

# Prediction of phase equilibria for mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures by cubic equation of state with $G^E$ type mixing rule based on COSMO-RS

Yusuke Shimoyama<sup>a</sup>, Yoshio Iwai<sup>a,\*</sup>, Satoshi Takada<sup>a</sup>, Yasuhiko Arai<sup>a</sup>,  
Tomoya Tsuji<sup>b</sup>, Toshihiko Hiaki<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

<sup>b</sup> College of Industrial Technology, Nihon University, 1-2-1 Izumicho, Narashino 275-8575, Japan

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## Abstract

The phase equilibria for the mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures were predicted by a cubic equation of state with an excess Gibbs free energy ( $G^E$ ) type mixing rule using information from the conductor-like screening model for real solvents (COSMO-RS) method. The systems predicted were water + hydrocarbon, water + alcohol, hydrocarbon + alcohol binary systems and water + hydrocarbon + hydrocarbon and water + hydrocarbon + alcohol ternary systems. COSMO-RS method was used to calculate activity coefficients of the mixtures. UNIQUAC equation was adopted as an activity coefficient model in  $G^E$  type mixing rule. The interaction parameters in UNIQUAC equation were determined with the activity coefficients calculated by COSMO-RS method. The modified Huron–Vidal mixing rule (MHV1) and a modified Soave–Redlich–Kwong (MSRK) equation of state were chosen as the  $G^E$  type mixing rule and the cubic equation of state, respectively. Further, the MHV1 mixing rule was modified to apply in high temperature regions.

It was found that the prediction method proposed here can represent the phase behavior of the mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures. The predicted results are compared with those calculated by a predictive Soave–Redlich–Kwong (PSRK) equation of state. The predicted results in this work are more accurate than those calculated by PSRK equation of state.

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## 1. Introduction

Chemical processes utilizing water near the critical point have been considered in various fields. Cracking processes of waste plastics, polyethylene and polypropylene, and heavy hydrocarbons have received much attention in the framework of the recycling of resources and environmental conservation [1–4]. Hydration processes of olefin in sub- and supercritical water have been also reported recently [5]. In these processes, low molecular weight hydrocarbons, such as alkanes, alkenes and alcohols are produced as products. Therefore, it is required for process design to elucidate the phase behav-

ior of the mixtures consisting of water and these compounds at high temperatures and pressures near the critical point of water.

In previous works, the phase equilibria for water + hydrocarbon [6,7], water + alcohol [8], water + hydrocarbon + hydrocarbon [9] and water + hydrocarbon + alcohol [10] systems at high temperatures and pressures were correlated using a modified Soave–Redlich–Kwong (MSRK) equation of state [11] with an exponent type mixing rule [12]. In the calculation model, the binary parameters were optimized by using the phase equilibrium data. However, there are few experimental data at high temperatures and pressures, and therefore the application of the model is confined to the systems of which phase equilibrium data are available.

Group contribution methods, such as ASOG [13] and UNI-FAC [14] activity coefficient models, a predictive SRK (PSRK)

\* Corresponding author. Fax: +81 92 802 2751.

E-mail address: [iwai@chem-eng.kyushu-u.ac.jp](mailto:iwai@chem-eng.kyushu-u.ac.jp) (Y. Iwai).

[15] and Peng–Robinson ASOG (PRASOG) [16] equation of states, are capable of solving the problem. Because it is considered that a molecule consists of several groups, and these methods can reduce the number of parameters needed to calculate the thermodynamic properties for the mixtures. Although group contribution methods are applicable to a large variety of the mixtures, the group parameters interested are not necessarily given. Klamt and Eckert [17–19] have proposed the conductor-like screening model for real solvents (COSMO-RS) method based on quantum calculations, without data fitting. It was confirmed from the recent publications that COSMO-RS method can be very useful tool to predict the thermodynamic properties of fluids and their mixtures [20–23]. However, the method cannot be applied in high pressure region, because the vapor phase is assumed as ideal gas. A method has been newly considered for phase equilibrium calculations at high pressure by Constantinescu et al. [24]. In the method, infinite dilution activity coefficients at low pressure calculated by COSMO-RS method were adopted to Huron–Vidal mixing rule [25], excess Gibbs free energy ( $G^E$ ) type mixing rule, with UNIFAC equation and the mixing rule was applied to the attractive term in SRK equation of state. This calculation method seems to be possible to predict the vapor–liquid equilibria for the mixtures containing polar compounds, such as water, alcohol and acetone at high pressures without data fitting.

In this work, a calculation method is constructed for the prediction of phase equilibria of the asymmetric mixtures, which consisting of water, hydrocarbons and alcohols at high temperatures and pressures. COSMO-RS method was applied for calculations of activity coefficients for the mixtures. UNIQUAC equation [26] was used to describe the activity coefficients. The interaction parameters in UNIQUAC equation were determined from the activity coefficients calculated by COSMO-RS method. A modified Huron–Vidal (MHV1) mixing rule [27,28] with UNIQUAC equation was adopted as a mixing rule of the attractive term in a modified Soave–Redlich–Kwong (MSRK) equation of state proposed by Sandarushi et al. [11]. In MHV1 mixing rule, one parameter was redetermined in order to extend the mixing rule to high temperature regions. The predicted systems are water + hydrocarbon, water + alcohol, hydrocarbon + alcohol binary systems and water + hydrocarbon + hydrocarbon and water + hydrocarbon + alcohol ternary systems. It is shown that the phase behavior for the asymmetric mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures can be represented by the method proposed in this work. The results predicted by the present method are compared with those by PSRK equation of state.

## 2. Calculation procedure

The calculation of the phase equilibria was carried out based on the following three steps.

- (1) Activity coefficients were calculated for the binary systems, water + hydrocarbon, water + alcohol, hydrocarbon + alcohol and hydrocarbon + hydrocarbon systems in variety compositions at 423–623 K by COSMO-RS method.

COSMO-RS calculations were performed based on COSMOtherm Version C2.1 program [29].

- (2) The interaction parameters in UNIQUAC equation were determined from the activity coefficients calculated in step 1 by Marquart method [30].
- (3) The phase equilibria were calculated by MSRK equation of state with MHV1 mixing using the UNIQUAC interaction parameters determined in step 2. The phase equilibrium calculations were performed with the thermodynamic relations given by the following equations.

$$py_i\varphi_i^V = px_i\varphi_i^L \quad \text{for vapor–liquid equilibria (VLE)} \quad (1)$$

$$px_i^I\varphi_i^I = px_i^{II}\varphi_i^{II} \quad \text{for liquid–liquid equilibria (LLE)} \quad (2)$$

and

$$\ln \varphi_i = \frac{1}{RT} \int_V^\infty \left\{ \left( \frac{\partial p}{\partial n_i} \right)_{T,V,n_{i \neq j}} - \frac{RT}{V} \right\} dV - \ln Z \quad (3)$$

where  $x$  and  $y$  denotes the mole fraction in liquid and vapor phases.  $n$ ,  $\varphi$  and  $Z$  are the amount of substance, the fugacity coefficient and the compressibility factor, respectively. Superscripts I, II, V and L mean the phases I and II, vapor and liquid phases, respectively. Subscript  $i$  denotes the component  $i$ .

## 3. Calculation method

### 3.1. COSMO-RS method

COSMO-RS method [17–19] has capabilities to predict thermodynamic properties of fluids from a statistical approach by quantum calculations, based on conductor-like screening model (COSMO) [31]. In these calculations, a charge density  $\sigma$  of a segment on the molecular surface is calculated in a virtual conductor. The distribution function  $P_i(\sigma)$  of the obtained  $\sigma$ , which is called  $\sigma$ -profile, for each molecule can give the  $\sigma$ -profile of the mixture  $P(\sigma)$  by using  $P_i(\sigma)$  and the mole fraction  $x_i$  of component  $i$  in the mixture.

$$P(\sigma) = \sum_i x_i P_i(\sigma) \quad (4)$$

Molecular interaction energies  $E_{\text{int}}$  are described as the summation of the three contribution terms, electrostatics  $E_{\text{misfit}}$ , which means the interactions by a difference between molecular surface charges, van der Waals interaction  $E_{\text{vdW}}$  and hydrogen bonding  $E_{\text{HB}}$ .

$$E_{\text{int}} = E_{\text{misfit}} + E_{\text{vdW}} + E_{\text{HB}} \quad (5)$$

The chemical potential of the contact surface segment  $\mu_S(\sigma)$  on the molecular surface are derived using Eqs. (4) and (5) as follows.

$$\exp\left(-\frac{\mu_S(\sigma)}{kT}\right) = \int P(\sigma') \exp\left[-\frac{E_{\text{int}}(\sigma, \sigma') - \mu_S(\sigma')}{kT}\right] d\sigma' \quad (6)$$

where  $k$  and  $T$  are the Boltzmann constant and the temperature, respectively.  $E_{\text{int}}(\sigma, \sigma')$  means the interaction energies

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