

Vapor–liquid equilibrium prediction at high pressures using activity coefficients at infinite dilution from COSMO-type methods

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Abstract

Predictions of vapor–liquid equilibria at high temperatures and pressures were obtained by applying a modified procedure using the Huron–Vidal mixing rule based on available activity coefficients at infinite dilution and low pressures. These activity coefficients were calculated with so-called conductor-like screening model for real solvents (COSMO-RS) and with a variation of this model, known as segment activity coefficient (COSMO-SAC) model.

In this work, the performances of the mixing rule (HVID model) coupled with the SRK equation of state and a reduced UNIQUAC model are presented for six binary systems and a ternary system, whose VLE data are available over a large temperature and pressure range.

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1. Introduction

Infinite dilution activity coefficients (γ^∞) are of great importance in both chemical and environmental engineering. If both infinite dilution activity coefficients are known for a binary system, parameters in a two-parameter activity coefficient model can be determined and then predictions of vapor–liquid equilibria over the entire composition range can be made.

The use of infinite dilution activity coefficients at low pressure in cubic equations of state was discussed by Ferioiu and Geană [1] in relation to the Stryjek and Vera [2] non-quadratic mixing rule. In previous papers [3–6], Ferioiu and Geană pro-

posed a modified procedure of using available activity coefficients at infinite dilution in the Huron–Vidal mixing rule (HVID). Following previous work [5,6], in which the activity coefficients at infinite dilution were calculated with one of the most successful predictive G^E models, i.e. UNIFAC'93 [7], we suggest here to make use of a novel method for the prediction of thermophysical data of liquids. This method, called 'conductor like screening model for real solvents' (COSMO-RS) was originally published in 1995 [8].

In contrast to the widely used group contribution methods, COSMO-RS gets the necessary information about the intermolecular interactions in solution from quantum mechanical calculations on the chemical compounds and thus is far less dependent on experimental data [9]. In a series of publications [9–12], it was shown that COSMO-RS is a valuable tool for handling of chemical and engineering thermodynamics problems concerning activity coefficients. In addition, it provides a great flexibility in treating systems of different chemical functionality. In a more recent paper [13] infinite dilution activity coefficients were predicted using the COSMO-RS model for over 400 binary systems.

Abbreviations: COSMO-RS, conductor-like screening model for real solvents; COSMO-SAC, segment activity coefficient model; GCS, group contribution solvation; HVID, Huron–Vidal mixing rule coupled with infinite dilution activity coefficients; No Dpt, number of data points; SRK, Soave–Redlich–Kwong equation of state; UNIQUAC, universal quasi chemical; UNIFAC, UNIQUAC functional group activity coefficients; VLE, vapor–liquid equilibria

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Lin and Sandler [14] proposed a variation of COSMO-RS called COSMO-SAC based on their previously developed group contribution solvation model GCS [15].

The application of the COSMO models in making a priori phase equilibrium predictions at low pressures was reported by Spuhl and Arlt [16]. The limitations of the COSMO method are, at present, on one hand its inability to account for high-temperature and high-pressure vapor–liquid equilibria, and on the other hand its inability to properly account for the thermodynamics of polymer systems. Panayiotou [17] incorporated free volume in the formalism and derived an equation of state that is applicable to polymer solutions.

The scope of this paper is to enlarge the fields of application of COSMO type methods to vapor–liquid equilibrium prediction at high pressures within the context of the proposed HVID model [3–6].

2. Calculation model

In this work, the cubic equation of state of Soave, Redlich and Kwong, SRK [18] was used:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (1)$$

The parameters for pure substances are

$$a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} [f(T_r)]^2; \quad b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (2)$$

where the Mathias and Copeman [19] temperature function $f(T_r)$ is given by

$$f(T_r) = 1 + C_1 y + C_1 y^2 + C_1 y^3 \quad \text{for } T_r \leq 1 \quad (3)$$

and

$$f(T_r) = 1 + C_1 y \quad \text{for } T_r \geq 1 \quad (4)$$

with

$$y = 1 - \sqrt{T_r} \quad (5)$$

The critical constants and the values of C_1 , C_2 , and C_3 constants were taken from Reid et al. [20] and Dahl et al. [21], respectively.

For mixtures, the Huron–Vidal mixing rules were used:

$$b = \sum_i x_i b_i \quad (6)$$

$$\frac{a}{bRT} = \sum_i x_i \left(\frac{a_i}{b_i RT} - \frac{\ln \gamma_i(P \rightarrow \infty)}{\ln 2} \right) \quad (7)$$

where $\ln \gamma_i(P \rightarrow \infty)$ is the activity coefficient of the component in the mixture at infinite pressure.

The corresponding expression for the activity coefficient, which relates the infinite dilution activity coefficient at infinite pressure $\ln \gamma_{i(j)}^\infty(P \rightarrow \infty)$ to its value at pressure $P(\gamma_{i(j)}^\infty)$,

is

$$\begin{aligned} \ln \gamma_{i(j)}^\infty(P) &= \frac{b_i}{b_j} (Z_j - 1) - \ln \left(\frac{V_j - b_j}{V_i - b_i} \right) \\ &- \left[\frac{a_i}{b_i RT} \ln \left(\frac{1 + b_j/V_j}{1 + b_i/V_i} \right) + \frac{\ln \gamma_{i(j)}^\infty(P \rightarrow \infty)}{\ln 2} \right] \\ &\times \ln \left(1 + \frac{b_j}{V_j} \right) \end{aligned} \quad (8)$$

Details about Eq. (8) can be seen in Refs. [3–5,22]. Moreover, if Eq. (8) is applied under the limiting condition $P \rightarrow 0$, it yields [1,2,22]:

$$\begin{aligned} \ln \gamma_{i(j)}^\infty(P \rightarrow 0) &= \left(1 - \frac{b_i}{b_j} + \ln \frac{b_i}{b_j} \right) - \ln \left(\frac{V_j/b_j - 1}{V_i/b_i - 1} \right) \\ &- \frac{a_i}{b_i RT} \ln \left(\frac{1 + b_j/V_j}{1 + b_i/V_i} \right) \\ &+ \frac{\ln \gamma_{i(j)}^\infty(P \rightarrow \infty)}{\ln 2} \ln \left(1 + \frac{b_j}{V_j} \right) \end{aligned} \quad (9)$$

where (V_i, V_j) are the solutions of Eq. (1) at $P \rightarrow 0$.

Feroiu and Geană [3,5] proposed a procedure to predict vapor–liquid equilibria at high pressure using the above mixing rule model and the infinite dilution activity coefficients at low pressures.

The activity coefficients in Eq. (7) are given by a reduced UNIQUAC model (only to its residual part, with the original values of q_i parameters) suitable for infinite pressure conditions:

$$\ln \gamma_i(P \rightarrow \infty) = q_i \left[1 - \ln \left(\sum_i \theta_j \tau_{ij} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (10)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \quad \tau_{ij} = \exp \left(-\frac{u_{ij}}{T} \right) \quad (11)$$

The temperature dependence of the parameter u_{ij} is expressed by

$$u_{ij} = u_{ij}^0 + u_{ij}^1 \frac{1}{T} \quad (12)$$

The procedure involves the following five steps:

1. Use the activity coefficient model (COSMO-RS, COSMO-SAC or UNIFAC'93) at low temperature/low pressure, to calculate the activity coefficient at infinite dilution $\gamma_{i(j)}^\infty(P \rightarrow 0)$ for several data sets.
2. Calculation of the corresponding values of $\ln \gamma_i(P \rightarrow \infty)$ with Eq. (9).
3. Calculation of the binary interaction parameters of the reduced UNIQUAC model at all temperatures.
4. Obtaining the linear temperature dependence of the interaction parameters (Eq. (12))

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