# Electrolyte Nonrandom Two-Liquid Activity Coefficient Model with Association Theory

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Pitzer model and electrolyte nonrandom two-liquid model (eNRTL) are the two most-used models for calculating the activity coefficient for electrolyte solutions. The eNRTL model improved over the Pitzer model and is applicable to the entire concentration range from pure salt to infinite dilution without ternary and higher order parameters. The eNRTL has shown a good representation for single-salt, single solvent, mixed-salt, and mixed-solvent systems. However, the modeling results are less satisfactorily at higher concentration above 6 molal especially for electrolytes that have strong charge density, suggesting the eNRTL does not correctly represent the water-ion interaction using the local composition theory when ion is highly hydrated.

A new model proposed in this work, association eNRTL model (AeNRTL), which considers the ion hydration using association theory will be presented. The AeNRTL has three contributions to excess Gibbs free energy, including the long-range interionic interaction, the short-range physical interaction, and the association interaction between species that associate. The long-range and the short-range interactions are calculated by Pitzer-Debye-Hückel equation and local composition theory, respectively. The ion hydration is calculated by association theory. We will present that the AeNRTL model outperforms eNRTL much by successfully correlating the activity coefficient data for electrolytes that have strong charge density such as lithium and magnesium salts up to high concentration. With the parameters obtained from single electrolyte system, the AeNRTL also successfully predicts the osmotic coefficient data for mixed-salt systems. The AeNRTL has shown significant advancement over eNRTL and has a great potential to be the next-generation activity coefficient model for electrolyte solutions.