The need for understanding of the nature of asphaltene in petroleum crude and it's role in EOR miscible gas flooding is well recognized according to the numerous research and developmental work underway in various laboratories. We have undertaken an interdisciplinary approach to the problem of asphaltene deposition from petroleum crudes. Our studies consist of the following topics:

(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. (iii) Experimental measurements and simulation in support of our studies which consist of the following: (iii-1) Measurement of phase behavior of crude and injection gas mixtures at high pressures and at different GOR and temperature conditions (iii-2) Experimental simulation of flow through porous media of asphaltene-containing crude and injection gas.

I. Introduction and Background

The mechanisms of oil recovery involved with miscible gas flooding are basically of three kinds [Simon, et al. (1978); Stalkup (1978, 1983)]: (i) The first-contact miscible gas drive; (ii) The condensing gas drive (or the enriched gas drive); (iii) The vaporizing gas drive or (the high pressure gas drive) process. The first and the 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 [Stalkup (1978, 1983)]. The most common problem in EOR miscible gas flooding is poor reservoir volumetric sweep efficiency which is due to channeling and viscous fingering because of the large difference between viscosities or densities of the displacing and displaced fluids. Introduction of a miscible fluid in the petroleum reservoirs in general will produce a number of alterations in the flow behavior, phase equilibrium properties, and the reservoir rock characteristics. One such alteration is the possibility of a reservoir in the course of oil recovery from the reservoir. [David (1973); Monger (1981); Orr, et al. (1980); Preckshot, et al. (1943); Shelton and Yarborough (1977); Stalkup (1983)]. In most of the instances observed asphaltene and wax precipitation may result in plugging or wettability reversal in the reservoir. 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 composition of crude and injection fluid, pressure, and temperature of the reservoir. With alterations in these parameters, asphaltene precipitation could occur during flooding operations.
in these parameters the nature of asphaltene and wax substances which precipitate will vary. Also, it is a proven fact that the precipitation of asphaltene is generally followed with polymerization, or flocculation, of the resulting precipitate which produces an insoluble material in the original reservoir fluid. 

Because of the complexity of the nature of asphaltic and wax substances the phenomena of precipitation and flocculation of these substances are not well understood. Also in view of the complexity of the petroleum reservoirs, study and understanding of the in situ precipitation of asphaltene and wax seems to be a challenging and timely task. Such an understanding will help to design a more profitable in situ precipitation route for miscible gas flooding projects.

II. Nature and Characteristics of Asphaltenes

Asphaltene was originally coined by Bousingault (1837) to describe the alcohol-insoluble but essence of turbentine soluble solids obtained from the distillation residue of an asphalt. Since then, the concept of asphaltene has been extended to define the low-molecular-weight n-paraffin insoluble and benzene-soluble fraction derived from various carbonaceous sources, such as petroleum, coal, and shale oil.

Asphaltenes must be classified by the particular precipitating solvent since different solvents cause different amounts of precipitation. Asphaltenes are both present as in petroleum, asphaltene-resin-tar association, and so on, depending on the precipitating solvent used. Recognizing the great complexity of asphaltene fractions, Speight and Moschopedis (1981) defined asphaltene in terms of elemental composition and molecular structure as well as by the carbonaceous source.

Table 1, reproduced from their paper, shows the fundamentally different elemental compositions of asphaltene fractions precipitated by different liquids from various sources of petroleum. Long (1981) proposed an overall concept of asphaltene by considering molecular weight and molecular polarity as separate properties of molecules. He demonstrated that asphaltenes contained a wide distribution of polarities and molecular weights. As shown in Figure 4, petroleum asphaltenes have higher molecular weight as well as wider molecular-weight distribution than coal asphaltenes. Nevertheless, asphaltenes from both sources lie within a region bounded by precipitation lines in a map of molecular weight versus polarity of the component as illustrated in Figure 5.

In the petroleum reservoir, asphaltenes have been observed to occur as micelles or colloidal suspensions in the crude oil. With concentration below the CMC, the asphaltene solution is 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, asphaltene-resin-tar association is significant. Waxman et al. (1980) have shown that asphaltene-resin preferentially over associates among themselves.

III. Field Experiences

Control of asphaltene and wax deposition can be difficult and costly in field EOR experiences. According to these figures concentrations of asphaltene and wax deposition can play a significant role in the production history and economics of a reservoir. In Figures 6 and 7 two ternary diagrams are presented in order to demonstrate composition of different classes of crude oils from oil field all around the world. According to these figures concentrations of asphaltenes and resins in most of the crude oils are significantly high.

As discussed in the above section, the asphaltene fraction of oil is defined as that part precipitated by the addition of a low-boiling (or low molecular-weight) paraffin solvent such as n-pentane. The asphaltene fraction generally consists of condensed aromatic and naphthenic molecules of molecular weights in the range of several hundred to several thousands gram per mole. Asphaltenes usually contain a significant number of heteroatoms of nitrogen, sulfur, and oxygen. Asphaltenes contain larger carbon-to-hydrogen ratio than is prevalent in...
crude oils. As a result, the low molecular weight paraffin solvents, which contain large amounts of hydrogen-to-carbon ratio than the crude oils, cause precipitation of the asphaltene colloids. This is thought to accompany with the removal (dissolution and desorption) of maldenites which are the soluble fraction of asphaltenes. In addition to the precipititative effects of low molecular weight paraffins, water, carbon dioxide and acids are observed to contribute to the precipitation of asphaltenes. Carbon dioxide, in addition to reducing the solubility of asphaltenes, cause rigid asphaltene film formations on the interfaces due to its effect on the PH value of the water present.

Asphaltene deposition was observed even before the introduction of EOR projects during the early life of the black oil production such as the case of the Ventura field in California [Katz and Beu (1945); Tuttle (1983) and Hassi-Mesahoud field in Algeria (Lihoreau, et al. (1967)]. In both of these fields the crude oil was highly undersaturated with respect to gas. In the case of Ventura field significant problems existed during the early production life of the wells. However, the problems were diminished after the bottom hole pressure (BHP) fell below the bubble-point of the crude. At Hassi-Mesahoud heavy asphaltene precipitation took place in a 450 m region of the tubing located just below the level at which the bubble point was reached. In addition, during gas injection period of the field a reduced injectivity, of the 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. Knowing that the Hassi-Messahoud crude is a light crude (API of 45) and has low asphaltene content of 0.2% by weight, is an indication of the serious problems which may arise in the EOR of light crude by miscible gas drives.

Asphaltene deposition is also observed in well acidizing practices. Use of hydrochloric acid as well stimulation fluid can cause severe damage in wells containing asphaltene crude oil. This is because the acid makes the asphaltene to precipitate and as a result produce a rigid film which causes a significant damage to the porous media around the well bore. Carbon dioxide in the presence of water also has acidizing effect on the reservoir. Injectable products by a factor of 3 following gas injection projects [Stalkup (1978)] and water alternate gas drives [Dyes, et al. (1972); Harvey, et al. (1977)]. These problems are associated mostly with field problems instead of 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 the wells that produce crude oils with high asphaltene contents to prevent plugging of the reservoir with precipitated asphaltene.

IV. Molecular Thermodynamic Modeling

Petroleum crude generally consists of many hydrocarbon components starting with methane up to very heavy hydrocarbons. There exist also a certain amount of sulfur, oxygen, and nitrogen-containing compounds with varying amounts in the crude [Speight (1980); Tissot and Welte (1978)]. The liquid state of the petroleum crude is a result of a delicate balance between its constituents which depend upon each other for solubility. By 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 asphaltenes from petroleum crude due to the introduction of a solvent can be understood by application of the principles of thermodynamics of multicomponent mixtures and phase equilibria. In the present section we first introduce a descriptive account of the asphaltene deposition phenomena, then we use molecular thermodynamic techniques [Haile and Mansoori (1983); Lan and Mansoori (1977); Mansoori and Leland (1972); Massih and Mansoori (1983)] in order to produce predictive equations for its quantitative interpretation.

It is understood that asphaltene precipitation is a phenomenon common to all complex organic solutions in general [Mckay, et al. (1978)]. 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.

It is generally assumed that two factors are primarily responsible for maintaining the mutual solubility of the compounds in a complex mixture such as the 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 [Mckay, et al. (1978)]. 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, 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 to 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 the petroleum crude we can take advantage of the theories of polymer
solutions [Samchez and Lacombe (1978); Scott and Magat (1945); Mansoori (1980)]. The first attempt of such modeling is due to Hirschberg, et al. (1983, 1984) in which they utilized the Flory-Huggins theory of polymer solutions in order to predict the onset of asphaltene deposition [Flory (1953)]. However, the Flory-Huggins theory is valid for the case of a homogeneous chain molecules of asphaltene of uniform molecular weight in a single uniform solvent. It is a well known fact that neither molecules of asphaltene consist of homogeneous chain molecules, nor the asphaltene-free crude and the injection fluid can be considered as a single uniform solvent [Hall and Herron (1981); Jacobs and Filby (1983); Kleinschmidt (1955); Newmann (1970); Tissot (1981); Wehah, et al. (1978)]. In reality asphaltene and the asphaltene free crude, both consist of mixtures of molecules with a virtually continuous molecular weight distributions. In order to formulate the phenomena of asphaltene deposition from petroleum crude we can utilize the thermodynamic theory of polymer solutions consisting of a polymer with heterogeneous distribution and a solvent. According to this theory, the chemical potential of fraction (i) of asphaltene in the precipitate phase is different from the liquid phase, then we can not set \( m_A^N \) equal to \( m_N \). In the special case when we set \( m_A^N = m_A^N = m \) and if we assume a uniform molecular weight distribution for the asphaltene \( \phi_A^S = \phi_A^L = 1 \) then we will derive the expression for volume fraction of asphaltene in the liquid phase according to the Flory-Huggins Theory [Hirschberg, et al. (1983)].

In the general case it can be shown that

\[
-\frac{S}{m_N} = \frac{\phi_A^S}{\phi_A^L/m_A^L} = \frac{\phi_A^S}{m_A^L [v_B^L \phi_A^L + (1-\phi_A^L) v_A^L]} = \frac{\phi_A^S}{v_B^L (1-\phi_A^L)}
\]

(10)

Eq's (8)-(10) express the volume fractions of different asphaltene fractions in the liquid and solid phases at the onset of asphaltene deposition. Let us now assume that the distribution of molecular weight of asphaltene in the liquid can be represented by

\[
dm = F(m_A^L) \, dm_A^L
\]

when \( dm \) is the volume of asphaltene fraction with molecular weight \( m_A^L \) and \( F(m_A^L) \) is a normalized function such that

\[
\int_0^\infty F(m_A^L) \, dm_A^L = 1
\]

(12)
We also write for the total volume of the ith fraction of asphaltene the following equation

\[ V_{Ai} = \phi_{Ai} V_A + \delta_{Ai} V_A \]  

(13)

According to the definition of \( F(m_{Ai}) \) we can also write

\[ V_A = V_A dW_i = \int_A F(m_{Ai}) dm_{Ai} \]  

(14)

By equating the above two equations we will derive the following equation

\[ \int_A F(m_{Ai}) dm_{Ai} = \phi_{Ai} V_A + \delta_{Ai} V_A \]  

(15)

We already have shown that

\[ \phi_{Ai} = \phi_{Ai} \exp(m_{Ai} \theta) \]  

where

\[ \theta = \frac{1}{\phi_B^2} - \phi_B^2 \left( \frac{1}{m_N} - \frac{1}{m_N} \right) \]  

(17)

As a result from equations (9)-(17) we can write

\[ \phi_{Ai} = \frac{\phi_{Ai} \exp(m_{Ai} \theta)}{1 + (\phi_B^2) \exp(m_{Ai} \theta)} \]  

(18)

This expression provides us with the maximum volume fraction of the ith fraction of asphaltene remaining in the liquid phase. In order to get the total volume fraction of asphaltene in the liquid phase we integrate eq. (18) over the entire molecular weight distribution range, i.e.

\[ \phi_{Ai} \text{ max} = \int_0 ^{\infty} \phi_{Ai} dm_{Ai} = \frac{\int_0 ^{\infty} F(m_{Ai}) \exp(m_{Ai} \theta) dm_{Ai}}{[1 + (1 - \phi_{Bi}) \exp(m_{Ai} \theta)]} \]  

(19)

Provide we have the molecular weight distribution of the asphaltene fractions \( F(m_{Ai}) \), we will be able to integrate eq. (19) in order to calculate the maximum volume fraction of asphaltene in the liquid phase at the onset of its deposition.

V. Transport Phenomena Modeling

Flow through Porous Media with Asphaltene Deposition

Fundamentally, there are no special equation 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 colloidal and interface sciences, 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, examined by the local volume-averaged equations of motion.

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-liquid 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 \( \mathbf{R}(f) \) the pores that contain fluid within \( S \); \( V(f) \) is the volume of \( \mathbf{R}(f) \).

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

\[ \langle B \rangle \]  

as the local volume average of \( B \) for the fluid phase, and

\[ \langle B \rangle \]  

as the intrinsic volume average of \( B \) for the fluid phase. By \( dV \) we indicate that a volume integration is to be performed. The local volume average and the intrinsic volume average are simply related in terms of the porosity.
of the porous medium:

\[ \bar{B} = \psi < B > \]  

(23)

The theorems for the local volume averages of a gradient and of a time derivative [Slattery (1967, 1968, 1981); Jiang, et al. (1984)] give

\[ \bar{\nabla} B = \nabla B - \frac{1}{V} \int_{S_w} B \xi dA \]  

(24)

\[ \frac{\partial B}{\partial t} = \bar{\nabla} \cdot \bar{B} - \frac{1}{V} \int_{S_w} \bar{B} \xi \cdot \xi dA \]  

(25)

The union of the pore walls within \( S \) is indicated by \( S \); \( \xi \) is the unit normal to \( S \) pointing into the fluid phase; \( \mu \xi \) is the speed of displacement of \( S \) directed into the fluid phase; \( dA \) indicates that an area integration is to be performed. The theorem for the local volume average of the divergence [Jiang, et al. (1984)] follows immediately.

Local Volume Averages of Equation of Continuity for Asphaltene Aggregates

Let us consider the fluid phase as a multicomponent mixture. The equation of continuity for asphaltene aggregates in the mixture requires

\[ \frac{\partial (\rho(A) \bar{\mathbf{v}})}{\partial t} + \nabla \cdot \rho(A) \mathbf{v}(A) = r(A) \]  

(27)

in which \( \rho(A) \) denotes the mass density of asphaltene aggregates, \( r(A) \) indicates the rate of production of asphaltene aggregates per unit volume by homogeneous polymerization or association reaction [Hirschberg (1983)], and

\[ \bar{n}(A) \equiv \rho(A) \chi(A) \]  

(28)

is the mass flux of asphaltene aggregates with respect to the fixed frame of reference. In Eq. (28) we have define \( \chi(A) \) as the velocity vector of asphaltene aggregates. The local volume average of Eq. (27) for the fluid phase takes the form

\[ \bar{\nabla} \cdot \bar{\rho}(A) \mathbf{v} + \nabla \cdot \bar{n}(A) = \bar{r}(A) - \bar{\alpha}(A) \]  

(29)

where we have introduced

\[ \bar{\alpha}(A) \equiv -\frac{1}{V} \int_{S_w} \rho(A) (\chi(A) - \mu) \cdot \xi dA \]  

(30)

as the net rate at which asphaltene aggregates deposit at the pore walls within the averaging surface \( S \).

The constitutive equation for the local volume-averaged mass flux vector \( \bar{\mathbf{v}}(A) \) depends on how we describe diffusion in multicomponent mixtures. If we assume conditions are such that it is appropriate to use Fick's first law in analyzing diffusion within the fluid contained by the permeable structure, we can express Eq. (28) as

\[ \bar{\mathbf{v}}(A) = \frac{\rho(A)}{D} \nabla \bar{w}(A) \]  

(31)

where

\[ \rho = \frac{N}{A=1} \rho(A) \]  

(32)

is the total mass density of the mixture of \( N \) components,

\[ \bar{w}(A) \equiv \frac{\rho(A)}{D} \]  

(33)

the mass fraction of asphaltene aggregates,

\[ N \chi = \frac{\bar{w}(A) \chi(A)}{A=1} \]  

(34)

the mass-averaged velocity, and \( D \) should be thought of as the diffusion coefficient for asphaltene aggregates in the multicomponent mixture. If we assume that the diffusion coefficient \( D \) is a constant, Eq. (24) allows us to write the local volume average of Eq. (31) as

\[ \bar{\mathbf{v}}(A) = \frac{\rho(A)}{D} \nabla \bar{w}(A) - \rho \nabla \bar{w}(A) \]  

(35)

Where we have defined

\[ \bar{\chi} = \frac{\rho}{D} \nabla \bar{w}(A) - \rho \nabla \bar{w}(A) \]  

(36)

If the mass density of asphaltene aggregates is not a strong function of position, the effect of the first four terms on the right of Eq. (36) can usually be discounted. The fifth term on the right of Eq. (36) may be thought of as the mass-density tortuosity vector for asphaltene aggregates that accounts for the twisting and turning of the passage through which the fluid moves.

With Eqs. (23) and (35), the local volume average of the equation of continuity for asphaltene aggregates in the form of Eq. (29)
may be expressed as
\[
\frac{\partial \langle \psi \rangle}{\partial t} + \text{div} \left( \langle \rho(A) \rangle \chi \right) =
\]
\[
- \text{div} \left( \bar{\chi}_e(A) - \bar{\chi}(A) \right) - \alpha(A)
\]
where the vector
\[
\bar{\chi}(A) = -<\rho> \text{div} \bar{W}(A) - \bar{\chi}_e(A)
\]
should be thought of as an "effective" mass flux vector with respect to \( \bar{\chi}_e \).

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 \( \bar{\chi}_e(A) \) and \( \chi(A) \). Either these additional relationships could take the form of empirical data correlations or they could be developed from an idealized structural model [Lin and Slattery (1982); Jiang, et al. (1984); Whitaker (1967)] for the porous medium within a given averaging surface S. Slattery (1981) gave examples of how experimental data can be used to prepare correlations for \( \bar{\chi}_e(A) \). For instance, in an isotropic (nonoriented) porous medium when convection can be neglected, it is shown that
\[
\bar{\chi}_e(A) = <\rho> D^*(A) \bar{W}(A)
\]
(39)
with
\[
D^*(A) = D^*(\psi, <\rho>, \bar{W}(A))
\]
(40)
as a function of the porosity \( \psi \) and a dimensionless group. In Eq. (40), \( \bar{\chi}_e \) can be thought of as a characteristic pore size. If conditions are such that Eq. (39) applies, the effective mass flux in the form of Eq. (38) can be expressed in terms of an effective diffusion coefficient
\[
D_{\text{eff}} = D(1 + D^*(A))
\]
(41)
as
\[
\bar{\chi}(A) = -<\rho> D_{\text{eff}} \bar{W}(A)
\]
(42)
\( \bar{\chi} \) is consistent with the common practice describing diffusion in the porous medium [Whitaker (1967)].
Local Volume-Averaged Equations of Motion

The local volume average of Cauchy's first law for an incompressible Newtonian fluid when all inertial effects are neglected can be written as [Slattery (1981)]

\[ \nabla \cdot (\mathbf{v} P) - \mu \text{div} (\mathbf{v} \mathbb{I}) + \mathbf{r} = 0 \]  

(43)

Here \( \mu \) is the viscosity of the fluid, \( P \) is the modified pressure

\[ P \equiv p + p_0 \]  

(44)

and

\[ \mathbf{r} \equiv \frac{1}{V} \int_S (\mathbf{r} \cdot \mathbb{I}) \cdot \mathbf{n} \, dA, \]  

(45)

can be identified as the force per unit volume that the fluid exerts upon the pore walls contained within \( S \) beyond the hydrostatic force. In Eq. (44), \( p \) is pressure and \( \phi \) is a scalar potential representing the external force per unit mass \( \mathbf{b} \) by

\[ \mathbf{b} = -\nabla \phi \]  

(46)

in Eq. (45), \( \mathbf{r} \) is the stress tensor and \( \mathbb{I} \) is the identity tensor, which transforms every spatial vector into itself.

A dimensional analysis shows that in Eq. (43), the magnitude of the second term is generally much smaller than that of \( \mathbf{r} \). If we are willing to neglect the second term in Eq. (43) with respect to \( \mathbf{r} \), Eq. (43) can be reduced to

\[ \nabla \cdot (\mathbf{v} P) - \mu \text{div} (\mathbf{v} \mathbb{I}) = \mathbf{r} \]  

(47)

Like \( \mu (A) \) and \( a(A) \), empirical correlations for \( \mathbf{r} (A) \) is required. For example, in a fixed isotropic (nonoriented) porous medium, we may write

\[ \mathbf{r} = \frac{1}{k} \mathbf{\tau} \]  

(48)

in which \( k \) is the permeability of the porous medium. Eq. (47) when joined with Eq. (48) is usually referred to as the Darcy's law.

Deposition of asphaltenes will not only change the porosity but also the permeability \( k \) of the porous formation. The pressure drop across the medium will therefore vary according to Eqs. (47) and (48).

VI. Experimental and Laboratory Measurements

In support of the Comprehensive research project proposed here for studying the asphaltene deposition and its role in EOR miscible gas flooding a number of experimental measurements are planned and they are under development in our laboratories. These experiments are of two categories. One category of the experiments consist of the measurement of the physiochemical characteristics of crude, asphaltene, reservoir core, the injection gases, and their interactions. The second category of experiments are of the simulation types trying to mimic the in situ asphaltene deposition at different temperatures, pressures, and other reservoir conditions.

Of the first category of experiments the following are presently under development:

1. Chromatographic analysis of crude oil and asphaltene for the purpose of specifying construction of molecular weight distributions of the asphaltene-free crude and asphaltene.
2. Measurement of solubility parameters of different fractions of asphaltene and crude for the purpose of comparisons with the theoretical prediction models.
3. Observation and specification of the onset of asphaltene deposition at different temperatures and pressures, and, with the use of different injection fluids.
4. Titration experiments for the purpose of measurement of the amount of asphaltene deposition.
5. Development of analytic techniques for the measurement of the rate of asphaltene polymerization and/or flocculation.
6. Effect of porosity, wettability, and other reservoir parameters on the rate of asphaltene deposition in a porous media.

Of the second category of experiments the following are presently under development:

1. A comprehensive core-flooding testing facility for simulation of the in situ asphaltene deposition at different temperatures, pressures, core porosity, and injection fluid to oil ratios.

Some of the above experiments have been completed. The ones with extensive hardware requirements await further external funding to be completed.

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**TABLE 1. ELEMENTAL COMPOSITIONS OF ASPHALTENE FRACTIONS PRECIPITATED BY DIFFERENT SOLVENTS**

(from Speight and Moschopedis (1981))

<table>
<thead>
<tr>
<th>Source</th>
<th>Precipitating Solvent</th>
<th>Composition (wt%)</th>
<th>Atomic Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Canada</td>
<td>n-pentane</td>
<td>79.5</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>78.4</td>
<td>7.6</td>
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<tr>
<td></td>
<td>n-pentane</td>
<td>83.8</td>
<td>7.5</td>
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<tr>
<td></td>
<td>n-heptane</td>
<td>84.2</td>
<td>7.0</td>
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<tr>
<td>Iraq</td>
<td>n-pentane</td>
<td>81.7</td>
<td>7.9</td>
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<tr>
<td></td>
<td>n-heptane</td>
<td>85.7</td>
<td>7.1</td>
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<tr>
<td>Kuwait</td>
<td>n-pentane</td>
<td>82.4</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>82.0</td>
<td>7.3</td>
</tr>
</tbody>
</table>

![Figure 1](image-url)
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 asphaltenes are generally of lower molecular weight but higher polarity, while petroleum asphaltenes are comparatively of lower polarity but higher molecular weight.

Figure 2: Macrostructure of asphaltene as proposed by Yen (1972). In this figure (A) represents a crystallite, including an intracluster (G) and forming a particle (C), (D) represents a micelle containing a metal (M) and a gap and hole (F), and (I) represents molecules of resin forming a particle (C).

Figure 3: Effect of the molecular weight of n-paraffin solvents on the amount of precipitation of asphaltene from Arabian light atmospheric residuum (Corbett and Petrossi, 1978). Similar effects can be observed for other petroleum crudes.

Figure 6: A ternary diagram categorizing six different classes of Crude Oils according to their aromatic, naphthenic, and paraffinic hydrocarbon contents. The dots in this diagram represent the composition of 342 oil fields around the world (Tissot and Welte, 1978).

Figure 7: A ternary diagram showing the gross composition of 636 Crude Oils from around the world; saturated hydrocarbons, aromatic hydrocarbons, and asphaltenes plus resins (weight % in the fraction boiling above 210°C); for construction of the iso-frequency contours a triangle unit of 10:10:10 was used (Tissot and Welte, 1978).