Molecular-Thermodynamic Framework for Asphaltene-Oil Equilibria

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Asphaltene precipitation is a perennial problem in producing and refining crude oils. To avoid precipitation, it is useful to know the solubility of asphaltenes in petroleum liquids as a function of temperature, pressure, and liquid-phase composition. In the novel molecular-thermodynamic framework presented here, both asphaltenes and resins are represented by pseudo-pure components while all other components in the solution are represented by a continuous medium that affects interactions among asphaltene and resin particles. The effect of the medium on asphaltene-asphaltene, resin-asphaltene, resin-resin pair interactions is taken into account through its density and dispersion-force properties. To obtain expressions for the chemical potential of asphaltene and for the osmotic pressure of an asphaltene-containing solution, the SAFT model is used in the framework of McMillan-Mayer theory, which considers hard-sphere repulsive, association and dispersion-force interactions. By assuming that asphaltene precipitation is a liquid-liquid equilibrium process, a variety of experimental observations can be explained, including effects of temperature, pressure, and composition on the phase behavior of asphaltene-containing fluids. For practical quantitative applications, the model outlined here requires molecular parameters that must be estimated from a few experimental data.

Introduction

For efficient production of petroleum, it is necessary to avoid precipitation of highly viscous asphaltenes lest they plug up reservoir wells and transfer lines. To prevent such precipitation, it may be useful to develop a new molecular-thermodynamic model that can describe the phase behavior of asphaltene-containing petroleum fluids. Although numerous studies have been reported (such as, Bunger and Li, 1981; Hirschberg et al., 1984; Mansoori et al., 1988; Park and Mansoori, 1988; Speight, 1991; Mushrush and Speight, 1995; Victorov and Firoozabadi, 1996; Mansoori, 1997; Pan and Firoozabadi, 1997), the mechanism of asphaltene deposition is not yet well understood. Traditional models based on classical equations of state or regular-solution theory cannot adequately represent the solubility of asphaltenes that are stabilized by resins. In this work we propose a new, promising alternative molecular-thermodynamic framework based on colloid theory.

Properties of asphaltenes

Crude oil contains a variety of substances with different chemical structure and molecular weight. Crude-oil composition varies widely depending on its source. For operational purposes, crude petroleum can be represented by three major fractions: oils, asphaltenes, and resins. Oils are mixtures of saturated hydrocarbons and aromatics of moderate molecular weight; asphaltenes refer to the fraction of crude oil insoluble in excess normal alkanes such as n-pentane or n-
heptane, but soluble in benzene or toluene at room temperature; and resins are the fraction of crude oil insoluble in liquid propane but soluble in \textit{n}-pentane at ambient conditions. Resins are often strongly adsorbed on surface-active material such as silica or alumina.

The chemical structure and physicochemical properties of asphaltenes are not well understood. However, NMR and infrared-spectroscopic data show that asphaltene molecules contain condensed polynuclear aromatic rings with alkyl side chains and heteroatoms such as N, O, S and Ni (Speight, 1991). Other experimental data suggest that asphaltene molecules can associate even at very small concentration in most solvents (Speight, 1994; Sheu et al., 1992a; Andersen and Birdi, 1991; Andersen and Speight, 1993). Asphaltene association may be due to hydrogen bonding and/or formation of charge-transfer complexes. Asphaltenes can be subfractionated into bases, acids, and neutral polar components by ion-exchange or HPLC (Mushrush and Speight, 1995).

Complex composition and chemical association make it difficult to measure accurately the molecular weights of asphaltenes. Association between asphaltene and resin molecules provides further complications. As a result, a wide range of asphaltene molecular weights has been reported (500-50,000 Da). However, data in highly polar solvents (such as pyridine) indicate that, although the molecular weights of asphaltenes are variable, they usually fall into the range 2,000 ± 500 Da (Mushrush and Speight, 1995; Acevedo et al., 1992). This conclusion is supported by mass spectrometry (Storm et al., 1991) and by molecular weights calculated from NMR measurements (Ali et al., 1990). Moreover, despite different sources, small-angle X-ray-scattering measurements suggest that all asphaltene molecules are of similar size and molecular weight (Lin et al., 1991).

X-ray diffraction experiments suggest that the structure of asphaltene can be represented by flat sheets of condensed aromatic systems interconnected by sulfide, ether, aliphatic chains, or naphthenic-ring linkages (Yen, 1990). However, some recent X-ray and neutron-scattering results suggest that asphaltene particles appear to be spherical with average radii in the range 3-6 nm (Sheu et al., 1992; Carnahan et al., 1993; Storm et al., 1994). Rheological and ultramicroscopic studies also suggest an essentially spherical shape of asphaltene particles in crude oil (Pfeiffer and Saal, 1940; Neumann et al., 1981).

There is much evidence to suggest that asphaltenes in crude oil are stabilized by resins with properties similar to those of asphaltenes, but with lower molecular weight and lower polarity (Pfeiffer and Saal, 1940). It has been shown that without a resin fraction, asphaltenes cannot dissolve in crude oil (Moschopedis and Speight, 1976; Speight, 1994). In addition, resin-asphaltene interactions appear to be preferred over asphaltene-asphaltene interactions (Moschopedis and Speight, 1976). Therefore, we expected that asphaltenes in crude oil exist as single molecules or small aggregates of asphaltene molecules peptized by resin molecules. It is likely that resin molecules associate with asphaltene molecules through electron-donor-acceptor complexes or through hydrogen bonding (Speight, 1994).

Asphaltenes can be peptized in \textit{normal-alkane} solvents by amphiphile molecules such as \textit{p}-(\textit{n}-dodecyl) benzene sulfonic acid (DBSA) and nonyl phenol (Chang and Fogler, 1994; Gonzalez and Middea, 1991). These authors found that the ability of an amphiphile to stabilize asphaltenes depends on the polarity of its head group and on the length of the alkyl tail; they suggested that the acid-base interactions between asphaltenes and natural resins may account for the stabilization of asphaltenes in crude oil.

The molecular structure of resin has received less attention than that of asphaltene (Speight, 1991). It has been postulated that resin molecules contain long paraffinic chains with naphthenic rings and polar groups (such as hydroxyl groups, acid or ester functions) interspersed throughout. The molecular weights of resins are about 800 daltons, substantially lower than those of asphaltenes (Speight, 1991). Unlike those for asphaltenes, the measured molecular weights of resins do not usually vary with the nature of the solvent or temperature. Therefore, chemical association between resin molecules is unlikely (Speight, 1991).

**Solubility of asphaltenes**

To avoid reservoir plugging and wettability reversal, much research has been directed to the solubility of asphaltenes in petroleum liquids as a function of temperature, pressure, and liquid-phase composition. The essential questions are what are the conditions for asphaltenes precipitation, and how much asphaltene precipitates at given operating conditions? Corresponding to these questions, two types of isothermal experiments are commonly used: the first measures the onset of asphaltene precipitation for a crude oil by adding a measured amount of \textit{normal-alkane} diluent or by gas injection; the second measures the amount of asphaltene precipitation obtained upon mixing a crude oil with a measured amount of a \textit{normal-alkane} diluent.

Both experimental methods are simple; extensive experimental data are reported in the literature. In general, for a given dilution ratio, the amount of asphaltene precipitated decreases as the molecular weight of the hydrocarbon diluent increases (Kokal et al., 1992). This is expected, because the solvent power (the ability of a solvent to dissolve asphaltenes) of a hydrocarbon increases with rising molecular weight of solvent. However, for the effect of normal alkanes on the onset of asphaltene precipitation, the dilution ratio (volume of diluent/volume of crude oil) at the onset point increases as the carbon number of light normal alkanes rises, and decreases with the carbon number of heavy normal alkanes (Hirschberg et al., 1984; Rassamdana et al., 1996). This observation cannot be explained by conventional solubility theory.

Concerning the effect of dilution ratio on the amount of asphaltene precipitated, it has been reported that asphaltenes, once precipitated, cannot be redissolved by an excess of diluent (Hirschberg et al., 1984; Kokal et al., 1992). Based on these experiments, it has been proposed that asphaltene precipitation is an irreversible process (Leontaritis, 1989). However, thermodynamic arguments suggest that it should be possible to redissolve asphaltene precipitated by a diluent if an excess amount of diluent is added. The observed effect of dilution ratio on the amount of asphaltene precipitation cannot be explained by Hildebrand solubility-parame-
Different trends have been reported concerning the effect of temperature on asphaltene yield (Andersen, 1995). In the propane-deasphalting process, the amount of asphaltene precipitated may rise as temperature increases. However, for normal-alkane diluents with carbon number above 5, the precipitated amount falls with increasing temperature (Fuhr et al., 1991; Ali and Al-Ghanam, 1981). Concerning the effect of pressure on asphaltene precipitation, if the pressure is higher than the bubble-point pressure of the crude oil, rising pressure raises the solubility of asphaltenes in the crude oil; on the other hand, below the bubble-point pressure, a reduction of pressure enhances solubility of asphaltenes (Hirschberg et al., 1984; Burke et al., 1990). Different effects of temperature and pressure are related to differences in liquid density and, along saturation curves, to composition. While we can qualitatively understand these experimental results (as shown below), quantitative representation is unsatisfactory when conventional theories are used.

**Models for asphaltene solubility**

Asphaltene precipitation has been the subject of numerous theoretical investigations. Most models in the literature are based on the classical Flory-Huggins polymer-solution theory coupled with Hildebrand regular-solution theory to describe the phase behavior of asphaltene-containing fluids (Hirschberg et al., 1984; Burke et al., 1990; Kokal et al., 1992; Andersen, 1994; Andersen and Stenby, 1996; Kawanaka et al., 1991; MacMillan et al., 1995). While these models can partially explain a few of the experimental results and have some use in describing selected asphaltene-precipitation phenomena in petroleum fluids, these solubility models are inadequate for explaining other experimental results.

The two main factors that determine the precipitation of asphaltenes from crude oil are not addressed in these classical models: one is the chemical association between asphaltene molecules and the other is the peptizing effect of resin molecules. Moreover, most classical models do not explicitly take into account the effect of liquid density. Therefore, it is not surprising that these models cannot provide quantitative representation of many experimental data.

An alternate method for describing solubility is provided by colloid theory. Some researchers consider asphaltenes to be solid-like particles that are suspended collooidally in the crude oil, stabilized by resin molecules. Irreversible deposition of asphaltenes has been described using colloid-science theories (Leontaritis and Mansoori, 1987). On the other hand, a thermodynamic micellization model proposed by Victorov and Firoozabadi (1996) assumes that micelles of asphaltene and resin molecules are always soluble in crude oil; asphaltene precipitation is due to the concentration of asphaltene monomers becoming higher than the solubility of asphaltenes in the crude oil without forming micelles. These micelle-based models are helpful for understanding the effect of resin on asphaltene precipitation and the mechanism of asphaltene precipitation from crude oil. While most of these models cannot readily explain the observed effect of oil density and oil composition on asphaltene-precipitation phenomena, a recent study by Pan and Firoozabadi (1997) indicates marked improvement.

We outline here a new molecular-thermodynamic framework to describe the phase behavior of asphaltene precipitation in petroleum fluids. While our model is not in final form, it shows promise because it can readily explain observed asphaltene-precipitation phenomena. Unlike other models, ours is based on an association model for particles in a continuous medium, following the McMillan-Mayer theory (Lee, 1988).

We assume that asphaltene precipitation is a liquid-liquid equilibrium process, that asphaltenes and resins can be represented by pseudo-pure components, and that all other components in the crude oil can be represented by a continuous medium that affects interactions among asphaltene and resin molecules. (While there has been speculation concerning crystallinity of the precipitated phase, there is no conclusive evidence that precipitated asphaltenes form crystals under normal conditions.) Strong associations between asphaltene molecules, and between asphaltene and resin molecules, are taken into account using the SAFT association theory (Chapman et al., 1988). Although our model follows from an idealized representation of asphaltene-containing fluids, comparison of theory and experiment indicates that essentially all experimental observations can be semiquantitatively explained. Development toward accurate quantitative representation, now in progress, requires suitable characterization of asphaltene-containing crude oils.

**Representation of Asphaltene-Containing Fluids**

To derive the thermodynamic properties for phase-equilibrium calculations, we use attractive hard spheres to represent asphaltene molecules, and attractive hard-sphere chains to represent resin molecules. Asphaltene molecules can associate with themselves and with resin molecules. All other components in the solution (oil) constitute the solvent; they are represented by a continuous medium whose density and dispersion-force properties influence interactions among asphaltene and resin molecules.

Figure 1a shows our model fluid. The large hard spheres with two black dots represent asphaltene molecules; the hard-sphere chains with one black dot at the head of each chain stand for resin molecules. The black dots denote association sites. We include asphaltene-asphaltene and asphaltene-resin associations, but there are no resin-resin associations. There are two association sites on each asphaltene molecule permitting aggregates beyond dimers. From experimental results, we expect that association between asphaltene and resin is preferred relative to that between asphaltene and asphaltene (Speight, 1994). Therefore, if present in sufficient concentration, resin molecules prevent extensive asphaltene self-association to form aggregates. In other words, asphaltene molecules are stabilized by resin molecules and become soluble in the crude oil.

The solvent power of the medium affects interactions among asphaltene and resin molecules. Suppose a diluent that dislikes both asphaltene and resin is added to the solution; in that event, both asphaltene and resin precipitate from the solution (Figure 1b). The volume of diluent required to initiate asphaltene precipitation depends on the solvent power of the diluent, that is, the dilution ratio at the onset point rises with increasing solvent power of the diluent. Light normal alkanes have low solvent power; they dislike both asphaltene
Figure 1. Two different ways of asphaltene precipitation by adding a diluent. Co-precipitated with resin (b); or predominant asphaltene precipitation with little or no precipitation of resin (c).

The diluent dislikes resin

(a)

The diluent likes resin

(b)

 solvent-rich phase

(c)

 asphaltene-rich phase

The potentials of mean force among asphaltene and resin molecules are represented by the sum of hard-sphere repulsions, van der Waals attractions, and associations. (We use potential of mean force instead of pair-interaction potential to indicate that all interactions among asphaltenes and resins occur in a medium of oil.)

Our model predicts that once asphaltenes are precipitated from a crude oil, they associate with each other to form large aggregates; these large aggregates cannot easily be redissolved by diluents. It has been observed that the amount of asphaltene precipitated is insensitive to the dilution ratio when it exceeds about 20 vol. of diluent per volume of crude oil, indicating that precipitated asphaltenes are difficult to redissolve.

Our model provides a reasonable explanation for effects of temperature and pressure. A change in temperature may result in two consequences: first, a rise in temperature improves miscibility; in the absence of specific intermolecular forces, two fluids mix more easily at high temperatures because the (negative) contribution of the entropy of mixing to the Gibbs energy of mixing increases with temperature, favoring mixing. Secondly, however, an increase in temperature also reduces liquid density, and that reduction decreases solvent power. At constant temperature, the solubility of asphaltenes decreases as the density of solvent falls. Therefore, even without considering the effect of temperature on associations, we have two opposing trends, explaining why, in some cases, raising temperature increases solubility while, in other cases, it decreases solubility.

To understand the effect of pressure at constant temperature, we first note that liquid density increases as pressure rises provided that there is no change in oil composition. Thus, at constant temperature and constant oil composition, an increase in pressure raises asphaltene solubility. However, if a vapor phase is present, an increase in pressure raises the solubility of a light vapor component (such as methane) changing oil composition toward reduced solvent power. Therefore, if a vapor phase is present, an increase in pressure is likely to reduce the solubility of asphaltene in oil.

**Molecular-Interaction Potentials**

The potentials of mean force among asphaltene and resin molecules are represented by the sum of hard-sphere repulsions, van der Waals attractions, and associations. (We use potential of mean force instead of pair-interaction potential to indicate that all interactions among asphaltenes and resins occur in a medium of oil.)

The hard-sphere potential is given by

\[ W_{ij}^{hs}(r) = \begin{cases} \infty & r < (\sigma_i + \sigma_j)/2 \\ 0 & r \geq (\sigma_i + \sigma_j)/2 \end{cases} \]  

(1)

where \( r \) denotes the center-to-center distance and \( \sigma \) is the diameter; \( i \) and \( j \) refer to two hard-spheres, here, an asphaltene molecule or one segment of a resin chain.

The attractive van der Waals potential between two large molecules in a medium can be calculated using McLachlan’s theory which relates the potential-of-mean-force function to
the dielectric properties of the molecules and the medium (Israelachvili, 1991). However, because the parameters in this theory are usually not well defined for petroleum fractions, we use a more conventional approach to calculate the van der Waals potential of mean force between two molecules in a medium, as shown in the Appendix. The potential of mean force due to van der Waals attractive interaction is

\[ W_{ij}^{vdw}(r) = -\frac{B_{ijm}}{r^6} \quad r \geq (\sigma_i + \sigma_j)/2. \]  

(2)

where \( B_{ijm} \) is an attractive energy parameter for large molecules \( i \) and \( j \) in medium \( m \).

Association between two sites is represented by a square-well potential

\[ W_{assoc}(r_{\alpha\beta}) = \begin{cases} -\xi_{\alpha\beta} & r_{\alpha\beta} < \delta_{\alpha\beta} \\ 0 & r_{\alpha\beta} \geq \delta_{\alpha\beta} \end{cases} \]  

(3)

where \( \alpha \) and \( \beta \) denote two association sites; \( r_{\alpha\beta} \) is the distance between the two sites, \( \delta_{\alpha\beta} \) is the square-well width, and \( \xi_{\alpha\beta} \) is the association energy. The minus sign signifies attractive interaction. All association sites are located on the hard-sphere surface.

**Molecular-Thermodynamic Framework**

Precipitation conditions are determined by chemical potentials of asphaltene and resin. When two liquid phases coexist at isothermal equilibrium, the chemical potential for each species is the same in both phases

\[ \mu_A' = \mu_A^*, \]  

\[ \mu_R' = \mu_R^*. \]  

(4)

(5)

where the single and double prime signs represent two equilibrated phases, \( \mu \) is chemical potential, and \( A \) and \( R \) denote asphaltene and resin chain, respectively. In addition, the osmotic pressures for the two equilibrated phases must be equal

\[ P' = P^*. \]  

(6)

where \( P \) denotes osmotic pressure. Both chemical potential and osmotic pressure can be obtained from Helmholtz energy \( A \)

\[ A = A^{id} + A^{hs} + A^{vdw} + A^{assoc} + A^{chain}. \]  

(10)

Superscripts in Eq. 10 are: \( id \) is the ideal-gas mixture of all particles prior to association and chain formation at the system temperature and concentration; \( hs \) is hard-sphere repulsions; \( vdw \) is the contribution from van der Waals attractions; \( assoc \) is the contribution from asphaltene-asphaltene, and asphaltene-resin associations; chain is the contribution from forming resin chains from hard spheres.

The Helmholtz energy for an ideal-gas mixture is given by (Lee, 1988)

\[ \frac{A^{id}}{kT} = \sum_{i=1}^{2} N_i \ln (\rho_i \Lambda_i^3) - N_i, \]  

(11)

where \( k \) is the Boltzmann constant; \( N_i \) is the number of particles \( i \), that is, asphaltene molecules, or resin segments; \( N_i \) is the total number of particles prior to any association; \( \rho_i = N_i/V \), is the number density; \( \Lambda_i \) is the de Broglie wavelength.

The contribution from repulsive hard-sphere interactions among all particles to the Helmholtz energy is obtained from the equation of Mansoori et al. (1971)

\[ \frac{A^{hs}}{kT} = \]  

\[ N_i \left[ \left( -\frac{\xi_3^2}{\xi_0^2} + \frac{3}{\xi_0} \right) \ln (1 - \xi_3) + \frac{3\xi_1\xi_2}{\xi_0(1 - \xi_3)} + \frac{\xi_2^3}{\xi_3\xi_0(1 - \xi_3)^2} \right] \]  

(12)

where

\[ \xi_n = \frac{\pi}{6} \sum_{i=1}^{2} \rho_i \sigma_i^n \quad n = 0, 1, 2, 3. \]

The contribution from van der Waals attractions in a medium is obtained from the random-phase approximation (RPA) (Grimson, 1983). In the RPA theory, the direct correlation function \( c_{ij}(r) \) is given by

\[ c_{ij}(r) = c_{ij}^0(r) - W_{ij}(r)/(kT) \]  

(13)

where \( c_{ij}^0(r) \) is the direct correlation function for the hard-sphere reference system and \( W_{ij}(r) \) is the perturbation potential of mean force for molecules \( i \) and \( j \) (prior to any association); here, \( W_{ij}(r) \) is the van der Waals interaction energy in
with a medium. Following standard thermodynamic relations, $A_{vdw}$ can be derived from Eq. 13 (Lee, 1988)

$$A_{vdw} = \frac{V}{kT} \sum_{i=1}^{2} \sum_{j=1}^{2} \rho_{i} \rho_{j} U_{ij},$$  \hspace{1cm} (14)

where $U_{ij} = 4\pi \int_{0}^{p_{f}} W_{r}^{vdw}(r) r^{2} dr$ with $\sigma_{ij} = (\sigma_{i} + \sigma_{j})/2$. In Eq. 14, $U_{ij}/V$ is the (mean-field) average pair potential energy for all $ij$ pairs; the summation gives the total potential energy of all different pairs. $U_{ij}$ is similar to parameter $a_{ij}$ in the van der Waals equation of state for mixtures.

We use the SAFT model to represent the contribution from association interactions. The Helmholtz energy due to association is given by (Wertheim, 1986; Chapman et al., 1988)

$$A_{assoc} = \frac{2}{kT} \left( \ln x_{a} + \frac{1 - x_{a}}{2} \right) + \frac{2}{kT} \left( \ln x_{b} + \frac{1 - x_{b}}{2} \right),$$  \hspace{1cm} (15)

where $x_{a}$ is the fraction of association sites $a$ (at asphaltenene molecule) that are not bonded; $x_{b}$ is the fraction of association sites $b$ (at resin molecule) that are not bonded. Association interaction can be understood as a reduction of the number of total particles; that reduction lowers the chemical potential and the compressibility factor.

In Eq. 15, $x_{a}$ and $x_{b}$ are given by (Chapman et al., 1990)

$$x_{a} = \left( 1 + 2\rho_{a} \Delta^{aa} x_{a} + \rho_{R} \Delta^{ab} x_{b} \right)^{-1},$$  \hspace{1cm} (16)

$$x_{b} = \left( 1 + 2\rho_{b} \Delta^{ab} x_{a} \right)^{-1},$$  \hspace{1cm} (17)

where $\rho_{a}, \rho_{b}$ are the number densities of asphaltenene molecules and resin chains, respectively; $\Delta^{aa}, \Delta^{ab}$ are given by

$$\Delta^{aa} = 8g_{ij}^{h} \sigma_{11} \left[ \exp(\xi^{aa}/kT) - 1 \right] \sigma_{11}^{3} \kappa^{aa},$$  \hspace{1cm} (18)

$$\Delta^{ab} = 8g_{ij}^{h} \sigma_{12} \left[ \exp(\xi^{ab}/kT) - 1 \right] \sigma_{12}^{3} \kappa^{ab},$$  \hspace{1cm} (19)

where $g_{ij}^{h}$ is the contact value of the pair correlation function in the reference system (Lee, 1988)

$$g_{ij}^{h} \left( \sigma_{ij} \right) = \frac{1}{1 - \xi_{3}} + \frac{2\sigma_{ij}}{\xi_{2}} \frac{\xi_{2}}{\left( \sigma_{i} + \sigma_{j} \right) \left( 1 - \xi_{3} \right)} \left( \frac{\sigma_{i} \sigma_{j}}{\sigma_{i} + \sigma_{j}} \right)^{2} \frac{\xi_{2}^{2}}{\left( 1 - \xi_{3} \right)^{3}},$$  \hspace{1cm} (20)

Here $\kappa^{aa}$ and $\kappa^{ab}$ are parameters related to the square-well widths for the association potentials. We assume that they are identical constants.

The contribution from the formation of the hard-sphere chain is given by (Chapman et al., 1988)

$$A_{chain} = \frac{N_{R} \left( 1 - l_{R} \right) \ln g_{22}^{h} \left( \sigma_{22} \right)}{kT},$$  \hspace{1cm} (21)

where $l_{R}$ denotes the number of segments per resin chain; $g_{22}^{h} \left( \sigma_{22} \right)$ is the contact value of the pair correlation function between resin segments. Equation 21 indicates the difference in Helmholtz energy between hard-sphere chains and a set of free hard spheres that make the chain; in the chain, each hard sphere must be in contact with its “bonded” neighbors, while in the set of free hard spheres, each hard sphere can move independently.

The molecular parameters used in our model are: size of asphaltenene particle and size of resin segment; Hamaker constants for asphaltenene, resin and medium; association-energy parameters for chemical associations; and the number of segments in each resin chain. The Hamaker constants and hard-sphere diameters of asphaltenene and resin are insensitive to temperature and pressure, but they may depend on the nature of oil. The association parameters can be assumed to be constants for a given crude oil. The Hamaker constant of the medium $H_{m}$ is calculated by adding all pair-interaction potentials (Israelachvili, 1991)

$$H_{m} = \sum_{i} \sum_{j} \pi_{2} B_{ij} \rho_{i} \rho_{j}$$  \hspace{1cm} (22)

where $i$ and $j$ indicate all components that comprise the medium and $B$ is a dispersion-energy parameter. Equation 22 indicates that the Hamaker constant of the medium depends on density and composition. For most cases, the oil is a mixture of hydrocarbons, that is, it is made of CH, CH$_{2}$, and CH$_{3}$ groups. Because the dispersion-energy parameters for all these groups are similar, for simplicity, we assume that they are the same. On the other hand, because the molecular weights of the three groups are close to each other, the total number density of these groups is determined only by the overall density of the medium. By neglecting the difference in molecular weight, the total number density of these groups can be approximated by that of the equivalent CH$_{2}$ group number density $\rho_{CH_{2}}$ given by

$$\rho_{CH_{2}} = \frac{1,000 \ N_{AV} \cdot d_{m}}{14}$$  \hspace{1cm} (23)

where $d_{m}$ is the mass-density of the hydrocarbon medium (oil free of asphaltenene and resin) in kg/m$^{3}$; $N_{AV}$ is the Avogadro constant. Density $\rho_{CH_{2}}$ depends on temperature and aromaticity.

**Effects of Medium and Temperature on Asphaltenene Precipitation**

Illustrative calculations serve to indicate the effect of medium and temperature on the phase behavior of asphaltenene-containing fluids. In Table 1, we assign reasonable, estimated molecular parameters: the Hamaker constants for as-

| Table 1. Estimated Molecular Parameters for Asphaltenene and Resin for Preliminary Calculations (7 = 298.15 K)* |
|-------------------------------|-----------------------------------|
| $\xi_{AA}/kT = 10$ | $\eta_{A} = 0.4$ | $H_{AA}/kT = 40$ | $\sigma_{A}/\sigma_{R} = 5$ |
| $\xi_{AB}/kT = 12$ | $\eta_{K} = 0.35$ | $H_{BR}/kT = 10$ | $l_{R} = 16$, $\kappa = 0.01$ |
* $\eta_{A}, \eta_{K}$ are packing fraction of “pure” asphaltenene and “pure” resin; $y = \pi \rho_{A} / \Sigma_{i} \sigma_{i}$ is the diameter of a resin segment.
phaltenes and resins are estimated from Eq. 22 using average molecular weight of 2,000 Da for asphaltene, 800 Da for resin, density of 1.2 g/mL for asphaltene and 1.0 g/mL for resin; the diameter of an asphaltene molecule is assumed to be 30 Å, as suggested by light-scattering data (Sheu et al., 1992b); and the diameter of a resin segment is assumed to be 6 Å. This estimate is for a molecule whose molecular weight is about 50 Da, because we assume that the number of segments for a resin molecule is equal to 16 and $16 \times 50$ is 800. Our use of 16 is arbitrary; it should be adjusted to experimental data as required. Pure component packing fractions $y_A$ and $y_R$ are estimated from density, molecular weight and diameters of asphaltene and resin molecules; energy parameters are in the range of chemical associations, and $K$ is in the range of those previously obtained when the SAFT model is applied to other systems.

Phase equilibria are calculated using Eqs. 4-6 coupled with three material-balance equations

$$ N_A + N_R = N_A^0, \quad (24) $$

$$ N_R' + N_R'' = N_R^0, \quad (25) $$

$$ N_m + N_m'' = N_m^0, \quad (26) $$

where superscript 0 indicates before phase separation; $N_m$ is the total number of medium molecules. Because it is difficult to predict accurately the density of a heavy crude oil, and the change in total volume usually is small after phase separation, we replace Eq. 26 with $V' + V'' = V^0$, where $V'$ and $V''$ are total volumes in phase ' and phase " respectively; $V^0$ is the total volume before phase separation. Given temperature, total volume, and the total numbers of asphaltene and resin molecules, from Eqs. 4-6 Eqs. 24-25, and $V' + V'' = V^0$, we can obtain $N_A', N_A'', N_R', N_R'', V'$ and $V''$.

Figures 2a and 2b show the effect of the medium on the phase envelopes of crude oils containing asphaltene and resin. Here, in the oil, $\eta_A$ is the packing fraction of asphaltene and $\eta_R$ is that of resin segments; $\eta_A = (\pi/6)\rho_A \sigma_A^3; \eta_R = (\pi/6)\rho_2 \sigma_2^3$ (2 refers to resin segments; the packing fraction of resin chains is the same as that of resin segments). The connected solid lines represent the phase boundary; the area inside the curve represents the two-phase region; the area outside the curve represents the one-phase region where no phase separation occurs. Figure 2a shows that, as the Hamaker constant of the medium increases, the two-phase region becomes smaller; in other words, the system becomes more miscible. However, Figure 2b shows that, as the Hamaker constant of the medium increases, the two-phase region becomes larger; therefore, the system becomes less miscible. For normal alkanes, the Hamaker constant varies approximately from 5 kT to 13 kT at ambient conditions; the Hamaker constants shown here could correspond to a medium that is a mixture of normal alkanes. The Hamaker constants in Figure 2a are close to those for light normal alkanes, whereas the Hamaker constants in Figure 2b correspond to those for heavy normal alkanes. The opposite trends in Figures 2a and 2b explain why there is a maximum dilution ratio at the onset of asphaltene precipitation when a crude oil is diluted with normal alkanes of rising carbon number.

Figures 3a and 3b show the effect of changing the medium on the amount of asphaltene and resin precipitation at given initial concentrations ($\eta_R^0 = 0.2$). At low resin concentration ($\eta_R^0 = 0.01)$, the amount of asphaltene precipitated (in the dense phase) declines as the Hamaker constant of the medium increases; the same holds for the resin. These results agree with experimental observations on the effect of diluent on the amount of asphaltene precipitation. However, our model also predicts that at somewhat higher resin concentrations ($\eta_R^0 = 0.0151$), the effect of medium on the amount of asphaltene precipitation becomes nonmonotonic. This nonmonotonic behavior may be induced by the maximum resin solubility near $H_m/kT = 10$. In general, the amount of asphaltene
characterized, and all model parameters must be obtained by correlation with some experimental data. Unfortunately, most crude-oil characterization data provide only very little information on the heavy-end components. In addition, accurate experimental data for asphaltene precipitation are often limited for a given oil. Therefore, although asphaltenes and resins may be quite different from one crude oil to another, we have assumed here that they have common molecular weight, density, molecular size, and number of association sites, as given in Table 2. We do not claim that these parameters are optimized or that they are accurate for any crude oil; however, our assumptions reduce significantly the number of unknowns in our model.

To illustrate, we compare model calculations with experimental data for the effect of diluent on asphaltene precipitation reported by Kokal et al. (1992). Oil-characterization data are given in Table 3. For each crude oil, we have two adjustable parameters, that is, association energies between asphaltene and asphaltene, and between asphaltene and resin. We assume that the asphaltene-resin association parameter is solvent-dependent, as given in Table 4. Figures 7 and 8 compare our calculated results with experimental data. Adjustable parameters are obtained from data regression. Calculated results agree well with experiments at high dilution ratios, but not at low dilution ratios, probably because of our oversimplified assumptions concerning crude-oil characterization.

Figure 9 shows detailed results for asphaltene-precipitation calculations. For our illustrative purposes here, we use Suffield crude oil (Table 3) titrated with n-hexane. In these calculations, densities were calculated using volume additivity (no excess volume). Figure 9a gives the overall densities of the asphaltene-rich phase and the solvent-rich phase. As shown on the ordinate, the density of the asphaltene-rich phase changes very little as the dilution ratio rises. The den-

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**Figure 6.** Phase diagrams for an asphaltene-resin-n-heptane ternary system at different temperatures.

**Table 2.** Pseudo-Universal Parameters for Asphaltene and Resin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Asphaltene</th>
<th>Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>2,000</td>
<td>800</td>
</tr>
<tr>
<td>$d$</td>
<td>1.25</td>
<td>1.0</td>
</tr>
<tr>
<td>$\eta_A$</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>$\eta_R$</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

*This refers to the diameter of a resin segment. We also assume that each resin chain has 16 segments.

**Table 3.** Characterizing Oil Parameters and Oil Specific Model Parameters for Suffield Oil and Lindbergh Oil

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Suffield</th>
<th>Lindbergh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL)</td>
<td>0.9474</td>
<td>0.968</td>
</tr>
<tr>
<td>(21°C and 1 atm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wt. % Asphaltene</td>
<td>13</td>
<td>21</td>
</tr>
<tr>
<td>wt. % Resin</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Molar Vol., m$^3$/kg·mol</td>
<td>0.38</td>
<td>0.51</td>
</tr>
<tr>
<td>Avg. molecular wt.</td>
<td>360</td>
<td>493</td>
</tr>
<tr>
<td>$\epsilon_4/\kappa T$ ($T = 294$ K)</td>
<td>8.5</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Table 4. Solvent-Dependent Asphaltene-Resin Association

<table>
<thead>
<tr>
<th>Parameter</th>
<th>gAflT (Y' = 294 K)</th>
<th>Y'</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>0.78</td>
<td>0.75</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.72</td>
<td>1.074</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.69</td>
<td>-1.071</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.85</td>
<td>-0.998</td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.88</td>
<td>-1.000</td>
</tr>
</tbody>
</table>

Table 4. Solvent-Dependent Asphaltene-Resin Association

Parameter $g_{AflT}$/$kT (T = 294 K)$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>4.5</th>
<th>4.2</th>
<th>4</th>
<th>3.88</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suffield Oil</td>
<td>7</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lindbergh Oil</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7. Calculated vs. experimental asphaltene precipitation by adding n-alkanes to Suffield crude oil.

Figure 8. Calculated vs. experimental asphaltene precipitation by adding n-alkanes to Lindbergh crude oil.

Figure 9. Densities and compositions of the coexisting phases after asphaltene precipitation for Suffield oil (Table 3) at ambient temperature and pressure.

Application of our model to more realistic systems, including the effect of temperature and pressure on asphaltene precipitation, is now under active investigation. We find that once model parameters are fixed from some experimental data, our model can predict the effects of temperature, pressure, and composition on the phase behavior of asphaltene-containing fluids.

Conclusions

A molecular-thermodynamic framework based on colloid theory and the SAFT model has been established to describe precipitation of asphaltene from crude oil. Calculated results indicate that essentially all observed experimental results on the phase behavior of asphaltene-containing fluids can be explained semiquantitatively by the current model. For practical quantitative applications, the framework outlined here requires molecular parameters that must be estimated from a few experimental data for the particular system of interest.

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Literature Cited


Appendix: van der Waals Interaction between Two Molecules in a Medium

Following well-established principles from the colloid theory (Israelachvili, 1991), Figure 1A shows how to relate the interaction between two molecules to that between two half-spaces in vacuum or in a medium. The left side represents the interaction between two hard spheres, and the interaction between two half-spaces in vacuum; the right side represents those interactions in a medium. Equation A1 gives \( W_{ij}^{vdw} \), the van der Waals potential energy between two

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molecules in vacuum (London’s equation), where $B_{ij}$ is an energy parameter. The interaction energy between two half spaces is calculated by adding all the pair interactions between molecules in different half spaces. The van der Waals interaction energy per surface area is given by Eq. A3 where $H_{ij}$ is Hamaker’s constant; $D$ is the distance between two parallel half-spaces. Equation A5 gives the relation between $B_{ij}$ and Hamaker’s constant $H_{ij}$, where $\rho_i$ and $\rho_j$ represent, respectively, the molecular number density of half space $i$ and $j$. Similar equations can be written for the interactions between two molecules or between two half spaces in a medium. The van der Waals interaction energy between two molecules in a medium can be written in the form of London’s equation according to McLachlan’s theory. In Eq. A4, $H_{imj}$ is the Hamaker constant of $i$ and $j$ interacting in a medium $m$. Hamaker constant $H_{imj}$ can be related by Eq. A6 to the molecular number densities of $i$ and $j$, and the interaction parameter between two molecules $i$ and $j$ in a medium $B_{imj}$. Equation A6 gives a theoretical combining rule to estimate the Hamaker constant in a medium from Hamaker constants of pure materials $i$, $j$ and medium $m$ in vacuum (Israelachvili, 1991). From these relations, we can calculate the van der Waals potential-of-mean force function between two molecules (attractive hard spheres) in a medium using the Hamaker constants of pure $i$, pure $j$ and pure medium, and from the number densities of $i$ and $j$.

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