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Prediction of water solubility in petroleum fractions and heavy crudes using cubic-plus-association equation of state (CPA-EoS)

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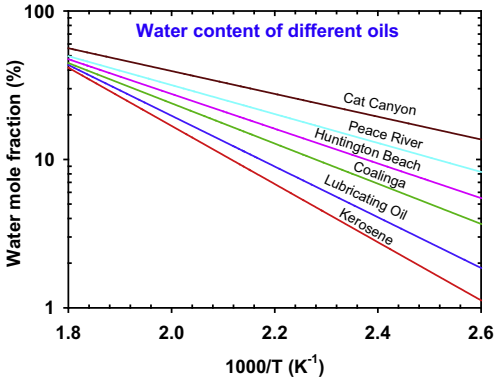
HIGHLIGHTS

- We propose application of CPA-EoS to predict water solubility in bitumen.
- CPA-EoS successfully reproduced experimental data of bitumen-water system.
- CPA-EoS works for a wide range of crude molecular weight and temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Knowledge of the solubility of water in hydrocarbon fluids is essential for the design, simulation, and optimization of thermal oil recovery processes. This study proposes the use of cubic-plus-association equation of state (CPA-EoS) to predict the mole fraction of water in hydrocarbon fluids with specific gravity and molecular weight as the correlating parameters. Experimental data for water solubility in petroleum fractions, heavy oils, and bitumens was represented with an absolute average relative deviation (AARD) of less than 6.8%. The binary interaction parameter between the water and hydrocarbons was determined for different crudes. The proposed model can be applied to petroleum fractions, heavy oils, and bitumens with molecular weights between 140 and 678 g/mol at temperatures up to 560 K, which is the practical range of many industrial applications.

1. Introduction

Water is used extensively in heavy oil and bitumen production, separation and refining. In fact, most of the thermal recovery processes including Steam Assisted Gravity Drainage (SAGD), Cyclic Steam Stimulation (CSS), and Expanded Solvent-Steam Assisted Gravity Drainage (ES-SAGD) are based on injecting saturated steam into bitumen and heavy oil reservoirs. Glandt and Chapman [1] reported that water dissolution in heavy oils and bitumens becomes significant at high temperatures ($T > 150$ °C). The water mole fraction in heavy crudes can reach 40 mole% at 250 °C [1]. Water that is dissolved in oil acts as a low viscosity component in the system and reduces the viscosity of the oleic phase. At high temperatures, this reduction in viscosity can be significant (~100% at 280 °C) [1] and have considerable effect on the performance of thermal recovery processes where the governing production mechanism is viscosity reduction. Luo and Barrufet [2] showed that

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water solubility in the oil phase has a remarkable effect on simulation results. Therefore, estimating water solubility in heavy oils and bitumens is a crucial step toward improving the simulation of thermal recovery processes.

In high temperature regions near the injection well, water dissolves in the bitumen reducing the viscosity of the hydrocarbon phase. However, when these fluids flow toward low temperature regions such as near the production well, the dissolved water comes out of the oleic phase and forms a water-in-oil emulsion with a higher viscosity. Important aspect of water dissolution in heavy crudes should be taken into account in reservoir simulations.

There are several models used to calculate water solubility in hydrocarbons [3–6]. Most of these models are too specific and must be re-tuned for each new hydrocarbon sample. Some of the models are only applicable to n-alkanes or have temperature limitations. Vega et al. [7] used the soft-SAFT (statistical associating fluid theory) to calculate mutual solubility of n-alkane hydrocarbons-water systems. This work shows the superiority to the original SAFT model. F-SAC (Functional-Segment Activity) model was applied for hydrocarbon-water systems by Possani et al. [8]. These models are applicable for well-defined hydrocarbons up to C_{12}.

Satyro et al. [9] proposed a technique for calculating water-hydrocarbon mutual solubility. The model is accurate for light hydrocarbons and crudes and does not suffer from most of aforementioned limitations. The model developed by Satyro et al. requires that the specific gravity and Watson characterization factor. Solubility predictions of water in heavy oils and bitumens using model of Satyro et al. [9] diverges from experimental data. They have re-tuned the model for heavy oils and bitumens and indicated that their model is not directly applicable for heavy oil and bitumen.

Amani et al. [10] proposed a generalized correlation for water solubility in ill-defined hydrocarbons but their correlation diverges from the experimental data for heavy crudes and bitumens. A comprehensive literature review on correlations and models for calculation of water-hydrocarbon mutual solubility can be found from Amani et al. [10] and Oliveira et al. [11].

In this work, we propose cubic-plus-association equation of state (CPA-EoS) to predict water dissolution in petroleum fractions, heavy oils and bitumens over the temperature range observed in thermal oil recovery processes. This equation of state has already been applied for systems of water and light well-known hydrocarbons [12,13]. Moreover, we have recently utilized the CPA-EoS to accurately calculate the solubility of CO_2 in heavy oils and bitumens [14]. In order to determine water solubility, we tuned the CPA-EoS to calculate the water dissolution in petroleum fractions, heavy oils and bitumens. Next, results for different oils are presented for a wide range of molecular weights. The accuracy of the proposed model makes it an attractive choice for predicting the solubility of water in hydrocarbons in thermal heavy oil and bitumen recovery applications.

2. Thermodynamic modeling

In this work we use the CPA-EoS as combination of the Soave-Redlich-Kwong equation of state (SRK EoS) [15] with the association term of Wertheim's first-order thermodynamic perturbation theory (TPT-1) [16] to represent the phase behavior of water-bitumen and water-heavy oil systems. Contribution of physical and association interactions on the intermolecular forces are taken into account using the SRK EoS and TPT-1, respectively. The CPA equation of state is expressed as [17]:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} - \frac{1}{2}\left(\frac{RT}{V}\right)\left(1 + \frac{1}{V}\frac{\partial \ln g}{\partial(1/V)}\right)\sum_i^n x_i \sum_{A_i}^s (1-\chi_{A_i}) \tag{1}$$

where V and T are the molar volume and absolute temperature, respectively; R is the universal gas constant; a and b are the energy and volume parameters of the SRK-EoS. In the association term of the CPA-EoS, g is the contact value of the radial distribution function of the hard-sphere mixture; x_i is the mole fraction of component i in the system; χ_{Ai} is the fraction of active site A on molecule i not bonded to the other active sites. n and s are number of components and types of association sites on the molecules, respectively. The fraction of non-bonded sites is calculated using the following equation:

$$\chi_{A_i} = \frac{1}{1 + \left(\frac{1}{V}\right)\sum_j^n x_j \sum_{B_j}^s \chi_{B_j} \Delta^{A_i B_j}} \tag{2}$$

where B_j is the summation over all association sites and Δ^{ij} is the association strength and calculated as follows:

$$\Delta^{ij} = g\beta_{ij} b_{ij}\left[\exp\left(\frac{\varepsilon_{ij}}{RT} - 1\right)\right] \tag{3}$$

where β and ε are the association volume and energy parameters, respectively; The values of $b_{ij} = (b_i + b_j)/2$ and g is given by:

$$g = \frac{1}{1 - 0.475 b\rho} \tag{4}$$

where ρ is the molar density. The van der Waals mixing rules were applied to calculate a and b parameters for the mixture required for the SRK-EoS as given by the following equation [17]:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{5}$$

$$b = \sum_i x_i b_i \tag{6}$$

where k_{ij} is the binary interaction parameter between molecules i and j.

The difference between CPA-EoS used in this work and the original form proposed by Kontogeorgis et al. [17] is in using critical properties for calculation of the parameters of equation of state. In the CPA-EoS proposed by Kontogeorgis et al. [17] these parameters are obtained from regression on the experimental saturation pressure and liquid density data. Implementation of the CPA-EoS requires the pure component critical properties (T_c, P_c), acentric factor (ω), binary interaction parameter (k_{ij}), and association parameters (ε and β). The parameters for water were obtained from the literature [17]. For bitumen and heavy oils, we followed the Zirrahi et al. method for CO_2-bitumen system [14]. The critical temperature and acentric factor were calculated using the Riazi and Al-Sahhaf [18] correlation provided below:

$$T_c = \frac{1080 - \exp(6.97996 - 0.01964 M^{0.6667})}{1.2 - \exp(-0.34742 - 0.02327 M^{0.55})} \tag{7}$$

$$\omega = -(0.3 - \exp(-6.252 + 3.64457 M^{0.1})) \tag{8}$$

where M is the molecular weight of the crude. This correlation gives reliable and accurate values for the critical temperature and acentric factor of heavy hydrocarbons and only requires the crude molecular weight. The critical pressure was adjusted to match the oil density as proposed by Li and Firoozabadi [19] and Zirrahi et al. [14].