

Modeling Asphaltene Precipitation by *n*-Alkanes from Heavy Oils and Bitumens Using Cubic-Plus-Association Equation of State

Zhidong Li and Abbas Firoozabadi*

Reservoir Engineering Research Institute (RERI) 385 Sherman Avenue, Suite 5, Palo Alto, California 94306

Received September 4, 2009. Revised Manuscript Received November 15, 2009

We apply a cubic-plus-association equation of state to study the asphaltene precipitation from *n*-alkane diluted model solutions (asphaltene+toluene), and heavy oils and bitumens. Heavy oils and bitumens are characterized in terms of saturates, aromatics/resins, and asphaltenes; *n*-alkanes are treated independently. The asphaltene precipitation is modeled as liquid–liquid phase equilibrium. The self-association between asphaltene molecules and the cross-association between asphaltene and aromatics/resins (or toluene) molecules are explicitly taken into account. There is no self-association between aromatics/resins (or toluene) molecules. Our model contains only one adjustable parameter, the cross-association energy between asphaltene and aromatics/resins (or toluene) molecules, which depends on the types of asphaltene and *n*-alkane, and possibly temperature but is independent of pressure and concentration. We successfully predict the amount of asphaltene precipitation over a broad range of compositions, temperatures, and pressures for *n*-alkane diluted model solutions, heavy oils, and bitumens.

I. Introduction

Asphaltenes are recognized as the heaviest, most polar, and most complicated fraction of a crude oil. They are operationally defined in terms of solubility in different solvents and represent a group of components insoluble in low-molecular-weight normal alkanes like *n*-pentane and *n*-heptane but soluble in aromatics like benzene and toluene. In general, asphaltenes are chemically composed of polynuclear aromatic rings, aliphatic rings and chains, and heteroatoms such as nitrogen, oxygen, sulfur, and various metals (vanadium, nickel, iron, copper, etc.).

Asphaltene flow assurance becomes a concern when asphaltene deposits onto solid surfaces, such as reservoir rocks, production tubing, flowlines, and surface equipment. Thus, asphaltene deposition may lead to serious plugging problems during the oil production, transportation, storage, and refining processes. Asphaltene precipitation is a necessary condition for deposition because sometimes asphaltene coming out of solution does not adhere to the surfaces. Asphaltene precipitation is described by bulk phase equilibrium thermodynamics, while asphaltene deposition includes mechanisms that depend on surface characteristics, phase behavior, flow regime, and rheology. This paper focuses on modeling the asphaltene precipitation. Asphaltene precipitation is mostly triggered by the compositional change and pressure decrease. Temperature generally does not play a significant role. It is suspected that the self-association of asphaltene constituents is the primary cause for the asphaltene aggregation. On the other hand, the cross-association with other polar components in the crude oil, such as aromatics and resins, may prevent the formation of asphaltene aggregates and may stabilize the asphaltene species in petroleum fluids.

Despite numerous publications and advances, theoretical investigation of asphaltene precipitation still represents a

challenging mission in petroleum engineering thermodynamics. Currently, the most popular approaches for asphaltene precipitation modeling include the solubility model^{1–12} and equation of state (EOS).^{13–26} In the solubility model, the

- (1) Hirschberg, A.; Dejong, L. N. J.; Schipper, B. A.; Meijer, J. G. *SPE J.* **1984**, *24*, 283.
- (2) Wang, J. X.; Buckley, J. S. *Energy Fuels* **2001**, *15*, 1004.
- (3) Correra, S.; Merino-Garcia, D. *Energy Fuels* **2007**, *21*, 1243.
- (4) Jamshidnezhad, M. J. *Jpn. Pet. Inst.* **2008**, *51*, 217.
- (5) Kraiwattanawong, K.; Fogler, H. S.; Gharfeh, S. G.; Singh, P.; Thomason, W. H.; Chavadej, S. *Energy Fuels* **2007**, *21*, 1248.
- (6) Akbarzadeh, K.; Alboudwarej, H.; Svrcek, W. Y.; Yarranton, H. W. *Fluid Phase Equilib.* **2005**, *232*, 159.
- (7) Akbarzadeh, K.; Dhillon, A.; Svrcek, W. Y.; Yarranton, H. W. *Energy Fuels* **2004**, *18*, 1434.
- (8) Mofidi, A. M.; Edalat, M. *Fuel* **2006**, *85*, 2616.
- (9) Nikookar, M.; Pazuki, G. R.; Omidkhah, M. R.; Sahranavard, L. *Fuel* **2008**, *87*, 85.
- (10) Alboudwarej, H.; Akbarzadeh, K.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W. *AIChE J.* **2003**, *49*, 2948.
- (11) Wiehe, I. A.; Yarranton, H. W.; Akbarzadeh, K.; Rahimi, P. M.; Teclemariam, A. *Energy Fuels* **2005**, *19*, 1261.
- (12) Correra, S. *Pet. Sci. Technol.* **2004**, *22*, 943.
- (13) Gonzalez, D. L.; Hirasaki, G. J.; Creek, J.; Chapman, W. G. *Energy Fuels* **2007**, *21*, 1231.
- (14) Gonzalez, D. L.; Ting, P. D.; Hirasaki, G. J.; Chapman, W. G. *Energy Fuels* **2005**, *19*, 1230.
- (15) Gonzalez, D. L.; Vargas, F. M.; Hirasaki, G. J.; Chapman, W. G. *Energy Fuels* **2008**, *22*, 757.
- (16) Ting, P. D.; Hirasaki, G. J.; Chapman, W. G. *Pet. Sci. Technol.* **2003**, *21*, 647.
- (17) Wu, J. Z.; Prausnitz, J. M.; Firoozabadi, A. *AIChE J.* **1998**, *44*, 1188.
- (18) Wu, J. Z.; Prausnitz, J. M.; Firoozabadi, A. *AIChE J.* **2000**, *46*, 197.
- (19) Buenrostro-Gonzalez, E.; Lira-Galeana, C.; Gil-Villegas, A.; Wu, J. Z. *AIChE J.* **2004**, *50*, 2552.
- (20) Gupta, A. K., Master of Science thesis, University of Calgary, Canada, 1986.
- (21) James, N. E.; Mehrotra, A. K. *Can. J. Chem. Eng.* **1988**, *66*, 870.
- (22) Godbole, S. P.; Thele, K. J. *SPE Annual Technical Conference and Exhibition*, SPE 24936; Washington, DC, October, 4–7, 1992).
- (23) Kohse, B. F.; Nghiem, L. X.; Maeda, H.; Ohno, K. *SPE Asia Pacific Oil and Gas Conference and Exhibition*, SPE 64465; Brisbane, Australia, October 16–18, 2000.
- (24) Du, J. L.; Zhang, D. *Pet. Sci. Technol.* **2004**, *22*, 1023.

*To whom correspondence should be addressed. Telephone: 650-326-9259. Fax: 650-326-9277. E-mail: af@rerinst.org.

crude oil is often treated as a mixture of two pseudocomponents, asphaltene and solvent. Most of the applications of solubility model are based on the Flory–Huggins polymer theory to describe the phase separation of asphaltene-containing petroleum fluids. The solubility model has been widely used to correlate and predict the onset and amount of asphaltene precipitation. However, the two-component fluid characterization is an oversimplification and may not be fit for direct use in compositional reservoir simulators. Besides, Flory–Huggins theory only considers the entropic effects and dispersion attractions but does not account for the association of asphaltene and other polar components. Moreover, the solubility model can not work independently for live oils below the bubble point pressure (i.e., when the gas phase forms). For that case, a traditional vapor–liquid phase split calculation is performed first often by a cubic EOS. Then the liquid phase is isolated to determine the molar volume and solubility parameter. Based on the assumption that asphaltene precipitation does not affect the vapor–liquid phase behavior, solubility model is used to check whether asphaltenes can precipitate from the liquid phase.

Since compositional reservoir simulators are primarily based on various EOS to solve the phase separation of hydrocarbon fluids, the EOS method has advantages over solubility model for modeling asphaltene precipitation. A modified version of the statistical association fluid theory (SAFT) has been adopted by Chapman et al. to study asphaltene precipitation.^{13–16} The dead oils are characterized based on SARA analysis (saturates, aromatics, resins, and asphaltenes). For live oils, several light pseudocomponents are included besides SARA. The onset of asphaltene precipitation is successfully correlated or predicted under various conditions. In these works, asphaltene phase behavior is assumed to be determined by dispersion attractions only and polar–polar interactions pertinent to asphaltenes and other polar components are assumed to be negligible.

Another line of attack based on SAFT for asphaltene precipitation is reported by Wu et al. on the McMillan–Mayer level.^{17–19} Only asphaltenes (represented by attractive and polar particles) and resins (represented by attractive and amphiphilic chains) are considered explicitly. The other components in the crude oil are regarded as a continuous medium which affects the effective dispersion attractions among asphaltene and resin molecules via the Hamaker constant. This model accounts for the polar–polar interactions of asphaltenes and resins and can quantitatively explain most of the phenomena relevant to the asphaltene separation for reservoir fluids. Like the solubility model, the two-component model is not sufficient to represent the crude oils. For live oils with gas phase formation, the model by Wu et al. can not work independently, either. Furthermore, SAFT has not been widely used in petroleum production and reservoir engineering calculations because the simple cubic EOS such as the Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations have higher accuracy and less mathematical complexity for hydrocarbon mixtures.

Traditional cubic EOS have also been used to study asphaltene precipitation.^{20–26} Some have even accounted for the self-association of asphaltenes through direct or

indirect ways. For instance, Vafaie-Sefti et al. and Du et al. have incorporated the chemical theory in the PR-EOS to investigate the asphaltene phase behavior under various conditions.^{24,25} Sabbagh et al. have divided asphaltenes into thirty subfractions to mimic the broad molar mass distribution due to self-association and applied the PR-EOS to examine asphaltene precipitation induced by *n*-alkanes from heavy oils and bitumens.²⁶ In both examples, the crude oils are represented by multicomponent mixtures. However, the polydisperse representation of asphaltenes increases the computational cost and may not reflect the nature of asphaltene association process. In addition, the stabilization of asphaltenes by other polar components like resins and aromatics can not be taken into account by either chemical theory or multiple subfractions.

Besides the solubility model and equation of state, other approaches have been employed to study asphaltene precipitation from petroleum fluids such as the scaling equation,^{27–29} micellization model,^{30–33} aggregation model,^{34,35} and integral equation theory.³⁶ These methods may qualitatively or even quantitatively describe the asphaltene phase behavior. However, they do not find broad applications in compositional reservoir simulators due to the theoretical limitation, mathematical complexity, or high computational cost.

In this work, we propose a cubic-plus-association EOS (CPA) to study asphaltene precipitation from model solutions (asphaltene+toluene), and real heavy oils and bitumens due to the injection of *n*-alkanes. CPA was originally developed to describe the thermodynamic properties and phase behavior of associating fluids.³⁷ Heavy oils and bitumens are characterized in terms of saturates, aromatics/resins, and asphaltenes. Precipitants (*n*-alkanes) are treated individually. The physical interactions are described by the PR-EOS.^{38,39} The self-association between asphaltenes and cross-association between asphaltenes and aromatics/resins (or toluene) are explicitly represented by the thermodynamic perturbation theory.^{40–45} Without self- and cross-association, the theory is reduced to the original PR-EOS. We examine the effects of temperature, pressure and *n*-alkanes on asphaltene precipitation. The EOS parameters of pseudocomponents are either from Sabbagh et al.,²⁶ or from fitting the pseudocomponent experimental mass densities, or reasonably assigned. The experiments are also from Sabbagh et al.²⁶ Our model contains only one adjustable parameter, the cross-association energy between asphaltene and aromatics/resins (or toluene) molecules, which depends on the types of asphaltene and *n*-alkane, and probably

(25) Vafaie-Sefti, M.; Mousavi-Dehghani, S. A.; Mohammad-Zadeh, M. *Fluid Phase Equilib.* **2003**, *206*, PII S0378.

(26) Sabbagh, O.; Akbarzadeh, K.; Badamchi-Zadeh, A.; Svrcek, W. Y.; Yarranton, H. W. *Energy Fuels* **2006**, *20*, 625.

(27) Hu, Y. F.; Guo, T. M. *Fluid Phase Equilib.* **2001**, *192*, 13.

(28) Hong, E.; Watkinson, P. *Fuel* **2004**, *83*, 1881.

(29) Menshad, A. K.; Mofidi, A. M.; Shariatpanahi, F.; Edalat, M. *J. Jpn. Pet. Inst.* **2008**, *51*, 102.

(30) Pan, H. Q.; Firoozabadi, A. *SPE Prod. Facil.* **1998**, *13*, 118.

(31) Pan, H. Q.; Firoozabadi, A. *SPE Prod. Facil.* **2000**, *15*, 58.

(32) Pan, H. Q.; Firoozabadi, A. *AIChE J.* **2000**, *46*, 416.

(33) Victorov, A. I.; Firoozabadi, A. *AIChE J.* **1996**, *42*, 1753.

(34) Rogel, E. *Langmuir* **2002**, *18*, 1928.

(35) Rogel, E. *Langmuir* **2004**, *20*, 1003.

(36) Duda, Y.; Lira-Galeana, C. *Fluid Phase Equilib.* **2006**, *241*, 257.

(37) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310.

(38) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fund.* **1976**, *15*, 59.

(39) Robinson, D. B.; Peng, D. Y.; Chung, S. Y. K. *Fluid Phase Equilib.* **1985**, *24*, 25.

(40) Wertheim, M. S. *J. Stat. Phys.* **1984**, *35*, 19.

(41) Wertheim, M. S. *J. Stat. Phys.* **1984**, *35*, 35.

(42) Wertheim, M. S. *J. Chem. Phys.* **1986**, *85*, 2929.

(43) Wertheim, M. S. *J. Stat. Phys.* **1986**, *42*, 459.

(44) Wertheim, M. S. *J. Stat. Phys.* **1986**, *42*, 477.

(45) Wertheim, M. S. *J. Chem. Phys.* **1987**, *87*, 7323.

temperature but is independent of pressure and concentration. Through adjusting this parameter, our model reproduces most of the experiments.

We have applied our CPA approach to investigate asphaltene precipitation from several live oils due to pressure decrease and mixing with gas at high temperature and pressure. Within a unified theoretical framework, we have successfully captured the saturation and onset pressures, amount of precipitated asphaltenes, and gas-oil-asphaltene three-phase coexistence. The application of our model to live oils will be presented in a forthcoming publication. Our model possesses significant advantages over the traditional methods mentioned above. The theory is based on the PR-EOS which is widely used in the compositional reservoir simulators. It has simple mathematical formalism which introduce only minor additional computational cost. The approach is directly applicable to multicomponent systems. The self-association of asphaltenes is explicitly described together with the effect of other polar components on asphaltene stabilization. As a unified method, the CPA method is expected to be a powerful tool for various phase behavior modeling in petroleum industry.

The remainder of this article is organized as follows. Section II describes the modeling and the formulation of our CPA for the asphaltene systems. Section III compares the calculations with the experiments for the asphaltene precipitation from model solutions (asphaltene+toluene) and from several heavy oils and bitumens induced by the injection of *n*-alkanes. In Section IV the main results and conclusions are summarized.

II. Modeling and Theory

The asphaltene precipitation from model solutions (asphaltene+toluene), and real heavy oils and bitumens by *n*-alkanes is treated as the traditional liquid–liquid phase separation. The heavy oils and bitumens are characterized in terms of three pseudocomponents, i.e., saturates, aromatics/resins, and asphaltenes. Because both aromatics and resins have polar–polar interactions (cross-association) with asphaltenes, we combine them as one pseudocomponent to reduce the number of adjustable parameters. The precipitants, *n*-alkanes, are considered independently.

In the framework of CPA, the excess Helmholtz free energy A^{ex} consists of two parts: the physical part describes the nonassociating molecular interactions such as short-range repulsions and dispersion attractions; the association part describes the polar–polar interactions (self-association and cross-association) of asphaltene and aromatics/resins (or toluene) molecules.

The physical contribution is represented by the PR-EOS^{38,39}

$$\frac{A_{\text{ph}}^{\text{ex}}}{nRT} = -\ln(1 - b\rho_c) - \frac{a}{2\sqrt{2}bRT} \ln\left(\frac{1 + (1 + \sqrt{2})b\rho_c}{1 + (1 - \sqrt{2})b\rho_c}\right) \quad (1)$$

where R is the universal gas constant, T is the absolute temperature, n is the total number of moles, and ρ_c is the molar density of the mixture. The energy and volume parameters of the mixture are denoted as a and b , respectively. They can be estimated by applying the van der Waals quadratic mixing rules: $a = \sum_{i,j} x_i x_j a_{ij}$, $b = \sum_{i,j} x_i x_j b_{ij}$, $a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$ and $b_{ij} = (b_i + b_j)/2$ where x_i , a_i and b_i stand for the mole fraction, energy parameter and volume parameter of component i , respectively, and k_{ij} is the binary interaction coefficient (BIC) between components i and j . a_i and b_i can be determined

from the critical properties and acentric factor of individual component

$$a_i = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} [1 + c_i(1 - \sqrt{T_{ri}})]^2, b_i = 0.0778 \frac{RT_{ci}}{P_{ci}} \quad (2)$$

$$\text{with } c_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2, & \omega_i \leq 0.5 \\ 0.3796 + 1.485\omega_i - 0.1644\omega_i^2 + 0.01667\omega_i^3, & \omega_i > 0.5 \end{cases}$$

where T_{ri} , T_{ci} , P_{ci} and ω_i denote the reduced temperature, critical temperature, critical pressure, and acentric factor of component i , respectively. In this work, all the values of k_{ij} are set to zero. This treatment can further reduce the number of adjustable parameters. Firoozabadi suggests that if the mixtures contain methane, N_2 , CO_2 and H_2S , the nonzero k_{ij} related to these species must be applied to correctly describe the phase behavior; otherwise, $k_{ij} = 0$.^{46,47} We have developed the software for the phase split computation and compositional reservoir simulation based on this suggestion and have used it in various industrial projects. The zero k_{ij} in this article is also consistent with Firoozabadi's suggestion and our previous works.

The contribution to the excess Helmholtz energy due to the association is obtained from the thermodynamic perturbation theory with the assumption that each asphaltene molecule has N_A identical association sites and each aromatics/resins (or toluene) molecule has N_R identical association sites^{40–45}

$$\frac{A_{\text{assoc}}^{\text{ex}}}{nRT} = N_A x_A \left(\ln \chi_A + \frac{1 - \chi_A}{2} \right) + N_R x_R \left(\ln \chi_R + \frac{1 - \chi_R}{2} \right) \quad (3)$$

The subscripts “A” and “R” represent asphaltene and aromatics/resins (or toluene), respectively. χ_A and χ_R are the mole fractions of asphaltene and aromatics/resins (or toluene) not bonded at one of the association sites, respectively. Association bonding occurs between two sites with one on asphaltene molecule and the other on either asphaltene molecule or aromatics/resins (or toluene) molecule. Similar to the work of Wu et al., the aromatics/resins (or toluene) molecules are assumed not to self-associate.^{17–19} Consequently, without the asphaltenes, the equation can be reduced to the original PR-EOS. As a result, χ_A and χ_R are given by

$$\chi_A = \frac{1}{1 + \rho_c N_A x_A \Delta^{\text{AA}} + \rho_c N_R x_R \Delta^{\text{AR}}}, \quad \chi_R = \frac{1}{1 + \rho_c N_A x_A \Delta^{\text{AR}}} \quad (4)$$

where $\Delta^{ij} = g \kappa_{ij} b_{ij} [\exp(\epsilon_{ij}/k_B T) - 1]$ ($i = \text{A}, j = \text{A or R}$) characterizes the “association strength” with k_B the Boltzmann constant, g the contact value of the radial distribution function of the hard-sphere mixture, and κ_{ij} and ϵ_{ij} the association volume and energy parameters, respectively. To simplify the calculations, g is approximated by that of the pure hard-sphere fluids as $g \approx (1 - 0.5\eta)/(1 - \eta)^3$ with $\eta = b\rho_c/4$.

(46) Firoozabadi, A., *Thermodynamics of Hydrocarbon Reservoirs*; McGraw-Hill: New York, 1999.

(47) Arbabi, S.; Firoozabadi, A. *SPE Adv. Technol.*, March, **1995**, 139–145.

Table 1. SARA Analysis (wt%) of Seven Different Heavy Oils and Bitumens

	saturates	aromatics/resins	asphaltenes	solids
Athabasca	16.3	68.3	14.6	0.8
Cold Lake	19.4	64.8	15.3	0.5
Lloydminster	23.1	61.2	15.1	0.6
Venezuela-1	15.4	69.4	15.0	0.2
Venezuela-2	20.5	57.6	21.8	0.1
Russia	25.0	68.2	6.8	0.0
Indonesia	23.2	72.1	4.7	0.0

III. Results and Discussion

The SARA analysis of the seven heavy oils and bitumens studied in this work are provided in Table 1.²⁶ The “solids” are assumed to precipitate directly and do not participate in the phase-split calculations. Same as in ref 26, in this work, the fractional precipitation of asphaltene from toluene is defined as the mass of precipitated asphaltenes divided by the mass of asphaltenes dissolved in toluene. The fractional yield of asphaltene precipitation from heavy oil or bitumen is defined as the mass of precipitated asphaltenes and solids divided by the mass of the heavy oil or bitumen.

The key step is the determination of the EOS parameters for pseudocomponents. The physical parameters include T_C , P_C , ω , and molecular weight M_W for each pseudocomponent. The association parameters include ϵ_{AA} , ϵ_{AR} , κ_{AA} , κ_{AR} , N_A , and N_R for asphaltenes and aromatics/resins (or toluene). In the physical part, T_C , ω , and M_W are taken from the literature directly for saturates and asphaltenes, or estimated from the molar average values of aromatics and resins from the literature for aromatics/resins.²⁶ The determination of M_W is a challenge in asphaltene chemistry. The complications are attributed to the compositional variance, size polydispersity, and more importantly, self-association of asphaltenes even at low concentrations. In the past, various techniques have been employed to determine the asphaltene M_W including vapor pressure osmometry, gel permeation chromatography, fluorescence depolarization, and mass spectrometry. These techniques give inferred M_W which may be different by an order of magnitude. Some authors also use different values of M_W in the theoretical studies. In our opinion reasonable value of asphaltene M_W probably lies between 1000 and 2000 g/mol.⁴⁸ In this work, $M_W = 1800$ g/mol for asphaltenes obtained from the vapor pressure osmometry is used.¹⁰ This value was reported by the same authors whose experiments of asphaltene precipitation from heavy oils and bitumens are used in this work. The values of P_C for all the three pseudocomponents are adjusted to match their experimental mass densities ρ_m at 296.15 K and 1 bar, that is, 880 kg/m³, 1010 kg/m³, and 1185 kg/m³ for saturates, aromatics/resins, and asphaltenes, respectively. Wu et al. provide the association parameters which may be used as a guide to develop our model despite the fact that those parameters do not have constant values.^{17–19} The number of association sites on each asphaltene molecule N_A is two, three, or six. The association volume parameters κ_{AA} and κ_{AR} are assumed identical and equal 0.005 or 0.024. The self-association energy of asphaltenes ϵ_{AA}/k_B varies between 1340 and 3725 K.^{17–19} In our work, we assume that $N_A = N_R = 4$, and $\kappa_{AA} = \kappa_{AR} = 0.01$, which are comparable to those by Wu et al. Although Wu et al. assume that each resin chain always carries one association site, we suggest four association sites for aromatics/resins or toluene molecules in

Table 2. Physical Parameters of Pseudo-Components

	saturates	aromatics/resins	asphaltenes
M_W (g/mol)	460	660	1800
T_C (K)	930	1074	1474
P_C (bar)	11.98	10.85	6.34
ω	0.9	1.5	2.0

Table 3. Association Parameters for Model Solutions (Asphaltene+Toluene) and Heavy Oils and Bitumens

asphaltene+toluene	$\epsilon_{AA}/k_B = 2800$ K, $\kappa_{AA} = \kappa_{AR} = 0.01$, $N_A = N_R = 4$
heavy oil and bitumen	$\epsilon_{AA}/k_B = 2000$ K, $\kappa_{AA} = \kappa_{AR} = 0.01$, $N_A = N_R = 4$

order to unify the model with that of asphaltenes. $N_A = N_R = 4$ may not relate to the molecular reality. The association energy between asphaltene molecules ϵ_{AA} reflects the highest association degree of asphaltenes and is dependent on asphaltene polarity. The magnitude should be in the range of normal hydrogen-bonding energy ($\epsilon_{AA}/k_B = 1500\sim 12000$ K).¹⁸ In reality, ϵ_{AA} is not a constant for the asphaltenes extracted from different reservoir fluids and subject to different separation and purification techniques. However, to simplify our model, we do not adjust ϵ_{AA} frequently. In the literature, we notice that when the asphaltenes are separated from the heavy oils, purified and then redissolved in toluene, they have much higher association degree (average associated molar mass) than in the original oil.²⁶ Thus, it is necessary to assign different values of ϵ_{AA} for the asphaltenes in a model oil and in a heavy oil. We use the experimental data for the maximum asphaltene precipitation amount at 296.15 K and 1 bar to estimate ϵ_{AA} . For the model solutions, the maximum asphaltene precipitation amount is not sensitive to the type of n -alkanes. For the real heavy oils, the resins will coprecipitate with asphaltenes when they are mixed with lower-molecular-weight n -alkanes.²⁶ We use the maximum asphaltene precipitation amount from mixing with n -heptane to correlate ϵ_{AA} for the heavy oils. We find that $\epsilon_{AA}/k_B = 2800$ K (asphaltene+toluene) and 2000 K (heavy oils and bitumens) can give results in agreement with most of the experiments for the maximum asphaltene precipitation amount. Interestingly, P_C of asphaltenes is not sensitive to ϵ_{AA} . When ϵ_{AA}/k_B varies from 0 to 12000 K, P_C change is only 0.0025 bar, which implies that the asphaltene precipitation is dominated by the asphaltene association. Tables 2 and 3 list the EOS parameters; they are kept constant in the following calculations. It should be mentioned that the physical parameters of asphaltenes and association parameters for heavy oils and bitumens, that is, $T_C = 1474$ K, $P_C = 6.34$ bar, $\omega = 2.0$, $M_W = 1800$ g/mol, $\epsilon_{AA}/k_B = 2000$ K, $\kappa_{AA} = \kappa_{AR} = 0.01$, and $N_A = N_R = 4$, have been used in our work of asphaltene precipitation from live oils. Same as in ref 26, T_C , P_C , and ω of all the three pseudocomponents are comparable to those from the existing correlations. As a result, our model contains only one adjustable parameter, the cross-association energy between asphaltene and aromatics/resins (or toluene) molecules ϵ_{AR} . ϵ_{AR} is assumed to be independent of pressure and concentration but depends on the types of asphaltenes and n -alkanes, and possibly temperature. The maximum asphaltene precipitation amount is not sensitive to ϵ_{AR} as mentioned above. Because the experimental mass densities of asphaltenes, aromatics/resins, and saturates have been reproduced by correlating their EOS parameters, there is no need to apply the volume translation for these three pseudocomponents.

(48) Yarranton, H. W. *J. Dispersion Sci. Technol.* **2005**, *26*, 5.

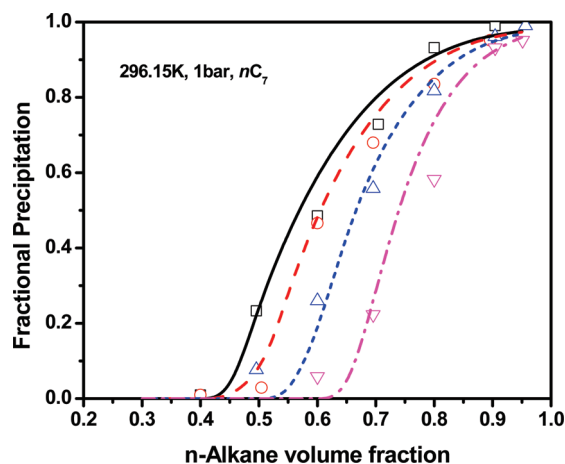


Figure 1. Fractional precipitation of asphaltenes from different sources in solutions of *n*-heptane and toluene at 296.15 K and 1 bar. Squares with solid line, circles with dash line, up-triangles with dotted line, and down-triangles with dash-dotted line are for Venezuela-1, Venezuela-2, Russian, and Indonesian asphaltenes, respectively.

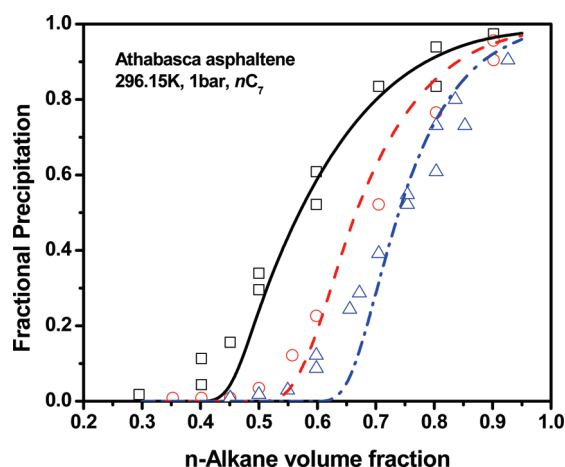


Figure 2. Fractional precipitation of Athabasca asphaltenes with different washing extents in solutions of *n*-heptane and toluene at 296.15 K and 1 bar. Squares with solid line, circles with dash line, and triangles with dotted line are for "Soxhlet washed", "filter-washed", and "unwashed" asphaltenes, respectively.

However, for toluene and *n*-alkanes, the volume translation must be used in order to obtain the correct volume and density.

The focus of this work is examining the effect of *n*-alkane, temperature, and pressure on the asphaltene precipitation from model solutions (asphaltene+toluene) and from seven heavy oils and bitumens. For the model systems, the asphaltene concentration in toluene is 10 kg/m³. In all the figures, symbols represent experiments from ref 26, and lines represent the results from our model. In Figures 1–3 and 5–11, we fit the experiments to obtain ε_{AR} for different asphaltenes and *n*-alkanes. Then in Figures 4 and 12–16, we predict the effect of temperature and pressure on asphaltene precipitation from the model and real heavy oils.

In Figure 1 we compare the calculated and measured fractional precipitation of asphaltenes Venezuela-1, Venezuela-2, Russian, and Indonesian crude in solutions of toluene and *n*-heptane at 296.15 K and 1 bar. Figure 2 depicts the fractional precipitation of asphaltenes Athabasca crude in

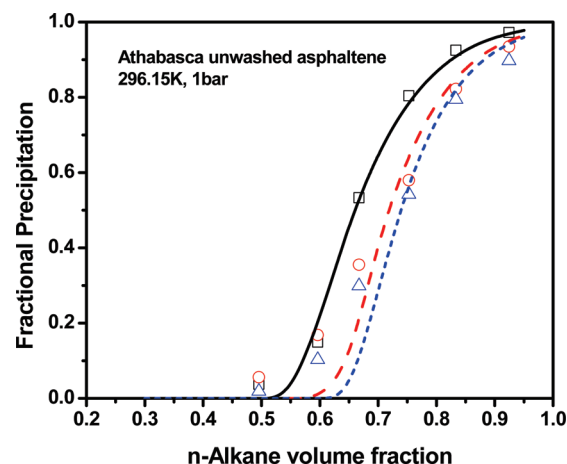


Figure 3. Effect of *n*-alkanes on the fractional precipitation of Athabasca unwashed asphaltenes in solutions of *n*-alkane and toluene at 296.15 K and 1 bar. Squares with solid line, circles with dash line, and triangles with dotted line are for *n*-pentane, *n*-hexane, and *n*-heptane, respectively.

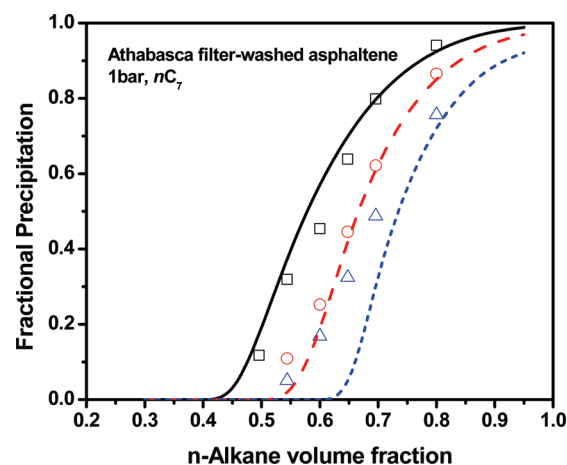


Figure 4. Effect of temperature on the fractional precipitation of Athabasca filter-washed asphaltenes in solutions of *n*-heptane and toluene at 1 bar. Squares with solid line, circles with dash line, and triangles with dotted line are for 273.15, 296.15, and 323.15 K, respectively.

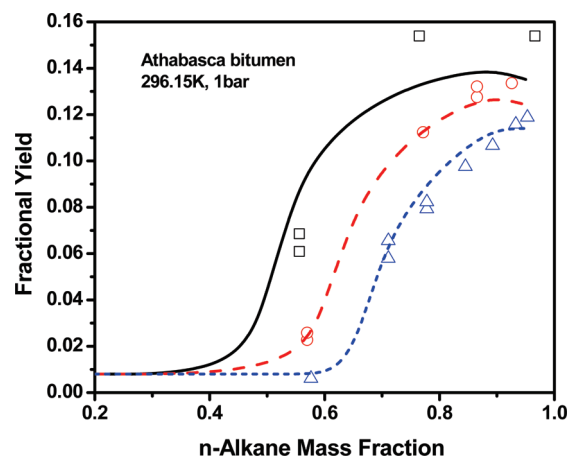


Figure 5. Effect of *n*-alkanes on the fractional yield for Athabasca bitumen at 296.15 K and 1 bar. Squares with solid line, circles with dash line, and triangles with dotted line are for *n*-pentane, *n*-hexane, and *n*-heptane, respectively.

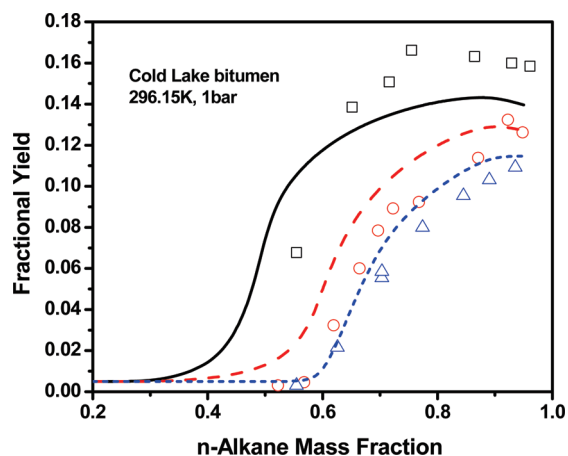


Figure 6. Same as Figure 5 but for Cold Lake bitumen. Squares with solid line, circles with dash line, and triangles with dotted line are for *n*-pentane, *n*-hexane, and *n*-heptane, respectively.

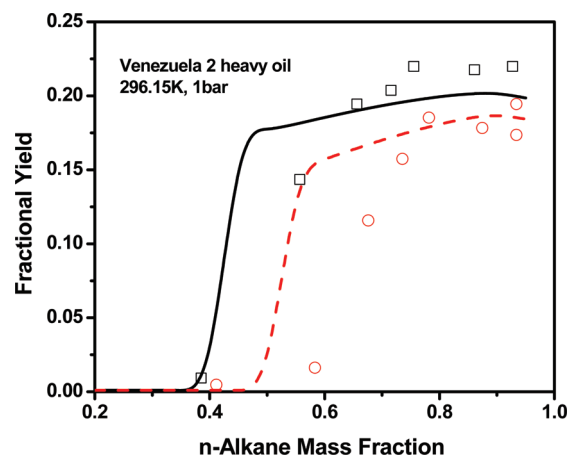


Figure 9. Same as Figure 5 but for Venezuela-2 heavy oil. Squares with solid line and circles with dash line are for *n*-pentane, and *n*-heptane, respectively.

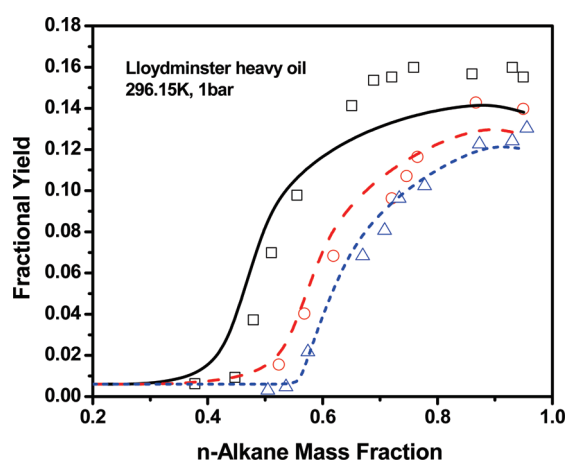


Figure 7. Same as Figure 5 but for Lloydminster heavy oil. Squares with solid line, circles with dash line, and triangles with dotted line are for *n*-pentane, *n*-hexane, and *n*-heptane, respectively.

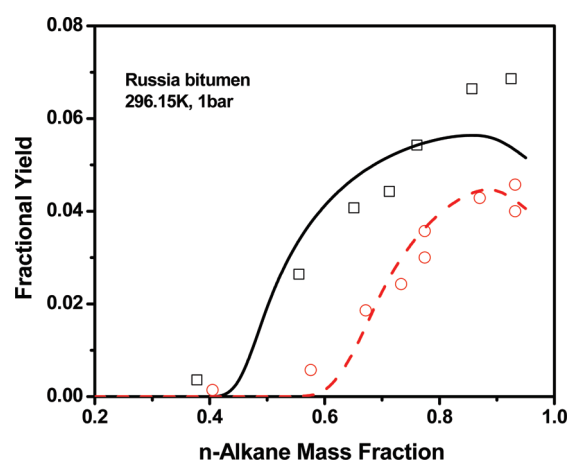


Figure 10. Same as Figure 5 but for Russia bitumen. Squares with solid line and circles with dash line are for *n*-pentane and *n*-heptane, respectively.

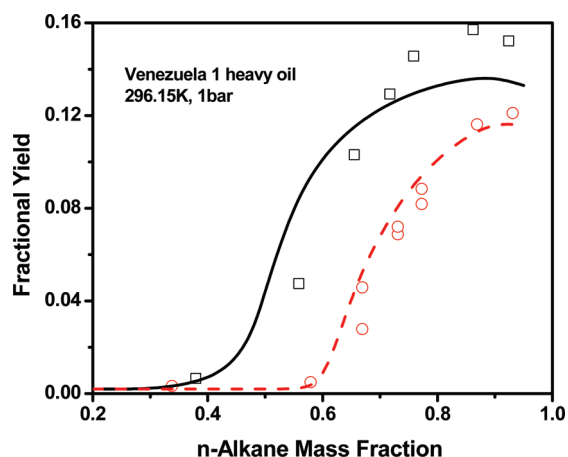


Figure 8. Same as Figure 5 but for Venezuela-1 heavy oil. Squares with solid line and circles with dash line are for *n*-pentane and *n*-heptane, respectively.

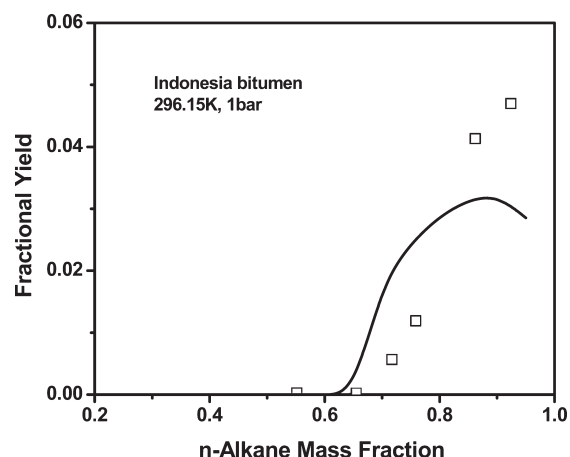


Figure 11. Fractional yield for Indonesia bitumen diluted with *n*-pentane at 296.15 K and 1 bar.

toluene by adding *n*-heptane at 296.15 K and 1 bar. The asphaltenes are subjected to different washing extent:

(49) Alboudwarej, H.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W. *Energy Fuels* 2002, 16, 462.

“Soxhlet-washed”, “filter-washed”, and “unwashed”, in the order from the most to the least.⁴⁹ The greater the washing extent, the “purer” the asphaltenes. The washing extent has significant effect on the asphaltene precipitation behavior. Figure 3 presents the effect of different *n*-alkanes on the

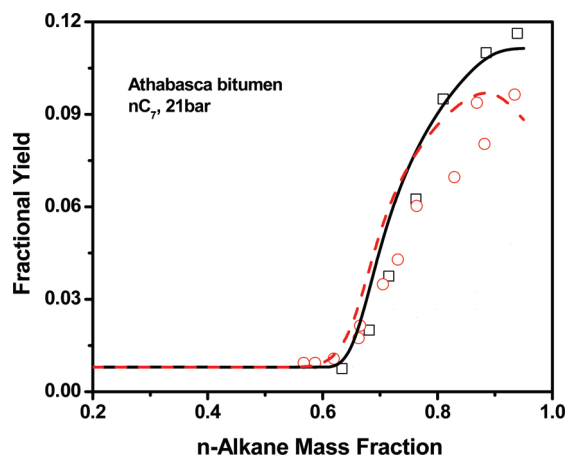


Figure 12. Effect of temperature on the fractional yield for Athabasca bitumen diluted with *n*-heptane at 21 bar. Squares with solid line and circles with dash line are for 296.15 and 323.15 K, respectively.

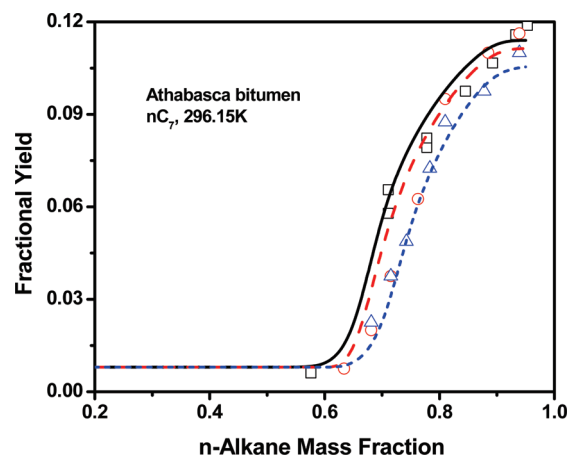


Figure 15. Effect of pressure on the fractional yield for Athabasca bitumen diluted with *n*-heptane at 296.15 K. Squares with solid line, circles with dash line, and triangles with dotted line are for 1 bar, 21 bar, and 69 bar, respectively.

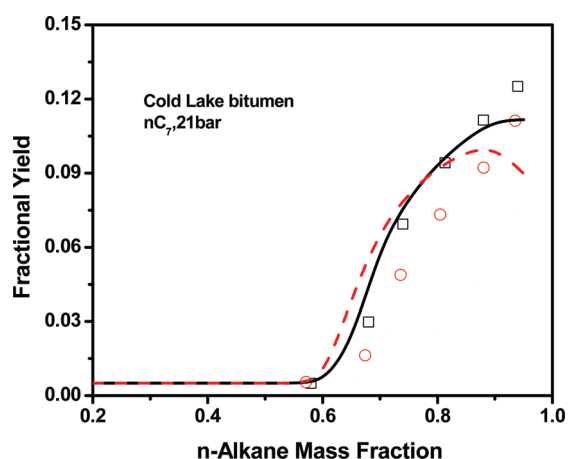


Figure 13. Same as Figure 12 but for Cold Lake bitumen. Squares with solid line and circles with dash line are for 296.15 and 323.15 K, respectively.

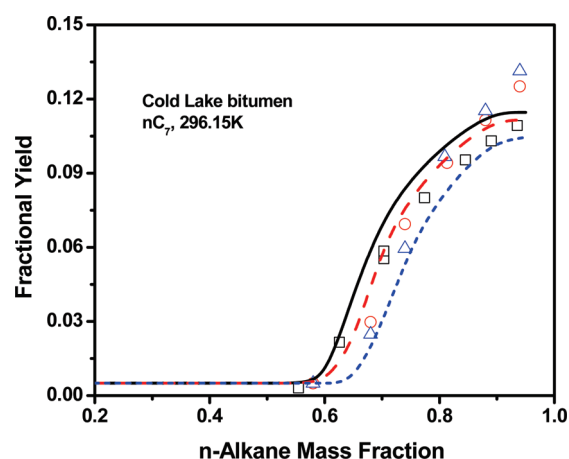


Figure 16. Same as Figure 15 but for Cold Lake bitumen. Squares with solid line, circles with dash line, and triangles with dotted line are for 1 bar, 21 bar, and 69 bar, respectively.

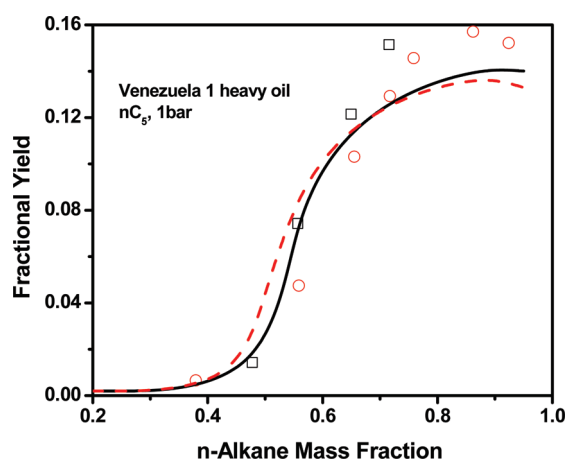


Figure 14. Same as Figure 12 but for Venezuela-1 heavy oil diluted with *n*-pentane at 1 bar. Squares with solid line and circles with dash line are for 273.15 and 296.15 K, respectively.

fractional precipitation for Athabasca unwashed asphaltenes in toluene at 296.15 K and 1 bar. Table 4 lists values of ϵ_{AR} for precipitation of different asphaltenes from toluene by adding

n-pentane, *n*-hexane, and *n*-heptane. The higher the *n*-alkane carbon number and the lower washing extent, the higher the cross-association energy. Through adjusting ϵ_{AR} , good agreement between calculations and measurements is achieved. In Figure 4 we predict the effect of temperature on fractional precipitation of Athabasca filter-washed asphaltenes from solution of toluene and *n*-heptane at 1 bar. The inhibition of asphaltene precipitation due to temperature increase is captured by the model.

Figures 5–11 exhibit the comparison between the experimental and calculated asphaltene and solid fractional yields for Athabasca, Cold Lake, Lloydminster, Venezuela-1, Venezuela-2, Russia, and Indonesia heavy oils and bitumens diluted with various *n*-alkanes at 296.15 K and 1 bar. Through adjusting ϵ_{AR} , most of the experiments are well reproduced. However, for *n*-pentane at very high mass fractions, the fractional yield is always underestimated. It is possibly because a nonnegligible amount of resins precipitates together with asphaltenes.²⁶ In our model, although we consider the partitioning of resins to the dense liquid phase which is rich in asphaltenes, we treat aromatics and resins as one pseudocomponent. For Venezuela-2 heavy oil, we predict that the precipitation starts at lower *n*-alkane mass fractions

Table 4. ε_{AR}/k_B (K) for Different Asphaltenes in Solutions of *n*-Alkane and Toluene

asphaltene	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane
Athabasca Soxhlet washed			760
filter washed			820
unwashed	820	860	880
Venezuela-1			760
Venezuela-2			780
Russia			820
Indonesia			880

Table 5. ε_{AR}/k_B (K) for Seven Heavy Oils and Bitumens Diluted with Different *n*-Alkanes

	<i>n</i> -pentane	<i>n</i> -hexane	<i>n</i> -heptane
Athabasca	1150	1250	1400
Cold Lake	1150	1300	1500
Lloydminster	1200	1300	1400
Venezuela-1	1150		1330
Venezuela-2	1300		1400
Russia	1000		1150
Indonesia	1100		

compared to the experiments. Venezuela-2 heavy oil is a special case. Because it contains a fairly high concentration of asphaltenes, only aromatics/resins may not be sufficient enough to prevent the asphaltene precipitation. Adjusting ε_{AR} and even ε_{AA} can not significantly improve the agreement. This might be one limitation of our model. It should be noted that our model predicts the asphaltene redissolution at very high *n*-alkane mass fractions, which is in agreement with the trends shown by the experiments. Table 5 provides values of ε_{AR} for the seven heavy oils and bitumens diluted with *n*-pentane, *n*-hexane, and *n*-heptane. Same as in Table 4, ε_{AR} increases with the carbon number of *n*-alkanes.

In Figures 12–14 we present the effect of temperature on the measured and predicted asphaltene and solid fractional yields for Athabasca and Cold Lake bitumens diluted with *n*-heptane at 21 bar and for Venezuela-1 heavy oil diluted with *n*-pentane at 1 bar. Temperature changes may result in either asphaltene precipitation or solubilization. When the temperature is not far from 296.15 K, that is, at 273.15 and 323.15 K, there is a satisfactory agreement between predictions and experiments. Because the temperature varies within a narrow range, it is hard to distinguish whether the asphaltene precipitation is strengthened or weakened with temperature through either experiments or predictions. The literature also reports the data at 373.15 K. The agreement between our predictions and measurements is poor. We also notice that adjusting ε_{AR} does not improve the agreement. Apparently the error in conducting the experiments at 373.15 K is high.²⁶ Additionally there may a deficiency in our parameters at high temperatures. We do not show the results at 373.15 K in order to avoid confusion. In our work on asphaltene precipitation from live oils, when ε_{AR} is assumed temperature-dependent and a simple linear function is applied to describe the $\varepsilon_{AR} \sim T$ relationship, the experiments can be reproduced over a wide range of temperatures and pressures without adjusting other parameters.

Figures 15 and 16 present the asphaltene and solid fractional yields for Athabasca and Cold Lake bitumens diluted with *n*-heptane at 296.15 K and various pressures. Generally, the experiments are well reproduced by our predictions. The influence of the pressure on asphaltene precipitation can be

explained readily. For heavy oils and bitumens which do not contain dissolved gases, it is well-known that the increase of pressure should improve the asphaltene solubility, which is reflected by measurements of Athabasca bitumen and our predictions. However, the experiments of Cold Lake bitumen show an opposite trend at high *n*-heptane mass fractions. Ref. 26 points that that the discrepancy could be due to the experimental error. To the best of our knowledge, the theoretical models cannot reproduce this trend.

The main objective of our work is applying CPA to study asphaltene precipitation amount when adding various *n*-alkanes. Our model reproduces the overall trend for most of the experiments. However, we do not match the “onset” points of the precipitation, and therefore our model has visible deviation at the beginning of the asphaltene precipitation in some cases. This deviation may be reduced through further adjustment of ε_{AR} . However, the overall performance might be sacrificed. It should be mentioned that onset data are determined by using more elaborate laboratory techniques such as fluorescence spectroscopy, conductivity measurements, acoustic-resonance, and light scattering. In our work on asphaltene precipitation from live oils, the performance of the CPA model on the onset points are systematically studied.

IV. Summary and Conclusions

We present the cubic-plus-association equation of state to model asphaltene precipitation by *n*-alkanes in model solutions (asphaltene+toluene) and in heavy oils and bitumens. The heavy oils and bitumens are characterized in terms of three pseudocomponents including saturates, aromatics/resins, and asphaltenes. The *n*-alkanes are considered independently. The physical interactions are described by the Peng–Robinson equation. The polar–polar interactions between asphaltene molecules and between asphaltene and aromatics/resins (or toluene) molecules are described by the thermodynamic perturbation theory. We assume that aromatics/resins (or toluene) molecules do not associate with themselves.

The parameters of equation of state for all the three pseudocomponents are from three sources: N_A , N_R , ε_{AA} , κ_{AA} , and κ_{AR} are reasonably assigned; T_C , ω , and M_W are directly or indirectly taken from the literature; P_C is obtained from matching the measured mass densities. As a result, our model contains only one adjustable parameter ε_{AR} . We reproduce most of the experiments for the amount of asphaltene precipitation by different *n*-alkanes from model solutions and seven heavy oils and bitumens over a wide range of temperatures, pressures and compositions through adjusting ε_{AR} .

We have also applied our model to asphaltene precipitation from several live oils induced by pressure decrease and mixing with gases. The temperature and pressure vary from 300 to 500 K and from 50 to 1000 bar, respectively, which covers a wide range of reservoir conditions. Our theory successfully predicts the saturation and onset pressures, asphaltene precipitation amount, and gas–liquid–asphaltene three-phase behavior within a unified framework. Our model for asphaltene precipitation from live oils will be discussed in a forthcoming publication.

Acknowledgment. We are grateful to the financial support from the industrial sponsors of RERI.