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Electrolyte-UNIQUAC-NRF model for the correlation of the mean activity coefficient of electrolyte solutions

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ABSTRACT

The new electrolyte-UNIQUAC-NRF excess Gibbs function is obtained for calculation of the activity coefficient of the binary electrolyte solutions. The excess Gibbs energy of the model consists of the Pitzer–Debye–Hückel equation, describing the long-range electrostatic contribution and the electrolyte-UNIQUAC-NRF model to account for the short-range contributions. With two adjustable parameters per electrolyte, the new model is applied to correlation of the mean activity coefficients of more than 130 binary aqueous electrolyte solutions at 25 °C. Also the binary parameters, obtaining from regression of mean activity data, are used for prediction of osmotic coefficient data for the same electrolytes. The results are compared with various local composition models such as the electrolyte-NRTL, electrolyte NRF-Wilson, electrolyte-NRTL-NRF, N-Wilson-NRF models. The comparison of the results with experiment demonstrates that the new model can correlate the experimental activity coefficient data and predict the osmotic coefficient data of binary electrolytes accurately.

1. Introduction

Electrolyte systems represent an important part in chemical, gas and petroleum industries such as natural gas treatment, extractive distillation, crystallization, desalination of water, hydrometallurgy, etc. [1,2]. The thermodynamics of electrolyte are used in the environmental protection industries and computation of liquid–liquid equilibria in aqueous two-phase systems for extraction of biomolecules in downstream processing in biotechnology [1]. Thus, the accurate representation of thermodynamic properties of electrolyte solutions is vital in design of several industrial processes. Calculation activity coefficient of salts, bases and acids in aqueous and nonaqueous solutions are based on Gibbs energy functions that are usually obtained from two-liquid theory using local composition concept. In the last decades many correlations have been developed to represent the nonideality of electrolyte solutions and for accurate calculations of activity coefficient of ionic species [1]. One class of models, which widely used in chemical industries, is the local composition models. These types of models are based on two terms of the long-range, electrostatic interactions, and the short-range interactions. The long-range contribution of activity coefficient is based on the electrostatic theory of Poisson which results the brilliant equation of Debye–Hückel or Pitzer–Debye–Hückel equation [2,3]. During recent decays, for the short-range interaction variety of the local composition excess Gibbs functions have been proposed for electrolyte and nonelectrolyte systems. The different excess Gibbs functions have been developed for molecular systems which have been successfully used in calculation of activity coefficient of nonelectrolyte systems [1]. These functions are the various versions of two-liquid theories such as Wilson, NRTL, UNIQUAC and UNIQUAC-NRF that are based on the Wilson local composition expression [4–7]. The two-liquid theory was used to develop the excess Gibbs function for binary single-electrolyte systems such as Cruz and Renon [8], Chen et al. [9,10], Haghtalab and Vera [11], Jaretun and Aly [12], Sadeghi [13], Haghtalab and Mazloumi [14]. Dissolution of electrolytes in a solvent dissociates into ionic or true species which with their physico-chemical behavior in the solution demonstrate different characteristic from original electrolyte. So, in developing the excess Gibbs functions, those models that used the pure ionic species as a reference state are not realistic such as electrolyte-NRTL and Cruz and Renon models [8–10]. Moreover, the pure ion reference state does not satisfy the electroneutrality principle. In the models such as the electrolyte-NRTL-NRF, the electrolyte-Wilson-NRF and the N-Wilson-NRF models [11,13,14], using the random state as a reference state, show the realistic behavior of ions in vanishing of local composition. In construction of an excess Gibbs function for electrolyte systems, two general approaches were applied. In the first method, the molecular local composition models were directly used for the electrolyte mixtures without changing the form of the excess Gibbs functions. At the other method, the configuration of the local cells was modified so that the new excess Gibbs functions were obtained for electrolyte solutions. Sander et al. [15], Macedo et al. [16] and Rasmussen [17] applied the original UNIQUAC equation to

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correlation of the mean activity coefficient of electrolyte solutions. Using ion pair assumption, Haghtalab and Mazloumi [14] developed a nonelectrolyte-local composition model for correlation of the activity coefficient data of electrolyte solutions that results accurate correlation of the mean activity coefficient of many binary electrolyte systems from dilute solution up to the saturation point of the solution. As mentioned, in the second class of models, based on two assumptions of the "like-ion repulsion" and "electroneutrality of solvent cell", the Wilson local composition expression was applied for ionic and molecular species, so that the electrolyte excess Gibbs functions were constructed by using the different versions of two-liquid theory [9–13].

In most electrolyte-local composition models such as electrolyte-NRTL [9], Electrolyte-NRTL-NRF [11] and the similar models the two adjustable energy parameters were used, however, in extended UNIQUAC [17,18] models the structural parameters of ionic species such as area and volume parameters of ions are used with binary interaction parameters as adjustable variables. So in UNIQUAC model, the four adjustable parameters per binary electrolyte system were used. As a summary, one may conclude, so far the developed local composition models used both molecular and electrolyte versions of Wilson [13,14], NRTL and UNIQUAC [9,17,18], nevertheless, the UNIQUAC-NRF [7] model has not been developed to correlation of binary electrolyte systems yet.

At this work, following approach of Haghtalab and Asadollahi [7], the electrolyte-UNIQUAC-NRF model is developed for the binary electrolyte solutions. In applying the model, the random state of ions is assumed as the reference state and the structural parameters of ions, volume and area, are estimated using van der Waals area and volume of ions. In contrast to electrolyte-UNIQUAC model [18] which used four adjustable parameters, only two energy parameters per electrolyte were used as the adjustable variables.

2. Electrolyte-UNIQUAC-NRF model

Following the general approach of the electrolyte-local composition models, the excess Gibbs energy of a binary electrolyte solution includes the contribution of two terms as:

$$g^{ex} = (g^{ex})_{\mathrm{PDH}} + (g^{ex})_{\mathrm{E\text{-}UNIQUAC\text{-}NRF}} \tag{1}$$

where the first term denotes the long-range contribution which is presented by the Pitzer–Debye–Hückel [3] and the second term denotes the contribution of the short-range interaction that is expressed by electrolyte-UNIQUAC-NRF model.

The short-range effects are originated by molecule–molecule, molecule–ion and ion–ion interactions. So at this work, following Haghtalab and Vera [11], for configuration of the species we assume the existence of three types of central cells. Two types of cells are those with a cation or anion as central species. For cation and anion cells the assumption of like ion repulsion leads to the local mole fraction of cation around cation and anion around anion vanishes. The third type of cell is the solvent molecules in the center of the cell and all the ionic and molecular species in surrounding. Following approach of the UNIQUAC-NRF model [7], one can express the excess internal energy for the each central cell as:

$$U_i^E = U_i - U_i^0 \quad i = C, A, W \tag{2}$$

Based on the like ion repulsion assumption, the effective local area fractions of like ions in ionic central cells are vanished, i.e. θ'_{CC}, $\theta'_{AA} = 0$. So, the internal energy of the cells are expressed in terms of the potential energies and the local area fractions as:

$$U_A = \theta'_{CA}U_{CA} + \theta'_{WA}U_{WA} \tag{3a}$$

$$U_C = \theta'_{AC}U_{AC} + \theta'_{WC}U_{WC} \tag{3b}$$

$$U_W = \theta'_{CW}U_{CW} + \theta'_{AW}U_{AW} + \theta'_{WW}U_{WW} \tag{3c}$$

Following the approach of Haghtalab and Vera [11], the energies of the reference cells in the random state are expressed as:

$$U_A^0 = \theta'_C U_{CA} + \theta'_W U_{WA} \tag{4a}$$

$$U_C^0 = \theta'_A U_{AC} + \theta'_W U_{WC} \tag{4b}$$

$$U_W^0 = \theta'_C U_{CW} + \theta'_A U_{AW} + \theta'_W U_{WW} \tag{4c}$$

By combining Eqs. (2)–(4), one can obtain the configurational excess Gibbs energy of the cells as:

$$U_A^E = (\theta'_{CA} - \theta'_C)(U_{CA} - U_{WA}) \tag{5a}$$

$$U_C^E = (\theta'_{AC} - \theta'_A)(U_{AC} - U_{WC}) \tag{5b}$$

$$U_W^E = (\theta'_{AW} - \theta'_A)U_{AW} + (\theta'_{CW} - \theta'_C)U_{CW} + (\theta'_{WW} - \theta'_W)U_{WW} \tag{5c}$$

After dissolution of m moles of a single electrolyte in a solvent with complete dissociation into N_A of anions and N_C of cations, the total excess internal energy of the mixture will be written as:

$$U^E = \frac{1}{2}zq_A N_A U_A^E + \frac{1}{2}zq_C N_C U_C^E + \frac{1}{2}zq_W N_W U_W^E \tag{6}$$

where "z" is the coordination number and usually set to 10.

By substitution of Eq. (5) into Eq. (6), the molar excess internal energy of the binary system is obtained as:

$$\begin{aligned} u^E &= q_A x_A\, \Delta u_{CA}(\theta'_{CA} - \theta'_C) + q_C x_C\ \Delta u_{AC}(\theta'_{AC} - \theta'_A) \\ &\quad + q_W x_W\ \Delta u_{EW}[(\theta'_{AW} - \theta'_A) + (\theta'_{CW} - \theta'_C)] \end{aligned} \tag{7}$$

where

$$\Delta u_{CA} = \frac{1}{2}z(U_{CA} - U_{WA})N_A \tag{8a}$$

$$\Delta u_{AC} = \frac{1}{2}z(U_{AC} - U_{WC})N_A \tag{8b}$$

$$\Delta u_{EW} = \frac{1}{2}z(U_{AW} - U_{WW})N_A = \frac{1}{2}z(U_{CW} - U_{WW})N_A \tag{8c}$$

Following the UNIQUACL-NRF model [7], the Wilson local area composition expression is written as:

$$\frac{\theta'_{ij}}{\theta'_{\ell j}} = \frac{\theta'_i}{\theta'_\ell}\tau_{ij,\ell j} \tag{9}$$

where

$$\tau_{ij,\ell j} = \frac{\Gamma_{ij}}{\Gamma_{\ell j}} = \exp\left[\frac{-(1/2)z(U_{ij} - U_{\ell j})}{KT}\right] = \exp\left(-\frac{a_{ij}}{T}\right) \tag{10}$$

where the effective local area fraction is defined as:

$$\theta'_{ij} = \theta'_i \Gamma_{ij} \tag{11}$$

The parameter "Γ", the nonrandom factor, is used for deviating of local composition from bulk composition. To show the effect of charge of ions on nonideality of electrolyte solutions, one can define the effective area fraction as:

$$\theta'_i = \frac{X_i q_i}{\sum_j X_j q_j} \tag{12}$$

where q_j is surface parameter of species j and X_i is the effective mole fraction that is presented by $X_i = C_i x_i$. $C_i = Z_i$ for ion "i" and $C_i = 1$ for water. The mole fractions of cation and anion are defined, respectively, as

$$x_A = \nu_A x_S \quad \text{and} \quad x_C = \nu_C x_S \tag{13}$$

Following Stockes and Robinson [19], the mole fraction of the electrolyte is defined as:

$$x_S = \frac{m}{\nu m + 1000/18.02} \tag{14}$$