Understanding the polydisperse behavior of asphaltenes during precipitation

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HIGHLIGHTS

- The PC-SAFT equation-of-state is used to study asphaltene phase behavior.
- The effect of asphaltene polydispersity on asphaltene phase behavior is studied.
- Results of monodisperse and polydisperse asphaltenes modeling are compared.
- A wide range of crude oils are considered for the study.
- An explanation for the observed behavior is provided based on Flory–Huggins theory.

ARTICLE INFO

ABSTRACT

Asphaltenes are a polydisperse fraction of the crude oil, the phase behavior of which is significantly affected by the changes in pressure, temperature and composition. The focus of this study is to model the polydisperse asphaltenes' precipitation onset condition and the amount of precipitate from solvent-diluted crude oils using the Perturbed Chain form of the Statistical Associating Fluid Theory (PC-SAFT) over a wide range of crude oil density. Heavy oil and bitumen production can involve diluting with paraffinic solvents. Different fractions of the polydisperse asphaltenes thus precipitated are predicted and when compared to the experimental data show a remarkable matching for different solvents. A comparison of monodisperse and polydisperse modeling is also performed. This work illustrates the successful application of PC-SAFT for predicting the phase behavior of polydisperse asphaltenes and in particular from heavy oil and bitumen.

1. Introduction

Asphaltenes, a polydisperse mixture of the heaviest and most polarizable fraction of the crude oil; are defined according to their solubility properties as being soluble in aromatic solvents, but insoluble in light paraffin solvents. Asphaltenes are well-known for their tendency to precipitate and deposit during oil production because of changes in pressure, temperature, and composition. It is desirable to prevent or mitigate asphaltene flow assurance problems, because remediation techniques are a significant cost factor. Therefore, as a first step it is necessary to predict the onset and amount of asphaltenes precipitation.

Thermodynamic models to understand the asphaltenes precipitation fall under one of two molecular thermodynamic frameworks, mirroring the two prevalent schools of thought regarding how asphaltenes are stabilized in crude oil. The first approach assumes that asphaltenes are solvated in crude oil and that these asphaltenes will precipitate if the quality of the oil solvent drops below a certain threshold. The Flory–Huggins-regular-solution based models and the equation of state based models are some examples of this approach [1–3]. Thermodynamic models in the second category take a colloidal approach to describe asphaltenes behavior. In this approach resins stabilize the asphaltenes in the crude oil [4,5]. The second approach was beneficial in the early stages of understanding asphaltene behavior. However, aspects like addition of toluene (not a resin) which can redissolve asphaltenes made the asphaltene research community tend towards the solubility approach (first approach).

In this work, the first approach is adopted and a SAFT based equation of state is used to model the asphaltenes behavior [6].

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Previous work by Ting et al. showed that the phase behavior of asphaltenes is different when considered as monodisperse and polydisperse [7]. Ting et al. considered the effect of asphaltenes' polydispersity for only model oil systems. Although Victorov and Smirnova modeled asphaltenes polydispersity in real crude oil systems, they could not obtain a good match with the presented data [8]. Wang and Buckley presented experimental data showing the effect of dilution ratio on different fractions of asphaltenes [9]. Good knowledge of the polydisperse behavior of the asphaltenes is important because different fractions precipitate in different amounts under different conditions. In this regard, limited modeling work is available in the literature. Hence, this article deals with PC-SAFT modeling of real crude oil systems containing polydisperse asphaltenes. A detailed explanation on their behavior is also presented based on the Flory–Huggins theory.

2. Modeling procedure

The focus of this work is to model the polydisperse asphaltenes based on the experimental data for titration of dead oils with various *n*-alkanes. The PC-SAFT characterization methodology is described elsewhere in detail [10]. Hence, this section discusses only about the asphaltenes and the parameter estimation of this polydisperse fraction.

2.1. Asphaltenes and their sub-fractions

For treating asphaltenes as polydisperse, asphaltenes are split into sub-fractions based on the precipitating solvents used. For example, when *n*-C_{10}, *n*-C_7 and *n*-C_5 are used as the titrating agents, asphaltenes are modeled as *n*-C_{10+} sub-fraction, *n*-C_{7-10} sub-fraction, and *n*-C_{5-7} sub-fraction. Here, the *n*-C_{10+} asphaltene sub-fraction represents *n*-decane insoluble asphaltenes. Asphaltenes from the combination of *n*-C_{10+} and *n*-C_{7-10} sub-fractions represent the *n*-heptane insoluble asphaltenes. Finally, the combination of *n*-C_{10+}, *n*-C_{7-10} and *n*-C_{5-7} sub-fractions represent the *n*-pentane insoluble asphaltenes.

2.2. Asphaltenes' parameter estimation

Asphaltene molecules aggregate forming nano-aggregates even in good solvents such as toluene. Along with polarizability, polarity of the asphaltenes may also play a role in forming the nano-aggregates, but steric effects are thought to prevent further aggregation of asphaltenes in solution [11]. Precipitation is a phenomenon dominated by polarizability creating microdomains of asphaltene rich phase [12]. Because of this, the association term in SAFT can be safely neglected in asphaltenes modeling work.

For every non-associating component, PC-SAFT has just three parameters, the temperature independent diameter of each molecular segment (σ), the number of segments per molecule (m), and the segment–segment dispersion energy (ε/k). When considering a compound which is not well defined like asphaltenes, these three parameters as well as asphaltenes' molecular weight are fit based on experimental data. But, when asphaltenes are considered as polydisperse, the number of parameters increases in multiples of the number of sub-fractions. To reduce the number of parameters, the PC-SAFT parameter correlations for Aromatics + Resins pseudo-component presented by Gonzalez et al. (Table 1) are used in this work to calculate the asphaltenes' parameters [13]. The aromaticity parameter of asphaltenes is kept constant for all the asphaltene sub-fractions of one oil (because the pseudo-components should have the same nature), and only the molecular weight of each sub-fraction along with the aromaticity are fit. The parameter of aromaticity (γ) used in these correlations determines the

Table 1
PC-SAFT parameters correlations for asphaltenes.

PC-SAFT Parameter	Correlation
M	$(1 - \gamma)(0.0223\,Mw + 0.751) + \gamma\,(0.0101\,Mw + 1.7296)$
σ (A)	$(1 - \gamma)(4.1377 - 38.1483/Mw) + \gamma\,(4.6169 - 93.98/Mw)$
ε/k (K)	$(1 - \gamma)(0.00436\,Mw + 283.93) + \gamma\,(508 - 234100/(Mw)^{1.5})$

component's tendency to behave as a poly-nuclear-aromatic ($\gamma = 1$) or as a benzene derivative ($\gamma = 0$).

It should be mentioned that in most cases of polydisperse asphaltenes, the correlations in Table 1 give the right values for asphaltene SAFT parameters. But, in some cases like Lagrave oil in Section 3.1, we need to treat the parameter σ as a separate fitting parameter to find a good match. One single value of σ should be used for all asphaltenes' sub-fractions and the correlation in Table 1 gives us a good initial estimate for σ. So in this case, we have one aromaticity and one σ besides molecular weights of asphaltenes' sub-fractions which need to be fitted to reproduce asphaltene instability experimental data. We will see later that even in the case of using the correlation in Table 1 for calculating the parameter σ, the obtained values for all asphaltenes' sub-fractions are equal if one rounds them off to two decimals which is a result of assuming the same aromaticity for each asphaltenes sub-fraction.

3. Results and discussion

3.1. Lagrave oil

3.1.1. Asphaltenes polydispersity

In the experiments performed by Wang, the asphaltenes for Lagrave oil are first separated into various solubility fractions using excess *n*-pentane, *n*-heptane, and *n*-pentadecane precipitants [14]. These sub-fractions are called *n*-C_5 insoluble asphaltenes, *n*-C_7 insoluble asphaltenes, and *n*-C_{15} insoluble asphaltenes, respectively. The asphaltenes instability onsets for mixtures of asphaltene, toluene, and *n*-alkanes (at ambient condition and an asphaltenes/toluene ratio of 1 g per 100 ml toluene) are then measured for each asphaltenes fraction.

Within the PC-SAFT model, polydisperse asphaltenes are modeled as three pseudo-components: *n*-C_{15+} sub-fraction, *n*-C_{7-15} sub-fraction, and *n*-C_{5-7} sub-fraction. The parameters of molecular weight and aromaticity are fit for the *n*-C_{15+} asphaltenes sub-fraction to reproduce the experimental data on the minimum volume fraction precipitant needed to induce asphaltenes instability (φ_v^{ppt}) for mixtures of *n*-C_{15} insoluble asphaltenes, toluene, and various *n*-alkanes. It should be mentioned that the fitting parameters were optimized to match all the experimental data points for all *n*-alkanes. The asphaltenes made from the combination of *n*-C_{15+} and *n*-C_{7-15} sub-fractions represent the *n*-C_7 insoluble asphaltenes. The molecular weight is fit for the *n*-C_{7-15} sub-fraction to reproduce (together with the previously fitted *n*-C_{15+} sub-fraction) the experimental φ_v^{ppt} data for a mixture of *n*-C_7 insoluble asphaltenes, toluene, and *n*-alkane. Finally, the molecular weight parameter of *n*-C_{5-7} sub-fraction is fit so that the combination of the *n*-C_{15+} (previous fit), *n*-C_{7-15} (previous fit), and *n*-C_{5-7} sub-fractions represent the *n*-C_5 insoluble asphaltenes and will reproduce the experimental φ_v^{ppt} data for a mixture of *n*-C_5 insoluble asphaltenes, toluene, and *n*-alkanes.

3.1.2. Parameters

In this section polydisperse asphaltenes are modeled as three pseudo-components, hence four adjustable parameters are used, one aromaticity value and three molecular weights for each of