

ASPHALTENE DEPOSITION AND ITS ROLE IN PETROLEUM PRODUCTION AND PROCESSING

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الخلاصة :

دعت الحاجة لفهم طبيعة الاسفلتين ودوره في انتاج ومعالجة الزيت الخام إلى معرفته عالمياً نتيجة للصعوبات الكثيرة الناتجة بسبب رواسب الاسفلتين ، ويظهر أن صناعة البترول في العالم سوف تتوجه بالتأكيد نحو استكشاف ، وحفر ، و انتاج ، ومعالجة الزيت الثقيل (المحتوي على نسبة عالية من الاسفلتين) واستخدام طرق حقن الغاز (أو اعادة الحقن) ، وطرق الدرجة الثانية والثالثة لاستخلاص كميات زيت أكبر من الحقول الموجودة حالياً .

تم دراسة وتحليل ترسيب الاسفلتين ودوره في مجال البترول ، وعرضت المتطلبات التقني لفهم الترسيب . ومن أجل الفهم الشامل لهذا الموضوع فلا بد من دراسة الآتي : (١) وصف تجزيي لخليط الاسفلتين مع الزيت الخام وغاز الحقن ومقارنة الوصف مع قياسات المختبر والحقل . (٢) وصف انتقال الزيت الخام المحتوي على حبيبات صغيرة جداً عالقة من الاسفلتين ، في المسامات ومدى مقاومة هذا الخليط لترسيب الاسفلتين ، وتغير خاصية الترطيب لجدران المسامات نتيجة لادمصاص الاسفلتين عليها . (٣) قياسات مخبرية ونماذج حسابية لتعزيد هذه الدراسات .

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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 crudes 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 Bousingault [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]. Asphaltenes 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 asphaltenes precipitated. According to this figure there is very little difference in the amount of asphaltenes 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].

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Table 1. Elemental Compositions of Asphaltene Fractions Precipitated by Different Solvents [33].

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

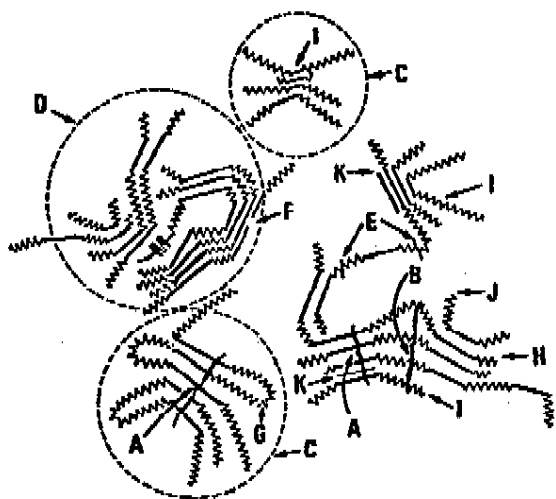


Figure 2. Microstructure of Asphaltene as Proposed by Yen [28]. (A) Represents a Crystallite, Including an Intracrystallite (G) and Forming a Particle (C); (D) Represents a Micelle Containing a Metal (M) and a Gap and Hole (F), and (I) Represents Molecules of Resin Forming a Particle (C). (B) is a Chain Bundle; (E) is a Weak Link; (H) is an Intercluster; (J) is a Single Layer; and (K) is a Petroporphyrin.

minor to large amounts depending on the nature of crude, the cloud and pour points of crude, the nature of the injection fluid and the operating (or reservoir) temperature and pressure. 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 the composition of different classes of crude oils from oil fields 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 an oil is defined as that part precipitated

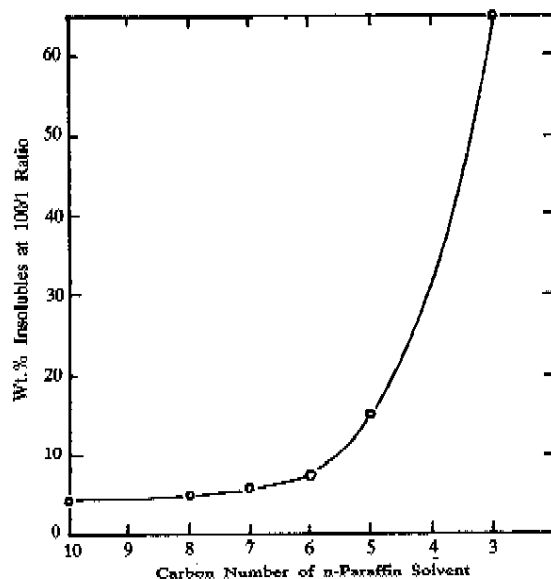


Figure 3. Effect of the Molecular Weight of n-Paraffin Solvents on The Amount of Precipitation of Asphaltene from Arabian Light Atmospheric Residuum (Corbett and Pertossi [31]). Similar Effects can be Observed for Other Petroleum Crudes.

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 thousand grams 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 larger hydrogen-to-carbon ratios than the crude oils, cause precipitation of the asphaltene colloids. This is thought to

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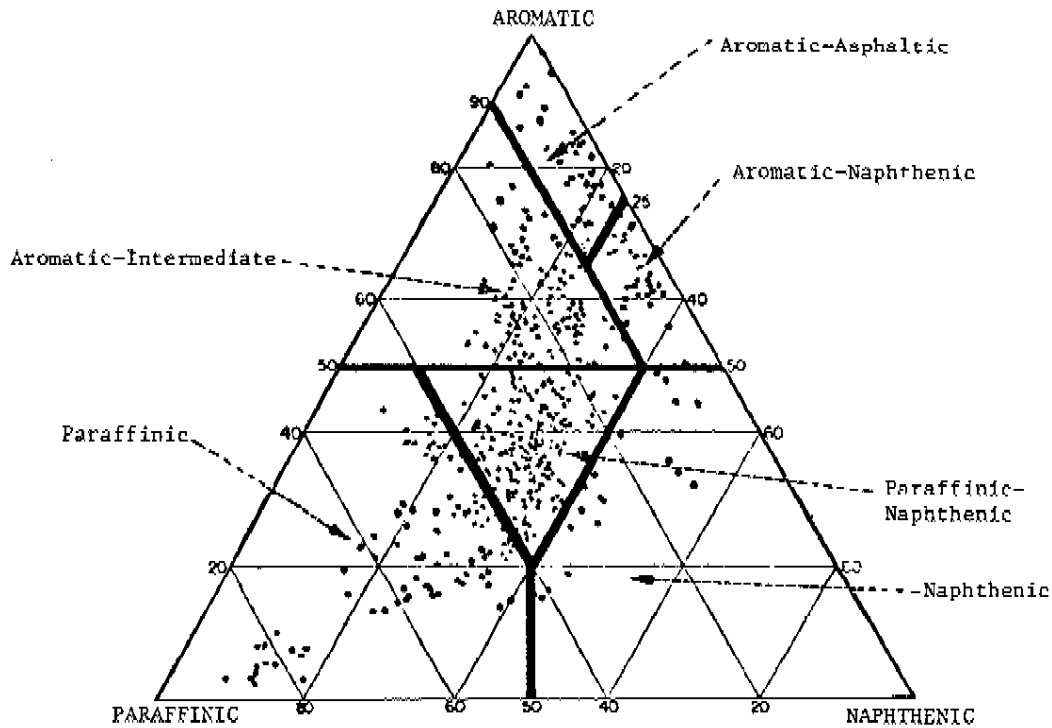


Figure 6. A Ternary Diagram Categorizing Six Different Classes of Crude Oils According to Their Aromatic, Naphthenic, and Paraffinic Hydrocarbon Contents. The Dots in This Diagram Represent the Composition of 541 Oil Fields Around the World (Tissot and Welte [51]).

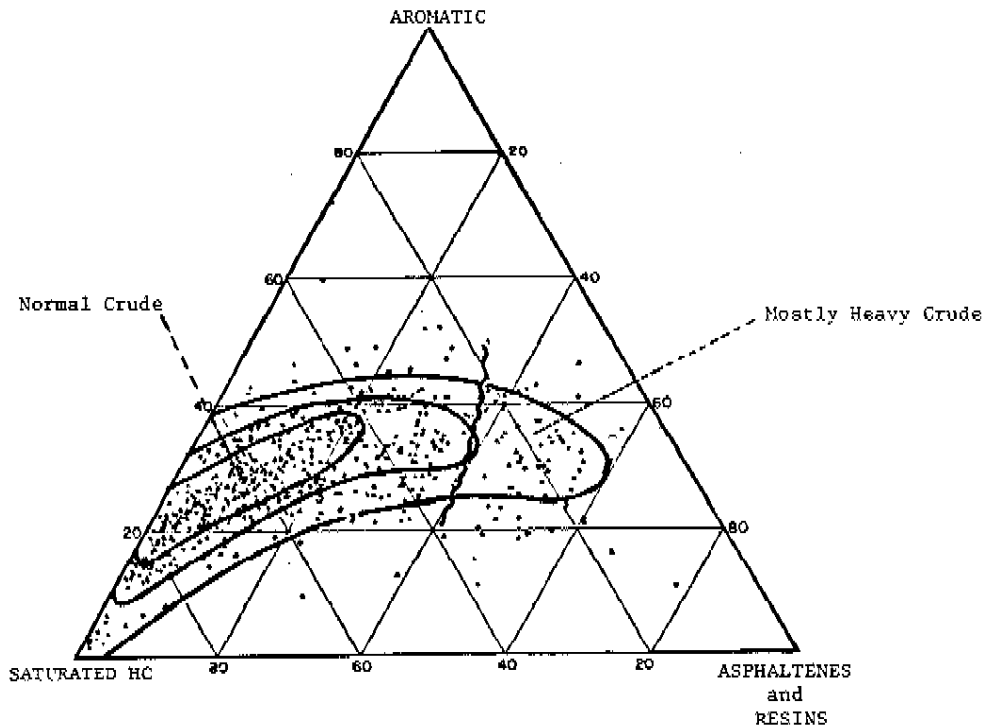


Figure 7. A Ternary Diagram Showing the Gross Composition of 636 Crude Oils from Around the World; Saturated Hydrocarbons, Aromatic Hydrocarbons, and Asphaltenes plus Resins (Weight % in the Fraction Boiling Above 210°C); for Construction of the Isofrequency Contours a Triangle Unit of 10:10:10 was Used (Tissot and Welte [51]).

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:

$$(\mu_{Ai} - \mu_{Ai}^s) = RT[\ln\phi_{Ai} + 1 - (m_{Ai}/m_N)(1 - \phi_B) - m_{Ai}\phi_B + f m_{Ai}\phi_B^2] \quad (1)$$

In this expression, ϕ_{Ai} is the volume fraction of the *i*th fraction of asphaltene and ϕ_B is the volume fraction of asphaltene-free crude such that

$$\sum_i \phi_{Ai} + \phi_B = 1, \quad (2)$$

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

$$m_N = \sum_i \phi_{Ai} / \sum_i (\phi_{Ai}/m_{Ai}) \quad (3)$$

and

$$f = 1/r + K v_B (\delta_A - \delta_B)^2 / RT, \quad (4)$$

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 δ_A and δ_B are the solubility parameters of the asphaltene and asphaltene-free crude, respectively. The solubility parameter is related to the internal energy of vaporization by the following expression

$$\delta_j^2 = \Delta U_j^{vap} / V_j. \quad (5)$$

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.*

$$\mu_{Ai}^s = \mu_{Ai}^l; \quad i = 1, 2, \dots \quad (6)$$

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

$$\begin{aligned} \ln\phi_{Ai}^s + 1 - (m_{Ai}^s/m_N^s)(1 - \phi_B^s) - m_{Ai}^s\phi_B^s + f^s m_{Ai}^s(\phi_B^s)^2 \\ = \ln\phi_{Ai}^l + 1 - (m_{Ai}^l/m_N^l)(1 - \phi_B^l) \\ - m_{Ai}^l\phi_B^l + f^l m_{Ai}^l(\phi_B^l)^2. \end{aligned} \quad (7)$$

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

$$\begin{aligned} \phi_{Ai}^s / \phi_{Ai}^l = \exp[m_{Ai}(1/m_N^s - 1/m_N^l) \\ - m_{Ai}(1 - 1/m_N^l)\phi_B^l + m_{Ai}f^l(\phi_B^l)^2]. \end{aligned} \quad (8)$$

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_N^s equal to m_N^l . In the special case when we set $m_N^s = m_N^l = m$ and if we assume a uniform molecular-weight distribution for the asphaltene ($\phi_{Ai}^l = \phi_{Ai}^s$; $\phi_B^s = 1$), then we can derive 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:

$$F_v(M_{Ai}) = (1/V_A^T)(dV_{Ai}^T/dM_{Ai}), \quad (9)$$

where, V_A^T is the total volume of asphaltene, and dV_{Ai}^T is the total volume of the *i*th fraction of asphaltene, whose molecular weight is between M_{Ai} and $M_{Ai} + dM_{Ai}$. We can also write for the total volume of the *i*th fraction of asphaltene as follows:

$$dV_{Ai}^T = dV_{Ai}^L + dV_{Ai}^S = V^L d\phi_{Ai}^L + V^S d\phi_{Ai}^S, \quad (10)$$

where V^L and V^S are the total volumes of the liquid phase and the asphaltene phase, respectively. According to Equations (9) and (10),

$$F_v(M_{Ai}) V_A^T dM_{Ai} = V^L d\phi_{Ai}^L + V^S d\phi_{Ai}^S. \quad (11)$$

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

$$d\phi_{Ai}^S = \exp(-m_{Ai}\theta) d\phi_{Ai}^L, \quad (12)$$

where

$$\theta = (1 - 1/m_N^l)\phi_B^l - f^l(\phi_B^l)^2 - (1/m_N^l - 1/m_N^s). \quad (13)$$

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

$$d\phi_{Ai}^L = [V_A^T / (V^L + V^S \exp(-m_{Ai}\theta))] F_v(M_{Ai}) dM_{Ai}. \quad (14)$$

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:

$$F_w(M_{Ai}) = (1/W_A^T)(dW_{Ai}^T/dM_{Ai}). \quad (15)$$

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

$$F_v(M_{Ai}) = F_w(M_{Ai}). \quad (16)$$

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.

$$\psi \equiv V_{(f)}/V \quad (22)$$

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

$$\langle \nabla B \rangle = \nabla \langle B \rangle - (1/V) \int_{S_w} B \xi dA \quad (24)$$

$$\langle \partial B / \partial t \rangle = (\partial B / \partial t) + (1/V) \int_{S_w} B u \cdot \xi dA. \quad (25)$$

The union of the pore walls within S is indicated by S_w ; ξ is the unit normal to S_w pointing into the fluid phase; $u \cdot \xi$ 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]

$$\langle \text{div } B \rangle = \text{div } \bar{B} - (1/V) \int_{S_w} B \cdot \xi dA \quad (26)$$

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

$$\partial \rho_{(A)} / \partial t + \text{div } n_{(A)} = r_{(A)}, \quad (27)$$

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

$$n_{(A)} \equiv \rho_{(A)} v_{(A)} \quad (28)$$

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

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

where we have introduced

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$$\alpha_{(A)} = -(1/V) \int_{S_w} \rho_{(A)} (v_{(A)} - u) \cdot \xi dA \quad (30)$$

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

$$n_{(A)} = \rho_{(A)} v - \rho D \nabla w_{(A)}, \quad (31)$$

where

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

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

$$w_{(A)} \equiv \rho_{(A)} / \rho \quad (33)$$

the mass fraction of asphaltene aggregates,

$$v \equiv \sum_{A=1}^N w_{(A)} v_{(A)} \quad (34)$$

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, Equation (24) allows us to write the local volume average of Equation (31) as

$$\bar{n}_{(A)} = \langle \rho_{(A)} \rangle \bar{v} - \langle \rho \rangle D \nabla \bar{w}_{(A)} - \delta_{(A)}, \quad (35)$$

where we have defined:

$$\begin{aligned} \delta_{(A)} \equiv & \langle \rho_{(A)} \rangle \bar{v} - \langle \rho_{(A)} v \rangle + \langle D \rho \nabla w_{(A)} \rangle - \langle \rho \rangle D \langle \nabla w_{(A)} \rangle \\ & - \langle \rho \rangle D / V \int_{S_w} w_{(A)} \xi dA. \end{aligned} \quad (36)$$

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

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]

$$\nabla(\psi(P)) - \mu \operatorname{div}(\nabla \bar{v}) + a = 0. \quad (46)$$

Here μ is the viscosity of the fluid, P is the modified pressure

$$P = p + \rho\phi, \quad (47)$$

and

$$a = (1/V) \int_{S_p} (\mathbf{T}_\perp - \rho\phi \mathbf{I}_\perp) \cdot \xi \, dA, \quad (48)$$

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 ϕ is a scalar potential representing the external force per unit mass b by

$$\mathbf{b} = -\nabla\phi. \quad (49)$$

In Equation (48), \mathbf{T}_\perp is the stress tensor and \mathbf{I}_\perp 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

$$-\nabla(\psi(P)) = a. \quad (50)$$

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

$$a = (\mu/k)\bar{v}, \quad (51)$$

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.

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