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Monodisperse Thermodynamic Model Based on Chemical + Flory–Hüggins Polymer Solution Theories for Predicting Asphaltene Precipitation

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Ⓢ Supporting Information

ABSTRACT: Asphaltene precipitation is traditionally modeled using the Flory–Hüggins polymer solution theory. The existing thermodynamic models, generally, do not take into account the aggregation/association phenomena in the system. This work aims at providing a monodisperse thermodynamic model for estimating asphaltene precipitation by taking into account the aforementioned phenomena. The chemical theory of associated solutions with physical interactions along with the Flory–Hüggins polymer solution theory is applied to develop this model. The results of this method are compared with some selected experimental data from the literature. It is shown that taking into account the aggregation/association phenomena in the system can lead to better predictions of the model. Moreover, it is shown that this method simplifies to the existing activity coefficient based models when ignoring the association.

■ INTRODUCTION

Crude oil is a complex mixture of hydrocarbons and other compounds. These components are often divided, somewhat arbitrarily, into saturates, aromatics, resins and asphaltenes (SARA).[1,2] The amorphous compounds that are toluene/benzene soluble but n-heptane/n-pentane insoluble are called asphaltenes (The portion which is soluble in normal alkane is termed as "maltenes", and the insoluble portion is called "asphaltenes").[1,2] They correspond to the most aromatic and highest molecular weight fraction of petroleum.[1,2] This fraction alone contains at least 100 000 different molecules.[1,2] Asphaltenes contain simple heteroatoms (C, H, N, O, and S) accompanied, most times, by metal constituents (Fe, Ni, and V) having aromatic cyclic structures with alkyl side chains.[1−4] The yield and quality of this fraction depend on how it was separated: the ratio of n-heptane/n-pentane to oil, the time before filtration, the pore size and material of the filter, etc.[1,2] This is also the case for resins, separated from n-heptane/n-pentane solution by adsorption on Attapulgus clay and desorbed by a mixture of toluene and acetone.[1,2] Saturates are the compounds that crystallize out of the remaining oil after evaporating the n-heptane/n-pentane and cooling a methyl ethyl ketone (MEK) solution of the oil to 195 K with dry ice.[1,2] The remaining oil is called the aromatics.[1−10]

Since the 1930s, it was recognized that asphaltenes and resins form micelle particles.[1,2,7−23] Asphaltene micelle particles have a core, which is formed by several aggregated asphaltene molecules; bipolar resin molecules are adhered on the surface of the core (the amount of monomeric asphaltenes is very small compared to the amount of asphaltene in micelles).[1,2,7−10] If not for the resins, most of the asphaltene material would immediately precipitate from the crude due to a low solubility of asphaltene monomeric molecules in the bulk of the petroleum fluid.[1,5−8]

Certain variations in operational parameters including pressure, temperature, and fluid composition changes may result in asphaltene precipitation. As a kinetic point of view, the formation of the asphaltene particles is generally a two-step process: phase separation and the growth of asphaltene particles.[23] Phase separation occurs when nanosize asphaltene particles from the crude oil bulk flocculate and grow into large aggregates. Large asphaltene particles are aggregates consisting of very small (submicrometer) size asphaltene particles.[23] Asphaltene precipitation can cause severe difficulties during oil production, transportation, and processing as follows: fouling in the reservoirs, wettability alterations, flow blockage with excess pressure drop in wellbore tubings, surface pipelines, and upstream process facilities, as well as poisoning of refinery catalysis.[1−8,11,15] As the oil pressure drops during production above the bubble point of some crudes oils, especially those containing high fractions of saturates, asphaltenes may precipitate.[1−16,20,21] During enhanced oil recovery when compressed gases, such as methane (or natural gas) or carbon dioxide, are injected into the reservoir, asphaltenes may also precipitate because it alters the reservoir fluid.[1,7,8,11] Once crude oils are brought to the surface, they are commonly mixed in the field, in tankers, and/or pipelines. Blending crudes can also upset the delicate balance and precipitate asphaltenes.[1,2,11]

Reversibility of asphaltene precipitation is often an issue. Observations show reversibility of asphaltene precipitation with pressure at high temperatures.[11] Reversibility with respect to composition at low temperatures is still unresolved,[12−14] although Ramos et al.,[16] Cimino et al.,[17] and Hirschberg et al.[11] comment that the titration experiments are reversible. It seems that the dissolution of the precipitated asphaltene at low temperature is a kinetically slow process and therefore the reversibility may require a very long time.[18] In addition, the reversibility of asphaltene precipitation at high temperatures (reservoir temperatures) with respect to pressure or composition has been confirmed by experimental observations.[19−21] The precipitated phase from a crude oil may have two different states. It may have a solid-like or a liquid-like state. Precipitation as a solid-like state would apply mainly to precipitation from crude oil at room temperature.[14,21] However, the liquid state is valid at high temperatures.[11,20−22] As mentioned before, the precipitated solid phase may be very slow to redissolve in the oil due to a large kinetic barrier to dissolution. Contrary to the solid state, the equilibrium between the precipitated liquid phase and the oil phase is achieved at a faster rate at high temperatures.[18] To the best of our knowledge, a detailed composition for the precipitated liquid phase has not yet been reported in the literature. It is likely that the precipitated phase, in addition to asphaltene and resin, may contain components as light as methane. However, the bulk of the precipitated phase consists of asphaltene and in certain cases resin may be present.

Asphaltene precipitation has therefore been the subject of many theoretical investigations. One of the fundamental difficulties encountered in describing the phase behavior of asphaltene-containing systems is the lack of suitable characterization parameters.[1,8,15,17−21,24−31] As a matter of fact, asphaltenes are not well-identified components/mixtures.[1,2,5,8] They consist of several polar components of aromatic nature with high molecular weight, as mentioned earlier.[1,5,8,11] In the majority of cases, the complexity of the asphaltene fraction leads to the assumption that the asphaltenes can be regarded as one single pseudocomponent (monodisperse).[1,5,8,11,27,30,31] The main drawback of most of the monodisperse models is that they do not take into account the aggregation phenomena of asphaltenes.[1,8] In fact, the aggregation process produces a molecular weight distribution of aggregates, which also causes a polydispersity in asphaltene properties.[1,8,26−29] A few models use a polydisperse concept in terms of asphaltene properties, especially molecular weight and size.[28,29]

Many studies have been done to predict asphaltene precipitation conditions. A preliminary study shows that the precipitation models/tools may fall into five categories: "equation of state (EoS)" based models, "activity coefficient" based models, "association" models, "colloidal/micellization" models, and "scaling laws, corresponding states and correlations".

Equations of state have been widely used in modeling of the heavy organic depositions due to the flexibility and simple application in simulation software. For instance, the Peng−Robinson (PR)[32] and Soave−Redlich−Kwong (SRK)[33] cubic equations of state were simultaneously used by Gupta,[34] who estimated the solubility of the asphaltenes in definite organic solvents. Nghiem et al.,[35−37] Godbole et al.,[20] Lindeloff et al.,[38] Sabbagh et al.,[39] and Soroush et al.[40] also applied the equation of state approach to model asphaltene precipitation. This approach and its extended versions have been used in many simulators (e.g., MULTIFLASH,[41] CMG,[42] etc.). Fahim and

Andersen[43] proposed a thermodynamic model based on the cubic-plus-association (CPA) EoS[44] to predict the region of asphaltene stability. Very recently, Li and Firoozabadi[45] have applied this EoS to study the asphaltene precipitation from n-alkane diluted model solutions (asphaltene + toluene) and heavy oils and bitumens. They have continued this work[46] in order to study the asphaltene precipitation in live oils from temperature, pressure, and composition effects. Other more advanced EoS based models are based on statistical associating fluid theory (SAFT) (e.g. the works of Wu et al.,[47,48] Ting et al.,[49] Buenrostro-Gonzalez et al.,[50] Christensen et al.,[51] Gonzalez et al.,[52] and Tabatabaei-Nejad and Khodapanah[53]). Another approach has been pursued by Vafaie-Sefti and Mousavi-Dehghani,[54] Eslamimanesh and Shariati,[55] and Eslamimanesh,[56] who have recently applied the PR EoS[32] in continuous form to take into account the aggregation of asphaltene particles, and by Nikookar et al.,[57] who modified the SRK EoS[33] to develop a more flexible equation of state for modeling asphaltene precipitation. The EoS based models require fluid characterization information generally up to C_{30+} (C_{29+} or C_{31+}), and this is one of their disadvantages. Convergence of some of these models is another problem encountered especially when the polydispersity of the asphaltene particles may be taken into account. However, the EoS-based models are especially appropriate for prediction of the pressure−temperature phase diagram of asphaltenes.

The activity coefficient based models, which are generally based on regular solution or polymer solution theories, (those of Scatchard−Hildebrand,[58,59] Flory−Hüggins,[24,25] and Scott−Magat[26]) are applied to model the phase behavior of asphaltene-containing fluids (e.g. see the works of Hirschberg et al.,[11] Burke et al.,[27,60] Kawanaka et al.,[28] and Park[29]). So far, a number of modifications for the Flory−Hüggins theory[24,25] and calculation procedures for the solubility parameters of the asphaltene fractions have been recommended to determine the effects of pressure and composition on the onset conditions and the amounts of the precipitations.[60−70] A good review of these kinds of models is available in the article by Andersen and Speight.[71] Activity coefficient based models normally do not require fluid characterization information up to C_{30+} (C_{29+} or C_{31+}), and this is one of their advantages. Having information on average molecular weight of asphaltenes is a key parameter for these kinds of thermodynamic models. The latter parameter is generally considered to be an "adjustable parameter". In the case that the polydispersity of the asphlatene particles is considered, more adjustable parameters are needed. In addition, proper distribution functions such as Gamma, Schulz, Weibull, Tung, etc.[12,72−78] should be introduced into the model to account for molar mass distribution in the phases present. This may result in some calculation problems because there is a need to change the form of the function according to the specific system containing oil and different solvents/gases.

The evidence for the asphaltene self-association phenomenon[2,8,10,12,13,23,79−83] resulted in presentation of more advanced association models. The CPA-EoS[44] based models[43,45,46] and thermodynamic models based on SAFT-EoS[47−53] as well as continuous[54]/semicontinuous[55,56] models based on EoS + an association term take into account this concept, as pointed out earlier. Having studied the proposed mechanisms of asphaltene self-association (hydrogen bonding, aromatic stacking, acid−base interactions, and van der Waals forces), Agrawala and Yarranton[82] developed an association model for asphaltene precipitation. They considered the aggregations to

be similar to linear polymerization, though without the initial step due to the fact that the association is not a reaction of free radicals. In their proposed model, the asphaltene monomers would be the propagators, and resin molecules would act as the terminators of the polymerization reactions. The authors then tried to calculate the average molar mass and molar mass distributions of asphaltene aggregates for two kinds of well-known crude oils (Athabasca and Cold Lake). In 2007, Fox[83] modified the original model (single-end association model) to a double-end association one in which two terminators might be linked together to form another kind of terminator (resin−resin terminators). The association models have also been applied for prediction of the effects of miscible gas injections and high pressures on asphaltene depositions.[72]

In 1987, Leontaritis and Mansoori[84] considered the resin molecules as the peptizing agents for suspension of the asphaltene particles in the bulk of crude oils. They presented a new class of thermodynamic model called a colloidal model in which a specific amount of resin molecules is supposed to attach to the surface of the asphaltene particles to prevent flocculation. These investigators asserted that the proposed model would be able to predict only the onset conditions of precipitation but not the amount of deposition upon addition of solvents. The colloidal model was later modified to a "fractal aggregation model" in the following years to make the previous model more exact and clarify the mechanism of the aggregations to some extent.[85] The latter model takes into account the theory of polymer polydispersity and the principles of the phase equilibria to predict the complex fractal shapes and size distributions of asphaltene particles. In addition to the above works, there are other investigations which considered the colloidal nature of asphaltene aggregates.[86,87] Furthermore, a similar model, in which the Scott−Magat[26] theory is employed to predict the asphaltene precipitation conditions was reported by Mohammadi and Richon.[88]

The thermodyanmic micellization model is another approach presented by Victorov and Firoozabadi,[89] in which the focus is on the stabilization of asphaltene micelles by resin molecules. According to this model, later continued by Pan and Firoozabadi,[18,90,91] asphaltene molecules are polar and lipophobic. Hence, they migrate from the crude bulk that includes nonpolar species such as paraffins to form the micellar core. The equilibrium calculations were done by initial derivation of the Gibbs energy equation of the asphalt-free oil phase and precipitated liquid phase. The original model is able to predict the amounts and compositions of the two phases accompanied by micellar size while the modified one is capable of determination of the effects of organic solvents and resins on the amount of asphaltene precipitation.[18,91] These calculations were performed by minimization of the total Gibbs energy equation obtained from thermodynamic relations and a proper equation of state.[18,90,91] Although the micellization model is capable of taking into account the micellar and aggregation natures of asphaltene, it contains many adjustable parameters and it also requires information on resin content of the oil sample, which may not always be available. Furthermore, there is a debate among the researchers about the origin of micellization of asphaltenes in oil systems. It is believed that micellization is a result of stronger intermolecular forces in the solvent than in the interior of the micelle for aqueous systems.[10] For "normal" micelles in water, the micelle limitation growth is due to the repulsion between the polar groups.[10] This concept may not be applicable to the association of asphaltenes

in toluene, since there is no reasonable mechanism that would give a reduction of the intermolecular forces with increased number of molecules added to a stacked association structure.[10] Therefore, there may be a limitation of the micelle growth by steric repulsion from the aliphatic chains.[10]

Predictive tools based on scaling equation, corresponding states, and correlations have also been reported in the literature.[12,13,92−102] These tools may, however, be limited to specific systems. Recently, application of mathematical correlations has been investigated for predictions of the amount of asphaltene precipitation.[98,103,104] Ashoori et al.[98] have used the artificial neural network (ANN) in comparison with the scaling laws and found out that the prediction results of the latter network are more accurate than the modified scaling equations proposed by Rassamdana et al.[92] and Hu et al.[96,97] However, ANN based models should be used very carefully because they may face over-fitting or under-fitting problems. For instance, in the case that the number of the ANN parameters are more than the number of treated experimental data for its training, the over-fitting problem may occur. The capability of the mathematical structure "BBN", which is a graphical probabilistic model, has been studied by Sayyad Amin and co-workers[105] to investigate the effects of pressure, temperature, dilution ratio, and injected fluid molecular weight on the amount of asphaltene precipitation.

It is currently obvious that perhaps none of the models presented so far is capable of predicting asphaltene precipitation satisfactorily, and therefore, there is still a need for a simple and robust model to estimate the asphaltene precipitation. In a previous work,[1] a monodisperse thermodynamic model based on the Flory−Hüggins[24,25] polymer solution theory was proposed, in which a distribution of asphaltene and non-asphaltene components in the oil and precipitated phases is considered. The aim of this new study is to provide a more general monodisperse thermodynamic model for predicting asphaltene precipitation. For this purpose, a discussion is made on chemical theory of associated solutions with physical interactions,[25] which has been used to model the associated systems such as hydrocarbon−alcohol mixtures and mixtures of complex polar substances, like coating materials. It is also shown that the existing Flory−Hüggins[24,25] based models may require some modifications in order to take into account the distributions of asphaltene and nonasphaltene components in the oil and precipitated phases.[1] A thermodynamic model is then introduced to solve this shortcoming. The main assumption in this model is that the asphaltene precipitation is considered as a reversible process, allowing the use of molecular thermodynamics. The results of this model are finally compared with some selected experimental data from literature.

■ FLORY−HÜGGINS POLYMER SOLUTION THEORY BASED MODELS

The Flory−Hüggins polymer solution theory[24,25] has been used traditionally to estimate asphaltene precipitation conditions. Two assumptions are normally used in modeling asphaltene precipitation:[1] (1) the precipitated phase consists of asphaltene only or (2) the precipitated phase consists of asphaltene and nonasphaltene components with the oil phase free of asphaltene (due to lower concentration of asphaltene than maltene concentration). The model developed by Hirschberg et al.[11] is perhaps one of the first developed models, which uses the first assumption, i.e., it is assumed that asphaltene volume fraction

Φ_a^{Asph} in the precipitated phase can be generally assumed equal to unity.[1] The second assumption has been used in the model developed by Cimino et al.[5,17] In this model, the oil phase can be safely assumed to be pure as typical asphaltene volume fraction Φ_a^{Oil} in oils is in the range of $10^{-2}-10^{-3}$ for oils with asphaltene weight percent from 1 to 10.[1,5,17] Furthermore, it is assumed that asphaltene volume fraction in precipitated phase is not very sensitive to oil systems, and it can be generally assumed to be constant.[1,5,17] A more detailed description of these two models is given in the Appendix.[1]

Figure 1 shows volume fraction of asphaltene in the precipitated phase versus interaction parameter (χ)
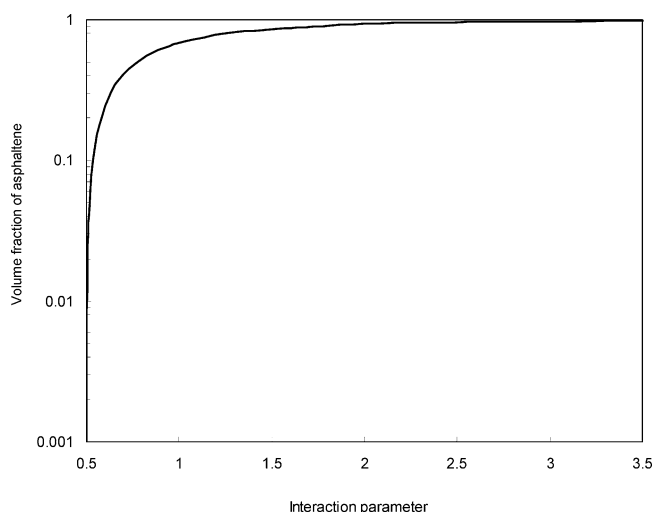

Figure 1. Typical volume fraction of asphaltene in the precipitated phase (Φ_a^{Asph}) versus interaction parameter (χ).[1] Limited solubility is often observed in macromolecule (polymer) containing systems. The Flory–Hüggins[24,25,109] theory indicates that, for a solvent–macromolecule system, the value of χ may not exceed 0.5 for miscibility in all proportions.[106]

using Flory–Hüggins[24,25] theory.[1] As can be seen, limited solubility is often observed in macromolecule (polymeric component) containing systems according to this theory. The Flory–Hüggins[24,25] theory indicates that, for a solvent–macromolecule system, the value of χ may not exceed 0.5 for miscibility in all proportions.[97] According to this figure, at $\chi \gg$ 0.5, $\Phi_a^{Asph} \cong 1$. That is, the Hirschberg et al. model[11] can be obtained.[1] However, at χ near 0.5, $\Phi_a^{Asph} \ll 1$, and therefore, using the latter assumptions may be conservative.[1] In other words, by taking into account the presence of maltene in the precipitated phase and the presence of asphaltene in the oil phase, a more comprehensive model can be obtained with respect to the models developed by Hirschberg et al.[11] and Cimino et al.[5,17] (See the Appendix[1]).

On the other hand, a similar approach based on the Scott–Magat[26] polymer solution theory can be pursued in order to deal with the prediction of the precipitation of asphaltene (or any organic deposition like wax). The detailed derivation of this approach and the corresponding equations are presented in the Supporting Information.

■ DEVELOPMENT OF A THERMODYNAMIC MODEL

From the point of view that the molecules in a liquid solution interact with each other to form new chemical species and that solution nonideality is a consequence of chemical reactions, Dolezalek[107] and van Laar[108] presented the chemical theory of the solutions. This theory implies that the chemically distinct species in a solution can be in chemical equilibrium.[25] In the original form, it assumes that these substances form an ideal solution and the nonideality of a solution is apparent because it is based on the apparent account of the solution's composition.[25]

Dolezalek's theory[107] is capable of taking into consideration both positive and negative deviations from ideality for molecules of similar kind, while the van Laar–Scatchard–Hildebrand theory of regular solutions[24,25,61,62,109] is applicable to mixtures containing polar and hydrogen-bonded liquids.[25] The properties of the solution can be evaluated without further consideration to interactions between the true species, once the mole fractions of these species are known. In contrast, the physical theory states that the true species are the same as the apparent species and while there are physical (van der Waals) intermolecular forces, there are no chemical reactions in the solution.[25]

To develop our model, we begin with the theory of polymer mixtures by Flory.[24,25,109,110] We consider a mixture consisting of an asphaltene fraction and a hydrocarbon (maltene) fraction with the following assumptions:[25]

1. The asphaltenes exist in solution in the form of linear, hydrogen-like bonded polymers a_1, a_2, ..., a_n as follows:

$$a + a_{n-1} \Leftrightarrow a_n \tag{1}$$

   It is an assumption that an asphaltene monomer reacts with an asphaltene $(n-1)$-mer to form an asphaltene n-mer. Therefore, we ignore the probability of the reaction between an m-mer and a k-mer (where "m" and "k" are arbitrary integer numbers).

2. The constant of the above reaction is independent of the number of species n, i.e. n-mer. This assumption is made to reduce the number of adjustable parameters.

3. The molar volume of an n-mer is given by the molar volume of the monomer multiplied by n.

4. There are physical interactions between all molecules.

Using Flory's results for entropy of mixing, the following expression has been derived for the equilibrium constant, $K(T)$:[25]

$$K(T) = \frac{\Phi_{a_{n+1}}}{\Phi_{a_n}\Phi_{a_1}}\frac{n}{n+1} \tag{2}$$

where Φ_a is the volume fraction of the monomer/n-mer of asphaltene. The molar excess Gibbs energy, g^E, taken relative to an ideal solution of asphaltene and maltene, can be separated into two contributions as follows:[25]

$$g^E = g_c^E + g_p^E \tag{3}$$

where g_c^E is the chemical and g_p^E is the physical contribution. The chemical contribution is evaluated as follows:[25]

$$\frac{g_c^E}{RT} = x_m\ln\frac{\Phi_m}{x_m} + x_a\ln\frac{\Phi_{a_1}}{\Phi_{a_1}^*x_a} + Kx_a(\Phi_{a_1} - \Phi_{a_1}^*) \tag{4}$$

In the preceding equation, T is temperature, R is the universal gas constant, Φ_m represents the volume fraction of maltene, x_a and x_m are the overall mole fractions of asphaltenes and

maltenes, respectively, Φ_{a_1} is the volume fraction of molecular species a_1, and

$$\Phi_{a_1}^* = \underset{x_m \to 0}{\text{limit}} \, \Phi_{a_1} \tag{5}$$

Applying the definition of equilibrium constant (eq 2), the volume fraction of the monomer of asphaltene (Φ_{a_1}) can be calculated as follows:

$$\Phi_{a_1} = \frac{1 + 2K\Phi_a - \sqrt{1 + 4K\Phi_a}}{2K^2\Phi_a} \tag{6}$$

where Φ_a is the overall volume fraction of asphaltenes. The $\Phi_{a_1}^*$, is then evaluated by

$$\Phi_{a_1}^* = \frac{1 + 2K - \sqrt{1 + 4K}}{2K^2} \tag{7}$$

The physical contribution is written using the following expression proposed by Scatchard:[25,110]

$$g_p^E = \beta \Phi_a \Phi_m (x_a v_a + x_m v_m) \tag{8}$$

where β is a physical interaction parameter related to the maltene−asphaltene monomer interaction, and v_a and v_m are the molar volumes of the two fractions. Substitution of eqs 4 and 8 into eq 3 and appropriate differentiation of Gibbs energy relation with respect to the number of moles of the two portions gives the following expression for evaluation of the activity coefficients:[25]

$$\ln \gamma_a = \ln \frac{\Phi_{a_1}}{\Phi_{a_1}^* x_a} + \Phi_m \left(1 - \frac{v_a}{v_m}\right) + K(\Phi_a \Phi_{a_1} - \Phi_{a_1}^*) + \chi \Phi_m^2 \tag{9}$$

$$\ln \gamma_m = \ln \frac{\Phi_m}{x_m} + \Phi_a \left(1 - \frac{v_m}{v_a}\right) + K \frac{v_m}{v_a} \Phi_a \Phi_{a_1} + \chi \Phi_a^2 \tag{10}$$

where γ is the activity coefficient and χ is a physical interaction parameter (as mentioned earlier), which describes the maltene solvent power with respect to the asphaltene ($\chi = \beta v_{m/a}/(RT)$) The subscripts a and m represent asphaltene and maltene, respectively. The parameter χ depends on the temperature, but for systems containing macromolecules, in which the molecular weight of the macromolecule is very large, it is nearly independent of the molecular weight of macromolecules.[111] In theory, this parameter is also independent of macromolecule concentration, but in fact, it often varies with concentration, especially in mixtures containing polar molecules, for which the Flory−Hüggins[24,25,110] theory provides only a rough approximation. This parameter can be calculated using the following equation:[8,25,97,110]

$$\chi = \frac{v_m[(\delta_m - \delta_a)^2]}{RT} \tag{11}$$

where δ stands for the solubility parameter. Substitution of eq 6 into eq 10 and using the relation $\Phi_m = 1 - \Phi_a$ gives

$$\ln \gamma_m = \ln\left(\frac{1 - \Phi_a}{1 - x_a}\right) + \Phi_a\left(1 - \frac{v_m}{v_a}\right)$$
$$+ \frac{v_m}{v_a}\left(\frac{1 + 2K\Phi_a - \sqrt{1 + 4K\Phi_a}}{2K}\right) + \chi \Phi_a^2 \tag{12}$$

Similarly, substitution of eqs 6 and 7 into eq 9 results in the following equation after appropriate mathematical rearrangements:

$$\ln \gamma_a = \ln\left[\frac{1 + 2K\Phi_a - \sqrt{1 + 4K\Phi_a}}{(1 + 2K - \sqrt{1 + 4K})\Phi_a x_a}\right] - (1 - \Phi_a)\left(\frac{v_a}{v_m}\right)$$
$$- \frac{\sqrt{1 + 4K\Phi_a} - \sqrt{1 + 4K}}{2K} + \chi(1 - \Phi_a)^2 \tag{13}$$

Considering the liquid−liquid equilibrium between the two fluid fraction phases, the following equations should be established in the system:[1,25]

$$x_a^{Oil} \gamma_a^{Oil} = x_a^{Asph} \gamma_a^{Asph} \tag{14}$$

$$x_m^{Oil} \gamma_m^{Oil} = x_m^{Asph} \gamma_m^{Asph} \tag{15}$$

Applying the derived eqs 6−13 and substituting into eqs 14 and 15 gives

$$\left[\frac{1 + 2K'\Phi_a^{Asph} - \sqrt{1 + 4K'\Phi_a^{Asph}}}{(1 + 2K' - \sqrt{1 + 4K'})\Phi_a^{Asph}}\right]$$
$$\times \exp\left[-\frac{\sqrt{1 + 4K'\Phi_a^{Asph}} - \sqrt{1 + 4K'}}{2K'}\right.$$
$$\left. - (1 - \Phi_a^{Asph})\frac{v_a^{Asph}}{v_a^{Asph}} + \chi'(1 - \Phi_a^{Asph})^2\right]$$
$$= \left[\frac{1 + 2K\Phi_a^{Oil} - \sqrt{1 + 4K\Phi_a^{Oil}}}{(1 + 2K - \sqrt{1 + 4K})\Phi_a^{Oil}}\right]$$
$$\times \exp\left[-\frac{\sqrt{1 + 4K\Phi_a^{Oil}} - \sqrt{1 + 4K}}{2K}\right.$$
$$\left. - (1 - \Phi_a^{Oil})\frac{v_a^{Oil}}{v_m^{Oil}} + \chi(1 - \Phi_a^{Oil})^2\right] \tag{16}$$

and

$$
\begin{aligned}
(1 - \Phi_a^{\text{Oil}}) &\times \exp\left[\left(1 - \frac{v_m^{\text{Oil}}}{v_a^{\text{Oil}}}\right)\Phi_a^{\text{Oil}} + \frac{v_m^{\text{Oil}}}{v_a^{\text{Oil}}}\right. \\
&\times \left.\left(\frac{1 + 2K\Phi_a^{\text{Oil}} - \sqrt{1 + 4K\Phi_a^{\text{Oil}}}}{2K}\right) + \chi\Phi_a^{\text{Oil}^2}\right] \\
&= (1 - \Phi_a^{\text{Asph}}) \times \exp\left[\left(1 - \frac{v_m^{\text{Asph}}}{v_a^{\text{Asph}}}\right)\Phi_a^{\text{Asph}}\right. \\
&+ \frac{v_m^{\text{Asph}}}{v_a^{\text{Asph}}}\left(\frac{1 + 2K'\Phi_a^{\text{Asph}} - \sqrt{1 + 4K'\Phi_a^{\text{Asph}}}}{2K'}\right) \\
&\left. + \chi'\Phi_a^{\text{Asph}^2}\right]
\end{aligned}
\tag{17}
$$

where K' and χ' represent, respectively, the equilibrium constant and the interaction parameter in asphaltene-rich phase. The two above equations are solved simultaneously for the volume fractions of the precipitated asphaltenes. The following equations can be used to calculate the volume fractions of asphaltene and maltene:[1,106]

$$
\Phi_a = \frac{x_a v_a}{x_a v_a + x_m v_m}
\tag{18}
$$

$$
\Phi_m = \frac{x_m v_m}{x_a v_a + x_m v_m}
\tag{19}
$$

It should be noted that in macromolecule containing systems, volume fractions are very different from mole fractions because the molar volume of a macromolecule is much larger than that of the solvent.[106] Furthermore, since the molecular weight of the macromolecule components is not known accurately, it is difficult to determine the mole fraction. Therefore, an equivalent definition of Φ is used.[106] Equations 18 and 19 can be also written as below:[1,106]

$$
\Phi_a = \frac{w_a/\rho_a}{w_a/\rho_a + w_m/\rho_m}
\tag{20}
$$

$$
\Phi_m = \frac{w_m/\rho_m}{w_a/\rho_a + w_m/\rho_m}
\tag{21}
$$

where w_a and w_m are the weight fractions of asphaltene and maltene, respectively, and ρ_a and ρ_m represent the mass densities of asphaltene (1.2 g/cm^3) and maltene, respectively.

It can be easily shown that the two well-known precipitation models of Cimino et al.[5,17] and Hirschberg et al.[11] are particular cases of the proposed model (see the Appendix).

■ FLUID CHARACTERIZATION

For calculating asphaltene solubility/precipitation, the solubility parameter of asphaltene, solubility parameter of maltene, and molecular volume of maltene are required. The solubility

parameter of asphaltene δ_a can be calculated using the following relation:[1,11]

$$
\delta_a = 20.04[1 - 1.07 \times 10^{-3}(T - 273.15)]
\tag{22}
$$

where T is in kelvin and δ_a is in MPa$^{0.5}$. The solubility parameter of the maltene can be calculated from[1,11]

$$
\delta_m = \sqrt{\frac{\Delta u_m^V}{v_m}}
\tag{23}
$$

where Δu_m^V is the energy change upon isothermal vaporization of one mole of the maltene to the ideal gas state and v_m is the molecular volume of the maltene. It is known that the two-parameter cubic PR EoS[32] gives better results for predicting v, whereas the results of the SRK EoS[33] for Δu^V are in better agreement with the reported experimental data.[11] However, a three-parameter cubic equations of state can also be used for calculation of the solubility parameter.[69] In this work, the PR EoS[32] has been used for this purpose as follows:[69]

$$
\delta = \left(\frac{a_c(1 + m(1 - T_r^{1/2}))(1 + m)}{[v(v + b) + b(v - b)]}\right)^{1/2}
\tag{24}
$$

where,

$$
a_c = \frac{0.457235R^2T_c^2}{P_c}
\tag{25}
$$

$$
b = \frac{0.077796RT_c}{P_c}
\tag{26}
$$

and the modified m is given by[112]

$$
m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3
\tag{27}
$$

In the above equations, the subscripts c and r represent critical point and reduced property, respectively. The parameters a and b are the attractive and repulsive parameters of the PR EoS,[32] respectively. The parameter ω is the acentric factor and P stands for pressure. To extend the concept of the solubility parameter to the mixtures (here is maltene consisting of subfractions), the following mixing rule is used:

$$
\delta_m = \sum_{i=1}^{N} \Phi_i\delta_i
\tag{28}
$$

where N is the number of maltene subfractions (components). Besides, the Twu's correlation[113] for critical properties and the Lee−Kesler correlation[114] for the acentric factor are used for the petroleum fractions, as recommended by Danesh.[115] The binary interaction parameters (BIPs) for the PR EoS,[32] which have been used in this work, were those derived from the work of Knapp and Döring.[116] For the BIPs between hydrocarbon−hydrocarbon molecules (excluding those reported in Knapp and Döring[116]), the correlation employed by Nghiem et al.[36] is used as follows:

$$
k_{ij} = 1 - \left(\frac{2v_{ci}^{1/6}v_{cj}^{1/6}}{v_{ci}^{1/3} + v_{cj}^{1/3}}\right)^e
\tag{29}
$$

where k is the binary interaction parameter, v is the molar volume, subscripts i and j refer to ith and jth hydrocarbon

fraction present in the investigated petroleum fluid, respectively, and e is considered as a tuning parameter. The values of e are generally evaluated by tuning the results of bubble point calculations (saturation pressures) for oil systems. Sample flash calculation results have been presented as a Supporting Information file. In the presented model, K (or K') and average molecular weight of the asphaltene fraction (M_w) are regarded as adjustable parameters.

■ RESULTS AND DISCUSSION

In the first step of the calculations, vapor−liquid equilibrium (flash) calculations are generally preformed on the fluids to obtain the amount and the compositions of the liquid phase at the investigated pressure−temperature conditions. The PR EoS[32] is used for this purpose. Later, liquid−liquid equilibrium calculations are applied on the obtained liquid phase from the previous computational step (there is almost a similar approach in all of precipitation models based on activity coefficient methods).

To show the capability of the model for estimating asphaltene precipitation, several case studies are reported here. The data of a tank oil[28] reported in Tables 1 and 2 were first used.

Table 1. Compositions of Tank Oil[28]

component	mole %
C_1	0.1
C_2	0.48
C_3	2.05
$i\text{-}C_4$	0.88
$n\text{-}C_4$	3.16
$i\text{-}C_5$	1.93
$n\text{-}C_5$	2.58
C_6	4.32
C_{7+}	84.5

Table 2. Properties of Tank Oil, Asphaltene, C_6 and C_{7+}[28]

property	value
average molecular weight	221.5
specific gravity	0.873
density of asphaltene, g/cm^3	1.2
molecular weight of C_6	84
total amount of asphaltene, wt %	4.023
molecular weight of C_{7+}	249.9
density of C_6, g/cm^3	0.685
density of C_{7+}, g/cm^3	0.868
bubble point temperature of C_6, K	337
bubble point temperature of C_{7+}, K	585
evaluated critical pressure of C_{7+}, MPa	1.27
evaluated critical temperature of C_{7+}, K	740
evaluated acentric factor of C_{7+}, K	0.7814

The model was tuned using the experimental titration data with *n*-pentane and *n*-decane. Figure 2 shows the results. The values of the adjustable parameters for the proposed sample are $K = 1000$ and average molecular weight of asphaltene = 2000 g/gmol. As can be seen, there is acceptable agreement between the experimental data and the model results. It is inferred from the calculations that the value of χ is about 3.46. This literally shows that the volume fraction of asphaltene in the asphaltene-rich phase is almost unity based on Figure 1.
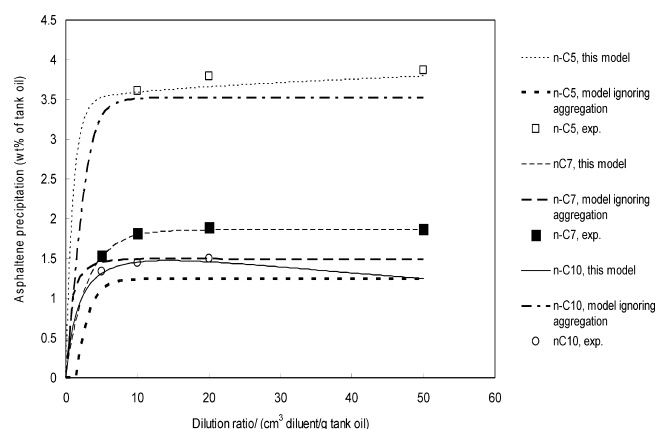

Figure 2. Experimental data[28] and model results with $K = 1000$ and average molecular weight of asphaltene = 2000 g/gmol and the results of the model ignoring aggregations ($K = 0$) for the weight percent of asphaltene precipitation from the tank oil mentioned in Tables 1 and 2. The value of χ has been calculated as 3.46. Symbols represent experimental data.[28] Curves represent model results. Calculations were performed at 298.15 K.

Therefore, we obtain eq A.12, which is the final equation to be solved according to the model proposed in this work (see the Appendix for details).

The deviations between experimental titration data of *n*-heptane and predictions can be attributed to the unreliability of the experimental data.[1] At high concentrations of *n*-decane, the weight percent of the precipitated asphaltene from the tank oil decreases. This behavior is in correct agreement with the results of the previous models.[8,11,28] In overall, the model results are in better agreement with the experimental data compared with the case where the aggregation is ignored. Moreover, the asphaltene volume fraction in the precipitated phase approaches unity for all titrations done on the tank oil.

To further demonstrate the capability of the model, asphaltene precipitation in a live oil system from the Middle East region was also studied.[117] The reservoir and fluid properties are presented in Tables 3 and 4. As mentioned earlier, the

Table 3. Characteristics of Live Oil[117]

property	value
reservoir temperature, K	389.15
reservoir pressure, MPa	62.05
bubble point pressure at reservoir temperature, MPa	22.68
gas/oil ratio (GOR), (m^3/ m^3)	195.9
API	39
saturates, wt % of STO^a	68.3
aromatics, wt % of STO	11.6
resins, wt % of STO	18.8
asphaltenes (*n*-pentane insoluble), wt % of STO	1.3
evaluated critical pressure of C_{7+}, MPa	1.40
evaluated critical temperature of C_{7+}, K	720
evaluated acentric factor of C_{7+}, K	0.7209

^{a}STO: stock tank oil.

methodology of the calculations for live oil was that first, flash calculations are performed on the investigated oil sample using the PR EoS.[32] Four bubble point experimental data[117] were used for tuning the EoS. Once the liquid/vapor split is

Table 4. Compositions of Live Oil System[117]

components	mole %
N_2	0.48
CO_2	0.92
C_1	43.43
C_2	11.02
C_3	6.55
i-C_4	0.79
n-C_4	3.7
i-C_5	1.28
n-C_5	2.25
C_6	2.7
C_{7+}	26.88
molecular weight	82.49
C_{7+} molecular weight	228.07
C_{7+} density	0.865

calculated, the asphaltene model calculations steps were followed to find the onset and the amount of asphaltene precipitation on the remaining liquid phase. In Figure 3, only
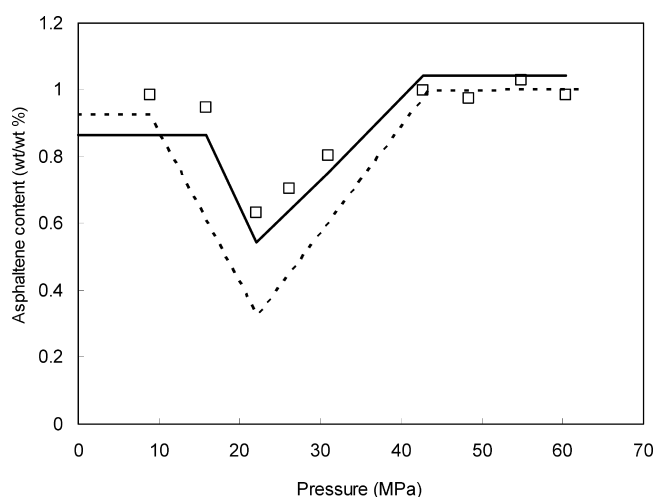

Figure 3. Experimental data[117] and model results for asphaltene content of live oil mentioned in Tables 3 and 4 as a function of pressure at reservoir temperature, 389.15 K. Values of adjusted parameters: $K = 1500$, average molecular weight of asphaltene = 1800 g/gmol. The value of χ has been calculated as 3.16. (curve) Model results; (dashed curve) results of the model ignoring aggregations ($K = 0$). Symbols: (□) experimental data.[117]

the experimental data at the onset of asphaltene precipitation were used for tuning. The values of the tuned parameters for this sample are $K = 1500$ and average molecular weight of asphaltene =1800 g/gmol. Our calculations show that the value of χ is about 3.16. This proves that the volume fraction of asphaltene in the asphaltene-rich phase is almost unity based on Figure 1. Therefore, the previous assumptions of the model are also validated for this live oil. Figure 3 shows that the model can correctly predict asphaltene precipitation/content behavior, i.e. when reducing pressure at a given temperature, asphaltene starts precipitating at the onset of asphaltene precipitation condition and therefore oil asphaltene content decreases. The asphaltene content of oil is reduced as the pressure decreases. The asphaltene content reaches a minimum near the bubble point pressure. The oil asphaltene content then increases as the pressure decreases further below the bubble point pressure. From this figure, it is clear that the model cannot reliably

predict the asphaltene content of oil, which can be attributed to the monodisperse nature of the model properties. However, the model results are in better agreement with the experimental data compared with the case where the aggregation is ignored. More reliable results would be expected by taking into account the polydispersity in asphaltene properties. Figure 4 shows the
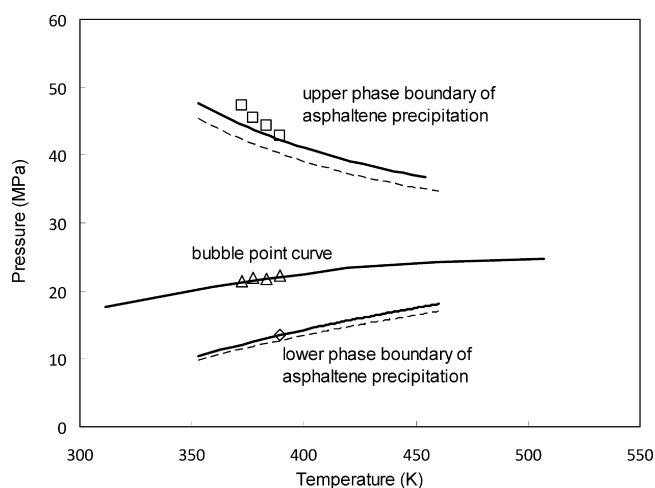

Figure 4. Experimental data[117] and model results for asphaltene precipitation phase boundaries of live oil mentioned in Tables 3 and 4 using the previously adjusted parameters: $K = 1500$, average molecular weight of asphaltene = 1800 g/gmol. The e parameter has been calculated as 2.2 for this oil. (solid curves) Model results; (dashed curves) results of the model ignoring aggregations ($K = 0$). Symbols:[117] (□) experimental data of upper phase boundary, (△) experimental data of saturation curve, (◇) experimental data of lower phase boundary.

predicted and experimental data[117] for the upper and lower asphaltene precipitation phase boundaries along with saturation conditions of the oil sample. These predictions were performed using the previously tuned parameters for this sample. The *predicted* results coincide well with the existing experimental data. Again, compared with the case where the aggregation is ignored, the model results are in better agreement with the experimental values. In overall, the asphaltene volume fraction in the precipitated phase approaches unity.

The effects of gas injection on asphaltene precipitation are also of significance for the petroleum industry. The capabilities of the proposed model for representation and prediction of the amount of precipitated asphaltenes from two live oil samples under methane and nitrogen injections have been also checked in this work. Table 5 reports the compositional data of the aforementioned samples.[118] It is worth pointing out that these petroleum samples contain non-negligible amounts of a hydrogen sulfide component, which make them very attractive to check their asphaltene content phase behavior. The calculation steps have been pursued based on the previous procedure. The obtained results of the effects of the pressure on asphaltene precipitation are interpreted in Figures 5−8. The corresponding model parameters are reported in the figure captions. As can be seen, the calculated/estimated model results acceptably coincide with the trends of the experimental data. The precipitated asphaltene amounts soar at the beginning of the pressure drop (in the higher pressure region) and later decrease with the continued pressure drop at constant amounts of injected methane or nitrogen. Normally, the maximum amounts of asphaltene

Table 5. Compositional Analysis and Characteristics of Live Oil Samples for Investigations of the Effect of Gas Injection on Asphaltene Precipitation[118]

components	mole %	
	sample A	sample B[a]
H_2S	2.70	0.59
N_2	0.21	0.06
CO_2	5.14	2.45
C_1	22.00	38.65
C_2	7.10	6.66
C_3	5.34	5.33
$i\text{-}C_4$	0.99	1.01
$n\text{-}C_4$	2.78	2.92
$i\text{-}C_5$	1.12	1.24
$n\text{-}C_5$	1.41	1.51
C_6	5.55	4.67
C_7	3.84	4.56
C_8	4.02	3.75
C_9	2.85	2.24
C_{10}	2.83	2.55
C_{11}	2.58	2.26
C_{12+}	29.54	19.56
molecular weight	149	75
C_{12+} molecular weight	418	300
C_{12+} SG	0.9760	0.9025

[a]The summation of the mole % values as reported in the original article is 100.01 %. Therefore, the normalized mole fractions are herein applied for the calculations.
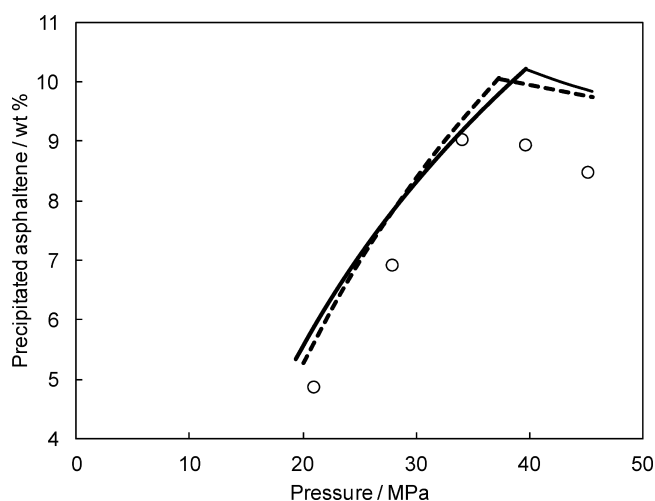

Figure 5. Effect of pressure on the amount of asphaltene precipitation from live oil sample (Table 5, sample A) under methane injection (43.3 mol %) at 397 K. Adjusted parameters: K = 1200, average molecular weight of asphaltene = 1600 g/gmol. The e parameter has been calculated as 1.9. (solid curve) Proposed model results, (dashed curve) results of the model ignoring association (K = 0). Symbols: (○) experimental data.[118]

precipitation are observed at the bubble point pressure of the fluid. It is now generally accepted[27] that the decrease in the amounts of precipitates after passing the maximum value may be due to vaporization of lighter oil components by decreasing of the pressure, which contribute to obtaining heavier liquid phase. Consequently, the solubility parameter of maltene fraction increases because of increasing the heavier components in liquid phase. Therefore, asphaltene particles can be better
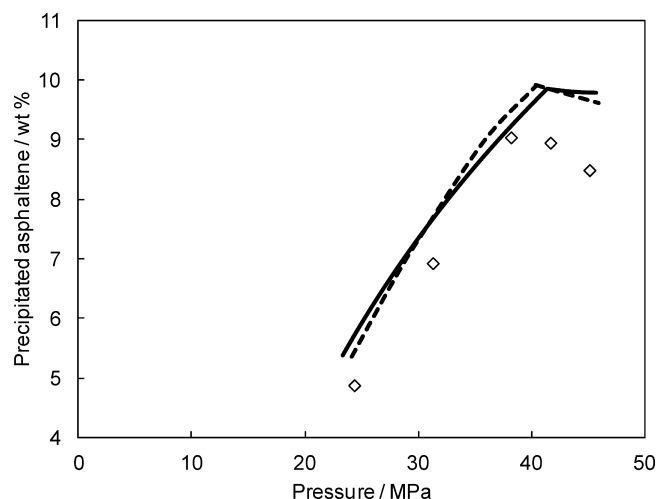

Figure 6. Effect of pressure on the amount of asphaltene precipitation from live oil sample (Table 5, sample A) under methane injection (43.3 mol %) at 355 K. Previously adjusted parameters using the corresponding data at T = 397 K (Figure 5): K = 1200, average molecular weight of asphaltene = 1600 g/gmol. The e parameter has been calculated as 1.9. (solid curve) Proposed model results, (dashed curve) results of the model ignoring association (K = 0). Symbols: (◇) experimental data.[118]
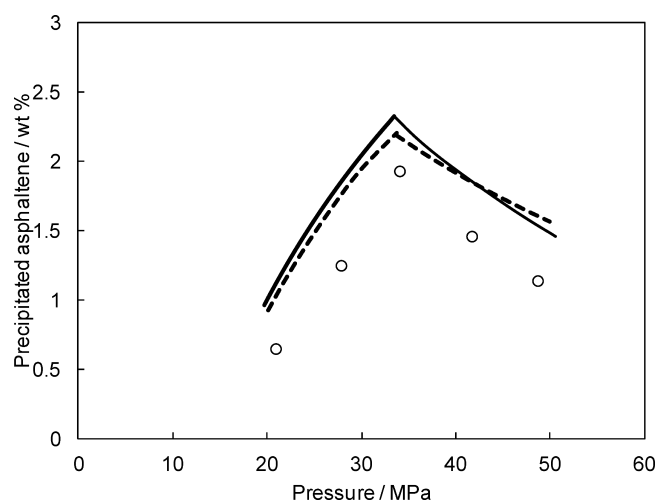

Figure 7. Asphaltene precipitation from live oil sample (Table 5, sample B) versus pressure under nitrogen injection (10 mol %) at 385.15 K. Adjusted parameters K = 1300, average molecular weight of asphaltene =1700 g/gmol. The e parameter has been calculated as 2. (solid curve) Proposed model results, (dashed curve) results of the model ignoring association (K = 0). Symbols: (○) experimental data.[118]

dissolved in the corresponding liquid phase (the liquid phase would be a better solvent for the asphaltene particles).

The polydispersity phenomenon can be introduced into the presented model to deal with the distribution of asphaltene particles in the system. However, more adjustable parameters and selecting a proper distribution function reduce the simplicity of the model. Of particular interest is the fact that taking into account the aggregation of all of the present n-mers in the system leads to cross reactions between these particles, which consequently lead to complicated tensor calculations to find the equilibrium concentrations. Finally, the concept of this paper can
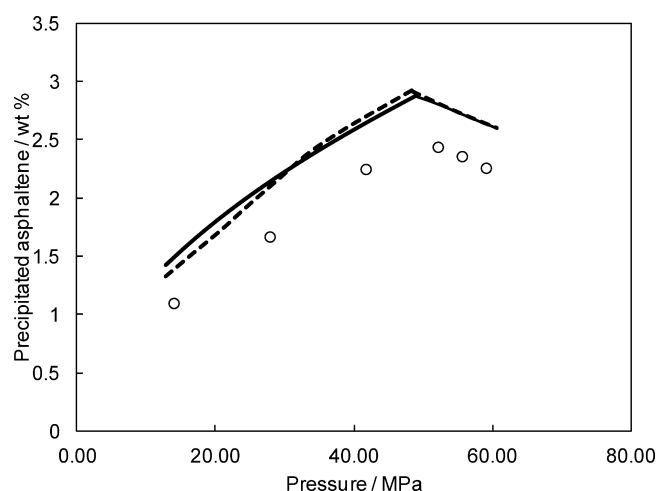
Figure 8. Asphaltene precipitation from live oil sample (Table 5, sample B) versus pressure under nitrogen injection (20 mol %) at 385.15 K. Previously adjusted parameters K = 1300, average molecular weight of asphaltene = 1700 g/gmol. The e parameter has been calculated as 2. (solid curve) Proposed model results, (dashed curve) results of the model ignoring association (K = 0). Symbols: (O) experimental data.[118]

be introduced to micellization[18,89−91] and colloidal[84−87] models to make them more general for prediction of asphaltene precipitation.

■ CONCLUSIONS

In this work, the following points are concluded:

1. A review was made on the thermodynamic models reported in the literature for estimating asphaltene precipitation.
2. It was confirmed that the traditional models based on the Flory−Hüggins[24,25,109] polymer solution theory,[4,5,11,27,71] which assume that either the precipitated phase consists of asphaltene only or the precipitated phase consists of asphaltene and nonasphaltene components and the oil phase is free of asphaltene (due to lower concentration of asphaltene than maltene concentration), may not be helpful for the conditions where χ is near 0.5 and may require some modifications.[1]
3. A thermodynamic model based on the chemical theory of associated solutions with physical interactions,[25,107,108] in which it is assumed that asphaltene forms a pseudocomponent and the precipitated and nonprecipitated phases contain asphaltene and nonasphaltene components was then introduced. The study shows that the existing traditional Flory−Hüggins[4,5,11,27,71] based models could be specific cases of the developed model.
4. Two main adjustable parameters are required in this model: the equilibrium constant and the average molecular weight of asphaltenes. The capability of this model for estimating asphaltene precipitation was examined (Figures 2−8) using some selected experimental data[28,117,118] from the literature (tank oil and live oils). It was shown that taking into account aggregation phenomena in our model improves the predictions.
5. It was argued that more reliable results would be expected by taking into account the polydispersity of asphaltene properties in our model. However, more adjustable parameters, a proper distribution function, and cross reactions between the n-mers in the system, which

consequently lead to complicated tensor calculations to find the equilibrium concentrations, would be required. These, however, may reduce the simplicity of the model.
6. It was also argued that the concept of this paper can be introduced to the micellization[18,89−91] and the colloidal[84−87] models to make them more general for prediction of asphaltene precipitation.

■ APPENDIX

Hirschberg et al.'s Model

In this thermodynamic model,[11] once the vapor/liquid split has been calculated, asphaltene precipitation is determined by a modified Flory−Hüggins[24,25,109] theory. The conditions for equilibrium between an asphaltene-rich phase A and a solvent-rich phase B are[11]

$$\mu_i^A = \mu_i^B \tag{A.1}$$

Following the Flory−Hüggins[24,25,109] theory, the chemical potential μ_i of component i is given by[11]

$$\frac{\mu_i - (\mu_i)_{ref}}{RT} = \ln(\Phi_i) + 1 - \frac{v_i}{v} + \chi_i \tag{A.2}$$

where $(\mu_i)_{ref}$ is the chemical potential at the reference state of pure liquid i. Φ_i is the volume fraction of component i. Hence[11]

$$\Phi_i = \frac{x_i v_i}{v} \tag{A.3}$$

The molar volume, v, of the mixture and the interaction parameter, χ_i, are calculated by using Hildebrand's approximation:[11]

$$v = \sum x_i v_i \tag{A.4}$$

and

$$\chi_i = \frac{v_i}{RT}(\delta - \delta_i)^2 \tag{A.5}$$

where T is the absolute temperature, R stands for the universal gas constant, and x_i is the mole fraction of component i and δ is given by eq 28.[11]

Assuming that the precipitated phase is pure asphaltene, $\mu_a^{Asph} = (\mu_a)_{ref}$ which in combination of above equations yields[11]

$$\Phi_a^{Oil} = \exp\left[\frac{v_a^{Oil}}{v_m^{Oil}} - 1 - \frac{v_a^{Oil}}{RT}(\delta_a - \delta_m^{Oil})^2\right] \tag{A.6}$$

where subscripts a and m represent asphaltene and maltene, respectively and superscript oil stands for oil phase.

Cimino et al.'s Model

According to this model,[5,17] thermodynamic equilibrium is described by means of the equality of chemical potentials relative to the two species (asphaltene and maltene) in the two phases, on phase splitting. Some simplification can be done by considering the physics of phase splitting. Considering a typical asphaltene volume fraction Φ_a^{Oil} in oil, it can be estimated in the range of 10^{-2} to 10^{-3} for oils with asphaltene weight percent from 1 to 10. It can be safely assumed to be pure solvent

(maltene), that is $\Phi_a^{Oil} = 0$. Such an assumption leads to the final equation, using Flory−Hüggins[24,25,109] theory:[5,17]

$$\ln[1 - \Phi_a^{Asph}] + \left(1 - \frac{v_m^{Asph}}{v_a^{Asph}}\right)\Phi_a^{Asph} + \chi'\Phi_a^{Asph^2} = 0$$

(A.7)

where the prime represents the asphaltene-rich phase and Φ_a^{Asph} is the volume fraction of asphaltenes in asphaltene-rich phase. The superscript Asph stands for asphaltene-rich phase. By solving the above equation, it is possible to see that Φ_a^{Asph} is not very sensitive for oil systems and it can be generally assumed to be constant. In the above equations, (v_m/v_a) is negligibly small compared with unity, and therefore, it may be neglected.[16] Mohammadi and Richon[70] applied the Scott−Magat[26] theory with Cimino et al.'s[5,17] assumptions and finally obtained the similar form of the eq A.7.

Mohammadi and Richon's Model

In this model, the liquid−liquid equilibrium is given by eqs 14 and 15, and using the activity coefficient expressions described earlier, one can write[1]

$$\ln\left(\frac{\Phi_m^{Oil}}{\Phi_m^{Asph}}\right) + \left(1 - \frac{v_m^{Asph}}{v_a^{Asph}}\right)(\Phi_a^{Oil} - \Phi_a^{Asph})$$
$$+ \chi'[(\Phi_a^{Oil})^2 - (\Phi_a^{Asph})^2] = 0$$

(A.8)

$$\ln\left(\frac{\Phi_a^{Oil}}{\Phi_a^{Asph}}\right) + \left(1 - \frac{v_a^{Oil}}{v_m^{Oil}}\right)(\Phi_m^{Oil} - \Phi_m^{Asph})$$
$$+ \chi[(\Phi_m^{Oil})^2 - (\Phi_m^{Asph})^2] = 0$$

(A.9)

where γ is the activity coefficient. The two above equations are simultaneously solved for obtaining the volume fraction of precipitated asphaltenes. The main assumption of this model is that asphaltene forms a pseudocomponent and the precipitated and oil phases contain asphaltene and nonasphaltene components.[1]

This Model

It can be easily shown that the two well-known precipitation models of Cimino et al.[5,17] and Hirschberg et al.[11] are particular cases of our proposed model. Using eq 15 as the equilibrium criterion of Cimino et al.'s model,[5,17] we can obtain eq 17. Assuming an asphaltene-free oil fraction ($\Phi_a^{Oil} = 0$) and after some mathematical rearrangements, one can obtain

$$\ln(1 - \Phi_a^{Asph}) + \left(1 - \frac{v_m^{Asph}}{v_a^{Asph}}\right)\Phi_a^{Asph} + \chi'\Phi_a^{Asph^2}$$
$$+ \frac{v_m^{Asph}}{v_a^{Asph}}\left(\frac{1 + 2K'\Phi_a^{Asph} - \sqrt{1 + 4K'\Phi_a^{Asph}}}{2K'}\right) = 0$$

(A.10)

If we assign $K = 0$ in the above equation and assume that $v_m^{Asph}/v_a^{Asph} \ll 1$, equation A.7 can be obtained, which is the final equation of the model proposed by Cimino et al.[5,17]

On the other hand, if we take eq 14 as the equilibrium criterion and substitute the derived equations for activity coefficient, the following relations is obtained:

$$x_a^{oil}\exp\left(\ln\left[\frac{1 + 2K\Phi_a^{Oil} - \sqrt{1 + 4K\Phi_a^{Oil}}}{(1 + 2K - \sqrt{1 + 4K})\Phi_a^{Oil}x_a^{Oil}}\right] - \left[\frac{\sqrt{1 + 4K\Phi_a^{Oil}} - \sqrt{1 + 4K}}{2K} + \frac{v_a^{Oil}}{v_m^{Oil}}\right] + \chi\right) = 1$$

(A.11)

and after suitable rearrangements

$$\left[\frac{1 + 2K\Phi_a^{Oil} - \sqrt{1 + 4K\Phi_a^{Oil}}}{1 + 2K - \sqrt{1 + 4K}}\right]$$
$$\times \exp\left[\frac{-\sqrt{1 + 4K\Phi_a^{Oil}} + \sqrt{1 + 4K}}{2K} - \frac{v_a^{Oil}}{v_m^{Oil}}\right.$$
$$\left. + \frac{v_a^{Oil}}{RT}(\delta_a - \delta_m^{Oil})^2\right] = \Phi_a^{Oil}$$

(A.12)

Equation A.12 is the main equation to be solved according to the proposed model in this work. Finally, taking the limit of the above function when K approaches zero yields equation A.6, which is the final equation of Hirschberg et al.'s[11] model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Three files including expressions based on the Scott−Magat polymer solution theory[26] for modeling asphaltene (and any other organic deposit like wax) precipitation (Supporting Information 1), the details of the derivations of the proposed model expressions (Supporting Information 2), and sample flash calculation results (Supporting Information 3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ACKNOWLEDGMENTS

■ NOMENCLATURE

ANN = artificial neural network
BIP = binary interaction parameter
CPA = cubic-plus-association equation of state

4051

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EoS = equation of state
GOR = gas−oil ratio
K = equilibrium constant
M = molecular weight (g/gmol)
MEK = methyl ethyl ketone
P = pressure (MPa)
PR = Peng−Robinson
SAFT = statistical associating fluid theory
SARA = saturates, aromatics, resins, and asphaltenes
SRK = Soave−Redlich−Kwong
STO = stock tank oil
R = universal gas constant (MPa·m^3/mol·K)
T = temperature (K)
a = attractive parameter of the PR EoS[32] (MPa·m^6/mol^2) or refers to n-mer of asphaltene particles in eq 1
b = repulsive parameter of the PR EoS[32] (m^3/mol)
e = tuning parameter in eq 29
g = molar Gibbs energy
k = binary interaction parameter of EoS
m = parameter defined in eq 27
n = refers to the number of n-mer
u = energy change upon isothermal vaporization of one mole of the maltene to the ideal gas state (kJ/mol)
v = molar volume (m^3/mol)
w = weight fraction
x = mole fraction

Greek Letters

β = physical interaction parameter in eq 8
Δ = difference
Φ = volume fraction
χ = interaction parameter in Flory−Hüggins theory[24,25,109]
δ = solubility parameter (MPa$^{0.5}$)
γ = activity coefficient
μ = chemical potential
ρ = density (g/cm^3)
ω = acentric factor

Superscripts

Asph = asphaltene-rich phase
E = excess property
Oil = oil
A = asphaltene-rich phase
B = solvent(maltene)-rich phase
V = vaporization

Subscripts

a = asphaltene
c = chemical contribution in eq 3 or critical point/property in eqs 25 and 26
m = maltene
p = physical
r = reduced property
ref = reference state
w = weight

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4055

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