Predicting Asphaltene Precipitation by Simple Algorithm Using Solubility Parameter Calculated Based on Peng-Robinson Equation of State

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Asphaltene precipitation is frequently the cause of increased cost of oil production in the petroleum industry. To avoid or minimize problems due to asphaltene precipitation, a model to predict the amount of asphaltene precipitation under the petroleum reservoir conditions is required. In this study, the Flory-Huggins solution theory with a correctly tuned equation of state for calculation of the solubility parameter of liquid oil and a second order polynomial equation for variations of asphaltene solubility with pressure were applied to model asphaltene precipitation. The advantage of this model is that expensive and time consuming experiments are not required to obtain the asphaltene and liquid oil solubility parameters. Routine pressure/volume/temperature (PVT) tests and the amount of asphaltene precipitated at the bubble point pressure are sufficient. Data generated by the model were compared to the experimental asphaltene precipitation data on two live oils under reservoir conditions, showing that the model could accurately represent the behavior of asphaltene precipitation in the reservoir.

Keywords
Asphaltene precipitation, Flory-Huggins solution theory, Solubility parameter, Bubble point pressure, Petroleum reservoir condition, Equation of state

1. Introduction

Asphaltenes are defined as the fraction separated from crude oil or petroleum products by addition of hydrocarbon solvents such as n-heptane. Resins are defined as the fraction of crude oil not soluble in ethyl acetate but soluble in n-heptane, toluene, and benzene at room temperature. Asphaltenes and resins are aromatic hetero-compounds with aliphatic substitutions and form the most polar fraction of crude oil. Resins have a strong tendency to associate with asphaltenes, which determines, to a large extent, their solubility in crude oil.

Field experiences and experimental observations have shown that asphaltene stability depends on a number of factors, including the composition of the surrounding fluid, pressure, and temperature. The effects of composition and pressure on asphaltene precipitation are generally believed to be stronger than the effect of temperature. Addition of paraffinic compounds changes the solubility of asphaltenes in bulk oil because the solvent power affects the interactions between asphaltenes and resins. If paraffinic compounds are good solvents for resins but not for asphaltenes, increasing volume of diluent will decrease both the interaction between resins and asphaltenes, and the capacity of the resin to stabilize the asphaltene molecules as small aggregates, causing the asphaltenes to precipitate. Only decreases in pressure can destabilize asphaltenes and are the most probable cause of asphaltene deposition in well-bore pipes.

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Several approaches for modeling asphaltene precipitation have been reported. A simple model for predicting asphaltene precipitation used three tuning parameters for pressure effects, temperature effects and reference pressure. The solid phase was treated as an ideal multicomponent mixture. However, the model could not match the experimental data. A two-component solubility model was developed to predict the phase behavior of asphaltene in crude oils. Coupled values of the asphaltene solubility parameter and molar volume were the adjustable parameters. The solubility parameter of the liquid phase was calculated from a linear relationship between solubility parameter and refractive index measured experimentally. The Flory-Huggins model was modified with three adjustable parameters to predict asphaltene precipitation in crude oil. The adjustable parameters were obtained by experimental values of asphaltene precipitation and optimization of an objective function. The solubility...
parameter of asphaltene was used as the input oil data. A thermodynamic modeling procedure for predicting asphaltene precipitation was proposed using a tuning procedure for calculating the molecular weight of asphaltene\textsuperscript{12}. Solubility parameter of the liquid phase (oil) was calculated by solving the set of equations derived from minimization of the Gibbs free energy relationship. The solubility parameter of asphaltene was again assumed as the input oil data. An onset-constrained colloidal asphaltene model was used for the prediction of asphaltene precipitation in upstream operations\textsuperscript{33}. Oil solubility was estimated from a linear relationship with respect to density, and the asphaltene solubility parameter was obtained as a fitting parameter from onset flocculation experiments. Experiments were performed at different conditions to determine the effect of pressure and temperature on the asphaltene solubility parameter. A new cubic equation of state with new parameters was proposed to calculate the density and solubility parameter of crude oil\textsuperscript{43}. Using the modified Flory–Huggins model and three adjustable (tuning) parameters, values of asphaltene precipitation were predicted in different ratios of solvents (n-C\textsubscript{5}, n-C\textsubscript{6}, n-C\textsubscript{7}) at constant temperature and pressure. Prediction of asphaltene precipitation by this model required the solubility parameter of asphaltene and three adjustable (tuning) parameters. These three tuning parameters were obtained from experimental data of asphaltene precipitation in the oil sample. No measurement or estimation of asphaltene solubility parameter was described.

All previous models required adjustable (tuning) parameters obtained from experimental data of asphaltene precipitation in the oil sample. Usually more experimental data results in more accurate tuning parameters. However, obtaining experimental data of asphaltene precipitation in the oil sample under reservoir conditions (usually high pressure and temperature) is expensive and time consuming.

The present study proposes a model for predicting asphaltene precipitation under reservoir conditions based on the Peng–Robinson equation of state and Flory–Huggins solution theory. Solubility parameter and other thermodynamic properties of crude oil are calculated from the Peng–Robinson equation of state, which is widely accepted for the convenient and flexible calculation of the phase behavior of reservoir fluids. Solubility parameter of asphaltene can be calculated from inexpensively measured data at the bubble point. The advantage of this model is that expensive and time consuming experiments are not necessary to obtain adjustable (tuning) parameters and solubility parameter of asphaltene. Routine pressure/volume/temperature (PVT) tests (which are usually performed on oil samples) and the amount of asphaltene precipitated at bubble point pressure are sufficient.

This paper summarizes the theory behind the model, and applications of the model to field operations.

2. Theory

This study defines asphaltene as the portion of crude oil that is insoluble in n-heptane but soluble in benzene or toluene. The model describes the precipitation mechanism by polymer solution theory. The large asphaltene molecules are similar in structure and behavior to polymer molecules. The remaining components in the crude oil act as a solvent in which the asphaltene is dissolved or suspended\textsuperscript{55}.

The overall model depends on two types of fluid equilibria: the vapor-liquid equilibrium of the total reservoir fluid, and the liquid-liquid equilibrium between the liquid oil and pseudoliquid asphaltene phases. The vapor-liquid equilibrium of the reservoir fluid was modeled first to obtain the composition and fluid properties of the liquid phase. The liquid-liquid equilibrium is considered to consist of two liquid phases: an oil-rich phase that acts as the solvent and an asphaltene-rich phase that behaves as the polymer. The polymer solution theory is a simplified version of the Flory–Huggins solution theory and is defined by the following Eq. (1)\textsuperscript{29}:

\[
\phi_L = \exp \left[ \frac{V_L}{V_L} - 1 - \frac{V_L}{RT} (\delta_a - \delta_L)^2 \right]
\]

In this equation, the volume fraction of precipitated asphaltene, \(\phi_L\), is calculated using the molar volumes of liquid oil, \(V_L\), and asphaltene, \(V_a\), the reservoir temperature, \(T\), and the solubility parameters of liquid oil, \(\delta_L\), and asphaltene, \(\delta_a\).

The solubility parameter is defined as a measure of the cohesive energy density or internal pressure that is exerted by molecules within a solution\textsuperscript{16}:

\[
\delta = C^{1/2} = \frac{\Delta u^V}{V_L}
\]

The solubility parameter has a clear physical meaning: if the difference between the solubility parameters of two substances is small, one can dissolve the other appreciably. The difference in solubility parameters is a measure of the solubility power.

In this study, saturated hydrocarbons, aromatics, resins and asphaltenes formed the oil component groups. The saturated hydrocarbons and aromatics were smaller and nonpolar hydrocarbons. The asphaltene fraction consisted of large, complex polar molecules. The resins are known to be chemically similar in structure to asphaltenes. Resins are important in the solubility of asphaltenes and must be present for the asphaltenes to remain in solution. Although the exact mechanism is unknown, the theory assumes that the resins act a mutual solvent or form stabilizing peptide bonds with
the asphaltenes\textsuperscript{17)}. Asphaltenes are dissolved or suspended in the crude oil in a reservoir fluid. This equilibrium can be modified by changes in pressure, composition or temperature.

In this study, the solubility parameter of liquid oil was calculated on the basis of the Peng–Robinson equation of state\textsuperscript{18}:

\[
P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + 2vb - b^2}
\]

\[
a(T) = 0.45724 \frac{R^2T^2}{P_c} \alpha(T)
\]

\[b = 0.0778 \frac{RT_c}{P_c}
\]

\[
\alpha(T) = (1 + m(1 - T_0^{0.5}))^2
\]

\[m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.0167\omega^3
\]

This equation was also used for the vapor-liquid equilibrium calculations. Parameter "\(b\)" was calculated using a linear mixing rule:

\[
b_m = \sum x_ib_i
\]

Parameter "\(a\)" was calculated from the pure component parameter \(a_i\) using the mixture rule:

\[
a_m = \sum \sum \left[ x_ix_j(a_ia_j)^{0.5} (1 - k_{ij}) \right]
\]

The interaction coefficients \(k_{ij}\) were calculated from the Chueh and Prausnitz equation\textsuperscript{19}:

\[
k_{ij} = 1 - \left( \frac{2\sqrt{\nu_i^{1/3} \nu_j^{1/3}}}{\nu_{ij}^{1/3} + \nu_{ij}^{1/3}} \right)^{a}
\]

The solubility parameter of liquid oil was then derived as the following equation\textsuperscript{20}:

\[
\delta_L = \left[ \frac{1}{2\sqrt{2b_mV_c^L}} (a - T \frac{da_m}{dT}) \ln \frac{V_c^L + (\sqrt{2/1 - \delta_m})}{V_c^L - (\sqrt{2/1 - \delta_m})} \right]^{0.5}
\]

The maximum amount of asphaltene occurs experimentally very near the bubble point\textsuperscript{21,22}. On this basis, any variations of the solubility parameter of asphaltene, \(\delta_m\), with respect to pressure were assumed to be given by a second order polynomial equation (based on experimental observations)\textsuperscript{23} as follows:

\[
\delta_m = A + BP + CP^2
\]

\[
\varphi = \frac{-w_{pal} \times MW_a \times V_c^L}{-w_{pal} \times MW_a \times V_c^L + w_{pal} \times MW_a \times V_c^L - 1000MW_a \times V_c^L}
\]

\[
d_b = \delta_x + \left( \frac{\ln(\varphi_c) - 1/2 \ln V_c^L + 1/1 \ln(RT_0)}{x_c \sqrt{2}} - V_c^L \right)
\]

\[
A = \frac{(-2b \times P_i \times P_{sat} + db \times P_{sat}^i + \delta_{STB} \times P_{sat}^i)}{P_i^2 - 2P_i \times P_{sat} + P_{sat}^i}
\]

\[
B = \frac{(-2\delta_{STB} \times db)P_i}{P_i^2 - 2P_i \times P_{sat} + P_{sat}^i}
\]

\[
C_c = \frac{(-2\delta_{STB} \times db)}{P_i^2 - 2P_i \times P_{sat} + P_{sat}^i}
\]

where \(\delta_{STB}\) is the solubility parameter of asphaltenes under stock tank conditions, \(P\) is pressure, \(P_{sat}\) is atmospheric pressure, \(P_i\) is bubble point pressure, \(MW_a\) is live oil molecular weight, \(MW_{as}\) is asphaltene molecular weight and \(w_{pal}\) is asphaltene precipitated at bubble point pressure. Solubility parameter of asphaltenes under stock tank conditions can be measured experimentally using a series of titration experiments on tank oil\textsuperscript{24}. Experimental methods for measuring live oil molecular weight, \(MW_L\), and asphaltene molecular weight, \(MW_{as}\), are described in the next section.

3. Experimental Data

Samples of reservoir hydrocarbon mixtures, collected at bottom hole or separator conditions, were generally flashed at laboratory conditions and the compositions and properties of the separated gas and liquid phases measured. The compositional analysis data of the separated phases were then recombined in the surface proportions of gas and liquid to determine the composition of the original reservoir fluid. The gas composition was determined by gas chromatography (GC) in form of discrete components. The oil composition was determined by distillation and reported as liquid fraction. The heaviest fraction, which forms the residue in distillation, was analyzed by liquid chromatography\textsuperscript{25}.

Measurement of asphaltene molecular weight was based on the work of Storm and Sheu\textsuperscript{26}. Asphaltene was precipitated from the vacuum residue (fraction with an atmospheric boiling point greater than 538°C) by mixing one part of residue with 40 parts of heptane, stirring the slurry overnight at room temperature, filtering the asphaltene from slurry, and finally washing the solid well with heptane. Then, mass spectroscopy of asphaltene was performed. Details of the experimental technique to evaluate the amount of asphaltene precipitation during the pressure depletion sequence at reservoir temperature were given previously\textsuperscript{20}.

The asphaltene detection system consisted of a variable volume, visual PVT cell retrofit with fiber optic light transmission probes (source and detector) to measure the onset of organic solid precipitation (due to tem-
Table 1  PVT Properties of Crude Oil No.1

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition [mol%]</th>
<th>Pressure [MPa]</th>
<th>Relative oil volume</th>
<th>Solution GOR</th>
<th>Oil density [kg/m³]</th>
</tr>
</thead>
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<tr>
<td>H₂S</td>
<td>2.25</td>
<td>34.4091</td>
<td>0.9623</td>
<td>1.363</td>
<td>754.9</td>
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<td>N₂</td>
<td>0.26</td>
<td>27.537</td>
<td>0.9712</td>
<td>1.3757</td>
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<td>CO₂</td>
<td>7.53</td>
<td>20.6855</td>
<td>0.9808</td>
<td>1.3894</td>
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<td>C₁</td>
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<td>17.2528</td>
<td>0.986</td>
<td>1.3986</td>
<td>736.6</td>
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<td>C₂</td>
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<td>13.8409</td>
<td>0.9915</td>
<td>1.4047</td>
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<td>i-C₄</td>
<td>1.98</td>
<td>12.4761</td>
<td>0.9939</td>
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<td>n-C₄</td>
<td>3.22</td>
<td>11.7937</td>
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<td>C₁₁</td>
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<td>C₁₂⁺</td>
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<td></td>
<td>2.06786</td>
<td>2.8965</td>
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</tbody>
</table>

Molecular weight of residual oil 234
Molecular weight of C₁₂⁺ fraction 360
Molecular weight of reservoir oil 116
Specific gravity of C₁₂⁺ fraction [15.5/15.5 °C] 0.9400

temperature, pressure, and/or compositional change) concurrently with fluid volumetric data. The incident laser was mounted on the front of the PVT cell so that its beam passed through the high-pressure sample chamber before reaching the light detector probe. Thus, any changes in the opacity of the crude oil resulting from a density change and/or suspended solids would be registered at the detector. A magnetically coupled impeller was used to rapidly mix the fluid to keep any solids suspended and to quickly drive the fluid to equilibrium following a composition or pressure change. The ultimate interpretation of asphaltene behavior was based on inspection of the resulting “light transmittance” plots which showed the amount of light received by the detector (i.e., transmitted through the sample) as a function of pressure during the depletion/repressurization cycles. Power of transmitted light (PTL) refers to the amount of light passing through the oil sample and captured by the receiving fiber optic cable.

Each fluid was screened for the tendency to precipitate asphaltenes during isothermal pressure depletion at reservoir temperature. The screening test was completed in conjunction with the standard constant composition expansion (CCE) experiment to measure the fluid bubble-point pressure as well as liquid density and compressibility values. CCE tests were used to determine the change in density of a single-phase fluid during depressurization to the bubble point. Initially, the visual PVT cell was completely cleaned and evacuated with the temperature of the air-bath set to the desired value. Subsequently, 50-70 cm³ of crude oil was isobarically and isothermally (at single-phase conditions) charged into the cell from the storage cylinder using a positive displacement pump. A sub-sample of known volume was then withdrawn isobarically and isothermally into an evacuated and preweighed pycnometer for gravimetric density measurement. The remaining sample volume in the PVT cell was measured using a cathetometer. Therefore, the mass of oil sample charged into the PVT cell could be calculated. The system components were mounted across the full-length PVT cell windows and a reference scan of the light transmittance through the oil performed. The pressure of the cell was then lowered isothermally at programmable rates (either continuously or in discrete steps) during continuous mixing of the cell contents. At each pressure step, the sample volume was measured and the corresponding density calculated. The experi-
Experimental data are presented on the phase behavior of two crude oils. The PVT properties of these oils are shown in Tables 1 and 2. Onset pressure experiment results and the amounts of asphaltene precipitation at various pressure steps for two live oils are presented in Tables 3 and 4.

### 4. Algorithm of the Model

Cubic equations of state (EOS) will not generally predict accurately laboratory data of oil/gas mixtures without tuning of the EOS parameters. The common practice is to adjust the properties of the components (usually the heavy fractions, e.g. critical pressure, critical temperature, acentric factor, etc.) to fit the experimental data.

The major problem associated with phase-behavior matching with a cubic equation of state is the selection of regression parameters. There are many parameters that can be selected as the optimum set, and so a dynamic parameter-solution scheme is desired to avoid tedious and time-consuming trial-and-error regression runs. Therefore, in this study, a regression technique with dynamic parameter selection was used to tune the parameters of the Peng–Robinson equation of state to match the differential liberation (Diff. Lib.) and constant composition expansion (CCE) data.

The regression was performed by minimizing the objective function:

\[
F = \sum_{j=1}^{N} w_i \left( \frac{X_i^{\text{calc}}(r_j) - X_i^{\text{meas}}}{X_i^{\text{meas}}} \right)^2
\]

where \( w_i \) is the weighting factor, \( X_i^{\text{calc}}(r_j) \) is property calculated based on regression parameters \( r_j \), and \( X_i^{\text{meas}} \) is property measured.
Table 5 Weighting Factors and Properties Used in Eq. (9)

<table>
<thead>
<tr>
<th>Property ($X_i$)</th>
<th>Bubble point</th>
<th>Solution GOR</th>
<th>Oil formation volume factor, $B_o$</th>
<th>Relative oil volume</th>
<th>Oil density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weighting factor ($w_i$)</td>
<td>50</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

is the measured (experimental) value. $N$ expresses the number of measured data points to be fitted.

In this study, $r_i$ are critical pressure, critical temperature, critical volume, acentric factor and molecular weight of plus fraction $C_{12}^+$ and hydrocarbon-hydrocarbon interaction coefficient exponent ($\theta$ in Eq. (6)) of all components. The number of measured data points to be fitted, $N$, is 163. $X_i$ and $w_i$ are shown in Table 5.

After tuning, the equation of state was used to calculate the vapor-liquid equilibrium. The solubility parameter of the liquid oil phase was calculated using Eq. (7) and the molar volume of the liquid phase from the tuned equation of state. In the final step, calculation of the asphaltene solubility parameter used Eq. (8). The solution algorithm is outlined in Fig. 1. The solution algorithm is outlined in Fig. 1.

5. Model Results

Figure 2 presents simulation of the PVT tests (Diff. Lib. and CCE tests) of crude No. 2 by the Peng–Robinson equation of state, and shows how the tuned equation of state correctly predicts the fluid phase behavior of this reservoir.

Model predictions for asphaltene behavior in the two live oils are compared to the experimental data at reservoir temperature (126.66°C) in Figs. 3 and 4. The model predictions match the experimental data very well.

6. Conclusions

The following conclusions can be drawn from this research:

- A new algorithm for asphaltene precipitation cal-
calculation was proposed.
• Using Flory–Huggins solution theory with a correctly tuned equation of state for calculation of the solubility parameter of liquid oil and a second order polynomial equation for variations of asphaltene solubility with pressure were essential to the successful application of this model.
• Expensive and time consuming experiments were not necessary to obtain asphaltene and liquid oil solubility parameters. Routine PVT tests and the amount of asphaltene precipitated at bubble point pressure were sufficient.
• The model could accurately represent the experimental behavior of asphaltene precipitation obtained from industry data of two live oils.

Nomenclatures

- $a$: attractive term parameter of equation of state [Pa·(m³/kmol)²]
- $A$: parameter defined in Eq. (8) [(Pa)^0.5]
- $b$: repulsive term parameter of equation of state [m³/kmol]
- $C$: cohesive energy density [Pa]
- $C_c$: parameter defined in Eq. (8) [(Pa)^2.5]
- $db$: parameter defined in Eq. (8) [(Pa)^2.5]
- $f$: fugacity [Pa]
- $F$: objective function, Eq. (9) [—]
- $k$: interaction coefficients [—]
- $m$: parameter defined in Eq. (3) [—]
- $MW$: molecular weight [—]
- $N$: number of measured data points to be fitted [—]
- $P$: pressure [Pa]
- $R$: universal gas constant [J/(mol·K)]
- $T$: temperature [K]
- $u$: cohesive energy [Pa·m³]
- $v$: molar volume [m³/kmol]
- $w$: weight factor [—]
- $w_{pbl}$: asphaltene precipitated at bubble point pressure [kg]
- $x$: mole fraction [—]
- $X$: calculated or measured value in regression technique, Eq. (9) [—]

<Greek>
- $\alpha$: temperature dependency coefficient of attractive term [—]
- $\delta$: solubility parameter [(Pa)^0.5]
- $\theta$: hydrocarbon-hydrocarbon interaction coefficient exponent [—]
- $\phi$: fugacity coefficient [—]
- $\omega$: acentric factor [—]

<Superscripts>
- L: liquid phase

<Subscripts>
- a: asphaltene
- atm: atmosphere conditions
- b: bubble point
- c: critical
- L: liquid phase
- stb: stock tank conditions

References

溶解パラメーター推算に Peng–Robinson 状態方程式を使用した
簡易アルゴリズムによるアスファルテン析出挙動の予測

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石油産業におけるアスファルテン析出の問題は、石油精製においてコスト上昇を招いている。そのため原油タンク中のアスファルテン量を予測するモデルの開発が必要とされている。本研究では、Peng–Robinson 状態方程式と Flory–Huggins 溶解理論に基づいてアスファルテン析出を予測する新たなモデルを開発した。このモデルでは、アスファルテンと液状オイルの溶解度パラメーターの値および原油の熱力学特性値が Peng–Robinson 状態方程式から計算されるので、従来に比べて大幅に時間を短縮され、それを用いた簡易なアルゴリズムによる計算が可能となった。二つの原油タンクからの実験データと比較した結果、高い精度でアスファルテン析出挙動を予測することができた。