0.1	0.561	0.553	0.535	0.500	0.538	0.513	0.555	0.542	0.539	0.516	0.532	0.518	0.536	0.522	0.539	0.522
0.2	0.520	0.520	0.460	0.444	0.474	0.465	0.511	0.509	0.476	0.469	0.473	0.473	0.479	0.479	0.483	0.479
0.3	0.513	0.517	0.424	0.419	0.446	0.446	0.502	0.502	0.450	0.450	0.451	0.454	0.459	0.463	0.463	0.463
0.5	0.536	0.536	0.393	0.397	0.430	0.435	0.520	0.523	0.436	0.440	0.445	0.450	0.458	0.462	0.461	0.464
0.7	0.583	0.578	0.384	0.391	0.436	0.442	0.562	0.562	0.445	0.448	0.462	0.463	0.479	0.479	0.482	0.482
1	0.680	0.680	0.391	0.395	0.466	0.469	0.651	0.649	0.479	0.479	0.509	0.506	0.532	0.531	0.535	0.536
1.4			0.419	0.419	0.529	0.529			0.548	0.542	0.600	0.596	0.634	0.634	0.636	0.647
1.8			0.461	0.449	0.613	0.609					0.719	0.719				
2.5																
3																
4																
5																

**Table 4.** Constants of Eq. (4) giving best fits to the parameter  $\alpha$

	$\alpha_{cation}$	$\delta_{cation}$	$\alpha_{anion}$
H <sup>+</sup>	0.306	1	
Li <sup>+</sup>	0.339	1	
Na <sup>+</sup>	0.604	1	
K <sup>+</sup>	0.998	1	
Rb <sup>+</sup>	-1.319	1	
Mg <sup>2+</sup>	0.457	0.802	
Ca <sup>2+</sup>	0.373	0.611	
Sr <sup>2+</sup>	0.297	0.480	
Ba <sup>2+</sup>	0.184	0.308	
Mn <sup>2+</sup>	1.854	2.105	
Fe <sup>2+</sup>	1.854	2.259	
Co <sup>2+</sup>	1.536	1.969	
Ni <sup>2+</sup>	1.579	2.017	
Cl <sup>-</sup>			0.180
Br <sup>-</sup>			0.120
I <sup>-</sup>			0.049

(RSQ = 0.9813). The parameter  $\alpha$  can also be divided into three parameters,  $\alpha_{cation}$ ,  $\alpha_{anion}$  and  $\delta_{cation}$ , representing parameters for the cation, the anion and the combination, respectively. The combination parameter  $\delta_{cation}$  is believed to

represent the dipole angular relation because its value is 1 for a 1:1 electrolyte. Table 4 lists the values for  $\alpha_{cation}$ ,  $\alpha_{anion}$  and  $\delta_{cation}$ . The equation is expressed as follows.

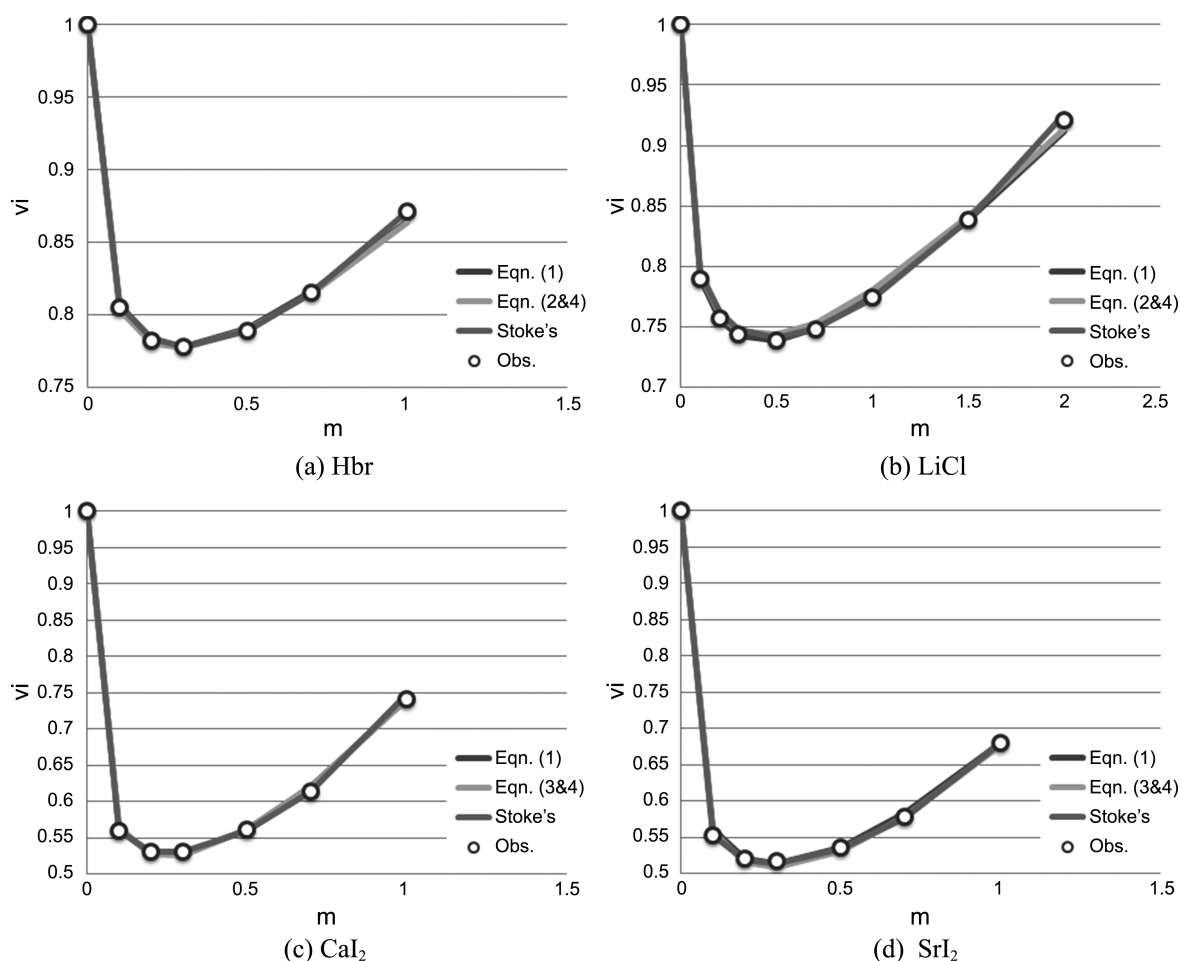
$$\alpha \times 10^{10} \cong \sqrt{\left(\frac{\delta_{cation}}{\alpha_{cation} + \alpha_{anion}}\right)^2} \quad (4)$$

Eq. (1) could be expressed with only one parameter,  $\alpha$ , which combines the cation and anion parameters as a semi-empirical form. Using Eqs. (1), (2), (3) and (4), the accuracy of the recalculated activity coefficients are shown in Table 1. In Figure 1, the calculated results using one and two parameters are shown for several ions by comparing the experimental results with the hydration correction by the Stokes and Robinson model.<sup>8</sup>

The combination parameter  $\delta_{cation}$  can also be expressed as a linear equation with  $\alpha_{cation}$ , as follows (RSQ = 0.9895).

$$\delta_{cation} \cong 1.1117 \cdot \alpha_{cation} + 0.1886 \quad (5)$$

The above equation allows the activity coefficient to be calculated using only one parameter. The use of statistical-mechanics-based simulations and computational methods may be more accurate,<sup>22,23</sup> but the simple proposed equation is expected to be more effective in real-world industry applications.



**Figure 1.** Calculated results using Eqn. (1) and Eqns. (1)–(4) for several ions by comparing the experimental results with the hydration correction by the Stokes and Robinson model for (a) HBr, (b) LiCl, (c) CaI<sub>2</sub>, (d) SrI<sub>2</sub>.

**Assumptions and Derivation #1: Empirical Trial and Error Approach.** The original Debye–Hückel equation is as follows.<sup>2</sup>

$$\ln \gamma_{\pm} = -\frac{z_{\pm}^2 e^2 \kappa}{2 \epsilon k T (1 + \kappa \alpha)} \quad (6)$$

Combining the constant terms into parameter C, Eq. (6) can be expressed as follows.

$$\ln \gamma_{\pm} = -C \cdot \frac{I^{1/2}}{1 + \kappa \alpha} \quad (7)$$

Through trial and error efforts, it was found that the  $(1 - \kappa \alpha)$  term can produce a rebound increase of Eq. (7). From the regression curve, the constant term C is also expected to be related with the term  $\alpha$ . Such expectations showed good agreement with the experimental results; consequently, we modified the original equation to Eq. (1).

**Assumptions and Derivations #2: Theoretical Trial and Error Approach.**

**Inside the Sphere:** The derivation of Eq. (1) was determined through trial and error. The theoretical approach was very rough, but the main goal of this work was to find a simple and useful equation that could be obtained from just one parameter. The derivation process was based on the

following two main assumptions.

**First Assumption**—In an electrolyte, ionic molecules form a spherical cluster, such as in the mean spherical model (MSM).<sup>24</sup> We assumed that the cluster produces a spherically symmetric potential surrounding the ions, and the potential behaves as a dipole moment. The moment includes the electric charge fraction as follows. The electric charge fraction is the degree of bias of shared pair electrons in molecules.

$$\mu_c \propto \delta \quad (8)$$

Here, we assume that the electron fraction is proportional to the intensity of the surrounding ions, or  $I^{1/2}$ . The constant  $\eta$  is a proportional factor.

$$\delta = \eta \cdot I^{1/2} \quad (9)$$

**Second Assumption**—The interaction is caused from the clustering of multiple molecules, and it should be numerically scaled down to a one molecule unit as in the original derivation, so the potential can be divided by a unitizing factor. Because  $\eta$  is treated as a regression parameter, it includes a functional term for unitization or scaling down which focuses on one dipole of the cluster. The cluster moment  $\mu_c$  could be changed to  $\mu_c$ , representing unitized cluster moment. The parameter  $\eta$  also serves as a propor-

tional factor including the other term of the moment,  $\mu_c$ . In conclusion, the moment could be expressed as follows.

$$\mu_c = \eta \cdot I^{1/2} \quad (10)$$

The electric potential of the dipole moment is expressed as follows,<sup>25</sup> where the parameter  $h$  is a proportional factor.

$$\varphi(r) = h \cdot \mu_c / r^2 \quad (11)$$

According to the Debye-Hückel theory, the ionic atmosphere is induced by a term that is independent of the distance, *i.e.*, is not governed by the distance. Therefore,  $A_0$ , a constant representing the ionic atmosphere, is added to the potential as follows.

$$\varphi_j(r) = h \cdot \mu_c / r^2 + A_0 \quad (12)$$

Then, by taking the derivative with respect to the radius, we obtain:

$$\frac{d\varphi_j}{dr} = -2h \cdot \frac{\mu_c}{r^3} \quad (13)$$

**Outside the Sphere<sup>1</sup>:** The region outside of the sphere is governed by the Poisson-Boltzmann equation. Thus,  $\psi_j$  represents the center potential outside of the sphere.

$$\nabla^2 \psi_j = -\frac{e}{\varepsilon} \sum_{i=1}^N z_i \rho_i e^{-z_i e \psi_j(r) / kT} \quad (14)$$

In the case that  $z_i e \psi_j(r) \ll 1$ , the right side can be expanded using a power series, and the higher order terms can be neglected. By maintaining the isotropy, Eq. (14) is expressed as follows:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{\partial \psi_j}{\partial r} \right) = -\frac{e}{\varepsilon} \sum_{i=1}^N z_i \rho_i \left( 1 - \frac{z_i e \psi_j}{kT} \right) \quad (15-1)$$

$$= \frac{e^2 \psi_j}{\varepsilon kT} \sum_{i=1}^N z_i^2 \rho_i \quad (15-2)$$

$$= \kappa^2 \cdot \psi_j \quad (15-3)$$

where

$$\kappa^2 = \frac{e^2}{\varepsilon kT} \sum_{i=1}^N z_i^2 \rho_i \quad (16)$$

Note that the general solution can be written as:

$$r \psi_j = c_1 e^{-\kappa r} + c_2 e^{+\kappa r} \quad (17)$$

However, since  $\psi_j \rightarrow 0$  if  $r \rightarrow \infty$ ,  $c_2 = 0$ . Hence, the above equation reduces to:

$$r \psi_j = c_1 e^{-\kappa r} \quad (18)$$

Thus, the potential outside the sphere can be written as follows.

$$\psi_j(r) = \frac{c_1 e^{-\kappa r}}{r} \quad (19)$$

By differentiating, we obtain:

$$\frac{d\psi_j}{dr} = -\frac{c_1 e^{-\kappa r} (1 + \kappa r)}{r^2} \quad (20)$$

**Ionic Atmosphere:** The boundary conditions at radius  $\alpha$  can be expressed as follows.

$$\psi_j(\alpha) = \varphi_j(\alpha) \quad (21)$$

$$\left( \frac{\partial \psi_j}{\partial r} \right)_{\alpha} = \left( \frac{\partial \varphi_j}{\partial r} \right)_{\alpha} \quad (22)$$

Using the first boundary condition,

$$-\frac{c_1 e^{-\kappa \alpha} (1 + \kappa \alpha)}{\alpha^2} = -2h \cdot \frac{\mu_c}{\alpha^3} \quad (23)$$

$$c_1 = 2h \cdot \frac{\mu_c}{\alpha} e^{\kappa \alpha} (1 + \kappa \cdot \alpha)^{-1} \quad (24)$$

The derivation can be further simplified using the second boundary condition:

$$\frac{c_1 e^{-\kappa \alpha}}{\alpha} = A_0 + h \cdot \frac{\mu_c}{\alpha^2} \quad (25)$$

$$c_1 e^{-\kappa \alpha} = A_0 \alpha + h \cdot \frac{\mu_c}{\alpha} \quad (26)$$

Then, by substituting for  $c_1$  and rearranging, we obtain:

$$2h \cdot \frac{\mu_c}{\alpha} (1 + \kappa \alpha)^{-1} = A_0 \alpha + h \cdot \frac{\mu_c}{\alpha} \quad (27)$$

where

$$A_0 = h \cdot \frac{\mu_c}{\alpha^2} \left( \frac{1 - \kappa \alpha}{1 + \kappa \alpha} \right) \quad (28)$$

By substituting Eq. (28) into the original equation as the ionic atmosphere term,  $(1 - \kappa \alpha)$  can be inserted. The parameters  $h$ ,  $\eta$  and other constant terms can be combined by introducing a new parameter,  $\beta$ . The parameter  $\beta$  can be expressed as a power function with  $\alpha$ , so Eq. (2) and (3) can be obtained.

**Galvani Potential:** With the Galvani potential, the activity coefficients can be calculated using the following equation, where the coupling parameter  $\lambda$  was optionally introduced for the reversible insertion, or charging process.<sup>2</sup>

$$kT \ln \gamma = \sum q_i \int_0^1 \varphi_{atmo} d\lambda \quad (29)$$

In Eq. (29),  $q_i = z_i e$  is the electrical charge of the surrounding ions and ionic atmosphere, and  $\varphi_{atmo}$  is the potential of the ionic atmosphere. For conventional use, we simplified the equation considering the mean ionic activity coefficient,  $\gamma_{\pm}$ . Since the interaction is the potential double of the other signs, the equation was multiplied by  $-1$ .

$$v \cdot kT \ln \gamma_{\pm} = -\sum v_i |z_i| e \int_0^1 A_0 d\lambda \quad (30)$$

Substituting  $A_0$  gives

$$\nu \cdot kT \ln \gamma_{\pm} = -\frac{1}{2} \cdot h \cdot \frac{\eta}{\alpha^2} I^{1/2} \left( \frac{1 - \kappa \alpha}{1 + \kappa \alpha} \right) \cdot e \sum \nu_i |z_i| \quad (31)$$

and dividing Eq. (31) by  $\nu$  results in

$$kT \ln \gamma_{\pm} = -\frac{1}{2} \cdot h \cdot \frac{\eta}{\alpha^2} I^{1/2} \left( \frac{1 - \kappa \alpha}{1 + \kappa \alpha} \right) \cdot e / \nu \sum \nu_i |z_i| \quad (32)$$

The equation could be further simplified by introducing the new parameter,  $\beta$ , which includes the  $h$ ,  $\eta$  and  $(\sum \nu_i |z_i| / \nu)$  terms. As a result, Eq. (32) was modified to Eq. (1) for simplicity as a semi-empirical equation.

### Conclusions

The most noticeable merits are the usefulness and simplicity in obtaining the activity coefficients using just one parameter. This equation could calculate results that fit experimental ones. Former empirical equations, such as the Guggenheim equation,<sup>3</sup> the Specific Interaction theory,<sup>4,5</sup> the Bromely equation<sup>6,7</sup> and so on, are polynomials or need more than two parameters.<sup>2</sup> This equation cannot yet be applied to a two-solvent system, but it can be utilized to calculate activity coefficients with one parameter, which represents each ion in an ionic solution.

### References

1. Debye, P.; Hückel, E. *Phys. Z.* **1923**, *24*, 185.
2. Balomenosa, E.; Paniasa, D; Paspaliaris, I. *Miner. Process. Extr. Metall. Rev.* **2006**, *27*, 1.
3. Guggenheim, E. A.; Turgeon, J. C. *Trans. Faraday Soc.* **1955**, *51*, 747.
4. Ciavatta, L. *Ann. Chim. (Rome)* **1980**, *70*, 551.
5. Scatchard, G. *J. Am. Chem. Soc.* **1968**, *90*, 3124.
6. Bromley, L. A. *AIChE J.* **1973**, *19*, 313.
7. Borge, G.; Castano, R.; Carril, M. P.; Cobillon, M. S.; Madariaga, J. M. *Fluid Phase Equilib.* **1996**, *121*, 85.
8. Stokes, R. H.; Robinson, R. A. *J. Am. Chem. Soc.* **1948**, *70*, 1870.
9. Stokes, R. H.; Robinson, R. A. *J. Solution Chem.* **1973**, *2*, 173.
10. Glueckauf, E. *Trans. Faraday Soc.* **1955**, *51*, 1235.
11. Nesbitt, H. W. *J. Solution Chem.* **1982**, *11*, 415.
12. Schönert, H. *Z. Phys. Chem.* **1986**, *150*, 163.
13. Lin, C. L.; Lee, L. S.; Tseng, H. C. *Fluid Phase Equilib.* **1993**, *90*, 57.
14. Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701.
15. Pitzer, K. S. *Acc. Chem. Res.* **1977**, *10*, 371.
16. Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
17. Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
18. Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. *AIChE J.* **1982**, *28*, 588.
19. Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
20. Ananth, M. S.; Ramachandran, S. *AIChE J.* **1990**, *36*, 370.
21. Narayanan, K. V.; Ananth, M. S. *Fluid Phase Equilib.* **1996**, *114*, 89.
22. Kantor, R. *Czech. J. Phys.* **1991**, *41*, 157.
23. Valeriani, C.; Camp, P. J.; Zwanikken, J. W.; Roij, R.; Dijkstra, M. *J. Phys. Condens. Matter* **2010**, *22*, 104.
24. Wertheim, M. S. *J. Chem. Phys.* **1971**, *55*, 4291.
25. Lin, C.; Lee, L.; Tseng, H. *Fluid Phase Equilib.* **1993**, *90*, 57.