Invited Lecture IL 11

Association-based Activity Coefficient Models for Nonelectrolyte and Electrolyte Solutions

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Key Word (3 words)

Association theory; Fluid phase equilibria; Nonrandom Two-Liquid activity coefficient model

Abstract (less than 300 words)

The classical nonrandom two-liquid (NRTL) activity coefficient model for nonelectrolyte solutions [1] and the electrolyte NRTL model for electrolyte solutions [2] have been considered the most versatile and widely practiced molecular thermodynamic models to correlate and predict phase equilibrium behavior of multicomponent systems in support of process simulation, design, and optimization. Derived from the two-liquid theory, these NRTL models rely on the "binary interaction parameters" to account for the combined short-range physical interactions and chemical associations that dedicate the liquid structure and energetics of the system at a microscopic level. However, without explicitly accounting for specific chemical associations such as hydrogen bonding and ion hydration, these NRTL models fail to accurately correlate and predict phase behavior of highly associating nonelectrolyte systems such as methanol – alkanes binaries and aqueous electrolyte solutions with highly charged ionic species such as lithium and magnesium salts.

Extensively applied to equations of state such as Statistical Associating Fluid Theory and Cubic Plus Association, Wertheim's perturbation theory has recently been integrated with the NRTL models to explicitly account for the associations. [3,4,5] Specifically, the association contribution is formulated with a water self-association reference term and species-specific association strengths for molecules and ions while the physical interaction contribution is captured with the NRTL binary interaction parameters. The resulting association NRTL models reduce to the classical NRTL models when the association strengths are negligible. With refined theoretical basis and superior accuracy over the classical NRTL models, the association models enable accurate correlation and prediction of fluid phase equilibria of multicomponent association systems with minimum numbers of adjustable parameters. This presentation shows the association NRTL models yield drastically improved correlative and predictive results for many highly associating multicomponent systems, electrolytes and nonelectrolytes.

References

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