

Prediction of Vapor-Liquid Equilibria in Complex Binary Mixtures by the Reaction Gibbs Ensemble Monte Carlo Method

M. Lisal,¹ W.R. Smith,² and K. Aim¹

¹*E. Hala Laboratory of Thermodynamics
Institute of Chemical Process Fundamentals
Academy of Sciences
165 02 Prague 6 - Suchbátka, Czech Republic*

²*Department of Mathematics and Statistics and School of Engineering
College of Physical and Engineering Science
University of Guelph
Guelph, Ontario N1G 2W1, Canada*

The “reaction Gibbs ensemble Monte Carlo” (RGEMC) method recently developed by Lisal et al. [J. Phys. Chem. 103 (1999) 10496-10505] has been employed to predict vapor-liquid equilibria in binary mixtures of methanol + ethane, methanol + carbon dioxide, methanol + water, methanol + ethanol, and ethanol + water over wide ranges of state conditions.

The RGEMC approach treats the phase equilibrium conditions as a special type of chemical reaction and incorporates knowledge of the pure-substance vapor pressure data into the mixture phase simulations. In addition to the P - t - x - y phase equilibrium data, the volumetric properties of mixtures are also calculated.

The investigated systems have been modeled as fluids constituted of multi-site Lennard-Jones plus Coulombic molecules with interactions between unlike atoms represented by standard combining rules. No adjustable binary interaction parameters were used in the calculations. The simulated vapor-liquid equilibria have been compared with direct experimental data on real systems and with the results of macroscopic-level predictive models.

Potentialities and limitations of the different approaches will be discussed in detail. General observations are as follows: (i) good to excellent mutual agreement of the vapor-liquid equilibria obtained by RGEMC with experimental data for the systems examined and (ii) comparable accuracy of predictions by the present molecular-based simulation technique with the results obtained from macroscopic-level models, even though such approaches make use of experimental information on mixtures.