A generalized regular solution model for asphaltene precipitation from \( n \)-alkane diluted heavy oils and bitumens

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Abstract

Regular solution theory with a liquid-liquid equilibrium was used to model asphaltene precipitation from heavy oils and bitumens diluted with \( n \)-alkanes at a range of temperatures and pressures. The input parameters for the model are the mole fraction, molar volume and solubility parameters for each component. Bitumens were divided into four main pseudo-components corresponding to SARA fractions: saturates, aromatics, resins, and asphaltenes. Asphaltenes were divided into fractions of different molar mass based on the gamma molar mass distribution. The molar volumes and solubility parameters of the pseudo-components were calculated using solubility, density, and molar mass measurements. The effects of temperature and pressure are accounted for with temperature-dependent solubility parameters and pressure-dependent diluent densities, respectively. Model fits and predictions are compared with the measured onset and amount of precipitation for seven heavy oil and bitumen samples from around the globe. The overall percent average absolute deviations (%AAD) of the predicted yields were less than 1.6% for the diluted heavy oils. A generalized algorithm for characterizing heavy oils and predicting asphaltene precipitation from \( n \)-alkane diluted heavy oils at various conditions is proposed.

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Keywords: Regular solution; Modeling; Asphaltene precipitation; Heavy oil; Bitumen; Fluid characterization

1. Introduction

As conventional oil reserves are depleted, oil sands bitumens and heavy oil resources are gaining prominence. Bitumens and heavy oils are rich in asphaltenes; the heaviest, most polar fraction of a crude oil. Asphaltenes are formally defined as a solubility class of materials that are insoluble in \( n \)-alkanes such as \( n \)-pentane and \( n \)-heptane but soluble in aromatic solvents such as toluene. Asphaltenes are known to self-associate forming aggregates containing approximately 6–10 molecules [1,2]. Asphaltenes also contribute significantly to the high viscosity and the coking tendency of heavy oils and bitumens. In some production and processing schemes, such as heavy oil upgrading, VAPEX processes or paraffinic oil sands froth treatment, asphaltenes are deliberately precipitated to obtain a lower viscosity and more easily refined product. In other cases, heavy oils are diluted with a solvent, such as condensate, in order to reduce viscosity for transport.

To optimize these processes, it is necessary to have accurate predictions of the amount of asphaltene precipitation as a function of the amount of solvent, temperature, and pressure.

One promising approach to modeling asphaltene precipitation is regular solution theory, first applied to asphaltenes by Hirschberg et al. [3]. They treated asphaltenes as a single component. Kawanaka et al. [4] applied the modified Scott and Maget model [5,6] to asphaltene precipitation using a molar mass distribution for the asphaltenes. More recently, Yarranton and Masliyah [7] successfully modeled asphaltene precipitation in solvents by treating asphaltenes as a mixture...
of components of different density and molar mass. Alboudwarej et al. [8] extended Yarranton and Masliyah’s model and the Hildebrand and Scott [9,10] regular solution approach to asphaltene precipitation from Western Canadian heavy oils and bitumens.

The input parameters for the Alboudwarej et al. model [8] were the mole fraction, molar volume and solubility parameters for each component. Bitumens were divided into four main pseudo-components corresponding to SARA fractions: saturates, aromatics, resins, and asphaltenes. Asphaltenes were divided into fractions of different molar mass based on the gamma molar mass distribution. The extent of asphaltene self-association was accounted for through the average molar mass of asphaltenes. Correlations for the molar volumes and solubility parameters of the pseudo-components were developed based on solubility, density, and molar mass measurements. The preliminary model results for Western Canadian and four international bitumens and heavy oils were in good agreement with experimental measurements. Akbarzadeh et al. [11] developed a model based on solubility, density, and molar mass measurements for each component. Bitumens were divided into four fractions of different molar mass based on the universal gas constant, temperature, and the density of each fraction (measured in toluene at 50°C).

3. Regular solution model

Details of the regular solution model are given in Alboudwarej et al. [8]. A brief summary is provided here. A liquid–liquid equilibrium is assumed between the heavy liquid phase (asphaltene-rich phase including asphaltenes and resins) and the light liquid phase (oil-rich phase including all components). It is still not certain that asphaltenes ‘precipitate’ as a liquid phase or a solid phase. Also, multiple phases, including V:L1-L2:S, have been observed [15,16] for crude oils. Typically, multiple phases appear particularly for mixtures that either contain very light hydrocarbons, such as methane and ethane, or for systems close to their bubble point. The existence or lack of multiple phases in the systems discussed in this work could not be confirmed experimentally. However, since the systems under investigation were well above the bubble point and contained no light hydrocarbons, it was assumed that there are only two phases at equilibrium. The equilibrium ratio, \( K_i^{hl} \), for any given component is then given by:

\[
K_i^{hl} = \frac{x_i^l}{x_i^h} = \exp \left\{ \frac{x_i^l - x_i^h}{\delta_i^l - \delta_i^h} + \left( \frac{v_i^l}{RT} - \delta_i^l \right) - \left( \frac{v_i^h}{RT} - \delta_i^h \right) \right\}
\]

where \( x_i^l \) and \( x_i^h \) are the heavy and light liquid phase mole fractions, \( R \) the universal gas constant, \( T \) temperature, \( \delta_i \) and \( \delta_i \) are the molar volume and solubility parameter of component \( i \) in either the light liquid phase (l) or the heavy liquid phase (h), and \( v_i^l \) and \( v_i^h \) are the molar volume and solubility...
Table 1

<table>
<thead>
<tr>
<th>Fractions</th>
<th>wt %</th>
<th>Density (kg/m³)</th>
<th>Molar mass a (g/mol)</th>
</tr>
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<tr>
<td>Athabasca Saturates</td>
<td>16.3</td>
<td>900</td>
<td>524</td>
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<tr>
<td>Aromatics</td>
<td>39.8</td>
<td>1003</td>
<td>550</td>
</tr>
<tr>
<td>Resin</td>
<td>28.5</td>
<td>1058</td>
<td>976</td>
</tr>
<tr>
<td>Asphaltenes b</td>
<td>14.7</td>
<td>1192</td>
<td>7900</td>
</tr>
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<td>Solids c</td>
<td>0.7</td>
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<tr>
<td>Cold lake Saturates</td>
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<tr>
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<tr>
<td>Venezuela 2 Saturates</td>
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<td>Aromatics</td>
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<td>Resin</td>
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<td>Resin</td>
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Table 2

<table>
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<tr>
<th>Temperature (°C)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
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<td>Saturates</td>
<td>Aromatics</td>
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<td>895.1</td>
</tr>
<tr>
<td>25</td>
<td>888.8</td>
</tr>
<tr>
<td>35</td>
<td>–</td>
</tr>
<tr>
<td>40</td>
<td>870.2</td>
</tr>
<tr>
<td>55</td>
<td>869.6</td>
</tr>
</tbody>
</table>

* For asphaltenes the corrected molar mass at 23°C is 20% higher than the measured value at 50°C [19].

b. Asphaltenes average molar mass measured at 50°C and 10/1kg/m³ as toluene.

c. Non-asphaltic solids.

Table 2

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Saturates</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>895.1</td>
<td>–</td>
</tr>
<tr>
<td>25</td>
<td>888.8</td>
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<tr>
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<td>1004.0</td>
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<tr>
<td>40</td>
<td>870.2</td>
<td>996.6</td>
</tr>
<tr>
<td>55</td>
<td>869.6</td>
<td>–</td>
</tr>
</tbody>
</table>

4. Fluid characterization

The first step in fluid characterization is to divide the fluid into components and pseudo-components. In this case, each solvent is an individual component with known properties. The bitumen or heavy oil was divided into pseudo-components based on SARA fractions (saturates, aromatics, resins, and asphaltenes). The saturates, aromatics, and resins were each treated as a single pseudo-component. However, it proved necessary to divide the asphaltene fraction into several pseudo-components in order to accurately predict yields.

The asphaltenes are here considered to be macromolecular aggregates of monodisperse asphaltene monomers. Therefore, the asphaltene fraction was divided into pseudo-components based on molar mass. The gamma distribution function [18] was used to describe the molar mass distribution:

\[
\begin{align}
\frac{1}{\Gamma(\beta)} \left( \frac{\beta}{M - M_{\text{monomer}}} \right)^\beta (M - M_{\text{monomer}})^{\beta-1} \\
\times \exp \left( \frac{\beta(M - M_{\text{monomer}})}{M - M_{\text{monomer}}} \right)
\end{align}
\]

where \(M_{\text{monomer}}\) and \(\hat{M}\) are the monomer molar mass and average ‘associated’ molar mass of asphaltenes, and \(\beta\) a parameter which determines the shape of the distribution. Since molar mass is an intrinsic property, it is preferable to consider a distribution of aggregation numbers given by:

\[
\begin{align}
\frac{1}{M_{\text{monomer}} \Gamma(\beta)} \left( \frac{\beta}{\hat{M} - M_{\text{monomer}}} \right)^\beta (\hat{M} - M_{\text{monomer}})^{\beta-1} \\
\times \exp \left( \frac{\beta(\hat{M} - M_{\text{monomer}})}{\hat{M} - M_{\text{monomer}}} \right)
\end{align}
\]

where \(\hat{M}\) is the number of monomers in an aggregate and is defined as follows:

\[
\hat{M} = \frac{M}{M_{\text{monomer}}}
\]

This formulation was used in the modeling work. However, since the monomer molar mass is not well established, the measured apparent or associated molar masses are used in...
the following discussion. As discussed elsewhere [8], the asphaltenes were discretized into 30 fractions ranging up to 30,000 g/mol. The asphaltene monomer molar mass was assumed to be 1800 g/mol. The asphaltene monomer molar mass was assumed to be 1800 g/mol. The average aggregation number (or associated asphaltene molar mass) depends on the composition and temperature[17] and must be measured or estimated for any given condition.

The value of $\beta$ is unknown although a value of 2 is recommended for polymer systems. However, the extent of asphaltene self-association and hence the asphaltene molar mass distribution depend on temperature. Therefore, the parameter $\beta$ was also assumed to be temperature dependent. The following correlation for $\beta$ was determined by fitting the model to precipitation data for mixtures of asphaltene–heptane–toluene at temperatures of 23 and 50 $^\circ$C, as shown in Fig. 1:

$$\beta(T) = -0.0259T + 10.178$$

where $T$ is the temperature in Kelvin. Note that the correlation has only been tested for temperatures between 0 and 100 $^\circ$C and cannot apply at temperatures exceeding 120 $^\circ$C because the predicted $\beta$ decreases below zero. More data at higher temperatures is required to extend the correlation appropriately.

The second step in the fluid characterization for regular solution models is to determine the mole fraction, molar volume, and solubility parameter of each component. The mole fractions of the components and pseudo-components are determined from the masses of the solvent and bitumen, the SARA analysis, and the measured or estimated molar masses. Molar volumes and solubility parameters are discussed in detail below.

![Fig. 1. Fractional precipitation of Athabasca asphaltenes from solutions of n-heptane and toluene at 0, 23, and 50 $^\circ$C.](image)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Molar Mass at 50 $^\circ$C (g/mol)</th>
<th>Density at 23 $^\circ$C (kg/m$^3$)</th>
<th>Solubility parameter at 23 $^\circ$C (MPa$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>460</td>
<td>889</td>
<td>15.9</td>
</tr>
<tr>
<td>Aromatics</td>
<td>522</td>
<td>990</td>
<td>20.2</td>
</tr>
<tr>
<td>Resin</td>
<td>1040</td>
<td>1044</td>
<td>19.6</td>
</tr>
</tbody>
</table>

4.1. Molar volumes

The molar volumes of the solvents were calculated using Hankinson–Brobst–Thomson (HBT) technique [20], which accounts for both the effect of temperature and pressure. The molar volumes of the saturates and the aromatics can be determined either from the individual measured molar masses and densities for fractions from each bitumen or heavy oil, given in Table 1, or from the average molar masses and densities given in Table 3. The average properties are used in this work.

The data from Table 2 was used to determine the temperature dependence of the densities. The following curve fit equations were found for the densities of the saturate and the aromatic fractions of an Athabasca bitumen sample as a function of temperature:

$$\rho_{sat} = -0.0259T + 10.178$$

$$\rho_{aro} = -0.0259T + 10.178$$

where $\rho_{sat}$ and $\rho_{aro}$ are the densities of Athabasca saturates and aromatics in kg/m$^3$, respectively. It was assumed that the change in density with temperature was the same for saturates and aromatics extracted from any heavy oil/bitumen. Hence, the correlations were modified as follows to match the average density of saturates and aromatics from Table 3 but retain the slopes from Eqs. (4) and (5):

$$\bar{\rho}_{sat} = -0.0259T + 10.178$$

$$\bar{\rho}_{aro} = -0.0259T + 10.178$$

where $\bar{\rho}_{sat}$ and $\bar{\rho}_{aro}$ are the average densities of saturates and aromatics in kg/m$^3$, respectively and $T$ the temperature in Kelvin.

The molar volumes of the asphaltenes and resins are determined from the following correlation of density to molar mass [8]:

$$\rho = 670M^{0.089}$$

where $\rho$ is the asphaltene or resin density in kg/m$^3$ and $M$ the molar mass in g/mol. The molar mass of an asphaltene fraction is the associated molar mass ($rM_m$) of that fraction. Note that the asphaltenes and resins are considered together because they are assumed to be a continuum of polynuclear aromatics. The change in asphaltene average density with temperature is accounted for with the change in average asphaltene molar mass with temperature, as will be discussed.
later. It was assumed that the change in density of the SARA fractions with pressure was negligible.

4.2. Solubility parameters

The solubility parameter is defined as follows:

\[ \delta = \left( \frac{\Delta H_{vap} \alpha - RT}{v} \right)^{1/2} \]  

(9)

where \( \Delta H_{vap} \alpha \) is the heat of vaporization. The solubility parameter of the solvents can be determined from existing correlations of heats of vaporization and molar volumes. However, the model predictions are very sensitive to small changes in the solubility parameter and an estimation of the sol-vent solubility parameter with an accuracy of approximately ±0.05 MPa\(^{0.5}\) is necessary. In this work, the following approach was found to give good predictions of the asphaltene yields.

First, the heats of vaporization were calculated using the Daubert et al. correlation [21]. Then, the molar volumes were determined using the HBT technique [20]. The solubility parameters obtained using these correlations and Eq. (9) agree with the literature values [22] for \( n \)-heptane at different temperatures and for \( n \)-hexane and \( n \)-pentane at 25 \( ^\circ \)C, as shown in Table 4. However, the predicted solubility parameters do not match the literature values for \( n \)-hexane and \( n \)-pentane at 0 \( ^\circ \)C. Therefore, an alternate method was applied. Solubility parameters are expected to vary linearly with temperature [22], and, therefore, the calculated solubility parameters for \( n \)-heptane were plotted versus temperature to obtain:

\[ \delta_h = 22.121 - 0.0232T \]  

(10)

where \( \delta_h \) is the solubility parameter of \( n \)-heptane in (MPa\(^{0.5}\)) and \( T \) the temperature in K. It was assumed that the change in solubility parameter with temperature was the same for all of the \( n \)-alkanes considered here. Hence, the following correlation was found for the solubility parameter of \( n \)-alkanes at different temperatures:

\[ \delta_s, T = \delta_s, 25 - 0.0232(T - 298.15) \]  

(11)

where \( \delta_s, T \) is solvent solubility parameter at temperature \( T \), \( \delta_s, 25 \) is solvent solubility parameter at 25 \( ^\circ \)C estimated from Eq. (9), and \( T \) the temperature in K. The predicted solubility parameters are compared with literature values in Table 4. The effect of pressure on the solvent solubility parameters is accounted for in the decrease in their molar volume with pressure.

The heats of vaporization of SARA fractions cannot be determined because the fractions decompose before the boiling point. Instead, the solubility parameters were determined by fitting the model to asphaltene solubility data for mixtures of asphaltenes and solvents.

The solubility parameter of the asphaltenes (and resins) was determined from the following correlation of solubility parameter to density recommended by Yarranton and Masliyah [7].

\[ \delta_s = \left( \frac{\Delta H_{vap} \alpha - RT}{v} \right)^{1/2} \frac{1}{\sqrt{rM_m/\rho}} \approx (\Delta H_{vap} \alpha - RT \frac{1}{rM_m/\rho})^{1/2} \]  

(12)

where \( \delta_s \) is the solubility parameter (MPa\(^{0.5}\)) of asphaltenes and \( A \) is approximately equal to the monomer heat of vaporization (kJ/g). (Since asphaltenes are considered to be aggregates of monomers with relatively low association enthalpies, the heat of vaporization of an aggregate is approximately the product of the number of monomers and the monomer heat of vaporization. The term \( RT/rM \) is much smaller than the monomer heat of vaporization and can be neglected.) It was assumed that the heat of vaporization of a resin was the same as that of an asphaltene monomer on a mass basis and therefore Eq. (12) is applied to resins as well. The correlation incorporates the effect of temperature and, for asphaltenes, the aggregation number of the given asphaltene fraction via the density. Since the asphaltene and resin densities are assumed to be independent of pressure, their calculated solubility parameters are also independent of pressure.

Parameter \( A \) depends on the temperature. The following correlation for \( A \) was determined by fitting the model to precipitation data for mixtures of asphaltene–heptane–toluene at temperatures of 23 and 50 \( ^\circ \)C as shown in Fig. 1:

\[ A(T) = -6.667 \times 10^{-4}T + 0.5614 \]  

(13)

where \( T \) is the temperature in Kelvin. Note that two parameters (\( \beta \) and \( A \)) were fitted to account for the effect of temperature. Increasing the magnitude of \( A \) shifted the fractional precipitation curve to lower heptane volume fractions. Increasing the magnitude of \( \beta \) led to a steeper slope on the fractional precipitation curve. To test the correlations (Eqs. (3) and (13)), the fractional precipitation curve was predicted.
for 0°C. Fig. 1 shows that the predicted fractional precipitation agrees well with the data.

Fig. 2 shows asphaltene precipitation data for mixtures of asphaltenes, saturates, and toluene as well as asphaltenes, n-heptane, and aromatics at 23 and 50°C. The saturates and aromatics solubility parameters found to fit the data are given in Table 5 and the corresponding model predictions are shown on Fig. 2. The solubility parameters in Table 5 differ slightly from those used in previous work [8,11] because additional solubility data was obtained allowing for a more accurate calculation. The following correlations were developed to estimate the solubility parameters of saturates and aromatics at different temperatures:

$$\delta_{sat} = 22.381 - 0.0222T$$  \hspace{1cm} (14)

$$\delta_{aro} = 26.333 - 0.0204T$$  \hspace{1cm} (15)

where $\delta_{sat}$ and $\delta_{aro}$ are the solubility parameters of saturates and aromatics in MPa$^{0.5}$ and $T$ the temperature in Kelvin. The saturate and aromatic solubility parameters are assumed to be independent of pressure.

Akbarzadeh et al. [11] showed that using the average values of density, molar mass, and solubility parameter for the SARA fractions provided in Table 3, rather than the individual values for each oil in Table 1, did not affect the model predictions significantly. To retain the generality of the model, the model predictions in this work are also based on these average values.

Table 5
Fitted solubility parameters for saturates and aromatics at 23 and 50°C

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Fitted solubility parameter (MPa$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23°C</td>
</tr>
<tr>
<td>Saturates</td>
<td>15.9</td>
</tr>
<tr>
<td>Aromatics</td>
<td>20.2</td>
</tr>
</tbody>
</table>

5. Results and discussion

Once the fluid characterization was completed, only one unknown parameter remained: the average associated molar mass ($\bar{r}_{Mm}$) of the asphaltenes in the bitumen or heavy oil. This parameter is temperature and source dependent because asphaltene association is temperature and source dependent. In general, smaller average molar masses expected at higher temperatures and in fluids with high resin content [2]. The following approach was taken to finalize the model:

1. The average associated asphaltene molar mass at 23°C was determined by fitting the model to asphaltene yields from n-heptane diluted bitumens and heavy oils at ambient conditions.
2. The temperature dependence of the average associated asphaltene molar mass was determined by fitting the model to asphaltene yields from n-heptane diluted Athabasca bitumen at various temperatures.
3. The model was tested on different bitumens and heavy oils diluted with n-pentane, n-hexane, n-heptane, or n-octane at various temperatures and pressures.
4. A generalized modeling approach is recommended for:
   (a) cases with some experimental yield data (average associated asphaltene molar mass is a fitting parameter); (b) cases with no experimental data (no adjustable parameters).

5.1. Fitting the average asphaltene associated molar mass at 23°C

Fig. 3 shows the asphaltene yields from various heavy oils/bitumens upon dilution with n-heptane (n-pentane in the case of Indonesian sample) at ambient conditions. Interestingly, the experimental onset of asphaltene precipitation...
Table 6
Fitted asphaltene molar mass in heavy oils/bitumens and average absolute deviation (AAD) for different systems

<table>
<thead>
<tr>
<th>Bitumen/heavy oil</th>
<th>Fitted asphaltene molar mass, M_{23} (g/mol)</th>
<th>%AAD^a</th>
<th>n-Heptane</th>
<th>n-Hexane</th>
<th>n-Pentane</th>
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<tr>
<td>Athabasca</td>
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<td>0.705</td>
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<tr>
<td>Cold Lake</td>
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<td>0.855</td>
<td>0.508</td>
<td>0.937</td>
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</tr>
<tr>
<td>Lloydminster</td>
<td>3005</td>
<td>0.522</td>
<td>0.690</td>
<td>0.552</td>
<td></td>
</tr>
<tr>
<td>Venezuela no. 1</td>
<td>3000</td>
<td>0.757</td>
<td>–</td>
<td>0.707</td>
<td></td>
</tr>
<tr>
<td>Venezuela no. 2</td>
<td>3025</td>
<td>0.690</td>
<td>–</td>
<td>0.883</td>
<td></td>
</tr>
<tr>
<td>Russia</td>
<td>2800</td>
<td>0.416</td>
<td>0.406</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Indonesia</td>
<td>2270</td>
<td>–</td>
<td>–</td>
<td>0.623</td>
<td></td>
</tr>
</tbody>
</table>

^a %AAD = 100 × (Σ |calculated − experimental| / N).

Based on average properties for saturates, aromatics, and resins presented in Table 3.

occurs at approximately the same heptane content (54 ± 4 wt.%) for all of the heptane diluted crude oils even though the ultimate yields vary significantly. Hence, it appears that the onset of precipitation does not depend significantly on the asphaltene content of the oil. Perhaps, the asphaltene molar mass distribution is the more significant factor in determining the onset point.

The fitted average molar mass for each system is provided in Table 6. All of the average molar masses are within 1.2% of 3000 g/mol except for the Russian and Indonesian sample. The Russian and Indonesian crude oils have the highest resin-to-asphaltene mass ratio (R/A ratio) of all the crude oils.

The extent of asphaltene association is known to decrease as the ratio of resins to asphaltenes increases [2]. Therefore, the calculated average asphaltene molar masses were plotted against the R/A ratio of each crude oil, as shown in Fig. 4. Most of the data is clustered and only two points corresponding to the Russian (R) and Indonesian (I) samples are spread out sufficiently to discern a clear trend. Nonetheless, the calculated molar mass decreases as the R/A ratio increases and

Fig. 4. The fitted asphaltene molar mass in bitumen versus the resin-to-asphaltene ratio. Ath = Athabasca, CL = Cold Lake, LM = Lloydminster, V1 = Venezuela no. 1, V2 = Venezuela no. 2, R = Russia, I = Indonesia.

decreases dramatically above an R/A ratio of approximately 5.

The following third degree polynomial fits the data of Fig. 4:

\[
M_{23} = -3.207(R/A)^3 + 25.943(R/A)^2 - 101.04(R/A) + 3099.4
\]  

where \(M_{23}\) is the average molar mass of asphaltenes in heavy oils/bitumens at 23°C in g/mol.

However, more data over a wide range of R/A ratio are required to test the applicability of the correlation.

5.2. Fitting the temperature dependence of the average asphaltene molar mass

The model was fitted to Athabasca bitumen/n-heptane system at 0, 23, 50, and 100°C, as shown in Fig. 5. The fitted molar masses are given in Table 7. The form of the temperature dependence of the average asphaltene molar mass is unknown. However, the data were observed to follow a linear trend versus temperature and were fitted with the following equation:

\[
M_{T,ath} = -10.599T + 6043.523
\]  

where \(M_{T,ath}\) is the average molar mass of asphaltenes in Athabasca bitumen in g/mol at temperature \(T\) in K.

Table 7
Fitted asphaltene molar mass in Athabasca bitumen at various temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Fitted molar mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3100</td>
</tr>
<tr>
<td>23</td>
<td>2960</td>
</tr>
<tr>
<td>50</td>
<td>2850</td>
</tr>
<tr>
<td>100(^a)</td>
<td>2070</td>
</tr>
</tbody>
</table>

^a Pressure = 2.07 MPa.
It was assumed that the change in average asphaltene molar mass with temperature was the same for all of the crude oils. Hence, the following general correlation is suggested for the temperature dependency of the average asphaltene molar mass:

$$M_T = M_{23} - 10.599(T - 296.15)$$

where $M_T$ is the average molar mass at temperature $T$, $M_{23}$ the average molar mass at 23°C reported in Table 6, and $T$ the temperature in Kelvin.

5.3. Model predictions

5.3.1. Solvent effect

Once the average molar mass of asphaltene in heavy oil/bitumen was determined, the model can be used to predict the onset and amount of precipitation from heavy oil/bitumen diluted with other $n$-alkanes with no other adjustment. Fig. 6 shows the asphaltene yields from Lloydminster heavy oil upon dilution with various $n$-alkanes at ambient conditions. The model was fitted to the heptane diluted data using an average asphaltene molar mass of 3005 g/mol giving an average percent absolute deviation (%AAD) of 0.27%. The model successfully predicted the onset of precipitation and asphaltene yields for the heavy oil/$n$-pentane, $n$-hexane, and $n$-octane solutions. The overall %AAD for Lloydminster-$n$-alkane systems is 0.46%. Similar results were obtained for other heavy oils/bitumens diluted with $n$-alkanes at ambient conditions [11].

Note that the predicted asphaltene yields in the $n$-octane system are higher than that in the $n$-heptane system even though the experimental yields for $n$-octane and $n$-heptane dilution are the same within the scatter of the data. Wiehe et al. [23] showed for $n$-alkane diluents, the onset of precipitation occurs at higher diluent content as the carbon number of the diluent increased up to 8–10 but then decreases at still higher carbon numbers. In other words, heptane is a better solvent than pentane but dodecane is a better solvent than decane. They also showed that this model correctly predicted the observed trend. Hence, the predicted in increase in asphaltene yield with $n$-octane diluent is likely the same trend emerging for the Lloydminster oil.

Also note that, in almost all the diluted bitumens, the asphaltene yield calculated from the model decreases at high $n$-alkane mass fractions while the experimental data level off or continue to increase with a small slope. The predicted yields decrease because the solutions are becoming dilute in bitumen and asphaltene and a small asphaltene solubility begins to affect the yield. The reason this effect is not observed in the data may be that asphaltenes self-associate to a greater extent as the diluent content increases. Increasing self-association would decrease asphaltene solubility and oppose the dilution effect.

5.3.2. Temperature effect

Figs. 7–13 show model predictions for asphaltene precipitation, respectively, from Athabasca bitumen, Cold Lake bitumen, Lloydminster heavy oil, Venezuela no. 1 bitumen, Venezuela no. 2 bitumen, Russia heavy oil, and Indonesia heavy oil diluted with various $n$-alkanes at various temperatures. The total %AAD’s for predictions based on the average properties and the suggested correlations are presented in Table 6. In almost all cases, the model predicted the amount of precipitation with a %AAD of less than 1%.

There is only one data set at 100°C, Fig. 8, and the model results do not match very well with the experimental data. It is possible that a liquid–liquid equilibrium no longer applies or that the property correlations begin to fail at temperatures
Fig. 8. Predicted fractional yield of precipitate from Cold Lake bitumen diluted with \( n \)-pentane and \( n \)-heptane at various temperatures; data at 50 and 100 °C from [14].

As high as 100 °C. On the other hand, there were some difficulties in obtaining consistent experimental data at 100 °C [14]. At this stage, it is not clear if the problem is with the model or the data.

At 0 °C the model under-predicted the ultimate amount of precipitation for most of heavy oils and bitumens diluted with \( n \)-pentane. One possible explanation for under-prediction is that at temperatures as low as 0 °C, resins may self-associate in a similar mechanism to asphaltenes. To account for self-association of resins in the model, the gamma distribution function (Eqs. (2a) and (2c)) was used to divide resins into five fractions based on the molar mass ranging up to 1900 g/mol. The resin monomer molar mass was assumed to be 200 g/mol. The average resin molar mass was assumed constant at 1040 g/mol as given in Table 3. Fig. 14 compares model predictions with and without resin precipitation for Athabasca and Russia samples diluted with \( n \)-pentane at 0 °C. The model predictions for Athabasca system are improved if resins are indeed self-associating and the self-association is taken into account. However, at this stage, there is insufficient supporting evidence to incorporate resin self-association into the model.

Fig. 9. Predicted fractional yield of precipitate from Lloydminster heavy oil diluted with \( n \)-pentane and \( n \)-heptane at various temperatures.

Fig. 10. Predicted fractional yield of precipitate from Venezuela no. 1 bitumen diluted with \( n \)-pentane and \( n \)-heptane at various temperatures; data at 23° from [11].

Fig. 11. Predicted fractional yield of precipitate from Venezuela no. 2 bitumen diluted with \( n \)-pentane and \( n \)-heptane at various temperatures; data at 23° from [11].
5.3.3. Pressure effect

The effect of pressure on asphaltene precipitation from Athabasca bitumen and Cold Lake bitumen is shown in Figs. 15 and 16, respectively. Although the only pressure dependency considered in the model is with the molar volume of the solvents, the model could accurately predict the amount of precipitation at moderate pressures (e.g. 2.1 MPa). However, the model under-predicted the ultimate amount of precipitation at high pressures (e.g. 6.9 MPa). Accounting for the effect of pressure on the pseudo-component parameters could improve the model predictions especially at high pressures. Nonetheless, the %AADs of the model predictions were less than 1.6% in all cases.

5.4. Generalized model

The implementation of the generalized model to predict the onset and amount of precipitation from diluted heavy oils or bitumens is summarized in the following algorithm:

1. Obtain a SARA analysis of the oil sample.
2. If the SARA properties (molar mass and density) are not available, use the average properties presented in Table 3.
Calculate the densities of saturates and aromatics at temperatures other than 23 °C from Eqs. (6) and (7).

3. Estimate solubility parameters of saturates and aromatics from Eqs. (14) and (15).

4. Estimate the average molar mass of asphaltenes at 23 °C from Eq. (16) and at the desired temperature from Eq. (18).

5. Subdivide asphaltenes (and resins if desired) using the Gamma distribution (Eqs. (2a), (2c) and (3)).

6. Determine densities and solubility parameters of asphaltene and resin sub-fractions from Eqs. (8), (12) and (13).

7. Calculate the liquid molar volumes and solubility parameters of the relevant n-alkane(s) from Hankinson-Brobst-Thomson (HBT) technique [18] and Eqs. (9) and (11), respectively.

8. Perform equilibrium calculations using Eq. (1) and standard techniques [8,15]. A bisection method may be required to converge the model.

9. Calculate the amount of precipitation at desired conditions (temperature, pressure, solvent mass fraction).

10. Check the accuracy of model predictions with experimental data if available. If necessary, adjust the average asphaltene molar mass to obtain a better fit.

The proposed asphaltene precipitation model is valid for a heavy oils and bitumens diluted with liquid n-pentane and higher carbon number alkanes at temperatures from 0 up to 100 °C and pressures up to 7 MPa. Since the model is based on property correlations determined for only this range of conditions and because only a liquid–liquid phase transition is considered, caution is recommended in extrapolating beyond these conditions. Within this range of conditions, the model is predictive in the same sense an EoS is predictive. It can provide an approximate solution if run using the steps 1–9. A more accurate solution may be obtained if the average molar mass is tuned to fit some data.

6. Conclusions

Seven bitumens/heavy oils were characterized in terms of SARA fractions. The molar volume and solubility parameter of the fractions were determined from molar mass, density, and asphaltene precipitation measurements. Since the molar mass of asphaltenes in bitumen is unknown, it was estimated by fitting the proposed regular solution model to precipitation data from solutions of bitumen and n-heptane at ambient conditions. A correlation was developed to estimate the average molar mass of asphaltenes in heavy oils and bitumens using the resin-to-asphaltene ratio. Asphaltenes were modeled for n-alkane diluted bitumens and heavy oils at various temperatures from 0 to 100 °C and pressures up to 7 MPa. The fitted and predicted onset and amount of precipitation were in reasonable agreement with the experimental data in most cases. In all cases, the percent average absolute deviations (%AAD) of the predicted yields were less than 1.6% for the diluted heavy oils and bitumens.

List of symbols

- $A$: parameter in Eq. (12)
- $AAD$: average absolute deviation
- $f$: mass frequency
- $K$: equilibrium ratio
- $M$: molar mass (g/mol)
- $P$: pressure (MPa)
- $r$: number of monomers in an asphaltene aggregate
- $R$: universal gas constant (cm$^3$ bar/mol K)
- $R/A$: resin-to-asphaltene mass ratio (wt./wt.)
- $T$: temperature (K)
- $v$: molar volume (cm$^3$/mol)
- $x$: mole fraction

Greek symbols

- $\beta$: parameter in gamma distribution function
- $\delta$: solubility parameter (MPa$^{0.5}$)
- $\Delta H^\text{vap}$: heat of vaporization (J/mol)
- $\Gamma$: gamma function
- $\rho$: density (kg/m$^3$)

Subscripts

- $23$: at 23 °C
- $25$: at 25 °C
- $a$: asphaltenes
- $aro$: aromatics
- $ath$: Athabasca
- $h$: heptane
- $i$: i-th component
- $m$: monomer
- $r$: resins
- $s$: solvent
At temperature \( T_{\text{sat}} \)

**Superscripts**
- \( h \) heavy phase
- \( l \) light phase

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**References**