

G. A. Mansoori, T. S. Jiang, and S. Kawanaka

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Of the second category, that of greatest importance is Comprehensive core-flood testing facility for simulation of the *in situ* asphaltene deposition at different temperatures, pressures, core porosity, and injection fluid to oil ratios.

With the implementation of the models presented in this report, along with the experimental measurements discussed, the following objectives could be accomplished:

1. Development of a thorough molecular thermodynamic model for asphaltene deposition and testing of the model against the laboratory and field measurements.
2. Development of a comprehensive transport phenomena model of the flow of crude oil containing asphaltene colloidal particles (or micelles) in porous media in the course of asphaltene deposition, studies on colloidal instabilities which may be the cause of asphaltene deposition, and studies on wettability alterations due to the adsorption of asphaltene on surfaces.
3. Physicochemical property measurements and laboratory simulations in support of the studies which will basically consist of:
  - (i) Measurement of the phase behavior of crude and injection gas mixtures at high pressures and at different GOR and temperature conditions;
  - (ii) Experimental simulation of miscible gas flooding of reservoir during the course of asphaltene deposition and flow through porous media of asphaltene containing crude and injection gas.

These experiments will enable the researchers to develop structural models for porous media and analysis of flow of miscible crude system containing asphaltene substances in colloidal states.

The present models are only the beginning of an effort to try to develop analytical predictive techniques on the phase and transport behavior of asphaltenes. Any investigation, theoretical or experimental, into the chemical structure and phase behavior of asphaltenes in crude oil is hindered by their complex nature. Despite the large volume of laboratory work that has been performed since 1930's to establish the physical and chemical nature of asphaltenes in oil [77], there are only qualitative descriptions and hypotheses given as to the physicochemical structure of asphaltenes. A comprehensive model that would describe the phase and

transport behavior of asphaltenes in oil must take into account the fact that there is generally a wide range of size distribution of asphaltenes in oil and the plausible speculation that one part of them is dissolved and the other is in a colloidal state.

#### ACKNOWLEDGEMENTS

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aggregates in the form of Equation (29) may be expressed as

$$\partial(\psi\langle\rho_{(A)}\rangle)/\partial t + \text{div}(\langle\rho_{(A)}\rangle\bar{v}) = \bar{r}_{(A)} - \text{div}(\mathbf{j}_{(A)}^{(e)}) - \alpha_{(A)}, \quad (37)$$

where the vector

$$\mathbf{j}_{(A)}^{(e)} = -\langle\rho\rangle D \bar{w}_{(A)} - \delta_{(A)} \quad (38)$$

should be thought of as "effective" mass flux vector with respect to  $\bar{v}$ .

With the introduction of local volume-averaged variables, we have eliminated the necessity for an explicit description of the microscopic structure of the pores. However, as in any averaging process, information has been lost. We are now faced with the necessity of introducing additional relationships for  $\delta_{(A)}$  and  $\alpha_{(A)}$ . Either these additional relationships could take the form of empirical data correlations or they could be developed from an idealized structural model [72-74] for porous medium within any given averaging surface  $S$ . Slattery [71] gave three examples of how experimental data can be used to prepare correlations for  $\delta_{(A)}$ . For instance, in an isotropic (nonoriented) porous medium when convection can be neglected, it is shown that

$$\delta_{(A)} = \langle\rho\rangle D D_{(A)}^* \bar{\nabla} \bar{w}_{(A)}, \quad (39)$$

with

$$D_{(A)}^* = D_{(A)}^* \langle\psi, [l_o \langle\rho\rangle |\bar{\nabla} \bar{w}_{(A)}| / \langle\rho_{(A)}\rangle]\rangle \quad (40)$$

as a function of the porosity and a dimensionless group. In Equation (40),  $l_o$  can be thought of as a characteristic pore size. If conditions are such that Equation (39) applies, the effective mass flux in the form of Equation (38) can be expressed in terms of an effective coefficient

$$D_{\text{eff}} = D(1 + D_{(A)}^*) \quad (41)$$

as

$$\mathbf{j}_{(A)}^{(e)} = -\langle\rho\rangle D_{\text{eff}} \bar{\nabla} \bar{w}_{(A)}. \quad (42)$$

This is consistent with the common practice in describing diffusion in a porous medium [74].

By similar arguments we can show that when convection is important,  $\delta_{(A)}$  can be expressed as

$$\delta_{(A)} = \langle\rho\rangle (D D_{(A)}^* \bar{\nabla} \bar{w}_{(A)} - l_o |\bar{\nabla} \bar{w}_{(A)}| D_{(A)}^* \bar{v}) \quad (43)$$

where, for  $i = 1, 2$ ;

$$D_{(A)}^* =$$

$$D_{(A)}^* (N_{pe}, \bar{v} \cdot \bar{\nabla} \bar{w}_{(A)} / (|\bar{v}| |\bar{w}_{(A)}|), l_o \langle\rho\rangle |\bar{\nabla} \bar{w}_{(A)}| / \langle\rho_{(A)}\rangle, \psi) \quad (44)$$

and

$$N_{pe} = l_o |\bar{v}| / D. \quad (45)$$

#### 5.4 Deposition Mechanisms

When a crude oil containing asphaltenes is flowing through porous media, precipitation can occur as discussed in section 2. The asphaltene aggregates formed may be brought into contact with the possible retention site on the pore walls. They either deposit there or are carried away by the flowing stream. The deposition process is therefore a sequence of the following mechanisms:

1. The contacting of asphaltene aggregates with the retention sites on the pore walls;
2. The fixing of asphaltene aggregates on the sites, and eventually;
3. The breaking away of previously deposited asphaltene aggregates.

Our objective here is to relate the deposition rate  $\alpha_{(A)}$  of asphaltene aggregates to the various factors which define the system. The factors considered should be the experimental parameters which are measurable and have an effect upon deposition process. For example, the crude oil is characterized by its viscosity  $\mu$ , mass density  $\rho$  and flow rate  $\bar{v}$ ; the asphaltene aggregates are defined by their concentration  $\langle\rho_{(A)}\rangle$  and surface properties; the porous medium is represented by its porosity  $\psi$ , permeability  $k$  and pore size distribution.

Before asphaltene aggregates deposit on the pore wall surface, they have to be brought into the immediate neighborhood of the wall. Possible mechanisms are hydrodynamic lateral diffusion in the mass-transfer boundary layer, as well as Brownian diffusion due to molecular thermal motion. Once asphaltene aggregates are brought into the immediate neighborhood of, or into contact with, the pore wall, deposition may occur due to the interaction of asphaltene aggregates with the solid surface or deposited asphaltenes. There has been evidence showing the surface activity of petroleum asphaltenes [38]. The van der Waals forces, which are always attractive, and the electrical forces (electrostatic or electrokinetic) which are either attractive or repulsive according to the physicochemical conditions,

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That is, for constant density of asphaltene, the volume distribution with respect to the molecular weight of asphaltene happens to be the same as the weight distribution. In order to get the total volume fraction of asphaltene in the liquid phase, we substitute Equation (16) into Equation (17) and integrate over the entire molecular-weight distribution range; *i.e.*,

$$(\phi_A)_{\max} = \int_0^{\infty} d\phi_{Ai}^L \\ = \int_0^{\infty} [V_{Ai}^T / \{V^L + V^S \exp(-m_{Ai}\theta)\}] F_w(M_{Ai}) dM_{Ai}. \quad (17)$$

Hence, for a given weight distribution of asphaltene fraction,  $F_w(M_{Ai})$ , we will be able to integrate Equation (17) in order to calculate the maximum volume fraction of asphaltene in the liquid phase at the onset of its deposition

Suppose the mole distribution of the asphaltene fraction be provided:

$$F_n(M_{Ai}) = (1/n_A^T)(dn_A^T/dM_{Ai}). \quad (18)$$

Then, we obtain

$$F_w(M_{Ai}) = F_i(M_{Ai}) = (M_{Ai}/\bar{M}_A) F_n(M_{Ai}), \quad (19)$$

where  $\bar{M}_A$  is the average molecular weight of asphaltene. For the derivation, the molar volume of the *i*th fraction of asphaltene,  $v_{Ai} = dV_{Ai}^T/dn_{Ai}^T$  is used and the constant value of the density of asphaltene  $\rho_A$  is again used. In order to obtain the maximum volume fraction of asphaltene in the liquid phase, integrate Equation (14) after the substitution of Equation (19).

## 5. TRANSPORT PHENOMENA MODELING

### 5.1 Flow Through Porous Media with Asphaltene Deposition

Fundamentally, there are no special equations needed to analyze transport processes in a permeable structure. The usual equations of change are believed applicable to the fluid phase moving through an individual pore. The problem is to describe geometrically the configuration of the pore walls bounding the flow.

For many purposes, only local averages of concentrations, velocities and pressures are important. This suggests the concept of local volume averaging, in which the equations of change are averaged over the immediate neighborhood of each point in the

structure. The advantage is that one can avoid specifying detailed configurations of the pore geometry. But a price is paid: information is lost that must be supplied empirically or from an idealized structural model for the local flow.

In what follows, the local volume-averaged mass-balance equations for the flow through porous media with asphaltene deposition will first be established. The elementary mechanisms which cause the deposition of asphaltenes in porous media are then identified. From the basic laws of the colloid and interface science, the general form of correlations governing the deposition phenomena will be proposed. With the combination of these deposition correlations and local averaged mass balance equations, the general behavior of flow through porous media with asphaltene deposition can be described. The pressure drop and its variation with asphaltene deposition will then be examined by the local volume-averaged equations of motion.

### 5.2 Local Volume Averages

Let us begin by thinking of a particular point *z* in the porous medium. It makes no difference whether this point is located in the solid phase, the fluid phase, or on the solid-fluid phase interface; the argument remains unchanged. Let us associate with this point *z* a closed surface *S* of arbitrary shape.

We will identify this averaging surface *S* with every point in the porous medium with a simple translation of *S* without rotation. The characteristic dimension of *S* should be sufficiently large that averages over the fluid enclosed by *S* vary smoothly with position. Whenever possible, it should be so small as to be negligible with respect to the macroscopic dimension of the porous medium.

Let us define *V* to be the volume enclosed by *S*. We will denote by  $R_{(t)}$  the pores that contain the fluid within *S*;  $V_{(t)}$  is the volume of  $R_{(t)}$ .

Assume that *B* is some scalar, vector, or tensor associated with the fluid. We will have occasion to speak of

$$\bar{B} = (1/V) \int_{R_{(t)}} B dV \quad (20)$$

as the *local volume average* of *B* for the fluid phase, and

$$\langle B \rangle = (1/V_{(t)}) \int_{R_{(t)}} B dV \quad (21)$$

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Injectivities reduced by a factor of three following gas injection have been observed in a number of carbon dioxide-injection projects [2] and water-alternate gas drives [50]. These problems are associated mostly with field problems rather than well-bore effects.

Asphaltene precipitation inside the reservoir can add significantly to field problems, specially if it occurs deep in the well or in the producing intervals. Extensive testing should be conducted before the start of miscible flooding or acidizing of wells that produce crude oils with high asphaltene contents, to prevent plugging of the reservoir with precipitated asphaltene.

#### 4. MOLECULAR THERMODYNAMIC MODELING OF ASPHALTENE DEPOSITION

Crude petroleum generally consists of many hydrocarbon components, from methane up to very heavy hydrocarbons. There exist also varying amounts of sulfur, oxygen, and nitrogen-containing compounds [24, 50]. The liquid state of the petroleum crude is a result of a delicate balance between its constituents, which depend upon each other for solubility. On introduction of a solvent into this mixture, such as carbon dioxide at high pressures, or *n*-pentane, the natural equilibrium of the mixture is upset and some compounds precipitate. Deposition of asphaltene from petroleum crude due to the introduction of a solvent can be understood by the application of the principles of the thermodynamics of multicomponent mixtures and phase equilibria. In the present section, we first introduce a descriptive account of the asphaltene deposition phenomena, then use molecular thermodynamic techniques [52, 56] in order to produce predictive equations for its quantitative interpretation.

It is understood that asphaltene precipitation is a general phenomenon common to all complex organic solutions [24]. Thus, interpretations which are made for the deposition of petroleum asphaltenes will also apply to coal-derived liquids, kerogen from shale oil, bitumen of tar sands, and any other complex solution of organic compounds.

There are two types of modeling for asphaltene deposition processes: the solubility model; and the colloidal model. The colloidal model is based on the fact that asphaltene is suspended due to the adsorption of resin on asphaltene and that asphaltene may have either a positive or a negative charge [41]. This

model is effective for asphaltenes, the molecular weights of which are several hundred. The solubility model uses the statistical mechanical theory, in which asphaltene is assumed to behave like polymer molecules, and the rule of heat of mixing. The solubility model is introduced in this section.

It is generally assumed that two factors are primarily responsible for maintaining the mutual solubility of the compounds in a complex mixture such as petroleum crude. They are the ratio of polar to nonpolar molecules and the ratio of the high-molecular-weight to low-molecular-weight molecules in the mixture [24]. Of course, polar and nonpolar compounds are basically immiscible, and light and heavy molecules of the same kind are partially miscible or immiscible depending on the difference between their molecular weights. However, in the complex mixture of petroleum crude all these compounds are probably mutually soluble so long as a certain ratio of each kind of molecule is maintained in the mixture. By introduction of a solvent into the mixture this ratio is altered. Then the heavy and/or polar molecules separate from the mixture, either in the form of another liquid phase or as a solid precipitate. Hydrogen bonding and the sulfur and/or the nitrogen-containing segments of the separated molecules could start to aggregate (or polymerize) and as a result produce the irreversible asphaltene deposits, which are insoluble in solvents.

In order to formulate the necessary model for prediction of the onset of deposition of asphaltene from petroleum crude we can take advantage of the theories of polymer solutions [57–59]. The first attempt at such modeling is due to Hirschberg and others [60, 61], in which they utilized the Flory–Huggins theory of polymer solutions in order to predict the onset of asphaltene deposition [62]. However, the Flory–Huggins theory is valid for the case of homogeneous chain molecules of asphaltene of uniform molecular weight in a single uniform solvent. It is a well-known fact that molecules of asphaltene neither consist of homogeneous chain molecules, nor can the asphaltene-free crude and the injection fluid be considered as a single uniform solvent [63–68]. In reality, asphaltene, and the asphaltene-free crude, both consist of mixtures of molecules with a virtually continuous molecular weight distribution. In order to formulate the phenomena of asphaltene deposition from petroleum crude, we can utilize the thermodynamic theory for polymer solutions consisting of a polymer with

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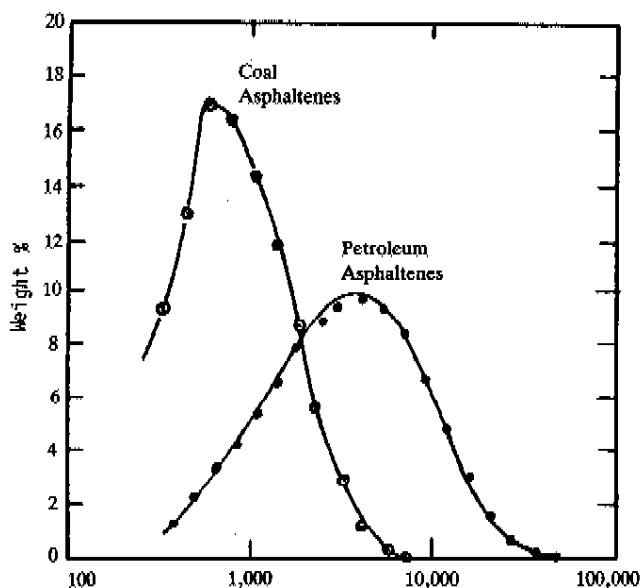


Figure 4. Comparison of Molecular Weight Distribution of Coal Asphaltene and Jobo Petroleum Asphaltene. For Petroleum Asphaltene the Solid Line Represents the Vacuum Residuum While the Dots Represent the Atmospheric Residuum (Long [23]).

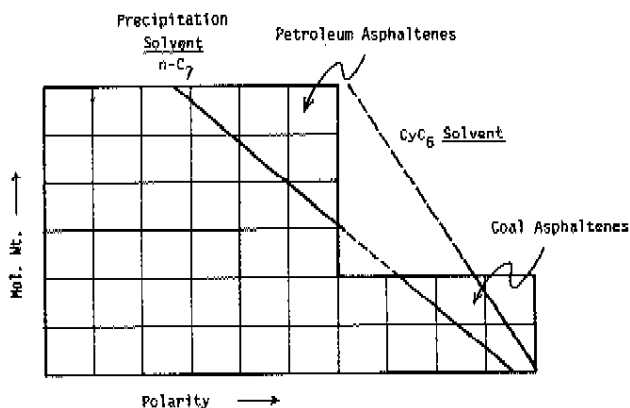


Figure 5. Comparison of Asphaltene Fractions Derived from Petroleum and Coal in a Spectrum of Molecular Weight, Polarity, and the Precipitation Solvent. According to this Figure, Coal Asphaltene are Generally of Lower Molecular Weight but Higher Polarity, While Petroleum Asphaltene are Comparatively of Lower Polarity but Higher Molecular Weight.

accompany the removal (dissolution and desorption) of maltenes, which are the soluble fraction of asphaltene. In addition to the precipitative effects of low molecular weight paraffins, water, carbon dioxide, and acids are observed to contribute to the precipitation of asphaltene. Carbon dioxide, in addition to reducing the solubility of asphaltene, cause rigid asphaltene film formation on the interface due to its effect on the pH value of the water present.

Asphaltene deposition occurs most readily when the pressure of the crude oils is at the bubble point. That is, maximum amount of asphaltene deposition is produced at the bubble point if there is asphaltene deposition. As a result of this fact, if the reservoir pressure is higher than the bubble point, asphaltene deposition may occur at the well or in pipes, since the pressure decreases during the oil production.

Asphaltene deposition was observed even before the introduction of enhanced oil recovery projects during the early period of black oil production, as in the cases of the Ventura field in California [21, 41, 49] and the Hassi Messaoud field in Algeria [12, 41, 45]. In both of these fields, the crude oil was highly undersaturated with respect to gas. In the case of the Ventura field, significant problems existed during the early production life of the wells. However, the problems diminished after the bottom-hole pressure (BHP) fell below the bubble-point was reached. In addition, during the gas-injection period of the field, a reduced injectivity, by a factor of 2, was observed. This seems to be a result of the original mixed wettability or oil wetness (wettability reversal) due to gas injection. The fact that Hassi Messaoud crude is a light crude ( $^{\circ}\text{API}$  of 45) and has a low asphaltene content of 0.2 wt% is an indication of the serious problems which may arise in the recovery of light crude by miscible gas drives.

Injection of solvents or gases may either increase or decrease the amounts of asphaltene deposition. Injection of naphthenes, such as cyclohexane, or aromatics, such as benzene, may reduce the asphaltene deposition because asphaltene is soluble to these solvents. Therefore, damaged reservoirs by asphaltene deposition may regain their lives by adding proper solvents. For instance, xylene injection has been carried out for the Prinos Field, North Aegean Sea, Greece [26, 41] to prevent the asphaltene deposition problem. On the other hand, injection of carbon dioxide may result in asphaltene deposition because of the insolubility of asphaltene in crude oils with miscible carbon dioxide.

Asphaltene deposition is also observed in well-acidizing practices. Use of hydrochloric acid as a well-stimulation fluid can cause severe damage in wells containing asphaltene crude oil. This is because the acid causes the asphaltene to precipitate, and as a result produce a rigid film, which causes significant damage to the porous media around the well bore. Carbon dioxide in the presence of water also has an acidizing effect on the reservoir.

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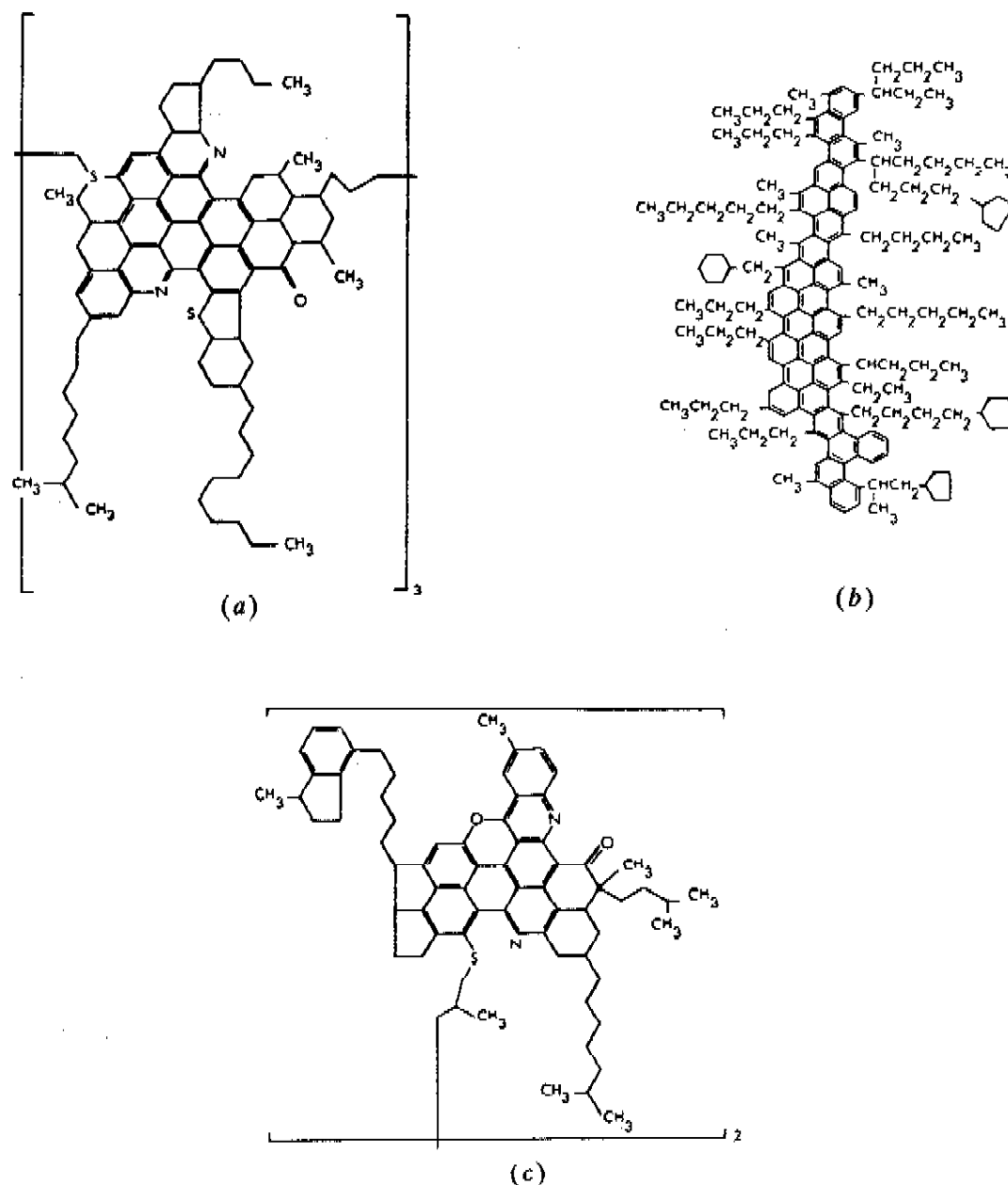


Figure 1. Hypothetical Structures for Asphaltenes from (a) Venezuelan Crude Oil, (b) Iraqi Crude Oil, and (c) California Crude Oil [Speight (1970)].

Measurement of the surface tension indicates that there exists the critical micelle concentration (CMC) for dilute solutions of asphaltenes in toluene [38]. With concentration below the CMC, the asphaltenes in the solution are in a molecular state, while above the CMC, associates and aggregates of asphaltenes may form. When resins and asphaltenes are both present as in petroleum, asphaltenes tend to associate with resins preferentially over association among themselves [33, 40]. This led Speight and his

co-workers to conclude that single asphaltene entities associated with resins molecules could be the dominant species which exist in the colloidal state in a crude oil.

### 3. FIELD EXPERIENCES WITH ASPHALTENE DEPOSITIONS

Control of asphaltene and wax depositions can be difficult and costly in field experience [10, 41–48]. The kind of precipitates observed can vary from very

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- $\phi$  = Scalar potential representing the external force per unit mass  $\mathbf{b}$ .
- $\phi_{Ai}$  = Volume fraction of the  $i$ th fraction of asphaltene in a phase.
- $(\phi_A)_{\max}$  = Maximum volume fraction of asphaltene held by a solvent rich phase.
- $\phi_B$  = Volume fraction of the mixture of asphaltene-free crude oil and solvent.
- $\psi$  = Porosity of the porous media.
- $\xi$  = Unit normal to  $S_w$  pointing into the fluid phase.

#### Mathematical Symbols

- $\langle \rangle$  Refers to an intrinsic volume average.
- $\nabla$  = Vector partial differential operator:  $i(\partial/\partial x) + j(\partial/\partial y) + k(\partial/\partial z)$ .
- div = Dot product of  $\nabla$  with a vector: e.g.  $\text{div}(\mathbf{B}) = \nabla \cdot \mathbf{B}$ .

#### Superscripts

- T Refers to whole phases.
- L Refers to liquid phase.
- S Refers to an asphaltene phase.
- Refers to local volume average.

#### Subscripts

- A Refers to asphaltene.
- $A_i$  Refers to the  $i$ th fraction of asphaltene.
- B Refers to asphaltene free liquid.

## 1. INTRODUCTION AND BACKGROUND

The key to solving many of the technical problems that face the petroleum and natural gas industries in our modern technological society today involves an understanding of the thermodynamic and transport aspects of these problems. Most of the irreplaceable energy resources available are mixtures of gases, liquids, and solids of varying physical and chemical properties contained in the crust of the earth in a variety of geological formations. Knowledge of the fluid-phase equilibrium thermodynamic and transport characteristics of these mixtures is a primary requirement for the design and operation of the systems which recover, produce, and process such mixtures.

There has been extensive progress in the past several years in the formulation of molecular thermodynamics of mixtures and transport phenomena modeling of multiphase flow in composite media.

This knowledge may now be applied to the understanding and prediction of the phase and transport behavior of reservoir fluids and other hydrocarbon mixtures. The present review is designed with the purpose of applying modern theoretical and experimental techniques of molecular thermodynamics, transport, and electrokinetic phenomena to develop methods that will predict asphaltene and asphalt flocculation during the production and processing of crude oil.

The mechanisms of gas injection and oil recovery involved with miscible gas flooding are basically of three kinds [1–3]: first-contact miscible gas drive; condensing-gas drive (or the enriched gas drive); and vaporizing-gas drive (or the high pressure gas drive). The first and second processes are based on the injection of hydrocarbons that are soluble in the residual oil, while the third process involves injection of a high-density gas, such as high-pressure nitrogen or carbon dioxide. In the case of the first-contact miscible process, a typical injection fluid is propane, which is completely soluble in oil. For the condensing-gas drive process, the injection fluid could be a natural gas containing relatively high concentration of intermediate hydrocarbons, such as ethane, propane, and butane.

Miscible flooding of petroleum reservoirs by carbon dioxide, natural gas, and other injection fluids has become an economically viable technique for enhanced oil recovery [2, 3]. The most common problem in petroleum recovery is poor reservoir volumetric sweep efficiency, which is due to channeling and viscous fingering because of the large difference between mobilities of the displacing and displaced fluids. Introduction of a miscible fluid in the petroleum reservoirs will in general produce a number of alterations in the flow behavior, phase equilibrium properties, and the reservoir rock characteristics. One such alteration is asphaltene and wax precipitation, which is expected to affect productivity of a reservoir in the course of oil recovery [3–8]. In most of the instances observed, asphaltene and wax precipitation may result in plugging or wettability reversal in the reservoir. The effect of asphaltene deposition could be positive or negative, depending on whether it could be controlled and predicted before it occurs.

The parameters that govern precipitation of asphaltene and wax appear to be the composition of crude and injection fluid and the pressure and temperature of the reservoir. With alterations in

*G. A. Mansoori, T. S. Jiang, and S. Kawanaka*

#### ABSTRACT

The need to understand the nature of asphaltene and its role in the production and processing of crude oil is well recognized around the world as manifested by the extensive problems resulting from asphaltene depositions. It appears certain that the trend in the petroleum industry worldwide now and in the future will involve the exploration, drilling, production, and processing of heavier oils (higher in asphaltene content), use of gas injection (or re-injection) techniques, and secondary and tertiary methods for recovering more oil from existing reservoirs.

The subject of asphaltene deposition and its role in the petroleum field is here analysed and the technical requirements for its understanding are presented. It is demonstrated that for a comprehensive understanding of this subject the following topics should be studied: (i) Molecular thermodynamic modeling of phase behavior of asphaltene + petroleum crude + injection gas systems and examination of the resulting successful models against the available laboratory and field data; (ii) transport phenomena modeling of the flow of crude in porous media containing asphaltene colloidal particles (or micelles), colloidal instability which may cause asphaltene deposition, and wettability alterations due to the adsorption of asphaltene on the pore walls, and (iii) experimental measurements and simulations in support of such studies.