

## Aggregation and Deposition of Heavy Organics in Petroleum Crudes

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*Abstract* Deposition of complex and heavy organic compounds which exist in petroleum crude can cause a number of severe problems. To prevent deposition inside the reservoir, in the well head, and inside the transmission lines it is necessary to be able to predict the onset and amount of deposition due to various factors. In the present paper the basic mechanisms of organic deposition are described based on two different microscopic theories; and their predictive capabilities are discussed. These models are the continuous thermodynamic (CT) model and the steric colloidal (SC) model. Utilization of kinetic theory of aggregation enables one to develop a fractal aggregation (FA) model which combines the ideas of the two proposed CT and SC models. The FA model is capable of describing several situations, such as the phenomena of organic deposition, growing mechanism of heavy organic aggregates, the geometrical aspects of aggregates, the size distributions of precipitated organics, and the solubility of heavy organics in an oil under the influence of miscible solvents.

**Keywords** Fractal aggregation theory; deposition of heavy organic; asphaltene; resin; continuous thermodynamics; statistical mechanics; colloidal suspension; petroleum.

### Introduction

One of the most worrisome problems in petroleum production and processing is heavy organic deposition which could cause permeability blocking between reservoir matrix and vugs and isolate the oil in the matrix from the principal flow channels (Lichaa and Harrera 1975). Asphaltene and other highly polar petroleum fractions pose many problems to the efficiency and cost of petroleum production. Considering the trend of the oil industry towards the utilization of deeper reservoirs (heavier asphaltic crudes) and the increased utilization of miscible flooding techniques for recovering oil, the role of organic deposition in the economic development of oil discoveries will be important and crucial (Preckshot et al. 1943; David 1973; Stalkup 1983; Leontaritis et al. 1986; Mansoori et al. 1988). As a result, there is a need for understanding the nature of heavy organic compounds and the mechanism of heavy organic deposition.

The parameters that govern precipitation of heavy organic substances appear to be compositions of crude and injection fluid, pressure, and temperature of the reservoir. With alterations in these parameters the nature of heavy organic substances which precipitate will vary. Also, it is a proven fact that the precipitation of asphaltene is generally followed with aggregation, or flocculation, of the resulting precipitate, which produces an insoluble material in the original reservoir fluid (Hirshberg 1984; Speight et al. 1984).

Over the last five decades a number of investigators have done research on the nature of heavy organic compounds and the mechanism of heavy organic deposition. There has been extensive progress made in the development of applied statistical mechanics and thermodynamics which is applicable in formulation and prediction of the organic deposition mechanism. Because of the complexity of the nature of heavy organic substances, the phenomena of the organic deposition are not well understood. Also in view of the complexity of the petroleum reservoirs, study and understanding of the in situ precipitation of organic substances seems to be a challenging and timely task. Such an understanding will help to design a more profitable route for miscible gas flooding projects. The extensively wide range of organic deposits suggest that such compounds may be partly dissolved and partly in colloidal state dispersed and stabilized primarily by resin molecules that are adsorbed on macromolecular surfaces.

The concept that heavy organic (asphaltic) compounds are present as a colloidal system is credited to Nellensteyn (1924). He proposed that asphaltic compounds were made of micelles protected by adsorbed resin and hydrocarbon materials, all dispersed in a hydrocarbon medium. He also found that the peptizing or precipitating properties of different common solvents with respect to asphaltic compounds are closely related to the surface tension. Swanson (1942) and Witherspoon and Munir (1960) proposed that resins were required for asphaltenes to dissolve in the distillate portion of a crude oil. According to Dickie and Yen (1967) petroleum resins provide a transition between the polar (asphaltene) and the relatively nonpolar (oil) fractions in petroleum, thus preventing the assembly of polar aggregates that would be nondispersible in the oil. Koots and Speight (1975) considered that asphaltene clusters associated with resin molecules could well be dominant species which allow the asphaltenes to exist in the colloidal state in a crude oil. Leontaritis and Mansoori (1987) proposed a thermodynamic-colloidal model which is capable of predicting the onset of asphaltene flocculation. According to their model asphaltenes exist in the oil as solid particles in colloidal suspension, stabilized by resins adsorbed on their surface.

The present report is designed with the purpose of describing the microscopic models of heavy organic deposition and application of modern theoretical and experimental techniques of statistical mechanics and thermodynamics to develop the methods that will predict organic deposition during the production and processing of petroleum crudes. First, a continuous thermodynamic (CT) model is presented in which the theory of heterogeneous polymer solutions is utilized for the predictions of the onset point and amount of organic deposits from a petroleum crude. Then, a steric colloidal (SC) model which is capable of predicting the onset of organic deposition is described. A combination of the two models results in a fractal aggregation (FA) model. Finally, an overview of the organic deposition problem is presented.

### Models of Organic Deposition

One major question of interest in the oil industry is "when" and "how much" heavy organics will flocculate out under certain conditions. Since the petroleum crude consists generally of a mixture of oil, aromatics, resins, and asphaltenes it has become possible to consider each of the constituents of this system as a continuous or discrete mixture interacting with each other. From the available laboratory and field data it is proven that the heavy organic substance which exists in oil consists of very many particles having molecular weights ranging from one thousand to several hundred thousands. As a result, distribution-function curves are used to report their molecular weight distribution. We have proposed two different models which are based on statistical mechanics of particles (monomers and polymers) dissolved or suspended in oil. A combination of the two models is general enough to predict the asphaltene-oil interaction problems (phase behavior or flocculation) wherever it may occur during oil production and processing. The principles of thermodynamics of multicomponent mixtures and phase equilibria, the theory of continuous mixtures, the statistical mechanical theory of monomer/polymer solutions, the theory of fractal aggregation kinetics are utilized here to analyze and predict the onset and amount of organic deposition from petroleum crudes.

#### *Continuous Thermodynamic (CT) Model*

Mansoori et al. (1988), Kawanaka, Park, and Mansoori (1988): The degree of dispersion of heavy organics in petroleum oils depends upon the chemical composition of the petroleum. Deposition of such compounds can be explained by an upset in the balance of oil composition. The ratio of polar to nonpolar molecules and the ratio of high to low molecular weight molecules in a complex mixture such as petroleum (see Figure 1) are the two factors primarily responsible for maintaining mutual solubility. The addition of miscible solvents will destroy these ratios, as is demonstrated in Figure 2. Then the heavy and/or polar molecules separate from the mixture either in the form of another liquid phase or into a solid precipitate. Hydrogen bonding and the sulfur and/or the nitrogen containing segments of the separated molecules could start to aggregate and as a result produce the irreversible heavy organic deposits which are insoluble in solvents.

Since heavy organics have a wide range of size or molecular weight distribution, one may consider such compounds as a heterogeneous polydisperse polymer. Then, in order to predict the phase behavior of heavy organics one can assume that the properties of heavy organic fractions are dependent on their molecular weights. To perform phase equilibrium calculation one needs to equate chemical potentials of every heavy organic fraction in the liquid phase,  $\mu_i^L$ , and the solid phase,  $\mu_i^S$ ;

$$\mu_i^S = \mu_i^L; i = 1, 2, \dots \quad (1)$$

In this model, the Scott and Magat theory (1945) of heterogeneous polydisperse polymer solutions is employed for calculation of chemical potentials of every heavy organic fractions. Since organic substances such as asphaltenes consist of mixtures of molecules with virtually continuous molecular weight distributions,

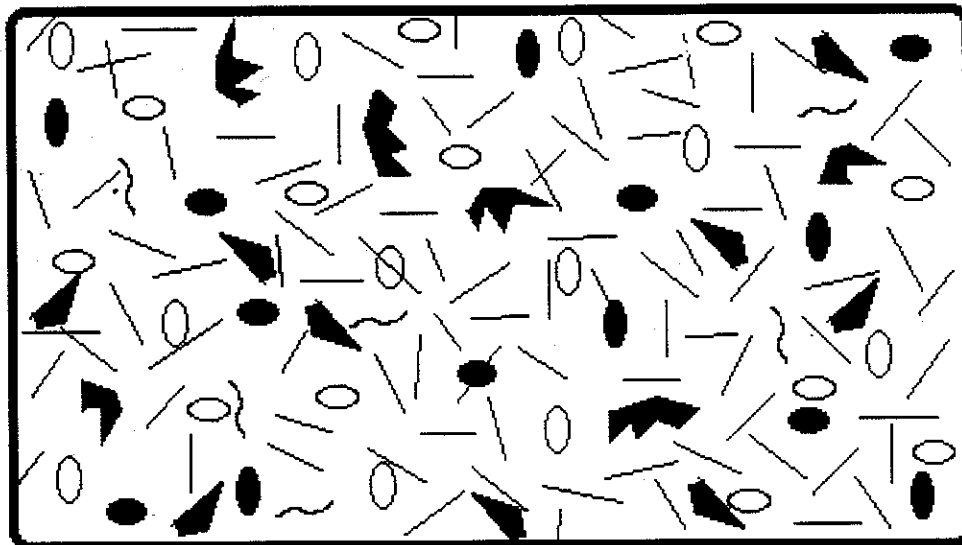



Figure 1. Composition of a petroleum crude containing heavy organics. In this figure --- and ~ represent the paraffinic molecules, ● represents the aromatic molecules, ○ represents the resin molecules and  represents the asphaltene molecules.

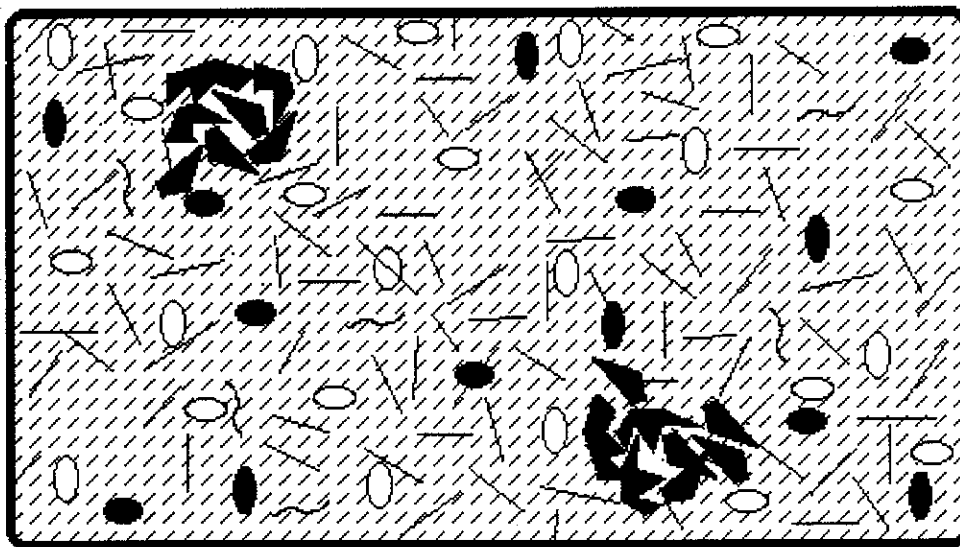

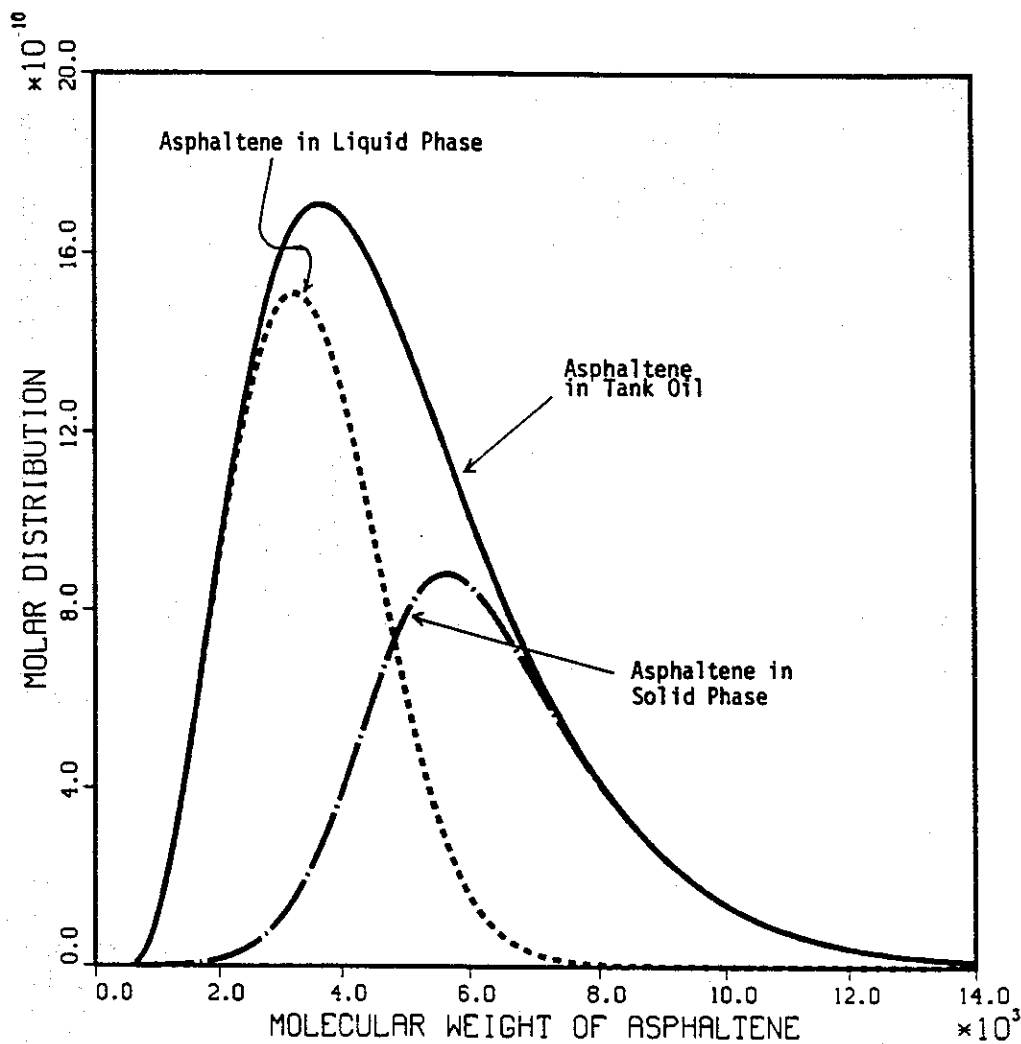
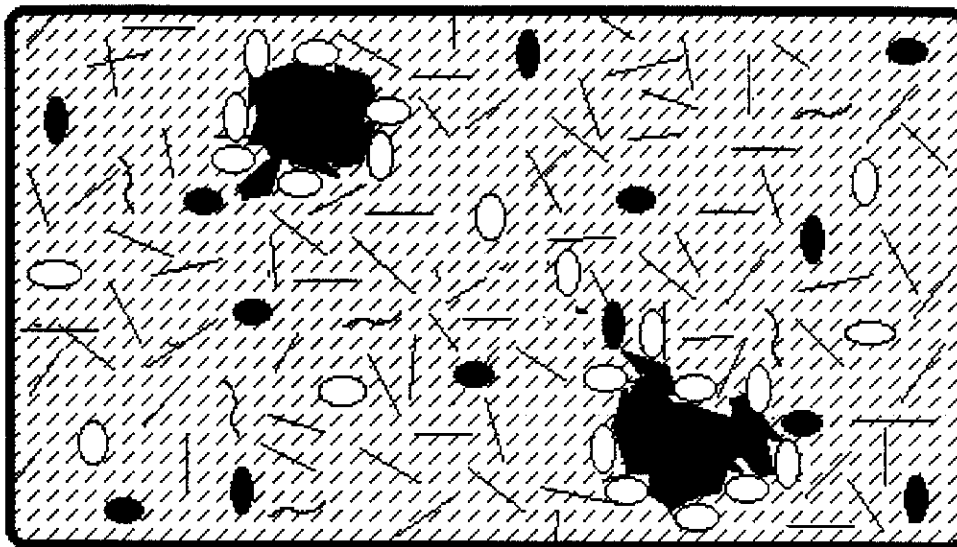


Figure 2. Precipitation of the heavy components of a petroleum crude due to the introduction of a miscible solvent. Molecular notations in this figure are the same as in Figure 1. The molecules of the miscible solvent are shown by .



**Figure 3.** Relations between molar concentration distributions of asphaltene in different phases in equilibrium resulting from the addition of a given amount of the miscible solvent (20.0 cc n-heptane) to one gram of the tank oil.

we can utilize the continuous mixture theory (Du and Mansoori 1986, 1987) joined with the thermodynamic theory of heterogeneous polymer solutions. Introduction of the continuous mixture theory results in a model that contributes toward better characterization of heavy organics and prediction of the onset of deposition and their phase behavior under the influence of miscible solvents. Figure 3 shows the comparison of the molecular weight of asphaltene from a petroleum crude oil before and after flocculation as predicted by the model. According to this figure the fractions of asphaltene with high molecular weights tend to deposit earlier than the fractions of asphaltene with lower molecular weight.



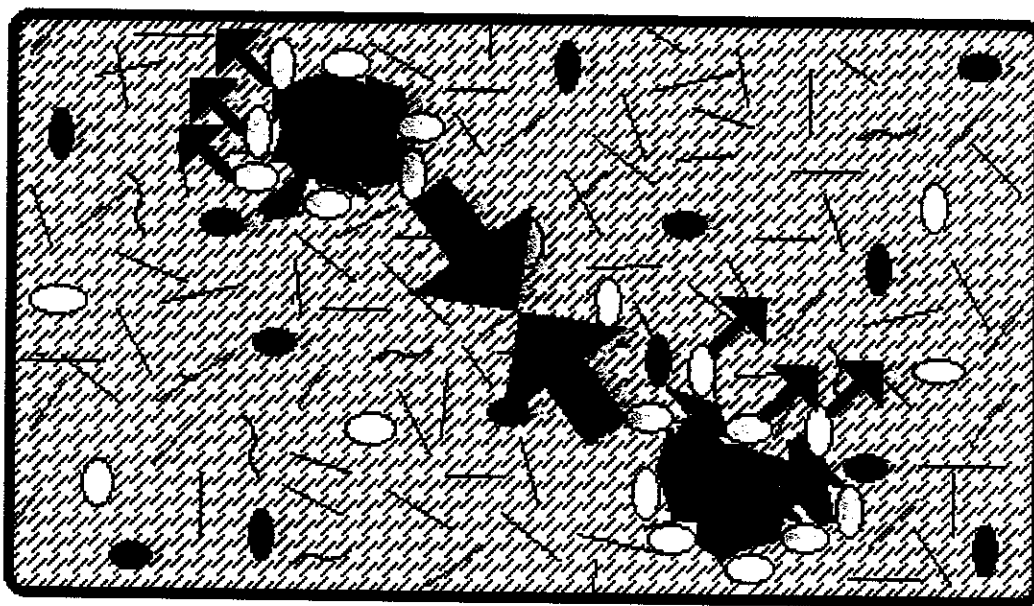
**Figure 4.** Steric colloidal model of heavy organic suspension in oil. Resin molecules in this case act as the peptizing agents. Molecular notations in this figure are the same as in Figures 1 & 2.

#### *Steric Colloidal (SC) Model*

Leontaritis and Mansoori (1987): This model is based upon the assumption that heavy organics (asphaltenes) exist as particles suspended in oil. Their suspension is assumed to be caused by resins (heavy and mostly aromatic molecules) which are adsorbed to the surface of heavy organic particles and keep them afloat because of the repulsive forces between resin molecules in the solution and the adsorbed resins on the macromolecular (asphaltene) surface (see Fig. 4). Stability of such a suspension is considered to be a function of concentration of resins in the solution, the fraction of asphaltene surface sites occupied by resin molecules, and the equilibrium conditions between the resins in solution and on the asphaltene surface. According to thermodynamics, a necessary condition for chemical equilibrium between two phases is that the chemical potential of each component in one phase is equal to its chemical potential in the other phase. Writing this condition for the resins in the asphaltene and oil phases we will have:

$$\mu_{\text{Resin}}^{\text{asphaltene phase}} = \mu_{\text{Resin}}^{\text{oil phase}} \quad (2)$$

The significance of the SC model is that the asphaltene particles will remain completely covered regardless of how the nature of the liquid mixture (i.e., add or remove miscible solvent) is changed, so long as the calculated chemical potential remains equal to (or above the) critical chemical potential, the colloidal asphaltene particles will remain completely covered. Calculation of the chemical potential of the resin in the solid phase would require utilizing small system thermodynamic techniques. However, this model requires only calculation of the chemical potential of the macroscopic asphaltene-free oil phase and as a result



**Figure 5.** Migration of some resin molecules (shown by small arrows) from the surface of asphaltene particles due to the change in their chemical-potential-balance between the bulk oil phase and the asphaltene-surface phase due to the introduction of additional miscible solvent. This causes the potential for aggregation (large arrows) of asphaltene particles due to development of free active sites on their surfaces, and their eventual flocculation as shown in Figure 6. Molecular notations in this figure are the same as in Figures 1 & 2.

macroscopic chemical potential calculations are adequate. Utilization of the SC model requires the following: (1) resin chemical potential calculation based on the statistical mechanical theory of polymer solutions; (2) studies regarding resin adsorption on asphaltene particle surface and measurement of the related Langmuir constants; (3) calculation of streaming potentials generated during flow of charged asphaltene particles; and (4) development and use of asphaltene colloidal and aggregation models for estimating the amount of asphalt which may be irreversibly aggregated and flocculated out according to Figure 5. The amount of resins adsorbed is primarily a function of their concentration in the liquid state (the oil). So, for a given system (i.e., fixing the type and amount of oil and asphaltenes) changing the concentration of resins in the oil will cause the amount of resins adsorbed on the surface to change accordingly. This means that we may drop the concentration of resins in the oil to a point at which the amount of resins adsorbed is not high enough to cover the entire surface of asphaltenes, as shown in Figure 5. This may then permit the asphaltene particles to come together (irreversible aggregation), grow in size (see Fig. 6), and flocculate.

#### **Fractal Aggregation (FA) Model**

A realistic model for the interaction of the heavy and light components of crude oil account for both the solubility effect and suspension characteristic of the heavy end in light components as shown by the series of Figures 1, 2, 4, 5, and 6. Such a model may be constructed by joining the concepts of continuous thermody-

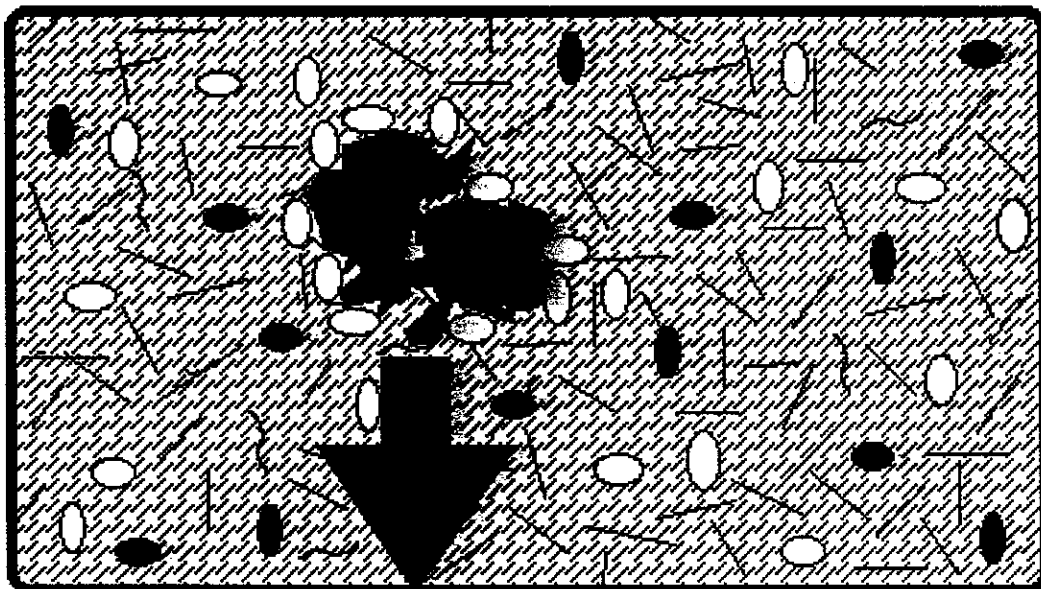


Figure 6. Flocculation and deposition (arrow) of very large asphaltene particles. See Figures 1, 2, 4, 5, and 6 for the historical events prior to this stage. Molecular notations in this figure are described in Figures 1 & 2.

namics, theory of liquid-solid phase transition, fractal aggregation theory of colloidal growth, and steric colloidal collapse and deposition models.

In the petroleum reservoir, heavy particles have been considered as colloidal particles, or micelles, being comprised of clusters of heavy particles associated principally via  $\pi$ - $\pi$  interactions (Dickie and Yen 1967). In their suspension, such particles are fully peptized by resin molecules and are able to remain suspended in the oil, thus preventing the aggregation of clusters of heavy particles because of the repulsive forces between resin molecules and the adsorbed resins on the macromolecular (heavy organic) surfaces. Stability of such a suspension is considered to be a function of the concentration of resins in the solution. When the concentration of resins changes due to the introduction of miscible solvents, the clusters of heavy particles will be subject to mutual interactions. This may result in a situation in which clusters of asphaltene molecules contact each other; they grow in size (irreversible aggregation) and flocculate. During the flocculation process the clusters of heavy particles are assumed to remain suspended in the solution randomly and independent of one another as Brownian particles due to the molecular induced thermal motion. Van der Waals attractive forces, and electrical (electrostatic or electrokinetic) repulsive (or attractive) forces would be the factors causing the aggregation and flocculation of the heavy organics. In order to account properly for the phenomena of heavy organic deposition, a model must incorporate the following: (1) the role of resin concentration in such deposition mechanism and its effect on the colloidal aggregation process of heavy particles under the influence of miscible solvents; (2) the growing size distribution of clusters of heavy particles by introducing the irreversible kinetic aggregation; and (3) determinations of the onset of heavy organic deposition, solubility of heavy organics in the solution, the size distributions of heavy organic deposits in the precipitated phase



and of heavy organics remaining soluble in the solution upon changes in pressure, temperature, and composition.

In order to formulate the necessary model for the prediction of phase behavior of the heavy organic deposition there is a need to study the mechanism of kinetic aggregation of clusters of heavy particles. There have been many attempts to understand the mechanism of kinetic aggregation of such particles. Up to now most of the studies on the Cluster-Cluster aggregation were concerned with the geometrical aspects of the aggregates. It has been noticed that an important characteristic of the colloidal aggregational model is the existence of a given shape for the size distribution of the clusters (Botet et al. 1984). We may consider a system consisting of  $N_C$  clusters of  $N_O$  heavy particles which are suspended in the solution randomly and are stabilized by resin molecules. The initial concentration of clusters of heavy particles in a system is considered sufficiently low so that one can observe the mechanism of flocculation. Introduction of miscible solvents into a system may result in a system that the clusters of heavy particles make them stick to each other, rigidly: that is, a cluster of mass  $m_i$  colliding with a cluster of mass  $m_j$  forms a single new cluster of a mass  $m_{i+j}$ . This process is then repeated. The heavy organic aggregation kinetic is assumed to obey the following model.



This model was originally proposed by Smoluchowski (1916) for coagulation and by Flory (1941) and Stockmayer (1943) for branched polymerization and it is extensively studied in the theory of aggregation, as well as in the theory of colloidal suspensions. The rate,  $R_{ij}$ , at which  $i$ -clusters of mass  $m_i$  and  $j$ -clusters of mass  $m_j$  may come into contact with each other and form  $(i + j)$ -clusters is given by  $R_{ij} = K_{ij}C_iC_j$ .  $A_j$  is the cluster of mass  $m_j$ , and  $K_{ij}$  is a concentration-independent collision kernel which describes the aggregation mechanism. Since the population of  $k$ -clusters ( $i + j = k$ ) increases by all collisions between  $i$ -clusters and  $j$ -clusters and decreases when a  $k$ -cluster combines with another cluster, then  $C_k(t)$  will satisfy

$$dC_k/dt = (\frac{1}{2})\sum_{i+j=k}K_{ij}C_iC_j - C_k\sum_{j=1}K_{kj}C_j \quad (4)$$

This expression is known as Smoluchowski's coagulation equation. This irreversible growth mechanism implies that the tendency of clusters to clustering of Brownian aggregates depends on their mass and the concentration of resins in the solution. The growth velocity,  $v$ , of the clusters of heavy particles can be expressed in the following functional form:

$$v = f(m, C_R) \quad (5)$$

where  $m$  is the cluster of asphaltene molecules of mass  $m$  and  $C_R$  is the resin concentration in the solution. All geometrical aspects may be contained in the expression of kinetic kernels,  $K_{mn}$ , which are proportional to the probability for two clusters of mass  $m$  and  $n$  to meet. The expression of kinetic kernels,  $K_{mn}$ , can be expressed in the following functional form:

$$K_{mn} = f(m, n, d, D, C_R) \quad (6)$$

where  $d$  is the euclidian dimension,  $D$  is the fractal dimension of clusters, and  $D$  is bounded by  $1 < D < d$ . The dynamical behavior of average cluster mass with respect to time can be expressed based on the hypothesis generally admitted for the kinetic treatment (Leyvraz and Hendriks 1981; Hendriks et al. 1984; Jullien et al. 1983) of coagulation using Smoluchowski's equation. From the time scaling (Botet and Jullien 1984), the increasing average cluster mass,  $\langle m \rangle$ , can be expected to have a following functional form:

$$\langle m \rangle = f(t, d, D, C_R) \quad (7)$$

The kinetic theory of fractal aggregation process can be utilized in order to describe properly the growing size distribution of clusters of heavy particles due to the influence of miscible solvent. Based on a global (space, time, and mass) scaling hypothesis and a general mean-field argument Smoluchowski's equation can be solved analytically, which gives us the expression of a "reduced size" distribution of clusters (Botet and Jullien 1984; Jullien et al. 1984). The analytic equation for the "reduced" size distribution of clusters of heavy particles can be expressed in the following functional form:

$$F = F(y, d, D, C_R) \quad (8)$$

where  $y = m/\langle m \rangle$  and  $\langle m \rangle$  is the average cluster mass.

In a heterogeneous polymer mixture, one can specify different fractions of polymer based on their molecular weight. Assuming that heavy organics behave as a heterogeneous polymer, one can equate chemical potentials of every heavy organic fraction in the oil phase,  $\mu_y^L$ , and the precipitated phase,  $\mu_y^S$ . This corresponds to the heavy organic remaining soluble in an oil phase in equilibrium with the heavy organic content of a precipitated phase.

$$\mu_y^S = \mu_y^L; y = m/\langle m \rangle, 0 < y < \infty \quad (9)$$

The statistical mechanical theory of heterogeneous polydisperse polymer solutions permits calculation of chemical potentials of heavy organic fractions. The "reduced" growing size distribution of clusters of heavy particles can be utilized with the statistical mechanical theory of polymer solutions and the principle of phase equilibria. Thus, this model can predict the solubility of heavy organic in the solution, the size distributions of heavy organic in the precipitated phase and of heavy organic remaining soluble in an oil mixture upon changes in pressure, temperature, and composition under the influence of miscible solvents. This may contribute significantly toward better prediction of the phase behavior heavy organic deposition mechanism under the influence of miscible solvents.

### Characterizations and Model Predictions

Asphaltic compounds (asphaltenes and resins) are not very amenable to the petroleum production field and are usually responsible for the heavy organic deposition problem. Therefore, considerable effort has been applied to determine their physical and chemical properties. The techniques which have been used are

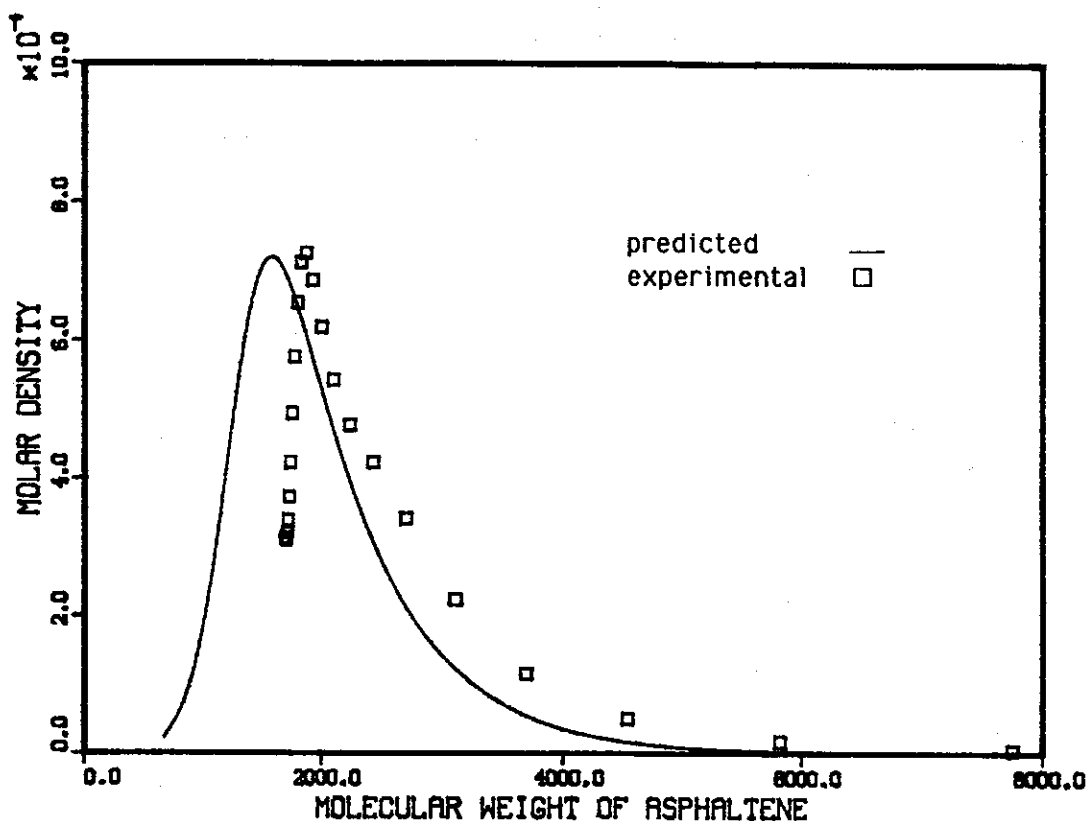


Figure 7. Comparison of experimental and predicted asphaltene molecular weight distributions. The asphaltenes were flocculated from Brookhaven oil with n-pentane using the standard method ASTM D-3279-83.

quite diverse, and it is difficult and erroneous to interrelate and classify these complex compounds. In the technique used in this laboratory the separation of asphaltenes and resins is accomplished by gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC). The detailed experimental methods used in this laboratory are reported in a previous publication (Leontaritis and Mansoori 1988).

Samples of n-pentane, n-hexane, and n-heptane asphaltenes flocculated from both crude oils were prepared and run through a Waters GPC. The obtained particle size distribution of Brookhaven oil samples was normalized in order to compare with the predicted particle size distributions by the proposed CT model. Figure 7 shows a comparison between the experimental and predicted molecular weight distributions of n-pentane asphaltene. The molecular size distributions for the different flocculant carbon numbers are plotted in Figure 8. Since the experimental molecular size distributions were determined relative to narrow dispersity polystyrene standards, the comparisons should focus on the trend of molar density with respect to molecular weight and of functional relationship of the flocculant carbon number. The molecular weight size distribution of resins was shown as a standard normal distribution, which indicates that, with respect to size, resins distribute evenly around their mean in the crude oil (Leontaritis and Mansoori 1988).

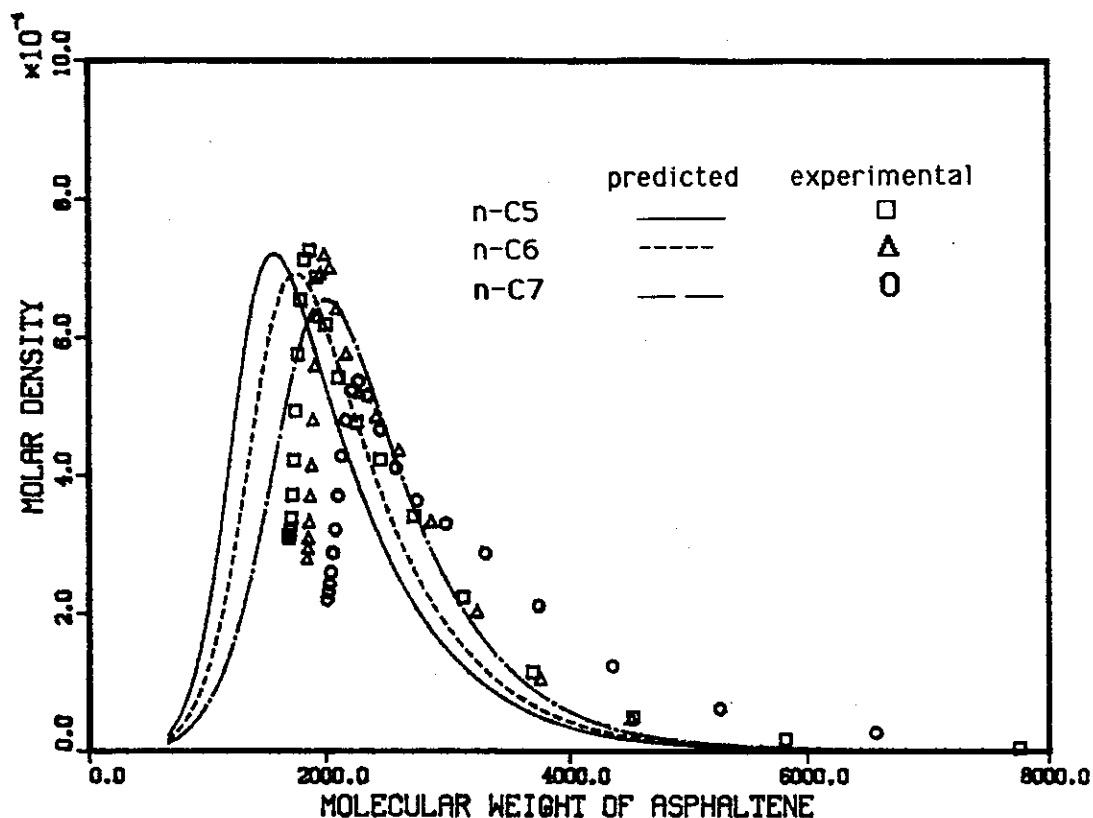


Figure 8. Comparison of experimental and predicted asphaltene molecular weight distributions. The asphaltenes were flocculated from Brookhaven oil with different n-paraffins using the standard method ASTM D-3279-83.

Using the proposed CT and SC models described we are able to predict the onset and amount of organic (asphaltene) deposition from petroleum crudes. Onsets of asphaltene deposition due to the different miscible solvents can be predicted by using the SC model in which only one experimental onset data is used for fitting to the model and the rest is predicted. Using the CT model, the onsets and amounts of asphaltene deposition are predicted and they are compared with the experimental data (Hirshberg et al. 1983) for Shell oil in Table 1. According to this table all the onsets and amounts of asphaltene deposition (except for n-heptane) are in good agreement with the experimental data. Figure 9 consists of the predictions of onsets and amounts of asphaltene deposition versus volumes of different n-paraffin solvents added to the tank oil. According to this figure the trend of the deposition predictions for different n-paraffins is consistent with their molecular weights. In Table 2, the predicted (by the CT model) amounts of asphaltene deposition for different normal paraffin solvents are listed with experimental titration data for Brookhaven oil which is generated in this laboratory. A comparison of the predicted values of amounts of asphaltene deposition with experimental data, also gives us fairly good agreement.

The trends of the asphaltene deposition shown in Tables 1 and 2 and Figure 9 can be explained from the viewpoint of our proposed CT and SC models. Ac-

**Table 1**  
The Experiment vs. Prediction of the Onset and Amount  
of Asphaltene Deposition from the Tank Oil

Dilution Ratio (cm <sup>3</sup> diluent/g tank oil)	n-C <sub>5</sub>		n-C <sub>7</sub>		n-C <sub>10</sub>	
	EXP <sup>a</sup>	CAL <sup>a</sup>	EXP	CAL	EXP	CAL
1.35						O.F
1.40				O.F	O.F	
1.90	N.T <sup>b</sup>	O.F <sup>c</sup>				
2.22			O.F			
5	—	3.31	1.53	1.52	1.34	1.30
10	3.61	3.67	1.82	2.28	1.45	1.53
20	3.79	3.75	1.89	2.43	1.50	1.45
50	3.87	3.73	1.87	2.29	—	1.13

The experimental titration data (wt% tank oil) are taken from Hirschberg et al. (1983).

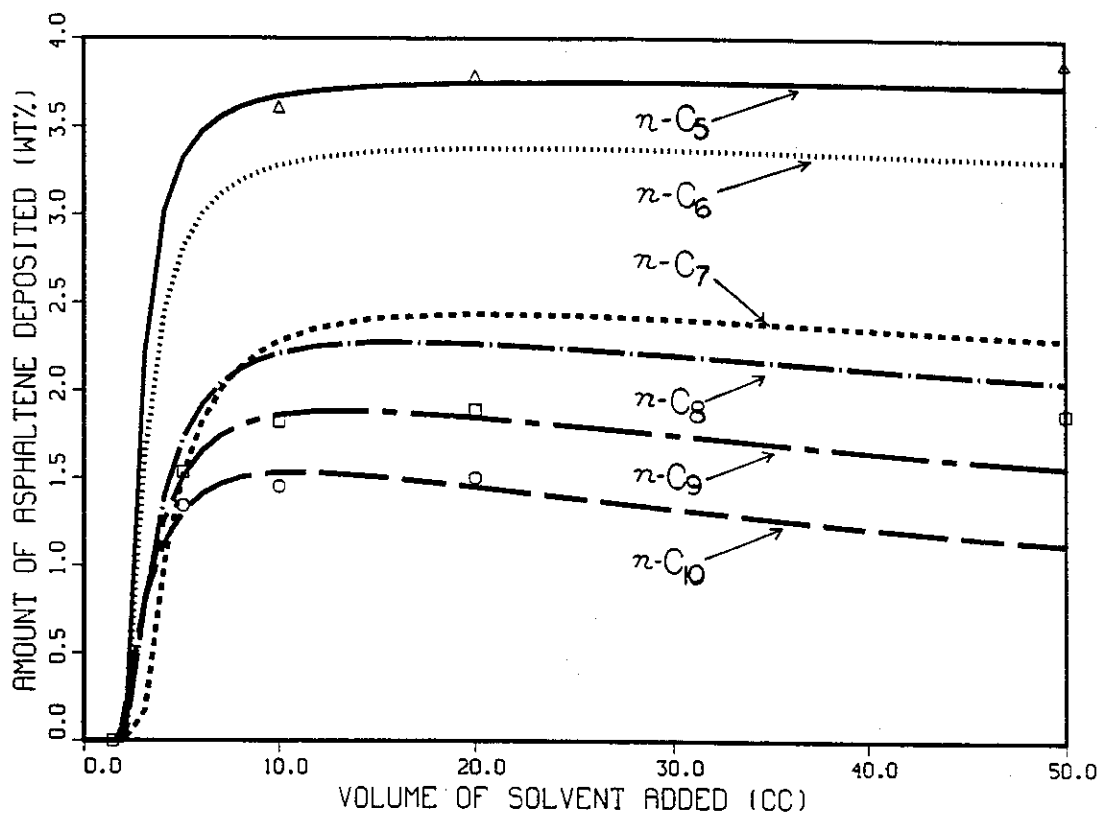
<sup>a</sup> EXP = experimental values; CAL = calculated values.

<sup>b</sup> N.T denotes that onset of asphaltene deposition is not determined.

<sup>c</sup> O.F denotes the onset of flocculation.

According to these models, the required amount of the miscible flocculant to arrive at the onset decreases as the molecular weight of the miscible flocculant increases. This trend can be explained by the SC model. In hydrocarbon mixtures (as in most mixtures), size difference between the components is a major factor affecting their solubility. In this case, resins are expected to be more soluble in heavier than lighter paraffins. As a result, it is expected to require smaller amounts of the heavier flocculants for dissolving the same amount of resins. Consequently, the required amount of flocculant for arriving at the onset will be inversely proportional to the flocculant molecular weight, provided that the amount of resins that needs to be desorbed from the asphaltenes in order to arrive at the onset is constant regardless of the flocculant used.

The tendency toward amounts of asphaltene deposition decreases as the molecular weight of the miscible flocculant increases. However, this tendency can be explained by the CT model. Since the high molecular weight molecules are less soluble in lower molecular weight solvents, the amount of asphaltene deposition by lower molecular weight solvent is bigger because the average molecular weight of an oil is lowered. This can also be expected because the lower molecular weight paraffins are more lyophobic with reference to asphaltene and, therefore, separate them more completely. The proposed CT and SC models can also apply for prediction of the pressure/composition region of asphaltene deposition at high pressures under the influence of a miscible gas. Figure 10 shows the predicted (by the CT model) pressure/composition region of asphaltene deposition from Brookhaven oil. The experimental data is taken from Monger and Fu (1987). There is good agreement between the experimental and predicted 3 $\Phi$ (vapor-liquid-solid phase) envelopes. Overall, the proposed models can be used successfully to predict the phase behavior of heavy organic deposition from the petroleum crudes under the influence of miscible solvents.



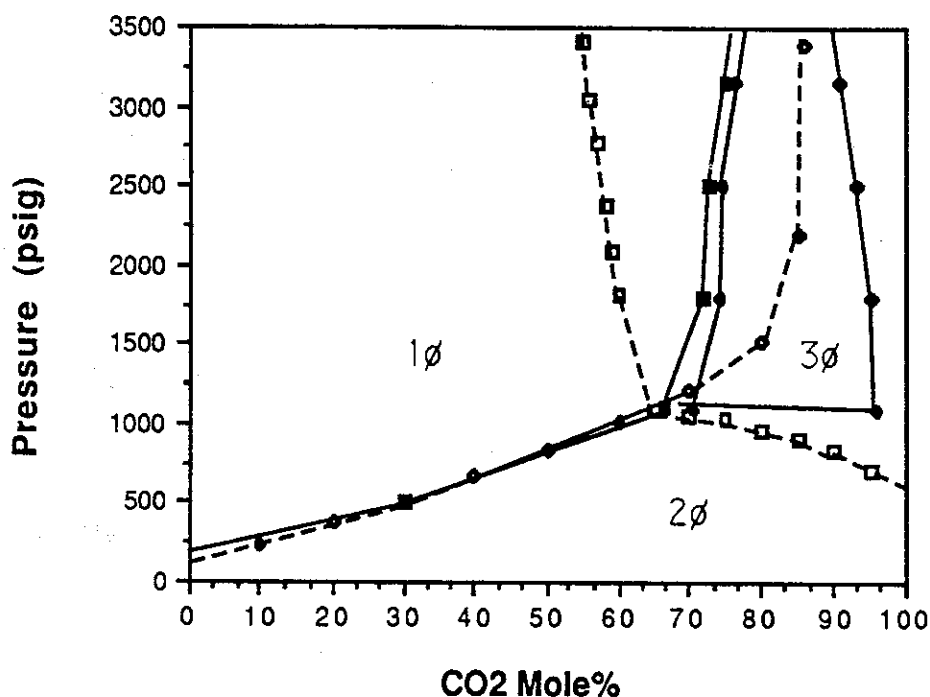
**Figure 9.** The prediction of the amount of asphaltene deposition from tank oil No. 1 versus the volume of six different n-paraffin solvents. The experimental asphaltene deposition data due to n-pentane, n-heptane, and n-decane additions are shown by  $\Delta$ ,  $\square$ ,  $\circ$ , respectively.

**Table 2**  
The Amount of Asphaltene Flocculant  
Obtained by Titration  
of a Brookhaven Oil with n-Paraffins

Flocculant	Wt% of Asphaltene	
	EXP <sup>a</sup>	CAL <sup>a</sup>
n-Pentane	1.65	1.41
n-Hexane	1.25	1.23
n-Heptane	0.95	0.99
n-Decane	0.72	0.69
n-Dodecane	0.60	0.63
n-Hexadecane	0.52	0.49

The experimental data are taken from Leon-taritis and Mansoori (1988).

<sup>a</sup> EXP = experimental values; CAL = calculated values.



**Figure 10.** Phase diagram for mixtures of Brookhaven stock tank oil and carbon dioxide at 317 K. Region 1 $\phi$  is the homogeneous liquid phase area, 2 $\phi$  is the liquid-vapor phase equilibrium area, and 3 $\phi$  is the liquid solid-vapor phase area. The region to the right of the vertical hollow square tick marks and to the top of the horizontal hollow square tick marks is the predicted 3 $\phi$  region. The diamond marks are the predicted bubble point pressures and the dark square marks are the experimental bubble point pressures. The experimental data is taken from (Monger and Fu (1987)).

## Conclusions

The proposed models for organic deposition from petroleum crudes are based on two different facts. In the CT model we consider the heavy organics to be dissolved in an oil which may or may not form a solid phase depending on the thermodynamic conditions of temperature, pressure, and composition. In the SC model we considered the heavy organics as solid particles of different sizes that are suspended colloiddally in an oil and stabilized by large polymeric molecules (i.e., resins) adsorbed on their surface. The proposed CT and SC models can provide the tool for making satisfactory prediction of the phase behaviors of heavy organic deposition.

Since the asphaltene problem is so elusive, it seems that before one can formulate a comprehensive model describing the problem the true asphaltene deposition mechanism must be clearly understood and backed by field and experimental data. Then an accurate and representative model can be formulated. Our objective here is to develop a comprehensive model which can properly describe the mechanism of heavy organic deposition. Utilization of kinetic theory of fractal aggregation has enabled the development of an FA model which combines ideas of the two proposed CT and SC models. The FA model allow us to properly describe several situations, such as phase behavior of heavy organic deposition,

growing mechanism of the heavy organic, the geometrical aspects of aggregates, the size distributions of precipitated deposits, and the solubility of heavy organic in the solution under the influence of miscible solvents. In general, the proposed models are applicable for predicting organic deposition (asphaltene, wax, resin) from petroleum crudes due to the changes of pressure, temperature, and composition.

### Acknowledgment

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