Fluid Phase Equilibria 425 (2016) 169–176

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modeling the solubility and volumetric properties of H_2 and heavy hydrocarbons using the simplified PC-SAFT

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ARTICLE INFO

Article history:
Received 8 March 2016
Received in revised form
16 May 2016
Accepted 17 May 2016
Available online 19 May 2016

Keywords:
The simplified PC-SAFT
Bitumen
Hydrogen
Solubility
Density
Compressibility
Thermal expansion coefficient

ABSTRACT

The solubility and volumetric properties of H_2 and heavy hydrocarbons are important to the design of many chemical processes. In this paper, a simplified Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) is chosen to model the solubility and volumetric properties of H_2/heavy alkanes and H_2/bitumen mixtures. The number of reduced density roots given by the simplified PC-SAFT is discussed and a robust procedure is employed to solve for the root with the lowest Gibbs free energy. The development of new H_2 parameters and the k_{ij} correlation of H_2-heavy alkane pairs for the simplified PC-SAFT is completed using extensive experimental data. The new parameters are applied with a developed bitumen characterization method to predict H_2 solubility in Athabasca Bitumen. The average absolute deviations (AADs) between the measured solubility data and the modeling results are within 0.57% for the five H_2/heavy alkane systems and 0.69% for the H_2/Athabasca bitumen systems. Finally, the density, thermal expansion coefficient, and compressibility of the systems are predicted over wide ranges of temperature and pressure.

1. Introduction

Unconventional oil resources, such as crude bitumen, are becoming increasingly important as conventional hydrocarbons become more scarce [1]. Although crude bitumen is an extra heavy oil that cannot be easily removed or transported [2], it can be hydrocracked to more valuable light components using refining [3]. This hydrotreatment process requires the knowledge of H_2 solubility in heavy hydrocarbons and their volumetric properties to determine hydrogen consumption [4]. Solubility and density are applied in mass-balance equations to design reformers, hydrocrackers, hydrotreaters and scrubbing units [5]. Furthermore, thermal expansion coefficient and compressibility give the dependence of density on temperature and pressure.

Limited data for H_2 solubility data in heavy alkanes and bitumens at elevated temperatures and pressures has reported [3,5,6]. It is very expensive to assemble an experimental apparatus for solubility measurement at temperatures up to 700 K and pressures up to 20 MPa. Additional difficulties are induced by high viscosity and thermal instability of bitumen. Appropriate experimental procedures must be applied to ensure measured data are reliable. Compared with experimental methods, modeling H_2 solubility using an Equation of State is an economical and efficient option.

From academic point of view, modeling the phase behavior of highly asymmetric mixtures can effectively test the capability of an Equation of State [7]. Bitumen is a mixture of various long-chain hydrocarbons which are characterized as pseudo-components, whereas hydrogen is the lightest gas. Furthermore, hydrogen has extremely low critical temperature but refining process is conducted at quite high temperatures. How well the simplified PC-SAFT predicts the phase behavior of H_2 and heavy hydrocarbons provides insights to its capability to correlate molecular features with macroscopic thermodynamic properties.

It is well known that cubic Equations of State do not produce reliable predictions over wide ranges of temperature and pressure or for high carbon numbers [6,8]. Compared with the empirical cubic equations, molecular models based on statistical mechanics are independent of thermodynamic conditions and can be used with confidence for asymmetrical systems due to their physical

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http://dx.doi.org/10.1016/j.fluid.2016.05.021
0378-3812/

meanings [8,9]. Previous studies have demonstrated that the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT [10]) has superior ability to predict the phase equilibrium and density of highly asymmetrical polymers, asphaltenes, and bitumen systems with solvents [11–15]. For example, Saajanlehto et al. successfully predicted the solubility of H_2 in Athabasca Bitumen using PC-SAFT, while a generalized characterization table for heavy oils significantly underpredicted the molar mass of bitumen [3].

This work employs a simplified version of PC-SAFT [16] to model the solubility and volumetric properties of H_2/heavy alkane and H_2/bitumen systems. As a relatively new model, the simplified PC-SAFT has not been applied to H_2/bitumen systems such that there are three major challenges associated with this model. First, SAFT Equations of State may exhibit more than three roots and must be solved numerically using quite tedious derivatives. Koak et al. reported the conditions for SAFT where up to five roots are found for pure methane and poly (ethylene-propylene) 790 [17]. Privat et al. demonstrated that PC-SAFT exhibits up to five different roots at very low temperatures for pure fluids [18]. Therefore, a generalized algorithm must be applied to find all possible roots and select the root with the lowest Gibbs free energy correctly. The second challenge is that there is a shortage of H_2 parameters for the simplified PC-SAFT. Although H_2 parameters (m, σ, and ε) were developed for PC-SAFT using vapor-liquid equilibrium data for the $H_2/C_{10}H_{22}$ system [8], they are not applicable for the simplified PC-SAFT because the two equations are different for modeling mixtures. In other words, the two equations can apply the same parameters only if the parameters are determined using pure component data [10,16]. Third, the complex phase behaviors and volumetric properties of bitumen with H_2 have not been investigated using the simplified PC-SAFT. A bitumen characterization method [15], where bitumen was characterized into pseudo-components and were applied to model for solvent/bitumen systems, must be tested for H_2/bitumen systems.

In this work, simple first-order and second-order derivatives for reduced density root of the simplified PC-SAFT are given and they are applied with Privat's method to solve for reduced density roots. In addition, the H_2 parameters are determined by matching $H_2/C_{10}H_{22}$ data [6] and a k_{ij} correlation for H_2–alkane pairs is proposed and determined by matching $H_2/n\text{-}C_{16}H_{34}$, $H_2/n\text{-}C_{28}H_{58}$, $H_2/n\text{-}C_{36}H_{74}$, and $H_2/n\text{-}C_{46}H_{94}$ data [6]. The previously developed bitumen characterization method [15], new H_2 parameters, and new k_{ij} correlation of the H_2–alkane pairs are applied to predict H_2 solubility in Athabasca Bitumen and tested against the measure data [5]. Finally, the density, thermal expansion coefficient, and compressibility of H_2 and heavy hydrocarbons are predicted over wide ranges of temperature and pressure.

2. Methodology

2.1. The simplified PC-SAFT

In Perturbed-chain Statistical Associating Fluid Theory (PC-SAFT), molecule chains are assumed to be composed of spherical segments which follow a square-well potential model [10]. In the case of non-associating systems, interactions between the spherical segments are described by a repulsive hard-chain contribution defined as a reference fluid without any attractions and an attractive dispersion contribution formulated as a perturbation to the reference system. Under PC-SAFT, a simplified version called the simplified PC-SAFT assumes that different species of molecular chains apply an average temperature-dependent segment diameter [16]. The simplified PC-SAFT has an advantage over PC-SAFT in computational efficiency and has been demonstrated to be as accurate as the PC-SAFT for modeling hydrocarbon systems [19]. The mathematical formulas for the simplified PC-SAFT in terms of pressure (including density, thermal expansion coefficient, and compressibility) are presented in Appendix A.

2.2. Root selection

The reduced density root is an independent variable in the simplified PC-SAFT which is solved and used for thermodynamics modeling. The number of reduced density roots of pure n-alkanes from CH_4 to $C_{44}H_{90}$, short-chain alkane/long-chain alkane binaries, alkane/CO_2 binaries, and bitumen/solvent systems is investigated. More than three reduced density roots are discovered for all of these systems at extremely low temperatures. However, a maximum of three roots are found in the fluid region and the root with the lowest Gibbs free energy is selected. These findings agree with those of Gross and Sadowski [11], where three reduced density roots are present for PC-SAFT in the case of argon at a reduced temperature (T/T_c) of 0.9.

The reduced density (η) can be expressed as a function of the specific volume (v, $m^3\ mol^{-1}$) [18],

$$v = 3.1532 \times 10^{-7} \cdot \left(\sum_{i=1}^{n_c} x_i m_i d_i^3 \right) \Big/ \eta \tag{1}$$

where n_c is the total number of components in the system; x is the mole fraction; m is the number of segments per chain; d is the T-dependent segment diameter; and i stands for the i-th component in the system.

Fig. 1 shows the CH_4 pressures at three different temperatures, $T_r = 0.95$, $T_r = 1.00$, and $T_r = 1.05$. Using the simplified PC-SAFT, P versus η is plotted on the left and P versus v is shown on the right, both by solid lines. In the right figure, the dashed lines indicate the results by Peng–Robinson EoS [20] and the open symbols are the data from the NIST correlation [21]. When T is less than T_c, a maximum of three η (or v) roots are found; otherwise, only one root is available. The P-v plots using the simplified PC-SAFT and Peng–Robinson EoS are quite similar and they present identical trends to the data using the NIST correlation.

The following procedure proposed by Privat et al. [18] is adopted to solve for the reduced density roots of the simplified PC-SAFT in the fluid region; (1) search for the extreme points (either zero or two points) and solve for them with Newton's method; (2) define the monotonous root intervals using the extreme points; (3) apply Newton's method to solve for the roots (either one or three roots); and (4) select the root with the lowest Gibbs free energy. This method is by no means the fastest approach. However, the definition of monotonous root regions is required for Newton's method, which is robust only if there are no extreme points located between a trial value and the solution.

The P-η plot of CH_4 at $Tr = 0.95$ is shown in Fig. 2 to demonstrate the algorithm. First, the analytical expression of the second-order derivative is used to solve for extreme points using Newton's method. Two extreme points ($\eta_{ep1} = 0.0955$, and $\eta_{ep2} = 0.2114$) are found in the reduced density region. Second, the two extreme points are used to define three monotonous regions (A, B, and C). Third, Newton's method is used to solve for the roots by applying the analytical expression of the first-order derivative. Although the analytical expressions of the first- and second-order derivatives of PC-SAFT have been published elsewhere [18], we have significantly predigested them for the simplified PC-SAFT (Appendix B). These simple reduced density derivatives can promote the application of the simplified PC-SAFT. In this work, an in-house simplified PC-SAFT toolbox is used for root selection, phase equilibrium, and physical properties calculation and optimization [22].