Prediction of asphaltene precipitation using Flory-Huggins thermodynamic model

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Abstract
Precipitation of asphaltene on the pore surfaces of a porous medium which can alter the rock wettability and its permeability is a critical problem in both oil recovery and refinery processes. Therefore, it is important to determine “how much” the asphaltenes precipitate at different conditions. A thermodynamic model based on the Flory-Huggins theory of polymer solutions is used in this study. Prediction of asphaltene precipitation was modeled for two crude oil samples which were diluted with different amounts of precipitants such as n-C5, n-C6 and n-C7. The influence of temperature was also investigated for the second oil sample.

Keywords: Asphaltene Precipitation, Precipitants, Thermodynamic Model, Flory-Huggins Model

Introduction
Asphaltene precipitation in the reservoirs is a serious problem because it can plug formation, flow lines, separators and decrease oil recovery while increasing production cost [1]. Asphaltene is colloidal particles in oil that can be dissolved in toluene and xylene but is not soluble in normal alkenes such as n-pentane and n-hexane [2]. Thermodynamic models of asphaltene precipitation can be used to predict the amounts of precipitated asphaltene. In general, there are four types of thermodynamic models [3]: 1) the solubility model 2) the solid model 3) the colloidal model and 4) the micellization models. The first category is based on the simplified Flory-Huggins polymer theory [3]. Hirschberg et al. [4] was the one who presented a solubility precipitation model based on the Soave equation of state [5]. Cimino et al. [6] and Kawanaka et al. [7] proposed a precipitation model on the basis of polymer-solution thermodynamics. This model is really a good application of the polymer-solution theory, so it can be a good representation of asphaltene-phase behavior. In this study, this thermodynamic model was used too.

Theory: Polymer-solution theory based on the Flory-Huggins model
Flory-Huggins [8] proposed a thermodynamic model of the lattice theory for mixtures of polymers and solvents. Hirschberg et al. [4] used this theory for prediction of asphaltene solubility in oil. According to this model, the solubility of asphaltene in oil is calculated as follow:

\[ \phi_c = \exp \left[ -1 + \frac{v_a}{v_t} - \frac{v_e}{RT} (\phi_a - \phi_e)^2 \right] \] (1)
where $\phi_a$, $v_a$, $v_1$, $\delta_a$, $\delta_1$, $R$ and $T$ are asphaltene solubility in oil, asphaltene molar volume, solvent molar volume, asphaltene solubility parameter, solvent solubility parameter, gas universal constant and absolute temperature, respectively.

Equation (1) is derived from original Flory-Huggins theory in which the partial molar Gibb’s free energy or chemical potential of component 1 is defined as:

$$\Delta \hat{\mu}_1 = \Delta \hat{H}_1 - T \Delta \hat{S}_1.$$  \hspace{1cm} (2)

The partial molar enthalpy ($\Delta \hat{H}_1$) and the partial molar entropy ($\Delta \hat{S}_1$) are:

$$\Delta \hat{H}_1 = v_1(\phi_a)^2(\delta_1 - \delta_2)^2$$ \hspace{1cm} (3)

$$\Delta \hat{S}_1 = -R \left[ \ln \phi_a + \left( 1 - \frac{\phi_1}{\phi_a} \right) \phi_a \right]$$ \hspace{1cm} (4)

Here (1) and (2) are asphaltene and asphaltene-free solvent, respectively.

After adding solvent, asphaltene precipitates because of the change in oil composition. In this state a solid-liquid equilibrium is reached in which chemical potential of asphaltene in liquid phase is equal to chemical potential of asphaltene in solid phase ($\Delta \mu_a^L = \Delta \mu_a^S$). Hirschberg et al. [4] assumed that the asphaltene phase is pure, so, $\Delta \mu_a^S = 0$ and derived the asphaltene solubility formula. Then, the weight percent of precipitated asphaltene ($w$) can be obtained [1]

$$w = \left( \frac{1 - \phi_2}{1 - \phi_2(a) \left( \frac{M_{S}}{v_a} \right)} \right) \left( \frac{M_{S}^{L}}{(1 - \phi_2(a) \left( \frac{M_{S}^{L}}{v_a} \right)) + \phi_2(a) \left( \frac{M_{W}^{L}}{v_a} \right)} \right)$$ \hspace{1cm} (5)

where $M_{S}^{L}$ and $M_{W}^{L}$ are molecular weight of solvent and molecular weight of asphaltene.

Molecular weight of asphaltene is considered to be 1389 g/mol for n-pentane, 1791 g/mol for n-hexane and 2105 g/mol for n-heptane [9]. Peng-Robinson equation of state and the mixing rules have been applied to calculate the molar volume of solvent.

**Results and discussion**

In this study, the influence of increasing temperature and precipitants n-pentane, n-hexane and n-heptane on the amount of precipitated asphaltene have been investigated. The properties of the two oil samples used can be seen in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Crude oil sample 1 (mol/mol) [1]</th>
<th>Crude oil sample 2 (mol/mol) [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C3</td>
<td>0</td>
<td>0.50336</td>
</tr>
<tr>
<td>i-C4</td>
<td>0.05</td>
<td>0.0661</td>
</tr>
<tr>
<td>n-C4</td>
<td>0.64</td>
<td>0.23299</td>
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<tr>
<td>i-C5</td>
<td>1.69</td>
<td>0.13881</td>
</tr>
<tr>
<td>n-C5</td>
<td>2.21</td>
<td>0.1837</td>
</tr>
<tr>
<td>n-C6</td>
<td>4.23</td>
<td>0.99874</td>
</tr>
<tr>
<td>C7+</td>
<td>91.18</td>
<td>97.8757</td>
</tr>
<tr>
<td>Va (m³/Kmol)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>C7+ MW</td>
<td>211.82</td>
<td>292.814</td>
</tr>
<tr>
<td>Oil MW</td>
<td>200</td>
<td>287.11</td>
</tr>
<tr>
<td>C7+ specific gravity</td>
<td>0.8778</td>
<td>0.8846</td>
</tr>
<tr>
<td>Asphaltene content (%wt)</td>
<td>11</td>
<td>10.39</td>
</tr>
</tbody>
</table>

Figures 1 to 4 shows the amount of asphaltene precipitation based on the Flory-Huggins model in different ratios of solvent. According to results, it is clear that increase in solvent volume to oil mass ratio (SR) increases weight percent of asphaltene precipitation. Also for a specific solvent, the amount of precipitation will reduce by increasing temperature. Nature of
liquid phase molecules, interactions between them and the amount of polar compounds in the solution are the reason for different amount of asphaltene precipitation obtained in same solvent ratios of different solvents [1].

Figure 1: Asphaltene precipitation obtained in different ratios of (a) n-pentane, (b) n-hexane and (c) n-heptane for crude sample 1

Figure 2: Asphaltene precipitation obtained in different ratios of n-pentane in temperatures of (a) 30 °C, (b) 50 °C and (c) 70 °C for crude sample 2
Figure 3: Asphaltene precipitation obtained in different ratios of n-hexane in temperatures of (a) 30 °C, (b) 50 °C and (c) 70 °C for crude sample 2.

Figure 4: Asphaltene precipitation obtained in different ratios of n-heptane in temperatures of (a) 30 °C, (b) 50 °C and (c) 70 °C for crude sample 2.
Conclusions
In this work, Peng-Robinson equation of state and Flory-Huggins theory have been applied to predict the amount of asphaltene precipitation in different solvent ratios (SR) for n-pentane, n-hexane and n-heptane in two oil samples and some temperatures in oil sample 2. The results showed that the asphaltene precipitation increases by increasing SR while decreasing by increasing temperature. Also, the results of the model were in good agreement with the experimental data.

References