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# Applying the PR-EoS to Asphaltene Precipitation from *n*-Alkane Diluted Heavy Oils and Bitumens

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The Peng–Robinson equation of state (EoS) was adapted using group contribution methods to model asphaltene precipitation from solutions of toluene and an *n*-alkane and from *n*-alkane diluted bitumens. A liquid–liquid equilibrium was assumed between a primary liquid phase and a second dense asphaltene phase. Bitumen was characterized in terms of solubility fractions: saturates, aromatics, resins, and asphaltenes. Critical properties of the saturates, aromatics, and resins were determined that fit their measured densities and compared well with existing critical property correlations. The saturate and aromatic critical properties were also tuned to fit asphaltene precipitation data from solutions of the saturate and toluene or the aromatic and heptane. Asphaltenes were divided into fractions of different molar masses using a gamma distribution function. EoS parameters for asphaltenes were determined that fit the measured densities, fit precipitation data for mixtures of asphaltenes, toluene, and heptane, and compared well with existing critical property correlations. The model successfully fitted and predicted the onset and amount of precipitation over a broad range of compositions, temperatures from 0 to 100 °C, and pressures up to 7 MPa. The model results were within the error of the measurements except for high dilutions with *n*-pentane.

## Introduction

Asphaltenes are a solubility class of crude oils and are defined as the fraction that precipitates upon the addition of an *n*-alkane (usually *n*-heptane or *n*-pentane), but dissolves in aromatic solvents such as toluene. They are a mixture of polynuclear aromatics, at least some of which are capable of self-association.<sup>1</sup> Asphaltenes can precipitate upon a change in pressure, temperature, and/or composition. For example, when pressure is drawn down around and within a wellbore, asphaltenes can precipitate and significantly reduce production. Also, when condensate diluent is added to heavy oils to reduce viscosity, asphaltene deposition can occur in surface facilities and pipelines. Treatment to remove or prevent the formation and deposition of solids increases operating costs. Therefore, it is desirable to prevent or mitigate asphaltene deposition. As a first step, it is necessary to predict the onset and amount of asphaltene precipitation.

There are a variety of approaches to modeling asphaltene precipitation that can be divided into two main camps: colloidal and macromolecular. In this work, we assume that asphaltenes can be treated as macromolecules and that their precipitation can be modeled as a conventional phase equilibrium between either two liquid phases or a liquid and a solid phase. There are two main conventional thermodynamic approaches for modeling asphaltene precipitation: regular solution theory and equations of state (EoS). Hirschberg et al.<sup>2</sup> and Griffith and Siegmund<sup>3</sup> first applied regular solution theory to asphaltenes. However, they treated asphaltenes as a single component.

Kawanaka et al.<sup>4</sup> applied the modified Scott and Maget model to asphaltene precipitation using a molar mass distribution for asphaltenes. Andersen and Speight<sup>5</sup> also tested the use of interaction parameters on asphaltene precipitation. Wang and Buckley<sup>6</sup> correlated solubility parameters to refractive index and used the results to model precipitation data. Yarranton and Masliyah treated asphaltenes as a mixture of components of different density and molar mass and successfully modeled asphaltene precipitation in solvents.<sup>7</sup> Others extended this approach to model asphaltene precipitation from Western Canadian heavy oils and bitumens diluted with various *n*-alkanes.<sup>8,9</sup> The heavy oils and bitumens were characterized on the basis of SARA fractionation, and a gamma distribution model was used to divide asphaltenes into pseudocomponent fractions. Asphaltene self-association was accounted for by using the average associated molar mass of the asphaltenes measured at or estimated for the given precipitation conditions. However, while the regular solution theory approach has proven fruitful, it is less convenient for use in process and reservoir simulation software, and most commercial process and reservoir simulation software employ the equation of state approach.

The EoS approach has not yet been applied successfully to asphaltene precipitation over a broad range of conditions. Gupta

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(1) Yarranton, H. W.; Alboudwarej, H.; Jakher, R. *Ind. Eng. Chem. Res.* **2000**, *39*, 2916–2924.

(2) Hirschberg, A.; DeJong, L. N. J.; Schipper, B. A.; Meijer, J. G. *SPE J.* **1984**, *June*, 283–293.

(3) Griffith, M. G.; Siegmund, C. W. *Marine Fuels: A Symposium*; ASTM Committee D-2 on Petroleum Products and Lubricants, Dec 7–8, 1983; Jones, C. H., Ed.; ASTM special technical publication 878; ASTM: Philadelphia, PA, 1985; pp 227.

(4) Kawanaka, S.; Park, S. J.; Mansoori, G. A. *SPE Reservoir Eng.* **1991**, *May*, 185–192.

(5) Andersen, S. I.; Speight, J. G. *J. Pet. Sci. Eng.* **1999**, *22*, 53–66.

(6) Wang, J. X.; Buckley, J. S. *Energy Fuels* **2001**, *15*, 1004–1012.

(7) Yarranton, H. W.; Masliyah, J. H. *AIChE J.* **1996**, *12*, 3533.

(8) Alboudwarej, H.; Akbarzadeh, K.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W. *AIChE J.* **2003**, *49*, 2948–2956.

(9) Akbarzadeh, K.; Alboudwarej, H.; Svrcek, W. Y.; Yarranton, H. W. *Fluid Phase Equilib.* **2005**, *232*, 159–170.

used the Peng–Robinson equation of state (PR-EoS) to calculate asphaltene solubility in solvents.<sup>10</sup> A solid–liquid equilibrium calculation was performed for a single nonassociating component with fixed molar mass. Gupta used a structural correlation for heavy components to estimate the critical properties of asphaltenes, even though this correlation was developed from the SRK-EoS. Nghiem and Coombe arbitrarily split the heaviest component in the oil into two parts: nonprecipitating and precipitating components.<sup>11</sup> The precipitating component was considered to be a pure dense asphaltene. Their model performed a three-phase vapor/liquid/solid flash calculation and required some experimental data for model tuning. Qin et al. attempted to implement the model of Nghiem and Coombe in their compositional model.<sup>12</sup> They treated asphaltenes as a pure component with the same critical properties as heavy hydrocarbons, except for the binary interaction parameters. They used the model to predict asphaltene precipitation in the reservoir during pressure depletion. However, none of these models account for asphaltene self-association.

Ting et al. used the statistical associating fluid theory (SAFT) equation of state to model asphaltene phase behavior in a live oil model and a recombined oil under reservoir conditions.<sup>13,14</sup> The theory predicts the change in free energy both upon bonding these segments to form chains and on the further association of the chainlike molecules. Ting et al. fitted the equation of state parameters for the asphaltene to precipitation data obtained from titration tests. The oil was characterized on the basis of SARA fractions, gas chromatography, and GOR data. The molar mass of the asphaltenes was back-calculated by fitting the density data. The model was used to predict the asphaltene onset pressure for various GOR values at 20 and 65.5 °C. This model requires a large number of parameters. Wu et al.<sup>15</sup> also proposed a fairly complex molecular-thermodynamic framework to describe asphaltene precipitation based on the SAFT equation of state and colloidal theory. Although the framework could theoretically explain the phase behavior of asphaltenes in oil, it could not be used for quantitative predictions due to the lack of some molecular parameters required for model predictions.

To date, there is no approach to modeling asphaltene precipitation that is easily adapted for reservoir and process simulation. The objective of this work is to apply the PR-EoS to asphaltene precipitation from heavy oils and bitumens over a range of temperatures and pressures. A methodology is developed to account for asphaltene self-association. While conventional oils are not considered here, this work is intended to be a first step in developing a broadly applicable and practical model for predicting asphaltene precipitation.

## Experimental Methods

The required data includes SARA analyses, molar masses, densities, fractional asphaltene precipitation in solvents, and asphaltene yields from alkane diluted heavy oils or bitumens. Almost

**Table 1. SARA Analysis (wt %) of Western Canadian<sup>8</sup> and Other Heavy Oils and Bitumens<sup>9</sup>**

sample	saturates	aromatics	resins	asphaltenes	solids
Athabasca	16.3	39.8	28.5	14.6	0.8
Cold Lake	19.4	38.1	26.7	15.3	0.5
Lloydminster	23.1	41.7	19.5	15.1	0.6
Venezuela 1	15.4	44.4	25.0	15.0	0.2
Venezuela 2	20.5	38.0	19.6	21.8	0.1
Russia	25.0	31.1	37.1	6.8	0.0
Indonesia	23.2	33.9	38.2	4.7	0.0

all of the data used in this work were obtained from Albouwarej et al.<sup>8</sup> and Akbarzadeh et al.<sup>9</sup> A few data points were added using the methods described in these articles. Asphaltenes were precipitated from each bitumen or heavy oil with the addition of *n*-pentane for SARA fractionation or *n*-heptane for solubility experiments and property measurements. Saturates, aromatics, and resins were extracted according to ASTM D2007M. Note that some native solids, such as clays, coprecipitate with the asphaltenes. Solid content was determined by dissolving asphaltene solids in toluene and centrifuging out the solids, as described elsewhere.<sup>8</sup> Molar mass and density were determined using a Jupiter model 833 vapor pressure osmometer and an Anton Paar DMA 46 density meter, respectively. In this work, the fractional precipitation is defined as the mass of precipitate divided by the mass of asphaltenes on a solids-free basis. The yield is defined as the mass of asphaltenes and solids divided by the mass of heavy oil or bitumen. The SARA fractions are repeatable to  $\pm 1$  wt % for saturates and asphaltenes and  $\pm 5$  wt % for aromatics and resins. Molar masses, densities, fractional asphaltene data, and asphaltene yields are repeatable to  $\pm 500$  g/mol (when at least five data points obtained),  $\pm 0.5$  kg/m<sup>3</sup>,  $\pm 0.05$ , and  $\pm 0.015$ , respectively.

In all, seven heavy oils and bitumens from around the world are considered. SARA analyses are provided in Table 1. Average molar masses and densities for each SARA fraction are listed in Table 2. Additional asphaltene molar masses are provided in Tables 3 and 4. Note that asphaltenes self-associate, and the apparent or self-associated molar mass is a function of asphaltene concentration, solvent, and temperature. The molar masses reported in Tables 3 and 4 were measured in 50 °C toluene at an asphaltene concentration of 10 kg/m<sup>3</sup>, the same concentration used in the asphaltene solubility experiments discussed later. The asphaltene molar masses are extrapolated to 23 and 0 °C based on the trends observed by Albouwarej et al.<sup>4</sup> The extrapolated molar masses at 23 and 0 °C are 20 and 45% higher, respectively, than the measured molar mass at 50 °C.

**Equation of State Model.** The PR-EoS<sup>16</sup> is given by:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (1)$$

where  $P$  is pressure,  $T$  is temperature,  $v$  is the molar volume,  $R$  is the universal gas constant, and  $a$  and  $b$  are the EoS parameters. The PR-EoS parameters for a pure component are defined as follows:

$$a_i = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} [1 + c_i (1 - T_{ri}^{0.5})]^2 \quad (2)$$

$$b_i = 0.07780 \frac{RT_{ci}}{P_{ci}} \quad (3)$$

where

$$c_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (4a)$$

and  $T_r$ ,  $T_c$ ,  $P_c$ , and  $\omega$  are the reduced temperature, the critical temperature, the critical pressure, and the acentric factor, respec-

(10) Gupta, A. K. A Model for Asphaltene Flocculation. M. Sc. Thesis, University of Calgary, Canada, 1986.

(11) Nghiem, L. X.; Coombe, D. A. SPE Fourth Latin American and Caribbean Petroleum Engineering Conference, Trinidad, Tobago, April 23–26, 1996; SPE Paper 36106.

(12) Qin, X.; Wang, P.; Sepehrnoori, K.; Pope, G. A. *Ind. Eng. Chem. Res.* **2000**, *39*, 2644–2654.

(13) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. *Fluid Phase Equilib.* **1989**, *52*, 31–38.

(14) Ting, P. D.; Hirasaki, G. J.; Chapman, W. G. *Pet. Sci. Technol.* **2003**, *21*, 647–661.

(15) Wu, J.; Prausnitz, J. M.; Firoozabadi, A. *AIChE J.* **1998**, *44*, 1188–1199.

(16) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

Table 2. Measured and Calculated Properties of Saturates, Aromatics, and Resins

	measured molar mass (kg/kmol)	calculated $T_c$ (K)	calculated $P_c$ (kPa)	calculated $\omega$	measured density at 23 °C (kg/m <sup>3</sup> )	calculated density at 23 °C (kg/m <sup>3</sup> )	error in calculated density (%)
saturates	460	930	1200	0.9	880	881	0.11
aromatics	522	999	1250	1.4	990	981	0.91
resins	1040	1279	818	1.76	1040	1011	2.8
asphaltenes	1800 <sup>a</sup>	1474 <sup>a</sup>	472 <sup>a</sup>	2.0 <sup>a</sup>	1185	1110	6.4

<sup>a</sup> Monomer properties.

Table 3. Average Associated Molar Masses of Athabasca Asphaltenes Washed with Different Methods

sample	measured at 50 °C	corrected to 23 °C	fitted at 23 °C	corrected to 50 °C	corrected to 0 °C
unwashed	5700	6800	6800	—	—
filter-washed	7900	9500	8100	6700	9700
sonicator-washed	7600	9100	9100	—	—
soxhlet-washed	9100	10 900	10 900	—	—

Table 4. Average Associated Molar Masses of Filter-Washed Asphaltenes from Four Non-Canadian Heavy Oils and Bitumens (All Corrected to 23 °C)

sample	molar mass (kg/kmol)
Venezuela 1	12 000
Venezuela 2	9200
Russia	7100
Indonesia	5500

tively. Equation 4a was later modified (eq 4b) to improve predictions for heavier components.<sup>17</sup>

$$c_i = 0.3796 + 1.485\omega_i - 0.1644\omega_i^2 + 0.01667\omega_i^3 \quad (4b)$$

The mixing rules used in this work to determine the PR-EoS parameters for a mixture of components are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$b = \sum_i x_i b_i \quad (6)$$

where

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \quad (7)$$

and  $k_{ij}$  is the binary interaction parameter between components  $i$  and  $j$ .

A liquid–liquid equilibrium was assumed between a dense liquid phase (asphaltene-rich phase) and a light liquid phase. The equilibrium calculation was performed using Heidemann's method with Michelsen's stability test.<sup>18</sup> However, due to the very large equilibrium ratios of the asphaltene fractions, a bisection method was used instead of a Newton–Raphson method to improve convergence. Note that only asphaltenes were allowed to partition to the heavy phase; that is, the heavy phase consists only of asphaltenes. This assumption increases the rate of convergence in the phase calculations. Note also that volume translation was not used here but is necessary if accurate solvent liquid density predictions are required (the equilibrium calculations are not altered with volume translation).

The input data required for the EoS are the temperature; pressure; mole fractions,  $a$  parameter, and  $b$  parameter for each component or pseudocomponent; and interaction parameters between each component and/or pseudocomponent. The first step is to divide the

fluid into components and pseudocomponents. The component EoS parameters are calculated from the component's critical properties. However, the EoS parameters for the pseudocomponents must be determined from a correlation or from fitting experimental phase behavior. The latter approach is used here. Finally, interaction parameters are set empirically to better fit the phase behavior data.

**Fluid Characterization. Choice of Pseudocomponents.** Each solvent is treated as an individual component. The bitumens and heavy oils are divided into pseudocomponents corresponding to the SARA fractions (saturates, aromatics, resins, and asphaltenes). Saturates, aromatics, and resins are each considered to be a single pseudocomponent. It was necessary to divide asphaltenes into several fractions to account for the broad molar mass distribution and to provide a means of incorporating the effects of asphaltene self-association. Asphaltenes were considered to be macromolecular aggregates formed from monodisperse asphaltene monomers. The asphaltenes were divided into 30 pseudocomponent fractions of different molar mass based on the following gamma distribution function:<sup>19</sup>

$$f(M) = \frac{1}{\Gamma(\beta)} \left[ \frac{\beta}{\bar{M} - M_m} \right]^\beta (M - M_m)^{\beta-1} \exp \left[ -\frac{\beta(M - M_m)}{\bar{M} - M_m} \right] \quad (8)$$

where  $f(M)$  is the mass frequency of the given molar mass,  $M_m$  and  $\bar{M}$  are the monomer molar mass and average associated molar mass of asphaltenes, respectively, and  $\beta$  is a parameter that governs the shape of the distribution curve. The recommended values for  $\beta$  are from 2 to 4. A value of 3 was found to give good results for the precipitation of asphaltenes from solvents (relatively high average molar mass asphaltenes), and a value of 4 was found for the precipitation of asphaltenes from bitumen (relatively low average molar mass asphaltenes). The asphaltene average monomer molar mass was taken to be 1800 g/mol based on vapor pressure osmometry data extrapolated to infinite dilution.<sup>8</sup> The measured average associated molar masses from Tables 3 and 4 were used for modeling precipitation from solutions of asphaltenes and solvents. The average molar mass was a fitting parameter for the diluted bitumen systems. The maximum molar mass was set to 30 000 g/mol. Note that using less than 30 asphaltene pseudocomponent fractions reduced the precision of the predicted yield curve at high solvent mass fractions.

Molar compositions for the bitumens and heavy oils were determined from the SARA analyses and molar masses from Tables 1–4.

**Asphaltene EoS Parameters.** Akbarzadeh et al. showed that asphaltenes can be modeled using group contribution methods.<sup>20</sup> An aggregation parameter ( $r$ ) can be defined for each asphaltene aggregate that is the molar mass of the aggregate, derived from molar mass distribution function, divided by the monomer molar mass:

$$r_i = \frac{M_i}{M_m} \quad (9)$$

where  $r_i$  is the aggregation parameter for each asphaltene aggregate. The equation of state parameters of each asphaltene fraction can

(17) Robinson, D. B.; Peng, D. Y. The Characterization of Heptanes and Heavier Fractions for the GPA Peng–Robinson Programs. Gas Processors Association (GPA) Research Report, Tulsa, OK, 1978; p 28.

(18) Heidemann, R. A.; Michelsen, M. L. *Ind. Eng. Chem. Res.* **1995**, *34*, 958–966.

(19) Whitson, C. H. *SPEJ, Soc. Pet. Eng. J.* **1983**, August, 683–694; SPE Paper 12233.

(20) Akbarzadeh, K.; Moshfeghian, M.; Ayatollahi, S.; Alboudwarej, H.; Yarranton, H. W. *J. Can. Pet. Technol.* **2004**, *43*, 31–39.



then be related to monomer parameters using group contribution theory as follows:<sup>21</sup>

$$a_i = (r_i)^2 a_m \quad (10)$$

$$b_i = r_i b_m \quad (11)$$

where  $a_i$  and  $b_i$  are the EoS parameters for each aggregate, and  $a_m$  and  $b_m$  are the EoS parameters for asphaltene monomer. With this approach, only the monomer EoS parameters remain to be determined.

EoS parameters are typically determined from the critical properties of the components. However, these properties are generally not known for heavy components, which decompose before they boil at atmospheric pressure. Since the monomer critical properties were unknown, the EoS parameters were determined for asphaltene monomers by matching the measured average asphaltene densities (Table 2) and solubility data for asphaltenes extracted from Athabasca bitumen in solutions of toluene and *n*-heptane (Figure 2).

There is not a unique solution for the EoS parameters. Examples of pairs of  $a$  and  $b$  values that provided acceptable fits to the data are listed in Table 5. To select one pair of values, the critical properties of an asphaltene monomer were back-calculated from the  $a$  and  $b$  values using eq 12 and an assumed value for  $\omega$  of 2. The calculated values, given in Table 5, were compared with the acentric factor and critical property correlations<sup>10,22–29</sup> shown in Figure 1. The pair of EoS parameters that best fit with the correlated trends are an  $a$  of 1 507 100 kPa·(m<sup>3</sup>/kmol)<sup>2</sup> and a  $b$  of 2.020 m<sup>3</sup>/kmol. The fit to the precipitation data is shown in Figure 2.

While parameter  $b$  is constant, parameter  $a$  is a function of temperature. The values of  $a$  for the asphaltene monomer were adjusted to fit the solubility data for solutions of asphaltenes in heptane and toluene at temperatures of 0, 23, and 50 °C. The average associated asphaltene molar mass at each temperature was taken from Table 3. A number of temperature functions were tested, including the original Peng–Robinson function and an exponential function. However, the following equation was found to best fit the adjusted values of  $a$  for the asphaltene monomer:

$$a_{\text{ASPH-mono}} = \frac{R^2 T_c^2}{P_c} |(1 + c(1 - T_r)^3)^{1/3}| \quad (12)$$

The resulting model fits are compared with precipitation data for solutions of asphaltenes in toluene and heptane at three different temperatures as shown in Figure 2. Note that an interaction parameter of  $-0.00256$  was used between heptane and each asphaltene pseudocomponent, as will be discussed later. All other interaction parameters were set to zero. Equation 12 can be applied at least up to the critical temperature, but only data from 0 to 100 °C were examined in this work, as shown later.

**Saturate, Aromatic, and Resin EoS Parameters.** Saturates and aromatics EoS parameters ( $a$  and  $b$ ) were determined that (1) fitted the average density of the fraction (Table 2), (2) fitted precipitation data for solutions of asphaltenes extracted from Athabasca bitumen, the given fraction, and either toluene or heptane (Figures 3 and 4),

(21) Pulis, J. C.; Greenkorn, R. A.; Chao, K. C. *Chem. Eng. Sci.* **1989**, *44*, 2553–2564.

(22) Alboudwarej, H. (now with Oilphase-DBR (Schlumberger)). Personal communication, Calgary, 2004.

(23) Kesler, M. G.; Lee, B. I. *Hydrocarbon Process.* **1976**, *55*, 153–158.

(24) Edmister, W. C. *Pet. Refiner* **1958**, *37*, 173–179.

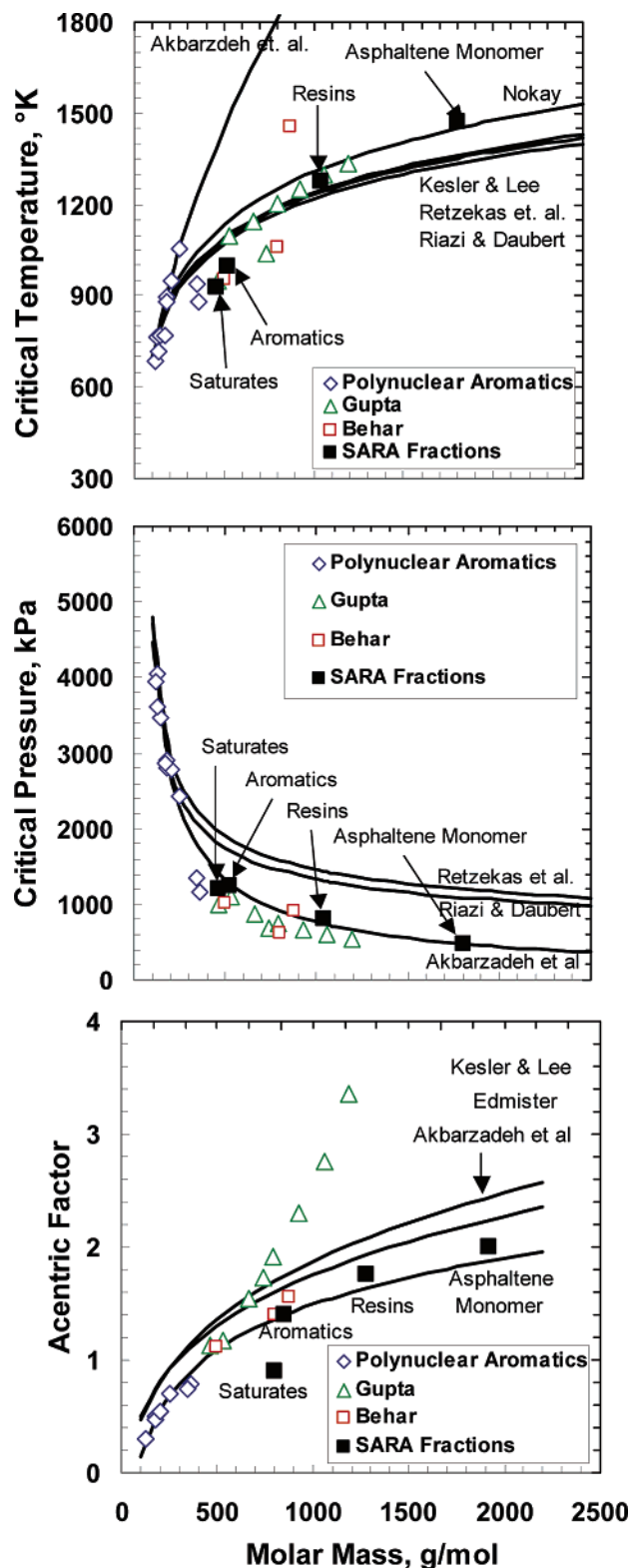
(25) Nokay, R. *Chem. Eng.* **1959**, *66* (Feb 23), 147–148.

(26) Retzekas, E.; Voutsas, E.; Magoulas, K.; Tassios, D. *Ind. Eng. Chem. Res.* **2002**, *41*, 1695–1702.

(27) Riazi, M. R.; Daubert, T. E. *Hydrocarbon Process.* **1980**, *59*, 115–116.

(28) Szweczyk, V.; Behar, E. *Fluid Phase Equilib.* **1999**, *158–160*, 459.

(29) Poling, B. E.; Prausnitz, J.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001; pp A.5–A.19.



**Figure 1.** Measured and correlated critical pressure, temperature, and acentric factor of heavy fractions versus molar mass (Alboudwarej<sup>22</sup>). Estimated SARA fraction properties from this work are shown with solid symbols.

and (3) followed the trends of the critical property correlations of Figure 1.

The asphaltene parameters and the binary interaction parameter between asphaltene pseudocomponents and heptane remained set at  $-0.00256$ . All other interaction parameters were set to zero. The average associated molar mass of the asphaltenes was taken from Table 3. Volume translation was not employed to match the

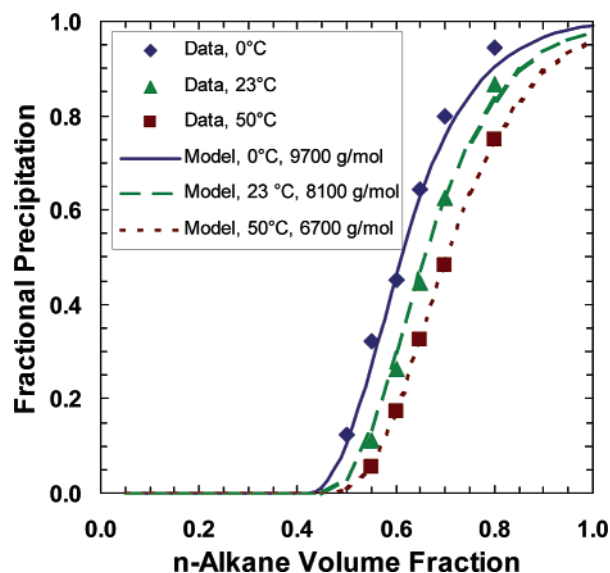


Figure 2. Effect of temperature on the fractional precipitation of Athabasca filter-washed asphaltenes in solutions of *n*-heptane and toluene.

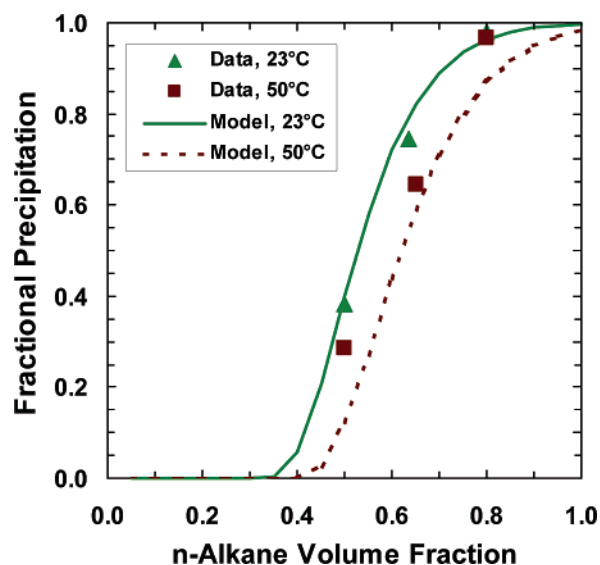


Figure 3. Fractional precipitation of Athabasca filter-washed asphaltenes in solutions of toluene and saturates at 23 and 50 °C, 0.1 MPa.

Table 5. Potential Combinations of EoS Parameters for the Average Asphaltene Monomer

parameter $a$ kPa·(m <sup>3</sup> /kmol) <sup>2</sup>	parameter $b$ (m <sup>3</sup> /kmol)	$T_c$ (K)	$P_c$ (kPa)
1 506 500	1.970	1490	490
1 507 100	2.020	1470	472
1 507 500	2.050	1460	463
1 508 400	2.110	1440	440

density because there is a high degree of uncertainty in applying volume translation to ill-defined high-density pseudofractions. The saturate and aromatic critical properties were back-calculated from eqs 2 and 3.

Note that any change in asphaltene self-association with the introduction of saturates or aromatics was assumed to be negligible. This assumption is not valid for resins, and therefore, asphaltene precipitation in the presence of resins could not be modeled using the molar masses from Table 3. Instead, a set of critical properties that reasonably matched existing correlations and also fitted the density data was found. Since resins are expected to be similar to

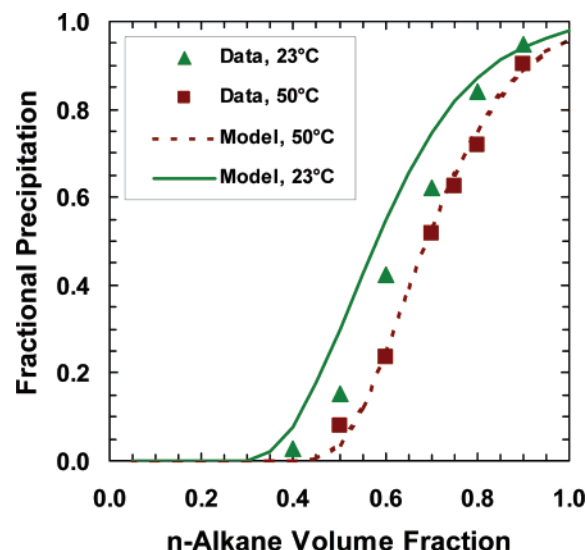


Figure 4. Fractional precipitation of Athabasca filter-washed asphaltenes in solutions of aromatics and *n*-heptane at 23 and 50 °C, 0.1 MPa.

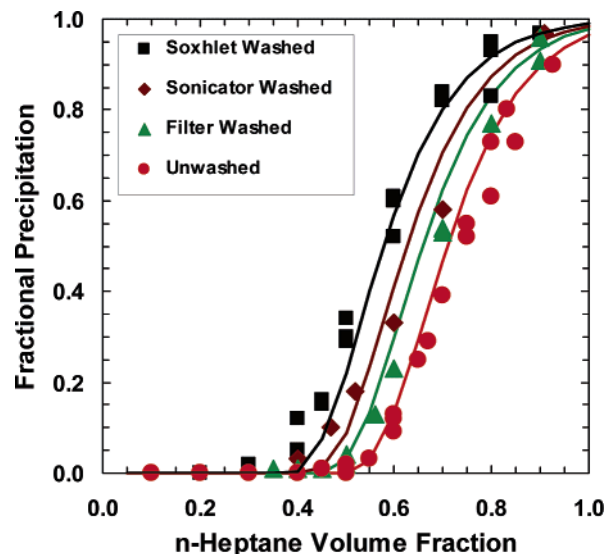


Figure 5. Fractional precipitation of Athabasca asphaltenes with different extents of washing in solutions of *n*-heptane and toluene at 23 °C and 0.1 MPa.

asphaltenes, eq 12 was used to calculate the value of the  $a$  parameter from the critical properties. The critical properties determined for saturates, aromatics, and resins are given in Table 2 and compared with the correlations in Figure 1. The fitted densities are compared with experimental data in Table 2. Figures 3 and 4 show the fitted precipitation data for saturates and aromatics, respectively.

## Results and Discussion

Before applying the model to heavy oils and bitumens, the asphaltene characterization is tested on a number of asphaltene samples of different molar mass. Then binary interaction parameters between asphaltenes and *n*-alkanes are set based on precipitation data for asphaltene solvent systems. Finally, a correlation for the asphaltene average associated molar mass in bitumen is developed, and the EoS model is tested on a number of heavy oils and bitumens diluted with *n*-alkanes.

**Testing the Asphaltene Characterization.** The average molar mass of an asphaltene sample depends on the source of heavy oil or bitumen and on the washing procedure used during the separation of the asphaltenes from the source oil. Alboud-

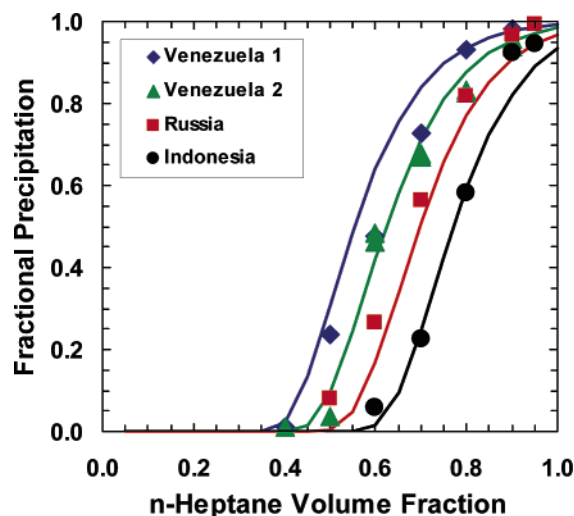


Figure 6. Fractional precipitation of asphaltenes from different sources in solutions of *n*-heptane and toluene at 23 °C and 0.1 MPa.

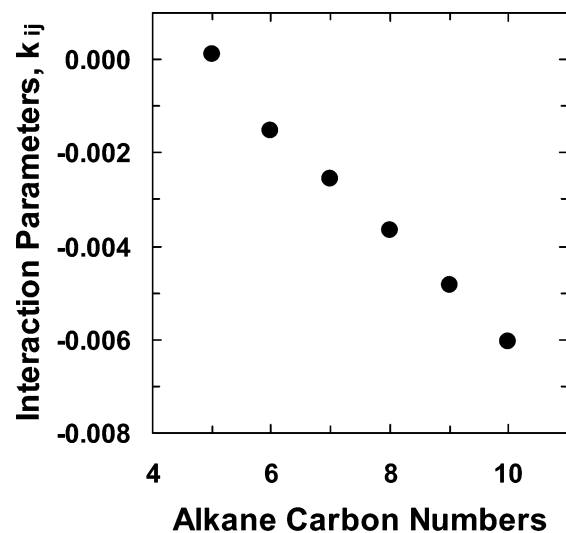


Figure 7. Binary interaction parameters between asphaltenes and *n*-alkanes.

warej et al. confirmed that asphaltenes with different molar masses have different fractional precipitation at a given solvent composition.<sup>8</sup> Figure 5 compares the fractional precipitation of unwashed, filter-washed, sonicator-washed, and soxhlet-washed athabasca asphaltenes (detailed descriptions are provided elsewhere<sup>8</sup>) in solutions of toluene and heptane. Note that the model parameters were fitted to the filter-washed data only. Figure 6 compares the predicted with the measured fractional precipitation of Venezuela 1, Venezuela 2, Russian, and Indonesian asphaltenes in solutions of toluene and heptane. All of the data in Figures 5 and 6 are at an asphaltene concentration of 10 kg/m<sup>3</sup> and a temperature of 23 °C. The measured average asphaltene molar masses (corrected to 23 °C) are given in Table 3 for the Athabasca asphaltenes and in Table 4 for asphaltenes from other heavy oils and bitumens.

The binary interaction parameter between each asphaltene fraction and *n*-heptane was set to  $-0.00256$ . The model was then applied using the measured molar masses without any other adjustment to the model parameters. The predictions are shown as lines in Figures 5 and 6. The model predicted the onset and amount of asphaltene precipitation with an absolute average deviation of less than 0.04 fractional precipitation units. (AAD is the average of the sum of the absolute value of the differences

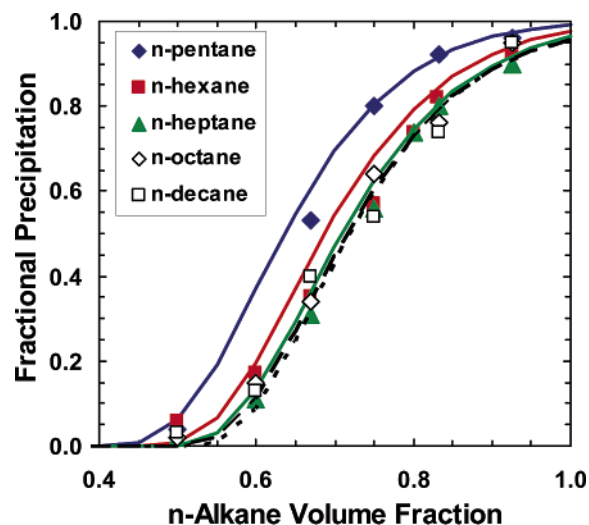


Figure 8. Fractional precipitation of Athabasca unwashed asphaltenes in solutions of toluene and *n*-alkanes at 23 °C and 0.1 MPa.

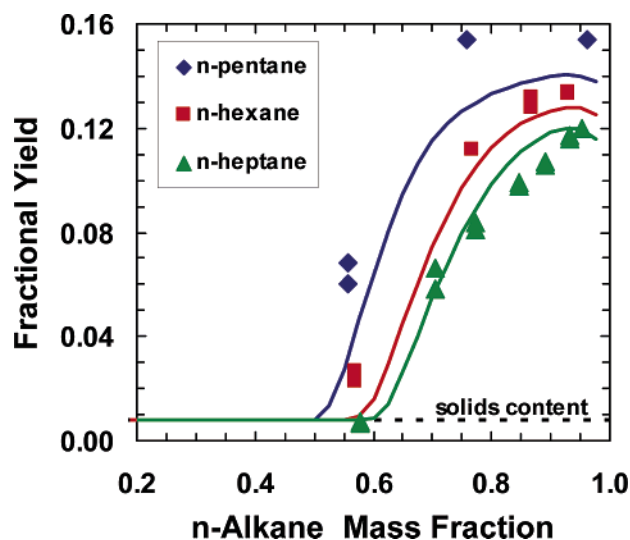


Figure 9. Fractional yield from Athabasca bitumen diluted with *n*-alkanes at 23 °C and 0.1 MPa.

Table 6. Fitted Asphaltene Associated Molar Mass in Bitumens and Heavy Oils

bitumen or heavy oil	asphaltene average associated molar mass (kg/kmol)
Athabasca	4200
Cold Lake	4050
Lloydminster	4000
Venezuelan 1	4290
Venezuelan 2	4290
Russian	4800
Indonesian	3960

between the calculated and experimental data points.) The success of the predictions indicates that the asphaltene characterization is applicable to a variety of asphaltenes.

**Setting Binary Interaction Parameters.** We found that the EoS could not predict asphaltene precipitation in the *n*-alkane series without the use of binary interaction parameters. Therefore, a set of interaction parameters was determined that fitted fractional asphaltene precipitation data for solution of toluene and *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, or *n*-decane. All of the data were collected at an asphaltene concentration of 10 kg/m<sup>3</sup> and a temperature of 23 °C. The tuned interaction parameters are shown in Figure 7, and the model fits are compared with the experimental data in Figure 8. The binary



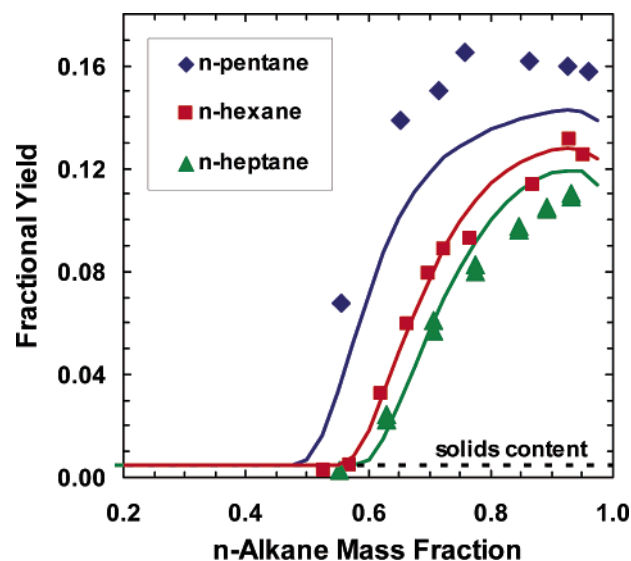


Figure 10. Fractional yield from Cold Lake bitumen diluted with *n*-alkanes at 23 °C and 0.1 MPa.

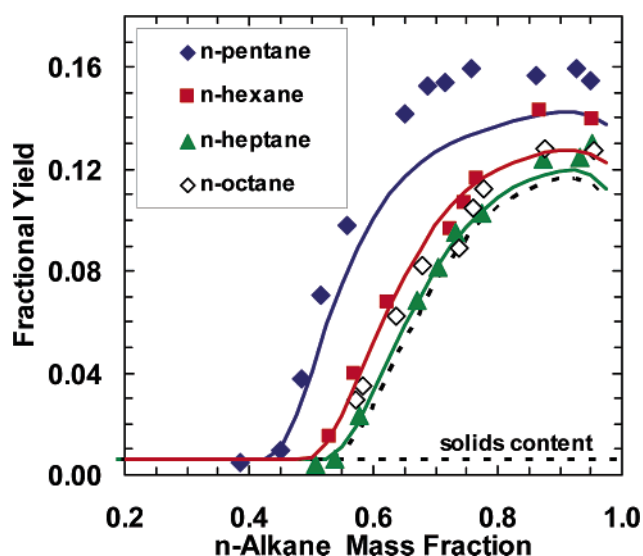


Figure 11. Fractional yield from Lloydminster heavy oil diluted with *n*-alkanes at 23 °C and 0.1 MPa.

interaction parameters were fixed at these values so that the model is now purely predictive for solutions of asphaltenes, toluene, and *n*-alkanes from *n*-pentane to *n*-decane. Furthermore, only one parameter is yet to be determined for *n*-alkane diluted bitumens; that is, the average associated molar mass of asphaltenes in bitumen.

**Average Associated Molar Mass of Asphaltenes in Bitumen.** Since there is no method available to measure the average molar mass of asphaltenes in bitumen, it was used as a fitting parameter. The molar masses used to fit the asphaltene yields from *n*-heptane diluted heavy oils or bitumens at 23 °C and atmospheric pressure are summarized in Table 6.

Asphaltene self-association is temperature-dependent, and it is expected that the average molar mass will decrease with temperature. The average associated molar masses were determined by fitting precipitation data from the *n*-heptane diluted bitumens and heavy oils at temperatures from 0 to 100 °C. Note that the 100 °C data was obtained at 2.1 MPa but the effect of pressure on precipitation is negligible, as discussed later. The data were normalized (divided by the molar mass at 23 °C) and curve-fitted to obtain the following correlation for the

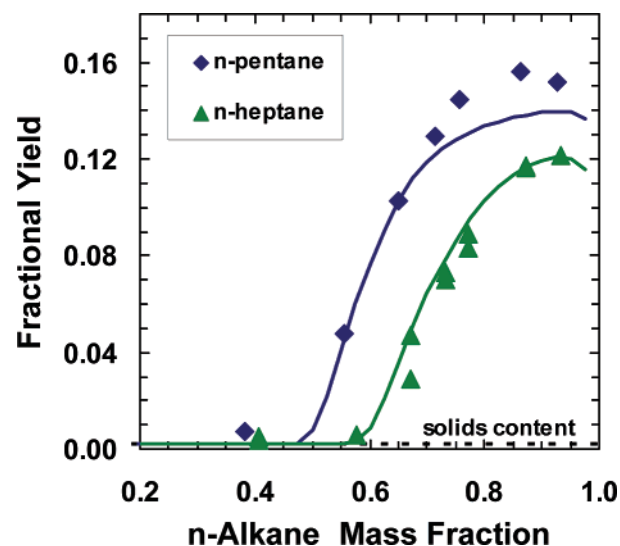


Figure 12. Fractional yield from Venezuela 1 heavy oil diluted with *n*-alkanes at 23 °C and 0.1 MPa.

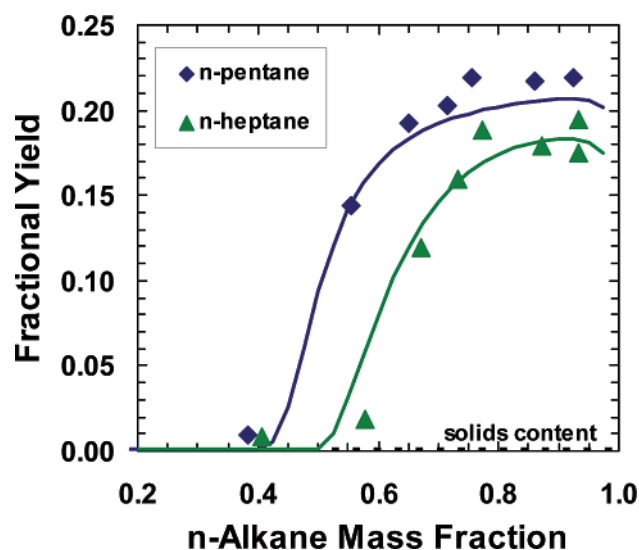


Figure 13. Fractional yield from Venezuela 2 heavy oil diluted with *n*-alkanes at 23 °C and 0.1 MPa.

average associated asphaltene molar mass as a function of temperature:

$$M = 1.03M_{23^\circ\text{C}}[1 - 1.60 \times 10^{-5} \exp(0.0248T)] \quad (13)$$

where  $T$  has units of Kelvin. All further predictions were made using eq 13 with the fitted molar masses from Table 6. Note that the form of eq 13 is empirical and has no physical significance.

***n*-Alkane Diluted Heavy Oils and Bitumens.** Figures 9–15 compare experimental and modeled asphaltene yields from Athabasca, Cold Lake, Lloydminster, Venezuela 1, Venezuela 2, Russia, and Indonesia heavy oils and bitumens, respectively, diluted with various *n*-alkanes at 23 °C and atmospheric pressure. In most cases, the AAD is less than 0.02. The greatest discrepancies occur at high *n*-pentane volume fractions. It is possible that resins are partitioning to the dense phase. The model does not account for resin precipitation. Alternatively, there may be a significant mass of trapped maltenes at the high yields observed in *n*-pentane. These maltenes may not be part of the dense phase and therefore would not be predicted by the model. A third possibility is the formation of multiple liquid

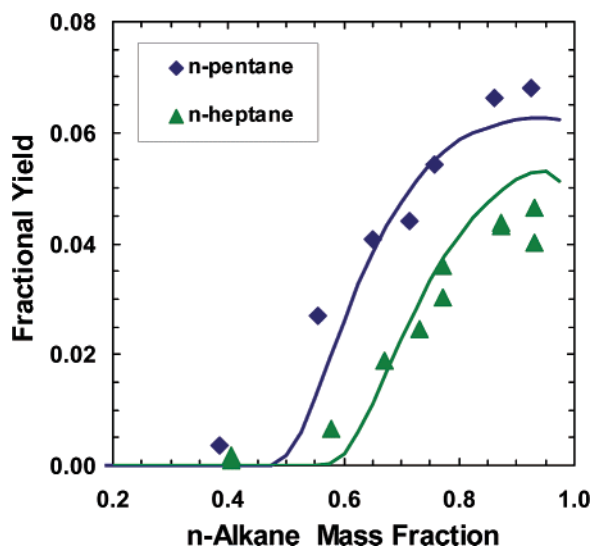


Figure 14. Fractional yield from Russia bitumen diluted with *n*-alkanes at 23 °C and 0.1 MPa.

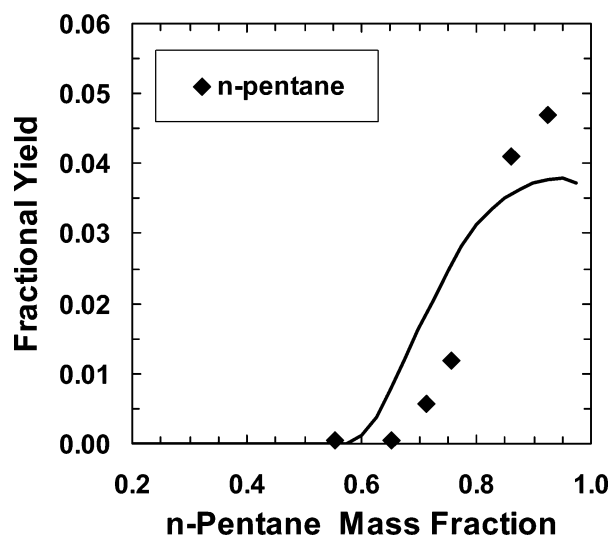


Figure 15. Fractional yield from Indonesia bitumen diluted with *n*-alkanes at 23 °C and 0.1 MPa.

and/or solids phases, which are not accounted for in the modeling.

Figures 16–18 show the effect of temperature on the measured and modeled asphaltene yields from Athabasca and Cold Lake bitumen diluted with *n*-heptane and Venezuela 1 heavy oil diluted with *n*-pentane. In most cases, the AAD is less than 0.02 (fractional yield). Again discrepancies are observed at high pentane volume fractions. There is also a poor match at 100 °C for the *n*-heptane diluted Athabasca bitumen. There was some difficulty in obtaining consistent data at 100 °C. It is also possible that eq 12 does not extrapolate correctly to 100 °C as it was based on the data collected at 0–50 °C.

Figures 19 and 20 show the effect of pressure on the measured and modeled asphaltene yields from Athabasca and Cold Lake bitumen, respectively, diluted with *n*-heptane at 23 °C. The measured and predicted asphaltene yields both decrease slightly with pressure. There is a discrepancy between the experimental data for Cold Lake bitumen and the predictions at 6.9 MPa. The discrepancy may be in the experimental data. For Cold Lake bitumen (Figure 20), the measured yields at 6.9 MPa overlap the yields at 2.1 MPa. However, the 6.9 MPa yields are lower than the 2.1 MPa yields for Athabasca bitumen (Figure 19). In

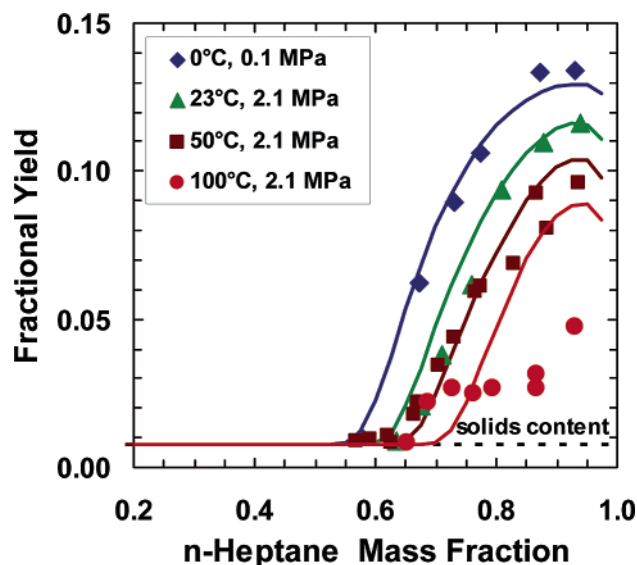


Figure 16. Fractional yield from Athabasca bitumen diluted with *n*-heptane at 0 °C and 0.1 MPa and at 23, 50, and 100 °C all at 2.1 MPa.

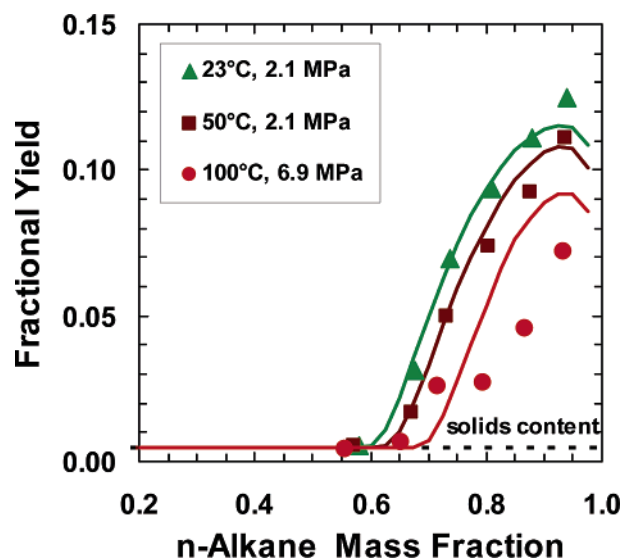


Figure 17. Fractional yield from Cold Lake bitumen diluted with *n*-heptane at 0 °C and 2.1 MPa, 23 °C and 2.1 MPa, and 100 °C and 6.9 MPa.

other words, the pressure effect is within the error of the experimental data. In all cases, the AAD is less than 0.02.

## Conclusions

The Peng–Robinson EoS was successfully adapted for the fitting and prediction of the onset and amount of asphaltene precipitation from both asphaltenes/toluene/*n*-alkane and bitumen/*n*-alkane systems. A liquid–liquid equilibrium model was assumed with only asphaltenes partitioning to the dense phase. The bitumens and heavy oils were characterized in terms of saturates, aromatics, resins, and asphaltenes. The saturates, aromatics, and resins were considered as single pseudocomponents. Asphaltenes were divided into pseudocomponents of different molar mass based on a gamma distribution function. The extent of self-association between asphaltene molecules was considered in the average associated asphaltene molar mass, an input parameter in the molar mass distribution function. Measured molar masses were used for the asphaltene solvent systems. The average asphaltene molar mass was used as a

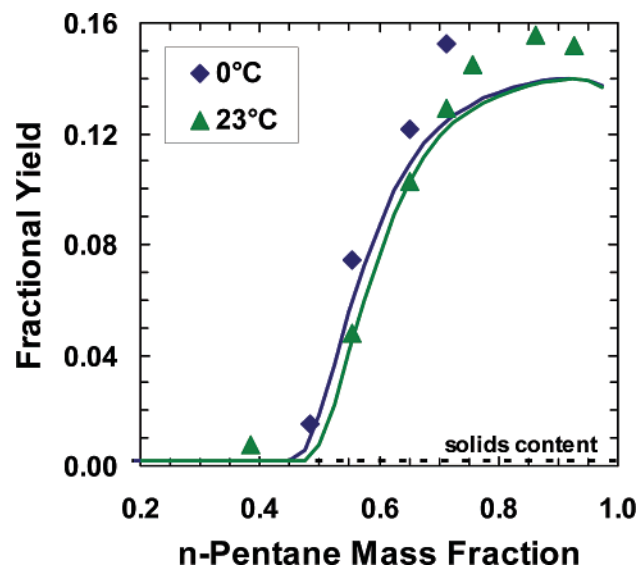


Figure 18. Fractional yield from Venezuela 1 bitumen diluted with *n*-pentane at 0 and 23 °C both at 0.1 MPa.

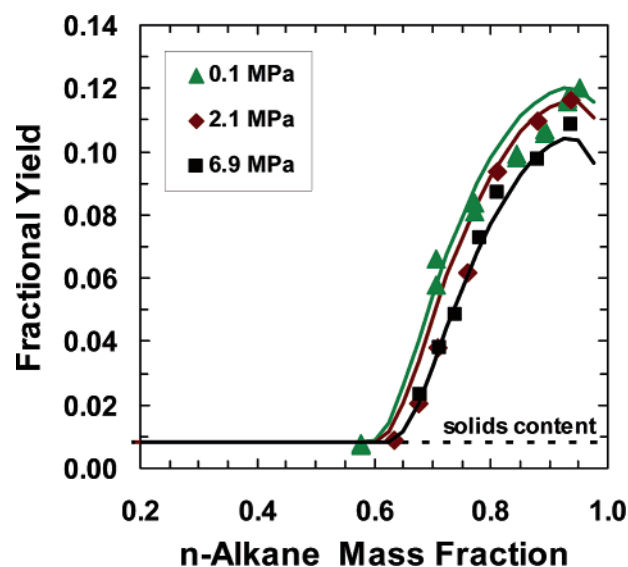


Figure 19. Fractional yield from Athabasca bitumen diluted with *n*-heptane at 23 °C and 0.1, 2.1, and 6.9 MPa.

fitting parameter for the bitumen solvent systems. Critical properties of saturates, aromatics, and resins and the EoS parameters of the asphaltene monomers were determined that fit density and asphaltene precipitation data and were consistent with existing critical property correlations. EoS parameters of associated asphaltenes were determined using group contribution methods.

Binary interaction parameters between asphaltene pseudocomponents and each *n*-alkane were determined by fitting the model to the experimental data for mixtures of Athabasca asphaltenes, toluene, and each *n*-alkane. The interaction parameters were then correlated to the carbon number of the *n*-alkane. The interaction parameters were held constant at various temperatures, pressures, and concentrations.

The model was tested on asphaltenes extracted from three Western Canadian oils (Athabasca, Cold Lake, and Lloydminster) and four other oils (Venezuela 1 and 2, Russia, and Indonesia). The model matched the measured fractional precipitations with an AAD of less than 0.04. The model successfully matched asphaltene yields for *n*-alkane diluted bitumens at temperatures from 0 to 100 °C and pressures up to 7 MPa.

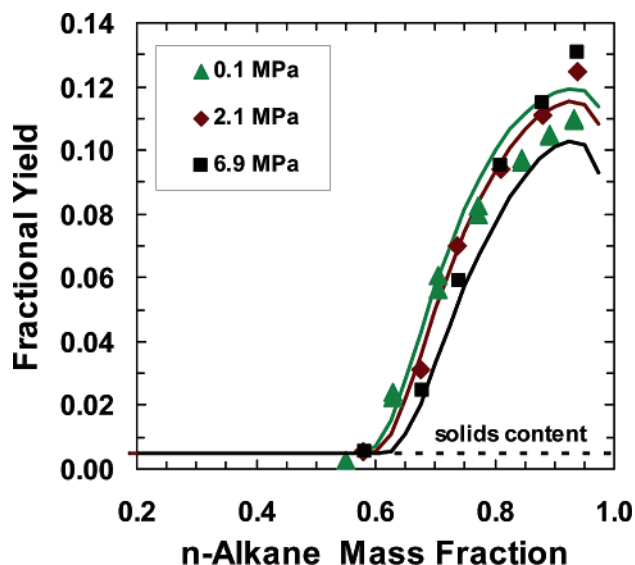


Figure 20. Fractional yield from Cold Lake bitumen diluted with *n*-heptane at 23 °C and 0.1, 2.1, and 6.9 MPa.

The model was tested on all of the Alberta and international crude oils with an AAD of less than 0.02 (fractional yield) in almost all cases. The model failed to fit yields from *n*-pentane diluted bitumen at high dilution ratios. It is probably necessary to account for resin precipitation at these conditions.

The proposed model is not a universal predictor; rather, a methodology is provided to correlate asphaltene yields from diluted heavy oils. At least one yield or onset measurement is required to tune the model. Interestingly, one set of asphaltene parameters was sufficient for asphaltenes from a variety of sources. However, it is likely that different parameters will be required for at least some sources. Also note that the model fits and predictions are no better than a previously developed regular solution model;<sup>8</sup> however, a PR-EoS-based approach is more readily adapted to most process simulation software.

**Acknowledgment.** We would like to thank Dr. R. A. Heide-mann for his technical help on phase behavior calculations and to acknowledge Dr. H. Alboudwarej for preparing much of Figure 1. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is appreciated. We also thank Syncrude Canada Ltd. and Imperial Oil Ltd. for supplying oil samples.

### Nomenclature

$a$  = parameter in Peng–Robinson EoS;  $\text{kPa}\cdot(\text{m}^3/\text{kmol})^2$   
 $b$  = parameter in Peng–Robinson EoS;  $\text{m}^3/\text{kmol}$   
 $c$  = constant (function of  $\omega$ )  
 $f$  = mole or number frequency  
 $k$  = binary interaction parameter  
 $M$  = molar mass;  $\text{kg}/\text{kmol}$   
 $P$  = pressure;  $\text{kPa}$   
 $r$  = aggregation parameter  
 $R$  = universal gas constant;  $\text{m}^3\cdot\text{kPa}/\text{kmol}\cdot\text{K}$   
 $T$  = temperature;  $\text{K}$   
 $v$  = molar volume  
 $w$  = weight fraction  
 $x$  = mole fraction

### Greek Symbols

$\alpha$  = temperature-dependent EoS parameter  
 $\beta$  = parameter in distribution function  
 $\Gamma$  = gamma function  
 $\omega$  = acentric factor

Subscripts

c = critical property

i = component

m = monomer

max = maximum

min = minimum

mix = mixture

r = reduced property

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