

Phase equilibria of associating fluid mixtures using the perturbed-hard-sphere-chain equation of state combined with the association model

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(Received 7 August 2006 • accepted 26 October 2006)

Abstract—For developing the equation of state which can be applicable to associating fluids, the Perturbed-Hard-Sphere-Chain-Association (PHSC-AS) equation of state is proposed by incorporating the association term of the SAFT model into the PHSC equation of state which has been widely used to describe phase equilibria for the fluid system containing a large molecule such as polymer. In this work, two different types of PHSC models have been examined. One is the original model proposed by Song et al., and the other is the modified model by Kim and Bae whose chain term was replaced with that of the SAFT model. As a result, two types of PHSC-AS models are obtained, and applied to the calculation of phase equilibria for the binary system containing a self-associating compound such as alcohol, amine and carboxylic acid, etc. The calculated results of vapour-liquid equilibria are in good agreement with the experimental data. The proposed models (PHSC-AS) are also compared to the PC-SAFT model.

Key words: PHSC-AS Equation of State, PHSC Model, Association, Phase Equilibria, PC-SAFT Model

INTRODUCTION

In chemical engineering practice, there is a strong need for an equation of state suitable to describing thermodynamic properties and phase behaviors of fluids. Especially, the equation of state provides useful tools for correlating and estimating phase equilibria of mixtures at a condition in the high pressure region. During the last thirty years, a great number of theoretical studies aimed at developing a molecular-based equation of state have been performed, and the details of which have well been reviewed in literature reported recently [Wei and Sados, 2000]. These studies have been mainly focused on theoretical models to account for the effects of molecular size, shape and molecular special interaction on bulk properties and phase behaviors.

Mixtures containing associating compounds are often encountered with the operation of an industrial chemical process, as well as are of great interest from the theoretical point of view for testing molecular-based statistical models. A molecular association phenomenon is ascribed to a strong attractive interaction between molecules such as hydrogen bonding interaction, and has an important effect on the phase behavior of pure fluids and mixtures. In pure fluid associations, hydrogen bonding between molecules results in the formation of molecular clusters that considerably affect their thermodynamic properties. In mixtures, a hydrogen bonding interaction may occur between molecules of the same species (self-association) or between molecules of different species (cross-association). A number of extensive and comprehensive investigations have been carried out during last two decades towards the development of models suitable for associating fluid systems. These models can be divided into three categories based on the theoretical background to account for the extent of hydrogen bonding [Economou and Donohue, 1991; Muller and Gubbins, 2001]: i) Chemical theory, ii) Lat-

tice or quasi-chemical theory and iii) Perturbation theory. In chemical theory, molecules in a fluid are assumed to interact with each other to form new chemical species such as dimer, trimer, etc. Accordingly, chemical theory postulates the existence of chemically distinct species that are assumed to be in chemical equilibrium. Heidemann and Prausnitz [1976] have shown that it is possible to solve the chemical equilibrium analytically and then to incorporate this analytic solution into the equation of state. Since their work, this approach has been used by many researchers [Ikonomou and Donohue, 1986; Anderko, 1989; Elliott et al., 1990] to develop an equation of state for a fluid system composed of associating chemicals. Lattice theory was also used to develop an equation of state for associating fluids. Panayiotou and Sanchez [1991] modified the Sanchez-Lacombe equation of state to account explicitly for hydrogen-bonding interactions. In their approach, a specific interaction is introduced between adjacent sites in a lattice, and the number of bonds determining the extent of hydrogen bonding is formulated based on the Veytsman [1990] lattice statistics. This approach has been applied for developing various Lattice-Fluid models suitable for associating fluids [Gupta and Johnston, 1994; Yeom et al., 1999; Yoo and Lee, 2000; Oh et al., 2003]. Recent advances in statistical mechanics have resulted in perturbation theories capable of accurately describing the thermodynamic properties of non-ideal fluids. Wertheim [1984, 1986] proposed theoretical expressions based on the cluster expansion and algebraic topology for hydrogen bonding fluids. Wertheim's theory (TPT1) was used as the basis to develop the Statistical-Associating-Fluid-Theory (SAFT), which is known to be accurate for real associating fluids [Chapman et al., 1990; Huang and Radosz, 1990, 1991]. After Huang's original SAFT model was presented, a number of significant works have been performed towards the improvement of SAFT, resulting in the development of various types of SAFT equations of state [Economou, 2002]. Apart from three types of theories previously reviewed, a different approach was taken by Kontogeorgis et al. [1996]. They presented the Cubic Plus Association (CPA) equation of state combining the Soave-Redlich-

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Kwong equation and an association term of the SAFT model. This equation of state has been utilized extensively in the modeling of phase equilibria for the associating fluid system.

As mentioned above, although a large number of publications have focused on the development of an accurate equation of state, this subject is still open for further investigation. In this work, for developing the equation of state for the associating fluid, the Perturbed-Hard-Sphere-Chain-Association (PHSC) equation of state developed by Song et al. [1994, 1996] has been extended to be applicable to the system containing associating components. The PHSC model was developed starting from the modified Chiew [1990] equation of state for the hard-sphere chain as a reference term, and using van der Waals-type perturbation to account for attractive forces. Many researchers [Gupta and Prausnitz, 1996; Favari et al., 2000; Feng et al., 2001] have shown that the PHSC equation of state can represent superior accuracy for the behavior of long-chain pure-component properties as well as small molecules, and also is suitable for describing the phase equilibria of polymer-containing mixtures. Although the PHSC equation of state has been successfully applied to the modeling of phase equilibria relation of the system composed of strong polar components including polymers, this equation has a limit of application on the associating fluid system. In this work, to extend the applicability of the PHSC equation of state to the system that contains polar and hydrogen-bonding molecule such as alcohol, amine, aldehyde and organic acid, etc., we modified the PHSC equation of state with a combination of the association term (based on Wertheim's TPT1 theory) of the SAFT model. Two different types of PHSC models have been examined. One is the original model proposed by Song et al. [1994] and the other is the modified model by Kim and Bae [2000], whose chain term was replaced with that of the SAFT model. The extended PHSC equation of state presented in this work is adopted for describing phase equilibria of associating fluid mixtures, and also compared to the PC-SAFT model [Gross and Sadowiski, 2001] which has been widely used for calculating phase equilibria of the associating fluid system.

THEORETICAL BACKGROUND

In the PHSC model, the molecule is assumedly constituted by a chain of freely jointed tangent hard-spheres (or segments). The PHSC model uses the modified Chiew equation of state [Chiew, 1990] for an athermal mixture of hard-sphere chains as the reference term and a van der Waals-type perturbation term to take into account the dispersion force between hard-spheres. The PHSC equation of state for a mixture of homonuclear chain molecules which consist of effective hard spheres of the equal size and potential energy is given by [Song et al., 1994]

$$Z_{PHSC} = Z^{ref} + Z^{pert} \quad (1)$$

with

$$Z^{ref} = 1 + r^2 b(T) \rho g^{hs}(d^+) - (r-1)[g^{hs}(d^+) - 1] \quad (2)$$

and

$$Z^{pert} = Z^{disp} = -\frac{r^2 a(T) \rho}{kT} \quad (3)$$

where $Z = (P/\rho kT)$ is the compressibility factor, $\rho = (N/V)$ is the num-

ber density of hard-spheres, k is the Boltzmann constant, and r is the number of effective hard-spheres per molecule.

The third term on the right hand of Eq. (2) is related to the chain composed of hard-spheres. Recently, Kim and Bae [2000] have replaced this term of Eq. (2) with the chain term of the SAFT model expressed as [Chapman et al., 1990]

$$Z^{chain} = -(r-1) \rho \left[\frac{\partial \ln g^{hs}(d^+)}{\partial \rho} \right]$$

They proposed a modified PHSC equation of state with a reference term in Eq. (2) to be transformed as:

$$Z^{ref} = 1 + r^2 b(T) \rho g^{hs}(d^+) - (r-1) \rho \left[\frac{\partial \ln g^{hs}(d^+)}{\partial \rho} \right] \quad (4)$$

Since the PHSC theory accounts only for weak attraction due to the van der Waals force as a perturbation to the dominating repulsive force, it does not account for strong attractive forces such as hydrogen bonding. In this work, considering this point, our attention has been paid to the extension of the PHSC equation of state to be applicable for the fluid system containing hydrogen-bonding components such as alcohol, amine and organic acid, etc. We modified the PHSC equation of state by combining the association term in the SAFT model, and obtained the resulting equation (Perturbed-Hard-Sphere-Chain-Association (PHSC-AS) equation of state) expressed as:

$$Z = Z_{PHSC} + Z^{assoc} \quad (5)$$

where the association term Z^{assoc} is defined based on the SAFT model [Chapman et al., 1990], as follows:

$$Z^{assoc} = \rho \sum_A \left[\frac{1}{X^A} - \frac{1}{2} \right] \left(\frac{\partial X^A}{\partial \rho} \right) \quad (6)$$

where X^A , a mole fraction of molecules not bonded at the association site A on the molecule, is expressed as:

$$X^A = [1 + \rho \sum_B X^B \Delta^{AB}]^{-1} \quad (7)$$

and Δ^{AB} is the association strength evaluated from the following expression:

$$\Delta^{AB} = g^{hs}(d^+) \left[\exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1 \right] (\sigma^3 \kappa^{AB}) \quad (8)$$

In the SAFT model, ε^{AB} and κ^{AB} are the association energy and the volume parameter between the association sites A and B on the self-associating molecules, respectively, and σ is the temperature independent diameter of segment (or hard-sphere).

As a result, we obtained two types of PHSC-AS models: PHSC-AS (model 1) from Eqs. (2), (3) and (6) expressed as:

$$Z^{model1} = 1 + r^2 b(T) \rho g^{hs}(d^+) - (r-1)[g^{hs}(d^+) - 1] - \frac{r^2 a(T) \rho}{kT} + \rho \sum_A \left[\frac{1}{X^A} - \frac{1}{2} \right] \left(\frac{\partial X^A}{\partial \rho} \right) \quad (9)$$

and PHSC-AS (model 2) from Eqs. (3), (4) and (6) expressed as:

$$Z^{model2} = 1 + r^2 b(T) \rho g^{hs}(d^+) - (r-1) \rho \left[\frac{\partial \ln g^{hs}(d^+)}{\partial \rho} \right] - \frac{r^2 a(T) \rho}{kT}$$

$$+ \rho \sum_A \left[\frac{1}{X^A} - \frac{1}{2} \right] \left(\frac{\partial X^A}{\partial \rho} \right) \quad (10)$$

In Eqs. (8), (9) and (10), $g^{hs}(d^+)$ is the radial distribution function of hard-spheres prior to bonding, and is obtained from the Carnahan-Stirling equation:

$$g^{hs}(d^+) = \frac{1 - 0.5\eta}{(1 - \eta)^3} \quad (11)$$

where η is the packing fraction of segments:

$$\eta = \frac{r\rho b(T)}{4} \quad (12)$$

The $a(T)$ term of Eq. (3) reflects the attractive force between non-bonded segments and the $b(T)$ term of Eq. (2) is the van der Waals covolume (or excluded volume) per segment. These terms are given by: [Song et al., 1994]

$$a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(Tk/\varepsilon) \quad (13)$$

$$b(T) = \frac{2\pi}{3} \sigma^3 F_b(Tk/\varepsilon) \quad (14)$$

where ε and σ are pair-potential parameters: ε is the depth of the minimum in the pair potential and σ is the separation distance between segment centers at this minimum with a physical meaning of the segment diameter similar to that in Eq. (8) related to the SAFT model. In Eqs. (13) and (14), $F_a(Tk/\varepsilon)$ and $F_b(Tk/\varepsilon)$ are the universal functions expressed as the following empirical formulas [Song et al., 1996]

$$F_a(Tk/\varepsilon) = 1.8681 \exp[-0.0619(Tk/\varepsilon)] + 0.6715 \exp[-1.7317(Tk/\varepsilon)^{3/2}] \quad (15)$$

$$F_b(Tk/\varepsilon) = 0.7303 \exp[-0.1649(Tk/\varepsilon)^{1/2}] + 0.2697 \exp[-2.3973(Tk/\varepsilon)^{3/2}] \quad (16)$$

The present PHSC-AS equation proposed in this work requires five parameters to describe self-associating chemicals: the number of effective hard-spheres per molecule, r ; segmental diameter, σ ; non-bonded segmental pair-interaction energy, ε ; association energy parameter, ε^{AB} ; and association volume parameter, κ^{AB} . Three parameters (r , σ and ε) are, however, needed for describing the non-associating chemicals as the case in the original PHSC equation.

For the mixture, Eqs. (9) and (10) are straightforwardly transformed as:

$$Z^{model1} = 1 + \rho \sum_{ij} x_i x_j r_i r_j b_{ij}(T) g_{ij}^{hs}(d_{ij}^+) - \sum_i x_i (r_i - 1) [g_{ii}^{hs}(d_{ii}^+) - 1] - \frac{\rho}{kT} \sum_{ij} x_i x_j r_i r_j a_{ij}(T) + \rho \sum_i x_i \sum_A \left[\frac{1}{X^{A_i}} - \frac{1}{2} \right] \left(\frac{\partial X^{A_i}}{\partial \rho} \right) \quad (17)$$

$$Z^{model2} = 1 + \rho \sum_{ij} x_i x_j r_i r_j b_{ij}(T) g_{ij}^{hs}(d_{ij}^+) - \sum_i x_i (r_i - 1) \rho \left[\frac{\partial \ln g_{ii}^{hs}(d_{ii}^+)}{\partial \rho} \right] - \frac{\rho}{kT} \sum_{ij} x_i x_j r_i r_j a_{ij}(T) + \rho \sum_i x_i \sum_A \left[\frac{1}{X^{A_i}} - \frac{1}{2} \right] \left(\frac{\partial X^{A_i}}{\partial \rho} \right) \quad (18)$$

where X^{A_i} and $\Delta^{A_i B_j}$ related to the association term in the mixture are expressed as:

$$X^{A_i} = \left[1 + \rho \sum_i x_i \sum_B X^{B_j} \Delta^{A_i B_j} \right]^{-1} \quad (19)$$

$$\Delta^{A_i B_j} = g_{ij}^{hs}(d_{ij}^+) \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT}\right) - 1 \right] \sigma_{ij}^3 \kappa^{A_i B_j} \quad (20)$$

The mathematical expression required for $g_{ij}^{hs}(d_{ij}^+)$ is given by the BMCS (Boublick-Mansoori-Carnahan-Stirling) equation for hard-sphere mixtures[Mansoori et al., 1971]

$$g_{ij}^{hs}(d_{ij}^+) = \frac{1}{1 - \eta} + \frac{3}{2} \frac{\xi_{ij}}{(1 - \eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1 - \eta)^3} \quad (21)$$

where

$$\eta = \frac{\rho}{4} \sum_i x_i r_i b_i \quad (22)$$

$$\xi_{ij} = \frac{\rho}{4} \left(\frac{b_i b_j}{b_{ij}} \right)^{1/3} \sum_i x_i r_i b_i^{2/3} \quad (23)$$

The $a_{ij}(T)$ and $b_{ij}(T)$ terms in Eq. (17) and (18) are obtained by the extension of Eqs. (13) and (14)

$$a_{ij}(T) = \frac{2\pi}{3} \sigma_{ij}^3 \varepsilon_{ij} F_a(Tk/\varepsilon_{ij}) \quad (24)$$

$$b_{ij}(T) = \frac{2\pi}{3} \sigma_{ij}^3 F_b(Tk/\varepsilon_{ij}) \quad (25)$$

where $F_a(Tk/\varepsilon_{ij})$ and $F_b(Tk/\varepsilon_{ij})$ are the same universal functions as Eqs. (15) and (16) for the pure component. The parameters representing interaction between a pair of unlike segments σ_{ij} and ε_{ij} are defined from the conventional combining rules:

$$\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) \quad (26)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} (1 - k_{ij}) \quad (27)$$

where k_{ij} is the adjustable binary interaction parameter introduced for each binary pair included in the mixture. Meanwhile, the cross-association parameters in the association strength of Eq. (20) can be defined as [Wolbach and Sandler, 1998]

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \quad (28)$$

$$\kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left[\frac{\sqrt{\sigma_i \sigma_j}}{(\sigma_i + \sigma_j)/2} \right]^3 \quad (29)$$

The general equation for calculating the Helmholtz free energy from the pressure-explicit equation of state is [Prausnitz et al., 1999]

$$A^{res} = \int_p^p \left[P - \frac{nRT}{V} \right] dV - nRT \ln Z \quad (30)$$

By inserting Eqs. (9) and (10) into Eq. (30), the residual Helmholtz free energy of the pure component is defined as:

$$A^{res}/nRT = r^2 b(T) W - (r-1) Q - r^2 a(T) \rho / RT + \left[\sum_A \left[\ln X^A - \frac{X^A}{2} \right] + \frac{1}{2} M \right] - \ln Z \quad (31)$$

where W and Q terms are related to the radial distribution function $g^{hs}(d^+)$ [Hino et al., 1994]. These terms are expressed as the following:

$$W = \int_0^{\infty} [\rho g^{hs}(d^+)] \frac{d\rho}{\rho} = \frac{\eta}{1 - \eta} + \frac{1}{4} \frac{\eta^2}{(1 - \eta)^2} \quad (32)$$

$$Q^{model1} = \int_0^{\rho} [g^{hs}(d^+) - 1] \frac{d\rho}{\rho} = -\ln(1-\eta) + \frac{3}{2} \frac{\eta}{1-\eta} + \frac{1}{4} \frac{\eta^2}{(1-\eta)^2} \quad (33)$$

$$Q^{model2} = \int_0^{\rho} \left[\rho \frac{\partial \ln g^{hs}(d^+)}{\partial \rho} \right] \frac{d\rho}{\rho} = \ln g^{hs}(d^+) \quad (34)$$

The fugacity equation for the pure component can be straightforwardly obtained from the above residual Helmholtz free energy relation.

For mixtures, Substituting Eqs. (17) and (18) into Eq. (30) yields

$$A^{res}/nRT = \rho \sum_{ij} x_i x_j r_i r_j b_{ij}(T) W_{ij} - \sum_i x_i (r_i - 1) Q_{ii} - \rho/kT \sum_{ij} x_i x_j r_i r_j a_{ij}(T) + \sum_i x_i \left[\sum_{A_i} \left[\ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_i \right] - \ln Z \quad (35)$$

with

$$W_{ij} = \frac{1}{\rho} \int_0^{\rho} g_{ij}^{hs}(d_{ij}^+) d\rho = \frac{-\ln(1-\eta)}{\eta} + \frac{3}{2} \frac{\xi_{ij}}{\eta^2} \left[\ln(1-\eta) + \frac{\eta}{1-\eta} \right] + \frac{1}{2} \frac{\xi_{ij}^2}{\eta^3} \left[-\ln(1-\eta) - \frac{\eta}{1-\eta} + \frac{1}{2} \frac{\eta^2}{(1-\eta)^2} \right] \quad (36)$$

and

$$Q_{ii}^{model1} = \int_0^{\rho} [g_{ii}^{hs}(d_{ii}^+) - 1] \frac{d\rho}{\rho} = -\ln(1-\eta) + \frac{3}{2} \frac{\xi_{ii}}{1-\eta} + \frac{1}{4} \frac{\xi_{ii}^2}{(1-\eta)^2} \quad (37)$$

$$Q_{ii}^{model2} = \int_0^{\rho} \left[\rho \frac{\partial \ln g_{ii}^{hs}(d_{ii}^+)}{\partial \rho} \right] \frac{d\rho}{\rho} = \ln g_{ii}^{hs}(d_{ii}^+) \quad (38)$$

where ξ_{ii} (or ξ_{ij}) is equal to a packing fraction of segments η when $i=j$.

Here, for mixtures, the fugacity coefficient of each component can be derived from the differentiation of the residual Helmholtz free energy with respect to the number of molecules of component. The resulting relation is obtained as follows:

$$\ln \hat{\phi}_k = 2 \rho \kappa_k \sum_i x_i r_i b_{ik}(T) W_{ik} + \rho \sum_{ij} x_i x_j r_i r_j b_{ij}(T) \left(N \frac{\partial W_{ij}}{\partial N_k} \right)$$

$$- \sum_i x_i (r_i - 1) \left(N \frac{\partial Q_{ii}}{\partial N_k} \right) - (r_k - 1) Q_{kk} - 2 r_k \rho / kT \sum_i x_i r_i a_{ik}(T) + \left[\sum_{A_i} \left[\ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_k \right] + \sum_{i \neq k} x_i \sum_{A_i} \left[\frac{1}{X^{A_i}} - \frac{1}{2} \right] \left(N \frac{\partial X^{A_i}}{\partial N_k} \right) - \ln Z \quad (39)$$

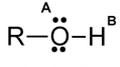
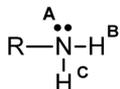
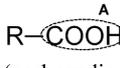
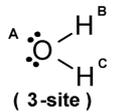
where the differential terms, $\left(N \frac{\partial W_{ij}}{\partial N_k} \right)$, $\left(N \frac{\partial Q_{ii}}{\partial N_k} \right)$ and $\left(N \frac{\partial X^{A_i}}{\partial N_k} \right)$ are summarized in APPENDIX A.

RESULTS AND DISCUSSION

1. Pure Chemical Components

For the self-associating pure fluids such as alcohol, amine and carboxylic acid, etc., the PHSC-AS equation of state (model 1 and 2) described in the previous section requires five adjustable molecular parameters: three parameters from the PHSC part (segment number per molecule r , segment diameter σ and non-bonded segment-segment interaction energy ε) and two association-based parameters (association energy ε^{AB} and association volume κ^{AB}). However, for non-self-associating fluids, the present models have three parameters (r , σ and ε) which are equivalent to that of the Song's model [1996]. Since the association part used in the present models is based on the SAFT theory, all relationships of the molecular associations are similar to the ones of the SAFT model summarized in Table 1. In this work, the five parameters of the self-associating fluids were estimated by simultaneously fitting the saturated vapour pressures and the liquid molar volumes data that were calculated from the correlating relations of the DIPPR data compilation [Daubert et al., 1995]. Generally, when searching for a pure component parameters of the equation of state characterized by the five parameters such as SAFT model, including the present models, the selection of an initial value is important because intermolecular terms (dispersive and association term) are intercorrelated. For example, the estimated liquid molar volume can be decreased by decreasing the segment diameter and also decreased by increasing the associa-

Table 1. Relations of association parameters for pure self-associating chemicals

Chemicals	Association parameters	Relations of X^A
 (alcohol)	$\varepsilon^{AA} = \varepsilon^{BB} = 0, \kappa^{AA} = \kappa^{BB} = 0$ $\varepsilon^{AB} \neq 0, \kappa^{AB} \neq 0, \Delta^{AB} \neq 0$	$X^A = X^B = \frac{-1 + \sqrt{1 + 4\rho\Delta^{AB}}}{2\rho\Delta^{AB}}$
 (amine)	$\varepsilon^{AA} = \varepsilon^{BB} = \varepsilon^{CC} = \varepsilon^{BC} = 0$ $\kappa^{AA} = \kappa^{BB} = \kappa^{CC} = \kappa^{BC} = 0$ $\varepsilon^{AB} = \varepsilon^{AC} \neq 0, \kappa^{AB} = \kappa^{AC} \neq 0$ $\Delta^{AB} = \Delta^{AC} \neq 0$	$X^B = X^C = \frac{-(1 - \rho\Delta^{AB}) + \sqrt{(1 - \rho\Delta^{AB})^2 + 8\rho\Delta^{AB}}}{4\rho\Delta^{AB}}$ $X^A = 2X^B - 1$
 (carboxylic acid)	$\varepsilon^{AA} \neq 0, \kappa^{AA} \neq 0, \Delta^{AA} \neq 0$	$X^A = \frac{-1 + \sqrt{1 + 4\rho\Delta^{AA}}}{2\rho\Delta^{AA}}$
 (water, 3-site)	$\varepsilon^{AA} = \varepsilon^{BB} = \varepsilon^{CC} = \varepsilon^{BC} = 0$ $\kappa^{AA} = \kappa^{BB} = \kappa^{CC} = \kappa^{BC} = 0$ $\varepsilon^{AB} = \varepsilon^{AC} \neq 0, \kappa^{AB} = \kappa^{AC} \neq 0$ $\Delta^{AB} = \Delta^{AC} \neq 0$	$X^B = X^C = \frac{-(1 - \rho\Delta^{AB}) + \sqrt{(1 - \rho\Delta^{AB})^2 + 8\rho\Delta^{AB}}}{4\rho\Delta^{AB}}$ $X^A = 2X^B - 1$

tion energy. Thus, owing to such an intercorrelation between parameters, a multiple set of parameters can be obtained. The present models also reveal an intercorrelation between the association energy and the segment diameter as described above. In this work, for determining an optimum set of pure component parameters, we calculated the heat of vaporization (ΔH^v), and then selected the parameter set with the smallest AAD (%) of ΔH^v as parameters of the pure component. Thus, using the method described above, five parameters for each model of the PHSC-AS equation of state were estimated for self-associating fluids; 12 alcohols, 7 primary amines, 7 carboxylic acids and water. The results are summarized in Table B-1 of Appendix B. Table B-1 presents only the results estimated from the model 1, but the results of mode 2 are not listed here. Table B-1 has shown that the present model 1 represents a significant correlation of vapour pressures and saturated liquid molar volumes with an admissible range of error within the experimental accuracy. Model 2, though its results are not shown here, was also found to give a reasonable trend similar to model 1.

Generally in the PHSC model, the segment number per mole-

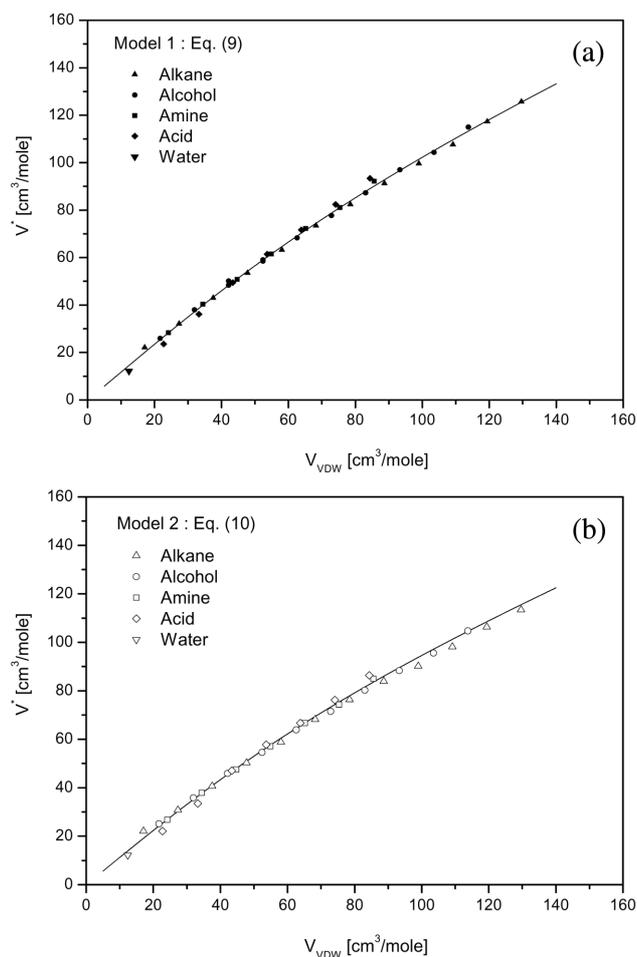


Fig. 1. (a) Correlations of the characteristic volume calculated from estimated molecular parameters (model 1) and van der Waals volume: solid line (—); correlated line. (b) Correlations of the characteristic volume calculated from estimated molecular parameters (model 2) and van der Waals volume: solid line (—); correlated line.

cule r and the segment diameter σ are known to reflect characteristic properties of molecules [Song et al., 1994]. When the characteristic volume, V^* and characteristic surface area, A^* are defined by the combination of r and σ , such as

$$V^* = (\pi/6)r\sigma^3N_w$$

$$A^* = \pi r\sigma^2N_w$$

the characteristic volume and the surface area of molecules can be related to the van der Waals volume and surface area, respectively. In Figs. 1 and 2, V^* and A^* obtained from the estimated parameters r and σ of the model 1 listed in Tables B were correlated with the

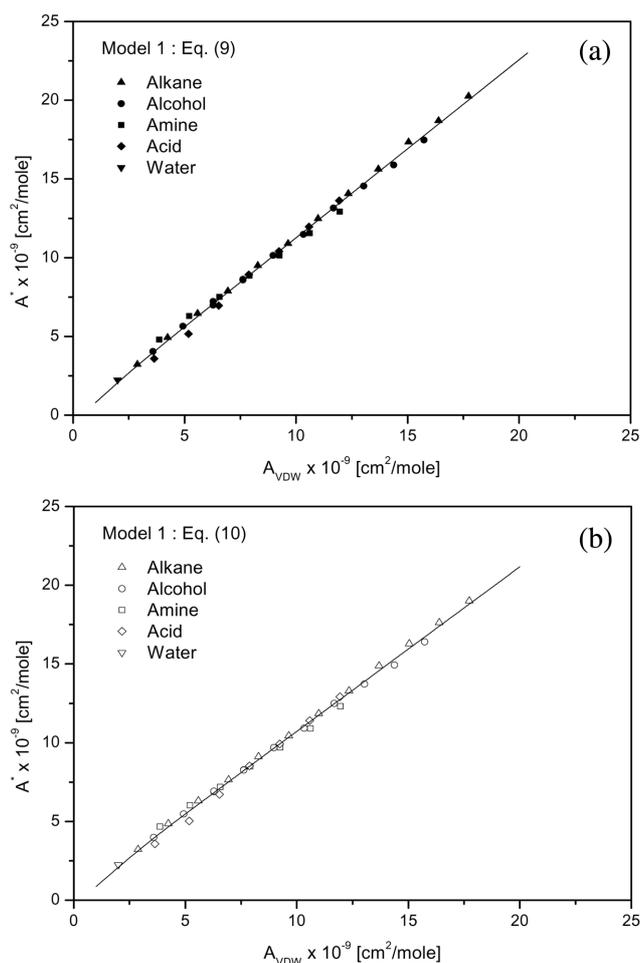


Fig. 2. (a) Correlations of the characteristic surface area calculated from estimated molecular parameters (model 1) and van der Waals surface area: solid line (—); correlated line. (b) Correlations of the characteristic surface area calculated from estimated molecular parameters (model 2) and van der Waals surface area: solid line (—); correlated line.

Table 2. Correlated constants of A^* based on Eq. (40)

Constant	Model 1	Model 2
c_1	1.3141	1.0911
c_2	-0.0495	0.2619
c_3	1.1311	1.0456

Table 3. Estimated 4-parameters (or 2-parameters) of the PHSC-AS (Model 1) EoS

Chemicals	Temp. range [K]	A_{vdW}^a $\times 10^{-9}$ [cm ² /mole]	σ^b [Å]	Adjustable parameters				AAD(%)	
				r [-]	ε/k [K]	ε^{AB}/k [K]	κ^{AB} [-]	ΔP^S	ΔV^I
《Alkanes》									
Methane	95-181	2.88	4.1793	0.9488	190.94	-	-	2.85	1.85
Ethane	153-290	4.24	4.0277	1.5406	220.84	-	-	2.46	2.10
Propane	185-351	5.59	4.0748	1.9958	228.81	-	-	2.31	2.27
Butane	213-404	6.94	4.0777	2.4794	232.50	-	-	2.16	2.86
Pentane	235-446	8.29	4.0460	3.0116	232.25	-	-	2.58	3.52
Hexane	254-482	9.64	4.0015	3.5831	230.46	-	-	2.55	3.96
Heptane	270-513	10.99	3.9113	4.2779	225.40	-	-	3.49	4.39
Octane	284-540	12.34	3.8634	4.9255	223.00	-	-	3.71	4.75
Nonane	297-565	13.69	3.7922	5.6734	219.16	-	-	3.77	5.19
Decane	309-587	15.04	3.7695	6.3100	218.26	-	-	3.90	5.16
Undecane	320-607	16.39	3.7300	7.0242	216.24	-	-	3.54	5.43
Dodecane	329-625	17.74	3.7086	7.6925	215.21	-	-	3.74	5.54
(overall average)								(3.09)	(3.92)
《Alcohols》									
Methanol	256-487	3.58	3.8349	1.4246	245.65	2708.27	0.023631	0.99	1.00
Ethanol	257-488	4.93	4.1292	1.7107	265.02	2750.66	0.009649	0.62	1.13
1-Propanol	268-510	6.28	4.1301	2.1853	262.28	2764.67	0.007910	0.97	2.22
2-Propanol	254-483	6.28	4.2605	2.0535	261.14	2693.06	0.005929	0.84	1.22
1-Butanol	282-535	7.62	4.1313	2.6538	255.99	2724.40	0.010059	0.71	3.10
2-Butanol	268-509	7.62	4.1187	2.6701	250.35	2600.42	0.006823	0.66	2.96
Pentanol	293-557	8.98	4.1046	3.1711	254.18	2567.56	0.013800	1.29	3.70
Hexanol	306-581	10.33	4.0472	3.7546	250.32	2524.29	0.014882	0.95	4.99
Heptanol	316-600	11.68	3.9735	4.4064	248.16	2603.08	0.010103	1.71	5.30
Octanol	326-620	13.03	4.0008	4.8506	245.64	2501.22	0.015525	1.16	5.25
Nonanol	334-635	14.38	3.9815	5.4069	242.34	2554.00	0.015120	2.10	6.48
Decanol	342-650	15.73	3.9534	6.0004	239.83	2535.53	0.015783	2.63	6.01
(overall average)								(1.22)	(3.61)
《Amines》									
Methanamine	215-409	3.86	4.1407	1.3224	317.67	1078.52	0.009098	0.79	1.20
Ethanamine	228-433	5.21	4.3629	1.6210	287.51	1034.75	0.020496	0.75	0.76
Propanamine	248-472	6.56	4.1280	2.2858	218.99	1291.86	0.075291	0.65	1.68
Butanamine	266-505	7.91	4.1980	2.6685	229.08	1229.53	0.092697	0.67	2.50
Pentanamine	278-527	9.26	4.0861	3.3002	212.35	1364.43	0.131496	1.31	2.68
Hexanamine	292-555	10.61	4.0014	3.9455	205.09	1430.58	0.187755	2.26	3.37
Heptanamine	304-577	11.96	3.9999	4.4530	206.48	1459.17	0.214974	1.90	3.22
(overall average)								(1.19)	(2.20)
《Carboxylic acid》									
Methanoic acid	294-559	3.6344	3.3465	1.9005	262.24	7071.09	0.026119	5.59	6.68
Ethanoic acid	296-562	5.18	3.9230	1.9932	327.04	2959.04	0.038403	2.02	0.43
Propanoic acid	300-571	6.53	3.9377	2.5005	288.67	4154.03	0.005968	1.68	1.24
Butanoic acid	308-585	7.88	4.0702	2.8279	297.43	4467.68	0.001599	1.36	1.60
Pentanoic acid	320-607	9.23	4.0631	3.3267	285.71	4689.65	0.001403	1.25	2.27
Hexanoic acid	330-626	10.58	4.0864	3.7724	287.65	5031.43	0.000443	2.27	3.10
Heptanoic acid	338-643	11.93	4.1517	4.1228	284.26	5114.31	0.000445	2.60	2.47
(overall average)								(2.39)	(2.53)
Water (3-site)	324-615	2.26	3.0179	1.3802	431.62	1545.95	0.037450	0.75	4.17
(Grand Average)								(1.99)	(3.27)

^aDIPPR data compilation [Daubert et al., 1995].^bCalculated values based on Eq. (40).

Table 4. Estimated 4-parameters (or 2-parameters) of the PHSC-AS (Model 2) EoS

Chemicals	Temp. range [K]	A_{vdW}^a $\times 10^{-9}$ [cm ² /mole]	σ^b [Å]	Adjustable parameters				AAD(%)	
				r [-]	ε/k [K]	ε^{AB}/k [K]	κ^{AB} [-]	ΔP^S	ΔV^I
《Alkanes》									
Methane	95-181	2.88	4.1966	0.9400	191.74	-	-	2.91	1.95
Ethane	153-290	4.24	3.9532	1.5725	222.68	-	-	2.70	2.41
Propane	185-351	5.59	3.9759	2.0374	233.35	-	-	2.80	2.66
Butane	213-404	6.94	3.9662	2.5250	239.39	-	-	2.77	3.15
Pentane	235-446	8.29	3.9208	3.0701	240.51	-	-	3.18	3.83
Hexane	254-482	9.64	3.8606	3.6676	239.29	-	-	3.16	4.30
Heptane	270-513	10.99	3.7523	4.4122	234.14	-	-	4.12	4.84
Octane	284-540	12.34	3.6888	5.1138	231.60	-	-	4.40	5.24
Nonane	297-565	13.69	3.6022	5.9377	227.33	-	-	4.54	5.73
Decane	309-587	15.04	3.5596	6.6696	225.83	-	-	4.69	5.79
Undecane	320-607	16.39	3.5058	7.4830	223.34	-	-	4.38	6.07
Dodecane	329-625	17.74	3.4712	8.2519	221.90	-	-	4.60	6.20
(overall average)								(3.69)	(4.35)
《Alcohols》									
Methanol	256-487	3.58	3.8691	1.3857	265.90	2665.26	0.020607	0.99	0.46
Ethanol	257-488	4.93	4.0193	1.7642	265.86	2777.80	0.010438	0.68	1.55
1-Propanol	268-510	6.28	4.0313	2.2186	269.04	2802.04	0.008136	0.78	2.54
2-Propanol	254-483	6.28	4.1493	2.0941	263.27	2747.98	0.006486	0.83	1.60
1-Butanol	282-535	7.62	4.0337	2.6728	266.43	2765.45	0.009966	0.78	3.42
2-Butanol	268-509	7.62	4.0255	2.6837	259.37	2660.89	0.006775	0.78	3.25
Pentanol	293-557	8.98	4.0244	3.1498	266.71	2652.43	0.012739	1.42	3.99
Hexanol	306-581	10.33	3.9480	3.7517	260.31	2628.18	0.015634	1.06	5.27
Heptanol	316-600	11.68	3.8583	4.4294	256.50	2658.14	0.014357	1.68	5.38
Octanol	326-620	13.03	3.8907	4.8487	258.66	2645.20	0.013990	1.32	5.56
Nonanol	334-635	14.38	3.8677	5.4053	254.66	2701.45	0.015041	2.34	6.77
Decanol	342-650	15.73	3.8203	6.0516	249.61	2688.78	0.018950	3.00	6.27
(overall average)								(1.31)	(3.84)
《Amines》									
Methanamine	215-409	3.86	4.1065	1.3272	319.54	1095.28	0.009678	0.77	1.17
Ethanamine	228-433	5.21	4.3311	1.6033	293.42	1081.90	0.020587	0.76	0.73
Propanamine	248-472	6.56	4.0570	2.2850	230.64	1293.75	0.073138	0.58	1.98
Butanamine	266-505	7.91	4.1124	2.6664	239.33	1270.82	0.090186	0.76	2.86
Pentanamine	278-527	9.26	4.0021	3.2816	225.19	1401.29	0.122694	1.82	3.08
Hexanamine	292-555	10.61	3.9040	3.9382	217.63	1481.93	0.173672	2.85	3.80
Heptanamine	304-577	11.96	3.8806	4.4812	217.56	1541.23	0.198631	2.44	3.70
(overall average)								(1.43)	(2.48)
《Carboxylic acid》									
Methanoic acid	294-559	3.6344	3.2730	1.9661	266.21	6419.96	0.036507	6.06	8.36
Ethanoic acid	296-562	5.18	3.8595	2.0078	340.47	2935.76	0.035488	2.15	0.46
Propanoic acid	300-571	6.53	3.8557	2.5187	302.94	4106.68	0.005926	1.89	1.25
Butanoic acid	308-585	7.88	3.9666	2.8554	309.54	4516.34	0.001576	1.41	1.85
Pentanoic acid	320-607	9.23	3.9492	3.3594	296.90	4809.39	0.001346	1.31	2.59
Hexanoic acid	330-626	10.58	3.9921	3.7559	301.65	5218.55	0.000384	2.39	3.34
Heptanoic acid	338-643	11.93	4.0513	4.1016	297.63	5379.27	0.000367	2.79	2.73
(overall average)								(2.57)	(2.94)
Water (3-site)	324-615	2.26	2.8665	1.5452	414.09	1466.25	0.050374	0.81	4.90
(Grand average)								(2.27)	(3.62)

^aDIPPR data compilation [Daubert et al., 1995].^bCalculated values based on Eq. (40).

van der Waals volume, V_{vdW} and the van der Waals surface area, A_{vdW} , respectively, based on the following:

$$Y^* = [1 - \exp(-c_1 X_{vdW})](c_2 + c_3 X_{vdW}) \quad (40)$$

where Y^* is the characteristic surface area, $A^* \cdot 10^{-9}$ [cm^2/mole] (or the characteristic volume, V^* [cm^3/mole]), and X_{vdW} is the van der Waals surface area, $A_{vdW} \cdot 10^{-9}$ [cm^2/mole] (or the van der Waals volume, V_{vdW} [cm^3/mole]). Additionally, in Figs. 1 and 2, V^* and A^* obtained from the model 2 also were correlated with van der Waals volume and surface area, respectively. In these figures, the characteristic volume and the surface area over all chemicals tested in this work are shown to be separately located around the correlated line. But the characteristic surface area are more well correlated with the van der Waals surface area rather than the case of the characteristic volume. In this work, to reduce the number of parameters of the present model, we used a correlation between the characteristic surface area calculated from the PHSC-AS parameters and the van der Waals surface area. Correlation constants, c_1 , c_2 and c_3 of Eq. (40) for the characteristic surface area, A^* are given Table 2, and these constants are universal constants to be available for all chemical compounds. If r or σ is selected as an adjustable parameter of the EoS, and the other is directly determined by the correlated relation of the characteristic surface area based on Eq. (40). In this work, the number of segment per molecules, r was assumed to be an adjustable parameter of the equation of state. As a result, the present equation of state has four adjustable parameters (r , ε/k , ε^{AB}/k , and κ^{AB}) for a self-associating fluid, and two parameters (r , ε/k) for a non self-associating fluid.

Four parameters (two parameters for a non self-associating fluid) were calculated by a method similar to the case for the five parameters (presented in Tables B-1 of Appendix B). The calculated results are given in Tables 3 and 4. From these tables, the 4-parameter PHSC-AS equation of state can be seen to give slightly poor correlations of saturated vapour pressures and liquid molar volume, compared to the 5-parameter PHSC-AS equation of state. However, it is likely that the 4-parameter PHSC-AS equation of state as well as the 5-parameter equation of state is useful for correlating saturated vapour pressures and liquid molar volumes within the error range to be generally allowable in the applied area of the equation of state. Also, the results of model 1 (of 4-parameter PHSC-AS EoS) listed in Table 3 are nearly similar to that of model 2 in Table 4. Meanwhile, the molecular weight dependency of the estimated 4-parameters was considered. Fig. 3 shows that the number of segments per molecule for n-alkane, alcohol, amine and carboxylic acid r has a significant correlation with the molecular weight. The number of hard-sphere segments increases smoothly along with the molar mass of molecules. The hard-sphere energy ε/k , playing an important role in the phase equilibria calculation, is in the ranges of 200-330 K for all self-associating chemicals, and 190-230 K for alkanes (refer to Table 3 and 4), while this parameter ε/k is not seen to be correlated with the molar mass of molecules. Also, association parameters, ε^{AB}/k and κ^{AB} , do not show a correlation with the molecular weight. In addition, for comparing the phase equilibria description capability for the present model (PHSC-AS) with the PC-SAFT model, we re-estimated parameters of the PC-SAFT EoS for self-associating compounds, over the temperature range which is equal to the range of the estimated parameters of the present equation of state. The

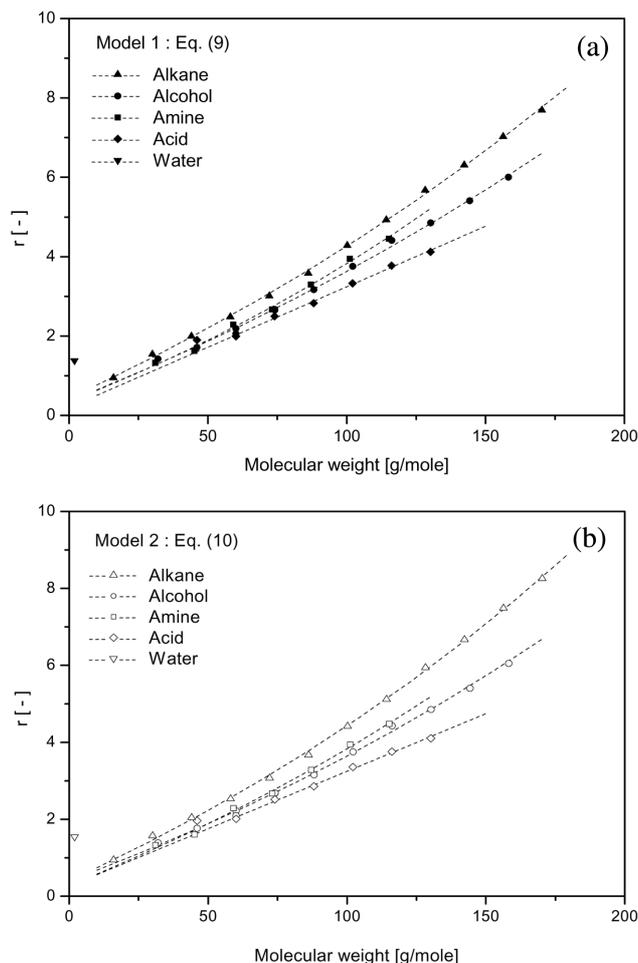


Fig. 3. (a) Plotting of the segment number r with the molecular weight for model 1. (b) Plotting of the segment number r with the molecular weight for model 2.

results are given in Table B-2 of APPENDIX B.

2. Phase Equilibria Calculations

The PHSC-AS equations of state, model 1 and 2 proposed in this work were applied to the calculation of vapour-liquid equilibria for the mixtures containing a associating chemicals such as Alcohol/Paraffin, Alcohol/Alcohol, Alcohol/Carboxylic acid, Amine/Alcohol and Alcohol/Water systems. The binary experimental data in these systems were obtained from the DECHEMA data collection [Gmehling et al., 1982]. All binary systems tested in this work, except for the Alcohol/Paraffin system, form a cross-association owing to hydrogen bonding between functional groups located in the molecules of different chemical components. In these systems, cross-association parameters, ε^{AB}/k and κ^{AB} were obtained from the combining rule of Eqs. (28) and (29). Then, in the calculations of VLE, the present PHSC-AS equations of state were coupled with pure component parameters listed in Tables 3 and 4, which were estimated along with the relation of Eq. (40). The VLE calculated results, optimized interaction parameters and the average deviations of pressure and composition, are summarized in Table 5 with comparisons of the results from models 1 and 2, as well as comparisons of results of the present models and that of PC-SAFT model. As shown in this table, the calculated results by using the present two

Table 5. Calculated results of VLE for the associating mixtures

Systems	Temp. [K]	Model 1			Model 2			PC-SAFT model		
		k_{12}	ΔP (%)	Δy	k_{12}	ΔP (%)	Δy	k_{12}	ΔP (%)	Δy
Methanol/Pentane	372.70	0.0485	2.293	0.0173	0.0459	2.906	0.0187	0.0541	1.446	0.0172
	397.70	0.0458	3.713	0.0193	0.0467	4.084	0.0193	0.0474	2.651	0.0204
	422.60	0.0533	4.594	0.0177	0.0538	5.514	0.0218	0.0553	1.616	0.0094
Methanol/Hexane	318.15	0.0378	1.015	-	0.0351	1.299	-	0.0444	0.710	-
	333.15	0.0434	2.743	0.0130	0.0404	3.196	0.0159	0.0498	2.126	0.0145
	343.15	0.0415	1.315	-	0.0394	1.836	-	0.0486	1.273	-
Ethanol/Heptane	313.15	0.0226	1.171	0.0140	0.0226	1.262	0.0138	0.0295	0.877	0.0150
	333.15	0.0238	1.260	0.0094	0.0240	1.236	0.0098	0.0316	1.556	0.0086
Ethanol/Octane	318.15	0.0237	2.369	0.0073	0.0241	2.347	0.0081	0.0293	2.267	0.0082
	328.15	0.0227	3.413	0.0110	0.0230	3.395	0.0116	0.0289	3.508	0.0119
	338.15	0.0273	1.493	0.0052	0.0278	1.368	0.0057	0.0340	1.689	0.0052
1-Propanol/Heptane	318.15	0.0171	1.112	-	0.0171	1.257	-	0.0203	2.445	-
	333.15	0.0143	1.917	0.0174	0.0151	2.067	0.0177	0.0271	3.451	0.0275
1-Butanol/Octane	373.15	0.0094	1.024	-	0.0102	1.029	-	0.0168	0.946	-
	383.15	0.0091	1.185	-	0.0100	1.106	-	0.0175	0.822	-
1-Pentanol/Octane	363.27	0.0021	1.158	-	0.0030	1.409	-	0.0129	2.895	-
	373.32	0.0020	1.053	-	0.0030	1.237	-	0.0264	3.349	-
1-Hexanol/Hexane	333.15	0.0036	2.155	-	0.0046	2.620	-	0.0077	1.810	-
	353.15	0.0027	1.626	-	0.0036	1.954	-	0.0087	2.214	-
(overall average)			(1.927)	(0.0132)		(2.164)	(0.0142)		(1.982)	(0.0138)
Methanol/Ethanol	373.15	0.0020	0.290	0.0023	-0.0016	0.334	0.0017	-0.0006	0.604	0.0030
	393.15	-0.0017	0.619	0.0026	-0.0054	0.875	0.0024	-0.0041	0.307	0.0024
Methanol/1-Propanol	333.17	0.0109	1.073	0.0022	0.0081	0.875	0.0016	-0.0066	0.995	0.0017
Methanol/2-Propanol	328.15	0.0102	0.887	0.0047	0.0057	0.956	0.0052	-0.0016	0.961	0.0056
Ethanol/1-Propanol	343.15	0.0185	1.282	0.0055	0.0185	1.128	0.0054	0.0107	0.719	0.0064
	353.15	0.0182	0.473	0.0053	0.0182	0.422	0.0054	0.0107	0.436	0.0073
2-Butanol/1-Butanol	313.15	0.0059	0.876	0.0035	0.0057	0.954	0.0034	0.0046	0.871	0.0050
(overall average)			(0.786)	(0.0037)		(0.792)	(0.0036)		(0.699)	(0.0045)
Propanamine/1-Propanol	302.15	-0.0559	2.336	-	-0.0559	2.250	-	-0.0470	2.196	-
	312.15	-0.0567	1.075	-	-0.0569	1.160	-	-0.0488	0.840	-
Butanamine/Ethanol	313.15	-0.0548	1.167	0.0076	-0.0553	1.051	0.0076	-0.0680	1.283	0.0125
Butanamine/1-Propanol	313.15	-0.0582	1.287	0.0090	-0.0586	1.218	0.0089	-0.0579	0.908	0.0054
	318.15	-0.0585	2.006	0.0042	-0.0589	1.869	0.0040	-0.0581	1.136	0.0035
Butanamine/Butanol	313.15	-0.0175	1.387	0.0062	-0.0180	1.322	0.0062	-0.0277	1.232	0.0053
(overall average)			(1.543)	(0.0068)		(1.478)	(0.0067)		(1.266)	(0.0067)
Methanol/Propanoic acid	308.21	0.0017	7.047	-	0.0015	7.046	-	-0.0026	6.888	-
	318.16	0.0012	6.516	-	0.0070	6.527	-	-0.0022	6.348	-
Ethanol/Ethanoic acid	308.15	-0.0297	3.276	0.0139	-0.0310	3.337	0.0140	0.0055	4.245	0.0120
	318.15	-0.0306	2.682	0.0139	-0.0319	2.720	0.0139	0.0046	4.630	0.0171
1-Butanol/Methanoic acid	308.15	0.0705	15.209	0.0307	0.0708	16.295	0.0283	0.0456	9.813	0.0380
	318.15	0.0794	7.144	0.0235	0.0802	8.127	0.0207	0.0512	8.986	0.0344
1-Butanol/Ethanoic acid	308.15	-0.0453	5.822	0.0257	-0.0452	5.708	0.0256	-0.0090	2.447	0.0182
	318.15	-0.0349	7.894	0.0431	-0.0350	7.892	0.0430	0.0038	4.010	0.0337
(overall average)			(6.949)	(0.0251)		(7.207)	(0.0243)		(5.921)	(0.0256)
Methanol/Water	312.91	-0.1032	2.235	0.0441	-0.0933	2.114	0.0429	-0.1115	2.985	0.0523
	333.15	-0.0971	1.180	0.0087	-0.0871	1.510	0.0095	-0.0986	2.381	0.0158
Ethanol/Water	328.15	-0.0755	3.052	0.0136	-0.0768	2.971	0.0121	-0.0721	3.438	0.0206
	343.15	-0.0705	2.914	0.0114	-0.0715	2.770	0.0105	-0.0651	3.219	0.0164
(overall average)			(2.345)	(0.0195)		(2.341)	(0.0188)		(3.006)	(0.0263)
(Grand Average)			(2.723)	(0.0141)		(2.882)	(0.0141)		(2.592)	(0.0157)

$$* \Delta P(\%) = 1/N \sum_i |(P_{exp} - P_{cal})/P_{exp}| \times 100, \Delta y = 1/N \sum_i |y_{cal} - y_{exp}|$$

models may have somewhat poor agreement with experimental data compared to the PC-SAFT model, but the present models have a

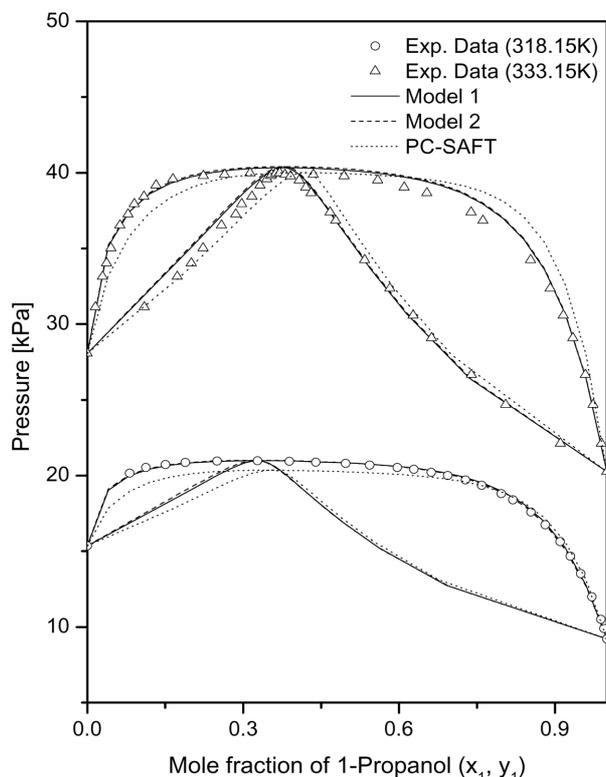


Fig. 4. Vapour-liquid equilibria of the 1-propanol(1)/heptane(2) system.

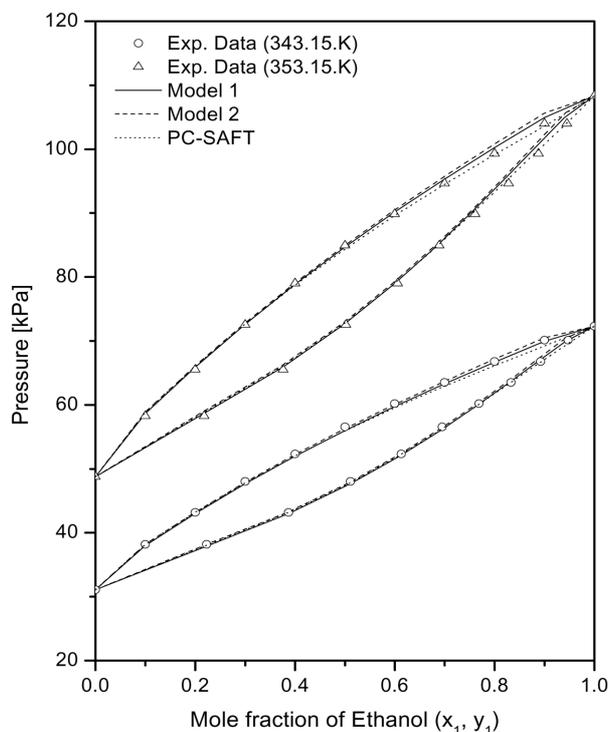


Fig. 5. Vapour-liquid equilibria of the ethanol(1)/1-propanol(2) system.

predictive capability of VLE with an accuracy to be generally acceptable in the procedure of phase equilibria calculating for chemical process design. Meanwhile, no differences between model 1 and 2 of the present PHSC-AS equation of state were found for all binary systems tested in this work. Fig. 4 shows the calculated results of the 1-propanol/heptane system which does not form cross-associations, and the present models yield a good agreement with experimental data. Fig. 5 shows the result of the ethanol/1-propanol systems which form a hydrogen bonding between OH groups. Fig. 6 also gives a comparison between the experimental vapour-liquid equilibria data and results using the present models for the butanamine/1-propanol system. This system shows a cross association between the OH group of alcohol molecules and the NH_2 group of amine molecules, and also a self-association between alcohol and amine molecules, respectively. As shown in Figs. 5 and 6, the present models provide a good correlation of VLE. Fig. 7 is the calculated results for the 1-butanol/methanoic acid mixtures which form a cross association between alcohol and carboxylic acid molecules, as in the alcohol/amine system. As seen in Fig. 7, the present models provide a slightly poor correlation for the 1-butanol/ethanoic acid system, while the PC-SAFT model shows a similar tendency. In Fig. 8, the calculated results for the ethanol/water system are compared to the experimental data, where the present models show a predictive capability of VLE comparable to the PC-SAFT model, for the azeotropic mixture.

CONCLUSIONS

In this work, the PHSC equation of state has been extended to

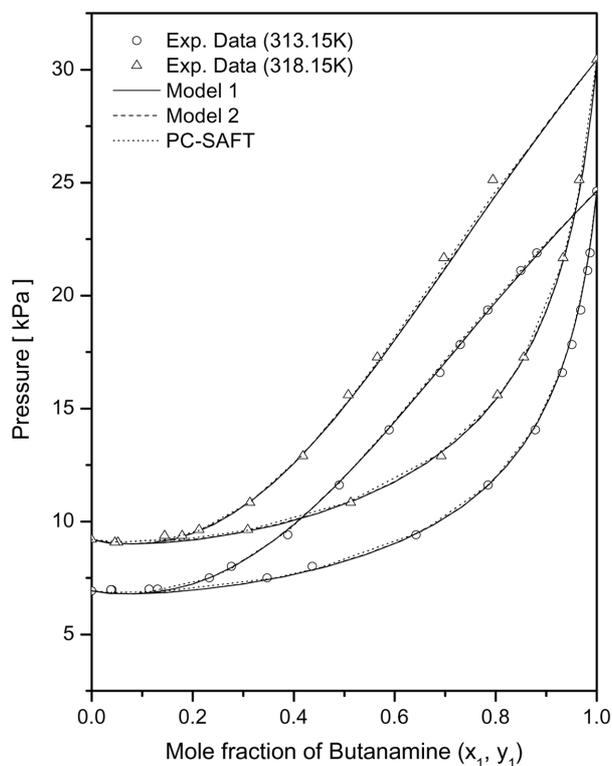


Fig. 6. Vapour-liquid equilibria of the butanamine(1)/1-propanol(2) system.

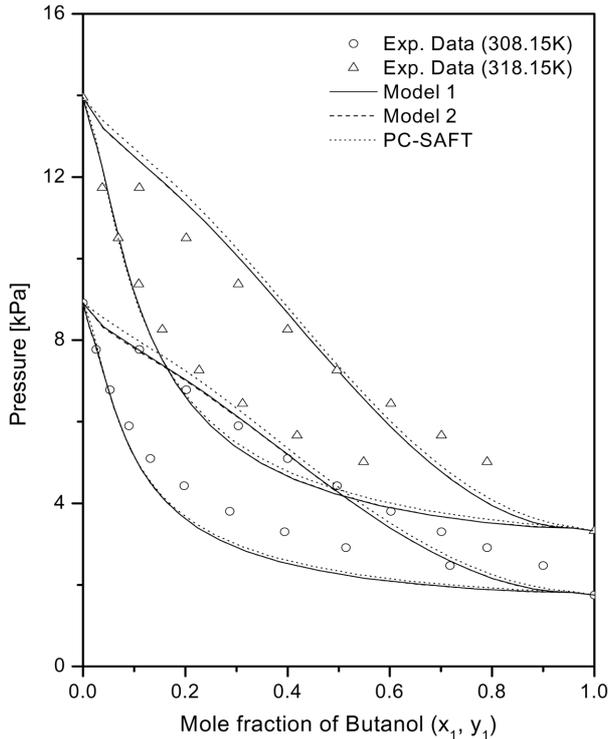


Fig. 7. Vapour-liquid equilibria of the 1-butanol(1)/methanoic acid (2) system.

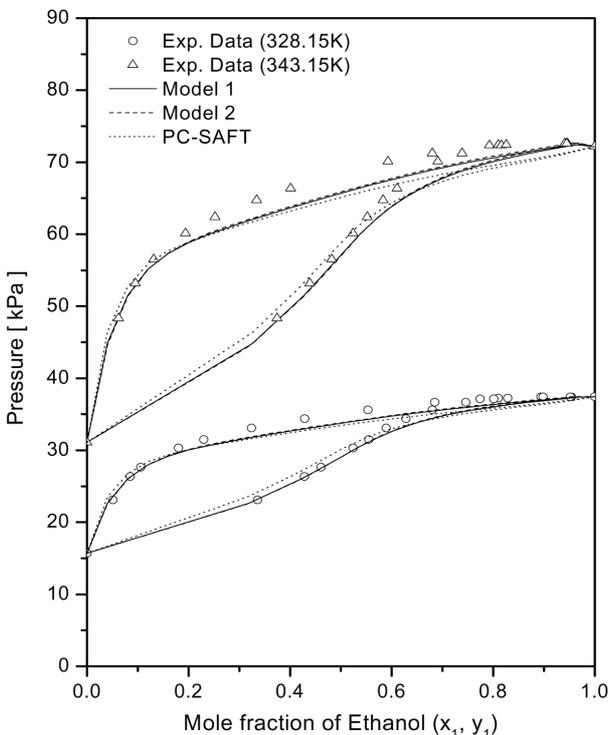


Fig. 8. Vapour-liquid equilibria of the ethanol(1)/water(2) system.

be adaptable to the associating fluid systems. We incorporated an association term of the SAFT model (based on Wertheim's TPT1 theory) into the PHSC model, and obtained the resulting equation

of state named as the PHSC-AS (model 1 and 2). The PHSC-AS equation of state is successfully applied to describing the vapour-liquid equilibria of binary systems containing associating chemical compounds, such as Alcohol/Paraffin, Alcohol/Alcohol, Amine/Alcohol, Alcohol/Carboxylic acid and Alcohol/Water systems. By comparing the calculated results of VLE and experimental data, it has been indicated that the present models (model 1 and 2) have the capability to predict VLE with an accuracy comparable to the PC-SAFT model. In this work, the PHSC-AS equations of state (model 1 and 2) are applied for only the mixture composed of the associating chemicals with a low molecular weight. Nevertheless, it is anticipated that the PHSC-AS model may be more useful for describing phase equilibria of the associating fluid system composed of the high molecular weight chemicals such as oligomers and polymers. Applications of the PHSC-AS equation of state to the associating polymer system will be accomplished in our next work.

APPENDIX A

W_{ij} of Eq. (36) has independent variables, η and ξ_{ij} . The differential of $W_{ij}(\eta, \xi_{ij})$ with respect to the number of molecule, N_k can be expressed as:

$$\left(N \frac{\partial W_{ij}}{\partial N_k}\right) = \left(\frac{\partial W_{ij}}{\partial \eta}\right) \left(N \frac{\partial \eta}{\partial N_k}\right) + \left(\frac{\partial W_{ij}}{\partial \xi_{ij}}\right) \left(N \frac{\partial \xi_{ij}}{\partial N_k}\right) \quad (\text{A-1})$$

with

$$\begin{aligned} \frac{\partial W_{ij}}{\partial \eta} = & \frac{1}{\eta(1-\eta)} + \frac{\ln(1-\eta)}{\eta^2} + \frac{3}{2} \frac{\xi_{ij}}{\eta^3} \left[-\frac{2\ln(1-\eta)}{\eta^3} + \frac{3\eta-2}{\eta^2(1-\eta)^2} \right] \\ & + \frac{1}{2} \frac{\xi_{ij}^2}{\eta^4} \left[\frac{3\ln(1-\eta)}{\eta^4} + \frac{4\eta^2-6\eta+3}{\eta^3(1-\eta)^3} - \frac{3}{2} \frac{1}{\eta^2(1-\eta)^2} \right] \end{aligned} \quad (\text{A-2})$$

$$\begin{aligned} \frac{\partial W_{ij}}{\partial \xi_{ij}} = & \frac{3}{2} \frac{1}{\eta^2} \left[\ln(1-\eta) + \frac{\eta}{1-\eta} \right] \\ & + \frac{\xi_{ij}}{\eta^3} \left[-\ln(1-\eta) - \frac{\eta}{1-\eta} + \frac{1}{2} \frac{\eta^2}{(1-\eta)^2} \right] \end{aligned} \quad (\text{A-3})$$

and the differential form of η and ξ_{ij} is defined from Eqs. (22) and (23), respectively, as follows:

$$N \frac{\partial \eta}{\partial N_k} = \frac{\rho r_k b_{kk}}{4} \quad (\text{A-4})$$

$$N \frac{\partial \xi_{ij}}{\partial N_k} = \frac{\rho}{4} \left(\frac{b_{ij} b_{ij}}{b_{ij}} \right)^{1/3} r_k b_{kk}^{2/3} \quad (\text{A-5})$$

The Q_{ij} terms defined in Eq. (37) or (38) are related to different functions according to model 1 and 2. Q_{ij}^{model1} is composed of independent variables, η and ξ_{ij} . Differentials of Q_{ij}^{model1} can be defined as:

$$\left(N \frac{\partial Q_{ij}^{model1}}{\partial N_k}\right) = \left(\frac{\partial Q_{ij}^{model1}}{\partial \eta}\right) \left(N \frac{\partial \eta}{\partial N_k}\right) + \left(\frac{\partial Q_{ij}^{model1}}{\partial \xi_{ij}}\right) \left(N \frac{\partial \xi_{ij}}{\partial N_k}\right) \quad (\text{A-6})$$

with

$$\frac{\partial Q_{ij}^{model1}}{\partial \eta} = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1-\eta)^3} \quad (\text{A-7})$$

$$\frac{\partial Q_{ij}^{model1}}{\partial \xi_{ij}} = \frac{3}{2} \frac{1}{(1-\eta)} + \frac{1}{2} \frac{\xi_{ij}}{(1-\eta)^2} \quad (\text{A-8})$$

and the differential of Q_{ij}^{model2} is obtained as:

$$N \frac{\partial Q_{ij}^{model2}}{\partial N_k} = \frac{1}{g_{ij}^{hs}(d_{ij}^+)} \left(N \frac{\partial g_{ij}^{hs}(d_{ij}^+)}{\partial N_k} \right) \quad (A-9)$$

where

$$N \frac{\partial g_{ij}^{hs}(d_{ij}^+)}{\partial N_k} = \left(\frac{\partial g_{ij}^{hs}(d_{ij}^+)}{\partial \eta} \right) \left(N \frac{\partial \eta}{\partial N_k} \right) + \left(\frac{\partial g_{ij}^{hs}(d_{ij}^+)}{\partial \xi_{ij}} \right) \left(N \frac{\partial \xi_{ij}}{\partial N_k} \right) \quad (A-10)$$

$$\frac{\partial g_{ij}^{hs}(d_{ij}^+)}{\partial \eta} = \frac{1}{(1-\eta)^2} + 3 \frac{\xi_{ij}}{(1-\eta)^3} + \frac{3}{2} \frac{\xi_{ij}^2}{(1-\eta)^4} \quad (A-11)$$

$$\frac{\partial g_{ij}^{hs}(d_{ij}^+)}{\partial \xi_{ij}} = \frac{3}{2} \frac{1}{(1-\eta)^2} + \frac{\xi_{ij}}{(1-\eta)^3} \quad (A-12)$$

Based on the SAFT model, X^{A_i} is the mole fraction of molecules not bonded at the association site A on the molecule of the component i. The differential of X^{A_i} is expressed as:

$$N \frac{\partial X^{A_i}}{\partial N_k} = \left(N \frac{\partial \rho_k}{\partial N_k} \right) \left(\frac{\partial X^{A_i}}{\partial \rho_k} \right) \quad (A-13)$$

$$N \frac{\partial \rho_k}{\partial N_k} = \rho \quad (A-14)$$

where $(\partial X^{A_i} / \partial \rho_k)$ is numerically evaluated from simultaneous algebra equations derived by Eq. (19).

APPENDIX B

Table B-1. Estimated 5-parameters (or 3-parameters) of the PHSC-AS (Model 1) EoS

Chemicals	Temp. range [K]	Parameters					AAD (%)		
		r [-]	σ [Å]	ε/k [K]	ε^{AB}/k [K]	κ^{AB} [-]	ΔP^s	ΔV^l	ΔH^v
《Alkanes》									
Methane	95-181	1.0000	4.1257	182.13	-	-	-	-	-
Ethane	153-290	1.6973	3.9139	206.02	-	-	0.65	1.32	2.14
Propane	185-351	2.1385	3.9939	218.33	-	-	0.94	1.99	9.85
Butane	213-404	2.4978	4.0816	231.26	-	-	1.49	2.49	1.05
Pentane	235-446	3.1509	3.9912	225.90	-	-	1.91	3.37	1.07
Hexane	254-482	3.5101	4.0486	233.11	-	-	1.79	3.42	1.25
Heptane	270-513	4.2055	3.9605	227.36	-	-	2.86	3.80	1.02
Octane	284-540	4.9173	3.8890	222.98	-	-	2.99	4.21	1.31
Nonane	297-565	5.6362	3.8271	219.65	-	-	3.06	4.56	1.54
Decane	309-587	6.6130	3.7236	212.83	-	-	3.11	4.87	1.54
Undecane	320-607	6.9827	3.7626	216.68	-	-	2.85	4.77	1.44
Dodecane	329-625	7.7203	3.7238	214.65	-	-	2.96	4.95	1.51
(overall average)							(2.24)	(3.61)	(2.16)
《Alcohols》									
Methanol	256-487	1.4426	3.8492	257.23	2628.79	0.021873	0.97	0.45	2.69
Ethanol	257-488	1.8213	4.0448	265.38	2644.31	0.010493	0.92	1.22	0.96
1-Propanol	268-510	2.3632	4.0178	259.35	2645.12	0.008734	0.54	2.49	1.39
2-Propanol	254-483	1.9821	4.3130	262.26	2736.79	0.005827	0.62	0.84	1.94
1-Butanol	282-535	2.7462	4.0738	254.05	2678.67	0.010513	0.49	3.31	3.65
2-Butanol	268-509	2.6765	4.1166	246.41	2629.67	0.007382	0.58	2.34	2.98
Pentanol	293-557	3.2857	4.0403	250.76	2527.71	0.014937	1.25	3.93	3.42
Hexanol	306-581	3.6791	4.0608	250.05	2556.76	0.016222	0.61	4.88	2.47
Heptanol	316-600	4.3870	3.9809	250.91	2592.95	0.008673	1.39	5.28	2.83
Octanol	326-620	4.7993	4.0024	249.55	2557.29	0.010973	1.27	5.35	4.35
Nonanol	334-635	5.4178	3.9378	242.56	2535.59	0.015996	2.09	6.18	1.25
Decanol	342-650	5.9332	3.9463	241.60	2629.53	0.012317	3.30	5.94	1.82
(overall average)							(1.17)	(3.52)	(2.48)
《Amines》									
Methanamine	215-409	2.0095	3.5489	216.28	993.89	0.062737	0.50	0.41	3.65
Ethanamine	228-433	2.2393	3.8529	215.18	1009.96	0.081764	0.36	0.58	2.73
Propanamine	248-472	2.4073	4.0599	217.17	1223.88	0.083034	0.39	1.63	2.59
Butanamine	266-505	2.7009	4.1639	225.58	1218.03	0.106736	0.46	2.04	1.89
Pentanamine	278-527	2.9321	4.2753	219.48	1517.00	0.096618	0.47	1.87	0.98
Hexanamine	292-555	3.4338	4.2156	210.91	1663.18	0.125893	1.02	2.40	0.16
Heptanamine	304-577	3.7312	4.2788	215.34	1763.11	0.124847	0.86	2.12	1.18
(overall average)							(0.58)	(1.58)	(1.88)

Table B-1. Continued

Chemicals	Temp. range [K]	Parameters					AAD (%)		
		r [-]	σ [Å]	ε/k [K]	ε^{AB}/k [K]	κ^{AB} [-]	ΔP^S	ΔV^I	ΔH^V
《Carboxylic acid》									
Methanoic acid	294-559	1.3055	3.8105	332.29	7444.00	0.002506	1.97	1.78	24.63
Ethanoic acid	296-562	1.7029	4.0032	297.78	4791.61	0.023000	1.89	2.65	7.96
Propanoic acid	300-571	2.0173	4.2690	324.51	4443.71	0.002835	0.58	0.23	31.58
Butanoic acid	308-585	2.7531	4.1370	312.15	4251.54	0.001258	1.07	1.14	34.16
Pentanoic acid	320-607	3.2126	4.1368	296.56	4585.19	0.001130	0.96	1.74	18.96
Hexanoic acid	330-626	3.7068	4.1307	294.97	4968.85	0.000323	1.69	2.58	14.90
Heptanoic acid	338-643	4.2560	4.1140	283.46	4995.71	0.000390	1.82	2.25	0.66
(overall average)							(1.43)	(1.77)	(18.98)
Water (3-site)	324-615	1.1073	3.2654	534.73	1579.18	0.015820	0.48	2.69	6.43
(Grand Average)							(1.40)	(2.84)	(5.42)

$$* \text{AAD}(\%) = (1/N) \sum_i^N |(X_{\text{exp}} - X_{\text{cal}}) / X_{\text{exp}}| \times 100; X = V^I, P^S \text{ or } H^V$$

Table B-2. Estimated parameters of the PC-SAFT EoS

Chemicals	Temp. range [K]	Parameters					AAD (%)		
		r [-]	σ [Å]	ε/k [K]	ε^{AB}/k [K]	κ^{AB} [-]	ΔP^S	ΔV^I	ΔH^V
《Alkanes》									
Pentane	235-465	2.7005	3.7544	230.87	-	-	0.12	0.46	2.99
Hexane	254-503	3.0636	3.7923	236.64	-	-	0.60	0.56	3.59
Heptane	270-535	3.4886	3.7967	238.33	-	-	0.27	0.61	2.74
Octane	284-563	3.8518	3.8240	241.62	-	-	0.28	0.60	2.22
《Alcohols》									
Methanol	256-508	1.5143	3.2564	193.76	2847.81	0.035224	0.79	0.42	4.97
Ethanol	257-509	2.3862	3.1698	198.00	2655.01	0.032422	0.40	0.13	0.98
1-Propanol	268-531	2.9989	3.2410	233.02	2287.60	0.015464	0.31	0.28	1.59
2-Propanol	254-503	3.1140	3.1986	207.25	2267.24	0.024655	0.32	0.67	2.74
1-Butanol	282-557	2.7346	3.6085	259.27	2566.99	0.006842	0.42	0.34	3.66
2-Butanol	268-531	2.7143	3.6080	250.44	2558.31	0.003991	0.71	0.48	3.52
《Amines》									
Ethanamine	228-452	2.6771	3.1464	221.52	754.00	0.015382	0.25	1.02	2.28
Propanamine	248-492	2.8153	3.3639	230.72	689.81	0.046583	0.67	0.23	2.55
Butanamine	266-527	2.9707	3.5214	247.70	904.52	0.014179	0.18	0.15	1.75
《Carboxylic acid》									
Methanoic acid	294-582	1.1279	3.5780	312.72	5699.27	0.011580	0.38	1.09	19.01
Ethanoic acid	296-586	1.5218	3.6754	281.86	5530.47	0.004598	0.46	0.40	2.77
Propanoic acid	300-595	2.4789	3.4365	252.26	4591.22	0.010296	0.26	0.60	16.93
Butanoic acid	308-610	3.1938	3.4153	255.35	4161.98	0.008720	1.28	0.97	32.12
Water (3-site)	324-641	1.2597	2.7124	371.82	1884.07	0.036563	0.46	2.12	10.32
(Average)							(0.49)	(0.64)	(7.88)

NOMENCLATURE

A^* : characteristic surface area [cm²/mole]

A_{vdW} : van der Waals surface [cm²/mole]

$a(T)$: attractive term

$b(T)$: van der Waals covolume (or excluded volume)

$F_o(Tk/\varepsilon)$: universal function for $a(T)$ term

$F_b(Tk/\varepsilon)$: universal function for $b(T)$ term

$g_{ij}^{hs}(d^i)$: radial distribution function

H^V : the heat of vaporization

k : Boltzmann constant

k_{ij} : binary interaction parameter between i and j components

M : number of association sites on the molecule

N : total number of molecules

N_{av} : Avogadro's number
 P : pressure
 r : number of segments with the molecule (segment number)
 R : gas constant
 T : absolute temperature
 V : total volume
 V^* : characteristic volume [cm^3/mole]
 V_{vdW} : van der Waals volume [cm^3/mole]
 X^d : mole fraction of the compound not bonded at the associating site A
 x_i : mole fraction of component i
 Z : compressibility factor

Greek Letters

ε : dispersion energy parameter
 ε^{AB} : energy parameter of the association between sites A and B
 ξ_{ij} : packing fraction
 η : reduced density
 κ^{AB} : volume parameter of the association between sites A and B
 ρ : number density (number of molecules in unit volume)
 σ : segment diameter
 ϕ : fugacity coefficient
 \sum_A : summation of all the sites (starting with A)

Superscripts

asso : association term
 chain : chain term
 disp : dispersion term
 hs : hard sphere term
 pert : perturbation term
 ref : reference term
 res : residual property

Subscripts

i, j : chemical component i, j
 vdW : van der Waals

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