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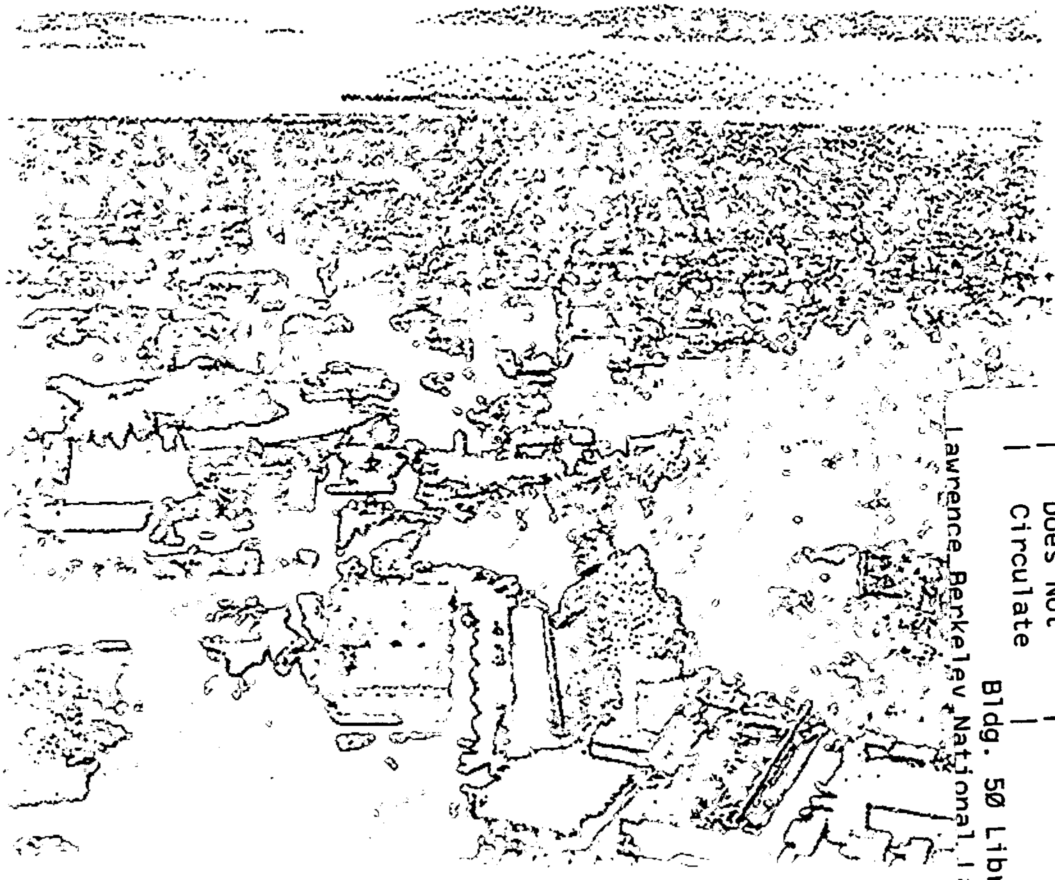

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ABSTRACT

Asphaltene precipitation is a perennial problem in production and refinery of crude oils. To avoid precipitation, it is useful to predict the solubility of asphaltenes in petroleum liquids as a function of temperature, pressure and liquid-phase composition. In the molecular-thermodynamic model presented here, both asphaltenes and resins are represented by pseudo-pure components, and all other components in the solution are represented by a continuous medium which 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 molecular-dispersion properties. To obtain expressions for the chemical potential of asphaltene and for the osmotic pressure of an asphaltene-containing solution, we use the integral theory of fluids coupled with the SAFT model to allow for asphaltene aggregation and for adsorption of resin on asphaltene particles. With these expressions, a variety of experimental

observations can be explained including the effects of temperature, pressure and composition on the phase behavior of asphaltene-containing fluids. For engineering application, the molecular parameters in this model must be correlated to some macro-properties of oil such as density and molecular weight. When such correlations are established, it will be possible to calculate asphaltene-precipitation equilibria at a variety of conditions for realistic systems.

Introduction

For efficient production of petroleum, it is necessary to avoid precipitation of solid-like asphaltenes lest they plug up reservoir wells and transfer lines. To prevent such precipitation, it is useful to develop a molecular-thermodynamic model which can describe the phase behavior of asphaltene-containing petroleum fluids. Although numerous studies have been reported(e.g., Bunger and Li, 1981; Hirschberg et al, 1984; Mansoori et al, 1988; Speight, 1991; Mushrush and Speight, 1995; Victorov and Firoozabadi, 1996), the mechanism of asphaltene deposition is not well understood; currently available models are not satisfactory for reliable engineering design. In this work we propose a not-previously-used molecular-thermodynamic framework which is promising for correlating asphaltene-oil phase behavior.

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 is often represented by three major fractions: oils, resins and asphaltenes. Oils are defined as all saturated hydrocarbons and aromatics of moderate molecular weight; asphaltenes are the fraction of crude oil insoluble in excess normal alkanes such as n-pentane or n-heptane at room temperature; and resins are the fraction of crude oil insoluble in liquid propane but soluble in n-pentane at ambient conditions.

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 (N, O, S, Ni etc.)(Speight, 1991). Other experimental data suggest that asphaltene molecules can associate with each other even at very small concentration in most solvents(Speight, 1994; Sheu et al, 1991; Andersen and Birdi, 1991; Andersen and Speight, 1994). 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. Also, associations between asphaltene and resin molecules provide further complications. As a result, a wide range of asphaltene molecular weights has been reported in the literature (500-50000 daltons). 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 2000±500 daltons (Mushrush and Speight, 1995; Acevedo et al., 1992). This conclusion is supported by mass spectrometry(Storm et al., 1990) and by molecular weights calculated from NMR measurements(Ali, et al, 1990). Moreover, small-angle X-ray-scattering measurements show that, despite different sources, there are fundamental units for asphaltenes with a radius of gyration near 4.0 nm (Lin et al., 1991). These results imply that different fractions of asphaltenes contain associated molecules whose units are of similar size and molecular weight.

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(Kwan and Yen, 1976). However, some recent X-ray and neutron scattering results on the shape and average size of asphaltene particles in vacuum residue or toluene suggest that asphaltene particles appear to be spherical with average radii in the range 3-6 nm (Sheu et al, 1992; 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 polarity (Nellensteyn, 1938; Pfeiffer and Saal, 1940; Ray et al, 1957; Yen, 1974). It has been shown that without a resin fraction, asphaltenes cannot dissolve in crude oil (Koots and Speight, 1975). In addition, resin-asphaltene interactions appear to be preferred over asphaltene-asphaltene interactions (Moschopedis and Speight, 1976).Therefore, it is likely that asphaltenes in crude oil exist as single molecules peptized by resin molecules. It seems that resin molecules associate with asphaltene molecules through electron-donor-acceptor complexes or through hydrogen bonding (Speight, 1994).

Asphaltenes can be peptized in normal alkane solvents by amphiphile molecules such as p-(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, and 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. It has been postulated that resin molecules contain long paraffinic chains with naphthenic rings, polar groups (such as hydroxyl groups, acid functions, ester functions et al.) interspersed throughout (Speight, 1991). The molecular weights of resins are about 800 daltons, substantially lower than those of asphaltenes. Unlike those for asphaltenes, the molecular weights of resins do not usually vary with the nature of the solvent or temperature. Therefore, chemical association between resin molecules is unlikely.

Solubility of Asphaltenes

Asphaltenes precipitated from crude oil can cause severe problems such as reservoir plugging and wettability reversal. Consequently, 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 first, what are the conditions for asphaltenes precipitation, and second, how much asphaltene precipitates at given operation conditions. Corresponding to these questions, two types of experimental studies are commonly reported in the literature: one measures the onset of asphaltene precipitation for a crude oil by adding a measured amount of normal-alkane diluent or by gas injection; the other measures the amount of asphaltene precipitation obtained upon mixing a crude oil with a measured amount of a normal alkane diluent.

Both experimental methods are simple; extensive experimental data are reported in the literature and in reports of petroleum companies. In general, it has been observed that, for a given dilution ratio, the amount of asphaltene precipitated decreases as the molecular weight of the hydrocarbon diluent increases (Mitchell and Speight, 1972; Lin et al, 1991; Kokal et al, 1992). This observation is expected because the solvent power of a hydrocarbon increases with rising molecular weight. However, for the effect of normal alkanes on the onset of asphaltene precipitation, it has been observed that 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 as the carbon number of heavy normal alkanes rises (Hotier and Robin, 1983; Norsk Hydro, 1988; Hirschberg et al, 1984; Rassamdana, 1996). This observation is not easily explained; as yet, no qualitative explanation has been reported in the literature.

Concerning the effect of dilution ratio on the amount of asphaltene precipitated, experiment shows that asphaltenes, once precipitated, cannot be redissolved by excess amount of diluents(Hirschberg et al, 1984; Kokal et al, 1992; Kamath et al, 1994). Based on these experiments, it has been proposed that asphaltene precipitation is an irreversible process(Leontaritis, 1989; Lichaa, 1977; Lichaa and Herrera, 1975).Thermodynamic arguments suggest that asphaltenes precipitated by a diluent should be redissolved if an excess amount of diluent is added, contrary to observation. The observed effect of dilution ratio on the amount of asphaltene precipitation cannot be explained by Hildbrand solubility-parameter theory.

Different trends have been reported concerning the effect of temperature on asphaltene yield (Andersen, 1994). In the propane deasphalting process, the amount of asphaltene precipitated rises 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-Ghannam, 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 asphaltene in the crude oil; on the other hand, below the bubble-point pressure, a reduction of pressure enhances solubility of asphaltene (Hirschberg et al, 1984; Burke et al, 1990). Different trends concerning the effect of temperature and pressure probably arise from differences in liquid density or composition. While we can qualitatively understand these experimental results, quantitative representation is still far from satisfactory.

Models for Asphaltene Solubility

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

An alternate method for describing solubility models is provided by colloid theory. Some researchers consider asphaltenes as solid particles that are suspended colloidally in the crude oil, stabilized by resin molecules. Deposition of asphaltene is an irreversible process that can be described using theories in colloid science (Leontaritis et al, 1989). On the other hand, a thermodynamic micellization model proposed by Victorov and Firoozabadi (1996) assumes that micelles made of asphaltene and resin molecules are always soluble in crude oil; asphaltene precipitation is due to the concentration of asphaltene monomer higher than the solubility of asphaltene in the crude oil without forming micelles. These colloid- based models are helpful for understanding the effect of resin on asphaltene precipitation and the mechanism of asphaltene precipitation from crude oil. However, these models cannot readily explain the effect of oil density and composition.

In this paper, we outline a new molecular-thermodynamic method to describe the phase behavior of asphaltene precipitation in petroleum fluids. Our model represents asphaltene and resin by pseudo-pure components, and all other components in the crude oil by a continuous medium that affects interactions among asphaltene and resin molecules. Strong associations between asphaltene molecules, and between asphaltene and resin molecules, are taken unto account using an association theory called SAFT (Chapman et al, 1986). Although our model provides an idealized representation of asphaltene-containing fluids, preliminary calculations indicate that essentially all experimental observations can be semi-quantitatively explained. Development toward accurate quantitative representation is now in progress.

Model Fluids

Thermodynamic properties of asphaltene-containing fluids are determined by intermolecular forces between the molecules of the mixture. To derive the thermodynamic properties for phase-equilibrium calculation, 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 that influences interactions among asphaltene and resin molecules.

Figure 1a gives a schematic representation of 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 the association between asphaltene and resin is preferred relative to that between asphaltene and asphaltene. Therefore, if present in sufficient concentration, resin molecules prevent extensive asphaltene self-association to form big 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 solution (Figure 1b). The volume of diluent required to initiate asphaltene precipitation depends on the solvent power of the diluent, i.e., the dilution ratio at the onset point rises with increasing the solvent power of the diluent. Light normal alkanes have low solvent power; they dislike both asphaltene and resin. Therefore, as observed in experiments, for light alkanes, the dilution ratio at the onset of asphaltene precipitation rises as the carbon number of normal-alkane diluents increases. However, if a diluent likes resin but dislikes asphaltene, only asphaltenes precipitate(Figure 1c). In that case, precipitation of asphaltene is due to a decrease in the interaction between asphaltenes relative to that between asphaltene and resin. As the solvent power of the diluent rises, attraction between resin and solvent becomes strong; the capacity of resin molecules to stabilize asphaltene molecules becomes weak, causing asphaltenes to precipitate. Because heavy normal alkanes are good solvents for resins but not for asphaltenes, the dilution ratio at the onset of asphaltene precipitation decreases as the carbon number of heavy normal alkane diluents rises.Later, we give a quantitative calculation of the effect of the medium (oil) on precipitation.

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. In experiments, it has been observed that the amount of asphaltene precipitated is insensitive to the dilution ratio when it exceeds about 20 volumes of diluent per volume of crude oil, indicating that asphaltenes precipitated are difficult to redissolve.

A similar qualitative analysis can be given to explain the effects of temperature and pressure. A change in temperature may result in two consequences: first, a rise in temperature leads to improve miscibility; two fluids mix more easily at high temperatures because the contribution of the entropy of mixing to free energy increases with temperature, favoring mixing. Second, an increase in temperature also reduces liquid density, and that reduction decreases solvent power. The solubility of asphaltenes decreases as the density of solvent falls. Therefore, we have two opposing trends, explaining why in some cases, raising temperature increases solubility while in other cases, it decreases solubility.

Concerning liquid pressure, liquid density increases as pressure rises provided that there is no change in composition. However, composition may readily change with pressure because an increase in pressure raises the solubility of a gas in the liquid phase.

Molecular-Interaction Potentials

Molecular interactions in our model fluids are represented by hard-sphere repulsions, van der Waals attractions in a continuous medium, and associations. The hard-sphere potential of mean force between two hard spheres i and j is given by:

$$W_{ij}^{hs}(r) = \begin{cases} \infty & r < (\sigma_i + \sigma_j)/2 \\ 0 & r \geq (\sigma_i + \sigma_j)/2 \end{cases}, \tag{1}$$

where r is the center-to-center distance, and σ is the diameter of an asphaltene molecule or of one segment of a resin molecule.

The attractive van der Waals energy between two large molecules in a medium can be calculated using McLachlan's theory which relates the potential function to the dielectric properties of the molecules and the medium (Israelachvili, 1991). However, the parameters used in this theory are usually not well defined for complicated petroleum fractions. Here we use a more conventional approach to calculate the van der Waals potential of mean force between two molecules in a medium. Figure A shows how to derive the desired equation for van der Waals attraction in a medium. The final equation for van der Waals attractive energy between two hard spheres in a medium is:

$$W_{ij}^{vdw}(r) = -\frac{B_{imj}}{r^6} \qquad r \geq (\sigma_i + \sigma_j)/2. \tag{2}$$

where B_{imj} is an attractive energy parameter for large molecules i and j in medium m. A derivation is given in Appendix A.

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

$$W_{\alpha\beta}^{assoc}(r_{\alpha\beta}) = \begin{cases} -\zeta_{\alpha\beta} & r_{\alpha\beta} < \delta_{\alpha\beta} \\ 0 & r_{\alpha\beta} \geq \delta_{\alpha\beta} \end{cases}, \tag{3}$$

where α and β denote two association sites; $r_{\alpha\beta}$ is the distance between the two sites; $\delta_{\alpha\beta}$ is the square-well width; and $\zeta_{\alpha\beta}$ 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. If two phases coexist at equilibrium,

$$\mu_A^{'} = \mu_A^{''} , \tag{4}$$

$$\mu_R^{'} = \mu_R^{''} , \tag{5}$$

$$P^{'} = P^{''} . \tag{6}$$

where ' and " represent two equilibrated phases, μ is chemical potential, and P is osmotic pressure.. Both the chemical potential and the osmotic pressure are obtained from the Helmholtz energy A

$$\mu_A = \left(\frac{\partial A}{\partial N_A} \right)_{T,V,N_R} \tag{7}$$

$$\mu_R = \left(\frac{\partial A}{\partial N_R} \right)_{T,V,N_A} \tag{8}$$

$$P = -\left(\frac{\partial A}{\partial V} \right)_{T,N_A,N_R} \tag{9}$$

where N is the number of molecules.

To derive the Helmholtz energy, we use perturbation theory. Our method is similar to that for the SAFT model for association and chain molecules (Chapman et al, 1990; Ghonasgi and Chapman, 1994). The reference system is a mixture of hard spheres with two different sizes. The big hard spheres represent asphaltenes, and the small ones represent the segments of resin molecules which are represented by short chains in our model fluid. Van der Waals attractions, associations, and chain connectivity are taken into account by perturbation methods. The total Helmholtz energy A contains five contributions,

$$A = A^{id} + A^{hs} + A^{vdw} + A^{assoc} + A^{chain} , \tag{10}$$

The superscripts in Eq (4) are: *id*, ideal-gas mixture of all particles prior to association and chain formation; *hs*, the contribution of hard-sphere repulsions; *vdw*, the contribution of van der Waals attractions; *assoc*, the contribution of associations of asphaltene-asphaltene, and asphaltene-resin; *chain*, the entropic contribution of forming a chain from hard spheres.

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

$$\frac{A^{id}}{kT} = \sum_{i=1}^{2} N_i \ln(\rho_i \Lambda_i^3) - N_t . \tag{11}$$

where k is the Boltzmann constant; T is absolute temperature; N_i is the number of particles i, 1=asphaltene, 2=resin segment; N_t is the total number of particles; $\rho_i = N_i/V$, is the number density where V is volume; Λ_i is the de Broglie wave length of particle i.

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

$$\frac{A^{hs}}{kT} = N_t \left\{ \left[\frac{\xi_2^3}{\xi_0 \xi_3^2} - 1 \right] \ln(1-\xi_3) + \frac{3\xi_1 \xi_2}{\xi_0 (1-\xi_3)} + \frac{\xi_2^3}{\xi_3 \xi_0 (1-\xi_3)^2} \right\}$$

$$\xi_n = \frac{\pi}{6}\sum_{i=1}^{2}\rho_i\sigma_i^n \qquad n=0,1,2,3 \tag{12}$$

where σ_i is the hard-sphere diameter of particle i.

The contribution of van der Waals attractions in a medium is taken into account using the random-phase-approximation(RPA) form of integral equation theory. (Grimson, 1983). In the RPA theory, the direct correlation function $c_{ij}(r)$ is given by:

$$c_{ij}(r) = c_{ij}^{0}(r) - W_{ij}(r)/(kT) \tag{13}$$

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 between molecules i and j. For A^{vdw}, we use Eq.(2), the van der Waals interaction energy in a medium. Following standard thermodynamic relations, A^{vdw} is,

$$\frac{A^{vdw}}{kT} = \frac{V}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}\rho_i\rho_j\frac{U_{ij}}{kT}. \tag{14}$$

where V is volume, $U_{ij} = 4\pi\int_{\sigma_{ij}}^{\infty} W_{ij}^{vdw}(r)r^2dr$; and $\sigma_{ij}=(\sigma_i+\sigma_j)/2$. The physical meaning of Eq(14) is clear: U_{ij}/V is the average pair potential energy for all ij pairs neglecting liquid structure, and 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.

As in the SAFT model, we use Wertheim's thermodynamic perturbation to represent the contribution of association interactions. The Helmholtz energy due to association is given by (Wertheim, 1984; Chapman, et al., 1988),

$$\frac{A^{assoc}}{kT} = 2N_A\left(\ln x_\alpha + \frac{1-x_\alpha}{2}\right) + N_R\left(\ln x_\beta + \frac{1-x_\beta}{2}\right) \tag{15}$$

where N_A is the number of asphaltene molecules; N_R is the number of resin molecules; x_α is the fraction of association site α (at asphaltene molecule) that is not bonded; x_β is the fraction of association site β (at resin molecule) that is not bonded. Physically, an association interaction can be understood as a reduction of the number of particles; that reduction lowers the chemical potential and the compressibility factor.

In Eq(15), x_α, and x_β are given by(Chapman et al, 1990)

$$x_\alpha = (1 + 2\rho_A \Delta^{\alpha\alpha} x_\alpha + \rho_R \Delta^{\alpha\beta} x_\beta)^{-1}, \tag{16}$$

$$x_\beta = (1 + 2\rho_A \Delta^{\alpha\beta} x_\alpha)^{-1}, \tag{17}$$

where ρ_A, ρ_R are the number densities of asphaltene and resin molecules; $\Delta^{\alpha\alpha}$, $\Delta^{\alpha\beta}$ are given by,

$$\Delta^{\alpha\alpha} = g_{11}^{hs}(\sigma_{11})[\exp(\zeta^{\alpha\alpha} / kT) - 1]\sigma_{11}^3 \kappa^{\alpha\alpha} \tag{18}$$

$$\Delta^{\alpha\beta} = g_{12}^{hs}(\sigma_{12})[\exp(\zeta^{\alpha\beta} / kT) - 1]\sigma_{12}^3 \kappa^{\alpha\beta} \tag{19}$$

where $g_{ij}^{hs}(\sigma_{ij})$ is the contact value of the pair correlation function in the reference system,

$$g_{ij}^{hs}(\sigma_{ij}) = \frac{1}{1-\xi_3} + \frac{3\sigma_i\sigma_j}{(\sigma_i+\sigma_j)}\frac{\xi_2}{(1-\xi_3)^2} + 2\left(\frac{\sigma_i\sigma_j}{\sigma_i+\sigma_j}\right)^2 \frac{\xi_2^2}{(1-\xi_3)^3}; \tag{20}$$

$\kappa^{\alpha\alpha}$ and $\kappa^{\alpha\beta}$ are parameters related to the square-well widths for the association potentials. Here we assume that they are a universal constant.

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

$$\frac{A^{chain}}{kT} = N_R(1-l_R)\ln\left[g_{22}^{hs}(\sigma_{22})\right], \tag{21}$$

where N_R is the number of resin molecules; l_R is the number of segments per resin molecule; $g_{22}^{hs}(\sigma_{22})$ is the contact value of the pair correlation function between resin segments. Physically, Eq(21) indicates the difference between a hard-sphere chain and a set of free hard spheres that make the chain; In the chain, each hard sphere must be present at the contact of its neighbors, while in the set of free hard spheres, it can move independently.

The molecular parameters used in our model are: size of asphaltene particles, and size of resin segment; Hamaker constants for asphaltene, resin and medium; association-energy parameters for chemical associations; and the number of segments in each resin molecule. The Hamaker constants and hard-sphere diameters of asphaltene and resin are insensitive to temperature, pressure and liquid composition, but they may vary from one oil to another. The association parameters can be assumed as constants for a given crude oil. The Hamaker constants of the medium depend on temperature and composition. If the medium is a simple mixture of hydrocarbons, the medium can be considered as a pure liquid of CH_2 groups. The number density of CH_2 group depends on temperature and composition (aromaticity). The Hamaker constant of this "pure liquid" can be calculated using Eq(A-5) in Figure A1. In this case, B_{ij}, the energy parameter between two CH_2 groups in vacuum, is a known constant; ρ_i or ρ_j is the number density of CH_2 groups in the hydrocarbon. ρ_{CH2} can be calculated using the mass density of the hydrocarbon by

$$\rho_{CH_2} = \frac{1000 \cdot N_{AV} \cdot d_m}{14} \tag{22}$$

where d_m is the mass density of the hydrocarbon medium in kg/m^3; 14 is the molecular weight of a CH_2 group in g/mol; N_{AV} is the Avogadro constant. If there are other components in the medium, the Hamaker constant of the medium can be calculated by

$$H_{mm} = \sum_i \sum_j \pi^2 B_{ij} \rho_i \rho_j \tag{23}$$

where i and j indicate all components that comprise the medium.

Effects of Medium and Temperature on Asphaltene Precipitation

Some preliminary calculations have been performed to establish the effect of medium and temperature on the phase behavior of asphaltene-containing fluids. In this primary stage of modeling the phase behavior of asphaltene-containing fluids, we assign reasonable estimated values to each molecular parameter used in our molecular-thermodynamic model. Table 1 gives these estimated parameters.

Phase equilibria are calculated using Eqs. (4), (5) and (6). The phase envelopes of fluids containing asphaltene and resin, and the amount of asphaltene precipitated at a given condition can be obtained by a flash calculation where the three equations of phase equilibrium (Eqs 7-9) are coupled with three material-balance equations:

$$N_A' + N_A'' = N_A^0 , \tag{24}$$

$$N_R' + N_R'' = N_R^0 , \tag{25}$$

$$N_m' + N_m'' = N_m^0 . \tag{26}$$

where superscript 0 denotes before phase separation, N_m is the total moles of medium molecules.

Figures 2a and 2b show the effect of the medium on the phase envelopes of crude oils containing asphaltene and resin. Here η_A is the packing fraction of asphaltene, and η_R is that of resin segments; $\eta_A = \frac{\pi}{6}\rho_1\sigma_1^3$; $\eta_R = \frac{\pi}{6}\rho_2\sigma_2^3$. 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 stable. However, Figure 2b shows that, as the Hamaker of the medium increases, the two-phase region becomes larger; therefore, the system becomes more unstable. 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. These two different trends explain why there is a maximum dilution ratio at the onset of asphaltene precipitation when a crude oil is titrated with normal alkanes.

Figure 3 shows the effect of the medium on the amount of asphaltene precipitation. In this case, we begin with a given concentration of asphaltene and resin which is in the two-phase region. We calculate the fractions of asphaltene and resin precipitated for different media. The amount of asphaltene precipitated (in the dense phase) rises as the Hamaker constant of the medium increases; the same holds for the resin. This calculation corresponds to the experiments which measure the amount of asphaltene precipitated for different normal alkanes at a given dilution ratio. The calculated result agrees with experimental observations on the effect of diluent on asphaltene precipitation.

Figure 4a shows the effect of dilution ratio on the amount of asphaltene precipitated. To explore the observation that asphaltenes, once precipitated from a crude oil, cannot be redissolved by diluents, we use a solution whose concentrations of asphaltene and resin are located in the two-phase region, and a diluent which is the same as the medium. The amount of asphaltene precipitated after phase separation is calculated for different dilution ratios. While the amount of asphaltene precipitated depends on the Hamaker constant of the medium or diluents, Figure 4a shows that, after the dilution ratio has reached 20, the amount of precipitation is insensitive to the dilution ratio for all solvents. In experiments reported in the literature, the maximum dilution ratio is about 50. Figure 4b shows that as the dilution ratio goes to 200, the amount of asphaltene precipitated declines, and the rate of change in the amount of precipitation depends on the solution power of the solvent. These results confirm the observed qualitative conclusions on the effect of diluent on asphaltene precipitation.

Figures 5a and 5b present the non-monotonic effect of temperature on asphaltene precipitation in different n-alkanes. Here the densities of propane and n-heptane are calculated using a method proposed by Aalto et al(1996). For propane, in the common temperature range used in experiments, the amount of asphaltene precipitated rises as temperature increases. However, for n-heptane, the solubility of asphaltene increases as temperature rises, or the amount of precipitate falls with increasing temperature. These results confirm the observed opposing trends concerning the effect of temperature on asphaltene precipitation when using n-alkane diluents.

Figure 6 shows the effect of temperature on the phase behavior of a ternary system containing asphaltene, resin and n-heptane. As the temperature rises, the two-phase region decreases and the system becomes more stable. This result also agrees with experimental observations.

All of the above calculated results are based on reasonable estimated molecular parameters. For good quantitative agreement with experiment, the parameters must be optimized.

Conclusions

A theoretically-based molecular-thermodynamic model has been established to describe the phase behavior of asphaltene precipitation from crude oil. Preliminary calculated results indicate that essentially all observed experimental results on the phase behavior of asphaltene-containing fluids can be explained by this model. For engineering application, the molecular parameters in this model must be correlated to some macro-properties of oil such as density and average molecular weight. With these correlations, asphaltene-precipitation equilibria can then be calculated at a variety of conditions for realistic systems.

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Appendix: van der Waals Interaction Between Two Molecules in a Medium.

Figure A1 shows how to relate the interaction between two molecules to that between two surfaces in vacuum and in a medium. The left side represents the interaction between two hard spheres, and the interaction between two surfaces in vacuum; the right side represents those interactions in a medium. Equation (A-1) gives W_{ij}^{vdw}, the van der Waals potential energy between two molecules in vacuum by London's equation, where B_{ij} is an energy parameter. The interaction energy between two surfaces is calculated by adding all the pair interactions between molecules in different surfaces. The van der Waals interaction energy per surface area is given by Equation (A-3) where H_{ij} is the Hamaker's constant; D is the distance between two parallel surfaces. Equation (A-5) gives the relation between B_{ij} and Hamaker's constant H_{ij}, where ρ_i and ρ_j represent, respectively, the molecular number densities of surface i and j. Similar equations can be written for the interactions between two molecules and between two surfaces 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 the exact McLachlan's theory. In Equation (F-4), H_{imj} is the Hamaker constant of i and j interacting in a medium m. That Hamaker constant can be related by Equation (A-6) to the molecular number densities of i and j, and the interaction parameter between two molecules in a medium, B_{imj}. Equation (A-6) gives a 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). By these steps, we can calculate the van der Waals potential function between two molecules(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.

Table 1 Estimated molecular parameters for asphaltene and resin for preliminary calculations (T=298.15 K)

$\zeta_{AA}/kT=10$	$y_A=0.4$	$H_{AA}/kT=40$	$\sigma_1/\sigma_2=5$
$\zeta_{AR}/kT=12$	$y_R=0.35$	$H_{RR}/kT= 10$	$l_R=16.$, $\kappa=0.01$

$y_A=\frac{\pi}{6}\rho_1^0\sigma_1^3$; $y_R=\frac{\pi}{6}\rho_2^0\sigma_2^3$;
superscript 0 denotes pure material.

Captions of Figures

Figure 1 Phase behavior of fluids containing asphaltene and resin.

Figure 2 Calculated phase diagrams of fluids containing asphaltene and resin (T=298.15 K, H_m is the Hamaker constant of the medium, $\eta_A=(\pi/6)\rho_1\sigma_1^3$; $\eta_R=(\pi/6)\rho_2\sigma_2^3$)

Figure 3 Calculated effect of medium on asphaltene precipitation

Figure 4 Calculated effect of dilution ratio on asphaltene precipitation

Figure 5 Calculated effect of temperature on amount of asphaltene precipitated (H_3, H_7 are the Hamaker constants of propane and n-heptane at 298.15 K, respectively)

Figure 6 Calculated effect of temperature on the phase behavior of asphaltene-resin-n-heptane ternary system

Figure 1 Phase behavior of fluids containing asphaltene and resin

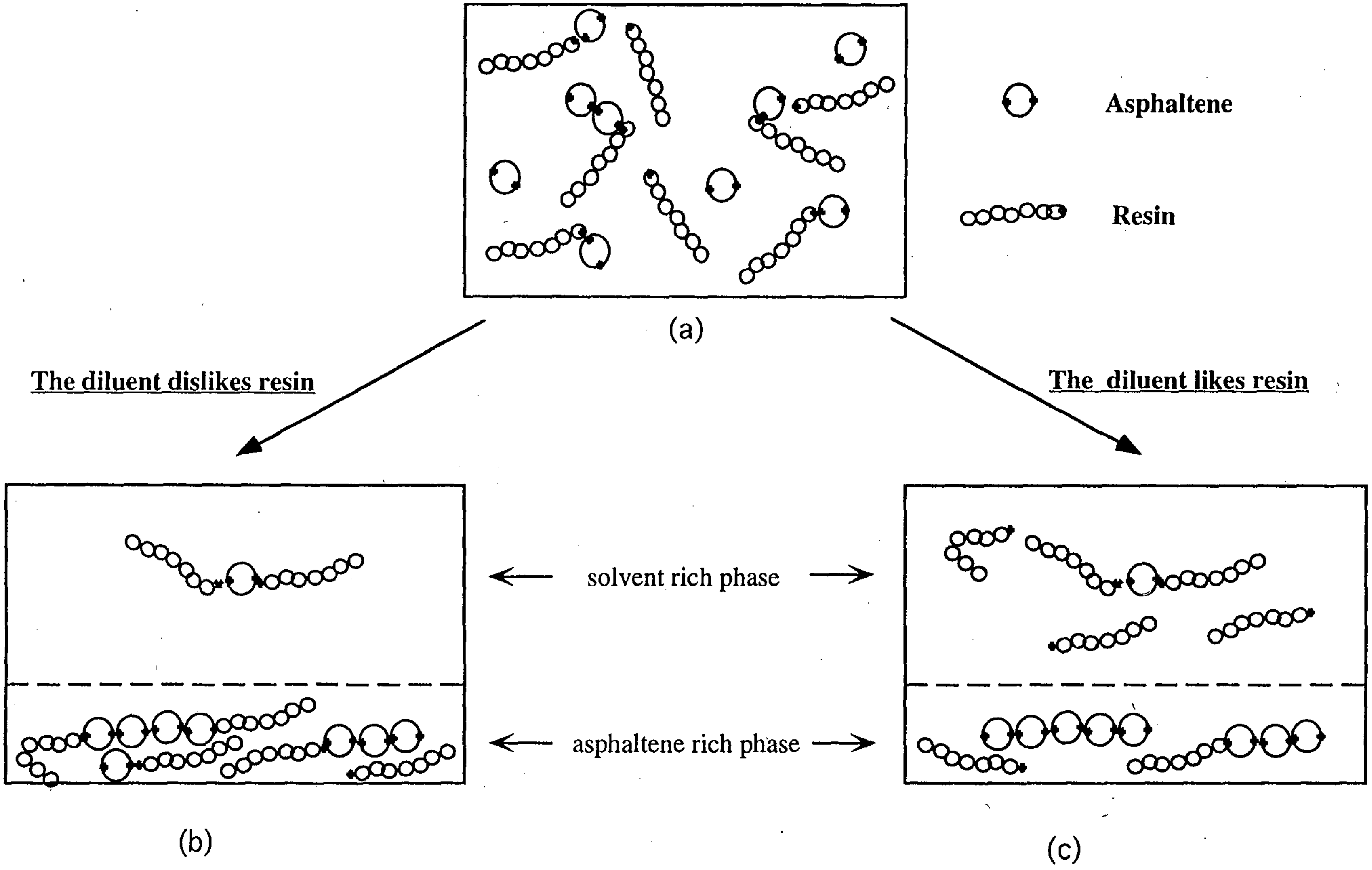


Figure 2

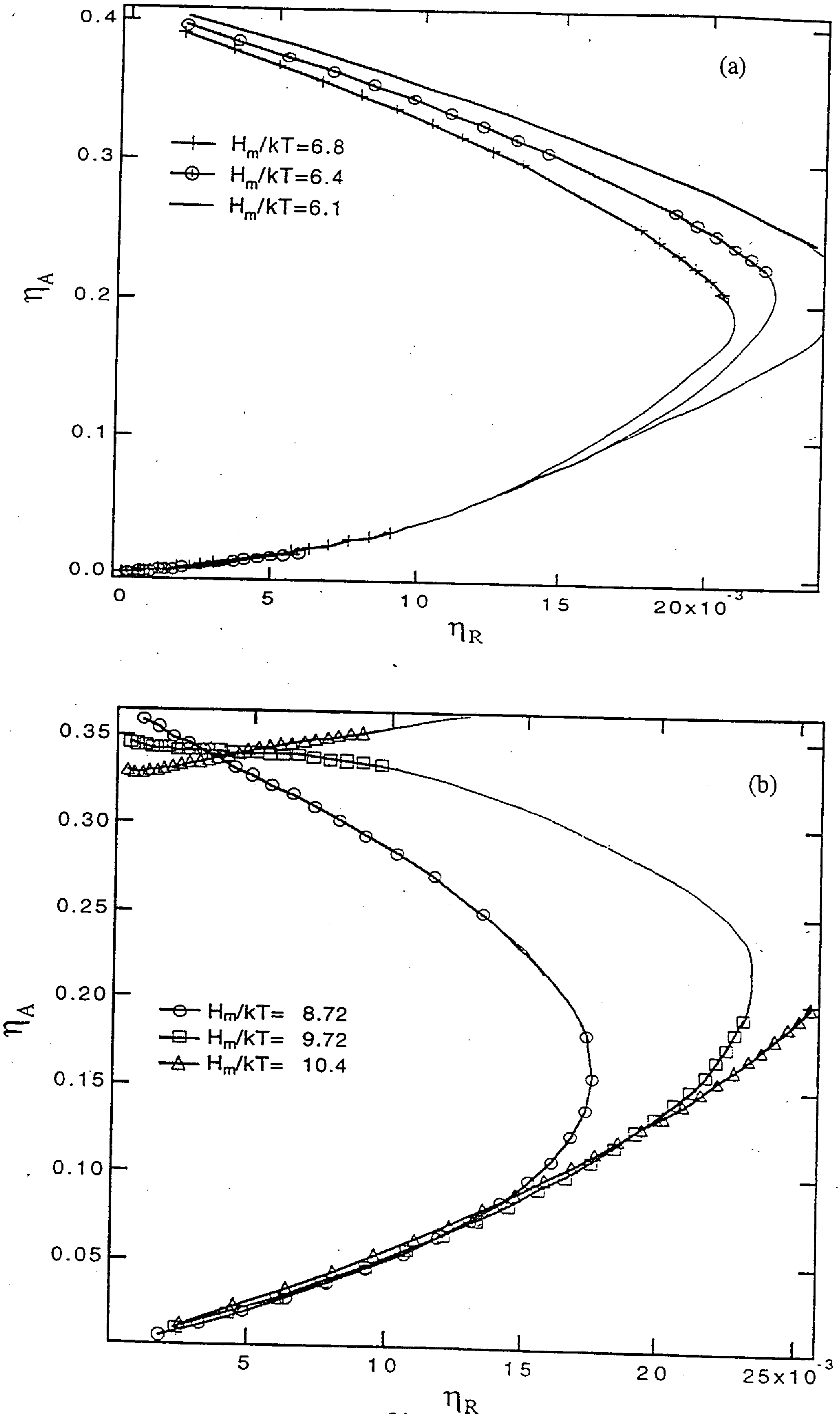
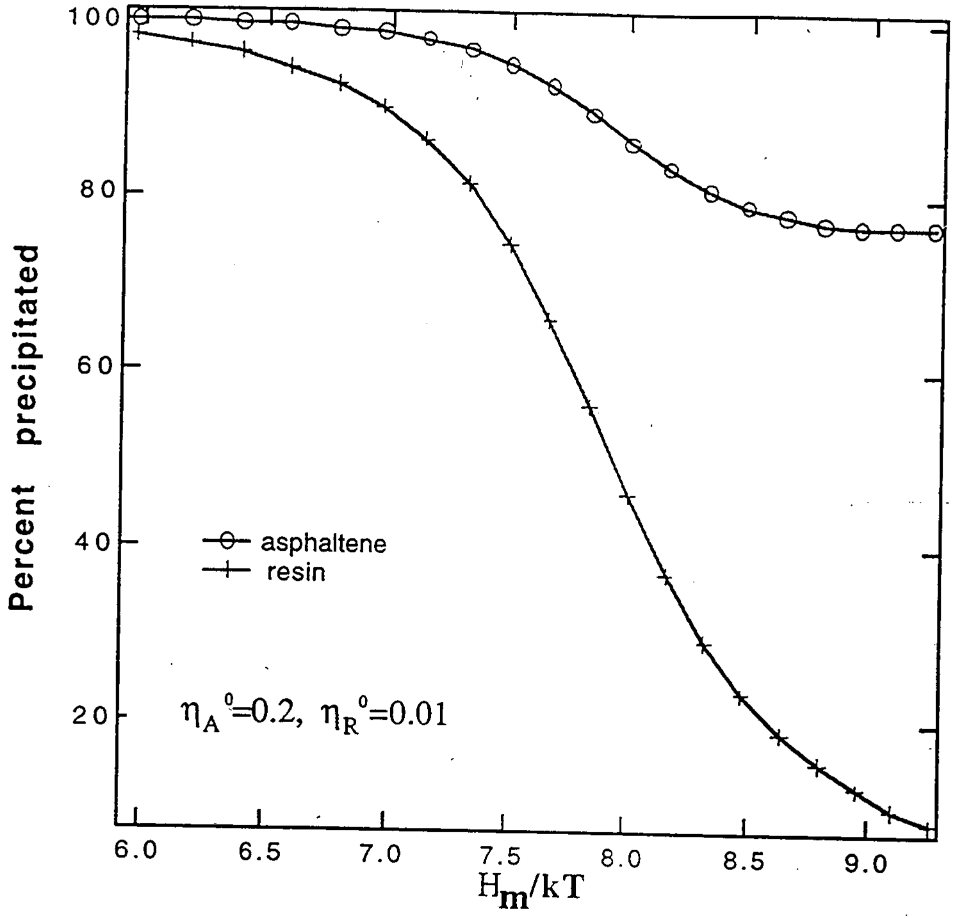

(a)
H_m/kT=6.8
H_m/kT=6.4
H_m/kT=6.1
η_A
0.4
0.3
0.2
0.1
0.0
η_R
0
5
10
15
20x10^-3
(b)
H_m/kT= 8.72
H_m/kT= 9.72
H_m/kT= 10.4
η_A
0.35
0.30
0.25
0.20
0.15
0.10
0.05
η_R
5
10
15
20
25x10^-3

Figure 3



100
80
60
40
20
Percent precipitated
6.0
6.5
7.0
7.5
8.0
8.5
9.0
H_m/kT
asphaltene
resin
$\eta_A{}^0=0.2,\ \eta_R{}^0=0.01$

Figure 4

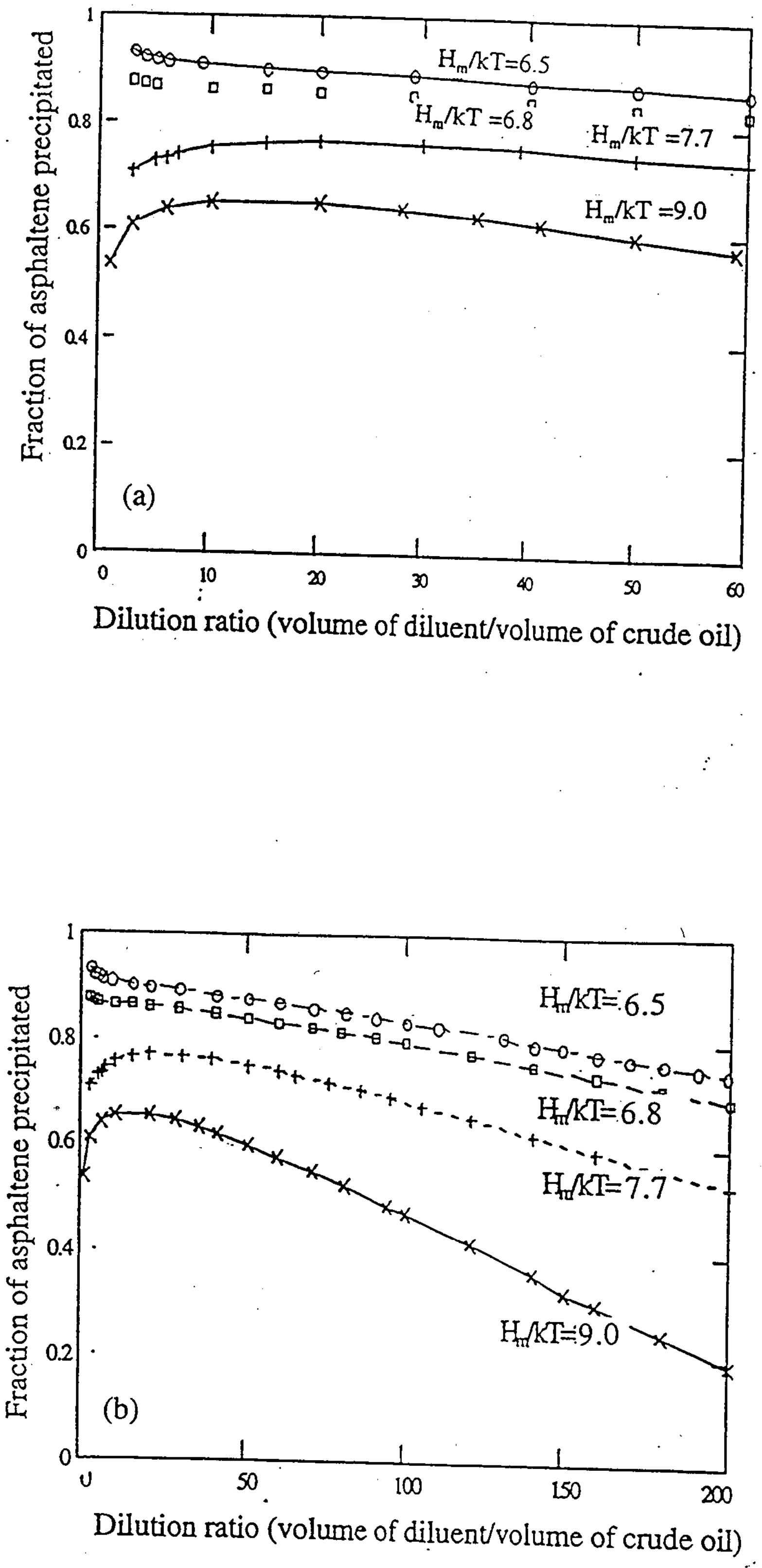
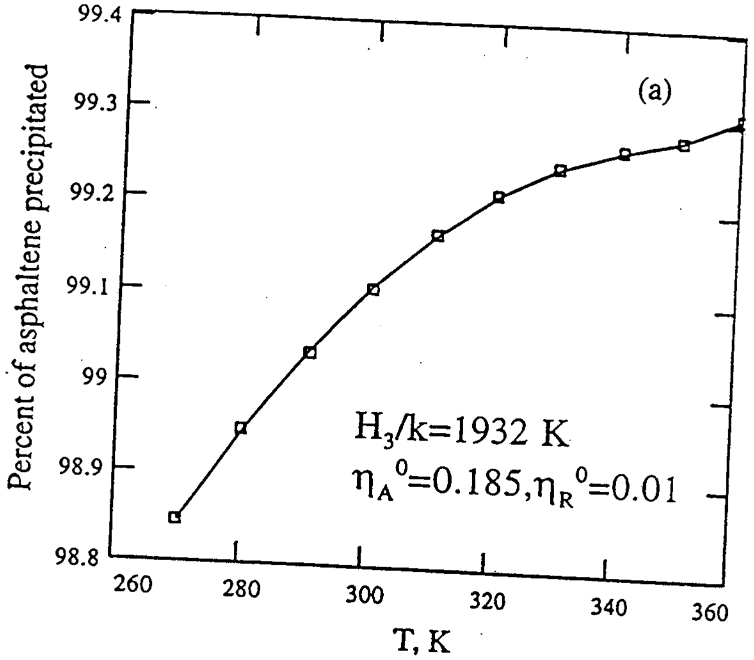
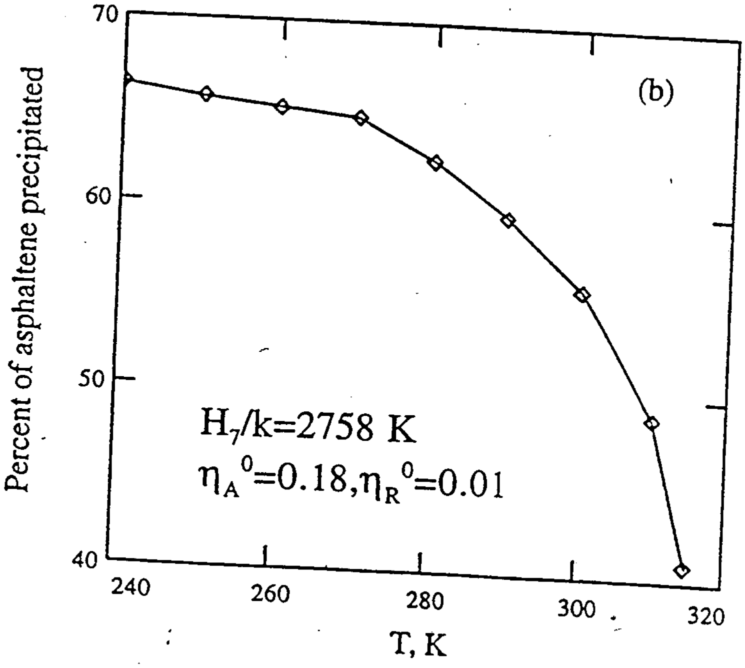

Fraction of asphaltene precipitated
0
0.2
0.4
0.6
0.8
1
H_m/kT=6.5
H_m/kT =6.8
H_m/kT =7.7
H_m/kT =9.0
(a)
0
10
20
30
40
50
60
Dilution ratio (volume of diluent/volume of crude oil)
Fraction of asphaltene precipitated
0
0.2
0.4
0.6
0.8
1
H_m/kT=6.5
H_m/kT=6.8
H_m/kT=7.7
H_m/kT=9.0
(b)
0
50
100
150
200
Dilution ratio (volume of diluent/volume of crude oil)

Figure 5



Asphaltene precipitation in propane at saturated pressure



Asphaltene precipitation in n-heptane at saturated pressure

Figure 6

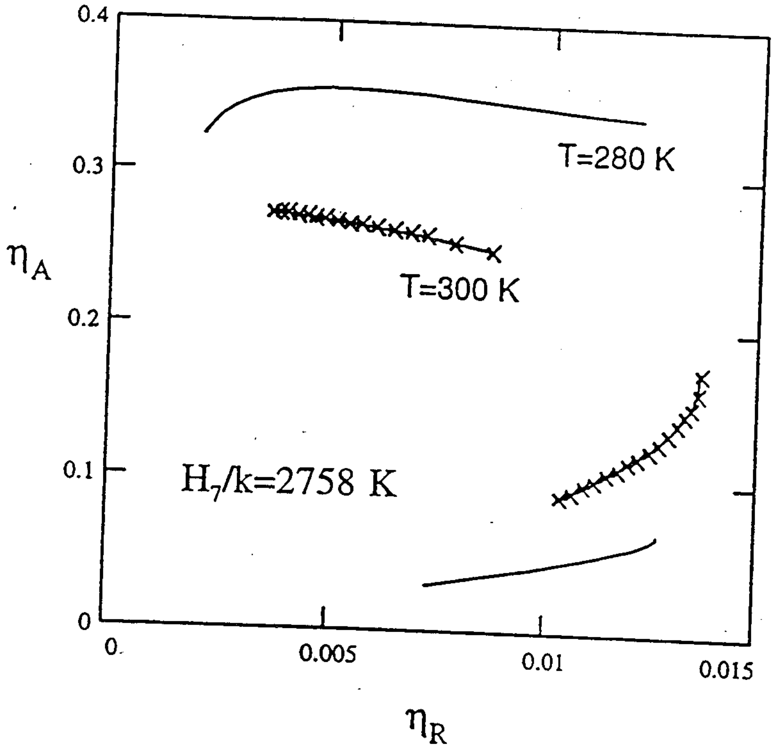
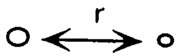
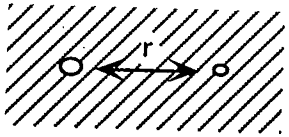


Figure A van der Waals interactions between molecules and surfaces in vacuum and in a medium

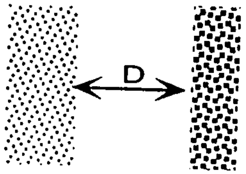


INTERACTION BETWEEN TWO MOLECULES

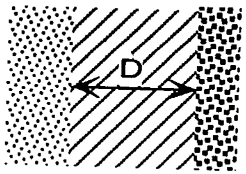


$$W_{ij}^{vdw}(r) = -\frac{B_{ij}}{r^6} \quad \text{(A-1)}$$

$$W_{ij}^{vdw}(r) = -\frac{B_{imj}}{r^6} \quad \text{(A-2)}$$



INTERACTION BETWEEN TWO SURFACES



$$W_{per\ unit\ area}^{vdw} = -\frac{H_{ij}}{12\pi D^2} \quad \text{(A-3)}$$

$$W_{per\ unit\ area}^{vdw} = -\frac{H_{imj}}{12\pi D^2} \quad \text{(A-4)}$$

$$H_{ij} \equiv \pi^2 B_{ij} \rho_i \rho_j \quad \text{(A-5)}$$

$$H_{imj} \equiv \pi^2 B_{imj} \rho_i \rho_j \quad \text{(A-6)}$$

IN VACUUM

IN A MEDIUM

$$H_{imj} \approx (H_{ii}^{1/2} - H_{mm}^{1/2})(H_{jj}^{1/2} - H_{mm}^{1/2}) \quad \text{(A-7)}$$

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