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Mixture Equations of State: Composition Dependence[1]

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This paper discusses theoretical models for the composition dependence of equations of state and compares the quality of predictions against experimental thermodynamic property data. The mean density approximation (MDA) and the van der Waals one-fluid (VDW1) model are compared with hybrid mixing rules (HMR), in which rigorous composition dependence is used for the second and third virial coefficients and the conformal solution model is used for equation-of-state density terms beyond the third virial term. It is found that when values of unity are used for all binary and three-body unlike interaction parameters, calculated densities for methane–normal heptane mixtures have average absolute deviations of 3.54% for MDA, 4.04% for VDW1, and 2.59% for HMR. When vapor–liquid equilibrium calculations were performed for the methane–normal heptane system, average absolute deviations of calculated *K* values from experimental values were 16.7% for methane and 36.4% for normal heptane using HMR, whereas when conformal solution model (CSM) mixing rules were used, the results were 34.8% for methane and 66.7% for normal heptane. When the binary interaction parameter for the characterization of interaction energies is determined, it is found to be less sensitive to state conditions in the case of HMR than either MDA or VDW1. These preliminary results suggest the potential of mixture equation-of-state methods which utilize rigorous composition dependence for the lower-order virial coefficients.

KEY WORDS: composition dependence; equation of state; hybrid mixing rules.

1. INTRODUCTION

Recently, there has been considerable interest in improving representations of the composition dependence of mixture equations of state [1–4]. The

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authors have initiated a study of equation-of-state composition dependence based on analysis of real fluid data using the macroscopic analogues of various plausible approximations introduced into the statistical mechanical expressions for mixture thermodynamic properties [4]. It has been shown that both the mean density approximation and the van der Waals one-fluid method are not accurate for describing equation-of-state composition dependence for mixtures of large and small molecules, such as the methane–normal heptane system [4]. The objective of the work presented here is to investigate methods for improving mixture equation-of-state composition dependence which retain a close relationship to theory while closely modeling the empirical data.

In Section 2, the theoretical mixture equation of state from statistical mechanics is reviewed in order to provide a rigorous starting point for the presentation. The mean density approximation is presented in Section 3 and the van der Waals one fluid model is presented in Section 4. In Section 5 new mixture equation-of-state mixing rules, referred to herein as hybrid mixing rules, are introduced. The hybrid mixing rules are compared with the mean density approximation and van der Waals one-fluid model in Section 6 utilizing *PVTx* data for the methane–normal heptane system. An evaluation of the hybrid mixing rules for predictions of vapor–liquid equilibrium is presented in Section 7 by comparisons with the conformal solution model using data for the methane–normal heptane system. Conclusions are presented in Section 8.

2. THEORETICAL MIXTURE EQUATION OF STATE

The statistical mechanical expression for the pressure of a fluid mixture in terms of the pair potentials, u_{ij}, and molecular pair correlation functions (pcf), g_{ij}, is

$$\frac{P}{\rho kT} = 1 - \frac{\rho}{6kT} \sum_i \sum_j x_i x_j \int dr\, r \frac{\partial u_{ij}}{\partial r} g_{ij}(r; \rho, T, x) \tag{1}$$

Fluids for which molecular orientation effects are important would involve integration over possible orientations; these are excluded to allow simpler equations. Note that the composition dependence in Eq. (1) has an "explicit" part, i.e., in the double summation, and an "implicit" part, contained in the arguments of the pair correlation functions, g_{ij}. The pressure equation written out in reduced form for the case in which u_{ij} is a two-parameter pair potential involving an energy parameter ε_{ij} and a size parameter σ_{ij} is the following:

$$\frac{P}{\rho kT} = 1 - \frac{4\pi}{6} \sum \sum x_i x_j \frac{(\rho \sigma_{ij}^3)\, \varepsilon_{ij}}{kT} \int dr_{ij}^*\, r_{ij}^{*3} \frac{\partial u_{ij}^*}{\partial r_{ij}^*} g_{ij}(r/\sigma_{ij}; \rho, T, x) \tag{2}$$

where $r_{ij}^* = r/\sigma_{ij}$ and $u_{ij}^* = u_{ij}/\varepsilon_{ij}$. The principal problem with explicit use of Eqs. (1) and (2) is the fact that the dependence of g_{ij} on composition is not known. The integrals in Eq. (2) are functions of temperature, density, and composition, denoted here by $F_{ij}(T, \rho, x)$. The mixture equation of state therefore can be written in the following form:

$$\frac{P}{\rho kT} = 1 - \frac{4\pi\rho}{6kT} \sum\sum x_i x_j \varepsilon_{ij} \sigma_{ij}^3 F_{ij}(T, \rho, x) \tag{3}$$

The composition dependences of various approximate mixture equations of state based on Eq. (2) are distinguished by the approximations used for g_{ij}.

3. THE MEAN DENSITY APPROXIMATION

Approximations for g_{ij} based on mappings of g_{ij} on g_0, the pure fluid pair correlation function, have been used extensively for mixture properties. In particular, the mean density approximation as proposed by Mansoori and Leland [5], for mixtures with two-parameter pair potentials of the same form in r_{ij}/σ_{ij}, corresponds to the following relation:

$$g_{ij}(r/\sigma_{ij}, \rho, T, x) = g_0(r/\sigma_x, \rho\sigma_x^3, kT/\varepsilon_{ij}) \tag{4}$$

where g_0 is the pure fluid pair correlation function. According to Eq. (4), $g_{ij} = g_0$ when $r/\sigma_{ij} = r/\sigma_x$, provided the pure fluid reduced temperature is $kT/\varepsilon = kT/\varepsilon_{ij}$ and the pure fluid reduced density is $\rho_x^* = \rho\sigma_x^3$. The commonly used relation for σ_x is

$$\sigma_x^3 = \sum\sum x_i x_j \sigma_{ij}^3 \tag{5}$$

which is suggested by consideration of hard sphere mixtures. The use of the mean density approximation in Eq. (2) leads to the following mean density approximation (MDA) equation of state for mixtures:

$$\frac{P}{\rho kT} = 1 - \frac{4\pi\rho}{6kT} \sum\sum x_i x_j \varepsilon_{ij} \sigma_{ij}^3 F_0(kT/\varepsilon_{ij}, \rho_x^*) \tag{6}$$

where $F_0(kT/\varepsilon_{ij}, \rho_x^*)$ is the pure fluid quantity evaluated at the reduced temperature kT/ε_{ij} and the mean reduced density ρ_x^*. Thus, the MDA equation of state has explicit composition dependence through the quadratic dependence on the mole fractions and implicit composition dependence through the dependence of the reduced density ρ_x^* on the composition.

4. THE VAN DER WAALS ONE-FLUID MODEL

The van der Waals one-fluid equation of state for mixtures corresponds to the following approximation:

$$g_{ij}(r/\sigma_{ij};\, \rho, T, x) = g_0(r/\sigma_x;\, \rho\sigma_x^3, kT/\varepsilon_x) \tag{7}$$

where ε_x is as yet undefined. The use of this approximation for g_{ij} in Eq. (2) leads to the following mixture equation of state:

$$\frac{P}{\rho kT} = 1 - \frac{4\pi\rho_x^*}{6T_x^*} \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j \varepsilon_{ij} \sigma_{ij}^3}{\varepsilon_x \sigma_x^3} F_0(T_x^*, \rho_x^*) \tag{8}$$

where $T_x^* = kT/\varepsilon_x$, $\rho_x^* = \rho\sigma_x^3$.

With the following definition of ε_x,

$$\varepsilon_x \sigma_x^3 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \tag{9}$$

Equation (8) for mixtures becomes conformal with the pure fluid equation of state and the van der Waals one-fluid eqution of state for mixtures results,

$$\frac{P}{\rho kT} = 1 - \frac{4\pi\rho_x^*}{6T_x^*} F_0(T_x^*, \rho_x^*) \tag{10}$$

where $T_x^* = kT/\varepsilon_x$ and $\rho_x^* = \rho\sigma_x^3$ and σ_x and ε_x are defined by Eqs. (5) and (9), respectively. The resulting VDW1 equation has implicit composition dependence through the dependence of both the reduced temperature T_x^* and the reduced density ρ_x^*.

5. HYBRID MIXING RULES

Neither the MDA nor the VDW1 mixture equation of state is rigorous in the composition dependence of the virial coefficients that result. For this reason, we have investigated the effects of utilizing the following mixture equation of state, which is a hybrid of the virial equation and the conformal solution model:

$$\frac{P}{\rho kT} = 1 + \rho \sum\sum\sum x_i x_j B_{ij} + \rho^2 \sum\sum\sum x_i x_j x_k C_{ijk} + Z_2(T_x^*, \rho_x^*) \tag{11}$$

The resulting hybrid mixing rules (HMR) provide rigorous composition dependence through the third virial term and the composition dependence of the conformal solution model for higher-order terms. Thus, it is anticipated that the low-density region of mixtures can be described more adequately by the HMR than the MDA or the VDW1 mixture equations of state.

To illustrate how the HMR mixture equation can be utilized, a three-parameter corresponding-states modified BWR equation of state [6] which has been used extensively with a conformal solution model (CSM) is utilized here. The pure fluid MBWR equation has the form,

$$Z = Z_0(T^*, \rho^*) + \gamma Z_\gamma(T^*, \rho^*) \tag{12}$$

where $T^* = kT/\varepsilon$ and $\rho^* = \rho\sigma^3$. The parameters ε, σ, and γ have been reported for numerous fluids [6]. For mixture calculations, the interaction second virial coefficients, B_{ij}, are required,

$$B_{ij} = \sigma_{ij}^3 B_{ij}^*(T_{ij}^*, \gamma_{ij}) \tag{13}$$

where B_{ij}^* is the reduced interaction second virial coefficient, $T_{ij}^* = kT/\varepsilon_{ij}$, $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$, $\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{1/2}$, and $\gamma_{ij} = (\gamma_{ii} + \gamma_{jj})/2$, where the subscripts *ii* and *jj* refer to the pure component parameters. Binary interaction parameters have not been used for the interaction parameters in this initial study. The interaction third virial coefficients, C_{ijk}, also are required:

$$C_{ijk} = \sigma_{ijk}^6 C_{ijk}^*(T_{ijk}^*, \gamma_{ijk}) \tag{14}$$

where C_{ijk}^* is the reduced interaction third virial coefficient, $T_{ijk}^* = kT/\varepsilon_{ijk}$, $\varepsilon_{ijk} = \Theta_{ijk}(\varepsilon_{ii} + \varepsilon_{jj} + \varepsilon_{kk})/3$, $\sigma_{ijk} = (\sigma_{ii} + \sigma_{jj} + \sigma_{kk})/3$, $\gamma_{ijk} = (\gamma_{ii} + \gamma_{jj} + \gamma_{kk})/3$. The parameter Θ_{ijk} is a three-body unlike interaction parameter for the energy parameter ε_{ijk}. The reduced virial coefficients are calculated using the chosen equation of state, in this case, the MBWR equation [6]. All terms in the MBWR equation higher order in density than the third virial term are grouped to calculate the term $Z_2(T_x^*, \rho_x^*)$ in Eq. (11). For the MBWR equation, this requires calculation of σ_x, ε_x, and γ_x, which in the present study were calculated using the following mixing rules:

$$\sigma_x^6 = \sum_{i=1}^{n} \sum_{i=1}^{n} x_i x_j \sigma_{ij}^6 \tag{15}$$

$$\varepsilon_x \sigma_x^6 = \sum_{i=1}^{n} \sum_{i=1}^{n} x_i x_j \varepsilon_{ij} \sigma_{ij}^6 \tag{16}$$

$$\gamma_x \sigma_x^3 = \sum_{i=1}^{n} \sum_{i=1}^{n} x_i x_j \gamma_{ij} \sigma_{ij}^3 \tag{17}$$

where the interaction parameters are defined by the following combining rules:

$$\varepsilon_{ij} = \zeta(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{18}$$

$$\sigma_{ij} = \xi(\sigma_{ii}\sigma_{jj})^{1/2} \tag{19}$$

$$\gamma_{ij} = \frac{\gamma_{ii} + \gamma_{jj}}{2} \tag{20}$$

ξ and ζ are binary interaction parameters. The values of the exponents in Eqs. (15)–(17) are different from those defined in the original VDW1 defined by Leland et al. [7]. It was shown by Lee et al. [8] that predictions of vapor–liquid equilibrium behavior for mixtures with molecules having large size differences can be improved by empirical determination of the exponents. We have determined the exponents in the HMR equation in a similar manner, with the resultant values shown in Eqs. (15)–(17). However, for the conformal solution model (CSM) applied to the total equation of state, which is used here for comparison purposes, the exponents are the values used by Lee et al. [8], 4.5, 4.5, and 3.5, instead of 6, 6, and 3, respectively.

6. COMPARISON OF HMR WITH MDA AND VDW1

One of the long-range goals of the present ongoing study of the composition dependence of mixture equations of state is that the mixing rules and combining rules lead to unlike interaction characterization parameters which will be true constants, rather than averages of quantities which are actually functions of state variables. When all unlike binary and three-body interaction parameters are taken to be unity, the average absolute deviations of predicted densities from experimental values [9] for the methane–normal heptane system are 3.54% for MDA, 4.04% for VDW1, and 2.59% for HMR. These results indicate that the use of rigorous composition dependence for the second and third virial coefficients, along with the use of the conformal solution model for the higher-order equation-of-state terms, offers potential advantages over the MDA and VDW1 mixtures equations of state when applied to mixtures with large molecular size differences.

7. COMPARISON OF HMR AND CSM

The van der Waals one-fluid model (VDW1) is a form of conformal solution model, that is, VDW1 is an attempt to map mixture properties on pure fluid properties. It has been noted that for mixtures of hydrocarbons with dissimilar molecular sizes, the exponent 4.5 on σ_{ij} in the mixing rules for σ_x and ε_x yields improved results for vapor–liquid equilibrium calculations over the VDW1 exponent of 3.0 and that the exponent 3.5 is best for γ_x [8]. Therefore, for a system such as methane–normal heptane, a comparison of the HMR with this conformal solution model (CSM) is a more stringent test of HMR than a comparison with VDW1. In this case, the results of flash calculations using HMR and CSM were compared with vapor–liquid equilibrium data for the methane–normal heptane system. With all binary and three-body unlike interaction parameters set equal to unity, the average absolute deviations of calculated K values from the experimental values were, for methane, 16.7% for HMR and 34.8% for CSM and, for normal heptane, 36.4% for HMR and 66.7% for CSM. Thus, with no parameters determined specifically from the methane–normal heptane data, the uncertainties in vapor–liquid equilibrium predictions using the HMR model are approximately one-half the uncertainties from CSM. Similar results are observed for other binary mixtures of methane with the normal paraffin hydrocarbons ethane through normal hexane. It is concluded that the HMR model offers advantages over the CSM mixture equation of state, especially for mixtures of fluids with large dissimilarities in molecular size.

8. CONCLUSIONS

The results presented here demonstrate some of the advantages of using rigorous composition dependence for second and third virial coefficients over approximations such as the mean density approximation (MDA) and conformal solution models (CSM), including the van der Waals one-fluid model (VDW1). The hybrid mixing rules (HMR) presented here utilize rigorous second and third virial composition dependence and the conformal solution model for higher-order density terms in the equation of state. It is found that with all binary and three-body unlike interaction parameters set equal to unity, the uncertainties in calculated liquid densities and K values using the HMR are roughly one-half the uncertainties using the MDA, VDW1, and CSM mixture equations of state. These results suggest the potential of mixture equation-of-state methods which utilize rigorous composition dependence for the lower order virial coefficients.

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