ASPHALTENE DEPOSITION AND ITS ROLE IN PETROLEUM PRODUCTION AND PROCESSING

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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 analyzed here 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.

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الخلاصة:

دعت الحاجة لفهم طبيعة الأسطوانين ودوره في إنتاج ومعالجة البترول إلى معرفة عالمياً نتيجة للمصموات الكبيرة الناتجة بسبب رواسب الأسطوانين، ويظهر أن صناعة البترول في العالم سوف توجه بالتأكيد نحو استكشاف، وحفر، وتنقيع والبحث، ومعالجة البترول الفئات (الغاز المنفصل) على نسبة عالية من الأسطوانين باستخدام نظام تشفير (أو إعادة التحنن)، وطرق الوقاية الثانية والثالثة لاستخلاص كميات زيت أكبر من الحقول الموجودة حاليًّاً.

تم دراسة وتحليل ترسب الأسطوانات في مجال البترول، وعرضت التنظيمات البيئية لفهم النسب. ومن أجل فهم الشاكلة لهذا الموضوع فلابد من دراسة الآتي: (1) وصف جزيئي لخلط الأسطوانات مع البترول الخام وغاز الحفر ومباشرة الطرح مع قياسات المختبر والقليل (2) وصف انتقال البترول الخام المنحل على حسابات صغيرة جداً عائدة من الأسطوانات في المساحات ومدى مقاومة هذا الخليط لترسب الأسطوانات، وتغير خاصة الترطب لحفر الحفار المساحات نتيجة للإمتصاص الأسطوانات عليها. (3) قياسات خشية ونتائج حسابية لتؤثر هذه الدراسات.
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NOTATION

\( A \) = Area on which an integration is performed.
\( a \) = Force per unit volume that fluid exerts upon the pore walls contained within \( S \) in excess of the hydrostatic force.
\( B \) = Scalar, vector, or tensor associated with a fluid.
\( B_\text{avg} \) = Local volume average of \( B \) for a fluid.
\( b \) = External force per unit mass.
\( D \) = Diffusion coefficient.
\( D'(\lambda) \) = Function of the porosity and a dimensionless group, as in Equation (40).
\( D_\text{eff} \) = Effective diffusion coefficient.
\( F_n(M) \) = Normalized mole distribution of the \( i \)th asphaltene fraction with respect to the molecular weight of asphaltene.
\( F_v(M) \) = Normalized volume distribution of the \( i \)th asphaltene fraction with respect to the molecular weight of asphaltene.
\( f \) = Intermediate parameter defined in Equation (4).
\( I \) = Identity tensor, which transforms every special vector into itself.
\( \text{div}(\mathbf{j}(\lambda)) \) = "Effective" mass flux vector with respect to \( \mathbf{v} \).
\( K \) = Empirical constant relating to the polarities of compounds.
\( k \) = Permeability of the porous medium.
\( l_0 \) = Characteristic pore size.
\( M_{\alpha_i} \) = Molecular weight of the \( i \)th fraction of asphaltene.
\( m_{\alpha_i} \) = Segment number of the \( i \)th fraction of asphaltene (=\( n_{\alpha_i}/v_\alpha \)).
\( m_c \) = Mole average segment number of asphaltene.
\( n_{\alpha} \) = Mass flux of asphaltene aggregates with respect to the fixed frame of reference.
\( n_\lambda \) = Total mole number of asphaltene.
\( n_i \) = Modified pressure defined by Equation (47).
\( p \) = Rate of production of asphaltene aggregates per unit volume by homogeneous polymerization or association reaction.
\( S_\alpha \) = Union of the pore walls within \( S \).
\( S_\alpha \) = Property defined by Equation (36).
\( S_\beta \) = Solubility parameter of the mixture of asphaltene free crude oil and solvent.
\( S_\gamma \) = Solubility parameter of component \( j \).
\( \theta \) = Intermediate parameter defined in Equation (17).
\( \mu_{\alpha_i} \) = Chemical potential of the \( i \)th fraction of asphaltene.
\( \rho \) = Total mass density of a mixture of \( N \) components.
\( \rho_\alpha \) = Density of asphaltene.
\( \rho_{\alpha} \) = Mass density of asphaltene aggregates.

Greek Letters

\( \alpha_{\alpha} \) = Net rate per unit volume at which asphaltenes deposit at the pore walls within the averaging surface \( S \).
\( \delta_{\lambda} \) = Solubility parameter of asphaltene.
\( \delta_{\alpha} \) = Property defined by Equation (36).
\( \delta_{\beta} \) = Solubility parameter of the mixture of asphaltene free crude oil and solvent.
\( \delta_{\gamma} \) = Solubility parameter of component \( j \).
\( \theta \) = Intermediate parameter defined in Equation (17).
\( \mu_{\alpha_i} \) = Chemical potential of the \( i \)th fraction of asphaltene.
\( \mu_{\alpha_i} \) = Chemical potential of the \( i \)th fraction of asphaltene at a standard state.
\( \rho \) = Total mass density of a mixture of \( N \) components.
\( \rho_\alpha \) = Density of asphaltene.
\( \rho_{\alpha} \) = Mass density of asphaltene aggregates.
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 irreplenishable 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
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 by polymerization, or flocculation, of the resulting precipitate, which produces an insoluble material in the original reservoir fluid [9-15]. 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 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 route for miscible gas flooding projects.

In section 2 of the present report, the nature of molecular characteristics of asphaltene and wax deposits from petroleum crude oils are presented. Field experiences with asphaltene and wax deposition and their related problems are discussed in section 3. In order to predict the phenomena of asphaltene deposition one has to consider the use of the molecular thermodynamics of fluid phase equilibria. In section 4, predictive approaches on the behavior of reservoir fluids and asphaltene depositions are discussed from a molecular thermodynamic point of view. This includes correlation and prediction of the effects of temperature, pressure, and composition of the miscible gas and crude on: the thermodynamic behavior of fluids; onset of asphaltene and wax deposition; and the mechanism of asphaltene flocculation. The in situ precipitation and flocculation of asphaltene is expected to be quite different from that in controlled laboratory experiments. This is primarily due to the multiphase flow through the reservoir porous media and the interactions of the precipitates with the reservoir material. In section 5, the transport phenomena modeling of the flow through porous media with in situ asphaltene deposition is presented. Successful predictive models for asphaltene deposition and flocculation require a number of experimental and laboratory measurements. In section 6, the experimental techniques envisioned in support of predictive models for asphaltene and wax deposition are discussed. Finally, in section 7, an overview of the asphaltene deposition problem is presented.

2. NATURE AND CHARACTERISTICS OF ASPHALTENE

The word "asphaltene", was originally coined by Bousinault [16] to describe the alcohol-insoluble, but essence of turpentine 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 [17-29]. Asphaltene must be classified by the particular precipitation solvent since different solvents cause different amounts of precipitation [30, 31]. In Figure 1, the hypothetical structures for asphaltenes from different regions of the world are presented. Figure 2, taken from Yen [28], shows how the asphaltene particles and the asphaltene micelles are structured due to the formation of the crystallites (A) of π-π associations among asphaltene molecules; on changing the conditions of solutions, the particles may grow to micelles, or the micelles may dissociate into particles. Figure 3, taken from Corbett and Petrossi [31], illustrates the effect of precipitation solvent on the amount of asphaltene precipitated. According to this figure there is very little difference in the amount of asphaltene precipitated by n-heptane and heavier n-paraffins. However, when n-pentane is used, additional material with less polarity and lower molecular weight is recovered in addition to n-heptane asphaltenes [23, 32]. Thus, there are n-pentane asphaltenes, n-hexane asphaltenes, n-heptane asphaltene, and so on, depending on the precipitation solvent used. Recognizing the great complexity of various asphaltene fractions, Speight and Moschopedis [33] defined asphaltenes 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 solvents from various sources of petroleum. Long [23] proposed an overall concept of asphaltenes by considering molecular weight and molecular polarity as separate properties of the 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 dissolved and as micelles or colloidal suspensions in the crude oil [22, 34-39].
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 petroleums, 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...
Table 1. Elemental Compositions of Asphaltene Fractions Precipitated by Different Solvents [33].

<table>
<thead>
<tr>
<th>Source</th>
<th>Precipitating Medium</th>
<th>Composition (wt %)</th>
<th>Atomic Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  H  N  O  S</td>
<td>H/C  N/C  O/C  S/C</td>
</tr>
<tr>
<td>Canada</td>
<td>n-pentane</td>
<td>79.5 8.0 1.2 3.8 7.5</td>
<td>1.21 0.013 0.036 0.035</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>78.4 7.6 1.4 4.6 8.0</td>
<td>1.16 0.015 0.044 0.038</td>
</tr>
<tr>
<td>Iran</td>
<td>n-pentane</td>
<td>83.8 7.5 1.4 2.3 5.0</td>
<td>1.07 0.014 0.021 0.022</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>84.2 7.0 1.6 1.4 5.8</td>
<td>1.00 0.016 0.012 0.026</td>
</tr>
<tr>
<td>Iraq</td>
<td>n-pentane</td>
<td>81.7 7.9 0.8 1.1 8.5</td>
<td>1.16 0.008 0.010 0.039</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>80.7 7.1 0.9 1.5 9.8</td>
<td>1.06 0.010 0.014 0.046</td>
</tr>
<tr>
<td>Kuwait</td>
<td>n-pentane</td>
<td>82.4 7.9 0.9 1.4 7.4</td>
<td>1.14 0.009 0.014 0.034</td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>82.0 7.3 1.0 1.9 7.8</td>
<td>1.07 0.010 0.017 0.036</td>
</tr>
</tbody>
</table>

Figure 2. Microstructure of Asphaltene as Proposed by Yen [28]. (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). (B) is a Chain Bundle; (E) is a Weak Link; (H) is an Intercluster; (J) is a Single Layer; and (K) is a Petroporphyrin.

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 Periosti [31]). Similar Effects can be Observed for Other Petroleum Crudes.
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 their 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 (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 asphalteneic 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.

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

![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.](image)
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 541 Oil Fields Around the World (Tissot and Welte [51]).

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 Isofrequency Contours a Triangle Unit of 10:10:10 was Used (Tissot and Welte [51]).
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
heterogeneous distribution and a solvent. According to this theory [58], the chemical potential of fraction \((i)\) of asphaltene in the mixture of asphaltene and solvent can be shown by the following expression:

\[
(\mu_{Ai} - \mu_{A0}) = \frac{RT}{\sum_i \phi_{Ai}} \ln \left( \frac{\sum_i \phi_{Ai} + \phi_B f_m A_i \phi_B^2}{\sum_i \phi_{Ai} + \phi_B} \right) - m_{Ai} \phi_B + m_{Ai} f_m A_i \phi_B^2 .
\]  

(1)

In this expression, \(\phi_{Ai}\) is the volume fraction of the \(i\)th fraction of asphaltene and \(\phi_B\) is the volume fraction of asphaltene-free crude such that

\[
\sum_i \phi_{Ai} + \phi_B = 1 ,
\]

(2)

also \(m_{Ai} = v_{Ai}/v_B\) where \(v_{Ai}\) is the molecular volume of the \(i\)th asphaltene fraction and \(v_B\) is molecular volume of asphaltene-free crude. Also we have

\[
m_{A0} = \sum_i \phi_{Ai}/\sum_i (\phi_{Ai}/m_{Ai})
\]

(3)

and

\[
f = 1/r + K v_B (\delta_A - \delta_B)^2/R T ,
\]

(4)

where \(r\) is the coordination number of the segments of the asphaltene molecule (about 3 to 4), \(K\) is an empirical constant relating to polarity of substances in mixture, and \(\delta_A\) and \(\delta_B\) are the solubility parameters of the asphaltene and asphaltene-free crude, respectively. The solubility parameter parameter is related to the internal energy of vaporization by the following expression

\[
\delta^f_i = \Delta U^{	ext{vapor}}/V_j ,
\]

(5)

At the onset of asphaltene deposition fractions of the asphaltene in the solid precipitate phase and in the liquid phase are in equilibrium, i.e.

\[
\mu_{Ai}^s = \mu_{Ai}^L ; \quad i = 1, 2, \ldots .
\]

(6)

From this equilibrium condition, by utilizing Equation (1) we can then write

\[
\ln \phi_{Ai}^s + 1 - (m_{Ai}^s/m_{A0}^s)(1 - \phi_B^s) - m_{Ai}^s \phi_B^s + m_{Ai}^s (\phi_B^s)^2 = \ln \phi_{Ai}^L + 1 - (m_{Ai}^L/m_{A0}^L)(1 - \phi_B^L) - m_{Ai}^L \phi_B^L + m_{Ai}^L (\phi_B^L)^2.
\]

(7)

At this stage we can assume that the solid phase is free of crude \((\phi_B^s = 0)\). We can assume that \(v_{Ai}^s = v_{Ai}^L = v_{Ai}\) and \(v_B^s = v_B^L = v_B\). As a result of these assumptions Equation (7) will simplify to the following form

\[
\phi_{Ai}^L/\phi_{Ai}^s = \exp\left[ m_{Ai}^s (1/m_{Ai}^s - 1/m_{Ai}^L) - m_{Ai}^L (1 - 1/m_{Ai}^s) \phi_B^L + m_{Ai}^L \phi_B^L \phi_B^L \right] .
\]

(8)

Since, in general, the molecular distribution of asphaltene in the precipitate phase is different from that in the liquid phase, we can not set \(m_{Ai}^s\) equal to \(m_{Ai}^L\). In the special case when we set \(m_{Ai}^s = m_{Ai}^L = m\) and if we assume a uniform molecular-weight distribution for the asphaltene \((\phi_{Ai}^L = \phi_{Ai}^s; \phi_{Ai}^L = 1)\), then we can drive the expression for volume fraction of asphaltene in the liquid phase according to the Flory–Huggins theory [60].

Let us now define the total volume distribution of asphaltene with respect to the molecular weight of asphaltene:

\[
F_s(M_{Ai}) = (1/V_{Ai}) (dV_{Ai}^s/dM_{Ai}) ,
\]

(9)

where \(V_{Ai}\) is the total volume of asphaltene, and \(dV_{Ai}^s\) is the total volume of the \(i\)th fraction of asphaltene, whose molecular weight is between \(M_{Ai}^s\) and \(M_{Ai}^{s+1}\). We can also write for the total volume of the \(i\)th fraction of asphaltene as follows:

\[
dV_{Ai}^s = dV_{Ai}^L + dV_{Ai}^s = V_{Ai}^L d\phi_{Ai}^L + V_s d\phi_{Ai}^s ,
\]

(10)

where \(V_{Ai}\) and \(V_s\) are the total volumes of the liquid phase and the asphaltene phase, respectively. According to Equations (9) and (10),

\[
F_s(M_{Ai}) V_{Ai} V_{Ai} dM_{Ai} = V_{Ai}^L d\phi_{Ai}^L + V_s d\phi_{Ai}^s.
\]

(11)

Equation (8) may be written as a differential form:

\[
d\phi_{Ai}^L = (1/m_{Ai}^L) d\phi_{Ai}^s \exp(-m_{Ai}^L \theta) ,
\]

(12)

where

\[
\theta = (1 - 1/m_{Ai}^L) \phi_B^L - \phi_B^L (\phi_B^L)^2 (1/m_{Ai}^L)^2 - (1/m_{Ai}^s - 1/m_{Ai}^L) .
\]

(13)

From Equations (11) and (12) we can write:

\[
d\phi_{Ai}^L = [V_{Ai}^L/(V_{Ai}^L + V_s \exp(-m_{Ai}^s \theta))] dF_s(M_{Ai}) dM_{Ai} .
\]

(14)

This expression provides us with the maximum volume fraction of the \(i\)th fraction of asphaltene remaining in the liquid phase. Assuming we have the weight distribution of the asphaltene fractions available as experimental data:

\[
F_s(M_{Ai}) = (1/V_{Ai}^L) (dW_{Ai}^L/dM_{Ai}) .
\]

(15)

The weight of the \(i\)th fraction of asphaltene is \(w_{Ai} = V_{Ai}^L / \phi_{Ai}^L\). Using the average density \(\rho_{Ai}\), or assuming the density is constant, we have the following from Equations (9) and (15):

\[
F_s(M_{Ai}) = w_{Ai} (M_{Ai}) .
\]

(16)
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.,

\[
(\phi_\lambda)_{\text{mix}} = \int_0^\infty \phi_\lambda^1(B) \, dB
\]

\[
= \int_0^\infty \left[ \frac{V_\lambda^V}{V_\lambda^c + V_\lambda^s \exp(-m_\lambda \theta)} \right] F_{\lambda}(M_\lambda) \, dM_\lambda. \tag{17}
\]

Hence, for a given weight distribution of asphaltene fraction, \( F_{\lambda}(M_\lambda) \), 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:

\[
F_{\lambda}(M_\lambda) = \left(1/n_\lambda^1\right)(dn_\lambda^1/dM_\lambda). \tag{18}
\]

Then, we obtain

\[
F_{\lambda}(M_\lambda) = F_v(M_\lambda) = (M_\lambda/M_\lambda^V) F_v(M_\lambda), \tag{19}
\]

where \( M_\lambda \) is the average molecular weight of asphaltene. For the derivation, the molar volume of the \( i \)-th fraction of asphaltene, \( \nu_\lambda^i = dV_\lambda^V/dn_\lambda^1 \), is used and the constant value of the density of asphaltene \( \rho_\lambda \) 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 \( R_{(f)} \) the pores that contain the fluid within \( S \); \( V_{(f)} \) is the volume of \( R_{(f)} \).

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

\[
\bar{B} = (1/V) \int_{R_{(f)}} B \, dV \tag{20}
\]

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

\[
\langle B \rangle = (1/V_{(f)}) \int_{R_{(f)}} B \, dV \tag{21}
\]
as the intrinsic volume average of $B$ for the fluid phase. By $d \mathbf{V}$ 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:

$$
\psi \equiv \frac{V(n)}{V} \quad (22)
$$

of the porous medium:

$$
\bar{B} = \psi \langle B \rangle \quad (23)
$$

The theorems for the local volume averages of a gradient and of a time derivative [69-72] give

$$
(\nabla \bar{B}) = \nabla \langle B \rangle - \left( \frac{1}{V} \right) \int_{S_w} \mathbf{B} \hat{\mathbf{\xi}} \, dA \quad (24)
$$

$$
\frac{\partial \bar{B}}{\partial t} = \frac{\partial \langle B \rangle}{\partial t} - \left( \frac{1}{V} \right) \int_{S_w} \mathbf{B} \mathbf{u} \cdot \hat{\mathbf{\xi}} \, dA \quad (25)
$$

The union of the pore walls within $S$ is indicated by $S_w$; $\hat{\mathbf{\xi}}$ is the unit normal to $S_w$ pointing into the fluid phase; $\mathbf{u} \cdot \hat{\mathbf{\xi}}$ is the speed of displacement of $S_w$ directed into the fluid phase; $dA$ indicated that an area integration is to be performed. The theorem for the local volume average of the divergence [72]

$$
(\text{div} \, \bar{B}) = \text{div} \, \langle B \rangle - \left( \frac{1}{V} \right) \int_{S_w} \mathbf{B} \cdot \hat{\mathbf{\xi}} \, dA \quad (26)
$$

follows immediately.

5.3 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

$$
\frac{\partial \rho(A)}{\partial t} + \text{div} \, \mathbf{n}(A) = r(A) \quad (27)
$$

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 [60], and

$$
n(A) = \rho(A) \mathbf{v}(A) \quad (28)
$$

is the mass flux of asphaltene aggregates with respect to the fixed frame of reference. In Equation (28) we have defined $\mathbf{v}(A)$ as the velocity vector of asphaltene aggregates. The local volume average of Equation (27) for the fluid phase takes the form

$$
\frac{\partial \rho(A)}{\partial t} + \text{div} \, \bar{n}(A) = \bar{r}(A) - \alpha(A) \quad (29)
$$

where we have introduced

$$
\alpha(A) = -\left( \frac{1}{V} \right) \int_{S_w} \rho(A) \left( \mathbf{v}(A) - \mathbf{u} \right) \cdot \hat{\mathbf{\xi}} \, dA \quad (30)
$$

as the net rate per unit volume 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 $\bar{n}(A)$ 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 Equation (28) as

$$
n(A) = \rho(A) \mathbf{v} - \rho \mathbf{D} \nabla \mathbf{w}(A) \quad (31)
$$

where

$$
\rho = \sum_{A=1}^{N} \rho(A) \quad (32)
$$

is the total mass density of the mixture of $N$ components.

$$
\mathbf{w}(A) = \frac{\rho(A)}{\rho} \quad (33)
$$

the mass fraction of asphaltene aggregates,

$$
\mathbf{v} = \sum_{A=1}^{N} \mathbf{w}(A) \mathbf{v}(A) \quad (34)
$$

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

$$
\bar{n}(A) = \left( \rho(A) \mathbf{v} - (\rho) \mathbf{D} \nabla \mathbf{w}(A) \right) - \delta(A) \quad (35)
$$

where we have defined:

$$
\delta(A) = \left( \rho(A) \mathbf{v} - (\rho) \mathbf{v} \right) - (\rho) \mathbf{D} \nabla \mathbf{w}(A) \quad (36)
$$

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 Equation (36) can usually be discounted. The fifth term on the right of Equation (36) may be thought of as mass-density tortuosity vector for asphaltene aggregates that accounts for the twisting and turning of the passages through which the fluid moves.

With Equations (23) and (35), the local volume average of the equation of continuity for asphaltene aggregates
aggregates in the form of Equation (29) may be expressed as
\[ \partial \psi / \partial t + \text{div}(\psi v) = - \text{div}(j_{(A)}^{(i)}) - \alpha(A), \]
where the vector
\[ j_{(A)}^{(i)} = - \langle \rho \rangle D \bar{w}_{(A)} - \delta(A), \]
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
\[ \delta(A) = \langle \rho \rangle D \bar{w}^*_{(A)} \bar{w}_{(A)} , \]
with
\[ D_{(A)}^* = D_{(A)}^*(\psi, [I_0(\rho)[\bar{w}_{(A)}]\langle \rho(A) \rangle]) \]
as a function of the porosity and a dimensionless group. In Equation (40), \( I_0 \) 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
\[ D_{eff} = D(1 + D_{(A)}^*) \]
as
\[ j_{(A)}^{(i)} = - \langle \rho \rangle D_{eff} \bar{w}_{(A)} . \]
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
\[ \delta_{(A)} = \langle \rho \rangle (D_{(A)}^* \bar{w}_{(A)} - I_0(\rho)[\bar{w}_{(A)}]D_{(A)}^* \bar{v}) \]
where, for \( i = 1, 2; \)

\[ D_{(A)}^* = \]
\[ D_{(A)}^*(\psi, [I_0(\rho)[\bar{w}_{(A)}]\langle \rho(A) \rangle]) \]
and
\[ N_{pe} = I_0(\rho)[\bar{w}_{(A)}] / D . \]

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 \( v \); the asphaltene aggregates are defined by their concentration \( \rho(A) \) 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,
could be the forces causing the deposition. This initial deposition can also be viewed as a monolayer adsorption with a similar picture to that for the chemisorption of gases [75]. However, the heat of adsorption from solution is usually fairly small, and is more comparable with heats of solution than with chemical bond energies. After a monolayer adsorption has been formed, the deposit can grow through hydrogen-bonding interaction with resins [33, 40, 60] or association with other asphaltenes similar to polymerization [60]. Because of the deposition, wettability of the surface coated with asphaltenes can be varied or even reversed. In some cases, the amount of deposition could be sufficiently large that plugging of small pores is possible, as discussed in section 3.

5.5 Local Volume-Average 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 [70]

$$\nabla \langle \psi(P) \rangle - \mu \text{div} (\nabla \nu) + a = 0 .$$  \hspace{1cm} (46)

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

$$P = p + \rho \phi ,$$  \hspace{1cm} (47)

and

$$a = \left( \frac{1}{V} \right) \int_{\delta_0} (T_n - \rho \phi L_n) \cdot \xi \, dA ,$$  \hspace{1cm} (48)

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 Equation (44), $p$ is pressure and $\phi$ is a scalar potential representing the external force per unit mass by

$$b = - \nabla \phi .$$  \hspace{1cm} (49)

In Equation (48), $T_n$ is the stress tensor and $L_n$ is the identity tensor, which transforms every spatial vector into itself.

A dimensional analysis shows that in Equation (46), the magnitude of the second term is generally much smaller than that of $a$. If we are willing to neglect the second term in Equation (46) with respect to $a$, Equation (46) can be reduced to

$$- \nabla \langle \psi(P) \rangle = a .$$  \hspace{1cm} (50)

As for $\delta_{AA}$ and $\alpha_{AA}$, empirical correlations for $a$ are required. For example, in a fixed isotropic (non-oriented) porous medium, we may write

$$a = (\mu/k) \nu ,$$  \hspace{1cm} (51)

in which $k$ is the permeability of the porous medium. Equation (50) when joined with Equation (51) 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 Equations (50) and (51). How the porosity and permeability of the porous formation change according to the deposition of asphaltenes is still under study. However, in order to obtain the onset point of asphaltene deposition, we may set the porosity and permeability of the porous media as constant.

6. DISCUSSION AND CONCLUSIONS

Implementation of the molecular thermodynamics and transport phenomena modelings of asphaltene flocculation and its role in petroleum recovery and processing industries presented in this paper require a number of experimental measurements [76–78]. Such experiments are in two categories. One consists of the measurement of the physicochemical characteristics of crude, asphaltene, reservoir core, the injection gases, and their interactions. The second category are of the simulation type, trying to mimic the in situ asphaltene deposition at different temperatures, pressures, and other reservoir conditions. Of the first category, the following are of greatest importance:

1. Chromatographic analysis of crude oil and asphaltene for the purpose of specification of 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 medium.
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.

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