

Methodology for the Characterization and Modeling of Asphaltene Precipitation from Heavy Oils Diluted with *n*-Alkanes

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A regular solution model, previously used to model asphaltene precipitation from Western Canadian bitumens, was tested on four international heavy oil and bitumen samples. The input parameters for the model are the mole fraction, the molar volume, and the solubility parameter for each component. Heavy oils and bitumens were divided into four main pseudo-components, corresponding to the SARA fractions (saturates, aromatics, resins, and asphaltenes). Asphaltenes were divided into fractions of different molar mass, based on a gamma molar mass distribution. The molar volumes and solubility parameters of the pseudo-components were calculated using solubility, density, and molar mass measurements and previously developed correlations. Model predictions were compared with the measured onset and the amount of asphaltene precipitation for solutions of asphaltenes in toluene and *n*-heptane and for heavy oils diluted with *n*-alkanes, all under ambient conditions. The overall average absolute deviations (AAD) of the predicted fractional precipitation or yields were <0.031 for the asphaltene solutions and <0.008 for the diluted heavy oils. A methodology for characterizing heavy oils and modeling asphaltene precipitation from *n*-alkane-diluted heavy oils is proposed.

Introduction

As conventional oil reserves are depleted, oil sands bitumen and heavy oil resources are gaining prominence. Bitumens and heavy oils are rich in asphaltenes, which is 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 are soluble in aromatic solvents such as toluene. Asphaltenes are known to self-associate, forming aggregates containing ~6–10 molecules.^{1,2} Asphaltenes 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 or paraffinic oil sands froth treatment, asphaltenes are deliberately precipitated to obtain a lower viscosity and more easily refined product. 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, which was 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 Magat model^{5,6} to asphaltene precipitation, using a molar mass distribution for the asphaltenes. The use of interaction parameters was also tested on asphaltene precipitation.^{4,7,8} More recently, Yarranton and Masliyah⁹ successfully modeled asphaltene precipitation in solvents by treating asphaltenes as a mixture of components of different density and molar mass. Alboudwarej et al.¹⁰ extended Yarranton and Masliyah's model and the Hildebrand and Scott^{11,12} regular solution approach to asphaltene precipitation from Western Canadian heavy oils and bitumens.

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The input parameters for the Alboudwarej et al. model¹⁰ were the mole fraction, the molar volume, and the solubility parameters for each component. Bitumens were divided into four main pseudo-components, corresponding to the 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 taken into consideration using the average molar mass of the 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 bitumens were in good agreement with experimental measurements under ambient conditions.

The correlations and modeling approach developed by Alboudwarej et al.¹⁰ were based exclusively on Western Canadian heavy oils and bitumens. One step in testing the general applicability of this model is to determine if it can be extended to other heavy oils and bitumens without adjustment. Alternatively, specific geographically grouped correlations for density and the solubility parameter may be required. In this work, the model is tested on four international bitumen and heavy oil samples: two bitumen samples from Venezuela, one heavy oil sample from Russia, and one heavy oil sample from Indonesia. Model predictions were compared with the measured amount of asphaltene precipitation for (i) asphaltenes in solutions of toluene and *n*-heptane and (ii) heavy oils diluted with various *n*-alkanes. A generalized approach is developed for modeling asphaltene precipitation from alkane-diluted heavy oils and bitumens.

Experimental Section

Chemicals and Materials. Venezuela No. 1 and Venezuela No. 2 bitumens were obtained from Imperial Oil, Ltd. and DBR Product Center, Schlumberger, respectively. The Russia heavy oil was obtained from the Scientific and Research Center for Heavy-Accessible Oil and Natural Bitumen Reserve in Tatarstan, Russia. The Indonesia heavy oil was obtained from PT. Caltex Pacific Indonesia in Jakarta, Indonesia. Toluene, *n*-heptane, *n*-pentane, and acetone were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were 99%+ pure.

SARA Fractionation. 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. Both C₅-asphaltenes and C₇-asphaltenes were "filter-washed" asphaltenes as defined by Alboudwarej et al.¹³ Saturates, aromatics, and resins were extracted according to ASTM D2007M. The SARA analysis of the bitumens and heavy oils are reported in Table 1.

Most asphaltene samples contain non-asphaltenic solids, including sand, clay, and adsorbed organics. To remove the solids, asphaltenes were dissolved in excess toluene and centrifuged for 6 min at 900 RCF (RCF = relative centrifugal force). The solids content of the asphaltenes from the different source oils are given in Table 1.

Table 1. SARA Analysis of Bitumens and Heavy Oil and Measured Molar Mass and Density of Each Fraction

fraction	content (wt %)	density (kg/m ³)	molar mass ^a (g/mol)
Western Canadian			
Athabasca			
saturates	16.3	900	524
aromatics	39.8	1003	550
resins	28.5	1058	976
asphaltenes ^b	14.7	1192	7900
solids ^c	0.7		
Cold Lake			
saturates	19.4	882	508
aromatics	38.1	995	522
resins	26.7	1019	930
asphaltenes ^b	15.5	1190	7400
solids ^c	0.3		
Lloydminster			
saturates	23.1	876	482
aromatics	41.7	997	537
resins	19.5	1039	859
asphaltenes ^b	15.3	1181	6660
solids ^c	0.4		
International			
Venezuela No. 1			
saturates	15.4	885	447
aromatics	44.4	1001	542
resins	25.0	1056	1240
asphaltenes ^b	15.2	1186	10005
solids ^c	0.2		
Venezuela No. 2			
saturates	20.5	882	400
aromatics	38.0	997	508
resins	19.6	1052	1090
asphaltenes ^b	21.8	1193	7662
solids ^c	0.1		
Russia			
saturates	25.0	853	361
aromatics	31.1	972	450
resins	37.1	1066	1108
asphaltenes ^b	6.8	1192	7065
solids ^c	0.0		
Indonesia			
saturates	23.2	877	498
aromatics	33.9	960	544
resins	38.2	1007	1070
asphaltenes ^b	4.7	1132	4635
solids ^c	0.0		

^a For asphaltenes, the corrected molar mass at 23 °C is 20% higher than the measured value at 50 °C. ^b Average molar mass of asphaltenes, measured at 50 °C and 10 kg/m³ in toluene. ^c Non-asphaltic solids.

Molar Mass Measurements. The molar masses of SARA fractions were measured using vapor pressure osmometry (VPO), as described elsewhere.¹³ All measurements were made in toluene at 50 °C. Molar masses of saturates, aromatics, resins, and asphaltenes are given in Table 1. Unlike the other SARA fractions, asphaltenes self-associate and the molar mass is dependent on both concentration and temperature.¹⁴ The molar mass of asphaltenes increases as the temperature decreases, because the level of asphaltene self-association changes. Therefore, the molar masses in Table 1 were increased by 20%¹⁴ from the measured value, to account for the change in molar mass between the VPO measurement at 50 °C and the solubility experiments at 23 °C.

Density Measurements. Densities were measured with an Anton Paar model DMA 46 densitometer that was calibrated with demineralized water and air. The instrument precision is ±0.0005 g/cm³. The densities of the saturates and

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aromatics were measured directly. The densities of the asphaltene and resins were calculated indirectly from the densities of mixtures of asphaltene or resins in toluene, as described elsewhere.⁹ Densities were accurate to $\pm 0.5 \text{ kg/m}^3$. Densities for the saturates, aromatics, resins, and asphaltene are given in Table 1.

Asphaltene Precipitation and Solubility Measurements. Asphaltene precipitation and solubility measurements were performed gravimetrically in (i) 10 kg/m^3 of asphaltene in solutions of toluene and *n*-heptane, and (ii) bitumen diluted with an *n*-alkane. The *n*-alkanes considered were *n*-heptane and *n*-pentane. All measurements were taken at 23°C and atmospheric pressure. After the mixtures were prepared, they were sonicated for 45 min and allowed to settle for 24 h. The mixtures then were centrifuged at 3500 rpm (900 RCF) for 6 min. The supernatant was decanted and the asphaltene was recovered, washed with the same solvent, and dried. For solutions of bitumen and solvents, asphaltene precipitation is reported as a yield: the mass of precipitate per mass of original bitumen. For solutions of asphaltene and solvents, asphaltene precipitation is reported on a fractional basis: the mass of precipitated asphaltene per total mass of asphaltene. The reported precipitation curves are corrected to a solids-free basis. Note that the precipitation of solids-free asphaltene and untreated asphaltene was compared. The solids precipitated with the first asphaltene to precipitate, but otherwise did not alter the onset or amount of asphaltene precipitation.

Safety Precautions. The main safety issues in this work were the handling of toxic and flammable chemicals. Laboratory coats, eye goggles, and gloves were worn while we were working with chemicals such as toluene and *n*-alkanes. Respiratory masks were used while we were working with toluene. Procedures that involved the liberation of volatile, flammable, or toxic materials were performed in a fume hood.

Regular Solution Model

Details of the regular solution model are given in the work by Alboudwarej et al.;¹⁰ however, a brief summary is provided here. A liquid–liquid equilibrium is assumed between the heavy liquid phase (the asphaltene-rich phase, including asphaltene and resins) and the light liquid phase (the oil-rich phase, including all components). The equilibrium ratio (K_i^{hl}) for any given component is then given by

$$K_i^{\text{hl}} = \frac{x_i^{\text{h}}}{x_i^{\text{l}}} = \exp \left[\frac{v_i^{\text{h}}}{v_m^{\text{h}}} - \frac{v_i^{\text{l}}}{v_m^{\text{l}}} + \ln \left(\frac{v_i^{\text{l}}}{v_m^{\text{l}}} \right) - \ln \left(\frac{v_i^{\text{h}}}{v_m^{\text{h}}} \right) + \frac{v_i^{\text{l}}}{RT} (\delta_i^{\text{l}} - \delta_m^{\text{l}})^2 - \frac{v_i^{\text{h}}}{RT} (\delta_i^{\text{h}} - \delta_m^{\text{h}})^2 \right] \quad (1)$$

where x_i^{h} and x_i^{l} are the heavy and light liquid-phase mole fractions, R is the universal gas constant, and T is temperature. The parameters v_i and δ_i are the molar volume and solubility parameter of component i in either the light liquid phase (l) or the heavy liquid phase (h), respectively, and v_m and δ_m are the molar volume and solubility parameter of either the light liquid phase or the heavy liquid phase, respectively.

Note that only asphaltene and resins were allowed to partition to the heavy phase. In reality, all the fractions could potentially partition; however, this assumption increases the rate of convergence in the phase calculations. Also, experimental observations indicate that the heavy phase consists primarily of asphaltene

and resins. The aforementioned formulation is equivalent to a solid–liquid phase equilibrium where the contribution of the heat of fusion to the equilibrium expression is negligible. When the equilibrium ratios are known, the phase equilibrium is determined using standard techniques.^{10,15}

Fluid Characterization

Components and Pseudo-components. Each solvent is treated as an individual component with known properties. The bitumens and heavy oils are divided into four main pseudo-components, corresponding to the SARA fractions (saturates, aromatics, resins, and asphaltene). Asphaltene is considered to be macromolecular aggregates of monodisperse asphaltene monomers and, therefore, are further divided into fractions of different molar mass, based on the following gamma distribution function:¹⁶

$$f(M) = \frac{1}{\Gamma(\beta)} \left[\frac{\beta}{M - M_m} \right]^\beta (M - M_m)^{\beta-1} \exp \left[-\frac{\beta(M - M_m)}{M - M_m} \right] \quad (2)$$

where M_m and $\bar{M}$ are the monomer molar mass and average molar mass of asphaltene, respectively, and β is a parameter that determines the shape of the distribution. The recommended value for β is 2 for systems that contain large aggregates. Details of the asphaltene discretization are discussed elsewhere.¹⁰

The mole fractions of the components and pseudo-components are determined from given volumes, the SARA analysis, and the measured molar masses. Note that the average asphaltene molar mass is dependent on the composition and temperature and must be measured or estimated for any given condition.

Molar Volumes. The molar volumes of the solvents are calculated using Hankinson–Brobst–Thomson (HBT) technique.¹⁷ The molar volumes of the saturates and the aromatics are determined from the molar masses and densities given in Table 1. The molar volumes of the asphaltene and resins are determined from the following correlation of density to molar mass:¹⁰

$$\rho = 670M^{0.0639} \quad (3)$$

where ρ is the asphaltene or resin density (in units of kg/m^3) and M is the molar mass (in g/mol). Note that the asphaltene and resins were considered together, because these fractions can be considered as a continuum of polynuclear aromatics.

Solubility Parameters. The solubility parameters of the solvents were calculated as follows:

$$\delta = \left(\frac{\Delta H^{\text{vap}} - RT}{v} \right)^{1/2} \quad (4)$$

where ΔH^{vap} is the heat of vaporization reported in the

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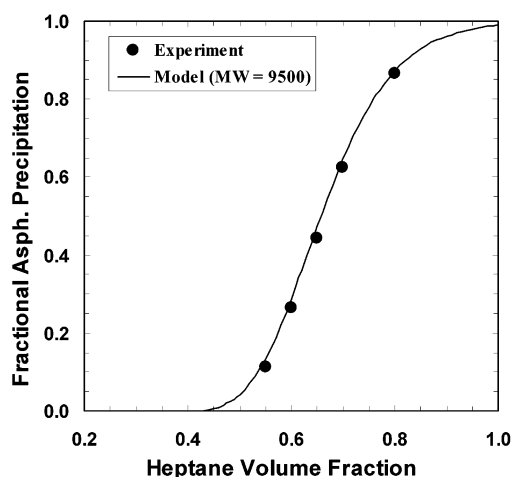


Figure 1. Fractional precipitation of Athabasca asphaltenes from solutions of *n*-heptane and toluene at 23°C.

literature.¹⁸ The solubility parameters of the saturates and aromatics were determined by fitting the solubility model to asphaltene–saturate–toluene and asphaltene–*n*-heptane–aromatics solubility data, respectively. The estimated values were determined to be 16.3 MPa^{0.5} for saturates and 20.9 MPa^{0.5} for aromatics.¹⁰ The solubility parameters of the asphaltenes and resins were determined from the following correlation of the solubility parameter δ to density ρ recommended by Yarranton and Masliyah:⁹

$$\delta = (A\rho)^{1/2} \quad (5)$$

where δ is the solubility parameter (MPa^{0.5}) and A is the monomer heat of vaporization (given in kJ/g). A value of $A = 0.366$ kJ/g was obtained by fitting the model to one set of asphaltene–*n*-heptane–toluene precipitation data¹⁰ at 23 °C.

Results and Discussion

The experimental data and the model predictions are presented for the mixtures of asphaltenes and solvents and then for the diluted heavy oils. A generalized approach for characterizing and modeling heavy oils and bitumens is developed.

Asphaltene + Toluene/*n*-Heptane Solutions. Figures 1–5 show the measured and predicted fractional precipitation of filter-washed Athabasca, Venezuela No. 1, Venezuela No. 2, Russia, and Indonesia asphaltenes, respectively, from solutions of toluene and *n*-heptane. The Athabasca results were used to develop the regular solution model and were published previously;¹⁰ they are provided here for the sake of comparison. The new samples (Venezuela No. 1, Venezuela No. 2, Russia, and Indonesia) were modeled without adjustment of input parameters or the use of interaction parameters.

The model predictions were in very good agreement with the measured fractional precipitation for all the new samples. The average absolute deviations (AADs) of the predicted values for Venezuela No. 1, Venezuela No. 2, Russia, and Indonesia samples were 0.027, 0.049, 0.018, and 0.027, respectively. The good predictions

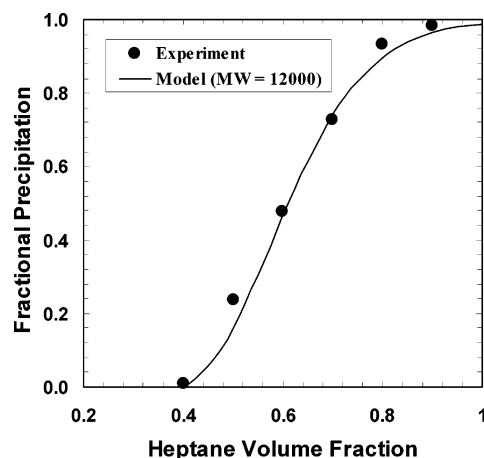


Figure 2. Fractional precipitation of Venezuela No. 1 asphaltenes from solutions of *n*-heptane and toluene at 23°C.

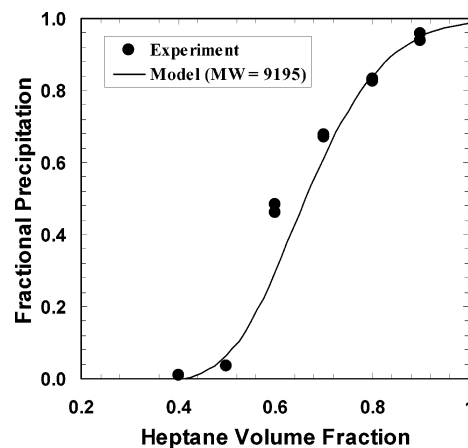


Figure 3. Fractional precipitation of Venezuela No. 2 asphaltenes from solutions of *n*-heptane and toluene at 23°C.

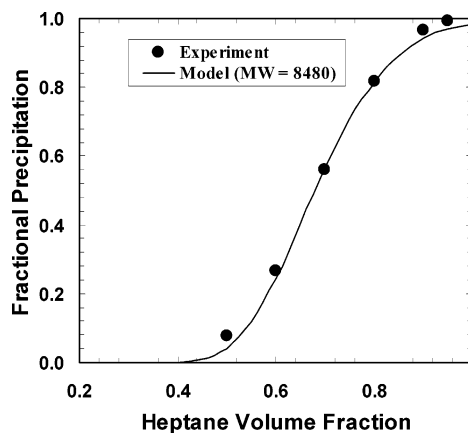


Figure 4. Fractional precipitation of Russia asphaltenes from solutions of *n*-heptane and toluene at 23°C.

demonstrate that the regular solution model can accurately predict asphaltene precipitation from solvent solutions, not only for asphaltenes from Western Canadian bitumens and heavy oils but also for asphaltenes from other heavy oil fields around the globe.

Heavy Oils Diluted with *n*-Alkanes. The asphaltene yields from various heavy oils and bitumens upon dilution with *n*-pentane and *n*-heptane are shown in Figures 6–12. The Western Canadian (Athabasca, Cold Lake, and Lloydminster) results were previously published¹⁰ and are provided here for the sake of compari-

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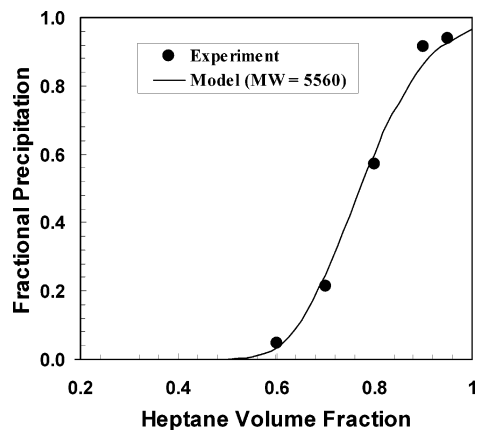


Figure 5. Fractional precipitation of Indonesia asphaltenes from solutions of *n*-heptane and toluene at 23°C.

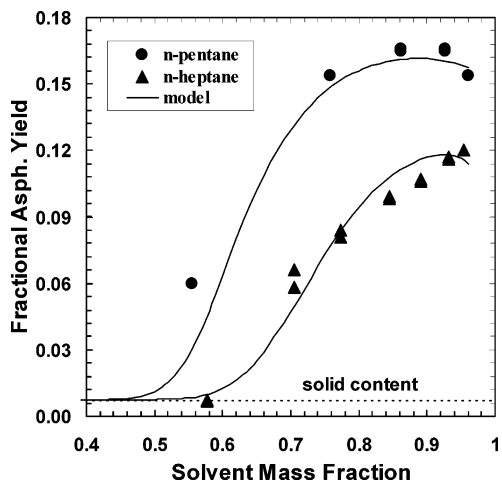


Figure 6. Fractional asphaltene yield from Athabasca bitumen diluted with (●) *n*-pentane or (▲) *n*-heptane.

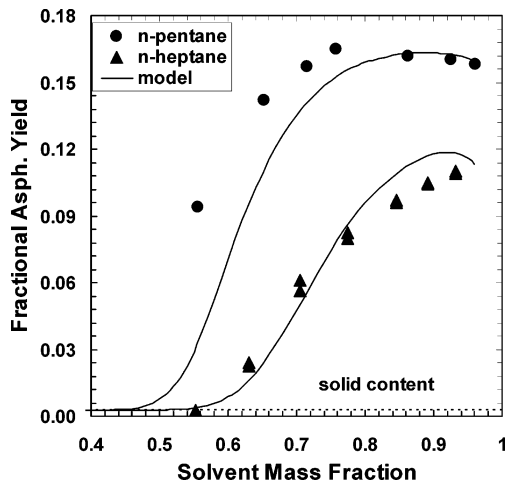


Figure 7. Fractional asphaltene yield from Cold Lake bitumen diluted with (●) *n*-pentane or (▲) *n*-heptane.

son. The results for Venezuela No. 1, Venezuela No. 2, Russia, and Indonesia samples are new. Note that the asphaltene yields from the Indonesian oil were so low that measurements were only taken for *n*-pentane-diluted mixtures.

The average molar mass of the self-associated asphaltenes in bitumen is unknown and cannot be measured. Therefore, the average molar mass of the asphaltenes becomes a fitting parameter. All other model

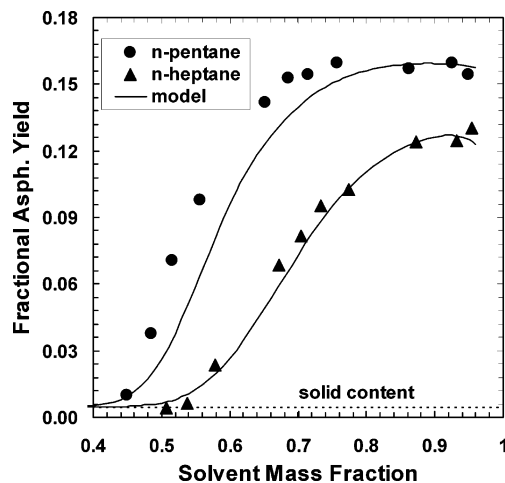


Figure 8. Fractional asphaltene yield from Lloydminster bitumen diluted with (●) *n*-pentane or (▲) *n*-heptane.

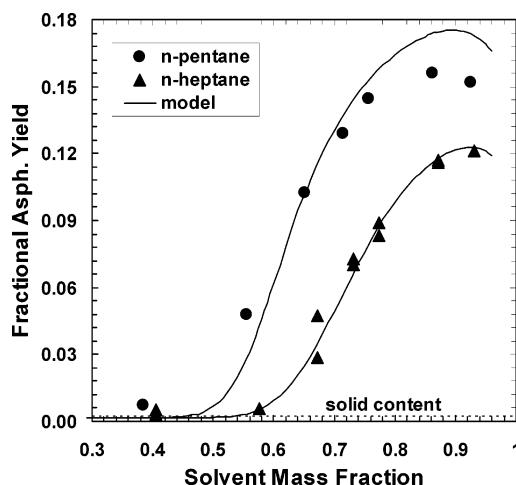


Figure 9. Fractional asphaltene yield from Venezuela No. 1 bitumen diluted with (●) *n*-pentane or (▲) *n*-heptane.

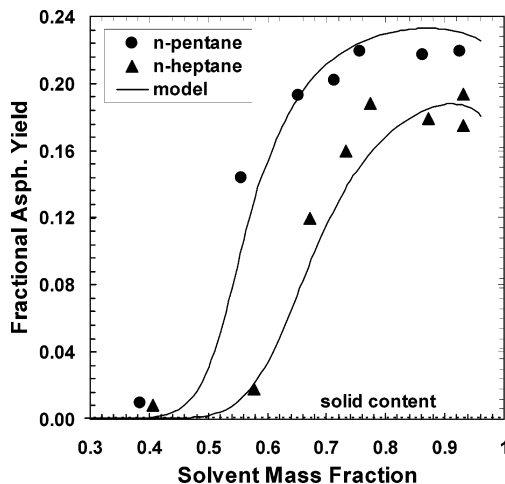


Figure 10. Fractional asphaltene yield from Venezuela No. 2 bitumen diluted with (●) *n*-pentane or (▲) *n*-heptane.

parameters are fixed. The model was fitted to the *n*-heptane-dilution data using the average asphaltene molar masses shown in Table 2. The asphaltene precipitation from heavy oils and bitumens diluted with *n*-pentane was predicted without further tuning of the model. Note that, for the Indonesian oil, the model was tuned to the *n*-pentane-diluted data. The AADs of the

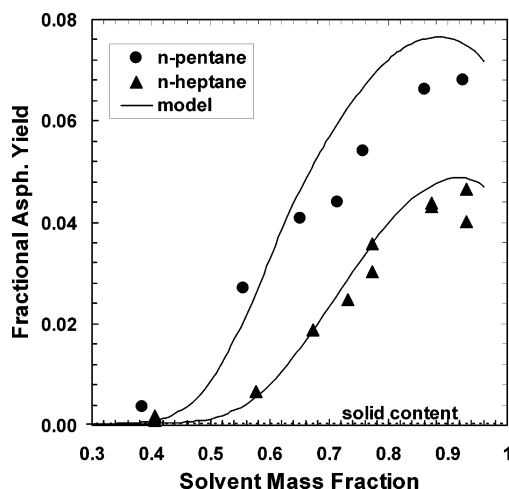


Figure 11. Fractional asphaltene yield from Russia bitumen diluted with (●) *n*-pentane or (▲) *n*-heptane.

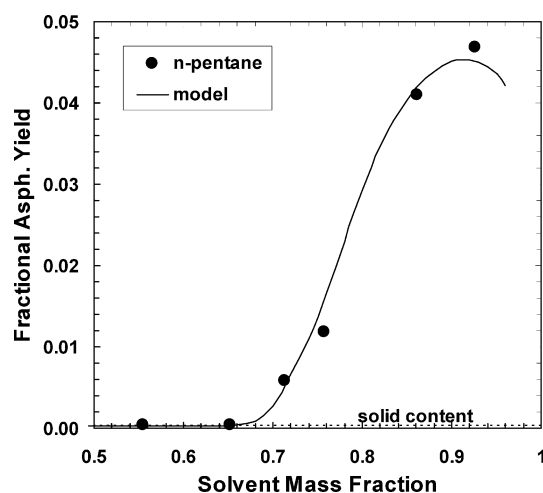


Figure 12. Fractional asphaltene yield from Indonesia bitumen diluted with *n*-pentane or *n*-heptane.

fitted or predicted yields for each diluted heavy oil or bitumen system and the average overall AADs for each diluent are shown in Table 2.

In most cases, the model fitted or predicted both the onset and the ultimate amount of precipitation with reasonable accuracy. However, for some of the pentane-diluted oils, the model underpredicted the amount of precipitation at intermediate solvent mass fractions. There are several possible explanations within the framework of the model:

(1) The molar mass distribution of the asphaltenes in bitumen may not always follow the gamma distribution with $\beta = 2$ (eq 2). A change in the shape of the distribution (change in β) will change the shape of the predicted yield curve.

(2) The average molar mass of the asphaltenes, which is a fitted constant in the model, may increase when an alkane is added to the bitumen. If the molar mass is greater than predicted, the model will underestimate the amount of precipitation at intermediate yields. The high yield prediction is less sensitive, because most of the asphaltenes precipitate at this point, regardless of the average molar mass.

(3) There may be a nonideal interaction between the asphaltenes and the diluent.

The effect of each of these factors is illustrated through a sensitivity analysis on the Lloydminster heavy oil data.

Sensitivity Analysis. The Lloydminster precipitation data was modeled using an average asphaltene molar mass of 3070 g/mol, no interaction parameters, and β values of 1, 1.5, 2, and 3. Figure 13 shows that the higher the value of β , the more sharply precipitation increases with increased mass fraction of diluent. A β value of 2 provides the best fit for the heptane-diluted oil, but a β value of 3 provides the best fit of the pentane-diluted oil.

Figure 14 shows the effect of changing the average molar mass of asphaltenes in bitumen on the model predictions. A higher asphaltene molar mass reduces the amount of solvent required to initiate precipitation and increases the amount of precipitation at any given solvent mass fraction. If the associated asphaltene molar mass increases as the solvent mass fraction increases, then the precipitation curves would become steeper.

The effect of an interaction parameter between the asphaltene and the oil is shown in Figure 15. A positive interaction parameter increases the solubility parameter of the mixture in the light phase (δ_m^l in eq 1) and increases the amount of precipitation at low to intermediate solvent-to-bitumen ratios.

Overall, the unadjusted model provides good predictions of both the onset of precipitation and the ultimate yield. Figures 13–15 demonstrate that, if desired, the model can be tuned to more closely fit a given data set. The simplest approach to match the data from a given alkane is to add an interaction parameter. However, it is quite possible that asphaltene self-association changes in different solvents. Both the average molar mass and the shape of the associated asphaltene molar mass distribution will then change. Hence, adjusting the average molar mass and the β value together may be the most physically meaningful approach.

Generalized Model. The proposed asphaltene precipitation model seems to be appropriate for a range of heavy oils and bitumens. To improve its generality, it is desirable to use average properties for the SARA fractions and develop a correlation for the average molar mass of asphaltenes in heavy oils. The solubility parameters of the correlations are already averages or are based on the molar mass and density of the fraction. Therefore, only average molar masses and densities are required. The use of average parameters and the possibility of a correlation for average asphaltene molar mass are discussed below, and a general approach to modeling asphaltene precipitation is recommended.

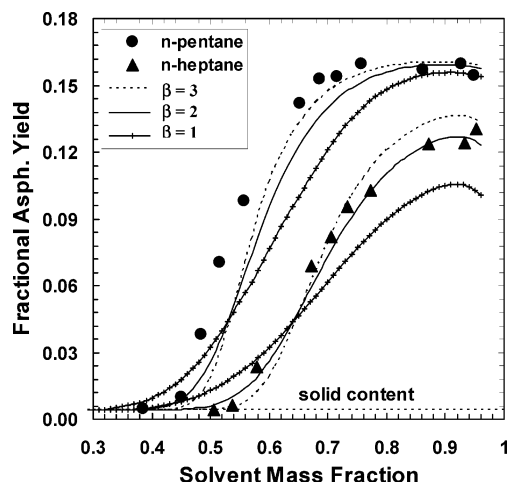
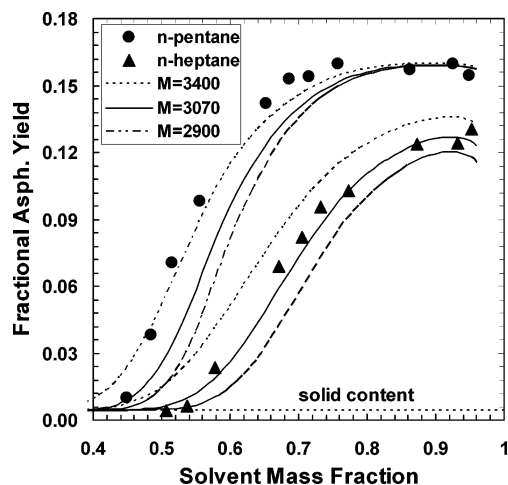
Akbarzadeh et al.¹⁹ suggested that the differences in the characteristics of Western Canadian heavy oils and bitumens were dependent mainly on the relative weight fraction of each solubility fraction, rather than on differences in the density or molar mass of the respective fractions from each oil. Hence, the use of average values of these properties for each fraction is not expected to affect the model predictions significantly. Model predictions were made for all of the diluted oils,

(19) Akbarzadeh, K.; Ayatollahi, Sh.; Moshfeghian, M.; Alboudwarej, H.; Yarranton, H. W. Estimation of the SARA Fraction Properties Using the SRK EOS. Accepted by *J. Can. Pet. Technol.*, 2003. (Presented at the Canadian International Petroleum Conference, Calgary, Canada, June 12–14, 2001, CIPC Paper No. 2001-122.)

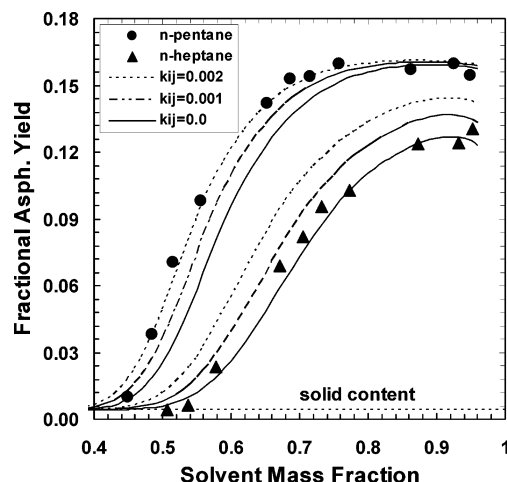
Table 2. Estimated Asphaltene Molar Mass in Heavy Oils/Bitumens and Average Absolute Deviations (AAD)^a for Different Systems

bitumen/heavy oil	fitted asphaltene molar mass (g/mol)	AAD, individual ^b		AAD, general ^c	
		<i>n</i> -heptane	<i>n</i> -pentane	<i>n</i> -heptane	<i>n</i> -pentane
Athabasca	2910	0.006	0.007	0.006	0.007
Cold Lake	2850	0.007	0.016	0.008	0.017
Lloydminster	3070	0.004	0.012	0.005	0.013
Venezuela No. 1	3070	0.004	0.012	0.004	0.006
Venezuela No. 2	3250	0.011	0.011	0.011	0.009
Russia	3000	0.002	0.008	0.002	0.008
Indonesia	2270	N/A	0.001	N/A	0.001
overall AAD		0.0057	0.0096	0.0060	0.0087

^a %AAD = $100 \times (\sum_1^N |\text{calculated} - \text{experimental}|/N)$. ^b Based on measured properties for saturates, aromatics, and resins. ^c Based on average properties for saturates, aromatics, and resins.

**Figure 13.** Effect of adjusting the parameter β on the predictions of asphaltene precipitation from Lloydminster heavy oil diluted with *n*-alkanes.**Figure 14.** Effect of adjusting the average molar mass on the predictions of asphaltene precipitation from Lloydminster heavy oil diluted with *n*-alkanes.

using the average densities and molar masses provided in Table 3. The total AAD for predictions based on the average properties are compared with the original AADs, based on the measured properties in Table 2. The total AAD for the bitumen/*n*-heptane systems increased from 0.0057 to 0.0060, whereas, for the bitumen/*n*-pentane systems, it decreased from 0.0096 to 0.0087. Predictions with less error were observed for the international samples. It is likely that the lower average resin molar mass improved the model predictions at

**Figure 15.** Effect of adjusting the interaction parameter on the predictions of asphaltene precipitation from Lloydminster heavy oil diluted with *n*-alkanes.**Table 3. Average Molar Masses, Densities, and Solubility Parameters of Saturates, Aromatics, and Resins**

fraction	molar mass (g/mol)	density (kg/m ³)	solubility parameter (MPa ^{0.5})
saturates	460	880	16.3
aromatics	522	990	20.9
resins	1040	1044	19.6

high solvent-to-bitumen ratios for these systems. In any case, the use of average properties did not significantly affect the accuracy of the model predictions.

An attempt was made to relate the estimated asphaltene molar masses in heavy oils and bitumens to other measurable parameters; however, no apparent correlation was observed. To illustrate, a correlation to the resin-to-asphaltene (R/A) ratio is considered. Asphaltene association is known to decrease as the R/A ratio increases. Hence, the average asphaltene molar mass is expected to be generally low in bitumens and lowest for bitumens with the highest R/A ratio. Figure 16 shows the estimated average asphaltene molar mass that was used to fit the precipitation data versus the R/A ratio of each heavy oil or bitumen. 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 trend. Unfortunately, the two outliers are scattered. If the Russian sample is neglected, the expected trend is observed. However, there is simply too little data to justify neglecting any data point. Similar difficulties occurred with any of the correlations that were attempted by the authors.

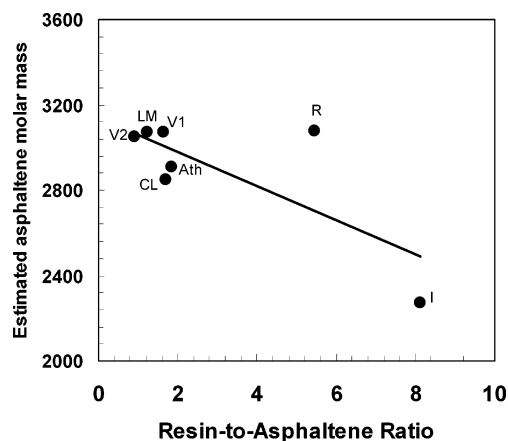


Figure 16. Fitted asphaltene molar mass in bitumen versus the resin-to-asphaltene ratio.

Given the lack of correlation for average asphaltene molar mass, the following approach to modeling asphaltene precipitation from diluted heavy oils or bitumens is recommended:

- (1) Obtain a SARA analysis and at least one precipitation data point.
- (2) If property data are not available, obtain average properties for SARA fractions from Table 3.
- (3) Set β equal to 2 and k_{ij} equal to zero; fit the model to the precipitation data point by adjusting the average asphaltene molar mass.
- (4) If more precipitation data are available, adjust β , the average molar mass, or the interaction parameter to obtain a better fit.

Conclusions

The correlations and modeling approach developed by Alboudwarej et al.¹⁰ were extended to some heavy oils

and bitumens from around the globe. The model successfully predicted asphaltene precipitation in solvent mixtures without adjustment (average absolute deviation of AAD < 0.049). The model was also fitted to asphaltene precipitation from four international bitumen and heavy oil samples that were diluted with *n*-heptane, using the average molar mass of asphaltenes in bitumen as a fitting parameter. Predictions were made for solutions of bitumen and *n*-pentane. The fitted and predicted onset and amount of precipitation were in good agreement with the experimental data in all cases (AAD < 0.016).

The effect of changing the shape of molar mass distribution, the average molar mass of asphaltenes in bitumen, or a nonideal interaction between solvent and asphaltenes was investigated through a sensitivity analysis. Although the unadjusted model provided good predictions of both the onset of precipitation and the ultimate yield, the model can be tuned to fit a given data set more closely. Adjusting the average molar mass and β together may be the most physically meaningful approach. A general approach to characterizing heavy oils and modeling asphaltene precipitation is recommended.

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