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G^{ex}-Model Using Local Area Fraction for Binary Electrolyte Systems

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The correlation and prediction of phase equilibria of electrolyte systems are essential in the design and operation of many industrial processes such as downstream processing in biotechnology, desalination, hydrometallurgy, etc. In this research, the local composition non-random two liquid-nonrandom factor (NRTL-NRF) model of Haghtalab and Vera was extended for uni-univalent aqueous electrolyte solutions. Based on the assumptions of the NRTL-NRF model, excess Gibbs free energy (g^{E}) functions were derived for binary electrolyte systems. In this work, the local area fraction was applied and the modified model of NRTL-NRF was developed with either an equal or unequal surface area of an anion to the surface area of a cation. The modified NRTL-NRF models consist of two contributions, one due to long-range forces represented by the Debye–Hückel theory, and the other due to short-range forces, represented by local area fractions of species through non-random factors. Each model contains only two adjustable parameters per electrolyte. In addition, the model with unequal surface area of ionic species gives better results in comparison with the second new model with equal surface area of ions. The results for the mean activity coefficients for aqueous solutions of uni-univalent electrolytes at 298.15 K showed that the present model is more accurate than the original NRTL-NRF model.

KEY WORDS: activity coefficient; anion; cation; excess Gibbs free energy; surface area fraction.

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1. INTRODUCTION

The correlation and prediction of the phase equilibria of electrolyte systems are essential problems in the design and operation of many separation processes in chemical engineering and other sciences and technologies; separation, concentration, and purification of proteins, cell organelles, and other biological products are just a few examples of cases for which a knowledge of the activity is needed for understanding of the phenomena. There are many models for estimation of the mean activity coefficient of electrolytes in aqueous solutions. The first group contribution models had four adjustable parameters such as the models of Cruz and Renon [1], and Jaretun and Aly [2]. In the model of Cruz and Renon, the free ions (cation and anion) were surrounded by solvent molecules only; in partially dissociated electrolytes, the ion pairs, if any, were taken into account as undissociated molecules and were surrounded by a solvent and other undissociated molecules.

Another group contribution model would be based on the local composition concept by means of NRTL or UNIQUAC. These types of physical models express the excess Gibbs free energy of the electrolyte systems as a contribution due to both long-range and short-range interactions. This group of models have two adjustable parameters such as the models of Chen et al. [3,4], Ball et al. [5], Sander et al. [6], Haghtalab and Vera [7,8], Haghtalab et al. [9], Narayanan and Ananth [10], and Jaretun and Aly [2,11] which have been used to predict the mean ionic activity of strong aqueous electrolyte solutions. Chen et al. and Haghtalab and Vera used the same assumption for distribution of ions around central species, but they implemented a different reference state. The reference state used in the model of Chen et al. is based on hypothetical pure ions, but the reference state which was proposed by Haghtalab and Vera is the random state of the cells. Moreover, in Haghtalab and Vera's model [7,8] named NRTL-NRF, the nonrandom factors show deviations of the local composition from the bulk composition. The random reference state is realistic, because the electroneutrality of the reference solutions has been considered along with a local composition approach to the bulk composition of species.

In this work, a new version of the local area fraction model was developed for aqueous binary electrolytes. We follow Haghtalab and Vera [7,8] with the assumption of the existence of three types of cells for binary electrolyte solutions and the assumption of either an equal or unequal surface area of an anion with the surface area of a cation. Excess Gibbs free energy functions and activity coefficients were derived on the basis of the assumptions of the NRTL-NRF model and the local area fraction of the species. Each of these models has two adjustable parameters and was applicable from the dilute region up to the saturation point. These parameters had been regressed by the Nelder-Mead optimization algorithm. Comparisons of results of the new models for binary systems with the original NRTL-NRF model and the models of Chen et al. and Jaretun show that the present model is more accurate.

2. NRTL-NRF MODEL BASED ON LOCAL AREA FRACTION

As a physical model, NRTL-NRF assumes that the excess Gibbs free energy of an aqueous electrolyte solution may be written as a sum of two contributions: one due to long-range interactions and the other due to short-range interactions. The Debye–Hückel expression is used to represent the contribution of long-range ion–ion interactions, while the local area fraction concept is employed to illustrate the short–range interactions. In this work, the local area fraction was applied and the NRTL-NRF was modified with the assumption of equality of the surface areas of the anion and cation. The molar excess Gibbs free energy is presented as follows:

$$\frac{g^{\mathrm{E}}}{RT} = \left(\frac{g^{\mathrm{E}}}{RT}\right)_{\mathrm{DH}} + \left(\frac{g^{\mathrm{E}}}{RT}\right)_{\mathrm{NRTL-NRF}} \tag{1}$$

By proper integration of the above equation, the activity coefficient of species i can be expressed as

$$\ln \gamma_i = (\ln \gamma_i)_{\mathrm{DH}} + (\ln \gamma_i)_{\mathrm{NRTL-NRF}} \quad (i = \mathrm{C, A, W}) \tag{2}$$

Following the work of Haghtalab and Vera [7,8], we assume the existence of three types of cells, depending on the central species, in the microstructure of an aqueous solution of a single electrolyte. Two types of cells are those with a cation or with an anion as the central species. For these cells, the like-ion repulsion leads to the assumption that the area fraction of a cation around a cation and of an anion around an anion is zero. Thus, only solvent molecules and counterion species surround a particular ion. The third type of cell has solvent central molecules with anions, cations, and solvent molecules in the surroundings. For a binary electrolyte system the excess Gibbs free energy for each central cell can be written as

$$G_i^{\mathrm{E}} = G_i - G_i^0 \tag{3}$$

where G_i and G_i^0 are the Gibbs free energies of the cell "i" in the nonrandom and reference states, respectively. Also, the Gibbs free energy of the cell in the nonrandom state can be written as

$$G_i = \sum_{\substack{j=1 \\ j\neq i \text{ for } i=1,2}}^{n} \theta'_{ji} G_{ji} \tag{4}$$

where θ'_{ji} is the effective local area fraction of species j and G_{ji} is the interaction energy between species i and j. The Gibbs free energy of the same cell in the reference state can be written as

$$G_i^0 = \sum_{\substack{j=1 \\ j\neq i \text{ for } i=1,2}}^{n} \theta'_j G_{ji} \tag{5}$$

where θ'_j is the bulk area fraction of species j. As one may see, we assume the random state as a reference state. The effective local area fraction is defined as

$$\theta'_{ji} = z_j \theta_{ji}\ (j = \text{ion}) \quad \text{and} \quad \theta'_{ji} = \theta_{ji}\ (j \neq \text{ion}) \tag{6}$$

where z is the charge number of an ion. In this study, the local area fraction is represented by means of nonrandom factors (NRF); thus, for i–j interactions, one can write

$$\theta'_{ji} = \theta'_j \Gamma_{ji} \tag{7}$$

Similarly,

$$\theta'_{ii} = \theta'_i \Gamma_{ii} \tag{8}$$

from which

$$\frac{\theta'_{ji}}{\theta'_{ii}} = \frac{\theta'_j}{\theta'_i} \frac{\Gamma_{ji}}{\Gamma_{ii}} \tag{9}$$

The nonrandom factors are evaluated using the Boltzmann factor as was proposed by Wilson [12],

$$\tau_{ji} = \frac{\Gamma_{ji}}{\Gamma_{ii}} \tag{10}$$

where

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{Z}\right); \quad a_{ji} = \frac{\Delta g_{ji}}{RT} \tag{11}$$

a_{ji} is the adjustable interaction parameter of the i–j pair, and Z is the coordination number.

The total excess Gibbs energy for a binary electrolyte system can be written as

$$G^{\mathrm{E}} = \frac{1}{2} Z \sum_{i=1}^{n} q_i N_i G_i^{\mathrm{E}} \tag{12}$$

where N_i and q_i are the number of species and the surface parameter of species "i", respectively. By substituting and combining Eqs. (3)–(5) and Eqs. (8)–(12), the molar excess Gibbs free energy is obtained as

$$g^{\mathrm{E}} = \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{\substack{j=1 \\ j \neq \text{solvent}}}^{n} q_i x_i \theta'_j \Gamma_{ji} \Delta g_{ji} \tag{13}$$

where

$$\Delta g_{ji} = g_{ji} - g_{ii} = \frac{1}{2} Z (G_{ji} - G_{ii}) N_{\mathrm{AV}} \tag{14}$$

By using the local electroneutrality assumption, which states that the distribution of cations and anions around a central molecule is such that the net local ionic charge is zero,

$$\underset{i,j \neq \text{Solvent}}{z_i \theta_{ij}} = \underset{i,j \neq \text{Solvent}}{z_j \theta_{ji}} \quad \text{or} \quad \theta'_{ij} = \theta'_{ji} \tag{15}$$

The surface area fraction of the ionic species is calculated as

$$\theta_i = \frac{x_i q_i}{\sum x_j q_j} \tag{16}$$

where $\theta'_i = z_i \theta_i$. Combining Eqs. (7), (15), and (16) and considering the expression for the overall electroneutrality of the solution $(Z_i \theta_i = Z_j \theta_j)$, for the first modification model based on the assumption of equal areas for the anion and cation, one finds

$$\Gamma_{\mathrm{CA}} = \Gamma_{\mathrm{AC}} = \Gamma_{\mathrm{E}} \tag{17}$$

$$\Delta g_{\mathrm{AC}} = \Delta g_{\mathrm{CA}} = \Delta g_{\mathrm{E}}; \quad \Delta g_{\mathrm{AW}} = \Delta g_{\mathrm{CW}} = \Delta g_{\mathrm{EW}} \tag{18}$$

Also, the second modification model based on the assumption of unequal areas of the anion and cation, one finds

$$q_A \Gamma_{AW} = q_C \Gamma_{CW}, \quad \Gamma_{CA} = \Gamma_E, \quad \Gamma_{CW} = \Gamma_{EW} \tag{19}$$

$$\Delta g_{AC} = \Delta g_{CA} = \Delta g_E; \quad \Delta g_{AW} = \Delta g_{CW} = \Delta g_{EW} \tag{20}$$

$$\Delta g_{AC} = \Delta g_E - ZRT \ln\left(\frac{q_C}{q_A}\right), \quad \Delta g_{AW} = \Delta g_{EW} - ZRT \ln\left(\frac{q_C}{q_A}\right) \tag{21}$$

For binary aqueous electrolytes solution, only two adjustable parameters are obtained as

$$a_E = \frac{g_E - g_{EW}}{RT} : \quad a_W = \frac{g_{EW} - g_{WW}}{RT} \tag{22}$$

Substituting Eqs. (17), (18), and (22) into Eq. (13) for the first model, one finds

$$\frac{g^E}{RT} = q_S\, x_S\, \theta'_E\, (\Gamma_E - 1)\, a_E - q_W\, x_W\, \theta'_W\, (\Gamma_{W-1})\, a_W \tag{23}$$

Substituting Eqs. (19)–(22) into Eq.(13), one finds

$$\frac{g^{ex}}{RT} = q_W x_W \theta'_W (1 - \Gamma_{WW})\, a_{EW} + q_S x_S \theta'_E \left(\Gamma_E - \frac{\nu q_A}{q_S}\right) a_E - \frac{Z q_W x_W \ln\left(\frac{q_C}{q_A}\right)}{2} \times \left(1 - \theta_W \Gamma_{WW} - \frac{2 q_A}{q_A + q_C}(1 - \theta_W)\right) - Z_E \theta_E q_C x_C \ln\left(\frac{q_C}{q_A}\right)\left(\Gamma_E - \frac{q_A}{q_C}\right) \tag{24}$$

where

$$q_S = \nu_1 q_1 + \nu_2 q_2 \tag{25}$$

We can write the local area balance for both ionic and nonionic central cells at nonrandom and random states as

$$\sum_{\substack{j=1 \\ j \neq i}}^{n} \theta'_{ji} = 1; \quad \sum_{j=1}^{n} \theta'_j = 1 \tag{26}$$

Using the above relations and expressing the local area fraction in terms of nonrandom factors,

$$\Gamma_{ij} = \frac{\tau_{ij}}{\sum_{i=1}^{n} \theta'_i \tau_{ij}} \tag{27}$$

So for a binary electrolyte system, one can obtain

$$\Gamma_{\mathrm{E}} = \frac{\tau_{\mathrm{E}}}{\theta'_{\mathrm{E}}\tau_{\mathrm{E}} + \theta'_{\mathrm{W}}}; \quad \tau_{\mathrm{E}} = \exp\left(-\frac{a_{\mathrm{E}}}{Z}\right) \tag{28}$$

$$\Gamma_{\mathrm{W}} = \frac{1}{\theta_{\mathrm{W}} + 2\theta_{\mathrm{E}}\tau_{\mathrm{W}}}; \quad \tau_{\mathrm{W}} = \exp\left(-\frac{a_{\mathrm{W}}}{Z}\right) \tag{29}$$

where a_{E} and a_{W} are the adjustable parameters for a binary electrolyte system. As discussed by Hala et al. [13], the mean ionic activity coefficient of an electrolyte in an aqueous solution can be obtained from the relation,

$$\nu \ln \gamma_{\pm} = \frac{\partial}{\partial n_{\mathrm{S}}}\left(\frac{n_t g^{\mathrm{E}}}{RT}\right)_{n_W} \tag{30}$$

It is necessary to normalize the contribution due to short-range interactions on the same basis as the contribution of long-range interactions to the activity coefficient, i.e., the Debye–Hückel model. Then, the unsymmetrical normalization is expressed as

$$\ln \gamma_{\pm}^{*} = \ln \gamma_{\pm} - \ln \gamma_{\pm}^{\infty} \tag{31}$$

By proper differentiation of Eq. (23) and using Eqs. (30) and (31), the mean ionic activity coefficient at infinite dilution for the first modification is obtained:

$$\nu \ln \gamma_{\pm}^{\infty} = -q_{\mathrm{S}} a_{\mathrm{EW}}\left(1 - \frac{2Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}}\right) \tag{32}$$

Similarly, by proper differentiation of Eq. (24) and using Eqs. (30) and (31), the mean ionic activity coefficient at infinite dilution for the second modification is obtained:

$$\begin{aligned} \nu \ln \gamma_{\pm}^{\infty} &= \frac{q_{\mathrm{S}}}{\nu}\left(\frac{2Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}} - 1\right)a_{\mathrm{EW}} - \frac{Zq_{\mathrm{S}}\ln\left(\frac{q_{\mathrm{C}}}{q_{\mathrm{A}}}\right)}{\upsilon} \\ &\quad \times \left(\frac{Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}} - \frac{q_{\mathrm{A}}}{q_{\mathrm{A}} + q_{\mathrm{C}}}\right) \end{aligned} \tag{33}$$

Finally, the equation for the mean activity coefficient in the unsymmetrical convention for the first modification is obtained as

$$\begin{aligned} \ln \gamma_{\pm}^{*} &= \frac{q_{\mathrm{S}}}{\nu}\theta'_{\mathrm{E}}a_{\mathrm{E}}\left\{(\Gamma_{\mathrm{E}} - 1)(1 + \theta'_{\mathrm{W}}) + \Gamma_{\mathrm{E}}^{2}\theta'_{\mathrm{E}}\theta'_{\mathrm{W}}\left(\frac{q_{\mathrm{S}}}{\beta_{\mathrm{E}}Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}} - 1\right)\right\} \\ &\quad + \frac{q_{\mathrm{S}}}{\nu}\theta'^{2}_{W}(\Gamma_{\mathrm{W}} - 1) - \frac{q_{\mathrm{S}}}{\nu}a_{\mathrm{EW}}\left(1 - \frac{2Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}}\right)(\Gamma_{\mathrm{W}}^{2}\theta_{\mathrm{W}}'^{3} - 1) \end{aligned} \tag{34}$$

And similarly, the equation for the mean activity coefficient in the unsymmetrical convention for the second modification is obtained as

$$\begin{aligned}\ln\gamma_{\pm}^{*} = {} & \frac{q_{\mathrm{S}}}{\nu}\theta'_{\mathrm{E}}a_{\mathrm{E}}\left\{\left(\Gamma_{\mathrm{E}}-\frac{\nu q_{\mathrm{A}}}{q_{\mathrm{S}}}\right)(1+\theta'_{\mathrm{W}})+\Gamma_{\mathrm{E}}^{2}\theta'_{\mathrm{E}}\theta'_{\mathrm{W}}\left(\frac{q_{\mathrm{S}}}{\beta_{\mathrm{E}}Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}}-1\right)\right\} \\ & +\frac{q_{\mathrm{S}}}{\nu}\theta'^{2}{}_{\mathrm{W}}(\Gamma_{\mathrm{W}}-1)\,a_{\mathrm{EW}}+\frac{q_{\mathrm{S}}}{\nu}\left(1-\theta'^{3}_{\mathrm{W}}\right)\left(1-\frac{2Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}}\right)a_{\mathrm{EW}}-Z\frac{q_{\mathrm{S}}}{\nu}Z_{\mathrm{E}} \\ & \times\ln\left(\frac{q_{\mathrm{C}}}{q_{\mathrm{A}}}\right)\theta'_{\mathrm{E}}\left\{(1+\theta'_{W})\left(\Gamma_{\mathrm{E}}-\frac{q_{\mathrm{A}}}{q_{\mathrm{C}}}\right)+\theta'_{\mathrm{E}}\theta'_{W}\Gamma_{\mathrm{E}}^{2}\left(\frac{q_{\mathrm{S}}}{\beta_{\mathrm{E}}Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}}-1\right)\right\} \\ & +Z\frac{q_{\mathrm{S}}}{\nu}\left(\frac{q_{\mathrm{C}}}{q_{\mathrm{A}}}\right)\left\{\frac{Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}}-\frac{q_{\mathrm{A}}}{q_{\mathrm{A}}+q_{\mathrm{C}}}\right\}-Z\theta'^{2}_{\mathrm{W}}\frac{q_{\mathrm{S}}}{2\nu}\ln\left(\frac{q_{\mathrm{C}}}{q_{\mathrm{A}}}\right) \\ & \times\left\{\Gamma_{\mathrm{W}}-\theta'_{\mathrm{W}}\Gamma_{\mathrm{W}}^{2}\left(1-\frac{2Z_{\mathrm{E}}\nu_{\mathrm{E}}q_{\mathrm{E}}\beta_{\mathrm{W}}}{q_{\mathrm{S}}}\right)-\frac{2q_{\mathrm{A}}}{q_{\mathrm{A}}+q_{\mathrm{C}}}\right\} \qquad (35)\end{aligned}$$

3. ELECTROSTATIC INTERACTIONS

The expression for long-range electrostatic interactions from Fowler and Guggenheim [14] is used to calculate γ_j^{LR}. For ionic species, the activity coefficient is calculated from

$$\ln\gamma_i^{\mathrm{LR}} = \frac{-z_i^2 A I^{\frac{1}{2}}}{(1+BI^{\frac{1}{2}})} \qquad (36)$$

where the subscript i stand for ionic species, z_j is the absolute charge number of ionic species j, and I is the ionic strength of the mixture, which can be obtained from the following equation:

$$I = \sum_{i=1}^{n} m_i z_i^2 \qquad (37)$$

Also, the experimental mean ionic activity coefficient is the molal mean ionic activity coefficient and it is calculated from the mole fraction mean ionic activity coefficient as follows:

$$\ln\gamma_{\pm} = \ln\gamma_{\pm m} + \ln\left(1+\frac{M_w \nu m}{1000}\right) \qquad (38)$$

4. RESULTS AND DISCUSSION

It is important to note that the Debye–Hückel constants are calculated from the physical properties of the solvent and fundamental data. Also, we used values of 1.2 and 1.174 for the Debye–Hückel constants B and A, respectively. A value of 8 for the coordination number Z was used for all binary electrolyte systems that gives minimum deviations for a majority of the electrolyte systems.

The optimization of the binary adjustable parameters in the representation of the experimental data was performed by the Nelder–Mead algorithm by minimization of the objective function [7]. So the binary parameters were obtained by minimizing the root-mean-square standard deviation as

$$\sigma_{\gamma_\pm} = \left[\frac{\sum \left(\ln \gamma_\pm^{\exp} - \ln \gamma_\pm^{\text{calc}} \right)}{N} \right]^{1/2} \tag{39}$$

where $\gamma^{\exp}$ and γ^{cal} are the experimental and calculated mole fraction mean activity coefficients, respectively, and N is the number of data points. For calculation of interaction parameters, the radii of the anion and cation in each salt are needed in the model reported by Marcus [15]. For calculation of surface area parameters, the equation of Bondi was used [16]. Nonrandom factors (NRF) which show the deviations of local surface area fractions from bulk surface area fractions are used in this model, and the random state of the species is considered as a reference state. In this work, the models developed with the assumption of either equal or unequal surface area of the anion with the surface area of the cation have been tested for uni-univalent electrolyte solutions. By fitting of the mean ionic activity coefficient for uni-univalent electrolytes, interaction parameters for both MNRTL-NRF models are shown in Table I. Results are represented by the standard average deviation between experimental and calculated quantities [7]. Table II shows the root-mean-square standard deviations for the present models, the original NRTL-NRF model, and the models of Chen and Jaretun. It should be noted that the parameters in the other models used in the comparisons were fitted to exactly the same data with the same objective function.

The details of both contributions, long-range and short-range forces, to the activity coefficients of NaCNS in an aqueous solution are shown in Fig. 1 for the MNRTL-NRF model with $q_A \neq q_C$. Also, the details of both contributions, long-range and short-range forces, to the activity coefficients of CsCl in an aqueous solution are shown in Fig. 2 for the MNRTL-NRF model with $q_A = q_C$. Some results for uni-univalent electrolytes up

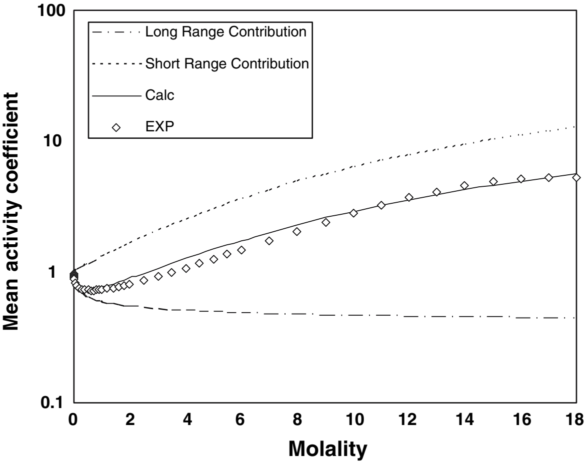

Fig. 1. Molality mean activity coefficient of aqueous solutions of NaCNS with long-range and short-range contributions at 298.15 K for the second modification of NRTL-NRF model ($\theta_A \neq \theta_C$).

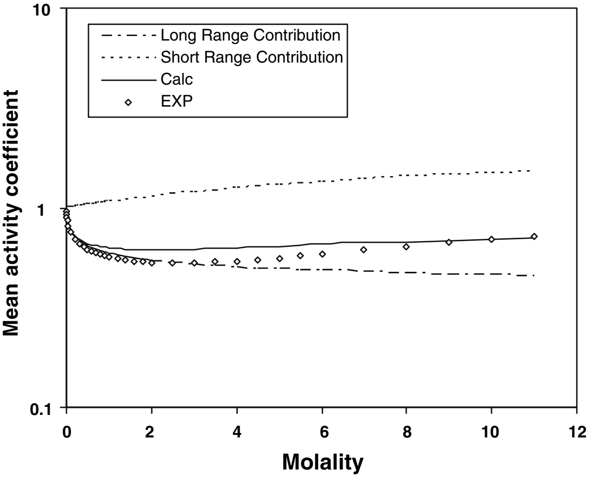

Fig. 2. Molality mean activity coefficient of aqueous solutions of CsCl with long-range and short-range contributions at 298.15 K for the first modification of NRTL-NRF model ($\theta_A = \theta_C$).

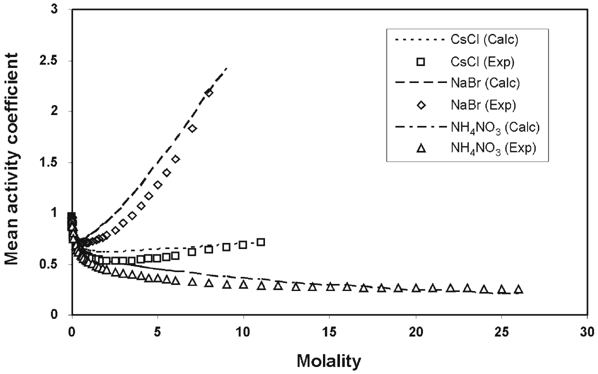

Fig. 3. Experimental [17] and calculated molality mean activity coefficients of various uni-univalent electrolytes for the first modification of the NRTL-NRF model ($\theta_A = \theta_C$).

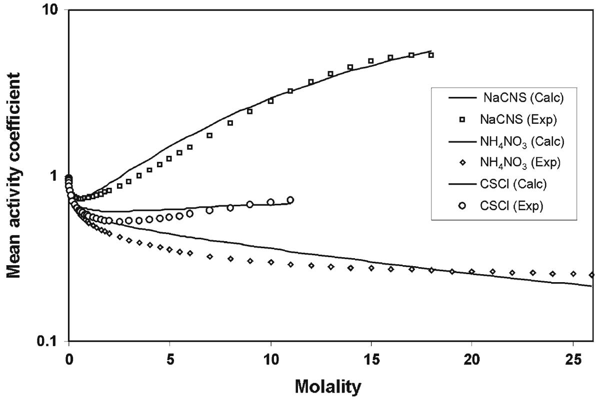

Fig. 4. Experimental [17] and calculated molality mean activity coefficients of various uni-univalent electrolytes for the second modification of NRTL-NRF model ($\theta_A \neq \theta_C$).

to molality 25 are shown for the MNRTL-NRF model in Figs. 3 and 4 for $q_A \neq q_C$ and $q_A = q_C$, respectively.

5. CONCLUSION

In this study new versions of the local area fraction models have been developed. Long-range interactions are accounted for by the Debye–Hückel theory. Local area fractions, expressed in terms of NRF, are used to represent the effect of short-range interactions in aqueous electrolyte

Table I. Interaction Parameters for Uni-univalent Electrolytes in the Two New MNRTL-NRF Models

Electrolyte	a_E [a]	a_{EW}	a_E [b]	a_{EW}
CsCl	−1.042	−2.574	−.042	−2.570
CsOH	−0.755	−3.992	−7.755	−3.992
KCl	−3.399	−4.655	−1.399	−4.655
KBr	−4.869	−5.530	−3.869	−5.530
KI	−9.352	−7.780	−8.352	−7.780
NaF	−6.382	5.405	−8.382	7.780
NaCl	−6.226	−8.940	−2.626	−8.940
NaBr	−3.869	−9.805	−1.869	−9.805
NaI	−13.646	−12.535	−10.646	−12.535
$NaClO_3$	−0.395	−7.909	−8.396	−5.909
$NaBrO_3$	−10.710	−7.955	−10.61	−4.155
NaH_2PO_4	−10.710	−8.340	−11.75	−8.45
NaCNS	−3.329	−10.599	−3.309	−9.899
$KClO_3$	−8.100	−3.350	−9.200	−3.350
$KBrO_3$	−9.005	−1.970	−9.805	−1.971
KH_2ASO_4	−9.315	−5.165	−9.314	−32.745
$TiClO_4$	−11.286	−6.799	−11.086	−6.899
NH_4ClO_4	−10.709	−7.520	−10.409	−7.522
NH_4NO_3	−7.157	−4.296	−6.407	−4.266
CsBr	0.045	−1.405	2.045	−0.409
CsF	3.261	−4.006	6.261	−3.006
$HClO_4$	100.200	−12.700	213.500	−14.580
KNO_3	6.450	−18.300	9.225	−2.295
KF	−10.897	24.515	−10.957	24.605
$NaClO_4$	−4.150	2.675	−15.150	2.655
$NaNO_3$	−4.051	1.095	−9.151	1.095

[a] First modification of the NRTL-NRF Model ($\theta_A = \theta_C$).
[b] Second modification of the NRTL-NRF Model($\theta_A \neq \theta_C$).

solutions. Each of the two models contains only two adjustable parameters per electrolyte. From the results of uni-univalent electrolyte solutions, it is clear that results for the modification of the model of NRTL-NRF are more accurate than of the original NRTL-NRF model. Also, the modified model of NRTL-NRF, based on the assumption of unequal surface areas of the anion and the cation, gives more accurate results than the modification model of the NRTL-NRF based on the assumption of equal surface areas of the anion and cation. The model is able to predict the mean ionic activity coefficients of salts beyond the traditional molality of 6 that has been the limit used by most investigations.

Table II. Root-Mean-Square Standard Deviations for the MNRTL-NRF Models, NRTL-NRF Model, and Other Models

Electrolyte	Chen et al. Model [4] $\sigma\gamma^*_\pm \times 10^5$	Jaretun/Aly Model [2] $\sigma\gamma^*_\pm \times 10^5$	NRTL-NRF [5] $\sigma\gamma^*_\pm \times 10^5$	MNRTL-NRF[a] $\sigma\gamma^*_\pm \times 10^5$	MNRTL-NRF[b] $\sigma\gamma^*_\pm \times 10^5$
CsCl	62	41	13	9	8
CsOH	74	9	12	3	2
KCl	28	8	21	4	3
KBr	44	6	14	6	4
KI	37	6	5	6	3
NaF	10	11	2	1	1
NaCl	159	6	11	9	7
NaBr	340	11	61	15	13
NaI	937	43	84	66	42
$NaClO_3$	39	5	5	3	1
$NaBrO_3$	9	7	4	4	2
NaH_2PO_4	14	13	3	7	6
NaCNS	673	419	39	44	22
$KClO_3$	11	9	2	1	1
$KBrO_3$	10	11	1	1	1
KH_2ASO_4	13	5	4	1	1
$TiClO_4$	22	5	1	1	1
NH_4ClO_4	92	8	7	5	3
NH_4NO_3	131	39	10	10	8
CsBr	53	26	5	5	4
CsF	67	17	7	9	1
$HClO_4$	5274	44	26	69	19
KNO_3	68	8	4	4	3
KF	1021	108	6	4	3
$NaClO_4$	327	45	9	4	3
$NaNO_3$	535	199	72	18	16

[a] First modification of the NRTL-NRF Model ($\theta_A = \theta_C$).
[b] Second modification of the NRTL-NRF Model($\theta_A \neq \theta_C$).

LIST OF SYMBOLS

a	Debye–Hückel constant
b	Debye–Hückel constant
a_E	electrolyte interaction energy parameter
a_{EW}	solvent interaction energy parameter
g^E	molar excess Gibbs energy
I	ionic strength
N	number of data points
R	gas constant

Greek Letters

γ	activity coefficient for component i
Γ	nonrandom factor
θ_i	surface area fraction of species i
θ'_i	effective surface area fraction of species i
θ'_{ij}	effective local surface area fraction of species i
τ_{ij}	binary interaction energy parameter
ν	stoichiometric number of electrolyte, $= Z_A + Z_C$
σ	mean standard deviation
θ'	effective surface area fraction of species i
Z	coordination number
M_W	molar mass of solvent
q	surface parameter of molecule
T	absolute temperature

Superscripts

cal	calculated
exp	experimental
LR	long range
$*$	unsymmetrical convention
∞	infinite dilution
0	reference state
E	excess

Subscripts

A	anion
C	cation
S	salt
W	solvent
$\pm$	mean ionic
i, j, l	any species

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