

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

Kamran Akbarzadeh¹, Hussein Alboudwarej²,
William Y. Svrcek, Harvey W. Yarranton^{*}

*Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive,
NW, Calgary, Alta., Canada T2N 1N4*

Received 22 September 2004; received in revised form 2 February 2005; accepted 9 March 2005

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.

© 2005 Elsevier B.V. All rights reserved.

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

1. 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; 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

^{*} Corresponding author. Tel.: +1 403 220 6529; fax: +1 403 282 3945.

E-mail address: hyarrant@ucalgary.ca (H.W. Yarranton).

¹ National Centre for Upgrading Technology, Canada.

² Oilphase-DBR, Canada.

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 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 at ambient conditions. Akbarzadeh et al. [11] extended the model to some heavy oils and bitumens from around the globe using the average molar mass of asphaltenes in bitumen as a fitting parameter.

The Alboudwarej et al. model has only been applied at ambient conditions. In this work, the model is extended to predict asphaltene yields from heavy oils and bitumens diluted with *n*-alkanes over a range of temperatures and pressures. Model fits and predictions are compared with the measured onset and amount of asphaltene precipitation for three Western Canadian and four international bitumens and heavy oils. A general approach to predicting precipitation from diluted heavy oils and bitumens is developed.

2. Experimental

Athabasca and Cold Lake bitumens and Lloydminster heavy oil were obtained from Syncrude Canada Ltd., Imperial Oil Ltd., and Husky Oil Ltd., respectively. Venezuela nos.1 and 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. The Athabasca bitumen was an oilsand bitumen that had been processed to remove sand and water. The Cold Lake and Russia samples were recovered from steam flooded reservoirs and had also been processed to remove sand and water. The Lloydminster heavy oil was a wellhead sample from a cyclic steam injection project and had not been processed. The Venezuela no. 1 bitumen was diluted and recovered by naphtha from an underground reservoir and had been processed to remove diluent and sand. The Venezuela no. 2 sample was a sample collected from a welltest of an exploratory well and had not been processed. The Indonesia heavy oil was a separator sample that had been processed to

remove water and sand. Toluene, *n*-heptane, *n*-pentane, and acetone were obtained from Aldrich Chemical Company and were 99%+ pure.

Saturates, aromatics, resins, and asphaltenes were extracted from each bitumen or heavy oil according to ASTM D2007M. The molar mass and density of each fraction were measured with a Jupiter 833 vapor pressure osmometer and an Anton Paar DMA 46 density meter, respectively. Details of the experimental methods are provided elsewhere [11–13]. Table 1 shows the SARA analysis of heavy oils and bitumens, the density of each fraction at 23 °C, and the molar mass of each fraction (measured in toluene at 50 °C). Table 2 provides the measured densities of saturate and aromatic fractions of an Athabasca sample at various temperatures.

The precipitation of asphaltenes from mixtures of asphaltene, toluene, and heptane at 0, 23 and 50 °C and from mixtures of bitumen/heavy oil and *n*-alkane at 0 and 23 °C was measured in a bench-top apparatus. In addition, asphaltene yields from *n*-heptane diluted Athabasca and Cold Lake bitumens and *n*-heptane at various temperatures and pressures were measured in a mercury-free PVT cell. Details of the experimental methods are provided elsewhere [12–14].

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:

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

where x_i^h and x_i^l are the heavy and light liquid phase mole fractions, R the universal gas constant, T temperature, 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), and v_m and δ_m are the molar volume and solubility

Table 1
SARA analysis of bitumens and heavy oils and measured molar mass and density of each fraction [11]

Fractions	wt. %	Density (kg/m ³)	Molar mass ^a (g/mol)
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		
Venezuela 1			
Saturates	15.4	885	447
Aromatics	44.4	1001	542
Resins	25.0	1056	1240
Asphaltenes ^b	15.0	1186	10005
Solids ^c	0.2		
Venezuela 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	1135
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 [19].

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

^c Non-asphaltic solids.

Table 2
Densities of saturate and aromatic fractions of an athabasca bitumen sample

Temperature (°C)	Density (kg/m ³)	
	Saturates	Aromatics
15	895.1	–
25	888.8	1006.4
35	–	1004.0
40	879.2	996.6
55	869.6	–

parameter of either the light liquid phase or the heavy liquid phase. Note that the above formulation is equivalent to a solid–liquid phase equilibrium where the contribution of the heat of fusion to the equilibrium expression is negligible.

It was assumed that only asphaltenes and resins partitioned to the heavy phase. In reality, all the fractions could potentially partition; however, allowing all components to partition significantly increases the time for the model to converge. Furthermore, experimental observations indicate that the heavy phase consists primarily of asphaltenes and resins. Once the equilibrium ratios are known the phase equilibrium is determined using standard techniques [8,17].

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:

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

where M_m , and $\bar{M}$ are the monomer molar mass and average ‘associated’ molar mass of asphaltenes, and β 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:

$$f(r) = \frac{1}{M_m \Gamma(\beta)} \left[\frac{\beta}{(\bar{r} - r_m)} \right]^\beta \times (r - r_m)^{\beta-1} \times \exp \left[-\frac{\beta(r - r_m)}{(\bar{r} - r_m)} \right] \quad (2b)$$

where r is the number of monomers in an aggregate and is defined as follows:

$$r = \frac{M}{M_m} \quad (2c)$$

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 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 β 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 β was also assumed to be temperature dependent. The following correlation for β was determined by fitting the model to precipitation data for mixtures of asphaltene–heptane–toluene at temperatures of 23 and 50 °C, as shown in Fig. 1:

$$\beta(T) = -0.0259T + 10.178 \quad (3)$$

where T is the temperature in Kelvin. Note that the correlation has only been tested for temperatures between 0 and 100 °C and cannot apply at temperatures exceeding 120 °C because the predicted β 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.

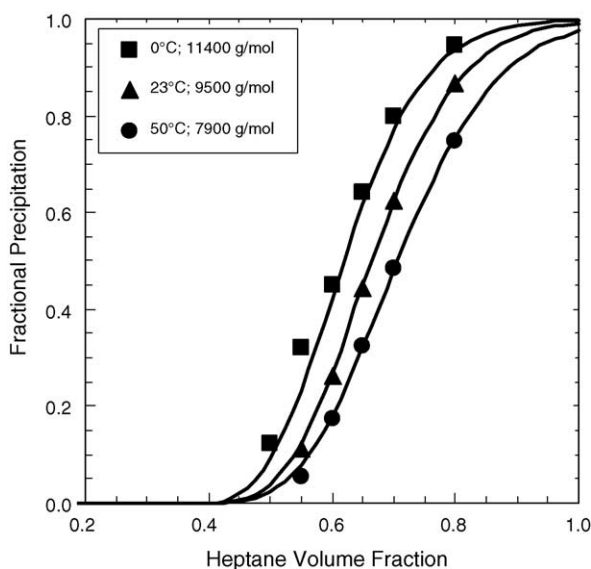


Fig. 1. Fractional precipitation of Athabasca asphaltenes from solutions of *n*-heptane and toluene at 0, 23, and 50 °C.

Table 3

Average molar masses, densities, and solubility parameters of saturates, aromatics, and resins

Fraction	Molar Mass at 50 °C (g/mol)	Density at 23 °C (kg/m ³)	Solubility parameter at 23 °C (MPa) ^{0.5}
Saturates	460	880	15.9
Aromatics	522	990	20.2
Resins	1040	1044	19.6

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:

$$\rho_{\text{sat}} = -0.6379T + 1078.96 \quad (4)$$

$$\rho_{\text{aro}} = -0.5942T + 1184.47 \quad (5)$$

where ρ_{sat} and ρ_{aro} are the densities of Athabasca saturates and aromatics in kg/m³, 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):

$$\bar{\rho}_{\text{sat}} = -0.6379T + 1069.54 \quad (6)$$

$$\bar{\rho}_{\text{aro}} = -0.5943T + 1164.73 \quad (7)$$

where $\bar{\rho}_{\text{sat}}$ and $\bar{\rho}_{\text{aro}}$ are the average densities of saturates and aromatics in kg/m³, 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]:

$$\rho = 670M^{0.0639} \quad (8)$$

where ρ is the asphaltene or resin density in kg/m³ 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:

$$\delta = \left(\frac{\Delta H^{\text{vap}} - RT}{v} \right)^{1/2} \quad (9)$$

where ΔH^{vap} is the heat of vaporization. The solubility parameters 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 solvent solubility parameter with an accuracy of approximately $\pm 0.05 \text{ MPa}^{0.5}$ 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 °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 °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:

$$\delta_h = 22.121 - 0.0232T \quad (10)$$

where δ_h is the solubility parameter of *n*-heptane (in $\text{MPa}^{0.5}$) 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:

$$\delta_{s,T} = \delta_{s,25} - 0.0232(T - 298.15) \quad (11)$$

where $\delta_{s,T}$ is solvent solubility parameter at temperature T , $\delta_{s,25}$ is solvent solubility parameter at 25 °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 below 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]:

$$\begin{aligned} \delta_a &= \left[\frac{\Delta H_m^{\text{vap}} - RT}{v} \right]^{1/2} = \left[\frac{r \Delta H_m^{\text{vap}} - RT}{r M_m / \rho} \right]^{1/2} \\ &= \left[\left(\frac{\Delta H_m^{\text{vap}}}{M_m} - \frac{RT}{r M_m} \right) \rho \right]^{1/2} \approx (A(T) \rho)^{1/2} \quad (12) \end{aligned}$$

where δ_a is the solubility parameter ($\text{MPa}^{0.5}$) 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 °C as shown in Fig. 1:

$$A(T) = -6.667 \times 10^{-4}T + 0.5614 \quad (13)$$

where T is the temperature in Kelvin. Note that two parameters (β 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 β led to a steeper slope on the fractional precipitation curve. To test the correlations (Eqs. (3) and (13)), the fractional precipitation curve was predicted

Table 4
Solubility parameters of *n*-alkanes at various temperatures

Solvent	Temperature (°C)	Solubility parameter ($\text{MPa}^{0.5}$)		
		Eq. (7)	Eq. (9)	Ref. [22]
<i>n</i> -Heptane	0	15.81	15.80	15.90
	25	15.20	15.20	15.20
	45	14.70	14.74	14.75
	60	14.31	14.39	14.41
	100	13.50	13.50	13.59
<i>n</i> -Hexane	0	15.55	15.46	15.42
	25	14.88	14.88	14.81
	45	14.31	14.41	14.50
	60	13.87	14.07	14.20
<i>n</i> -Pentane	0	15.15	14.95	15.00
	25	14.37	14.37	14.35
	45	13.71	13.91	13.81

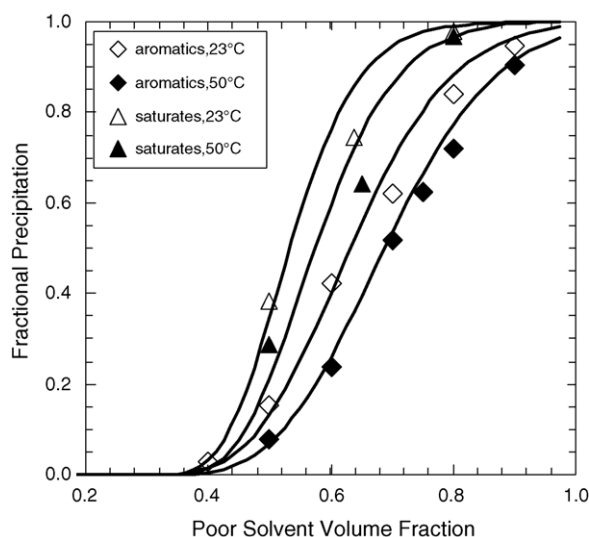


Fig. 2. Fractional precipitation of Athabasca asphaltenes from solutions of *n*-heptane/aromatics and saturates/toluene at 23 and 50 °C.

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:

$$\delta_{\text{sat}} = 22.381 - 0.0222T \quad (14)$$

$$\delta_{\text{aro}} = 26.333 - 0.0204T \quad (15)$$

where δ_{sat} and δ_{aro} are the solubility parameters of saturates and aromatics in $\text{MPa}^{0.5}$ 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

Fraction	Fitted solubility parameter ($\text{MPa}^{0.5}$)	
	23 °C	50 °C
Saturates	15.9	15.25
Aromatics	20.2	19.7

5. Results and discussion

Once the fluid characterization was completed, only one unknown parameter remained: the average associated molar mass ($\bar{r}M_m$) 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

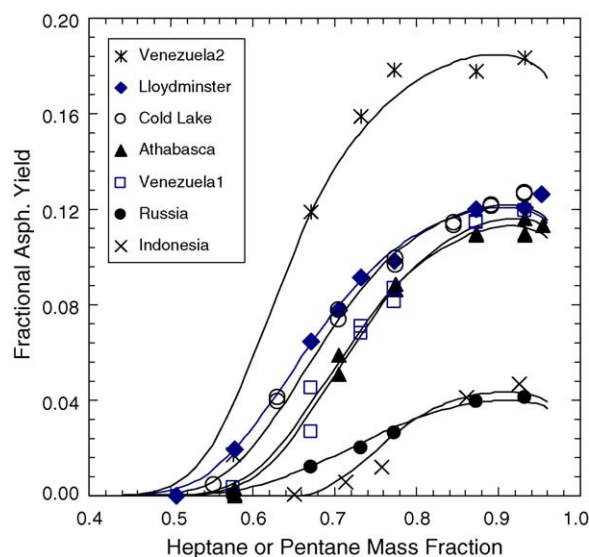


Fig. 3. Fractional yield of precipitate from various oils diluted with *n*-heptane (or *n*-pentane for Indonesian oil) at 23 °C.

Table 6
Fitted asphaltene molar mass in heavy oils/bitumens and average absolute deviation (AAD)^a for different systems

Bitumen/heavy oil	Fitted asphaltene molar mass, M_{23} (g/mol)	%AAD ^b		
		<i>n</i> -Heptane	<i>n</i> -Hexane	<i>n</i> -Pentane
Athabasca	2965	0.534	0.494	0.705
Cold Lake	2990	0.855	0.508	0.937
Lloydminster	3005	0.522	0.690	0.552
Venezuela no. 1	3000	0.757	—	0.707
Venezuela no. 2	3025	0.690	—	0.883
Russia	2800	0.436	—	0.496
Indonesia	2270	—	—	0.623

^a %AAD = $100 \times (\sum^N |\text{calculated} - \text{experimental}|/N)$.

^b 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

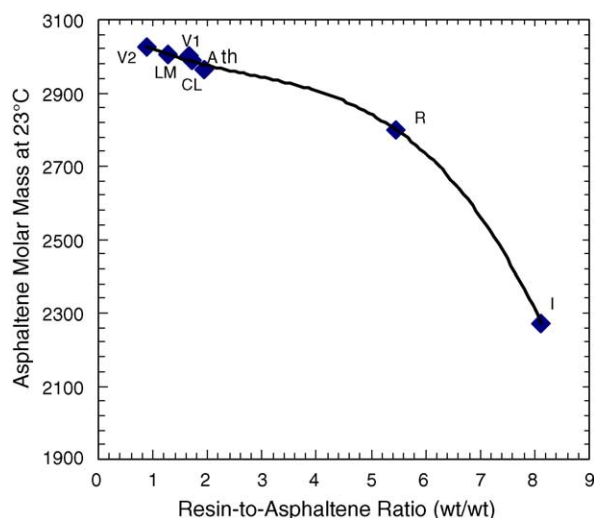


Fig. 4. The fitted asphaltene molar mass in bitumen versus the resin-to-asphaltene ratio. Ath = Athabasca, CL = Cold Lake, LM = Lloydminster, V1 = Venezuela no. 1, V2 = Venezuela no. 2, R = Russia, I = Indonesia.

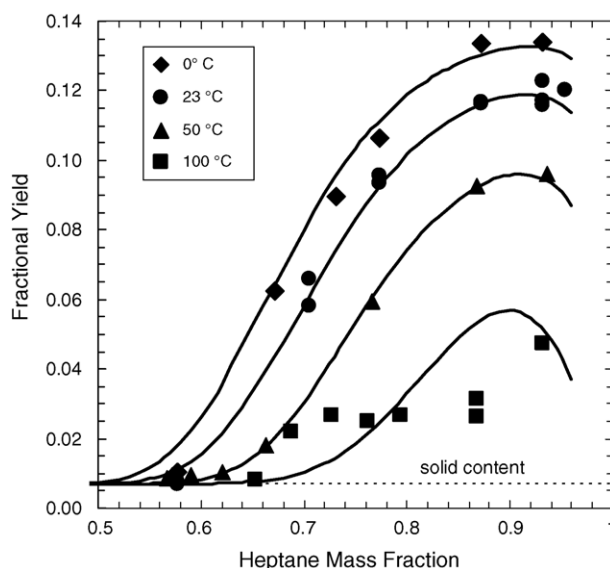


Fig. 5. Effect of temperature on the yield of precipitation from Athabasca bitumen diluted with *n*-heptane; data at 50 and 100 °C from [14].

decreases dramatically above an *R/A* ratio of approximately 5. The following third degree polynomial fits the data of Fig. 4:

$$M_{23} = -3.207(R/A)^3 + 25.943(R/A)^2 - 101.04(R/A) + 3099.4 \quad (16)$$

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:

$$M_{T,ath} = -10.599T + 6043.523 \quad (17)$$

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

Temperature (°C)	Fitted molar mass (g/mol)
0	3100
23	2960
50	2630
100 ^a	2070

^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:

$$M_T = M_{23} - 10.599(T - 296.15) \quad (18)$$

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 asphaltenes 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 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 asphaltenes 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

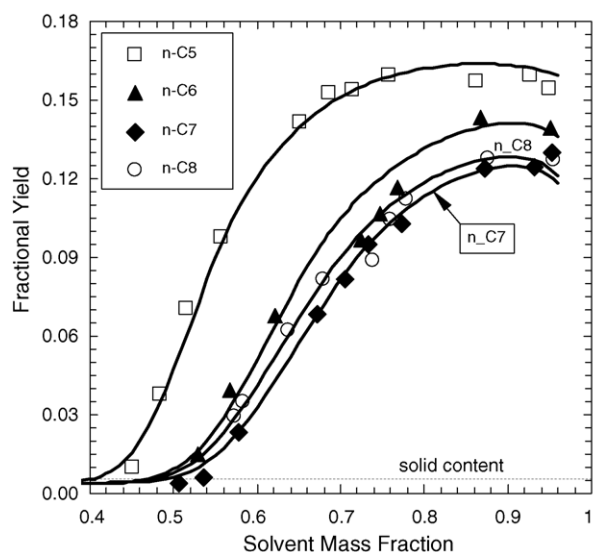


Fig. 6. Fractional yield of precipitate from Lloydminster bitumen diluted with n -alkanes at ambient conditions; data from [8].

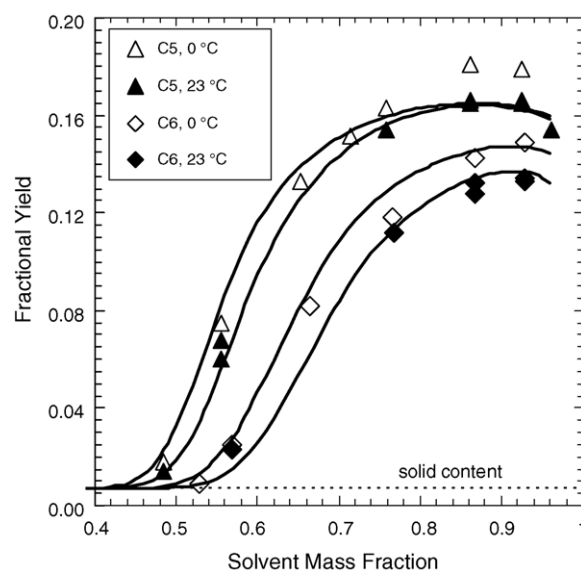


Fig. 7. Predicted fractional yield of precipitate from Athabasca bitumen diluted with n -pentane and n -hexane at 0 and 23 °C.

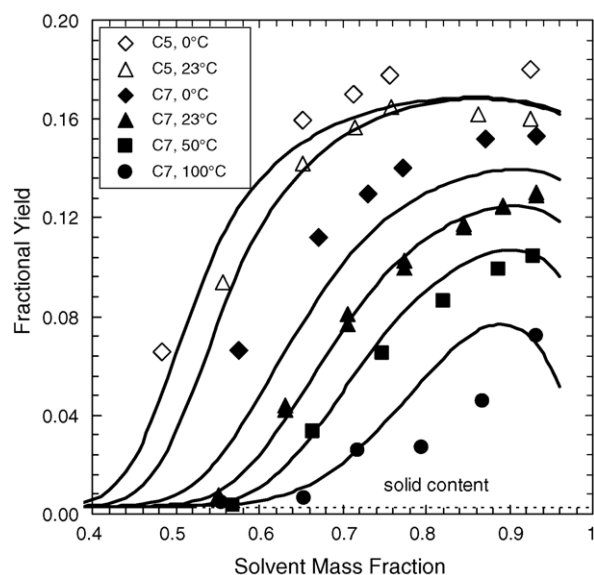


Fig. 8. Predicted fractional yield of precipitate from Cold Lake bitumen diluted with *n*-pentane and *n*-heptane at various temperatures; data at 50 and 100 °C from [14].

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

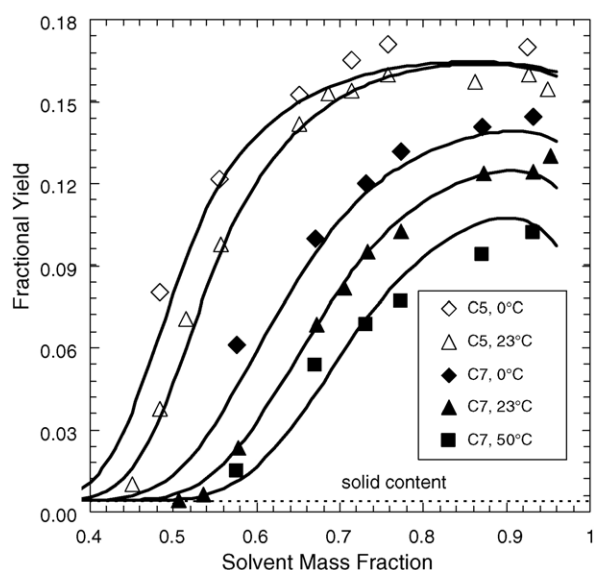


Fig. 9. Predicted fractional yield of precipitate from Lloydminster heavy oil diluted with *n*-pentane and *n*-heptane at various temperatures.

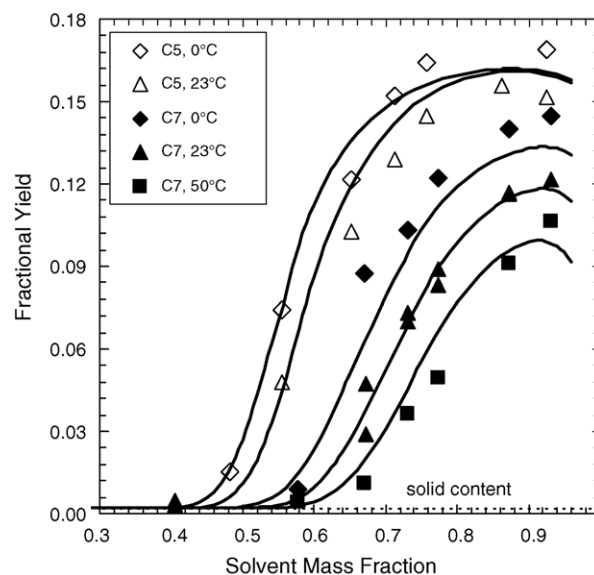


Fig. 10. Predicted fractional yield of precipitate from Venezuela no. 1 bitumen diluted with *n*-pentane and *n*-heptane at various temperatures; data at 23° from [11].

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.

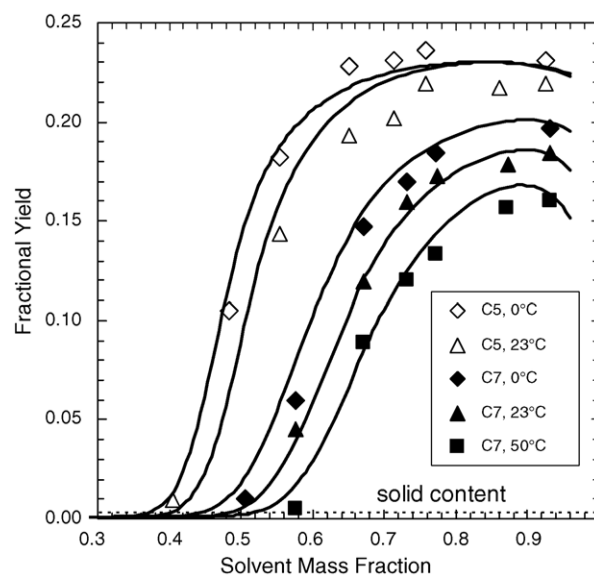


Fig. 11. Predicted fractional yield of precipitate from Venezuela no. 2 bitumen diluted with *n*-pentane and *n*-heptane at various temperatures; data at 23° from [11].

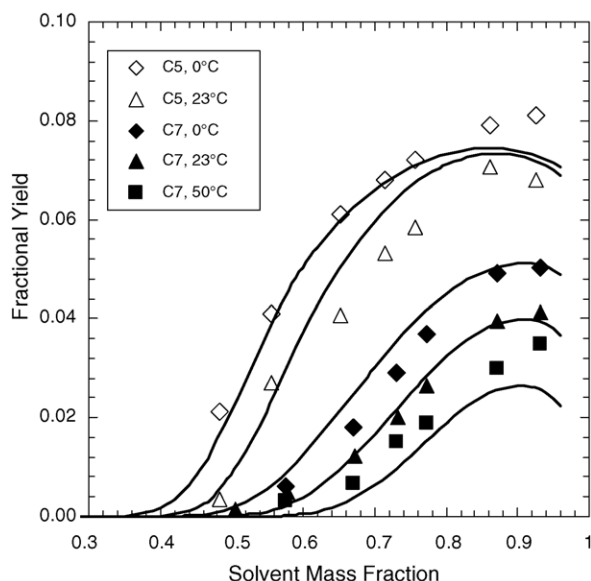


Fig. 12. Predicted fractional yield of precipitate from Russia heavy oil diluted with *n*-pentane and *n*-heptane at various temperatures; data at 23 °C from [11].

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

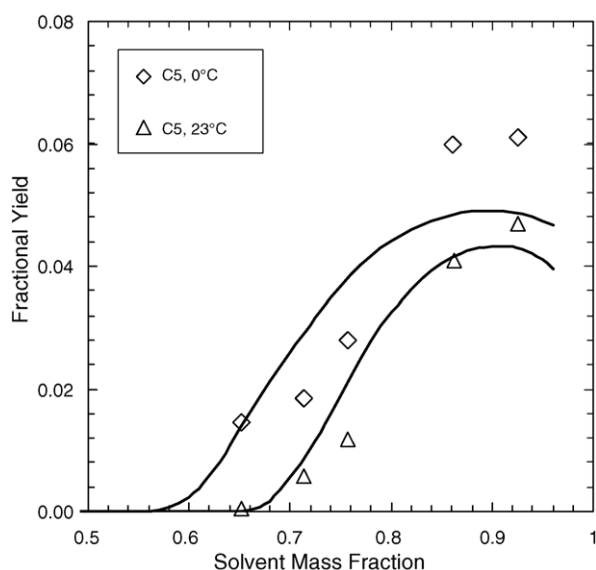


Fig. 13. Predicted fractional yield of precipitate from Indonesia heavy oil diluted with *n*-pentane *n*-heptane at 0 and 23 °C; data at 23 °C from [11].

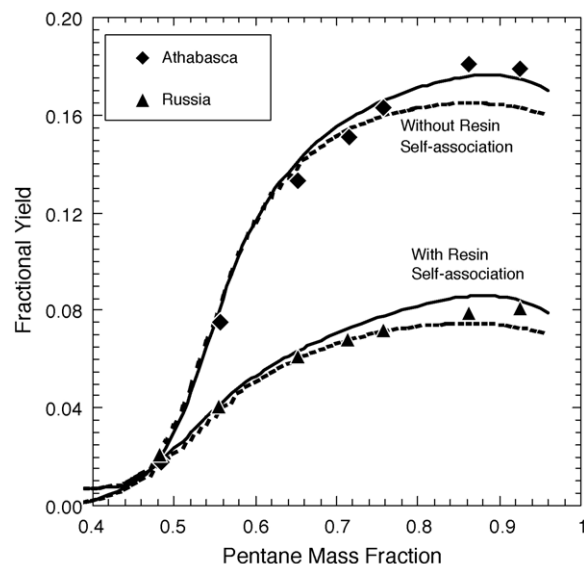


Fig. 14. Predicted fractional yield of precipitate from Athabasca and Russia samples diluted with *n*-pentane at 0 °C with and without resin self-association.

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.

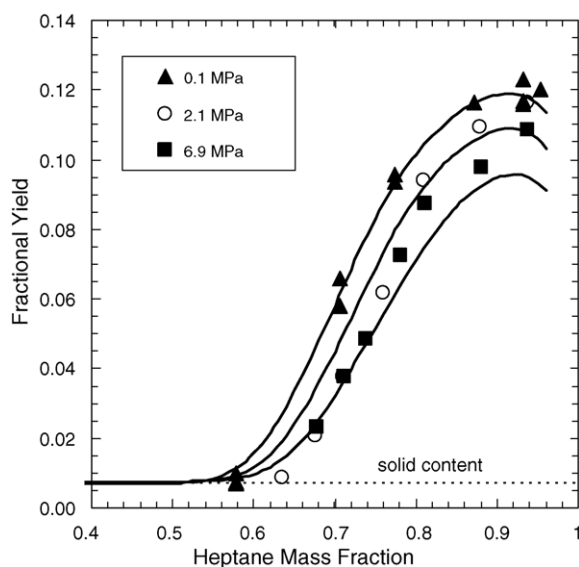


Fig. 15. The effect of pressure on the predicted fractional yield of precipitate from Athabasca bitumen diluted with *n*-heptane at 23 °C; data from [14].

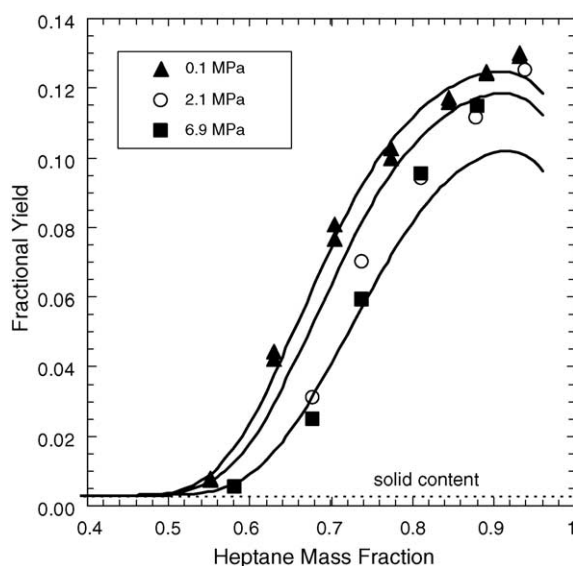


Fig. 16. The effect of pressure on the predicted fractional yield of precipitate from Cold Lake bitumen diluted with *n*-heptane at 23 °C; data from [14].

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-Brost-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. Asphaltene yields 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

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

Greek symbols

β	parameter in gamma distribution function
δ	solubility parameter (MPa) ^{0.5}
ΔH^{vap}	heat of vaporization (J/mol)
Γ	gamma function
ρ	density (kg/m ³)

Subscripts

23	at 23 °C
25	at 25 °C
<i>a</i>	asphaltenes
<i>aro</i>	aromatics
<i>ath</i>	Athabasca
<i>h</i>	heptane
<i>i</i>	<i>i</i> -th component
<i>m</i>	monomer
<i>r</i>	resins
<i>s</i>	solvent

T at temperature T
 sat saturates

Superscripts

h heavy phase
 l light phase

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Alberta Energy Research Institute (AERI) is appreciated. The authors also thank Syncrude Canada Ltd., Imperial Oil Ltd., Husky Oil Ltd., DBR Product Center, Schlumberger, the Scientific and Research Center for Heavy-Accessible Oil and Natural Bitumen Reserve in Tatarstan, and PT. Caltex Pacific Indonesia for supplying oil samples.

References

- [1] J.G. Speight, *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker, New York, 1999.
- [2] M. Agrawala, H.W. Yarranton, Asphaltene association model analogous to linear polymerization, *Ind. Eng. Chem. Res.* 40 (2001) 4664–4672.
- [3] A. Hirschberg, L.N.J. DeJong, B.A. Schipper, J.G. Meijer, Influence of temperature and pressure on asphaltene flocculation, *SPE J.* (1984) 283–293.
- [4] S. Kawanaka, S.J. Park, G.A. Mansoori, Organic deposition from reservoir fluids: a thermodynamic predictive technique, *SPE Res. Eng.* (1991) 185–192.
- [5] R.L. Scott, M. Magat, The thermodynamics of high-polymer solutions. I. The free energy of mixing of solvents and polymers of heterogeneous distribution, *J. Chem. Phys.* 13 (1945) 172–177.
- [6] R.L. Scott, M. Magat, The thermodynamics of high-polymer solutions. II. The solubility and fractionation of a polymer of heterogeneous distribution, *J. Chem. Phys.* 13 (1945) 178–187.
- [7] H.W. Yarranton, J.H. Masliyah, Molar mass distribution and solubility modeling of asphaltenes, *AIChE J.* 42 (1996) 3533–3543.
- [8] H. Alboudwarej, K. Akbarzadeh, J. Beck, W.Y. Svrcek, H.W. Yarranton, Regular solution model for asphaltene precipitation from bitumens and solvents, *AIChE J.* 49 (2003) 2948–2956.
- [9] J. Hildebrand, R. Scott, *Solubility of Non-Electrolytes*, 3rd ed., Reinhold, New York, 1949.
- [10] J. Hildebrand, R. Scott, *Regular Solutions*, Prentice-Hall, Englewood Cliffs, NJ, 1962.
- [11] K. Akbarzadeh, A. Dhillon, W.Y. Svrcek, H.W. Yarranton, Methodology for the characterization and modeling of asphaltene precipitation from heavy oils diluted with *n*-alkanes, *Energy Fuels* 18 (2004) 1434–1441.
- [12] H. Alboudwarej, K. Akbarzadeh, J. Beck, W.Y. Svrcek, H.W. Yarranton, Sensitivity of asphaltene properties to extraction techniques, *Energy Fuels* 16 (2002) 462–469.
- [13] K. Akbarzadeh, O. Sabbagh, J. Beck, W.Y. Svrcek, H.W. Yarranton, Asphaltene precipitation from bitumen diluted with *n*-alkanes, in: *Proceedings of the Canadian International Petroleum Conference, CIPC paper no. 2004-026*, June 8–10, Calgary, Canada, 2004.
- [14] H. Alboudwarej, Asphaltene deposition in flowing system. Ph.D. Thesis, University of Calgary, Calgary, Alta., Canada, April 2003.
- [15] J.L. Shelton, L. Yarborough, Multiple phase behavior in porous media during CO₂ or rich-gas flooding, *JPT (SPE #5827)*, September 1977, 1171–1178.
- [16] J.M. Shaw, T.W. deLoos, J. de Swaan Arons, An explanation for solid–liquid–liquid–vapour phase behaviour in reservoir fluids, *Pet. Sci. Technol.* 15 (1997) 503–521.
- [17] M.P.W. Rijkers, R.A. Heidemann, in: K.C., Chao, R.L., Robinson, Jr., (Eds.), *Convergence behavior of single-stage flash calculations*, Article in *Equations of State*, *Proceedings of the Theories and Applications ACS Symposium Series 300*, Washington, D.C., 1986.
- [18] C.H. Whitson, Characterizing hydrocarbon plus fractions, *SPE J.* (1983) 683–694.
- [19] H.W. Yarranton, H. Alboudwarej, R. Jakher, Investigation of asphaltene association with vapor pressure osmometry and interfacial tension measurements, *Ind. Eng. Chem. Res.* 39 (2000) 2916–2924.
- [20] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, 4th ed., Mc Graw-Hill, New York, 1989.
- [21] T.C. Daubert, R.P. Danner, H.M. Sibul, C.C. Stebbins, *DIPPR Data Compilation of Pure Compound Properties*, Project 801 Sponsor Release, July 1993, Design Institute for Physical Property Data, AIChE, New York, NY.
- [22] A.F.M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, 1983.
- [23] I.A. Wiehe, H.W. Yarranton, K. Akbarzadeh, P. Rahimi, A. Teclemariam, The Maximum in volume with carbon number of *n*-paraffins at the onset of asphaltene precipitation, in: *Proceedings of the 5th International Conference on Phase Behavior and Fouling*, June 13–17, Banff, Alta., Canada, 2004.