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A nonelectrolyte local composition model and its application in the correlation of the mean activity coefficient of aqueous electrolyte solutions

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ABSTRACT

The local composition models have been widely used for the correlation of activity coefficient of nonelectrolyte and electrolyte solutions. A new equation for the excess Gibbs energy function is developed based on the local composition expression of Wilson and the random reference state. This new function, the nonelectrolyte Wilson nonrandom factor (N-Wilson-NRF) model, is presented in the form of a molecular framework so that it can be used for both nonelectrolyte and electrolyte solutions. Without any particular assumptions for ionic solutions, the new function is used to described the short-range contribution of the excess Gibbs energy of electrolyte solutions. The long-range contribution is represented by Pitzer–Debye–Hückel model. With two adjustable parameters per electrolyte, the new model is applied to correlate the mean activity coefficients of more than 150 binary aqueous electrolyte solutions at 25 °C. The results are compared with various local composition models such as the electrolyte-NRTL, electrolyte NRF-Wilson and electrolyte-NRTL-NRF models. The comparison of the results with experiment demonstrates that the new model can correlate the experimental data accurately. Moreover, the model shows high precision of predictability for the osmotic coefficient of binary electrolyte solutions.

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1. Introduction

Accurate representation of thermodynamic properties of electrolyte solutions is vital in design of several industrial processes such as natural gas treatment, extractive distillation, crystallization, desalination of water, hydrometallurgy, etc. Thermodynamic modeling of electrolyte solutions can be carried out by two different general approaches [1,2]: First the models based on the excess Gibbs energy that may be categorized into the semiempirical local composition models [1] and the models which are based on the extension of Debye–Hückel theory. In these class of the models such as the Pitzer ionic interaction and hydration models [1] is taken into account the physical interaction or chemical reactions between ionic and molecular species. In these semiempirical models the molar excess Gibbs energy is the sum of two contributions, one arising from long-range electrostatic forces (which are represented by the Debye–Hückel theory or its extension) and the other from short-range forces which are expressed by local composition models. The second group of models is those based on residual Helmholtz free energy [3,4]. While all excess Gibbs energy functions are semi-empirical, the residual Helmholtz energy models have been developed by fundamentals. The excess Gibbs energy models are well established and are applicable in many industrial processes.

In the local composition models, the short-range physical interaction are described by different versions of Wilson local composition expression. Some of the local composition models are limited to electrolyte molality smaller than six of electrolyte such as the Cruz and Renon [5], Electrolyte-NRTL [6], Electrolyte-Wilson [7], Electrolyte-NRF-Wilson models [8]. Moreover, there are some local composition models which are applicable over the whole range of concentration up to the saturation point of the electrolyte such as the Electrolyte-NRTL-NRF [9], Liu et al. [10] and Jaretun and Aly [11] models.

In these local compositions models, assumptions of speciation of ions and the specific assumptions such as "the ion repulsion of ions around an ionic central cell" and the "electroneutrality" around a solvent central cell were used [6–9]. However in this work the electrolyte solution is treated as mixture of undissociated ion pairs and solvent molecules. Moeover, although the Electrolyte-NRTL [6] model was extended to multicomponent electrolyte mixtures, the extension of the other electrolyte local composition models to multicomponents electrolyte mixture isn't simple and straightforward. So, the present molecular approach may simplify the modeling of electrolyte systems for binary and multicomponents systems. In this work, based on the local composition concept, we developed a new version of local composition that is easily applicable to both

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