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Molecular Thermodynamics for Prevention of Asphaltene Precipitation

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Progress Report

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Molecular Thermodynamics for Prevention of Asphaltene Precipitation

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Introduction

Crude petroleum is a complex mixture of compounds with different chemical structures and molecular weights. Asphaltenes, the heaviest and most polar fraction of crude oil, are insoluble in normal alkanes such as n-heptane, but they are soluble in aromatic solvents such as toluene. The molecular nature of asphaltenes and their role in production and processing of crude oils have been the topic of numerous studies[1-3]. Under some conditions, asphaltenes precipitate from a petroleum fluid, causing severe problems in production and transportation[4-6]. Our research objective is to develop a theoretically-based, but engineering-oriented, molecular-thermodynamic model which can describe the phase behavior of asphaltene precipitation in petroleum fluids, to provide guidance for petroleum-engineering design and production.

In this progress report, particular attention is given to the potential of mean force between asphaltene molecules in a medium of asphaltene-free solvent. This potential of mean force is derived using the principles of colloid science[7-9]. It depends on the properties of asphaltene and those of the solvent as well as on temperature and pressure. The effect of a solvent on interactions between asphaltenes is taken into account through its density and through its molecular dispersion properties.

Based on an integral theory of fluids called the random-phase-approximation (RPA)[10-11], coupled with the potential of mean force between asphaltene molecules, a molecular-thermodynamic model has been developed for calculating the chemical potential

of asphaltene and the osmotic pressure of asphaltene-containing fluids. Using this model, we can calculate asphaltene-precipitation equilibria; these are used to correlate the solubilities of asphaltenes in n-alkanes, and the amount of asphaltene precipitated by adding n-alkanes to crude oils. At its present incomplete state of development, this model over-predicts the solubilities of asphaltenes at high dilution ratios of precipitants. Possible improvements on the current model are indicated, and a direction of our future work is outlined.

Interactions between asphaltene molecules

In our initial modeling of phase behavior of asphaltene-containing fluids, asphaltenes are represented by a pseudo-pure component, and all the other components in the solution are represented by a medium which affects the interaction between asphaltene molecules. The potential of mean force $W(r)$ between asphaltene molecules includes two parts: one is a repulsive interaction represented by hard-sphere potential $W^{hs}(r)$; the other is a van-der-Waals-type attractive interaction $W^{vdw}(r)$ which can be derived from the concept of dispersion interaction between two particles in a medium.

The hard-sphere repulsion between asphaltene molecules is represented by

$$W^{hs}(r) = \begin{cases} \infty & r \le \sigma_A \\ 0 & r > \sigma_A \end{cases}$$

(1)

where r is the center-to-center distance of separation; σ_A is the diameter of an asphaltene molecule; superscript hs denotes hard-sphere and subscript A denotes asphaltene. This repulsive interaction depends only on the size of asphaltene molecules.

The dispersion potential between two asphaltene molecules in an asphaltene-free solvent depends on the properties of the medium. This medium-dependent potential of mean force can be derived by the following procedure.

First, the dispersion interaction between two molecules in vacuum is given by London's approximation

$$W^{vdw}(r) = -\frac{B}{r^6}$$

(2)

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where B is a characteristic constant of the molecule, independent of temperature. superscript *vdw* denotes van der Waals attractive interaction. Compared with the well-known Lennard-Jones potential function, Equation (2) can also be written as

$$W^{vdw}(r) = -\varepsilon\left(\frac{\sigma}{r}\right)^6$$

(3)

where ε is the Lennard-Jones energy parameter, σ is the diameter of the molecule, and $B = \varepsilon\sigma^6$.

Consider now two large identical particles, each one composed of numerous Lennard-Jones molecules of the same material 1. As discussed in texts on colloid science, the potential energy of interaction between the two large particles is calculated by assuming that every molecule in one particle interacts with every molecule in the other. The total dispersion energy is obtained by summing the contributions from all possible pairs of molecules belonging to different particles.

$$\Phi = \int_\Omega\int_\Omega \rho_I^2 W^{vdw}(|\mathbf{r}_I - \mathbf{r}_{II}|)d\mathbf{r}_I d\mathbf{r}_{II} = -\rho_I^2 B \int_\Omega\int_\Omega \frac{1}{|\mathbf{r}_I - \mathbf{r}_{II}|^6} d\mathbf{r}_I d\mathbf{r}_{II}$$

(4)

where Φ is the dispersion potential energy which depends on the separation and orientation between two particles; Ω is the volume of the particle; ρ_I is the number density of molecules inside each particle; $\mathbf{r}_I$ and $\mathbf{r}_{II}$ are two vectors locating the molecules in particle I and in particle II, respectively; and $|\mathbf{r}_I - \mathbf{r}_{II}|$ is the center-to-center distance between two molecules.

Hamaker's constant H for interaction between two particles of the same material through a vacuum is defined by

$$H = \pi^2\rho^2 B$$

(5)

With this definition, Equation (4) can be rewritten as

$$\Phi = -(H/\pi^2)\int_\Omega\int_\Omega \frac{1}{|\mathbf{r}_I - \mathbf{r}_{II}|^6} d\mathbf{r}_I d\mathbf{r}_{II}$$

(6)

Hamaker's constant plays a central role in colloid science in the description of van der Waals forces between particles. Equation (6) shows that the interaction potential between

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two large particles in vacuum Φ is equal to Hamaker's constant multiplied by a geometric factor which depends on the distance of separation and orientation between two particles.

If two particles are separated by a medium of different molecules, the attractive force between these particles becomes smaller. A relatively simple way to describe the effect of a medium on the interaction potential between two large particles of the same material is to use the relation [7,8]

$$H_{121} \approx (H_{11}^{1/2} - H_{22}^{1/2})^2 \tag{7}$$

where H_{11} is the Hamaker's constant for interaction between two particles of material 1 in a vacuum, and similarly for H_{22}. Then, the interaction potential between two large particles of material 1 immersed in a medium 2 is given by replacing H with H_{121} in Equation (6):

$$\Phi_{121} = -(H_{121}/\pi^2) \int_\Omega \int_\Omega \frac{1}{|\mathbf{r}_I - \mathbf{r}_{II}|^6} d\mathbf{r}_I d\mathbf{r}_{II} \tag{8}$$

Following the same idea to calculate the interaction between two particles in vacuum by summing all the pair interactions between molecules in different particles, Equation (8) is equivalent to

$$\Phi_{121} = -\rho_1^2 \varepsilon_{121} \sigma_1^6 \int_\Omega \int_\Omega \frac{1}{|\mathbf{r}_I - \mathbf{r}_{II}|^6} d\mathbf{r}_I d\mathbf{r}_{II} . \tag{9}$$

In writing Equation (9), we assume that the dispersion interaction between two molecules of material 1 in a medium 2 is given by,

$$W_{121}(r) = -\varepsilon_{121} \left(\frac{\sigma_1}{r}\right)^6 \tag{10}$$

ε_{121} can be obtained by comparing Equation (9) with Equation (10),

$$\varepsilon_{121} = H_{121}/\pi^2 \rho_1^2 \tag{11}$$

Equations (3) and (10) give the dispersion interactions between two identical molecules in a vacuum and that in a medium, respectively. Based on Equation (7), and with the relations between Hamaker's constants and energy parameters given by Equations (5) and (11), ε_{121} is now given by

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$$\varepsilon_{121} = \left(\varepsilon_{11}^{1/2} - \frac{\rho_2 \sigma_2^3 \varepsilon_{22}^{1/2}}{\rho_1 \sigma_1^3} \right)^2$$

(12)

Based on this analysis, the dispersion interaction between two asphaltene molecules in a solvent medium is given by

$$W_{AMA}^{vdw}(r) = -\varepsilon_{AMA} \left(\frac{\sigma_A}{r} \right)^6$$

(13)

where subscript M represents medium, and subscript A represents asphaltene. Similar to Equation (12), ε_{AMA} is given by

$$\varepsilon_{AMA} = \left(\varepsilon_{AA}^{1/2} - \frac{\rho_M \sigma_M^3 \varepsilon_{MM}^{1/2}}{\rho_A \sigma_A^3} \right)^2$$

(14)

Equations (13) and (14) give an explicit expression indicating the dependence of interactions between asphaltene molecules on the properties of the medium as well as those of asphaltene. Because asphaltene particles are relatively incompressible compared with the medium, for a particular asphaltene, ε_{AA} and $\rho_A \sigma_A^3$ can be assumed as constants, essentially independent of temperature and pressure. The density of the medium ρ_M at different temperatures and pressures can be found from any one of several well-known equations of state[12-13], while the remaining terms in Equation (14) are insensitive to changes in temperature and pressure. This potential of mean force may be useful for predicting phase behavior of asphaltene-containing fluids at high temperatures and pressures based on some experimental data at ambient conditions.

Equation of state

Knowing the potential of mean force between asphaltene molecules, we can construct a molecular-thermodynamic model to calculate the phase behavior of asphaltene-containing fluids. To obtain a useful engineering result, we employ a simplified analytic form of the integral theory of fluids known as the random-phase-approximation (RPA) theory [10-11]. It is a perturbation theory which uses an assembly of hard spheres as

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the reference system, while the remaining spherically symmetric interactions are treated as perturbations. In RPA, the direct pair correlation function $c(r)$ is approximated by

$$c(r)=c_0(r)-\beta*W_I(r) \tag{15}$$

where $\beta=1/kT$; here T is the absolute temperature and k is Boltzmann constant; $W_I(r)$ is the perturbation part of the total potential, i.e. the dispersion interaction given by Equation (13); and $c_0(r)$ is the direct pair correlation function for hard spheres. Compared with other well-known perturbation theories, e.g. those by Barker-Henderson and Chandler-Weeks-Anderson[14], RPA is much simpler; it provides a relatively good first approximation. This theory has been used previously to describe the liquid-liquid phase equilibrium of protein precipitation[10-11].

The equation of state and chemical potential needed for phase-equilibria calculations can be related to the direct correlation function using equations given in books on statistical mechanics[15]. For an one-component system*, the isothermal compressibility is expressed as

$$\beta(\partial P/\partial\rho)_T = 1-4\pi\rho\int c(r)r^2 dr \tag{16}$$

where P is the osmotic pressure; and ρ is the number density of the asphaltene molecules in solution. Here ρ is different from ρ_A which is defined as the number density of asphaltene molecules in a solvent-free large asphaltene particle. From Equations (15) and (16), the equation of state for our simplified model of asphaltene-containing fluids is given by

$$\frac{P}{\rho kT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - 4\eta\frac{\varepsilon_{AMA}}{kT}, \tag{17}$$

where η is the packing fraction given by $\eta=\pi\rho\sigma_A^3/6$. The first term in the right hand side of Equation (17) is the contribution of the reference system given by the Carnahan-Starling equation[14]; the other term represents the perturbation contribution of dispersion interaction. The chemical potential of asphaltene μ is related to the direct pair correlation function $c(r)$ by

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* We are considering here a one-component system: asphaltene in a continuous medium of constant composition.

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$$\beta(\partial\mu / \partial\rho)_T = 1/\rho - 4\pi\int c(r)r^2 dr .\qquad(18)$$

From Equations (15) and (18), the chemical potential of the asphaltene is obtained:

$$\beta\mu = \ln(\Lambda^3) + \ln\rho + \eta(8-9\eta+3\eta^2)/(1-\eta)^3 - 8\eta\varepsilon_{121}/kT\qquad(19)$$

where $\Lambda^2 = \beta h^2/2\pi m$, with h denoting Planck's constant and m the mass of one asphaltene molecule. At equilibrium, we have

$$\mu'=\mu''\qquad(20)$$

$$P'=P''.\qquad(21)$$

Here ' and '' denote the two equilibrated phases. Using Equations (20) and (21), we can find whether one or two phases are present. If two phases coexist, the asphaltene concentration in each phase can be calculated(In equation (20), Λ cancels out).

Based on the equation of state given by Equation (17), the critical conditions for phase separation can be found by letting the first and second order derivatives of P with respect to ρ equal zero:

$$\frac{1+4\eta+4\eta^2-4\eta^3+\eta^4}{(1-\eta)^4}-8\eta\varepsilon_{121}/kT=0\qquad(22)$$

$$4\frac{2+5\eta-\eta^2}{(1-\eta)^5}-8\varepsilon_{121}/kT=0\qquad(23)$$

In this simple one-component model, the attractive interaction is taken into account by making a mean-field approximation using only one parameter ε_{121}. The critical asphaltene packing fraction η and ε_{121}/kT are two constants which can be obtained by solving Equations (22) and (23); they are $\eta=0.13$, $\varepsilon_{121}/kT=2.65$. Figure 1 presents the phase envelope for the one-component RPA model, that is, the binodal curve(dashed line) and isothermal curves (solid lines) at ε_{AMA}/kT equal to 2.5 and 3.0 respectively. The reduced osmotic pressure (or compressibility) is defined as Pv_0/kT where $v_0 = \pi\rho\sigma_A^3/6$ is the molecular volume of asphaltene.

When ε_{AMA}/kT is smaller than the critical value 2.65, the osmotic pressure is a single-valued increasing function of packing fraction η; phase separation will not occur (The top solid line in Figure 1). Above the critical value of ε_{AMA}/kT, the curves exhibit

familiar van der Waals loops. Upon phase separation, the concentration of asphaltenes in each equilibrated phase can be found from the binodal curve as determined from Equations (20) and (21).
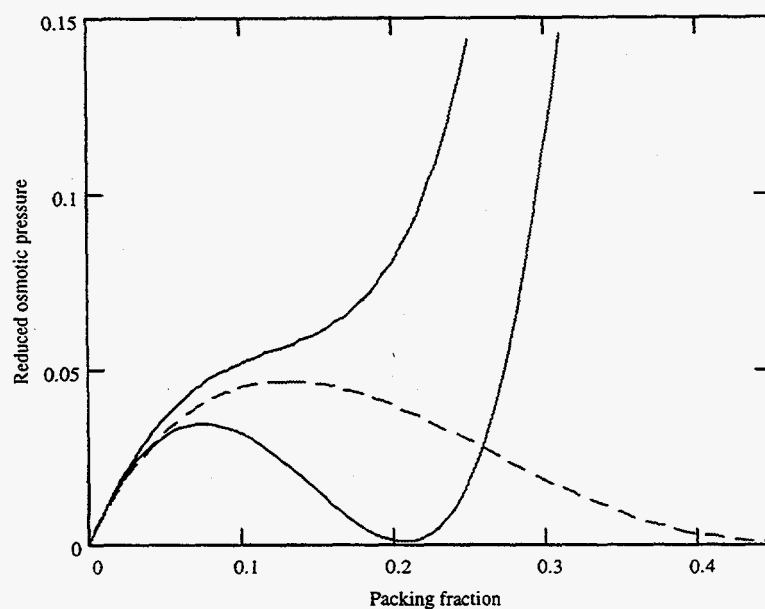

Figure 1 *Phase diagram from one-component RPA theory*

Solubility of asphaltene in n-alkanes: semiquantitative study of asphaltene precipitation

The previous section indicates how to calculate the solubility of asphaltenes in a solvent (medium) if the molecular properties of both asphaltene and solvent are available. Unfortunately, in the oil industry, neither the asphaltene nor the medium are well defined pure substances. To test performance of this model, the necessary molecular properties for solvents are estimated from some established methods. Following the method introduced by Prausnitz et al[12], the molecular parameters ε and σ are related to the macroscopic properties T_c and P_c by

$$\varepsilon/k=0.77T_c \tag{24}$$

$$\varepsilon/\sigma^3=7.42P_c \tag{25}$$

where T_c is the critical temperature, and P_c is the critical pressure. The critical properties of solvents are obtained from Reid et al[16]. Because asphaltenes are of high molecular weight and polarity, Equations (24) and (25) are inappropriate for estimating ε_{AA} and σ_A. Here we use the critical data given by Victorov and Firoozabadi[17] to calculate the second virial coefficients using the correlation developed by Pitzer and Curl[12]. Then the molecular parameters of asphaltenes are obtained by correlating these second virial coefficients. Table 1 gives the macroscopic properties and the estimated molecular properties of asphaltene and several normal alkanes.

Based on those parameters listed in Table 1, the solubility of asphaltenes in n-alkanes can be calculated as shown in Figure 2. For n-dodecane and n-tetradecane. ε_{AMA}/kT calculated is below the critical value which means asphaltenes are fully miscible in these two solvents. Although asphaltenes may not completely dissolve in dodecane or tetradecane, our calculated results indicate that the solubility of asphaltene in n-alkanes increases with carbon number, consistent with experimental results. Our results show that, at the same dilution ratio, the percent of asphaltene precipitated in a crude oil by adding n-alkane, decreases with alkane carbon number.

Table 1 *Macro and molecular parameters of asphaltene and several n-alkanes*

	n-C5	n-C7	n-C9	n-C10	n-C12	n-C14	asphaltene
Molecular weight (g/mol)	72.2	100.2	128.3	142.3	170.3	198. 4	850
T_c (K)	469.7	540.3	594.6	617.7	658.2	693	1003
P_c (bar)	33.7	27.4	22.9	21.2	18.2	14.4	8.8
density at 25 °C (kg/m³)	620.8	678.2	716.9	727.5	745.7	760.2	1200
ε/k (K)	361.7	416.0	457.8	475.6	506.8	533.6	2981.5
σ (A)	5.8	6.6	7.2	7.5	8.0	8.83	10.6

Knowing the molecular parameters of asphaltene and solvents, we also can predict the effect of temperature and pressure on asphaltene solubility. For this prediction, we need an equation to calculate the densities of solvents at different temperatures and pressures. Here we use a method developed by Aalto et al[18]. Figures 3 and 4 show the

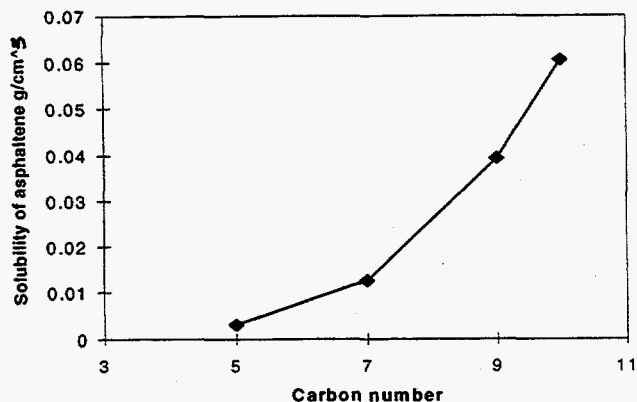effect of temperature and pressure on the solubility of asphaltene in n-heptane.
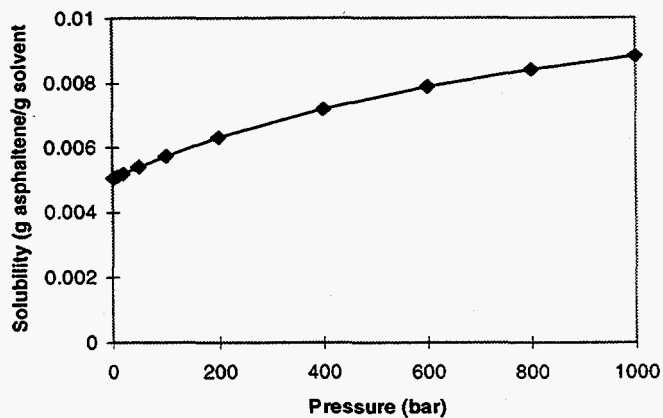

Figure 2 *Solubilities of asphaltenes in n-alkanes*

Figure 3 *Effect of pressure on the solubility of asphaltene in n-heptane at 25 °C*
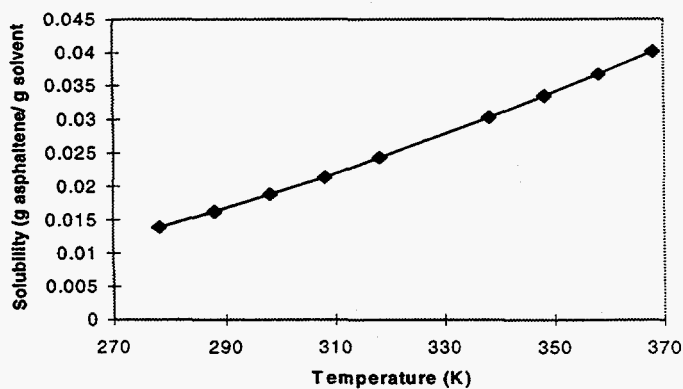

Figure 4 *Effect of temperature on the solubility of asphaltene in n-heptane at 1 atm*

In Figures 3 and 4, we assume that the density of asphaltene is independent of temperature and pressure because, compared with n-alkanes, the density of asphaltene is relatively insensitive to external conditions. The solubility of asphaltene in n-heptane increases with temperature and pressure. These trends coincide with most experimental results for the effect of temperature and pressure on the precipitation of asphaltenes: the amount of asphaltene precipitated decreases at high temperatures and pressures. From Figures 3 and 4, we can also see that the effect of pressure is much smaller than that of temperature, because pressure only slightly changes the density of a solvent, while temperature changes both density and β. If the solvent is near its critical state, or if an increase in pressure is due to raising methane concentration in the liquid, the qualitative conclusions reached here with heptane are not applicable.

As temperature increases, the density of solvent decreases(Figure 5). If the temperature is well below the solvent critical temperature, the decline of density due to temperature increase is small. The overall effect of rising temperature on the right side of Equation (14) is that ε_{AMA}/kT decreases. Therefore, the solubility of asphaltene in the solvent increases. However, when the temperature is close to the solvent's critical temperature, the density of the solvent decreases abruptly with increasing temperature. In this temperature range, the overall effect of temperature on the right side of Equation (14) raises ε_{AMA}/kT. Figure 6 gives the effect of temperature on the dispersion parameter ε_{AMA}/kT over a wide temperature range for several normal alkanes. Figure 6 shows that because for n-C5, n-C7, or n-C9, ε_{AMA}/kT is always larger than the critical value(2.65), asphaltenes are only partly soluble in these solvents; in low temperatures, the solubility of asphaltene increases with temperature, but the trend reverses near the solvent's critical temperature. Figure 6 also shows that for n-C10, n-C12 or n-C14, there is a temperature range where ε_{AMA}/kT is smaller than the critical value, where asphaltenes are fully miscible in the solvent. The lower boundary temperature is known as the lower-critical-solution-temperature(LCST), and the upper boundary temperature is known as the upper-critical-solution-temperature(UCST). Figure 7 shows the critical solution temperatures, the one-phase region, and the two-phase regions for n-decane. Because the upper-critical-

temperature is smaller than the solvent's normal freezing temperature for n-C12 or n-C14. only an lower-critical-solution-temperature exists for these systems.
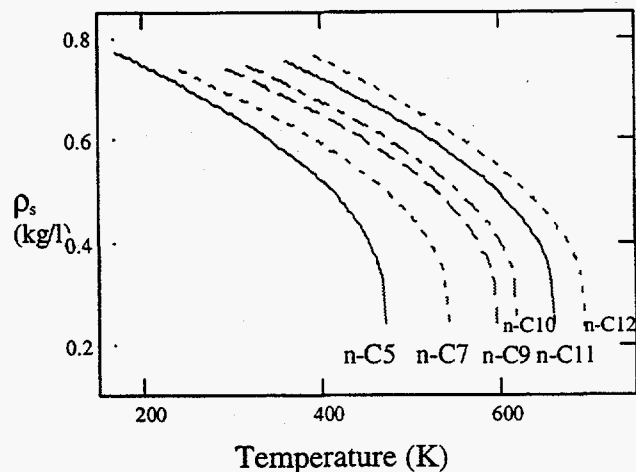

Figure 5 *Density of solvent ρ_s vs. temperature*

(Here we use the Valderrama and Abu-Sharkh(1989)[24] correlation for liquid density which is applicable for n-alkanes from the normal freezing temperature to the critical temperature)
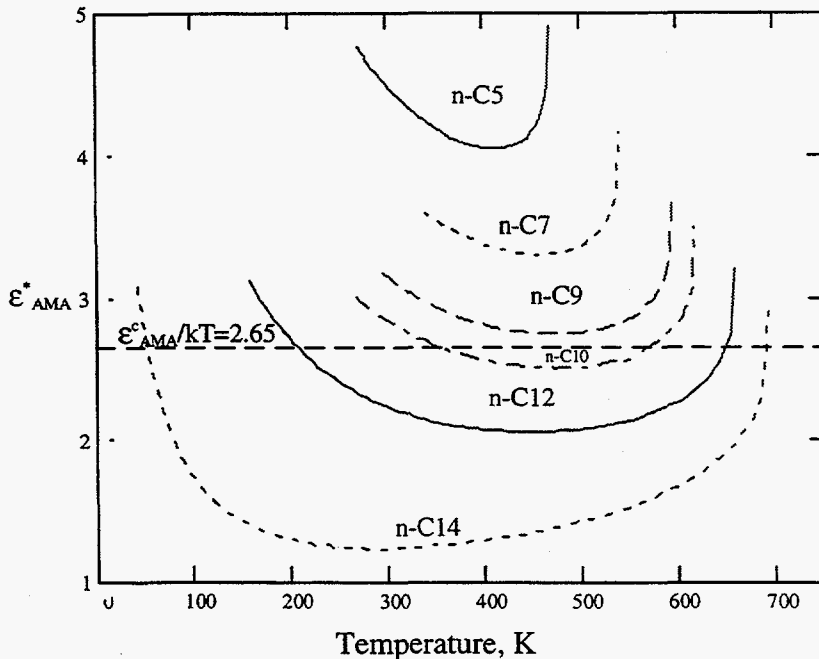

Figure 6 *The temperature dependence of reduced dispersion parameter $\varepsilon^{*}_{AMA}=\varepsilon_{AMA}/kT$ for several n-alkanes*
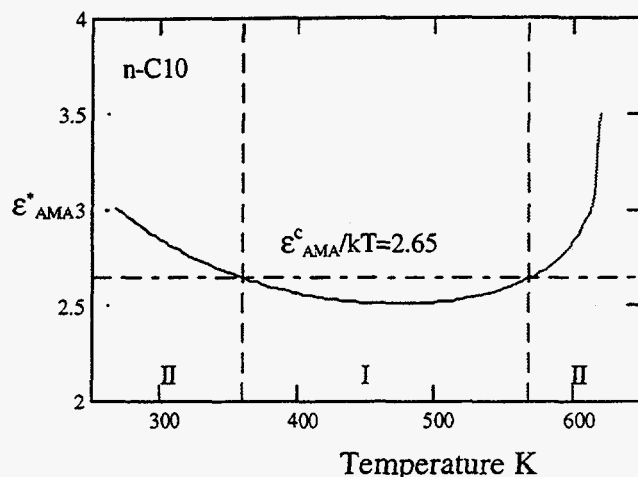
Figure 7 *The temperature dependence of reduced dispersion parameter $\varepsilon^{*}_{AMA}=\varepsilon_{AMA}/kT$ for n-C10. I denotes one-phase region, II denotes two-phase region. The upper-critical-solution-temperature is 360 K, and the lower-critical-solution-temperature is 568 K.*

Asphaltene precipitation by adding n-alkanes

Titration experiments are often carried out as the first step to study asphaltene-precipitation phase behavior. In these experiments, crude oils are titrated with various n-alkanes and the amount of asphaltene precipitated is determined by a gravity-filtration method. In the following section, the titration data given by Hirschberg et al[19] and Kokal et al[20] are used to test further the performance of our current model.

The method used in the previous section to estimate molecular properties is not suitable for high-molecular-weight species like asphaltene, nor is it appropriate for the average properties of a mixture. To apply our method to the phase behavior of asphaltene precipitation, the molecular parameters of both the asphaltene and the medium must be related to some macroproperties which are measured in the oil industry. Good candidates for such properties are molecular weight and density. However, because correlations are empirical in nature, some coefficients must be obtained by fitting to experimental asphaltene- precipitation data. In Equation (14), ε_{AA} is the dispersion parameter, a molecular property of pure asphaltene, independent of temperature and pressure. Because the density of asphaltene is insensitive to changes of temperature and pressure, $\rho_A \sigma_A^3$ also can be assumed constant. The medium density ρ_M is the only term in Equation (14) which is sensitive to temperature and pressure changes. For normal alkanes, σ and ε can be

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related to the molecular weight, but such correlations cannot be reliably extended to a mixture such as crude oil because other properties besides molecular weight also affect σ and ε. In our correlation of experimental asphaltene-precipitation data, we tested several empirical functions to obtain the best fit with as few parameters as possible. A simple relation is found between the second term in the right side of Equation (14) and the mass density and average molecular weight of the medium:

$$\frac{\rho_M \sigma_M^3}{\rho_A \sigma_A^3} \left(\frac{\varepsilon_{MM}}{kT} \right)^{1/2} = F(d_M, M_M) = k' + k''d_M + k'''M_M$$

(26)

where d_M is the density of medium in g/cm^3, and M_M is the mass-averaged molecular weight in g/mol; k', k'', k''' are empirical constants independent of temperature and pressure. The $\rho_A \sigma_A^3$ term is included in Equation (26) because we assume for now that those molecular properties of asphaltene are universal; that is, values of ε_{AA}, ρ_A, σ_A used in the previous section are applied to all asphaltenes in different crude oils. It is surely not a good approximation, considering that the nature of asphaltenes varies with its source. However, we make this approximation now because very little information is available for different asphaltenes, and the number of experimental data points for asphaltene precipitation for each crude oil is severely limited. Moreover, if values of ε_{AA}, ρ_A, σ_A are changed with different crude oils, only a proportionality constant is required in Equation (26). Following our approximation, the number of unknown parameters to be fixed is greatly reduced.

Table 2 shows coefficients k', k'', k''' for three different crude oils. Results based on Equation (26) are given in Figures (8) and (9). It is interesting to see that the coefficients listed in Table 2 nearly obey the relation,

$$\frac{k_i'}{k_j'} = \frac{k_i''}{k_j''} = \frac{k_i'''}{k_j'''}$$

(27)

where i and j refer to the oil. This is confirmed by Figure (9), where the three lines are nearly parallel; and Figure (8) also shows the three slopes are close. This result implies that if we use different values of ε_{AA}, ρ_A, σ_A for the asphaltene molecules in different crude oils, $F(d_M, M_M)$ could be a universal function. Figures (10)-(12) show the calculated and

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experimental percent of asphaltene precipitated from different crude oils by adding n-alkanes.

Table 2 *Linear coefficients for different crude oils*

	k'	k''	k'''
Tank oil No. 1[19]	-6.43	12.5	-0.013
Lindbergh oil[20]	-2.25	5.47	-0.0047
Suffield oil[20]	-3.59	7.48	-0.006

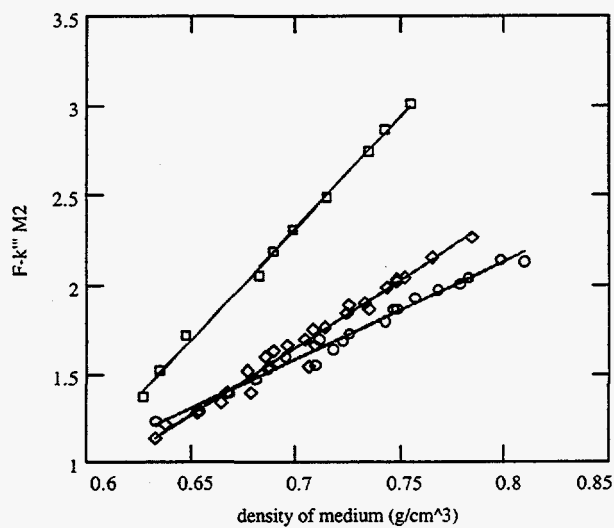**Figure 8** *F(d_M,M_M)-$k'''M_M$ vs. density of medium*

(□ : *Hirschberg's Tankoil No. 1*, ◊ : *Lindbergh oil, o: Suffield oil. The straight lines show calculated results.*)

Figure 9 $F(d2,M2)-k''d_2$ vs. molecular weight of medium

($\square$: Hirschberg's tankoil No. 1, $\lozenge$: Lindbergh oil, o: Suffield oil. The straight lines show calculated results.)
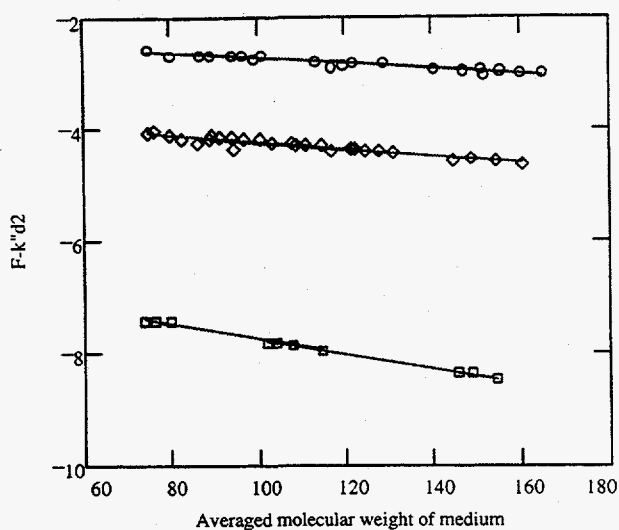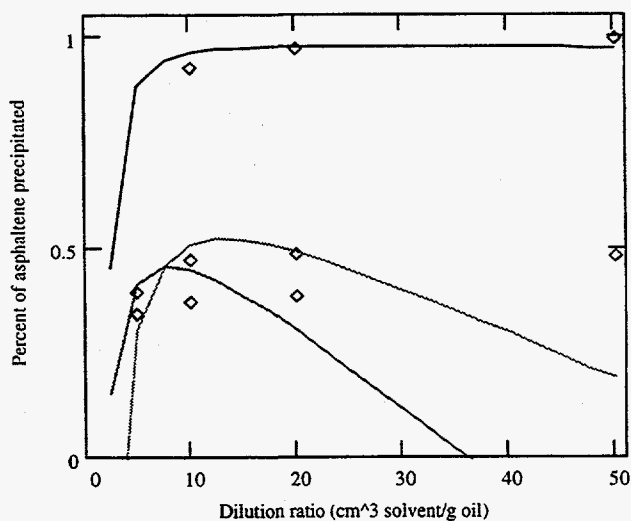

Figure 10   Liquid titration of Hirschberg's Tankoil No.1

(From top to bottom, the solvents used are n-C5, n-C7 and n-C10; solid lines are calculated, points are experimental.)
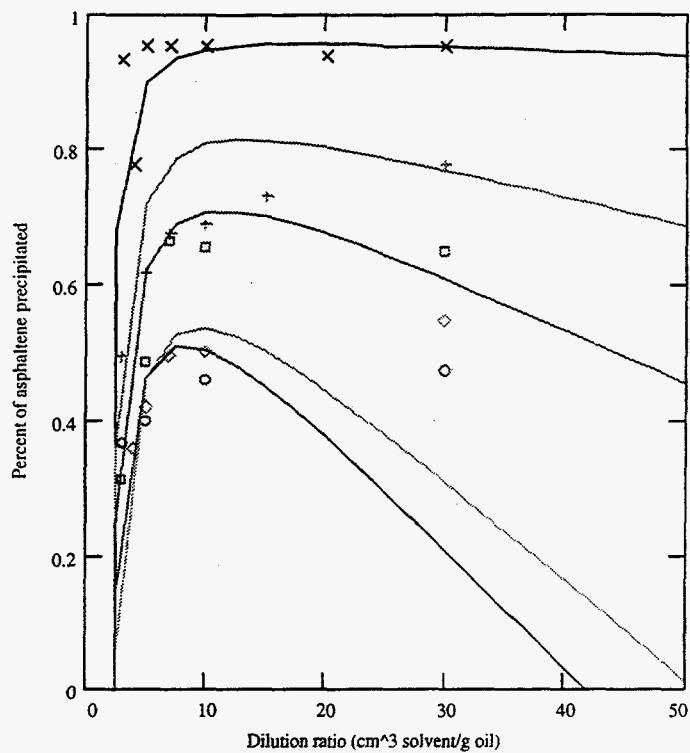
Figure 11 *Liquid titration of Suffield heavy oil*
(From top to bottom, the solvents used are n-C5, n-C6, n-C7, n-C8 and n-C10; solid lines are calculated, points are experimental.)
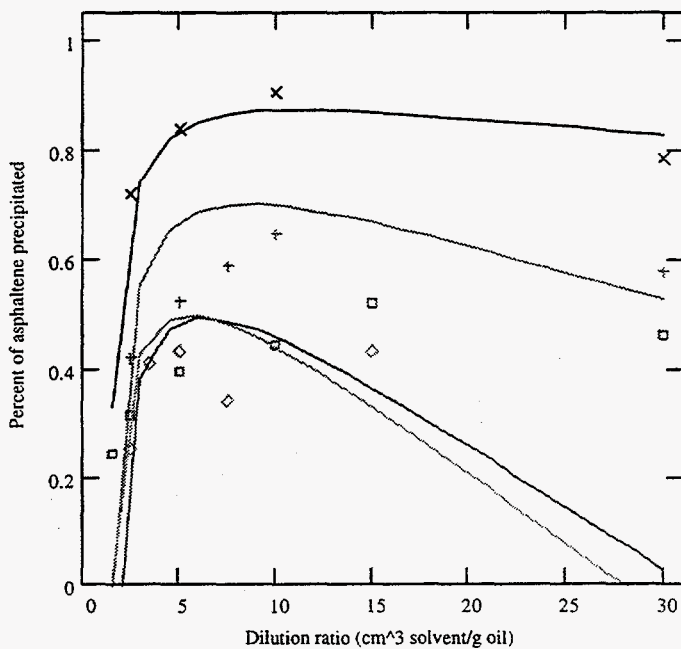

Figure 12 *Liquid titration of Lindbergh heavy oil*
(From top to bottom, the solvents used are n-C5, n-C6, n-C7, n-C8 and n-C10; solid lines are calculated, points are experimental.)

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Figures (10)-(12) show that for n-C5 titrations where essentially all asphaltenes are precipitated, calculated results agree well with experiment. However, our model fails to follow the experimental data at high dilution ratios for other n-alkanes which can dissolve part of asphaltenes. When excess amounts of n-alkanes are added, the observed amount of asphaltene redissolved is much smaller than that predicted. The reason for this difference is probably due to the association of asphaltene molecules, forming insoluble asphaltene "polymers". It is well known that asphaltenes in crude oil are stabilized by another polar fraction of heavy oil called resins, and asphaltene molecules may self-associate to form aggregates. In our current first model, only dispersion interaction between asphaltene molecules are considered. Based on this model, precipitated asphaltenes remain in monomer form in the dense phase, in contrast to real systems where most asphaltenes precipitate in aggregated (or in polymer) form, difficult to redissolve in n-alkanes.

Future work

To improve our current model, we plan to introduce association interactions between asphaltene molecules. Several different methods are available for this purpose, including the micelle model[17,21], the classical method for association fluids using the idea of chemical equilibrium[12], the integral-equation theory of sticky-hard-sphere model[22], and the perturbation theory for associated fluids[23]. Micellization seems most promising because it can represent most of the physical properties of asphaltene-containing fluids. However, because micelle formation is due to association between resin and asphaltene molecules, the last two methods may be more appropriate for improving our first current model.

It has been known for a long time that resin has a significant effect on the solubility of asphaltenes in solution. To consider the effect of resin on asphaltene precipitation, we need to extend our pseudo-one-component model to a multi-component model. Such extension can be done based on the principles of statistical mechanics[15].

For a two-component model with asphaltene and resin, in addition to interactions between asphaltene molecules as given in the previous section (for dispersion interaction), there are interactions between resin and asphaltene, resin and resin also. Similar to asphaltenes, we can give the dispersion potential resin molecules,

$$W_{RMR}(r) = -\varepsilon_{RMR} \cdot (\frac{\sigma_R}{r})^6 \tag{28}$$

$$\varepsilon_{RMR} = (\sqrt{\varepsilon_{RR}} - \frac{\rho_M \sigma_M^3}{\rho_M \sigma_M^3} \sqrt{\varepsilon_{MM}})^2 \tag{29}$$

In Equations (28) and (29), subscript R represents resin molecule.

The interaction between asphaltene and resin molecules can be derived by following the procedure given by Israelachvili [8]. Hamaker's constant for dispersion interaction between two large particles A and R in a medium M is given by

$$H_{AMR} \approx (\sqrt{H_{AA}} - \sqrt{H_{MM}}) \cdot (\sqrt{H_{RR}} - \sqrt{H_{MM}}) \tag{30}$$

From Equation (30), and the definition of Hamaker's constant, the attractive dispersion potential function between asphaltene and resin molecules in a solvent medium is given by

$$W_{AMR}(r) = -\varepsilon_{AMR} \cdot (\frac{\sigma_{AR}}{r})^6 \tag{31}$$

where

$$\sigma_{AR} = (\sigma_A + \sigma_R)/2 \tag{32}$$

$$\varepsilon_{AMR} = (\sqrt{\varepsilon_{AA}} - \frac{\rho_M \sigma_M^3}{\rho_A \sigma_A^3} \sqrt{\varepsilon_{MM}}) \cdot (\sqrt{\varepsilon_{RR}} - \frac{\rho_M \sigma_M^3}{\rho_R \sigma_R^3} \sqrt{\varepsilon_{MM}}) \tag{33}$$

The association interactions between asphaltene and resin molecules, and between asphaltene and asphaltene molecules can be considered in different ways depending on which theory is used. For the micelle model and the chemical equilibrium method, a chemical equilibrium constant can be used for considering association between molecules, while the statistical-mechanics methods use an interaction potential function, such as the sticky potential function or the square-well potential function.

To obtain the contribution of dispersion force to the osmotic pressure and chemical potential, we need to evaluate the integral $U_{ij} = 4\pi \int_{\sigma_{ij}}^{\infty} W_{ij}(r) \cdot r^2 dr$, which is given by

$$U_{ij} = \frac{4\pi\sigma_{ij}^3}{3}\varepsilon_{imj} \tag{34}$$

The final equation of state is given by

$$\beta \cdot P = \frac{6}{\pi}\left[\frac{\xi_0}{\Delta} + \frac{3\xi_1\xi_2}{\Delta^2} + \frac{\xi_2^3(3-\zeta_3)}{\Delta^3}\right] + \frac{\beta}{2}\sum_{i=A,R}\sum_{j=A,R}\rho_i\rho_j U_{ij} + \beta P^{ass} \tag{35}$$

where P^{ass} represents the contribution of association to osmotic pressure; the exact expression for this term can be derived using one of the methods for association.

$$\xi_l = \frac{\pi}{6}\sum_{k=1}^{2}\rho_k\sigma_k^l \qquad (l = 0,1,2,3) \tag{36}$$

$$\Delta = 1 - \xi_3 \tag{37}$$

The chemical potential for species i is given by [14]

$$\beta\mu_i = \ln(\frac{\rho_i\Lambda_i^3}{q_i^{int}}) - \ln\Delta + \frac{\pi \cdot P^0\sigma_i^3}{6kT} + \frac{3\xi_2\sigma_i}{\Delta} + \frac{3\xi_1\sigma_i^2}{\Delta} + \frac{9\xi_2^2\sigma_i^2}{\Delta^3} + \sum_{j=A,R}\rho_j U_{ij} + \beta\mu^{ass} \tag{38}$$

where $\Lambda_i^2 = \beta \cdot h / 2\pi \cdot m_i$ is the thermal de Broglie wave length of i, q_i^{int} is the partition function due to the internal coordinates of I; μ^{ass} represents the contribution of association. In phase-equilibrium calculations, the quantity $\ln(\frac{\rho_i\Lambda_i^3}{q_i^{int}})$ cancels out.

This extended model may explain the unexpected observed behavior of the solubility of asphaltenes at high dilution ratios. In crude oils, asphaltenes and resins are two polar species which can associate with each other. However, the association energy between asphaltene and resin molecules is higher than that between asphaltene self-association. Therefore, the presence of resins in crude oils prevents asphaltene from self-association. When a diluent is added to a crude oil, phase separation will occur as expected by our previous model. However, resins are more soluble than asphaltenes in n-

alkanes, yielding an uneven distribution of asphaltenes and resins between the two equilibrated phases. Resin molecules remain in the solvent-rich phase, and therefore. asphaltene molecules aggregate with each other in the dense phase. Because the interaction energy between asphaltene and solvent is much smaller than that for asphaltene association, asphaltene does not redissolve in the solution. This proposed extended model is consistent with the well-established experimental conclusion that asphaltenes are stabilized by resins in crude oil.

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Appendix: Experimental data on asphaltene precipitation from literature

I. Effect of solvents on the amount of asphaltene precipitated

a) At fixed dilution ratio of the solvents, the amount of asphaltene precipitated decreases with increasing carbon numbers for nonaromatic solvents. (Corbett L W and Petrossl U. 1978; Kokal S L et al, 1992; Hirschberg A et al, 1983; Norsk Hydro data)

b) The ability of a solvent to dissolve asphaltene:

2-methyl paraffin< n-paraffin<terminal olefin (Mitchell D L and Speight J G. 1972)

xylene<toluene<tetralinete (Cimino R et al, 1995)

Gonzalez G et al(1991) found that 1wt% of nonyl phenol can stabilize 0.1 g/l of asphaltene in n-heptane and toluene mixture. This study indicates that at least 250 molecules of nonyl phenol are involved in the peptization of each asphaltene molecule.

Chang C L and Fogler H S(1994) reported that, for best amphiphile DBSA, about 2 wt% of amphiphile can stabilize 0.15% of asphaltene in n-heptane.

II. . Effect of solvents on the onset of asphaltene precipitation

Rassamdana et al (1995) showed that the dilution ratio for the onset of asphaltene precipitation increases for n-C5 to n-C8, then decreases for n-C8 to n-C10. Data are extrapolated from titration experiments.

Norsk Hydro data show that the maximum dilution ratio at onset of precipitation occurs at n-C10.

Hirschberg A et al (1983) reported that the dilution ratio for onset of flocculation decreases from n-C7 to n-C16.

Cimino R et al(1995) reported that the amount of asphaltene precipitated increases with increasing dilution ratio of n-pentane. However, aromaticity and nitrogen content of asphaltene decrease with dilution ratio.

III. Effect of temperature

In general, the amount of asphaltene precipitated decreases with increasing temperature. However, the molecular weight and aromaticity of asphaltene increase. (Fuhr B J et al, 1991; Andersen S I, 1994 & 1996, MacMillan D J et al, 1995)

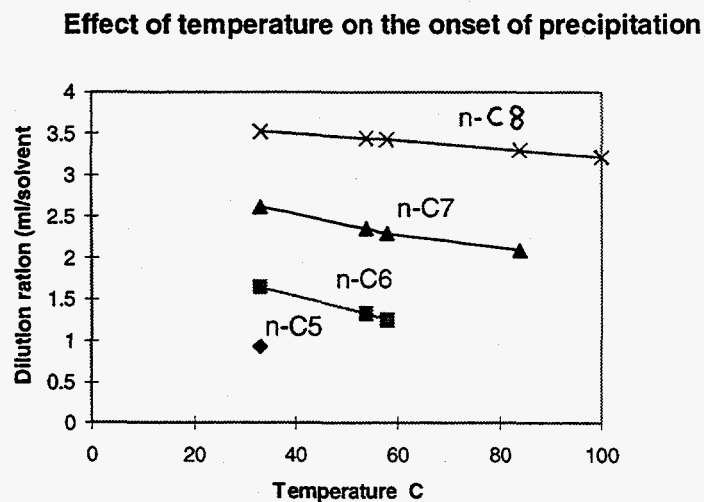The experimental data by Fuhr B J et al(1991) are shown in following two figures.

Effect of temperature on the onset of precipitation

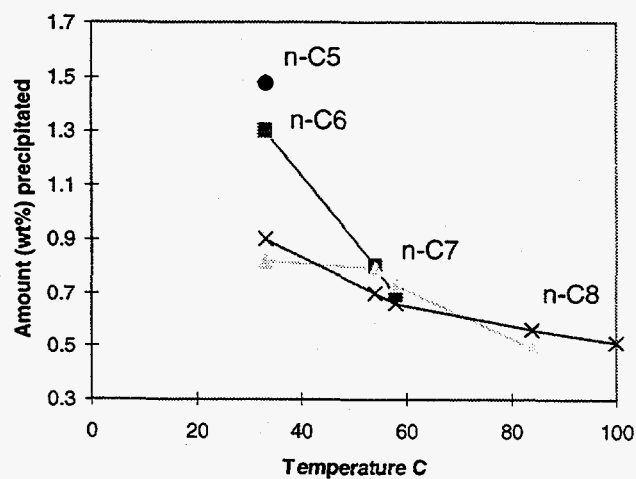**Figure A1** (Data from Fuhr B J et al(1991))

Figure A2 Effect of temperature on amount of asphaltene precipitated

(Fuhr B J et al ,1991)

Ali L H and Ghannam K A (1981) studied the effect of temperature on asphaltene precipitation for two different crude oils, one light and one heavy. For light crude oil. a lower asphaltene precipitated was observed at higher temperatures. However the heavy oil, the amount of asphaltene precipitated increased at higher temperatures. They suggested that the reason for "abnormal" temperature behavior was cracking of heavy oil at higher temperatures.

Kokal et al(1992) showed the effect of temperature and pressure on the onset of asphaltene precipitation for methane, propane, C2/C3 mixture and CO_2. For propane and C2/C3 mixture, they found that the pressure at onset point first increased with temperature($25-50^{\circ}C$), then decreases at higher temperatures($50-100^{\circ}C$). But in Hirschberg's experiments(1983), the pressure at onset of asphaltene precipitation increases with temperature for propane, and propane/decane mixture.

IV. Effect of pressure

For gas titration in general, the maximum likelihood of asphaltene precipitation occurs at the bubble point pressure of gas precipitant.(Hirschberg et al 1983, Kokal et al. 1992, Burke N E et al ,1990)

Srivastava R K et al (1995) showed the percent of asphaltene flocculated increases with the saturation pressure or concentration of CO_2

For liquid titration, the amount of asphaltene precipitated decreases with increasing pressure. The dilution ratio at onset of precipitation increases with pressure.

V. Size and molecular weight distribution of asphaltene molecules in solution

Carnahan N F et al (1993) found that as the pressure of the near critical solution is isothermally decreased from 400 to 25 bar, the average asphaltene molecule radius increases from 20.5 to 22.1 A. Association between asphaltenes increases with decreasing pressure. These results are obtained by using a small angle X-ray scattering(SAXS) method.

Storm D A et al (1992) showed that the polydispersity of asphaltene molecular size in vacuum residue can be correlated with Schultz distribution functions. The average

molecular radius of asphaltenes varies from 30 to 60 A for different crude oils. Also they found the average size increases slightly with asphaltene concentration.

Sheu E Y et al (1992) showed that the average asphaltene molecular radius in toluene is about 50 A, almost independent of temperature (25 to 180 °C). Small angle neutron scattering(SANS) was used in their experiments.

VI. Size of asphaltene particles precipitated from crude oil

Ferworn K A et al (1993), using a laser particle analyzer and paraffinic diluents, showed that particle size distributions can be correlated by a log-normal distribution function from about 100 to 800 μm, the average diameter is about 256 μm. Effects of paraffin carbon number and dilution ratio on particle size distribution were also investigated. The average particle size precipitated decreases from 300 μm for n-C5 to 180 μm for n-C16. On the effect of dilution ratio, it increases from 180 μm for volume ratio of n-heptane/bitumen equal 8 to about 280 μm for very high volume ratios.

Nielsen B B et al(1994) showed that the mean asphaltene particle size precipitated from crude oils increases with pressure, and decreases slightly with temperature.