Prediction of Solid Paraffin Precipitation Using Solid Phase Equation of State

Mohsen Vafaie Sefti, a Hamid Mehdizadeh, a Ali Mousavi, b

aDepartment of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
bIran’s Research Institute of Petroleum Industry, Pazhooheshgah, Blvd.Khairabad Junction, Old Qom Road, Tehran, Iran

Abstract

In the traditional methods for wax precipitation prediction, the fugacity of solid is calculated using a hypothetical thermodynamic cycle. In this study, a new method based on TST solid equation of state is proposed to calculate the fugacities of solid phases. The multi-solid approach is used for description of solid phases. Obtained parameters for this equation of state is useful for future works.

Keywords: wax precipitation, solid equation of state, multi-solid

1. Introduction

Wax deposition from gas and oil production facilities and pipelines is undesirable. The flow-lines and process equipments may be plugged by wax deposition. Different physical and chemical methods have been proposed to remove deposited solids, which increases operating costs. A reliable model for wax precipitation calculations is highly valued for design and operation of flowlines. Since 1990s, so many efforts have been done to predict conditions under which the waxes can precipitate and the amount of precipitated wax in functions of pressure, temperature and composition. At first, the calculations were based on the solid-liquid equilibrium assumption. Later on, the gas phase was included in the calculations [1, 2]. There are two clearly defined assumptions for the determination of the thermodynamic equilibrium wax–liquid in established multi-component hydrocarbons systems: solid solution, and the formation of multiple solid phases. In the former case, different methods were proposed based on the activity coefficient model assuming the non-ideality of liquid and solid phases [3, 4]. Solid phase transition and vapor phase were then considered in other works [5-7]. The non-ideality was defined using Wilson or UNIQUAC equations. Lira-Galeana et al. [8] developed the multi-solid approach in 1996. In this model, it is assumed that the solid wax consists of several pure solid phases, in which the number and nature of them will be obtained from phase stability analysis. Coutinho showed that the solid phase is a multi-solid solution in nature and supported by experimental data [9].
In this work, the wax-precipitation model based on solid phase equation of state will be presented. The multi-solid approach is used because of its wide acceptability and limitation of using solid phase equation of state. The parameters of the equation of state are obtained in the case that vapor, liquid and solid phases are included in the system.

2. Solid Phase Equation of State

The equations of state that can be applied to a system containing solid, liquid and vapor phases simultaneously are scarce [10,11]. In this project, TST\(^1\) equation of state is used [11]. The general form of the equation is as below:

\[
P = \frac{RT}{v-b} \left( \frac{a}{(v+ub)(v+wb)} \right)
\]  

(1)

In this equation, \(u\) and \(w\) are 3 and -0.5 respectively. Also,

\[
a_c = 0.470507 R^2 T_c^2 / P_c
\]  

(2)

\[
b_c = 0.0740740 RT_c / P_c
\]  

(3)

\[
Z_c = 0.296296
\]  

(4)

\[
a = \alpha \ a_c
\]  

(5)

Alpha function for liquid and vapor phases could be used in conventional polynomial form or in exponential form. In this equation, a new alpha function is introduced for the solid phase, which will be discussed later.

In order to calculate fugacity of each component in pure solid state, the following equation is used [12].

\[
d \ln f = - \frac{\Delta H}{RT^2} dT + \frac{v}{RT} dP
\]  

(6)

Where,

\(f\): fugacity

\(\Delta H\): enthalpy change in result of change in system temperature

\(v\): partial molar volume

By integrating the above equation from the triple point pressure to the system pressure for liquid and solid phases and dividing the two equations, the following relation will be obtained. In this equation, \(\Delta H^l\) and \(\Delta v\) are supposed to be independent of pressure and temperature.

\[
\ln \frac{f_s^L}{f_s^L} = - \frac{\Delta H^l}{RT} \left( 1 - \frac{T}{T_r} \right) \frac{\Delta v P}{RT}
\]  

(7)

\(^1\) Twu-Sim-Tassone
Suppose that the pressure system is equal to zero, we will have
\[
\ln \frac{f^S}{f^L} = -\frac{\Delta H^f}{RT} \left(1 - \frac{T}{T_r}\right)
\]  

(8)

This equation is similar to the equation that was proposed by Prausnitz et al. [13] for the calculation of solid phase fugacity. If the fugacity is calculated at zero pressure,
\[
\ln \left(\frac{f^S}{P}\right) = -1 - \ln b^* - \ln (v^{*S} - 1) - \frac{1}{(w-u)} \frac{a^{*S}}{b^*} \ln \left(\frac{v^{*S} + w}{v^{*S} + u}\right)
\]  

(9)

Where,
\[
 v^{*S} = \frac{1}{2} \left(\frac{a^{*S}}{b^*} - u - w\right) - \left[\left(u + w - \frac{a^{*S}}{b^*}\right)^2 - 4 \left(uw + \frac{a^{*S}}{b^*}\right)\right]^{1/2}
\]

(10)

\[
a^* = \frac{Pa}{R^2T^2}
\]

(11)

\[
b^* = \frac{Pb}{RT}
\]

(12)

And,
\[
 u \text{ and } w \text{ are the parameters of the equation of state. By equalizing the two equations, we will get}
\]
\[
-1 - \ln b^* - \ln (v^{*S} - 1) - \frac{1}{(w-u)} \frac{a^{*S}}{b^*} \ln \left(\frac{v^{*S} + w}{v^{*S} + u}\right) = \ln \left(\frac{f^L}{P}\right) - \frac{\Delta H^f}{RT} \left(1 - \frac{T}{T_r}\right)
\]

(13)

The only unknown variable in the above equation is $a^{*S}$. Therefore, the equation is solved to obtain $a^{*S}$ for different temperatures. The parameters of predefined solid alpha function are calculated by correlating the data to the following equation
\[
\alpha^S(T) = 1 + l_s (1 - T_{r,j}^{0.5}) + m_s (1 - T_{r,j})^{a_s} (0.7 - T_{r,j})
\]

(14)

In which $\alpha^S$ can be calculated using
\[
\alpha^S = a^c / a_s
\]

(15)

\[
a^S = \frac{a^{*S} R^2T^2}{P}
\]

(16)

In order to calculate the optimum parameters, the following goal function was used to minimize the difference between the presented data and the calculated data from eq. 9.
\[
f(x) = \sum\left(1 + l_s (1 - T_{r,j}^{0.5}) + m_s (1 - T_{r,j})^{a_s} (0.7 - T_{r,j}) - \alpha^S_i\right)^2
\]

(17)

The simplex-Nelder-Mead algorithm was utilized to obtain the optimum parameters, which minimizes the goal function. Due to the nonlinearity of the function, the results
will drastically depend on the initial guess for the optimal parameters. To avoid this problem, the optimization problem is run for different starting points.

3. Wax Precipitating Model

The following expressions are used to describe the system in which vapor, liquid and pure solids are in equilibrium state.

Mass balance for precipitating components:

\[ y_i^v n_v^i + x_i^l n_l^i + n_i^s - z_i^f n_f^i = 0 \]  \( i = 1, \ldots, N_c, \quad j = 1, \ldots, N_P \)

Where

- \( N_P \): Number of precipitated solids
- \( N_c \): Number of components

Mass balance for non-precipitating components:

\[ y_i^v n_v^i + x_i^l n_l^i - z_i^f n_f^i = 0 \]  \( i = 1, \ldots, N_c \)

Equality of fugacities in the liquid and gas phases for each component:

\[ f_i^l - f_i^g = 0 \]  \( i = 1, \ldots, N_c \)

Equality of fugacities in the liquid and solid phases for precipitating components:

\[ f_i^l - f_i^s = 0 \]  \( i = 1, \ldots, N_c \)

Summation of mole fractions in liquid and gas phases are equal to unity

\[ \sum_{i=1}^{N_c} x_i - 1 = 0 \]  \( i = 1, \ldots, N_c \)

\[ \sum_{i=1}^{N_c} y_i - 1 = 0 \]  \( i = 1, \ldots, N_c \)

All the equations above constitute a system of equations, which should be solved in order to define the equilibrium system completely. An error function is introduced to check the convergence of the system of equations.

\[ f(\delta) = \sum_{i=1}^{2N_c + N_P + 2} |\delta_i| \]

Where \( \delta_i \)’s are the right hand expressions in equations 13-17.

4. Results and Discussions

The composition of oil samples and some synthetic mixtures, which were used in this project are shown in tables 1-4. Since the references are different, the components considered for each sample are not the same.
Prediction of Solid Paraffin Precipitation Using Solid Phase Equation of State

Table 1. Mole fractions for two synthetic mixtures [7]

<table>
<thead>
<tr>
<th>Component</th>
<th>Mixture C</th>
<th>Mixture B</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C_{10}</td>
<td>0.5876</td>
<td>0.5101</td>
</tr>
<tr>
<td>n-C_{18}</td>
<td>0.0513</td>
<td>0.0819</td>
</tr>
<tr>
<td>n-C_{19}</td>
<td>0.0486</td>
<td>0.0694</td>
</tr>
<tr>
<td>n-C_{20}</td>
<td>0.0463</td>
<td>0.0590</td>
</tr>
<tr>
<td>n-C_{21}</td>
<td>0.0440</td>
<td>0.0506</td>
</tr>
<tr>
<td>n-C_{22}</td>
<td>0.0418</td>
<td>0.0433</td>
</tr>
<tr>
<td>n-C_{23}</td>
<td>0.0397</td>
<td>0.0373</td>
</tr>
<tr>
<td>n-C_{24}</td>
<td>0.0378</td>
<td>0.0319</td>
</tr>
<tr>
<td>n-C_{25}</td>
<td>0.0359</td>
<td>0.0274</td>
</tr>
<tr>
<td>n-C_{26}</td>
<td>0.0342</td>
<td>0.0236</td>
</tr>
<tr>
<td>n-C_{27}</td>
<td>0.0327</td>
<td>0.0202</td>
</tr>
<tr>
<td>n-C_{28}</td>
<td>0</td>
<td>0.0176</td>
</tr>
<tr>
<td>n-C_{29}</td>
<td>0</td>
<td>0.0148</td>
</tr>
<tr>
<td>n-C_{30}</td>
<td>0</td>
<td>0.0127</td>
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Table 2. Mole fractions for a synthetic mixture [14]

<table>
<thead>
<tr>
<th>Component</th>
<th>Bim 13</th>
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<tbody>
<tr>
<td>C_{10}</td>
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<tr>
<td>C_{18}</td>
<td>7.09</td>
</tr>
<tr>
<td>C_{19}</td>
<td>6.09</td>
</tr>
<tr>
<td>C_{20}</td>
<td>5.220</td>
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</tbody>
</table>

Table 3. Mole fractions of heavy oil fractions [5]

<table>
<thead>
<tr>
<th>Peusocomponent</th>
<th>Oil 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole percent</td>
</tr>
<tr>
<td>P-C_{10}</td>
<td>4.4627</td>
</tr>
<tr>
<td>N-C_{10}</td>
<td>6.4827</td>
</tr>
<tr>
<td>A-C_{10}</td>
<td>15.126</td>
</tr>
<tr>
<td>P-C_{15}</td>
<td>2.9096</td>
</tr>
<tr>
<td>N-C_{15}</td>
<td>3.8627</td>
</tr>
<tr>
<td>A-C_{15}</td>
<td>8.9664</td>
</tr>
<tr>
<td>P-C_{20}</td>
<td>1.5426</td>
</tr>
<tr>
<td>N-C_{20}</td>
<td>2.1514</td>
</tr>
<tr>
<td>A-C_{20}</td>
<td>5.0199</td>
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<td>P-C_{25}</td>
<td>0.7856</td>
</tr>
<tr>
<td>N-C_{25}</td>
<td>1.389</td>
</tr>
<tr>
<td>A-C_{25}</td>
<td>3.2409</td>
</tr>
<tr>
<td>P-C_{30}</td>
<td>0.3528</td>
</tr>
<tr>
<td>N-C_{30}</td>
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<tr>
<td>A-C_{30}</td>
<td>1.4348</td>
</tr>
<tr>
<td>P-C_{35}</td>
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<td>P-C_{40}</td>
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<tr>
<td>N-C_{40}</td>
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<td>A-C_{40}</td>
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<td>P-C_{45}</td>
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<tr>
<td>A-CP1</td>
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</tr>
<tr>
<td>N-CP2</td>
<td>0.2257</td>
</tr>
<tr>
<td>A-CP2</td>
<td>1.3396</td>
</tr>
</tbody>
</table>
Table 4. Mole fractions of heavy oil fractions [5]

<table>
<thead>
<tr>
<th>Pseudocomponent</th>
<th>Mole percent</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-CP1</td>
<td>3.5922</td>
<td>157.0</td>
</tr>
<tr>
<td>N-CP1</td>
<td>4.7712</td>
<td>157.0</td>
</tr>
<tr>
<td>A-CP1</td>
<td>4.7712</td>
<td>157.0</td>
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<tr>
<td>P-CP2</td>
<td>2.7858</td>
<td>201.0</td>
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<tr>
<td>N-CP2</td>
<td>4.5495</td>
<td>201.0</td>
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<tr>
<td>A-CP2</td>
<td>4.5495</td>
<td>201.0</td>
</tr>
<tr>
<td>P-CP3</td>
<td>1.8055</td>
<td>252.0</td>
</tr>
<tr>
<td>N-CP3</td>
<td>2.9829</td>
<td>252.0</td>
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<tr>
<td>A-CP3</td>
<td>4.4744</td>
<td>252.0</td>
</tr>
<tr>
<td>P-CP4</td>
<td>1.2238</td>
<td>300.0</td>
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<tr>
<td>N-CP4</td>
<td>2.9018</td>
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<td>A-CP4</td>
<td>4.3527</td>
<td>300.0</td>
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<tr>
<td>P-CP5</td>
<td>0.3674</td>
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<tr>
<td>N-CP5</td>
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<td>563.0</td>
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<td>A-CP5</td>
<td>5.1937</td>
<td>563.0</td>
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<td>P-CP6</td>
<td>0.0581</td>
<td>654.0</td>
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<td>A-CP6</td>
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<td>P-CP7</td>
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<td>A-CP7</td>
<td>2.8634</td>
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<td>N-CP8</td>
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<td>744.0</td>
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<tr>
<td>A-CP8</td>
<td>2.1707</td>
<td>744.0</td>
</tr>
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</table>

The parameters of the equation of state \((l_s, m_s, n_s)\) are calculated as discussed in the previous section. The optimal values for the mentioned parameters for the oil samples are in tables 5-9. The initial guess for the system of equilibrium equations is given from the results of a two-phase flash calculation. Then, the dogleg method [15] is applied to check the convergence criteria, i.e. the right-hand side expression in equation 19 should be less than 1e-7. If the criterion is not met, the program will shift to simplex algorithm that uses the results of the previous step as the initial points. There is a normalizing step, which filters the incoming physically unacceptable data. The physical properties data are derived from databooks or are estimated from proposed methods in the literature.

Table 5. Parameters of EOS for mixture B

<table>
<thead>
<tr>
<th>Component</th>
<th>(l_s)</th>
<th>(m_s)</th>
<th>(n_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n-C_{10})</td>
<td>-9.4224</td>
<td>13.239</td>
<td>-0.18762</td>
</tr>
<tr>
<td>(n-C_{18})</td>
<td>7.1395</td>
<td>-0.44956</td>
<td>-4.3144</td>
</tr>
<tr>
<td>(n-C_{19})</td>
<td>-8.9293</td>
<td>15.535</td>
<td>-0.035543</td>
</tr>
<tr>
<td>(n-C_{20})</td>
<td>7.9884</td>
<td>-0.52493</td>
<td>-4.2596</td>
</tr>
<tr>
<td>(n-C_{21})</td>
<td>-9.2735</td>
<td>16.518</td>
<td>-0.016801</td>
</tr>
<tr>
<td>(n-C_{22})</td>
<td>8.6106</td>
<td>-0.57798</td>
<td>-4.2509</td>
</tr>
<tr>
<td>(n-C_{23})</td>
<td>-9.5182</td>
<td>17.335</td>
<td>-0.0037988</td>
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<tr>
<td>(n-C_{24})</td>
<td>9.4021</td>
<td>-0.64356</td>
<td>-4.223</td>
</tr>
<tr>
<td>(n-C_{25})</td>
<td>-9.7652</td>
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<td>0.006465</td>
</tr>
<tr>
<td>(n-C_{26})</td>
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<td>-4.209</td>
</tr>
<tr>
<td>(n-C_{27})</td>
<td>-9.7534</td>
<td>18.749</td>
<td>0.019831</td>
</tr>
<tr>
<td>(n-C_{28})</td>
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Table 5. Parameters of EOS for mixture B (contd.)

<table>
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<tr>
<th>Component</th>
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<th>(m_c)</th>
<th>(n_c)</th>
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<tbody>
<tr>
<td>(n-C_{29})</td>
<td>-9.9905</td>
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<tr>
<td>(n-C_{30})</td>
<td>11.444</td>
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<td>-4.1968</td>
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Table 6. Parameters of EOS for mixture C

<table>
<thead>
<tr>
<th>Component</th>
<th>(i_c)</th>
<th>(m_c)</th>
<th>(n_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n-C_{10})</td>
<td>-9.4224</td>
<td>13.239</td>
<td>-0.18762</td>
</tr>
<tr>
<td>(n-C_{18})</td>
<td>7.1395</td>
<td>-0.44956</td>
<td>-4.3144</td>
</tr>
<tr>
<td>(n-C_{29})</td>
<td>-8.9293</td>
<td>15.535</td>
<td>-0.035543</td>
</tr>
<tr>
<td>(n-C_{20})</td>
<td>7.9884</td>
<td>-0.52493</td>
<td>-4.2596</td>
</tr>
<tr>
<td>(n-C_{21})</td>
<td>-9.2735</td>
<td>16.518</td>
<td>-0.016801</td>
</tr>
<tr>
<td>(n-C_{22})</td>
<td>8.6106</td>
<td>-0.57798</td>
<td>-4.2509</td>
</tr>
<tr>
<td>(n-C_{23})</td>
<td>-9.5182</td>
<td>17.335</td>
<td>-0.003799</td>
</tr>
<tr>
<td>(n-C_{24})</td>
<td>9.4021</td>
<td>-0.64356</td>
<td>-4.223</td>
</tr>
<tr>
<td>(n-C_{25})</td>
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<td>18.107</td>
<td>0.006465</td>
</tr>
<tr>
<td>(n-C_{26})</td>
<td>10.112</td>
<td>-0.70408</td>
<td>-4.209</td>
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<td>(n-C_{27})</td>
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Table 7. Parameters of EOS for bim13

<table>
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<th>(m_c)</th>
<th>(n_c)</th>
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</thead>
<tbody>
<tr>
<td>(C_{10})</td>
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<td>-0.20581</td>
</tr>
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<td>(C_{18})</td>
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<td>-4.2847</td>
</tr>
<tr>
<td>(C_{29})</td>
<td>6.4639</td>
<td>-0.29946</td>
<td>-4.5263</td>
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<tr>
<td>(C_{30})</td>
<td>8.0223</td>
<td>-0.53895</td>
<td>-4.2522</td>
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<td>(C_{14})</td>
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<td>-4.151</td>
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<td>(C_{15})</td>
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<td>(C_{16})</td>
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Table 8. Parameters of EOS for Oil 5

<table>
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<th>Pseudocomponent</th>
<th>(i_c)</th>
<th>(m_c)</th>
<th>(n_c)</th>
</tr>
</thead>
<tbody>
<tr>
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Table 9. Parameters of EOS for Oil 6

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$\alpha^S$ is independent of pressure and it can be used for the solid volume prediction [11]. The error function for lighter components, like $C_{10}$, are greater than heavy fractions. The reason is that the calculations are done in a temperature far from the melting point.

Figure 1. Experimental and calculated amount of precipitated wax for Oil 5
Prediction of Solid Paraffin Precipitation Using Solid Phase Equation of State

Figure 2. Experimental and calculated amount of precipitated wax for *Oil 6*

Figure 3. Experimental and calculated amount of precipitated wax for *bim13*

Figure 4. Experimental and calculated amount of precipitated wax for *mixture B*
5. Conclusion

Complex behavior of solid phase in oil mixture and wide range of its application in solid precipitation and deposition petroleum fluids (wax, asphaltene, …) need to be modeled via applicable and efficient methods. Here application of a solid EOS for description of solid phase was tested for wax precipitation in petroleum mixtures. In this work, TST solid equation of state is used for describing wax precipitation phenomena in some synthetic and real oil mixtures. This solid equation of state is based on an alpha function. Using thermodynamic cycle for pure solid fugacity from pure liquid fugacity, the TST parameters were tuned before its application for wax precipitation prediction. The multisolid phase approach is used for determination of the nature and number of solid phases. As it can be seen in the previous sections, the obtained results in this work are in good agreements with the experimental data.

References


