



Generalized Electrolyte-UNIQUAC-NRF model for calculation of solubility and vapor pressure of multicomponent electrolytes solutions

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ABSTRACT

The Electrolyte-UNIQUAC-NRF model proposed by Haghtalab and Peyvandi, Fluid Phase Equilib., 281, 2009 is modified and extended to represent the excess Gibbs energy function of multicomponent electrolyte solutions. Using the experimental mean activity coefficient of aqueous binary electrolyte systems in the extensive domain of temperature and molality, the adjustable temperature dependent parameters are obtained for the several binary electrolyte systems. Furthermore, the osmotic coefficient and vapor pressure of some binary systems are predicted at the wide range of temperature and molality using the adjustable parameters. Having the binary interaction parameters, the solubility of electrolytes in ternary aqueous electrolyte solutions are predicted at 298 K and the higher temperatures so that the phase diagram of the salt solubility are obtained for the several ternary aqueous-salt systems. The results of the solubility, osmotic coefficient and vapor pressure for the electrolyte systems demonstrate that the generalized Electrolyte-UNIQUAC-NRF model can be successfully applied for prediction of the thermodynamic properties of multicomponent electrolyte systems with very good accuracy.

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1. Introduction

Electrolyte systems represent an important role in chemical, gas and petroleum industries such as natural gas treatment, extractive distillation, crystallization, desalination of water, hydrometallurgy, enhanced oil recovery, etc [1]. In the oil production at petroleum industries, particularly in secondary oil recovery by water injection, several mineral scales are formed in pores of the reservoir rocks and at the metal surfaces of the separators and heat exchangers. In these types of systems, aqueous solutions of multi-electrolyte accompanying dissolved ions are encountered. Calculation of the solubility of salts in these systems is very significant in that it allows one to predict scaling tendencies and amount of electrolytes in produced water in the oil process industry. Moreover, estimation of salt solubility in brines is needed in the design of hydrometallurgy, water desalination, crystallization and the other chemical processes. Thus, accurate representation of thermodynamic properties of electrolyte solutions is vital in the design of several industrial processes [2]. The Pitzer ion interaction model has been widely applied in calculation of thermodynamic properties and solubility of electrolytes in natural water and aqueous multicomponent systems [3]. However, the tertiary interaction parameters of Pitzer [4] activity coefficient model are not available for some multicomponent systems in the literature. It is very important that the interaction parameters for a multicomponent

system would be accessible from the binary parameters of its constituent systems and no higher order parameters would be required.

Consequently, using two-liquid theory, the local composition Gibbs energy functions have been developed so far that allows one to calculate the activity coefficient of electrolyte for prediction of the salt solubility in electrolyte solutions. In the last decades, the two-liquid theory have been widely used to develop the excess Gibbs function for binary single electrolyte systems such as Cruz [5] and Renon [6], Chen et al. [7,8], Haghtalab and Vera [9], Jaretun and Aly [10], Messnaoui and Ouiazane [11], Sadeghi [12], Haghtalab and Mazloumi [13], Haghtalab and Peyvandi [14]. In the most electrolyte-local composition models such as E-NRTL [7], E-NRTL-NRF [9] and the similar models, the two adjustable energy parameters were used for a binary electrolyte solution. Since the binary interaction parameters could be practical to prediction of the properties of multicomponent systems, the demand for accurate electrolyte models that is extendable to multicomponent systems is higher than ever.

Chen et al. developed the generalized E-NRTL model [8] to represent the excess Gibbs energy of aqueous multicomponent electrolyte systems. In this model, the interaction parameters of the solvent-salt and salt-solvent can be obtained by correlation of the activity coefficient data of binary systems. Using suitable mixing rule and the binary parameters allows one to predict the solubility of salts for multicomponent systems. Moreover, the salt-salt parameters in the generalized E-NRTL model can be attained by fitting the experimental solubility data of multicomponent system.

Jaretun et al. [15] proposed a new local composition model for electrolyte solutions and extended to multicomponent systems. This

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model was based on modification both the E-NRTL [8] and E-NRTL-NRF models [9]. Similar to the other local composition models, using the binary interaction parameters and the mixing rule, the activity coefficient of electrolytes were calculated for the multicomponent mixture [15]. Moreover, for systems with common ion, the interaction energy among all kinds of ions with the molecular solvent was assumed to have the same value so that using this assumption, the activity and osmotic coefficients of twenty two binary aqueous electrolyte systems were simultaneously correlated and the salt–solvent parameters were calculated [15].

Messnaoui et al. [11] developed a modified E-UNIQUAC model to describe the behavior of the single and multicomponent electrolyte systems. The assumptions proposed by Chen et al. [8] were used in their work to reduce the number of the adjustable parameters involving in the residual contribution of the UNIQUAC model. However, the structural parameters of the ionic species such as the area and volume parameters of ions were adjusted together with the binary interaction parameters. In this model, by introducing a mixing rule, the molecule–ion interaction parameters were expressed in terms of the ion–solvent binary parameters.

Haghtalab and Peyvandi [14] developed the E-UNIQUAC-NRF model to correlation of the mean activity coefficient of the binary electrolyte systems. In the development of the model, the random state of ions was assumed as the reference state and the structural parameters of ions, volume and area, were estimated using van der Waals area and volume of ions [16] using the ionic radii that are obtained from Yizhak Marcus [17]. In contrast to E-UNIQUAC model developed by Messnaoui [11], which used four adjustable parameters, only two energy parameters per electrolyte were used as the adjustable variables so that the results of the model is in very good agreement with the experiment.

Although the E-UNIQUAC-NRF model [14] has been precisely used for correlation of the experimental data of the activity coefficient and osmotic coefficient for the binary aqueous electrolyte solutions at 298.15 K, but to have better prediction of the solubility of salts for ternary systems, the E-UNIQUAC-NRF model [14] is refined by minor changes in the casting of the equations. This leads to the consistency and accuracy of the model for the binary aqueous electrolyte solutions so that the model can be readily extendable to multi-electrolyte solutions. Thus, the main objective of this study is extension of the E-UNIQUAC-NRF model to represent the excess Gibbs energy of aqueous multicomponent electrolyte systems. In this approach, the temperature dependent binary parameters are correlated by the experimental data of mean activity coefficient at a wide range of temperature and salt concentration (up to the saturation point) for the binary solutions. These parameters are used in prediction of the osmotic coefficient and vapor pressure of the binary systems at 298 K and the higher temperatures. Moreover, the generalized model can accurately predict the solubility of the salts in the ternary aqueous electrolyte systems by using only the binary parameters without using any more fitting parameters for the ternary systems and applying any mixing rules. Thus, the estimation of the solubility in the ternary solutions is directly attainable from the binary adjustable parameters so that lacking of mixing rule for multicomponent mixtures is the advantage of the present work. Finally, this new model is used for prediction of the vapor pressure and osmotic coefficient of the electrolyte systems at 298 K and the higher temperatures.

2. Electrolyte-UNIQUAC-NRF activity coefficient 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

$$g^{ex,*} = (g^{ex})_{PDH} + (g^{ex,*})_{E-UNIQUAC-NRF} \quad (1)$$

where the first term denotes the long-range contribution which is presented by the Pitzer–Debye–Hückel [4] and the second term is used for the contribution of the short-range interaction that is expressed by the E-UNIQUAC-NRF model. By proper differentiation of the short-range excess Gibbs function and using the Pitzer–Debye–Hückel equation [4], the activity coefficient of ionic or molecular species for an electrolyte system can be written as

$$\ln \gamma_i = (\ln \gamma_i)_{PDH} + (\ln \gamma_i)_c + (\ln \gamma_i)_r; \quad i = A, C, W \quad (2)$$

where the Pitzer–Debye–Hückel equation [7] for ionic species is presented as

$$(\ln \gamma_i)_{PDH} = -A_\phi \left(\frac{1000}{M_w} \right)^{0.5} \left(\frac{2z_i^2}{\rho} \ln(1 + \rho I_x^{1/2}) + \frac{z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right) \quad (3)$$

and using Gibbs–Duhem equation, the long-range activity coefficient of water is obtained as

$$\begin{aligned} (\ln \gamma_w)_{PDH} \\ = -\frac{1}{x_w} \left[\left(\sum_k x_k \right) \left(\frac{1000}{M_w} \right)^{0.5} \frac{4A_\phi I_x}{\rho} \ln(1 + \rho I_x^{1/2}) + \sum_{i \neq W} x_i (\ln \gamma_i)_{PDH} \right] \end{aligned} \quad (4)$$

where A_ϕ and ρ are the Debye–Hückel parameters. M_w is the molecular weight of solvent and I_x are the mole fraction ionic strength that is defined as

$$I_x = \frac{1}{2} \sum_i x_i z_i^2 \quad (5)$$

2.1. Modified Electrolyte-UNIQUAC-NRF model

Following the UNIQUAC-NRF model [18], to obtain the local area fraction, the Wilson local area composition expression is written as

$$\frac{\theta'_{ij}}{\theta'_{ij}} = \frac{\theta'_i}{\theta'_\ell} \tau_{ij,\ell} \quad (6)$$

where Boltzmann factor, $\tau_{ij,\ell}$ is defined as

$$\tau_{ij,\ell} = \frac{\Gamma_{ij}}{\Gamma_{lj}} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) = \exp(-\lambda_{ij}) \quad (7)$$

where Γ_{ij} is the nonrandom factor which presents deviation of the area local composition from bulk area fraction. Thus, one can write as

$$\theta'_{ij} = \theta'_i \Gamma_{ij} \quad (8)$$

where the effective area fraction is obtained as

$$\theta'_i = \frac{X_i q_i}{\sum_j X_j q_j} \quad (9)$$

where q and X represent the surface parameter and the effective mole fraction, respectively, so that the effective mole fraction of species i is presented by $X_i = C_i x_i$, where $C_i = Z_i$ for ions and $C_i = 1$ for water. The mole fractions of cation and anion are expressed, respectively, as

$$x_A = \nu_A x_5 \quad \& \quad x_C = \nu_C x_5 \quad (10)$$

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