Modelling of Solid Precipitation from Reservoir Fluid

X. ZHOU, F.B. THOMAS
Hyca! Energy Research Laboratories
R.G. MOORE
University of Calgary

Abstract

A solid precipitation model is proposed for liquid-solid equilibrium based on the Flory-Huggins polymer solution theory along with a modification to account for the colloidal suspension effect of partial soluble solid compounds in the fluid mixture. The colloidal effect is dependent on the estimation of the critical resins concentration. A linear variation of the free volume is assumed in terms of the component molecular weight for the evaluation of volume fraction in the polymer solution formulation. The binary interaction energy coefficient is introduced to allow for positive or negative deviation from the ideal solution. The effect of heat capacity difference between the liquid and solid phases and the effect of pressure correction are included in the model. New correlations have also been developed for the model.

A multimodel multiphase flash algorithm is formulated using an equation of state for vapour-liquid equilibrium and the proposed model for liquid-solid equilibrium. A detailed discussion of the model performance and the effect of the model parameters on the fitting to experimental results are also presented.

Introduction

Solid precipitation from reservoir crudes has been a serious problem in the oil industry. In reservoir engineering, the original reservoir fluid is well-stabilized after it has formed and migrated geologically to the reserve area where it is found. The production of the reservoir fluid alters the storage conditions which may cause solid deposition. These deposits can cause formation damage and in situ plugging which result in the loss of reservoir permeability and degradation of the porous media. The deposition of the heterocompounds on the surface of the media may reverse its wettability and decrease the transmissivity. In miscible gas flooding, solvents are injected into the reservoir in order to reduce the interfacial tension of the reservoir fluids and to recover more crude oil from the formation. This process can significantly change the fluid phase behaviour and result in asphaltenes, or other solid compounds, instability in the solution, thus increasing the potential for solid deposition in the reservoir.

The solid problem is frequently observed in the wellbore and well tubing. It may plug wells, increasing the fluid pressure gradient which can result in significant reduction in well productivity. It can also cause operation problems in the subsurface and surface equipment. In these cases, costly well workovers or other production treatments may be required.

Review

Many investigators have done considerable research on the nature of heavy organic compounds and the mechanisms of the solid deposition. The complexity of the solid compounds has impeded progress toward accurate prediction and efficient treatment of solid deposition during oil recovery. The precipitated solid usually constitutes the heavy organic compounds of waxes, asphaltenes and resins.

Waxes—are defined as normal paraffins and other molecules containing long chain alky1 groups usually ranging from C16 to about C40. Upon cooling below their cloud point temperature, the solid waxes crystallize and precipitate. Waxes can dissolve in many kinds of hydrocarbon solvents to form a homogeneous solution. Wax solubility in crude oil depends on the chemical composition of the crude oil, pressure and temperature. Waxes can precipitate as crystalline or amorphous solid.

Asphaltenes—are defined to be soluble in benzene and insoluble in low molecular weight n-alkanes. Asphaltenes are classified by the particular solvent used to precipitate them. Different solvents and different purification processes can result in different characteristics and amounts of asphaltenes. Asphaltenes precipitated by various solvents are usually characterized by two major properties—polarity and average molecular weight. The polarity of asphaltenes is due to the presence of hetero-atoms and condensed aromatic rings. Some metal elements, such as vanadium, nickel, copper and uranium, can exist and associate with asphaltenes. The determination of asphaltenes molecular weight is a difficult task due to the low solubility in liquids, the adsorption of resins and the association of asphaltenes. The chemical bonding and aromatic sheet association, as well as electrostatic association, result in the high molecular weight. Asphaltenes molecular weight can range from 1,200 to 2,700 and their distribution can extend from no lower than 300 to no higher than 10,000,000. Asphaltenes particle size was examined in the range of 30 - 65 Å in diameter which suggested that the colloidal suspended solid compounds were present in petroleum crude.

Resins and Their Relation with Asphaltenes

Resins are pentane soluble but ethylacetate insoluble products. They have a relatively smaller average molecular weight and less polarity than asphaltenes. Resins can form true solutions with certain solvents. There are two different interpretations of how resins and asphaltenes interact in the crude oil. One is that resins in solution increase the polarity of the mixture which forms sufficient polarity to dissolve asphaltenes. This implies that the resins fraction functions as a cosolvent. The other is that resins in the crude oil solution tend to adsorb on the surface of asphaltenes.
to provide a transition between the polar asphaltenes and the relatively non-polar oil fractions. They therefore peptize the asphaltenes compounds and form micellization in the liquid.\textsuperscript{15, 29}

**Solid Phase Behaviour**

Solid precipitated from the reservoir fluid can be viewed as a full profile of constituents which contains primarily the complex heterocompounds of waxes, resins and asphaltenes. The experimental evidence shows that the broad distribution of solid compounds is partly dissolved and partly colloidal suspended by the peptizing resins. Waxes and resin compounds can form a solution in the crude oil. For asphaltenes, it is generally agreed that the lower molecular weight fraction of asphaltenes is soluble while the heavier compounds may not be soluble.

The parameters that govern the precipitation of heavy organic compounds from the reservoir crude appear to be composition, the nature of the crude oil system, pressure and temperature. Electrokinetic phenomena and other factors may promote the peptization of the polar asphaltic compounds or may induce solid precipitation.

There are two common approaches to modelling solid and/or asphaltene precipitation. One is based on the assumption that the solid, including waxes and asphaltenes, is dissolved in crude oil in a true solution state and may be precipitated as a result of changing thermodynamical conditions. The other mechanism considers solid asphaltenes to exist in crude oil in a colloidal state in which the solid compounds are suspended and stabilized by the adsorbed resins molecules. When the absorbed resins are diluted in the solution, asphaltene compounds tend to aggregate mechanically or by electrostatic attraction and begin to precipitate.

**Other Models**

A number of mathematical solid models have been proposed. Fussel used an equation of state (EOS) to describe the solid phase behaviour in the crude oil system.\textsuperscript{60} This approach was based on the rigorous thermodynamic derivation. However, using that EOS for a solid phase may not be an appropriate procedure. Gupta\textsuperscript{71} (based on asphaltene solubility) developed a solid phase fugacity correlation for a particular oil of interest. The empirical correlation may only be valid for this particular oil. A considerable amount of experimental work is required to build the correlation. The thermodynamic solution model is widely accepted in the modelling of solid precipitation from reservoir fluid, in which both the regular solution\textsuperscript{22, 30, 33} and the polymer solution\textsuperscript{6, 8, 9, 11, 13, 17, 19, 20} were employed to formulate the activity coefficient. The regular solution theory of Scatchard and Hildebrand was developed for mixtures of nonpolar liquid with similar sizes of molecules. This theory assumes regularity (\(S^{\text{free}} = 0\)) and the isometric mixing (\(V^{\text{free}} = 0\)) at constant temperature and pressure. The polymer solution theory was developed based on the statistical mechanical theory of mixtures and the concept of the quasicrystalline lattice as a model for a liquid. It can be applied for flexible nonpolar molecules that differ significantly in size and shape, which is similar to a reservoir fluid containing heavy organic compounds.

Leontaritis et al.\textsuperscript{15} developed a thermodynamic colloidal suspension model to predict the onset of colloidal asphaltene flocculation in the crude oil. The solid particles aggregation is based on the critical resins concentration or chemical potential regardless of how the characteristics of the liquid mixture is changed.

In this work, the polymer solution theory is employed with modifications to incorporate both the solubility effect of soluble heavy organic compounds and the colloidal suspension nature, or the micellization process, of partial soluble solid compounds.

**Model Development**

A thermodynamic solution model is considered to be the primary factor which governs the solid precipitation along with a correction for the colloidal part of solid asphaltenes precipitation.

**Thermodynamic Relation**

For the liquid-solid phase equilibrium the equal fugacity of the \(i^\text{th}\) component in liquid and solid phases results in the following expression:

\[
y_i^L \xi_i \frac{y_i^s \xi^s}{RT} \exp \left[ \frac{y_i^s \xi^s}{RT} \right] = y_i^L \xi^L \frac{y_i^L}{RT} \exp \left[ \frac{y_i^L}{RT} \right]
\]

The solid-liquid equilibrium constant \(K_{sL}\) is then:

\[
\ln K_{sL} = \ln \left( \frac{y_i^L}{y_i^s} \right) + \ln \left( \frac{\xi_i^L}{\xi_i^s} \right) \frac{y_i^s}{RT} \exp \left[ \frac{y_i^s}{RT} \right] \exp \left[ \frac{y_i^L}{RT} \right]
\]

The first term on the right hand side of Equation (2) represents the composition effect. The second term gives the temperature effect. The last term is the pressure effect.

The relation between the standard state fugacity in the solid phase and in the liquid phase can be derived from a thermodynamic cycle\textsuperscript{23}.

\[
\ln \left( \frac{f_i^L}{f_i^s} \right) = \frac{\Delta H_i}{RT} \left( 1 - \frac{T_f}{T} \right) + \frac{\Delta C_i}{RT} \Delta T \left( 1 - \frac{R}{T} \right) \frac{\Delta C_i}{R} \Delta T
\]

where \(\Delta H_i\), \(T_f\) and \(\Delta C_i\) are correlated in the Appendix. The Poynting correction in Equation (2) cannot be evaluated accurately due to inability to correlate the molar volume difference \(V_i^L - V_i^s\).

Alternatively, this can be evaluated from the equation of state. The integral over pressure can be eliminated by considering the incompressible nature of the liquid and solid phases. Thus,

\[
P F = \int_0^{\frac{V_i^L}{RT}} \frac{\Delta V_i^s}{RT} \cdot dP = C_{PF} \frac{\Delta V_i^s}{RT}
\]

where \(C_{PF}\) is an adjustable coefficient due to the uncertainty of \(\Delta V_i^s\).

**Development of Activity Coefficient Model:**

The similarity of the heavy organic compounds in the crude oil and the polymer solution leads to the following formulation of Gibbs free energy of mixing. The Flory-Huggins polymer solution theory is applied along with a modification to account for the surface phenomena for polar asphaltene compounds in the mixture. From Hildebrand's derivation of polymer solutions, the free volume (which is defined as the difference between the actual volume of the liquid and the minimum volume which it would occupy if all the molecules per unit volume of liquid were packed firmly in contact with each other) is assumed to be the same between different components with the assumption of an athermal solution. However, the free volumes for molecules with different size can be significantly different which result in different degrees of thermal expansion\textsuperscript{23}. A linear change of the free volume with respect to the molecular weight is assumed to account for the free volume shift between different molecules.

In the reservoir fluid system, resins are assumed to be responsible for the peptization of the insoluble part of asphaltene compounds; the micellization process can result in a rearrangement of interaction between the unlike species in the solution. The interaction of the encapsulated asphaltene compounds with the rest of the constituents becomes the interaction between asphaltenes and resins if the resins concentration is higher than the critical micellization concentration (CMC). It is further assumed that there is no reaction occurring during the micellization process. The correction for Gibbs free energy change will then be primarily due to the interaction between the resins and the asphaltene compounds in the mixture and the increase in the surface energy of the free polar asphaltene compounds in the liquid. When evaluating the latter effect, it is assumed that the surface energy of the asphaltene...
compounds inside micelles is zero. The expression of Gibbs free energy of mixing is:

\[
\Delta G_m = v_n \left( \frac{1}{2} \sum_{j=1}^{m} \chi_j \phi_j \right) E_m + RT \sum_{j=1}^{m} (\phi_j \ln \phi_j) + n_{\text{m, mic}} V_m + n_{\text{r, mic}} V_r + \frac{1}{2} n_{\text{C, mic}} V_c
\]

where \( v_n \) is the molar volume of the mixture and \( v_{\text{m, mic}} \) is the molar volume of the micelles.

\[
\phi_{\text{r, mic}} = \frac{n_{\text{r, mic}} V_r}{2 v_{\text{m, mic}}}, \quad \phi_{\text{c, mic}} = \frac{n_{\text{c, mic}} V_c}{v_{\text{m, mic}}}
\]

The component volume fraction is:

\[
\phi_i = \frac{n_i^c \phi_i \phi_i^c + \phi_i}{\sum_j n_j^c \phi_j \phi_j^c + 1}
\]

The linear change of free volume can be expressed as a function of the molecular weight.

\[
c_f = 1 + C_f \left( \frac{1}{MW_f} - \frac{1}{MW_{\phi}} \right)
\]

where \( C_f \) is an adjustable coefficient. \( \phi_i \) is the volume fraction when \( n_{\text{C, mic}} = 0 \) and \( n_{\text{r, mic}} = 0 \). \( n_i^c \) is the moles of the \( i \)th component in the solution system. The resins compound, due to the micellization, only half of \( n_{\text{C, mic}} \) is in contact with the liquid solution. The colloidal part of asphaltene compounds which are surrounded by the resins molecules is only in contact with resins in the micelle form. Thus

\[
n_i^c = n_i - \frac{1}{2} n_{\text{C, mic}}, \quad n_i^c = n_i - n_{\text{C, mic}}
\]

\( E_f \) is the interaction energy change upon fluid mixing which can be written as:

\[
E_f = \left( \delta_i - \delta_j \right)^2 + 2d_{ij} \delta_i \delta_j
\]

d_{ij} is the binary interaction energy parameter. The value of \( d_{ij} \) becomes larger when the difference between solubility parameters \( \delta_i \) and \( \delta_j \) increases. Hence, by setting \( n_{\text{C, mic}} = 0, n_{\text{r, mic}} = 0 \) and \( e_i = 0 \) Equation (5) represents the solubility model. Otherwise, the equation gives the combination of solubility and colloidal system.

The activity coefficient of the \( k \)th component in the liquid phase can be derived from the Gibbs free energy of mixing.

\[
RT \ln \gamma_i = \left( 1 + \ln \frac{\phi_i}{x_i} \right) \frac{1}{x_i} - \left( \frac{\phi_i}{x_i} \right) \phi_i - E_f + W_f
\]

where \( W_f = n_i/\chi_i \) is the \( k \)th component in the solution, and \( \delta_n \) and \( \delta_c \) are the Kronecker deltas. \( e_i \) is the surface energy of polar asphaltene compounds.

This equation is applicable to the liquid phase. For the solid phase, an ideal mixing is considered. Thus the equilibrium constant \( K_{SL} \) can be evaluated using Equation (2) along with the correlations in the Appendix.

\[
Q(\beta) = \sum_{i=1}^{n} \frac{\beta_i}{\phi_i} \ln(E_i)
\]

where:

\[
E_i = \sum_{j=1}^{n} \frac{\beta_j}{\phi_j} \phi_j
\]

The component mole fractions in each phase can then be calculated as:

\[
x_i = \frac{\zeta_i}{\phi_i} E_i
\]

which satisfies the material balances:

\[
z_i = \sum_{j=1}^{n} \zeta_j x_j = 1 \quad (i = 1, 2, \ldots, N)
\]

The flash scheme can be made with Newton's optimization applied to the objective function.

\[
\Delta \beta = -H^{-1} \nabla Q(\beta)
\]

where \( \Delta \beta \) is the search direction vector, and \( H \) is the Hessian matrix, for which the elements are:

\[
H_{jk} = \frac{\partial^2 Q}{\partial \beta_j \partial \beta_k} = \sum_{i=1}^{n} \frac{z_i}{E_i} \phi_j \phi_k
\]

\( \nabla Q \) is the first derivative vector of the objective function.

For a multimodel flash calculation where the solid phase is calculated with a solid model, the solid phase fugacity coefficients
TABLE 1: Summary of cloud point temperature determination of oil #1.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Experiment ±0.5°C</th>
<th>Best Fit °C</th>
<th>Reset Cc °C</th>
<th>Reset Ct °C</th>
<th>Reset Cpf °C</th>
<th>Reset Tb °C</th>
<th>Reset td °C</th>
<th>7-Component °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>327.40</td>
<td>32.5</td>
<td>31.5</td>
<td>30.4</td>
<td>28.7</td>
<td>22.9</td>
<td>3.8</td>
<td>52.3</td>
<td>33.1</td>
</tr>
<tr>
<td>273.00</td>
<td>32.9</td>
<td>31.1</td>
<td>29.9</td>
<td>28.4</td>
<td>23.1</td>
<td>3.1</td>
<td>50.2</td>
<td>31.0</td>
</tr>
<tr>
<td>136.60</td>
<td>33.1</td>
<td>32.2</td>
<td>31.0</td>
<td>28.2</td>
<td>2.5</td>
<td>4.4</td>
<td>30.1</td>
<td></td>
</tr>
<tr>
<td>78.05</td>
<td>34.1</td>
<td>35.2</td>
<td>34.3</td>
<td>33.6</td>
<td>2.5</td>
<td>4.4</td>
<td>33.4</td>
<td></td>
</tr>
<tr>
<td>1.70</td>
<td>42.6</td>
<td>43.9</td>
<td>43.3</td>
<td>43.8</td>
<td>11.4</td>
<td>55.3</td>
<td>47.4</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2: Characterization of oil #1 (6 pseudo-components).

<table>
<thead>
<tr>
<th>Pseudo-Component</th>
<th>Mole Fraction</th>
<th>Specific Gravity</th>
<th>( T_b ) (°K)</th>
<th>( P_c ) (atm)</th>
<th>( T_e ) (°K)</th>
<th>( V_c ) (litre/mole)</th>
<th>Acentric Factor</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 - C_1 )</td>
<td>0.8013</td>
<td>0.25970</td>
<td>45.185</td>
<td>189.920</td>
<td>0.06882</td>
<td>0.00065</td>
<td>16.270</td>
<td></td>
</tr>
<tr>
<td>( CO_2 - C_3 )</td>
<td>0.1095</td>
<td>0.47056</td>
<td>46.821</td>
<td>325.662</td>
<td>0.16234</td>
<td>0.11589</td>
<td>39.393</td>
<td></td>
</tr>
<tr>
<td>( C_4 - C_5 )</td>
<td>0.0246</td>
<td>0.58769</td>
<td>35.747</td>
<td>430.956</td>
<td>0.27269</td>
<td>0.20066</td>
<td>55.180</td>
<td></td>
</tr>
<tr>
<td>( C_6 - C_11 )</td>
<td>0.0386</td>
<td>0.75949</td>
<td>29.233</td>
<td>578.816</td>
<td>0.43384</td>
<td>0.30521</td>
<td>125.848</td>
<td></td>
</tr>
<tr>
<td>( C_{12} - C_{17} )</td>
<td>0.0158</td>
<td>0.85103</td>
<td>18.701</td>
<td>743.030</td>
<td>0.72952</td>
<td>0.53089</td>
<td>199.008</td>
<td></td>
</tr>
<tr>
<td>( C_{18}^+ )</td>
<td>0.0096</td>
<td>0.93158</td>
<td>13.906</td>
<td>848.987</td>
<td>1.11443</td>
<td>0.82665</td>
<td>335.706</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3: Binary interaction parameters \( \delta \) for oil #1.

<table>
<thead>
<tr>
<th>Component</th>
<th>( N_2 - C_1 )</th>
<th>( CO_2 - C_3 )</th>
<th>( C_4 - C_5 )</th>
<th>( C_6 - C_11 )</th>
<th>( C_{12} - C_{17} )</th>
<th>( C_{18}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 - C_1 )</td>
<td>0.0018</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>( CO_2 - C_3 )</td>
<td>0.1591</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>( C_4 - C_5 )</td>
<td>0.2603</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>( C_6 - C_11 )</td>
<td>0.2113</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>( C_{12} - C_{17} )</td>
<td>0.3479</td>
<td>0.1001</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>( C_{18}^+ )</td>
<td>0.0096</td>
<td>0.93158</td>
<td>0.1001</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

The results indicate that the pressure effect is fairly small for this system in the higher pressure range. The experimental data show an increasing CPT as the pressure decreases, while the model predictions appear to have a small increase at the high pressure end. However, this increase is not quite obvious when considering the temperature measurement precision. The trend is consistent with the predicted values. The reason is that for the dew point system, the liquid drop out has a maximum value at some pressure level which is at approximately 25,330 to 28,370 kPa (250 to 280 atm) in this case. From a perspective of solubility behaviour, more liquid volume tends to dissolve more solid constituents. Yet it is not necessary that more solid be present at higher or lower pressure. The behaviour depends on the dominant effect of liquid volume or the amount of solid constituents in the condensed phase. At lower pressures, more light to medium components evolve which leaves the condensed phase more waxy.

Results and Discussions

Solid precipitation experiments for reservoir crudes using a laser detection technique have been conducted for the evaluation of this model.

Oil #1

A waxy reservoir fluid had a dew point pressure of 51,270 kPa (506 atm) at 138°C. The molecular weight is 28.98. From a compositional analysis the waxy components extend to at least \( C_{28} \). The results of cloud point temperature at various pressures are summarized in Table 1.

The fluid is characterized as in Table 2 with six pseudo-components for which properties are calculated using the Lee-Kesler correlations. The Peng-Robinson EOS is fitted to the dew point. The waxes solubility mechanism is applied to the vapor-liquid-solid flash calculation. To fit the CPT, the \( T_b \) of the heavy hypothetical component is increased by about 2.57% from the original value of \( C_6 \). The interaction energy coefficients \( (\delta J) \) are inputted as in Table 3. The \( \Delta C_p \) correction is suppressed for this system, and the \( C_{pf} \) is corrected by a coefficient of 0.35. The \( C_6 \) is adjusted to 0.0065. This set of input data yield the reasonable fit to experimental CPTs as shown in Figure 1.

The results indicate that the pressure effect is fairly small for...
This effect starts to dominate the liquid volume effect of solubility, thus more solid phase is precipitated.

In terms of the effects of model parameters, using the best fit data set as a base, the effect of each adjusting parameter is examined by decoupling it from the data set. The results are summarized in Table 1 and Figure 2. It indicates that:

1. Resetting \( C_c \) has a slight effect on the CPT profile for this system. From Equation (3), the \( 1^{st} \) term on the right hand side is dominant, the other terms involving \( \Delta C_p \) are relatively small and tend to cancel each other. Increasing \( \Delta C_p \) effect tends to increase the solid solubility in the liquid phase at the pressure above 20,265 kPa (200 atm), with little effect at low pressures as indicated with "Reset \( C_c \)" in Figure 2.

2. The pressure correction \( C_{PF} \), or rather \( \Delta v_{LS} \), affects the curve primarily on the high pressure end as expected. Decreasing this effect increases the solid solubility. Although this correction does not directly affect the vapor-liquid distribution in the EOS calculation, in order to get the incipient CPT, the system temperature has to be reduced due to the enhanced solid solubility. This temperature change leads to the redistribution of the three phase equilibrium.

3. Increasing the free volume coefficient \( C_f \) results in a smaller volume fraction as the component gets heavier. This effect increases the possibility for heavy solid compounds to precipitate. The reduction in the volume fraction of heavy compounds can decrease the average liquid phase solubility parameter \( \delta_m \) and increase the solubility parameter difference between the heavy component and the overall liquid, thus increasing the interaction contribution to the activity coefficient.

4. \( T_b \) adjustments can affect the model prediction dramatically as shown in Figure 2 in which \( T_b \)'s are reset to the original values calculated from the Kesler-Lee correlations. This is because the dominant contribution of \( \Delta H_i \) and \( T_b \) is calculated from \( T_b \). These adjustments are considered to be adequate due to the possible deviation of the correlations from the real system for which Pedersen et al.\(^{[22]}\) indicated a fairly large difference between the experimental and the calculated values, and due to the possible inaccuracy in estimating \( T_b \) from Lee-Kesler correlations for high molecular weight heavy components.

5. \( d_i \)'s are examined by setting all of them to zero, which results in geometric mean of interaction solubility parameters. The curve (Figure 2) has been changed dramatically. This implies that a certain degree of solid phase nonideality may exist, or more likely there are some other parameters the model has not accounted for.

6. Like the phase behaviour calculation using an EOS, characterization can also affect the solid precipitation calculation.

This fluid characterization results in the underprediction of solid precipitation. This effect is examined by characterizing the fluid system with seven pseudo-components. The same model parameters were used except that \( T_b \) of the heavy compounds are reduced by about 5.9% in order to get an approximate fit to the experimental data (Figure 2 with "second characterization"). Pedersen et al.\(^{[22]}\) also reported similar phenomena in four out of 17 cases of reservoir fluids. More detailed characterization can lead to the overprediction of the model.

The analyses above indicate that \( C_c \), \( C_{PF} \) and \( C_f \) only affect the trend of the incipient solid precipitation profile, while \( T_b \) primarily shifts the whole curve and \( d_i \) can alter the curve trend and the degree of the solid precipitation.

**Oil #2**

This is a crude oil system with a bubble point of 10,436 kPa (103 atm) at 86°C. A series of titration tests was performed with various solvents of \( C_2 \), \( C_3 \), and a multicomponent with 47.2% \( C_1 \). A summary of experimental results is listed in Table 4. Using the characterization in Table 5, this fluid is first fitted to the saturation pressure. A three phase flash calculation is performed to fit the ethane titration results with some adjustments procedure similar to Oil #1. The other two solvent titration experiments are fitted with the same set of parameters and components properties except the slight adjustments on the binary interaction parameters between "asphalt" and \( C_1 \) and "asphalt" and \( C_3 \) components. The model prediction results, as presented in Table 4, show:

1. A lighter solvent requires less solvent fraction to obtain the incipient solid precipitation during the titration test. This indicates that a lighter solvent is a stronger precipitant. Figure 3 shows the incipient conditions of the titration tests with respect to \( T_b \) of the solvents.

2. At the pressure above the bubble point, the amount of solvent required for the incipient solid precipitation increases with increasing pressure, which indicates an increasing liquid solubility as it becomes more compressed. Figure 4 depicts this effect for \( C_2 \), \( C_3 \) and \( C_5 \) titration. The \( C_3 \) curve above \( C_2 \) agrees with the result in No.1.

3. At the pressure below the saturation pressure, a small change in the incipient solvent fraction is observed as the pressure decreases. Unfortunately, only one measurement is done for the \( C_5 \) titration. At this pressure level, a three phase vapour-liquid-solid equilibrium is involved. For solubility dominated solid compounds, a decrease in the pressure results in the decrease in the liquid phase volume which in turn decreases the solid solubility. The change in the liquid phase volume can change the composition distribution and characteristics of the phase. Reducing pressure results in more light components evolving to the vapor phase which leaves a heavier liq-
TABLE 4: Summary of titration results of oil #2.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_c$ (K)</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Solvent Fraction</th>
<th>Model Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2$</td>
<td>306.4</td>
<td>174.33</td>
<td>86.0</td>
<td>0.33 ± 0.38</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130.40</td>
<td>86.0</td>
<td>0.16 ± 0.18</td>
<td>0.192</td>
</tr>
<tr>
<td></td>
<td></td>
<td>87.44</td>
<td>86.0</td>
<td>0.17 ± 0.22</td>
<td>0.175</td>
</tr>
<tr>
<td></td>
<td></td>
<td>174.33</td>
<td>60.0</td>
<td>0.43 ± 0.46</td>
<td>0.458</td>
</tr>
<tr>
<td>$C_3$</td>
<td>369.8</td>
<td>174.33</td>
<td>86.0</td>
<td>0.50 ± 0.65</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>135.27</td>
<td>86.0</td>
<td>0.58 ± 0.63</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106.35</td>
<td>86.0</td>
<td>0.19 ± 0.24</td>
<td>0.243</td>
</tr>
<tr>
<td>Multi-component</td>
<td>279.0</td>
<td>174.33</td>
<td>86.0</td>
<td>0.16 ± 0.22</td>
<td>0.21</td>
</tr>
</tbody>
</table>

TABLE 6: Characterization of Oil #2.

<table>
<thead>
<tr>
<th>Pseudo-Component</th>
<th>Mole Fraction</th>
<th>Specific Gravity</th>
<th>$T_b$ (°K)</th>
<th>$P_b$ (atm)</th>
<th>$T_c$ (°K)</th>
<th>$V_a$ (litre/mole)</th>
<th>Acentric Factor</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$ - $C_{10}$</td>
<td>0.10680</td>
<td>0.9976</td>
<td>273.25</td>
<td>35.499</td>
<td>440.11</td>
<td>0.2768</td>
<td>0.2102</td>
<td>64.01</td>
</tr>
<tr>
<td>$C_{11}$ - $C_{16}$</td>
<td>0.18583</td>
<td>0.7216</td>
<td>373.35</td>
<td>28.731</td>
<td>550.04</td>
<td>0.4119</td>
<td>0.3328</td>
<td>104.50</td>
</tr>
<tr>
<td>$C_{17}$ - $C_{18}$</td>
<td>0.15200</td>
<td>0.8037</td>
<td>474.47</td>
<td>22.352</td>
<td>655.38</td>
<td>0.5819</td>
<td>0.5066</td>
<td>156.01</td>
</tr>
<tr>
<td>$C_{19}$ - $C_{27}$</td>
<td>0.08264</td>
<td>0.4741</td>
<td>545.19</td>
<td>10.356</td>
<td>745.98</td>
<td>0.8588</td>
<td>0.7179</td>
<td>221.82</td>
</tr>
<tr>
<td>Asphalt</td>
<td>0.00200</td>
<td>1.07485</td>
<td>1473.74</td>
<td>7.031</td>
<td>1154.00</td>
<td>1.4234</td>
<td>2.1665</td>
<td>1434.00</td>
</tr>
</tbody>
</table>

The solid compound is analysed to be extended at least to $C_{10}$. A small number of solid particles are present which implies that the solid compounds are partly soluble and partly colloidal suspended. For the purpose of the model match, the original fluid is characterized with resins and asphaltenes separated for the initialization of solubility-colloidal mechanism in Table 7.
of reservoir fluid systems using one set of parameter correlations. It may be necessary in the solid modelling that some of the parameters are adjusted due to correlations that are not well-defined at the present knowledge level (such as the detailed characterization or description of components and the lack of definition of the structure of asphaltenes compound). For all cases in this work, the boiling point temperatures of the heavy components are altered somewhat. This adjustment changes the freezing point temperature and the heat of fusion of the component used in the solid model. Because of the lack of experimental data on very heavy components in establishing the correlations, these correlations may not be accurate for heavy components like waxes and asphaltenes.

Pedersen et al.\(^{(22)}\) indicated a significant difference for the heat of fusion between the experimental and calculated values. However, another factor has to be considered. The boiling point temperature as calculated from the Kesler-Lee correlation may not be accurate for the heavy compounds. In addition, these compounds contain various hydrocarbons such as paraffins, aromatics, naphthenes, etc., which are difficult to analyse in reservoir fluids.

Two correction coefficients are placed in the terms of the Poynting effect and the \( \Delta C_p \) effect. In some fluid systems, this correction may be significant in the prediction of solid precipitation. Although a correlation has been developed which expresses \( \Delta C_p \) in terms of molecular weight and temperature, the correlation is based on a very limited number of data, hence an adjustable constant is introduced to correct the deviation of \( \Delta C_p \) for the heavy components. The light component usually has a very small \( \Delta C_p \) which does not affect the solid phase behaviour as significantly as the heavy component. It is evident that the \( \Delta C_p \) correction is very important when the model matching is strongly temperature dependent. Thomas et al.\(^{(30)}\) and Pedersen et al.\(^{(22)}\) also indicated the relevance of the inclusion of \( \Delta C_p \) term in Equation (3). Similar reasoning leads to the inclusion of \( C_{\text{PP}} \) in the model. Laboratory experiment shows

that for some fluid systems, solid precipitation is pressure sensitive under high pressure conditions. For these systems, the inclusion of the Poynting effect should not be neglected. The temperature effect is an important factor in waxes precipitation behaviour. For an asphaltene dominant solid compound in the fluid system, this effect is not as important as for waxy fluids. From this point of view, the introduction of an adjustable coefficient may be necessary for the model to work for all fluid systems. The adjustment of modelling parameters indicate that more effective fluid characterization may be required.

Quantitative data on the amount and composition of the solid precipitates are highly selective for the evaluation of the solid model. However, these data are difficult to obtain accurately. As a compromise, a series of titration tests to determine the incipient solid precipitation condition appears to be a practical data set for model fitting. The ability to match the experimental incipient precipitation conditions implies that a more precise solid precipitation locus can be obtained through model predictions at various reservoir conditions. Thus the model can be applied for the evaluation of solid formation in oil production and transportation processes.

To evaluate the validity of the model, more experiments are required to examine the effects of pressure, temperature and composition. This is especially true for the colloidal system where further information is required on the critical resins concentration. Quantitative measurements need to be done regarding the amount of the precipitated solid phase in order to evaluate the capability of quantitative prediction of the model. With more experimental data available, accurate correlations can be established for the improvement and generalization of model predictions.

Conclusions

1. A solid precipitation model is proposed for liquid-solid equilibrium based on polymer solution theory. Modifications are incorporated to account for the effect of surface phenomena on colloidal suspensions. Adequate fits of this model to the experimental data have been obtained.

2. Characterization of the heavy fraction in the reservoir fluid can affect the solid model prediction. A larger experimental data base is required to generalize the modelling parameters.

3. The solid precipitation of the light waxy fluid is primarily governed by the liquid phase volume and temperature.

4. Results from Oil #2 conclude that lighter hydrocarbon solvents (less \( T_s \)) are more powerful precipitants than the heavier ones.

5. At \( P>P_{\text{cr}} \), the solid solubility increases with increasing pressure. For three phase equilibrium \( (P<P_{\text{cr}}) \), the solubility depends on the dominant effect of liquid volume or the characteristics of the liquid phase in the fluid system.

6. Highly aromatic asphaltenes precipitation (Oil #3) is strongly pressure dependent despite the high system temperature.

7. The temperature effect for asphaltene dominant Oil #3 is not as significant as for the waxy Oil #1.
Acknowledgements

The authors thank Hycal Energy Research Laboratories Ltd. for the permission to present these results. Valuable comments from Dr. Heidemann and Dr. Trebble (University of Calgary) are gratefully acknowledged.

NOMENCLATURE

C = constant, heat capacity
f = fugacity
G = Gibbs free energy
H = enthalpy, Hessian matrix
K = equilibrium constant
MW = molecular weight
n = moles
N = number of components
p = pressure
Q = flash objective function
R = gas constant
T = temperature
v = molar volume
x = phase composition
z = feed composition

Greek Symbols

β = phase mole fraction
γ = activity coefficient
δ = solubility parameter, Kronecker delta
Δ = difference
ϕ, Φ = volume fraction
ρ = fugacity coefficient

Superscripts

L = liquid
S = solid
O = standard state

Subscripts

a = asphaltenes
b = boiling
c = heat capacity correction
coll = colloidal
f = fusion, free
i,k = component index
m = mixture
PF = Poynting factor
r = resins
ref = reference

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Appendix

Model Parameters Correlations

Solubility parameter $\delta$ can be evaluated using an EOS. For PR EOS, it can be expressed as:

$$\delta^2 = \frac{a}{2\sqrt{2} b \nu_l} \left( 1 - \frac{T \left( \frac{d a}{dT} \right)}{a} \right) \ln \left( \frac{v_L + (1+\sqrt{2})b}{v_L + (1-\sqrt{2})b} \right)$$

where $a$ and $b$ are the EOS parameters, and the liquid molar volume $v_L$ is calculated using the EOS with a volume translation to improve the accuracy.

Alternatively, a correlation of the solubility parameter based on the literature data\(^{33, 35, 36}\) is developed in terms of the molecular weight and corrected for the effect of temperature. The correlation has also considered the curve trend which allows for the solubility parameter profile to be extended up to $C_{60}$ without a serious offset.

$$\delta_f = \frac{\delta_{9700PC}}{2.0820 + 0.000325 \times \ln(MW)} \times (T - 25)$$

$$\delta_{9700PC} = 8.021 \times \frac{59.5}{MW} + 0.008 \cdot MW^{-0.6972} \quad \text{(cal/cm}^3)$$

Resins Critical Micellization Concentration (CMC) can be estimated from the relation:

$$n_{CMC} = \frac{v \delta^2}{v_{np} \delta^2_{np}}$$

where $v_{np}$ and $\delta_{np}$ are the system mean molar volume and polar solubility parameter excluding the asphaltenes.

Surface Energy of Solid Compounds per unit volume is given empirically as\(^{35}\):

$$\sigma_s = 0.01649 \cdot \delta_s^2 \quad \text{(cal/cm}^3)$$

Heat Capacity Difference $\Delta C_p$ is regressed as a function of temperature and molecular weight based on the limited experimental data\(^{22}\):

$$\Delta C_p = \left( 0.38\cdot0.44 \cdot MW^{0.982} - 4.31507 \right) \left( 1 - \frac{T - 150}{35.38 + 102.26 \cdot MW^{0.128}} \right) \quad \text{C}_c$$

$\Delta C_p$ in this correlation is restricted to positive value. $C_c$ is an adjustable correction coefficient.

Temperature of Fusion $T_f$ and Heat of Fusion $\Delta H_f$ are regressed using literature data of paraffins, aromatics and naphthenes\(^{33, 35}\). The resulting correlations are:

$$\begin{align*}
T_f &= \frac{3080.04 - 1.305 \cdot MW - 709.77 \cdot \ln(T_f) + 10.722 \cdot T^2}{-107.22} \\
\Delta H_f &= (7.4181 \cdot MW^{0.43} - 46.95) \cdot T_f
\end{align*}$$

where $T_f$ and $\Delta H_f$ are in K and cal/gmole, respectively.

Authors' Biographies

Xuelong Zbou has worked in the area of fluid phase behaviour for over ten years. He has been involved in research and development related to phase equilibria, EOS modelling and miscible flooding since he joined Hycal Energy Research Laboratories Ltd. in 1991. He received his M.Sc. in Chemical and petroleum engineering from the University of Calgary in 1995. He is a member of The Petroleum Society and SPE.

Brent Thomas holds a doctorate in chemical engineering. He has worked on enhanced oil recovery applications for the last ten years, including gas injection, chemical flooding, solids precipitation and thermal applications. He is presently vice president of Hycal Energy Research Laboratories Ltd.

R.G. Moore has been a professor in the Department of Chemical and Petroleum Engineering at The University of Calgary since 1970. For the past four years, he has also been head of that department.

In his research, Dr. Moore works in the area of thermal recovery with a specialty in situ combustion, as well as environmental, flammability and safety related issues. He has consulted to more than 40 companies worldwide in the area of enhanced oil recovery. Dr. Moore lectures both undergraduate and graduate students and has been awarded several "Best Instructor" awards by the students.

Dr. Moore currently serves on the board of governors of The Petroleum Society. He served as chairman of the Calgary Section and as a director on the National Board. In 1989 he was awarded the CIM District V Proficiency Medal, and in 1995 was awarded The Petroleum Society Distinguished Service Award and was given a CIM Fellowship. He is a registered professional engineer in the Province of Alberta and is a member of the SPE, CSCHE and AIChE.