

## Predicting Asphaltene Precipitation from Heavy Oils Diluted by n-Heptane Using a Four-Parameter EOS

Esmaeili S\* and Maaref S

Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Canada

### Article Info

**\*Corresponding author:****Sajjad Esmaeili**

Department of Chemical and Petroleum  
engineering  
University of Calgary  
Calgary, Canada  
Tel: (+1)-587-9690662  
E-mail: Sajjad.Esmaeili1@ucalgary.ca

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### Abstract

The aim of this study is to apply the regular solution theory with a liquid-liquid equilibrium to model the asphaltene precipitation and estimate the onset point of asphaltene precipitation for four Canadian bitumens diluted by *n*-heptane using a four-parameter equation of state. The heavy oil/bitumen is characterized in terms of SARA fractions and divided into four different pseudo-components as Saturates, Aromatics, Resins, and Asphaltenes. To calculate the values of solubility parameters, molar volume and density of each SARA fractions, a four-parameter equation of state developed by Adachi et al. is employed for the first time. These properties are required to estimate the onset point of asphaltene precipitation by adding *n*-heptane solvent to the bitumen. The density calculation of SARA fraction indicates that the average absolute relative error for these bitumens/heavy oils is less than 1.2% and for whole system is about 1%. Furthermore, the results of onset point calculation for different heavy oils demonstrates acceptable predicted values with the average absolute relative error less than about 0.8%. Therefore, the model developed here is found to be successful in fitting and predicting the onset point and amount of asphaltene precipitation which were reported by previous researchers.

**Keywords:** Asphaltene Precipitation, Onset Point, Regular Solution Theory, Four-Parameter Equation of State.

### Introduction

Asphaltenes are defined as the heaviest compounds in the crude oil which can be dissolved completely in aromatic solvents such as toluene, while deposit upon adding paraffinic solvents like *n*-alkanes [1-8]. Any thermodynamic changes in pressure [9-11], temperature or oil composition, can cause asphaltene precipitation, resulting in many problems in transmission, production, and processing facilities in the oil industry [12-16].

There are large number of experimental techniques such as gravimetric, acoustic resonance [17-19], IFT measurement, dynamic method [20], high-pressure microscopy and infrared spectroscopy [19, 21-23] to detect the asphaltene precipitation. In addition to experimental measurements, a large number of thermodynamic models have been employed to model asphaltene precipitation and predict its onset point, which include solid model [24], micellization model [25], colloidal model [26], solubility model, and equation of state models [27-36].

The solid model is the simplest model for predicting asphaltene precipitation which treats asphaltenes as a single solid component and estimates the behavior of other phases by the equation of state. However, the problem associated with this model is that it needs many empirical parameters and experimental data for tuning [24]. The micellization model assumes that asphaltene aggregates form with a micelle core coated with resin molecules

[25]. The colloidal model which has been introduced by Leontaritis [26], uses a VLE calculation and an EOS to estimate the liquid composition. In this model, asphaltenes are treated as solid colloidal particles which are surrounded by large resin molecules and suspended in the crude oil [37]. In the solubility model on the other hand, asphaltenes are dissolved in a solvent liquid state and creates a uniform solution [9, 38, 39].

Among many thermodynamic approaches employed to predict asphaltene precipitation, the regular solution theory in conjunction with the equation of state models, are the most prevalent techniques [40-43]. It has been confirmed that the regular solution theory can be adapted to the polymer-like system such as solutions composed of solvent/asphaltene [44]. This model uses the solubility parameter or concept of cohesion energy density to describe the asphaltene solubility [40]. Similar to other thermodynamic models, mole fraction, solubility parameters, molecular weight and density of each fraction in the solution are required in this model. Generally, a liquid-liquid equilibrium (LLE) is generated between an asphaltene phase and another liquid phase containing rest of the diluted oil [45]. Hirschberg et al. [2] were the first scholars who employed the regular solution theory to predict the asphaltene precipitated from a crude oil, assuming a single component asphaltene fraction. Later on, it was used to predict the asphaltene precipitation amount and its onset undergoing a composition change [29, 46, 47].

In this study, the Hildebrand and Scott [48, 49] regular solution theory is applied to model asphaltene precipitation diluted by adding n-heptane into four different Canadian bitumens with same properties as mentioned by Greaves et al. [50]. Each bitumen is divided into four main pseudo components corresponding to SARA fractions. A four-parameter EOS developed by Adachi et al. [51] is used for the first time to calculate the solubility parameters, molar volumes and densities of SARA fraction. It is notable that the SRK-EOS [52] and the PR-EOS [53] were generally used in previous studies to predict the onset of asphaltene precipitation. However, they required a volume shift term to enhance the accuracy of their liquid density calculations, while this four-parameter equation of state does not require this correction and can yield a better representation of mixture properties. The molar volume and solubility parameters from this four-parameter equation of state are input values in the regular solution model. The outcomes of the developed model are compared with the experimental results as well as the modeling results of previous researches.

## Model Description and Methodology

### The Four-Parameter Equation of State

The four-parameter equation of state has been introduced by Adachi et al. [51] in 1983 to predict the properties of pure substances as well as the mixtures and resolve the deficiency of other two- and three-parameter equation of states in liquid density estimation. Although this equation of state contains four parameters, Adachi et al. have endeavored to keep this equation of state in form of a cubic EOS and involve just one

temperature dependent parameter similar to other two- and three-parameter equation of states (i.e. SRK-EOS, PR-EOS and PT-EOS). This four-parameter equation of state is described as below.

$$P = \frac{RT}{V - b_1} - \frac{a(T)}{(V - b_2)(V + b_3)} \quad (1)$$

where  $R$  is gas constant ( $\text{cm}^3 \cdot \text{MPa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ),  $P$  is pressure (MPa),  $T$  is temperature (K) and  $V$  is the four-parameter EOS molar volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ). It should be pointed out that this equation of state contains four parameters as  $a$ ,  $b_1$ ,  $b_2$  and  $b_3$ , where  $a$  is a temperature dependent parameter. The definition of each parameter and relevant concepts are mentioned in the Appendix section.

By rearranging Eq. (1) and defining  $A$ ,  $B_1$ ,  $B_2$  and  $B_3$  parameters as a function of operational condition (pressure and temperature), the general cubic form of this four-parameter EOS can be derived based on the z-factor. Therefore, the compressibility factor of SARA fraction can be calculated using Eq. (2).

$$Z^3 + (B_3 - B_2 - B_1 - 1)Z^2 + (B_1B_2 - B_3B_2 - B_3B_1 - B_3 + B_2 + A)Z + (B_1B_2B_3 + B_2B_3 - AB_1) = 0 \quad (2)$$

$$A = \frac{aP}{R^2T^2} \quad B_1 = \frac{b_1P}{RT} \quad B_2 = \frac{b_2P}{RT} \quad B_3 = \frac{b_3P}{RT}$$

## Extension of the Four-Parameter EOS to Asphaltene Aggregates

As it is known, asphaltenes tend to self-associate and the aggregates can be analogous to polymer-like compounds. It has been shown that asphaltene association can be modeled same as linear polymerization [43, 44, 46, 50, 54, 55]. Since the structure of asphaltene monomers is repeated throughout the structure of asphaltene aggregates, the asphaltene monomers can be considered as a group, for which the Van der Waals forces are involved in the association mechanism instead of chemical bonding. Due to the similar molecular bonding, the critical properties of asphaltene aggregates are same as their monomers. Therefore, four parameters of the Adachi et al. EOS can be used for asphaltene monomers using the group contribution method [50]. By applying the group contribution method on  $a$ ,  $b_1$ ,  $b_2$  and  $b_3$  parameters of the four-parameter EOS, the modified form of these variables can be derived as follow.

$$a_a = \bar{r}^2 a_m \quad (3)$$

$$b_{1a} = \bar{r} b_{1m} \quad (4)$$

$$b_{2a} = \bar{r} b_{2m} \quad (5)$$

$$b_{3a} = \bar{r} b_{3m} \quad (6)$$

In the above equations,  $\bar{r}$  shows an average number of monomers in a given aggregate, which can be calculated based on Eq. (7), and subscript  $m$  and  $a$  refer to the monomer and aggregate; respectively.

$$\bar{r} = \frac{\bar{M}^{agg}}{M_m} \quad (7)$$

By substituting the modified forms of the four parameters into Eq. (1), the extended four-parameter EOS can be obtained as Eq. (8), which is able to calculate the molar volume of asphaltene aggregate. The general cubic form of the extended four-parameter EOS is also derived by rearranging Eq. (8) based on the Z-factor and presented in Eq. (9).

$$P = \frac{RT}{\bar{r}(v - b_{1m})} - \frac{a_m(T)}{(v - b_{2m})(v + b_{3m})} \quad (8)$$

$$Z^3 \cdot \bar{r} + (B_3 \cdot \bar{r} - B_2 \cdot \bar{r} - B_1 \cdot \bar{r} - 1)Z^2 + (B_1 B_2 \cdot \bar{r} - B_3 B_2 \cdot \bar{r} - B_3 B_1 \cdot \bar{r} - B_3 + B_2 + A \cdot \bar{r})Z + (B_1 B_2 B_3 \cdot \bar{r} + B_2 B_3 - A B_1 \cdot \bar{r}) = 0 \quad (9)$$

$$A = \frac{a_m P}{R^2 T^2} \quad B_{1m} = \frac{b_{1m} P}{RT} \quad B_2 = \frac{b_{2m} P}{RT} \quad B_3 = \frac{b_{3m} P}{RT}$$

where  $v = V/\bar{r}$  is the monomer molar volume. To solve Eq. (9), the average number of monomers in each asphaltene aggregate must be determined and we used the reported values by Greaves et al. [50] for the four Canadian bitumens in this study.

Table 1. SARA analysis of heavy oils and bitumens (weight percent) and average number of monomer ( $\bar{r}$ ) [50].

	Athabasca	Cold Lake	Lloydminster	Peace River
Saturates	16.3	19.4	23.1	20.8
Aromatics	39.8	38.1	41.7	41.1
Resins	28.5	26.7	19.5	22.1
C5-Asphaltenes <sup>a</sup>	15.4	15.8	15.7	16.0
Solids <sup>b</sup>	4.9	3.0	3.8	2.1
$\bar{r}$	12	11	9	8

a) Asphaltenes+Solids extracted by *n*-pentane

b) Weight percent of total C5-Asphaltene and Solids

### Calculating the Critical Properties of SARA Fraction

Four bitumens/heavy oils used in this study are categorized into four chemically distinct fractions as Saturates, Aromatics, Resins, and Asphaltenes (SARA analysis). The description of the SARA fraction of the four bitumens including Athabasca, Cold Lake, Lloydminster, and Peace River are presented in Table 1. In addition, the values of molecular weight and measured density for SARA fractions of these bitumens are reported in Table 2 [50].

Table 2. The density (kg/m<sup>3</sup>) and molecular weight (g/mol) of SARA fraction for four bitumens (a) measured value at 296.15 K, b) measured value at 323.15 K [50].

Bitumen		Athabasca	Cold Lake	Lloydminster	Peace River
Saturates	Density <sup>a</sup>	900	882	876	881
	Mw <sup>b</sup>	524	508	482	490
Aromatics	Density <sup>a</sup>	1003	995	997	1004
	Mw <sup>b</sup>	550	522	537	542
Resins	Density <sup>a</sup>	1058	1019	1039	1051
	Mw <sup>b</sup>	976	930	859	1120
C7-Asphaltenes	Density <sup>a</sup>	1192	1190	1181	1182
	Mw <sup>b</sup>	2200	1400	1800	1900
	Mw <sup>c</sup>	21900	19200	16900	15200

\* Molecular weight at 50 kg/m<sup>3</sup>

The first step in employing the four-parameter EOS to calculate the onset of asphaltene precipitation is to estimate the critical properties of SARA fraction including the critical pressure, critical temperature and acentric factor. Based on the previous section, critical properties of asphaltene aggregates are same as their monomers. It is worthwhile noting that the asphaltene fraction is also separated into pseudo-components based on molar mass and the gamma distribution function ( $\Gamma(\beta)$ ) is employed for this purpose to describe the molar mass distribution function as shown in Eq.(10). This study discretizes the asphaltene distribution into 35 fractions where the molar mass varies between 1600 and 25000 g/mol. This number of fractions is consistent with previous researches [44, 46, 54-56].

$$f(M) = \frac{1}{M_m \Psi(\beta)} \left( \frac{\beta}{(\bar{r} - r_m)} \right)^\beta (r - r_m)^{\beta-1} \exp\left( -\frac{\beta(r - r_m)}{(\bar{r} - r_m)} \right) \quad (10)$$

To estimate the critical properties of saturate fraction, an accurate correlation introduced by Riazi and Al-Sahhaf [57] is used as expressed by Eq.(11). This correlation is a function of the saturate compound molecular weight and is able to calculate critical temperature, critical pressure, acentric factor, and boiling point. The four constants of Eq. (11) are expressed in Table 3.

$$\theta = \theta_\infty - \exp(\phi_1 - \phi_2 M^{\phi_3}) \quad (11)$$

Table 3. Values of constants involved in Eq. (11) to calculate the critical properties of saturate component.

$\theta$	$\theta_\infty$	$\phi_1$	$\phi_2$	$\phi_3$
$T_b$	1070	6.98291	0.02013	0.67
$\frac{T_b}{T_c}$	1.15	-0.41966	0.02436	0.58
$-P_c$	0	4.65757	0.13423	0.5
$-\omega$	0.3	-3.06826	-1.04987	0.20

It should be pointed out that a simple and accurate correlation have not been determined yet for the rest of SARA fractions including aromatics, resins and asphaltenes. However, a proper empirical correlation has been proposed by Garnier et al. [58] based on the group contribution method for polynuclear aromatics, which can be used to calculate the critical properties of SARA fraction as a function of molecular weight. Eq. (12) through Eq. (15) show these correlations for the critical temperature, critical pressure, critical volume, and acentric factor of SARA fractions.

$$T_c (K) = 77.856M^{0.4708} \quad (12)$$

$$P_c (bar) = 1891.4M^{-0.7975} \quad (13)$$

$$V_c (cm^3/mol) = 2.4988M + 116.8879 \quad (14)$$

$$\omega = c_f (0.5837 \ln(M) - 2.5389) \quad (15)$$

where  $c_f$  is a correction factor for the acentric factor of aromatic, resin and asphaltene, which is introduced due to the small structural differences between polynuclear compounds and SARA fraction [50, 55]. Note that the correction factor for each SARA fraction can be determined through matching the value of the estimated density to the experimentally measured density, which will be expressed in the following sections.

### The Regular Solution Model

To calculate the amount of asphaltene precipitation under the LLE or SLE using the regular solution model, the equilibrium ratio of SARA fractions must be determined, which can be evaluated as Eq. (16).

$$K_i = \frac{x_i^s}{x_i^l} = \exp \left[ 1 - \frac{V_i^l}{V_{mix}^l} + \ln \left( \frac{V_i^l}{V_{mix}^l} \right) + \frac{V_i^l}{RT} (\delta_i - \delta_{mix})^2 \right] \quad (16)$$

According to the Flory-Huggins theory, the chemical potential of SARA fractions in a bitumen/pure solvent mixture can be calculated by Eq. (17).

$$\frac{\mu_i - \mu_i^0}{RT} = 1 - \frac{V_i^l}{V_{mix}^l} + \ln \left( \frac{x_i^l V_i^l}{V_{mix}^l} \right) + \frac{V_i^l}{RT} (\delta_i - \delta_{mix})^2 \quad (17)$$

where  $\mu_i$  is the chemical potential,  $x_i$  is the mole fraction,  $V_i$  is the liquid molar volume, and  $\delta_i$  is the solubility parameter of the  $i^{\text{th}}$  SARA fraction. Moreover,  $V_{mix}$  and  $\delta_{mix}$  show the liquid molar volume of the bitumen/solvent mixture and the solubility parameter of the bitumen/solvent mixture; respectively.

Hildebrand, Prausnitz, and Scott proposed a liquid solubility parameter for a non-polar solvent as a function of the internal energy of vaporization and the molar volume of the liquid phase, which can be calculated from Eq. (18). Based on the definition of internal energy of vaporization  $\Delta U^{lv}$  and also calculating the relevant integral, the general form of the solubility parameter for the four-parameter EOS can be derived as Eq. (22).

$$\delta^l = \left( \frac{\Delta U^{lv}}{V^l} \right)^{1/2} \quad (18)$$

$$\left( \frac{\Delta U^{lv}}{V^l} \right)^{1/2} = \frac{1}{V^l} \left[ \int_{\infty}^{V_c} \left( T \left( \frac{\partial P}{\partial T} \right)_V - P \right) dV - \int_{\infty}^{V_c} \left( T \left( \frac{\partial P}{\partial T} \right)_V - P \right) dV \right] \quad (19)$$

$$\frac{\Delta U^{lv}}{V^l} = \frac{1}{V^l} \int_{V_1}^{V_c} \left( \frac{T(da/dT) - a}{(V + b_3)(V - b_2)} \right) dV \quad (20)$$

$$\frac{\Delta U^{lv}}{V^l} = \frac{1}{V^l} \left( \frac{T(da/dT) - a}{(b_3 + b_2)} \ln \left( \frac{V^l - b_2}{V^l + b_3} \right) \right) \quad (21)$$

$$\delta^l = \left( \frac{\Delta U^{lv}}{V^l} \right)^{1/2} = \left( \frac{1}{V^l} \left( \frac{T(da/dT) - a}{(b_3 + b_2)} \ln \left( \frac{V^l - b_2}{V^l + b_3} \right) \right) \right)^{1/2} \quad (22)$$

Yang et al. [42] mentioned that if one assumes asphaltene fraction as a pure component, the onset point of asphaltene

precipitation can be determined by satisfying Eq. (23). If we substitute Eq. (23) into Eq. (17), the onset point of asphaltene precipitation can be determined when the  $F$  coefficient in Eq. (24) is zero.

$$\frac{\mu_i - \mu_i^0}{RT} = 0 \quad (23)$$

$$F = \ln \left( \frac{x_i V_i}{V_{mix}} \right) + 1 - \frac{V_i}{V_{mix}} + \frac{V_i}{RT} (\delta_i - \delta_{mix})^2 \quad (24)$$

Based on Eq. (24), a negative value of  $F$  is known as a stable condition of asphaltene in the bitumen/pure solvent mixture, while a positive value of  $F$  is referred to an unstable condition of asphaltene, which causes asphaltene precipitation. This is a simple approach to determine the onset point of asphaltene precipitation.

It should be mentioned that to determine the whole liquid phase properties such as the solubility parameter, molar volume, density, and molecular weight, the mixing rule is utilized as shown in Eq. (25) through Eq. (28).

$$M_{mix} = \sum_{i=SARA} x_i M_i \quad (25)$$

$$\frac{1}{\rho_{mix}} = \sum_{i=SARA} \frac{w_i}{\rho_i} \quad (26)$$

$$V_{mix} = \sum_{i=SARA} x_i V_i \quad (27)$$

$$\delta_{mix} = \sum_{i=SARA} \frac{x_i V_i \delta_i}{V_{mix}} \quad (28)$$

where,  $x_i$  denotes the mole fraction,  $\rho_i$  is the phase density,  $w_i$  is the mass fraction of  $i^{\text{th}}$  SARA fraction, and  $\delta_{mix}$  is the solubility parameter of the bitumen/solvent mixture. It is notable that the value of asphaltene molar volume is  $V_a = \bar{r} V_a$  in these correlations.

## Results and Discussions

### Model Validation

To validate the model, the estimated values of molar volume and solubility parameters of SARA fractions and a given solvent are compared to the measured or calculated values from literature, which are mentioned in the following subsections. The molecular weight and density of SARA fractions are extracted from Table 2. To calculate the molecular weight of asphaltene, the molar mass distribution of asphaltene is required. In this study, the molar mass of the first asphaltene precipitated from the crude oil is estimated by the trial and error and the approximated value of asphaltene molecular weight is found to be around 1600 g/mol, which is consistent with the existed literature [44, 46, 50, 54, 55, 57, 59]. It is notable that this value is used for all bitumens in this study.

### Density calculation

Due to the small structural difference between the polynuclear compounds and the SARA fraction, some critical properties of SARA fraction including the critical pressure, critical temperature and acentric factor can be tuned before the onset point calculation. The acentric correction factor is tuned here by fitting the calculated density to the measured density for each bitumen and the average value is used for each bitumen. The acentric correction factor, calculated density and measured density for each bitumen using the four-parameter EOS are reported in Table 4, which reveals that the relative errors are less than 2%. Moreover, the table demonstrates that the four-parameter EOS without the volume shift term can accurately determine the density of SARA fraction and the whole bitumen. The average values of acentric correction factor for previous studies which employed the PR-EOS and the SRK-EOS was found to be 0.9024, 0.8098, 0.7910 and 0.7940 for Saturate, Aromatic, Resin and Asphaltene; respectively. It is notable that the acentric correction factor obtained in this study are different from the PR-EOS and the SRK-EOS [59] results.

Table 4. The acentric correction factor, calculated density ( $\text{kg}/\text{m}^3$ ), relative deviation (%RD) and average absolute deviation (%AAD) of whole bitumens and SARA fraction at 296.15 K from the four-parameter EOS.

	$C_f$	Athabasca %RD	Cold Lake %RD	Lloydminster %RD	Peace River %RD	%AAD
Saturates	1.1985	893.61 (-0.70%)	887.19 (0.59%)	877.44 (0.16%)	880.35 (-0.07%)	0.38%
Aromatics	1.0594	1000.99 (-0.20%)	998.05 (0.31%)	999.63 (0.26%)	1000.16 (-0.38%)	0.29%
Resins	1.0628	1043.52 (-1.37%)	1039.46 (2.01%)	1033.07 (-0.57%)	1055.86 (0.46%)	1.10%
C7-Asphaltenes	1.1395	1186.93 (-0.43%)	1185.41 (-0.38%)	1183.69 (0.23%)	1188.78 (0.57%)	0.40%
Whole Oil		1024.243 (-0.17%)	1017.203 (1.62%)	1006.826 (1.90%)	1007.05 (0.40%)	1.02%

According to the absolute deviation of the density of SARA fraction calculated from the four-parameter EOS in Table 4, this four parameter EOS like the PR-EOS and the SRK-EOS is reliable for density calculation of SARA fraction after evaluating the acentric correction factor.

### Solubility parameter calculation

In this section, the performance of the four-parameter EOS is examined in prediction of solubility parameters of some pure substances such as *n*-pentane, *n*-heptane, *n*-octane and other substances to confirm its reliability in calculating the onset point and predicting asphaltene precipitation. Prior to calculating the solubility parameter, the acentric correction factors of SARA fraction is tuned based on the previous section and the molecular weight of first asphaltene precipitated of four bitumens is determined as mentioned previously. It should be also pointed out that the liquid molar volume is needed for calculating the solubility parameter.

Table 5 compares the experimental [60, 61] and calculated values of solubility parameters for six different pure substances at atmospheric pressure and temperature of 298.15 K. Note that the value of solubility parameters obtained by the PR-EOS and SRK-EOS are reported based on the previous studies [62] and

relevant data of the four-parameter EOS is only calculated in this study. To improve the accuracy of liquid molar volume calculation from the PR-EOS and SRK-EOS, the Peneloux volume correction [63] factor is employed. According to Table 5, the four-parameter EOS is more accurate than the PR-EOS and the SRK-EOS in solubility parameter calculation for pure solvents.

Table 5. The experimental value of solubility parameter ( $\text{MPa}^{0.5}$ ) [60, 61] and the relative deviation of solubility parameter calculated by various EOSs for six pure substances at ambient condition.

	Experiment ( $\text{MPa}^{0.5}$ )	Absolute Relative deviation (%)		
		PR	SRK	This Study
<i>n</i> -pentane	14.40	1.69	1.71	0.24
<i>n</i> -heptane	15.20	1.78	1.78	1.44
<i>n</i> -octane	15.40	2.48	2.5	1.46
<i>n</i> -Eicosane	16.50	7.00	7.98	2.58
Cyclopentane	16.50	1.86	1.85	0.91
Cyclohexane	16.80	6.01	7.32	1.84
Ethyl benzene	17.85	3.57	3.62	2.57
<i>O</i> -xylene	18.09	0.86	0.92	0.88
Toluene	18.32	1.86	1.86	3.50
Benzene	18.41	2.4	2.41	1.57
Acetone	19.95	12.98	13.45	6.93
AAR (%)		3.86	4.12	2.17

### Calculating the Onset Point of Asphaltene Precipitation

The onset point of asphaltene precipitation by adding a specific amount of *n*-heptane to the four bitumens is calculated using the four-parameter EOS at 296.15 K and atmospheric pressure. To determine the onset point of bitumen diluted by *n*-heptane based on the regular solution theory, the molar volume and solubility parameter of SARA fraction for a given bitumen is calculated firstly using Eq. (8) and Eq.(22). The mole fractions of SARA fraction and pure solvent are then updated by adding a particular mass of *n*-heptane to the bitumen and the equilibrium ratio of each component is calculated based on Eq. (16). Afterwards, the Rachford-Rice equation is applied assuming that the solid phase is a pure asphaltene substance and the amount of asphaltene precipitation is calculated and the new liquid composition is evaluated. This procedure is repeated until no variation occurs in the amount of asphaltene precipitation. The onset point is then known as the volume of a solvent in which the asphaltene precipitation first occurred.

Table 6. The measured onset point [50] and calculated onset point using *n*-heptane at 296.15 K from the four-parameter EOS.

	Onset H/B ( $\text{cm}^3$ (Solvent)/g (Bitumen))			Onset $W_H$ (Mass fraction of Solvent)		
	Measured	Predict	% RD	Measured	Predict	% RD
Athabasca	1.90	1.9140	0.74	0.565	0.564	0.20
Cold Lake	1.75	1.7645	0.83	0.545	0.544	0.22
Lloydminster	1.65	1.6402	0.59	0.530	0.525	0.83
Peace River	1.75	1.7305	1.12	0.545	0.539	1.11
%AAD			0.82			0.59

Table 7. The measured and calculated onset point using *n*-heptane at 296.15 K from the four-parameter EOS, SRK-EOS and PR-EOS.

	Onset H/B ( $\text{cm}^3$ (Solvent)/g (Bitumen))			
	Measured	SRK-EOS [50]	PR-EOS [54]	This study
Athabasca	1.90	1.92	1.93	1.9140
Cold Lake	1.75	1.82	1.71	1.7645
Lloydminster	1.65	1.66	1.61	1.6401
Peace River	1.75	1.70	1.71	1.7305

The measured and calculated values of asphaltene onset point for the four bitumens diluted by *n*-heptane at 23° C and atmospheric pressure are mentioned in Table 6. It should be noted that the measured values in this table are extracted from the study conducted by Greaves et al. [50]. According to Table 6, the four-parameter EOS can accurately estimate the onset point of each bitumen since the deviation values are less than 1.2%. Figure 1 also demonstrates the value of F coefficient versus the dilution ratios in which the zero value of F coefficient occurs at the onset point of asphaltene precipitation. The comparison between the onset point estimation from the SRK-EOS, PR-EOS, and the four-parameter EOS is shown in Table 7. Although the SRK and the PR equation of state can also determine the onset point of each bitumen [50] with considering volume shift and the acentric correction factor, the current research demonstrates that the four-parameter EOS can predict the onset point more accurately due to more reliable density and molar volume calculations and without requiring the Rackett compressibility factor.

Table 8. Solubility parameters (MPa<sup>0.5</sup>) of SARA fraction for the four bitumens calculated by the four-parameter EOS and SRK-EOS [50] at ambient condition.

	Athabasca	Cold Lake	Lloydminster	Peace River	
SRK-EOS	Saturates	16.54	16.44	16.38	16.34
	Aromatics	20.78	20.76	20.77	20.77
	Resins	20.50	20.50	20.49	20.51
	Asphaltenes	20.97	20.96	20.96	20.96
Four-parameter EOS	Saturates	16.24	16.31	16.42	16.38
	Aromatics	21.52	21.55	21.53	21.53
	Resins	20.85	20.94	21.07	20.59
	Asphaltenes	20.81	20.83	20.85	20.78

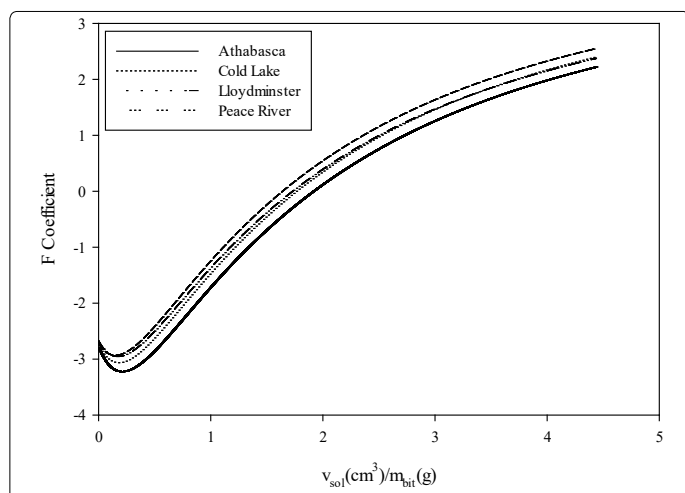


Figure 1. The value of F coefficient for different bitumens using *n*-heptane at atmospheric condition.

The calculated values of solubility parameters of SARA fractions of four bitumens using the four-parameter EOS in the present study and the SRK-EOS and PR-EOS from the study done by Greaves et al. [50] and Sabbagh et al. [54] are reported in Table 8. The results show that the four-parameter EOS is an appropriate equation of state to be used in the regular solution theory for estimating the asphaltene precipitation onset by adding *n*-heptane. Figure 2 also reveals the fractional precipitation of asphaltene for four bitumens using pure *n*-heptane versus the dilution ratio by

applying the four-parameter EOS. According to this figure, the whole asphaltene is expected to be precipitated by adding an infinite volume of solvent to the bitumen.

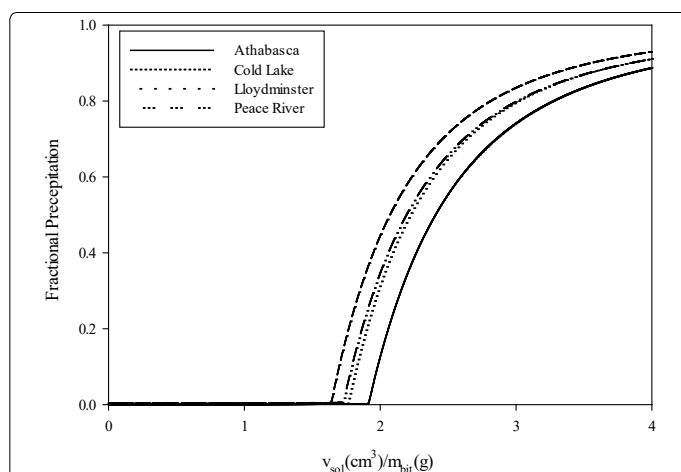


Figure 2. Fractional precipitation of asphaltene for Athabasca bitumen using *n*-heptane under ambient condition.

## Conclusion

The performance of a four-parameter equation of state was examined in the regular solution theory to predict the onset point of asphaltene precipitation diluted by *n*-heptane. Four Canadian bitumens including the Athabasca, Cold Lake, Lloydminster, and Peace River were characterized in terms of SARA fraction and their molar volumes, densities, and solubility parameters were determined using molecular weight and density data reported by Greaves et al. [50]. To validate the model, the calculated values of molar volume and solubility parameters of SARA fractions were compared with the measured values reported in the previous studies. The results showed that the density and molar volume of SARA fraction for each bitumen as well as the solubility parameter of pure solvents were estimated accurately using the four-parameter equation of state. Using the validated model, the onset point of asphaltene precipitation diluted by *n*-heptane was calculated for the four Canadian bitumen, which showed great consistency with that previously calculated using the PR- and SRK-EOSs. Moreover, this four-parameter EOS did not need the volume shift expression for correcting the calculated liquid density and it showed more advantageous over the PR-EOS and the SRK-EOS.

## Nomenclatures

$P$	Pressure
$T$	Temperature
$V^l$	Liquid molar volume
$b_1$	" $b_1$ " parameter in EOS
$b_3$	" $b_3$ " parameter in EOS
$B_1$	" $B_1$ " parameter in PT-EOS
$B_3$	" $B_3$ " parameter in PT-EOS

$\bar{r}$	Average number of monomer
$M$	Molecular weight
$x$	Mole fraction
$x^l$	Mole fraction of liquid phase
$\Delta U^{lv}$	Internal energy of vaporization
$R$	Gas constant
	Volume
$a$	"a" parameter in EOS
$b_2$	"b <sub>2</sub> " parameter in EOS
$A$	"A" parameter in PT-EOS
$B_2$	"B <sub>2</sub> " parameter in PT-EOS
$Z$	Gas compressibility factor
$M_m$	Monomer molecular weight
$C_f$	Acentric correction factor
$x^s$	Mole fraction of solid phase
$w$	Mass fraction

#### Subscripts

$i$	i <sup>th</sup> component
$c$	Critical property
$m$	Monomer
$mix$	Mixture
$b$	Boiling point
$a$	Aggregate property

#### Greek Symbols

$\rho$	Density
$\omega$	Acentric factor
$\lambda_{b_1}$	A coefficient for "b <sub>1</sub> " parameter
$\lambda_{b_3}$	A coefficient for "b <sub>3</sub> " parameter
$\beta$	Shape of distribution function
$\delta$	Solubility parameter
$\lambda_a$	A coefficient for "a" parameter
$\lambda_{b_2}$	A coefficient for "b <sub>2</sub> " parameter
$\mu$	Chemical potential
$\psi(\beta)$	Gamma distribution function

#### Abbreviations

EOS	Equation of State
VLE	Vapor-Liquid Equilibrium

SLE	Solid-Liquid Equilibrium
SRK-EOS	Soave-Redlich-Kwong Equation of State
AAD	Average Absolute Deviation
H/B	Volume of solvent per unit mass of bitumen
IFT	Interfacial Tension
LLE	Liquid-Liquid Equilibrium
PR-EOS	Peng-Robinson Equation of State
RD	Relative Deviation
$W_H$	Mass fraction of solvent

## Appendix A

The definition of  $a_c$ ,  $b_1$ ,  $b_2$  and  $b_3$  parameters for the four-parameter EOS are provided as follow.

$$a_c = \lambda_a \frac{R^2 T_c^2}{P_c} \quad b_1 = \lambda_{b_1} \frac{R T_c}{P_c} \quad b_2 = \lambda_{b_2} \frac{R T_c}{P_c} \quad b_3 = \lambda_{b_3} \frac{R T_c}{P_c}$$

where  $\lambda_a$ ,  $\lambda_{b_1}$ ,  $\lambda_{b_2}$  and  $\lambda_{b_3}$  can be determined by Eq. (A.1) through Eq. (A.4).

$$\lambda_a = 0.44869 + 0.04024\omega + 0.01111\omega^2 - 0.00576\omega^3 \quad (A.1)$$

$$\lambda_a = 0.08974 - 0.03452\omega + 0.00330\omega^2 \quad (A.2)$$

$$\lambda_a = 0.03686 + 0.00405\omega - 0.01073\omega^2 + 0.00157\omega^3 \quad (A.3)$$

$$\lambda_a = 0.15400 + 0.14122\omega - 0.00272\omega^2 - 0.00484\omega^3 \quad (A.4)$$

In addition, the following correlations are also required to calculate  $a$  parameter in the four-parameter EOS.

$$a = a_c \alpha(T) \quad (A.5)$$

$$\alpha(T) = 1 + m \left( 1 - \left( \frac{T}{T_c} \right)^{0.5} \right)^2 \quad (A.6)$$

$$m = 0.4070 + 1.3787\omega - 0.2933\omega^2 \quad (A.7)$$

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