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Application of the Pitzer and the MSA-Based Models in Predicting the Activity and the Osmotic Coefficients of Aqueous Electrolyte Solutions

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The GV-MSA, the BMCSL-MSA and the Pitzer models were used to correlate the individual, the mean ionic activity coefficients and the osmotic coefficients of symmetric and asymmetric electrolyte solutions. In order to compare the results obtained from the GV-MSA with those obtained from the Pitzer and the BMCSL-MSA models, the same experimental data and the same minimization procedure were used and the new sets of parameters for the BMCSL-MSA and the Pitzer models were also reported. The values for the osmotic coefficients of electrolyte solutions were calculated directly using the values of the mean ionic activity coefficients obtained from the models studied in this work. The results for the individual and the mean ionic activity coefficients, as well as the osmotic coefficients up to saturation concentration obtained from the GV-MSA model, compared with those of the BMCSL-MSA, the Pitzer and the Khoshkbarchi-Vera models.

INTRODUCTION

Electrolyte solutions play an important role in chemical engineering processes. The phase behavior study is an essential step towards the design of the industrial processes involving electrolyte solutions. Many attempts have been made to represent the activity and the osmotic coefficients of the electrolyte solutions. Among them, the Pitzer model received a great deal of attention in the last decades [1,2]. Using the Mean Spherical Approximation (MSA) theory for electrolyte solutions has also received extensive attention [3-5]. Waisman and Lebowitz [6] provided an analytical solution for the MSA theory, based on the perturbation and the integral equation theory proposed by Barker and Henderson [7]. Because of including the excluded volume of the ions and the short-range, as well as long-range, interaction effects in the MSA theory, unlike the Debye-Huckel (DH) model, it can be used for concentrated electrolyte solutions.

In the MSA model, the effect of the excluded volume of the ions is represented by a Hard-Sphere (HS) Equation Of State (EOS). Therefore, using an accurate EOS for mixtures of hard spheres is the first essential step for the development of the MSA model to represent correctly the behavior of the electrolyte solutions.

The Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) EOS for mixtures of hard spheres is commonly used as the reference part of the MSA model, to predict the mean ionic activity coefficients and the osmotic coefficients by Simonin [8] Lee [9] and Gering et al. [10]. In the development of the MSA-based models, Taghikhani and Vera [11] proposed the K-MSA model. In this model, the generalized formalism developed by Khoshkbarchi and Vera [12] to extend their EOS [13] to mixtures of hard spheres has been used as a reference part.

In a recent publication, Ghotbi and Vera [14] showed that the generalized formalism developed by Khoshkbarchi and Vera [12], produced poor predictions of the simulation results. In addition, for certain conditions, the combination of the Khoshkbarchi and Vera EOS with the different mixing rules showed significant positive deviations, in comparison with the other EOS for mixtures of hard spheres.

Ghotbi and Vera developed, recently, two new hard sphere equations of state. The proposed EOS by

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Ghotbi and Vera, unlike the Carnahan Starling hard sphere EOS, satisfies the ordered close-packed limit, i.e., the highest possible density [15]. They extended, accurately, their EOS to mixtures, using the Santos et al. [16] and the Barrio and Solana [17] mixing rules.

In this work, the Ghotbi and Vera EOS [15] have been used, combined with the Barrio and Solana [17] mixing rule as a reference system, perturbed with the MSA theory to correlate the mean ionic activity coefficients and the individual activity coefficients of ions and to calculate the osmotic coefficients of symmetric and asymmetric single electrolyte solutions. In addition, the BMCSL-MSA and the Pitzer models were used in correlating the activity coefficients data, as well as calculating the osmotic coefficients. The new sets of parameters for these models were also reported.

THEORY

According to the MSA model, the residual chemical potential of an ion in an electrolyte solution is represented by:

$$\frac{\mu_i^r}{kT} = \left(\frac{\mu_i^r}{kT}\right)^{hs} + \left(\frac{\mu_i^r}{kT}\right)^{\text{elec}}. \tag{1}$$

The contribution of the hard sphere term to the residual chemical potential in the GV-MSA model, coupled with the Barrio and Solana contribution [17], is represented by the following sets of equations:

$$\begin{aligned} Z_p = & \frac{\beta P}{\rho} = 1 + B_2^*\xi + B_3^*\xi^2 + B_4^*\xi^3 + B_5^*\xi^4 \\ & + \frac{8.85\xi^5}{1-\xi} - \frac{0.62\xi^7}{(1-\xi)^2} + \frac{0.04\xi^{10}}{(1-\xi)^3}, \end{aligned} \tag{2}$$

$$\begin{aligned} Z_{\text{mix}} = & 1 + \left(1 - \frac{3}{2}\eta\right)(Z_p - 1)\left(\frac{1+3Y_1}{4}\right) \\ & + \frac{3}{2}\eta(Z_p - 1)\left(\frac{Y_1 + Y_2}{2}\right), \end{aligned} \tag{3}$$

where, Z_p and Z_{mix} are, respectively, the compressibility factor for one-component (pure) hard-sphere fluid and mixtures of hard spheres. In the above equations, one has:

$$\xi_i = \frac{1}{\sqrt{2}} \sum_j \rho_j \sigma_j^i, \quad (i = 0, 1, 2, 3) \quad \text{and} \quad \xi = \xi_3, \tag{4}$$

$$\eta_i = \frac{\pi\sqrt{2}}{6}\xi_i \qquad \text{and} \qquad \eta = \eta_3, \tag{5}$$

$$Y_1 = \frac{\xi_1 \xi_2}{\xi_0 \xi}, \tag{6}$$

and:

$$Y_2 = \frac{\xi_2^3}{\xi_0 \xi^2}. \tag{7}$$

Using Equations 2 and 3, the residual chemical potential for mixtures of hard spheres with a correct, ordered, close-packed limit is as follows:

$$\begin{aligned} \frac{\mu_i^r}{kT} = & \frac{A^r}{NkT} + \frac{3M_{1,i}}{4}K_1 + \frac{3}{2}\left(\frac{2M_{2,i} - M_{1,i}}{4}\right)K_2 \\ & + \left(\frac{1+3Y_1}{4}\right)\left(\frac{\partial K_1}{\partial \rho_i}\right)_{T,V,\rho_{j\notin i}} \\ & + \frac{3}{2}\left(\frac{2Y_2 - Y_1 - 1}{4}\right)\left(\frac{\partial K_2}{\partial \rho_i}\right)_{T,V,\rho_{j\notin i}}, \end{aligned} \tag{8}$$

where:

$$\frac{A^r}{NkT} = \left(\frac{1+3Y_1}{4}\right)K_1 + \frac{3}{2}\left(\frac{2Y_2 - Y_1 - 1}{4}\right)K_2, \tag{9}$$

$$M_{1,i} = Y_1(R_2 + R_1 - R_3 - R_0)_i, \tag{10}$$

$$M_{2,i} = Y_2(3R_2 - R_0 - 2R_3)_i, \tag{11}$$

$$R_{k,i} = \frac{\sigma_i^k}{\sum_j x_j \sigma_j^k}, \tag{12}$$

and:

$$\left(\frac{\partial K_1}{\partial \rho_i}\right)_{T,V,\rho_{j\notin i}} = R_{3,i}(Z_p - 1). \tag{13}$$

As Z_p is expressed in terms of ξ, the derivative $(\frac{\partial K_2}{\partial \rho_i})_{T,V,\rho_{j\notin i}}$ takes the form:

$$\left(\frac{\partial K_2}{\partial \rho_i}\right)_{T,V,\rho_{j\notin i}} = R_{3,i}\xi(Z_p - 1). \tag{14}$$

For Equation 8, K_1 and K_2 have the form:

$$\begin{aligned} K_1 = & -10.11\xi - 3.34\xi^2 - 1.28\xi^3 - 0.50\xi^4 - 0.17\xi^5 \\ & - 0.02\xi^6 - 0.006\xi^7 - 14.01\ln(1-\xi) \\ & - \frac{0.98}{1-\xi} + \frac{0.02}{(1-\xi)^2} + 0.96, \end{aligned} \tag{15}$$

and:

$$\begin{aligned} K_2 = & -14.01\xi - 5.05\xi^2 - 2.23\xi^3 - 0.96\xi^4 - 0.40\xi^5 \\ & - 0.14\xi^6 - 0.02\xi^7 - 0.005\xi^8 - 14.99\ln(1-\xi) \\ & - \frac{1.02}{1-\xi} + \frac{0.02}{(1-\xi)^2} + 1.00. \end{aligned} \tag{16}$$

In order to calculate the osmotic coefficients of the electrolyte solutions directly from the values of the mean ionic activity coefficients, the following Gibbs-Duhem equation was used:

$$\phi = 1 + \frac{1}{m}\int_0^m m d \ln \gamma_\pm . \tag{17}$$

The electrostatic term for the MSA model is expressed as [18]:

$$\left(\frac{\mu_i^r}{kT}\right)^{\text{elec}} = \frac{Z_i e^2}{DkT}\left(\frac{2\Gamma a_i}{\sigma_i \alpha^2} - \frac{Z_i}{\sigma_i}\right) - \frac{P_n \sigma_i}{4(1-\eta)}\left(\Gamma a_i + \frac{\pi}{12(1-\eta)}\alpha^2 P_n \sigma_i^2\right), \tag{18}$$

where:

$$\alpha^2 = \frac{4\pi e^2}{DkT}, \tag{19}$$

$$P_n = \frac{1}{\Omega}\sum_{j=1}^{N} \frac{\rho_j \sigma_j Z_j}{1+\Gamma\sigma_j}, \tag{20}$$

$$\Omega = 1 + \frac{\pi}{2(1-\eta)}\sum_{j=1}^{N}\frac{\rho_j \sigma_j^3}{1+\Gamma\sigma_j}, \tag{21}$$

and:

$$a_i = \frac{\alpha^2\left[Z_i - (\frac{\pi}{2(1-\eta)})\sigma_i^2 P_n\right]}{2\Gamma(1+\Gamma\sigma_i)}. \tag{22}$$

In the above equations, the sums run over all ionic species; σ_i represents the hydrated diameter or size parameter of the ion $i; Z$ is the charge number; e is the electric charge of the electron; T is the absolute temperature; k is the Boltzmann constant; ρ is the number density and Γ is the inverse shielding length defined as:

$$\Gamma = \frac{\alpha}{2}\left\{\sum_{j=1}^{N}\rho_j\left[\frac{Z_j - (\frac{\pi}{2(1-\eta)})\sigma_j^2 P_n}{1+\Gamma\sigma_j}\right]^2\right\}^{1/2}. \tag{23}$$

This term, which is similar to the Debye inverse length, represents the long-range electrostatic interactions.

The term P_n, defined by Equation 20, represents short-range interactions and makes the mathematical expression of the MSA to be highly nonlinear. This is considered to be a shortcoming of the model for engineering applications. An important simplification to the MSA, which drastically simplifies its analytical complexity and reduces the calculation time for engineering applications, was introduced by Lee [9] and studied further by others [19-21]. This simplification neglects the short-range interaction term of the model. Lee [9] showed that the value of P_n can be set to zero when the ratio of the size of the ions is close to unity or the Bjerrum length, $Z_i Z_j e^2/DkT$, is large. With this simplification, the mathematical expression for the electrostatic term, in the simplified GV-MSA (SGV-MSA) form, becomes:

$$\left(\frac{\mu_i^r}{kT}\right)^{\text{elec}} = \frac{Z_i e^2}{DkT}\left(\frac{2\Gamma a_i}{\sigma_i \alpha^2} - \frac{Z_i}{\sigma_i}\right). \tag{24}$$

Since the GV-MSA and the BMCSL-MSA are derived in the McMillan-Mayer (MM) framework with temperature, volume, solute mole numbers and solvent chemical potential as independent variables, it is necessary to transform the activity coefficients calculated with the MSA from the MM framework to the Gibbs framework. The Gibbs framework uses temperature, pressure and mole numbers as independent variables and the Lewis-Randall (LR) standard state for the chemical potentials. While the transformation of the mean ionic activity coefficients from MM to LR is theoretically necessary, it was shown that this transformation does not affect the numerical results and, for practical applications, it can be neglected to a very good approximation.

APPLICATION OF THE NEW MODEL TO THE EXPERIMENTAL DATA

In this study, the GV-MSA, the BMCSL-MSA and the Pitzer models were used to correlate the ionic activity coefficients of symmetric and asymmetric single electrolyte solutions. In the case of the mean ionic activity coefficients, based on the established convention, the diameter of anion is kept constant and equal to the crystallographic Pauling diameter, while the diameter for cation changes with electrolyte concentration in the solutions, according to the following equation:

$$\sigma_+ = \sigma_{+0} + \sigma_{+1}c + \sigma_{+2}c^2, \tag{25}$$

where σ_+ is the hydrated diameter of the cation and c is the concentration of electrolytes based on molarity. The parameters $\sigma_{+j}(j = 0,1,2)$ are considered to be adjustable.

In the case of the individual ionic activity coefficient, it is necessary to introduce a composition dependent anion diameter in addition to that of cation, according to the relation as follows:

$$\sigma_- = \sigma_{-0} + \sigma_{-1}c, \tag{26}$$

where $\sigma_{-j}(j = 0,1)$ are adjustable parameters. The values of the adjustable parameters were obtained by fitting the experimental data of the mean and the individual ionic activity coefficients available in the literature [22-24] and by minimizing the following average absolute relative deviation of the calculated activity coefficients from the experimental data (AARD):

$$\mathrm{AARD}(\%) = \frac{100}{NP}\sum_{i}^{NP}\frac{\left|\gamma_i^{\mathrm{exp}} - \gamma_i^{\mathrm{calc}}\right|}{\gamma_i^{\mathrm{exp}}}. \tag{27}$$

In the above equation, NP refers to the number of the experimental points.

While the experimental data for the individual and the mean ionic activity coefficients available in the literature are based on the molality scale, the activity coefficients, calculated from the MSA model, are based on the molarity scale. Thus, the following conversion criterion is used to change the concentration scale of the activity coefficients [25,26]:

$$\ln\gamma_i^c = \ln\gamma_i^m + \ln\frac{m_i d_o}{c_i}. \tag{28}$$

In Equation 28, the superscripts, m and c, stand for the molality and molarity scales and d_0 is density of water. m and c are the molality and molarity of the ions of the electrolyte in the solution, respectively.

In order to calculate the osmotic coefficient of the electrolyte solutions, the values for the mean ionic activity coefficients obtained from the models were directly used. The osmotic coefficients reflect the non-ideality behavior of the electrolyte solutions in nature and can be exactly obtained by the well-known isopiestic experimental method. The conventional numerical method was used to solve the integration part of Equation 17.

RESULTS AND DISCUSSION

Figure 1 shows the correlation of the mean ionic activity coefficients of NaCl, KBr and $Ca(NO_3)_2$ as a function of molality obtained from the GV-MSA model. As seen from the figure, the model can accurately correlate the mean ionic activity coefficient of the electrolyte solutions, in comparison with the experimental data, up to saturation.

Figure 2 shows the results of the simplified version of the GV-MSA model for the RbCl solution, obtained by setting the electrostatic short range term, i.e., P_n in the MSA part of the model to zero. It can be inferred from the figure that the term, which introduces an extra complexity in the model, does not have a significant effect on the results. It can be also seen that the simplified form of the model represents the experimental data with good accuracy.

Table 1 represents the values of the adjustable parameters of Equation 25 for a number of symmetric and asymmetric aqueous electrolyte solutions obtained from the least square fitting of the model to the experimental data, together with the percent of absolute average relative deviation of the calculated activity coefficients from the experimental data. Table 1 also compares the results of the GV-MSA model with those of the BMCSL-MSA and the Pitzer models. The results for the mean ionic activity coefficients of the GV-MSA and the BMCSL-MSA models were obtained with constant anion diameter, independent of concentration and with the composition dependent of the diameters for cations, i.e., Equation 25. In order to do a fair comparison between the results obtained from the studied models, the same minimization procedure was employed to adjust the parameters of the three studied models. The parameters for the BMCSL-MSA and the Pitzer models are presented in Table 2. It is worth mentioning that the results obtained from the GV-MSA and the BMCSL-MSA models are more accurate than those obtained from the Pitzer model for the electrolyte solutions with high saturation concentration. Thus, the GV-MSA model produces almost the same errors as the BMCSL-MSA model in correlating the activity coefficients. It should be noted

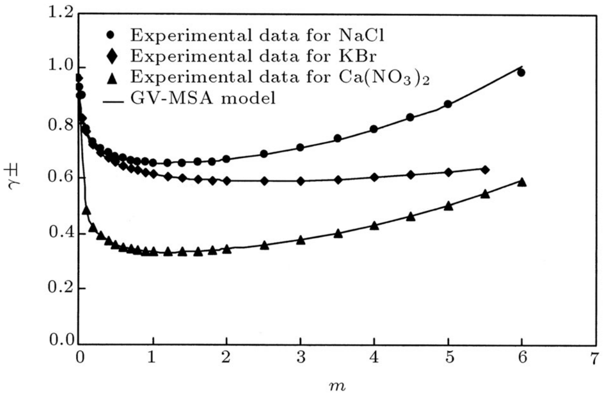

Figure 1. Correlation of the mean ionic activity coefficient of NaCl, KBr and $Ca(NO_3)_2$ in aqueous solutions as a function of molality.

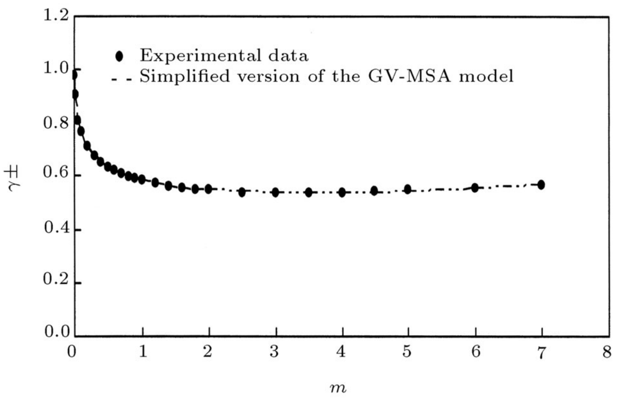

Figure 2. Correlation of the mean ionic activity coefficient of RbCl in aqueous solutions as a function of molality.

Table 1. The GV-MSA parameters for cations and the percent of average absolute relative deviations of the calculated activity coefficients from the experimental data obtained from the GV-MSA, the BMCSL-MSA and the Pitzer models for symmetric and asymmetric single electrolytes at 298.15 K.

	GV-MSA Parameters				**AARD (%)**		
Electrolyte	σ_{+0} **(Å)**	σ_{+1} **(Å mol^{-1} L)**	σ_{+2} **(Å mol^{-2} L^2)**	$\mathbf{m_{max}}$	**GV-MSA**	**BMCSL-MSA**	**Pitzer**
LiCl	4.119	0.001	-0.006	19.2	1.82	1.99	4.73
LiBr	4.289	0.107	-0.013	20.0	3.28	3.18	7.17
LiI	5.501	-0.699	0.187	3.0	0.62	0.62	0.56
NaCl	3.561	-0.294	0.040	6.0	0.95	0.95	0.53
NaBr	3.738	-0.116	0.019	9.0	0.74	0.76	0.40
NaI	3.766	0.084	0.001	12.0	1.14	1.15	0.67
$NaNO_3$	3.857	-0.659	0.096	11.0	1.80	1.79	2.60
KCl	3.062	-0.371	0.053	5.0	0.19	0.18	0.04
KBr	3.186	-0.283	0.047	5.5	0.23	0.23	0.05
KI	3.270	-0.189	0.037	4.5	0.20	0.20	0.05
KOH	4.064	-0.019	-0.003	20.0	0.52	0.53	1.98
$KClO_3^*$	2.298	-2.590	0.979	0.7	0.24	0.24	0.30
$KBrO_3^*$	2.745	-1.809	-0.877	0.5	0.21	0.23	0.25
RbCl*	2.941	-0.074	0.031	7.8	0.21	0.21	0.16
RbBr*	2.903	0.086	0.058	5.0	0.14	0.13	0.14
CsBr*	2.360	0.216	0.072	5.0	0.68	0.68	0.78
CsI*	2.030	0.345	-0.001	6.0	0.71	0.74	0.78
HCl	4.542	-0.095	-0.001	20.0	1.08	1.09	1.72
Li_2SO_4	4.781	-0.848	0.194	3.0	0.85	0.85	0.38
Na_2SO_4	4.101	-1.363	0.366	4.0	1.22	1.22	0.39
K_2SO_4	4.166	-2.074	1.069	0.7	0.50	1.83	1.94
$Rb_2SO_4^*$	4.704	-1.799	0.841	1.8	0.23	0.23	0.31
$Cs_2SO_4^*$	5.030	-1.576	0.841	1.8	1.02	1.02	1.03
$MgCl_2$	5.992	-0.077	-0.013	5.0	0.89	0.89	0.43
$MgBr_2$	6.664	-0.037	-0.012	5.0	0.60	0.61	0.26
$CaCl_2$	5.496	0.049	-0.026	6.0	1.41	1.44	1.22
$CaBr_2^*$	6.159	0.045	0.060	6.0	0.71	0.83	0.89
$Ca(NO_3)_2$	5.965	-0.306	0.057	6.0	0.37	0.37	1.26
$BaCl_2$	5.435	-0.451	0.178	1.8	0.20	0.19	0.27
$BaBr_2$	5.476	0.695	-0.056	2.0	1.89	1.88	1.20

* Due to lack of density data, the density of pure water at 298.15 K was used as the density for these electrolyte solutions.

that while the GV-MSA model can accurately predict the mean ionic activity coefficients of the electrolyte solutions, it has an advantage over the BMCSL-MSA model in that it satisfies, also, the closed packed ordered limit [14]. To obtain the parameters of the models mentioned in Table 1, the experimental density data of the electrolyte solutions were used to convert the concentration scales. However, due to the lack of density data for a few electrolyte solutions, the density of pure water was used in the calculations. Going through the values for the parameters of Equation 25 for different cations, it can be inferred that

Table 2. The BMCSL-MSA and the Pitzer parameters for symmetric and asymmetric electrolytes at 298.15 K.

Pitzer Parameters				**BMCSL-MSA Parameters**			
Electrolyte	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	C_{MX}^{ϕ}	σ_{+0} (Å)	σ_{+1} (Å mol^{-1} L)	σ_{+2} (Å mol^{-2} L^{2})	m_{max}
LiCl	0.1987	0.0577	-0.0036	4.100	0.007	-0.006	19.2
LiBr	0.2219	0.0171	-0.0015	4.240	0.124	-0.014	20.0
LiI	0.1621	0.5747	0.0160	5.503	-0.706	0.189	3.0
NaCl	0.0757	0.2747	0.0014	3.547	-0.276	0.036	6.0
NaBr	0.1013	0.2673	-0.0002	3.769	-0.141	0.023	9.0
NaI	0.1277	0.2961	-0.0002	3.772	0.078	0.003	12.0
$NaNO_3$	-0.0105	0.2452	0.0036	3.857	-0.659	0.096	11.0
KCl	0.0461	0.2216	-0.0003	3.061	-0.371	0.053	5.0
KBr	0.0550	0.2353	-0.0014	3.196	-0.297	0.050	5.5
KI	0.0732	0.2655	-0.0040	3.268	-0.188	0.037	4.5
KOH	0.1668	0.1076	-0.0021	4.061	-0.018	-0.003	20.0
$KClO_3$	-0.1076	0.2724	0.0081	2.286	-2.534	0.925	0.7
$KBrO_3$	-0.0992	0.2146	-0.0398	2.635	-1.208	-1.664	0.5
RbCl	0.0450	0.1505	-0.0013	2.937	-0.070	0.031	7.8
RbBr	0.0391	0.1594	-0.0014	2.903	-0.087	0.058	5.0
CsBr	0.0249	0.0553	0.0006	2.360	0.215	0.072	5.0
CsI	0.0208	0.0587	-0.0027	2.112	0.299	0.011	6.0
HCl	0.2027	0.1682	-0.0037	4.527	-0.091	-0.001	20.0
Li_2SO_4	0.1377	0.6594	-0.0061	4.781	-0.848	0.194	3.0
Na_2SO_4	0.0149	0.5551	0.0054	4.101	-1.363	0.366	4.0
K_2SO_4	0.1529	0.0292	-0.0819	4.161	-2.050	1.042	0.7
Rb_2SO_4	0.0645	0.5066	-0.0039	4.681	-1.731	0.769	1.8
Cs_2SO_4	0.0941	0.5112	-0.0088	5.050	-1.649	0.899	1.8
$MgCl_2$	0.3462	1.1446	0.0058	5.983	-0.070	-0.013	5.0
$MgBr_2$	0.4234	1.2582	0.0045	6.665	-0.048	-0.009	5.0
$CaCl_2$	0.3129	1.0479	-0.0001	5.519	0.027	-0.022	6.0
$CaBr_2$	0.3396	1.2975	0.0102	6.196	0.007	0.048	6.0
$Ca(NO_3)_2$	0.1635	1.0838	-0.0065	5.964	-0.315	0.058	6.0
$BaCl_2$	0.2633	0.8968	-0.0215	5.418	-0.404	0.146	1.8
$BaBr_2$	0.3129	1.0492	-0.0003	5.447	0.723	-0.065	2.0

the hydrated diameter of a cation decreases as its concentration increases. This phenomenon is the so-called hydration of ions. The decreasing trend of the size parameters of the cations indicates that the number of the hydration water molecules decrease at higher concentrations of the cation. The dehydration of a cation with an increase in its concentration is better presented, according to the hydrated diameter, in comparison with the Pauling diameter, σ_P, by an effective hydration layer thickness, λ, according to the following relation:

$$\sigma = \sigma_P + \lambda. \tag{29}$$

Figure 3 shows the variation of λ with concentration for the sodium ion in aqueous solutions of NaCl. As shown in this figure, the hydration layers around the cations become thinner as the salt concentration

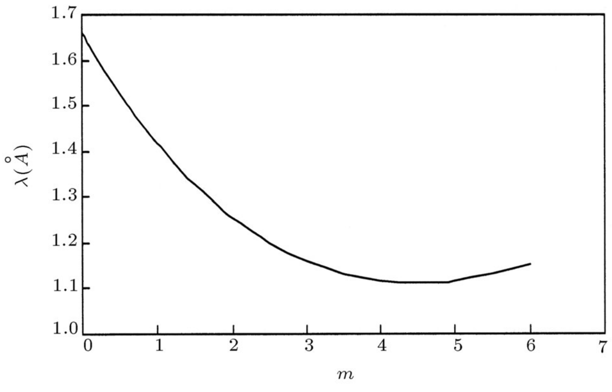

Figure 3. Variation of the hydration layer thickness for Na^+ in aqueous solution of NaCl as a function of molality.

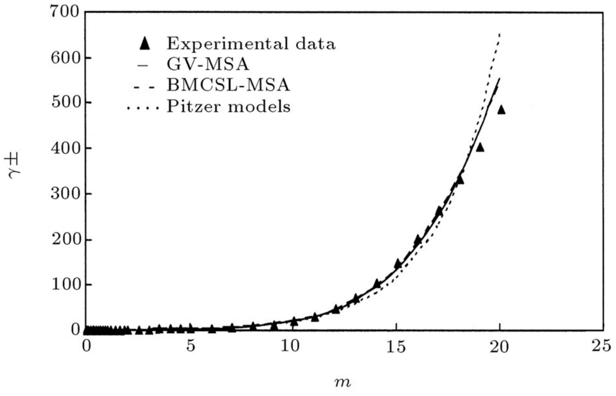

Figure 4. Correlation of the mean ionic activity coefficient of LiBr solution as a function of molality.

increases. It should be noted that an increasing trend for the hydration layer is observed at near saturation concentrations. Higher deviations of the results of the studied models from the experimental data near saturation concentrations plausibly justify such anomaly behavior.

Figure 4 shows the results of the correlation of the mean ionic activity coefficient of LiBr solution obtained from the models studied in this work. As seen from the figure, the GV-MSA and the BMCSL-MSA models can more accurately correlate the mean ionic activity coefficients of the electrolyte solutions at high electrolyte concentrations, in comparison with the Pitzer model.

The GV-MSA parameters for Equations 25 and 26 for different individual ions are represented in Table 3, along with the percent of average absolute relative deviation produced from the GV-MSA, the BMCSL-MSA and the Khoshkbarchi-Vera models, with respect to experimental data [27-30]. Different values for the parameters of the MSA-based models for anion and cation from those reported in Tables 1 and 2 were given for the individual ionic activity coefficients in the electrolyte solutions studied in this work. As observed

Table 3. The GV-MSA parameters for individual ions and the percent of average absolute relative percent deviation with respect to the experimental data of the activity coefficients calculated with the GV-MSA, the BMCSL-MSA and the Khoshkbarchi-Vera models.

Electrolyte	Ions	σ_0	σ_1	σ_2	GV-MSA AARD%	BMCSL-MSA AARD%	Khoshkbarchi-Vera AARD%
LiCl	Li^+	6.733	-0.606	0.075	0.33	0.34	1.00
	Cl^-	0.804	0.085	—	0.62	0.62	0.80
NaCl	Na^+	5.962	-0.723	0.082	2.45	2.40	9.00
	Cl^-	1.088	0.229	—	1.05	0.94	3.40
NaBr	Na^+	5.129	-0.182	0.024	1.68	1.68	7.70
	Br^-	2.136	0.083	—	1.40	1.42	4.30
KCl	K^+	2.278	-0.358	0.149	1.28	1.33	1.00
	Cl^-	4.468	-0.306	—	0.38	0.43	1.00
KBr	K^+	2.602	-2.161	0.495	1.17	6.08	1.00
	Br^-	4.913	0.308	—	2.71	2.02	2.00
$MgCl_2$	Mg^{2+}	9.493	-1.364	0.216	4.42	4.46	5.00
	Cl^-	0.498	0.341	—	0.62	0.63	1.40
$CaCl_2$	Ca^{2+}	8.375	-0.761	0.114	4.37	5.60	4.00
	Cl^-	0.997	0.176	—	1.14	1.35	1.70
$BaCl_2$	Ba^{2+}	6.956	0.678	-0.423	3.28	3.29	2.00
	Cl^-	1.704	-0.243	—	0.65	0.64	1.00

Table 4. The percent of average absolute relative deviation of the GV-MSA, the BMCSL-MSA and the Pitzer models with respect to experimental data of osmotic coefficients for symmetric and asymmetric single electrolyte solutions.

		AARD (%)		
Electrolyte	**m_{max}**	**GV-MSA**	**BMCSL-MSA**	**Pitzer**
LiCl	19.2	1.73	1.72	2.77
LiBr	20.0	1.85	1.87	3.03
NaCl	6.0	1.82	1.79	1.96
$NaNO_3$	11.0	2.62	4.09	3.88
KBr	5.5	1.94	1.96	4.66
KCl	5.0	2.07	2.07	2.12
KOH	20.0	1.49	1.49	1.61
RbCl	7.8	2.15	2.14	2.12
CsBr	5.0	2.48	2.48	2.40
HCl	20.0	1.29	1.33	1.38
Li_2SO_4	3.0	4.77	4.77	6.06
Na_2SO_4	4.0	5.27	5.27	7.46
Rb_2SO_4	1.8	6.33	6.30	6.97
$MgCl_2$	5.0	3.37	3.39	3.83
$Ca(NO_3)_2$	6.0	4.10	4.11	4.85
$BaCl_2$	1.8	5.02	5.03	5.26

from Table 3, while the Khoshkbarchi-Vera model fails to correlate accurately the experimental values for both cationic and anionic activity coefficients, the results obtained from the two MSA-based models are in good agreement with the experimental data.

The results obtained for the osmotic coefficient for some electrolytes were reported in Table 4, together with the percent of average absolute relative deviation of the GV-MSA, the BMCSL-MSA and the Pitzer models, with respect to the experimental data [22-24]. It can be seen that the results obtained from the MSA-based models are generally more accurate than those obtained from the Pitzer model.

CONCLUSION

The GV-MSA model was used to accurately correlate the experimental data of the individual and the mean ionic activity coefficients, as well as to calculate the osmotic coefficients of the symmetric and asymmetric electrolyte solutions studied in this work. In this study, the size parameters of the cation were considered to be concentration-dependent, using a simple polynomial expression in correlating the experimental data for the mean ionic activity coefficients. In the case of the individual ionic activity coefficients, both the cationic and the anionic diameters varied with concentration of electrolyte solutions. The size parameters for the ions were calculated by fitting the GV-MSA model to the experimental data of the mean ionic activity coefficients. In order to do a fair comparison between the results of the GV-MSA model and those of the BMCSL-MSA and the Pitzer models, the same minimization procedure and the same experimental data were employed to adjust the parameters of the above mentioned models. The results obtained for the MSA-based models suggest that the cation hydrates in aqueous solutions and their hydration numbers depend on the nature of the ion and its counter ions. It was found that the size parameters of the cation decrease with an increase in concentration. The results obtained from the rigorous GV-MSA model and simplified version of the GV-MSA (SGV-MSA) model show that the effect of the P_n term is insignificant on the performance of the GV-MSA model.

The osmotic coefficients were also calculated from the values of the mean ionic activity coefficient using the exact Gibbs-Duhem relation for the electrolyte solutions. It was shown that the GV-MSA model can correlate the experimental activity coefficient data and also calculate the osmotic coefficients with high accuracy.

NOMENCLATURE

A	Helmholtz free energy (erg mol^{-1})

B_n^*	reduced nth Virial coefficients
c	molarity (mol lit^{-1})
d	density (g cm^{-3})
D	dielectric constant
e	basic electric charge (esu)
k	Boltzmann constant (erg K^{-1})
m	molality (mol kg^{-1})
N_A	Avogadro's number
N	number of ionic species
NP	number of experimental data points
R	universal gas constant (erg mol^{-1} K^{-1})
T	absolute temperature (K)
Z	charge of ion, compressibility factor

Greek Letters

γ	activity coefficient
Γ	inverse shielding length (cm^{-1})
κ	Debye inverse length (cm^{-1})
λ	hydration layer thickness (cm)
η	packing fraction
ξ	packing fraction in the GV-MSA model
μ	chemical potential (erg mol^{-1})
ρ	number density
σ	ionic size parameter (cm)
ϕ	osmotic coefficient

Subscripts

i, j, k	component index
p	pure
$\circ$	pure solvent
$\pm$	mean ionic

Superscripts

c	molarity scale
m	molality scale
r	residual
S	solvent

Abbreviations

AARD	average absolute relative deviation
calc	calculated
elec	electrostatic
exp	experimental
hs	hard sphere
LR	Lewis-Randall
mix	mixture
MM	McMillan-Mayer

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