Modeling of asphaltene precipitation from *n*-alkane diluted heavy oils and bitumens using the PC-SAFT equation of state

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ARTICLE INFO

ABSTRACT

In this work, the PC-SAFT equation of state was applied to the modeling of asphaltene precipitation from *n*-alkane diluted heavy oils and bitumens. Liquid–liquid equilibrium was assumed between a dense liquid phase (asphaltene-rich phase) and a light liquid phase. The liquid–liquid equilibrium calculation, in which only asphaltenes were allowed to partition to the dense phase, was performed using an efficient method with Michelsen's stability test. The bisection or Newton–Raphson method was used to improve convergence. Experimental information of the heavy oils and bitumens, characterized in terms of solubility fractions (saturates, aromatics, resins, and asphaltenes), was taken from the literature. Asphaltenes were divided into fractions of different molar masses using a gamma distribution function. Predictions of the PC-SAFT equation of state using linear correlations of the binary interaction parameters between asphaltene subfractions and the *n*-alkane were compared with the measured onset of precipitation and the amount of precipitated asphaltene (fractional yield) of the heavy oils and bitumens diluted with *n*-alkanes. Results of the comparison showed a satisfactory agreement between the experimental data and the calculated values with the PC-SAFT equation.

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1. Introduction

Asphaltenes are defined as the fraction of crude oil or bitumen that precipitates with the addition of a low-chain liquid *n*-alkane (*n*-pentane or *n*-heptane) and dissolves in aromatic solvents as toluene or benzene. In practice, there are different aspects of the asphaltene precipitation that are important for the oil industry such as the prevention of the plugging in transport pipelines and the damages caused in the refinery facilities due to the asphaltene precipitation process. A major problem is when different crude oils having different densities and viscosities are mixed and they are, in turn, mixed with light liquid hydrocarbons (e.g., natural gasolines) to reduce the viscosity of the crude oil blends, since asphaltene precipitation may occur due to the instability of the crude oil mixtures [1].

To overcome such a problem, various research groups have developed different approaches to predict and quantify the onset and amount of precipitated asphaltene in crude oils. This task was started with the approach of Hirschberg et al. [2], who applied the regular solution theory for modeling asphaltene precipitation in crude oils. Later, this modeling approach was improved by other authors to predict (1) the amount of precipitated asphaltene from *n*-alkane diluted heavy oils and bitumens [3,4], (2) the asphaltenes dissolved in pure solvents [5,6], and (3) the stability of crude oil blends [1,7]. In particular, Yarranton and co-workers [1,3,4] proposed approaches to predict asphaltene precipitation by treating them as a mixture of subfractions with different densities and molar masses. These approaches have been successfully applied to several heavy oils and bitumens diluted with *n*-alkanes [3,4]. The heavy oils and bitumens were characterized based on SARA analysis and the polidispersity of the asphaltene fraction was included through the use of a gamma distribution function.

Other approaches in which the asphaltene precipitation is understood as a result of self-assembly and instability of resinous–asphaltene aggregates in the crude oil have also been

used. For instance, Leontaritis and Mansoori [8] presented a colloidal model based on the assumption that the insoluble solid asphaltene particles are suspended in the crude oil; the suspended solid asphaltene particles being stabilized by the adsorbing resins on their surface. In this model, resins are necessary for the asphaltenes to exist in solution. Subsequently, Victorov and Firoozabadi [9], Pan and Firoozabadi [10], and Victorov and Smirnova [11], among others, presented thermodynamic models to predict asphaltene precipitation in petroleum fluids by assuming that asphaltene precipitation from petroleum fluid is a micellization process. These models, however, although have shown promising results in explaining most of the experimentally observed results, they are still far from provides satisfactory quantitative representation.

On the other hand, the application of an equation of state to calculate the asphaltene solubility in solvents was studied by Gupta [12] considering a solid–liquid equilibrium calculation. Nghiem and co-workers [13–15] applied a modeling technique based on the representation of the precipitated asphaltene as a pure dense phase. In this approach, the heaviest component in the oil is divided into two fractions, the non-precipitating and the precipitating fraction. The precipitating fraction is considered as pure asphaltenes and the prediction precipitation process is quantified by a three phase flash calculation. Sabbagh et al. [16] applied in their approach a liquid–liquid equilibrium calculation, where one of the liquid phases is considered a light phase or a non-precipitating phase and the other liquid phase is considered a heavy liquid phase or a precipitating phase. The precipitating phase is considered a phase where only asphaltenes are present. They used the PR equation of state [17] to represent the asphaltene-rich liquid phase by relating the equation of state parameters of each asphaltene fraction to monomer parameters using group contribution theory. Ting et al. [18] modeled the asphaltene phase behavior in a model live oil and a recombined oil under reservoir conditions by using the SAFT equation of state [19]. In this case, the parameters of the equation of state for the asphaltenes were adjusted to precipitation data from oil titrations with n-alkanes at ambient conditions.

By using a molecular-thermodynamic framework based on the SAFT equation of state and colloidal theory, Wu et al. [20,21] calculated the solubility of asphaltenes in petroleum liquids as a function of temperature, pressure, and liquid-composition. In this approach, asphaltenes and resins were represented by pseudo-pure components while all other components in the solution were represented by a continuous medium that affects interactions among asphaltene and resin particles. The effect of the medium on asphaltene–asphaltene, resin–asphaltene, and resin–resin pair interactions was taken into account through its density and dispersion-force properties. The SAFT model was used in the framework of McMillan–Mayer theory, which considers hard-sphere repulsive, association and dispersion–force interactions. In their calculations, Wu et al. assumed that asphaltene precipitation is a liquid–liquid equilibrium process.

Buenrostro-Gonzalez et al. [22] used an approach similar to that suggested by Wu et al. for modeling the asphaltene precipitation from n-alkane diluted Mexican crude oils. They used the statistical association fluid theory for potentials of variable range (SAFT-VR) equation of state [23] in the framework of the McMillan–Mayer theory in the calculations to represent the asphaltene precipitation envelopes and bubble point pressures of the two oils investigated. By matching a single titration curve or two precipitation onset points with this SAFT-VR equation of state, satisfactory predictions of asphaltene precipitation over wide temperature, pressure, and composition intervals were obtained.

Li and Firoozabadi applied the cubic-plus-association (CPA) equation of state [24] to study the asphaltene precipitation from solutions of toluene and an n-alkane and from n-alkane diluted heavy oils and bitumens [25], and the asphaltene precipitation in live oils from temperature, pressure, and composition effects [26]. Heavy oils and bitumens were characterized in terms of saturates, aromatics/resins, and asphaltenes, whereas the live oils were characterized by considering the pure components, the pseudo-hydrocarbon components, and the hydrocarbon residue. In the case of heavy oils and bitumens, the asphaltene precipitation was modeled as liquid–liquid equilibrium. By using a single adjustable parameter—the cross association energy between asphaltene and aromatics/resins (or toluene), the amount of asphaltene was successfully predicted over a broad range of temperatures, pressures, and compositions for n-alkane diluted model solutions, heavy oils, and bitumens. In the case of live oils, the asphaltene precipitation was modeled as liquid–liquid equilibrium between the upper onset and bubble point pressures and as gas–liquid–liquid equilibrium between the bubble point and lower onset pressures. The amount and onset pressures of asphaltene precipitation in several live oils were reasonably reproduced over a broad range of composition, temperature, and pressure conditions.

More recently, Panuganti et al. [27] presented a procedure to characterize crude oils and plot asphaltene envelopes using the PC-SAFT equation of state. The results obtained with the proposed characterization method showed a satisfactory matching with the experimental data points for the bubble point and asphaltene precipitation onset curves studied.

The aim of this work is to apply the PC-SAFT equation of state [28] to predict the asphaltene precipitation from n-alkane diluted heavy oils and bitumens by using linear correlations of the binary interaction parameter as a function of n-alkane concentration. It is assumed that there exists liquid–liquid equilibrium coexistence between a light non-precipitating liquid phase and a heavy precipitating liquid phase, where only asphaltenes are allowed to partition, and that the effect of self-association is included in the asphaltene molar mass distribution to model the asphaltene precipitation from solvent diluted heavy oils and bitumens. The oils are characterized in terms of saturates, aromatics, resins, and asphaltenes (SARA) fractions, and the asphaltenes are, in turn, treated as nano-aggregates formed from asphaltene monomers and divided into subfractions of different aggregation number based on a gamma distribution function.

2. Thermodynamic model

2.1. PC-SAFT equation of state

In the PC-SAFT equation of state [28], the molecules are considered to be chains composed of spherical segments, in which the pair potential for the segment of a chain is given by a modified square-well potential [29]. Non-associating molecules are characterized by three pure component parameters, namely, the temperature-independent segment diameter σ, the depth of the potential ε, and the number of segments per chain m.

The PC-SAFT equation of state written in terms of the Helmholtz energy for an N-component mixture of non-associating chains consists of a hard-chain reference contribution and a perturbation contribution to account for the attractive interactions. In terms of reduced quantities, this equation can be expressed as

$$\tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} \tag{1}$$

The hard-chain reference contribution is given by

$$\tilde{a}^{hc} = \langle m \rangle \, \tilde{a}^{hs} - \sum_{i=1}^{N} x_i \, (m_i - 1) \ln g_{ii}^{hs} \, (d_{ii}) \tag{2}$$