A Model for the Excess Gibbs Energy at High Pressures

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Extended Abstract

Liquid-Liquid equilibrium at low pressures is usually described by activity coefficient models. At high pressures equation-of-state models are usually the only alternative. However, equations of state are not as accurate as activity coefficient models for complex mixtures.

In this work, a new model for the excess Gibbs free energy that covers high and low pressures is proposed. The model is based on a combination of a recently suggested volume-explicit equation for hard non-spherical molecules with exact pair correlation integrals. Molecular shape, size and specific interactions are accounted for in this model.

Typically equations of state are separated into repulsive and attractive terms:

$$Z = Z_{HB} + Z_{Att} \tag{1}$$

The volume-explicit equation developed by Hamad (1998) can successfully be used as the repulsive part in developing excess Gibbs energy models for mixtures consisting of hard bodies. The equation is expressed in terms of dimensionless pressure and a parameter m to take care of the non-sphericity of the molecules.

$$Z_{HB} = 1 + 4mp + \frac{3}{4} mp \ln\left[\frac{3+p}{3+25p}\right] + \frac{216(m-1)p}{(3+p)(3+25p)(16+\ln[(3+p)/(3+25p)]} \tag{2}$$

The reduced pressure is defined by $p = \left(P/mRT\right)\sum v_i x_i$. The parameter m is related to the non-sphericity parameter $\alpha = \sum x_i \bar{r}_i \sum s_i / \sum v_i$ by the expression

$$m = \frac{(6\alpha + 5)}{11} \tag{3}$$

where $\bar{r}_i$ is the mean radius of curvature, s_i is the surface area and v_i is the volume of a molecule.

For real molecules the attractive contribution at high densities should be similar to that of one-dimensional fluid. Based on an exact solution for one-dimensional square well fluid (Thompson,1972) we approximate the attractive contributions by the following:

$$Z_{Att,ij} = \frac{p(\lambda_{ij} - 1)q_{ij}}{q_{ij} - \exp\{(\lambda_{ij} - 1)p\}} \tag{4}$$

where

$$q_{ij} = 1 - \exp(-\frac{T_{ij}^*}{T}) \tag{5}$$

and T* is the reduced temperature.

The attractive contribution to the mixture equation of state is given by

$$Z_{Att} = \sum\sum Z_{Att,ij} x_i x_j \tag{6}$$

The overall equation of state can then be written as:

$$\begin{aligned} Z = 1 + 4mp + \frac{3}{4}mp \ln\left[\frac{3+p}{3+25p}\right] + \frac{216(m-1)p}{(3+p)(3+25p)(16+\ln[(3+p)/(3+25p)]} \\ + \sum\sum x_i x_j \frac{p(\lambda_{ij} - 1)q_{ij}}{q_{ij} - \exp\{(\lambda_{ij} - 1)p\}} \end{aligned} \tag{7}$$

Based on the equation of state presented above we can derive the Gibbs energy model using the following thermodynamic relation:

$$\frac{G^{EX}}{RT} = \int_0^p \left[Z - \sum_i x_i Z_i \right] \frac{dP}{P} \tag{8}$$

This model can be used to predict the LLE for systems at low and high pressure. Results will be presented for a number of binary systems.

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Literature Cited

Hamad, E. Z., "Volume-Explicit Equation of State for Hard Spheres, Disks and Mixtures of Hard spheres", *Ind & Eng Chem Res*., **36**, 4385 (1997).

Hamad, E. Z., "Volume-explicit equation of state for hard chains, their mixtures, and copolymers," AIChE *J,* **44**, 2766 (1998).

Thompson, C. J., "One-dimensional Models – Short Range Forces," In *Phase Transitions and Critical Phenomena*, Domb C., and M. S. Green (Eds), Academic Press, NY, Chap 5, 184, (1972).