

DEVELOPMENTS IN
PETROLEUM SCIENCE

40 B

ASPHALTENES AND ASPHALTS, 2

Edited by

Teh Fu YEN

George V. CHILINGARIAN

School of Engineering

University of Southern California

Los Angeles, CA 90089-2531

USA



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Chapter 12

PRECIPITATION OF ASPHALTENES IN HEAVY OIL AND TAR SANDS

NORMAN F. CARNAHAN

INTRODUCTION

Asphaltenes precipitate from petroleum mixtures as a result of complex phenomena involving at least three categories of mechanisms, individually and in various combinations: (1) classical solid–fluid and fluid–fluid equilibrium, including nucleation, agglomeration, precipitation, and interfacial phenomena; (2) ionic and/or electrochemically induced agglomeration; and (3) mechanical shear-induced agglomeration.

Each of these precipitation mechanisms for asphaltenes can be described in terms of fundamental physical and thermodynamic principles. The present work shall attempt to summarize some of the principles involved in asphaltenes separation from crude petroleum mixtures. First, it is necessary to define some terms that will be discussed.

Definition of terms

Asphaltenes are herein defined as those petroleum components, that are residues, determined using industry-accepted analytical laboratory procedures, typically using *n*-heptane or *n*-pentane as the precipitation-inducing fluid. Asphaltenes are essentially polynuclear aromatic components of the C_7^+ fraction, which contain very few alkyl groups per aromatic ring. Asphaltene structures also contain sulfur, nitrogen, oxygen, and certain metals (nickel, vanadium, etc.). They are lipophobic [1] polar macromolecules, having average carbon numbers in the range of about 40 to 80. They are very solubilizable in toluene, but exhibit very limited solubility or solubilizability in low carbon number normal alkanes. In crude oil, asphaltenes commonly exist as aggregates of 2 to 100 individual macromolecular asphaltenes ‘adhesive particles’ or platelets. Other polar constituents of the heavy fraction are resins and aromatics¹.

Petroleum resins exhibit structural similarities to asphaltenes. They are polynuclear aromatic structures; however, resins contain more alkyl attached groups (side-chains) per aromatic ring. They contain fewer nonhydrocarbon atoms per molecule. The effect of the alkyl groups is such that the resins exhibit lipophilic behavior [1] and have average molecular weight values lower than those of asphaltenes. Petroleum resins appear to form a nonadhesive skin or peptide coating of the asphaltenes aggregates.

Aggregates of lipophobic asphaltenes physically combine with lipophilic resins to form a reverse micelle, which is dispersed in the asphaltenes-free petroleum fluid, apparently as a colloidal system in crude oil.

¹ One must exercise caution in reading the literature on asphaltenes, paying special attention to which solvent is used for obtaining the material referred to as ‘asphaltenes’.

MECHANISMS

Fig. 12-1 describes an idealized spherical micellar configuration of an asphaltene-resins amphiphilic complex. Aggregated asphaltenes are depicted as the dark central sphere. Resins are depicted as an idealized concentric film or zone that surrounds the core of asphaltenes. The outermost portion of the resinous film is in contact with the continuous hydrocarbon or crude oil phase, whereas the innermost portion of the resinous film is in contact with the asphaltene core material. At equilibrium, micelles composed of asphaltenes and resins are assumed to be dispersed in the continuous hydrocarbon fluid.

Phase separation, aggregation, and precipitation of asphaltenes from heavy oils and tar sands depend upon the composition, thermal and mechanical conditions, which existed at the time of formation of the original mixture. The phenomenon also depends upon the composition, thermal and mechanical histories of the system until the time that conditions change sufficiently to result in nucleation, agglomeration, phase separation and/or precipitation of asphaltenes as solids or pseudo-solids. After phase separation occurs, the precipitation and/or deposition mechanisms are governed by viscosity and diffusion characteristics of the asphaltene-free petroleum fluid. In lighter petroleum liquids, aggregated asphaltenes can precipitate and deposit with relative ease; however, in heavy crudes and tar sands, even though phase separation and agglomeration of asphaltenes occur, transport mechanisms (e.g., convection and diffusion) proceed at a slower rate and inhibit the precipitation process.

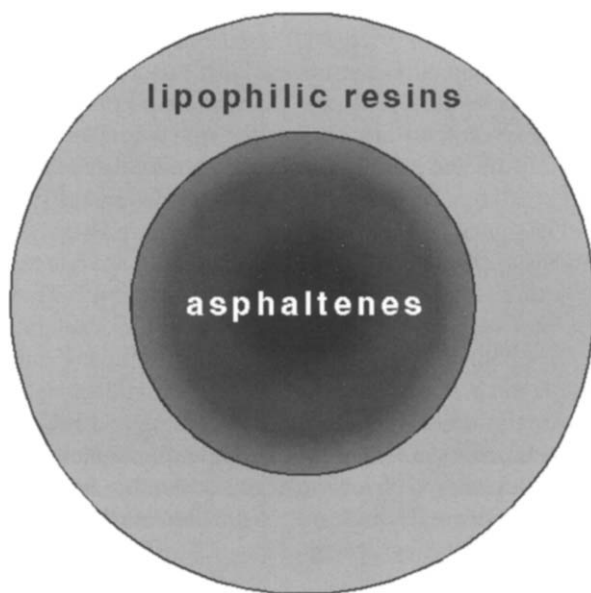


Fig. 12-1. Model of asphaltenes + resins micelle. Resins act as an amphiphilic agent between the continuous hydrocarbon fluid phase and the asphaltene aggregate complex.

Solid–fluid and fluid–fluid phase equilibrium

In petroleum reservoir fluids, asphaltenes can exist in at least two distinct forms: (1) as dissolved asphaltenes monomers and low-order ‘enmers’, and (2) as solubilized amphiphilic structures, such as reverse micelles, composed of resins and asphaltenes, for example. The latter is the more commonly encountered form.

A distinction must be made between the concepts of *solubility* and *solubilization*, as the terms are used herein. In the case of *solubility*, a substance is truly in solution (i.e., dissolved) in a continuous fluid solvent. The dissolved substance is usually very compatible with the solvent phase. In the case of *solubilization*, a substance may exist in a dispersed or colloidal state suspended (solubilized) in a continuous fluid medium. The solubilized substance can be solid, an immiscible liquid phase, or micellar complexes, etc.

Macroscopically, especially in the case of microemulsions and colloidal suspensions in obscure fluids, many outward appearances and behaviors of solutions and solubilized systems appear to be the same.

Solubility theory and asphaltenes

A number of studies have successfully used a macroscopic approach to correlate apparent asphaltenes precipitation behavior, assuming that asphaltenes are soluble in crude oil; however, using the classical solution theory in that manner is not in accord with experimental evidence obtained on the microscopic scale. Solution theory methods are indeed applicable on the macroscopic and microscopic scale; however, in that case, the ‘solute’ is resinous material, naphthenates, and other substances that act as natural amphiphiles and peptize asphaltenes agglomerates, inhibiting their aggregation and precipitation from the petroleum system.

The following review outlines the basis for application, on the macroscopic scale, of the classical solution theory to this phenomenon and presents an alternate interpretation of the physical evidence, using a point of view that is consistent with experimental results obtained on the microscopic scale. For reasons of simplicity, a hypothetical 3-component system composed of asphaltenes, resins and asphaltenes-free oil will be considered.

Solubility of resins and asphaltenes

Solution theory predicts that high molecular weight, relatively nonvolatile hydrocarbon components, such as macromolecular paraffins, resins and, perhaps, some low molecular weight asphaltenes, are of limited solubility in lower molecular weight solvents, such as paraffinic and aromatic lighter ends of naturally-occurring petroleum reservoir fluids. In terms of chemical structure, asphaltenes are complex polynuclear aromatic, high molecular weight petroleum components, which include hydrocarbon, and nonhydrocarbon groups, such as nitrogen, oxygen, sulfur, vanadium, nickel, etc.

A minor amount of asphaltenes may be truly dissolved in lighter ends, especially in highly aromatic reservoir fluids. When conditions change, such that the solubilizing capacity of the lighter ends decreases, the system becomes effectively supersaturated.

From the supersaturated system, nucleation, agglomeration and precipitation of the excess amount of solubilized components (e.g., asphaltenes, resins, and/or macromolecular paraffins) will result, in accordance with principles of macroscopic phase behavior.

A change in the solubilizing capacity of the continuous external phase (e.g., the asphaltenes-free fluid), can result from: (1) variation of the temperature of the solution; (2) addition of components which compete with asphaltenes for the solvent, or which affect the solubilizing power of the solvent such that the characteristic solubility parameters of the solvent and the solute become increasingly similar or dissimilar; and/or (3) variation of the pressure of the system, such that the density of the solvent phase varies sufficiently to affect the solubilizing power of the continuous fluid phase.

Macroscopic point of view

Hirschberg and Hermans [2] and others have presented macroscopic models for calculation of solid-liquid phase equilibrium, assuming that asphaltenes are indeed soluble in crude oil and that precipitation is thermodynamically reversible. Fussel [3] describes solid-liquid equilibrium for asphaltenes in terms of vapor-liquid and liquid-liquid phase behavior. Others have described the phenomenon in terms of Flory-Huggins and/or regular solution concepts developed for polymer solutions. Labout [4], Mitchell and Speight [5], Rogacheva et al. [6], Waxman et al. [7], Burke et al. [8], Thawer et al. [9] and Kawanaka et al. [10] describe asphaltene precipitation mechanism(s) in terms of solubility parameter variations between solubilized asphaltenes and the solvent portion of several crudes. Hirschberg and Hermans [2] applied such a model to describe asphaltenes precipitation from an Iranian crude oil and a North Sea crude oil. Using the macroscopic point of view, one can examine the applicability and consequences of using the classical solution theory to correlate experimental results for apparent solubility of asphaltenes in crude oils and liquid hydrocarbons. Solubility is consistent with reversible solid-liquid phase behavior. In the absence of complex formation in the precipitate, solubility would mean that the precipitate could be redissolved in the liquid by restoring the system to the initial conditions.

Microscopic point of view

As early as 1923, Nellensteyn [11] defended the point of view that asphaltenes are not in solution in crude oil; rather, they exist in the form of a colloidal suspension in crude oil. If true, then classical solution theory should not apply to the phase equilibrium for asphaltenes precipitation from crude oil. Yet, solution theory might be useful to describe the phase equilibrium between amphiphilic resins and crude oil. The interfacial phenomenon requires simultaneous consideration of Langmuir-type adsorption equilibrium between amphiphilic resins and 'crude oil insoluble' material(s), including asphaltenes. Thus, one needs to solve interfacial adsorption equilibrium equations for the resins + asphaltenes system simultaneously with solubility phase equilibrium equations for the resins + oil system. Solubilization is consistent with irreversible solid separation from the liquid phase.

Characterization of the petroleum heavy fraction

Regardless of which point of view one adopts, the complex nature of the petroleum system, in the case of crude oils and tar sands, requires careful characterization in terms of the components and/or pseudo-components contained therein. Traditionally, crude oils have been characterized on the basis of a distillation curve. More recently, it is becoming well recognized that detailed analysis of many narrow boiling cuts is necessary for proper phase equilibrium and thermodynamic calculations. For the oils considered by Hirschberg and Hermans [2], extended composition analyses, derived from regression of mole percents vs. carbon number, result in the following correlation formulas:

$$\text{Iran: Mol.\%} = 10.29 \times [10^{(-0.106 \text{ CN})}]$$

$$\text{North Sea: Mol.\%} = 8.75 \times [10^{(-0.107 \text{ CN})}]$$

The exponents indicate that the slopes of the composition correlations for these two crude oils, on a semi-logarithmic graph, are very similar. The major difference is the magnitude of the pre-exponential coefficient, which relates to the intercept on the vertical axis of a semi-logarithmic graph. Although the oils in the examples used by Hirschberg and Hermans [2] are inherently different, their estimated distribution of higher carbon number components appears to be semi-logarithmic. The semi-logarithmic distribution of macromolecules in petroleum fluids was empirically observed by Whitson [12] and has been justified on theoretical grounds by Levelt-Sengers and de Swaan-Arons [13]. Correlation of extended composition of the high carbon number components in this manner supports the applicability of polymer solution theory for macroscopic description of these phenomena.

Calculation method — macroscopic model

Hirschberg summarizes, from a macroscopic point of view, the apparent effects of temperature, pressure and composition on the deposition of asphaltenes from liquid petroleum.

Hirschberg [14] used the Soave equation of state for VLE calculations, assuming a negligible amount of solid asphaltenes-rich phase, based on a 22-component representation of the crude oil. Light ends, methane through hexanes, including nitrogen and carbon dioxide, were determined by PVT analysis. The C_7^+ fraction was subdivided into six paraffin pseudocomponents and six aromatic pseudocomponents. Alternatively, one can characterize the C_7^+ fraction as a continuous mixture, using semi-logarithmic correlations (as previously described), and subportions (e.g., boiling point cuts) of the semi-continuous mixture can be characterized according to their paraffin/naphthene/aromatic (PNA) distributions, as pointed out by Mansoori and Jiang [15]. The PNA ratio for various petroleum fractions can be defined experimentally or estimated in terms of exhibited PVT properties, using such correlations as presented by Yarborough [16]. No matter how the C_7^+ fraction is characterized, it is necessary to properly define the amount of resins and asphaltenes in the heavy end fractions.

Solid–fluid phase equilibrium can be approximated using rigorous thermodynamic criteria for phase equilibrium. The presence of a solid phase or an immiscible liquid phase has a similar mathematical definition in terms of phase equilibrium calculations.

Consider the following analysis:

$$\mu_i^A = \mu_i^{CO} \quad (12-1)$$

Subscript i pertains to the i -th component and superscripts 'CO' and 'A' pertain to the 'crude oil-rich phase' and the 'asphaltenes-rich phase', respectively.

Considering size-related entropy effects, it is proposed that:

$$\frac{\mu_i - \mu_i^o}{RT} = \ln \phi + 1 - \frac{V_i}{\langle V \rangle} + \chi_i \quad (12-2)$$

where: μ_i^o = chemical potential of pure-component i as a liquid; ϕ_i = volume fraction of component i in the liquid mixture [$x_i V_i / \langle V \rangle$]; V_i = molar volume of pure-component i as a liquid; x_i = mole fraction of component i in the liquid phase,

$$\langle V \rangle = \sum_i x_i V_i \quad (12-3)$$

and

$$\chi_i = \frac{V_i}{RT} [\langle \delta \rangle - \delta_i]^2 \quad (12-4)$$

where

$$\langle \delta \rangle = \sum_i \phi_i \delta_i \quad (12-5)$$

$$\delta_i^2 = \frac{\Delta U_{\text{vap}}^o}{V_i} \quad (12-6)$$

ΔU_{vap}^o = molar internal energy difference due to isothermal vaporization between the liquid state and the ideal gas state.

It is assumed, in this method, that the 'asphaltenes-rich phase' is 100% asphaltenes; therefore,

$$\mu_i^A = \mu_A = \mu_A^{CO} \quad (12-7)$$

Hirschberg [14] and Kawanaka et al. [10] present an estimation of the maximum volume fraction of asphaltenes in solution with degassed crude oil, i.e.,

$$(\phi_A)_{\text{max}} = \exp \left\{ \frac{V_A}{V_{CO}} \left[1 - \frac{V_{CO}}{V_A} - \frac{V_{CO}}{RT} (\delta_A - \delta_{CO})^2 \right] \right\} \quad (12-8)$$

The composition of degassed crude oil remains practically invariant above the bubble point. The numerical value of the solubility parameter of the crude oil is inversely proportional to the molar volume of the liquid, which normally decreases with increasing pressure. Therefore, the apparent solubility parameter of live crude oil usually increases with increasing pressure. Likewise, the apparent solubility parameter of live crude oil usually decreases as pressure decreases.

Apparent solubility parameter for asphaltenes

The apparent solubility parameter of asphaltenes, determined via correlation of macroscopic thermodynamic data using a regular solution theory model, is approximately 10 hildebrands [1 hildebrand = $0.1 (\text{cal}/\text{cm}^3)^{0.5}$]. Hirschberg et al. [19] report the apparent solubility parameter of asphaltenes in crude oil to be about 9.8 hildebrands (20 MPa^{0.5}). Burke et al. [8] found the apparent solubility parameter of 'asphaltenes sludge' to be about 10.0 hildebrands (20.5 MPa^{0.5}).

Solubility parameters of petroleum fluids

Solubility parameter values for light crude components depend on composition, and are often in the range of about 6–8 hildebrands. Lower molecular weight alkanes exhibit solubility parameters of lower numerical value, relative to those of higher molecular weight hydrocarbons. Hirschberg and Hermans [2], Burke et al. [8], Thawer et al. [9], and Kawanaka et al. [10] have noted the relationship between the composition (*or molecular weight*) of the continuous fluid, and the ability of crude oil to maintain asphaltenes in apparent solution. Solubility parameter values for medium and heavy oils are greater than those for light oils. Only a limited amount of reliable experimental data has been reported, although none for asphaltenes phase behavior in heavy oils and tar sands. The expected value of the solubility parameter of such heavy petroleum fluids is about 8–10 hildebrands.

Table 12-1 shows the general effect reported by Wuithier [35] which demonstrates the significant role of molecular weight (*hence the solubility parameter*) on hydrocarbon fluid compatibility with asphaltenes. Table 12-2 lists solubility parameters for several hydrocarbons, showing that the solubility parameter characteristically increases with molecular weight and/or carbon number for alkanes. Aromatic substances exhibit solubility parameters similar to the apparent solubility parameter for asphaltenes.

TABLE 12-1

Amount of asphaltenes precipitated vs. solvent molecular weight at 323.15 K (122°F) [35]

Solvent (mol wt.)	Asphaltenes precipitated (mass percent)
30 (<i>n</i> -C ₂)	90.0
44 (<i>n</i> -C ₃)	22.5
58 (<i>n</i> -C ₄)	10.0
72 (<i>n</i> -C ₅)	4.0
86 (<i>n</i> -C ₆)	1.0
100 (<i>n</i> -C ₇)	less than (1.0)

TABLE 12-2

Solubility parameters of various alkane and aromatic hydrocarbons

Component	δ (hildebrands)	Component	δ (hildebrands)
Propane	6.0	<i>n</i> -Heptane	7.45
<i>n</i> -Butane	6.7	<i>n</i> -Octane	7.55
<i>i</i> -Butane	6.25	<i>n</i> -Nonane	7.65
<i>n</i> -Pentane	7.05	<i>n</i> -Hexadecane	8.00
<i>i</i> -Pentane	6.75	Benzene	9.15
neo-Pentane	6.25	Toluene	8.90
<i>n</i> -Hexane	7.30	Naphthalene	9.90

Alkanes typically exhibit lower solubility parameter values than aromatic hydrocarbons, which macroscopically appear to be more compatible with heavy crude oils and asphaltenes. The linear mixing rule, according to their volume fractions in the mixture, enables blending of solvent mixtures to obtain a desired value of the effective solubility parameter. Such blending of solvents was used by Burke et al. [8], who reported experimental results of asphaltenes deposition from simulated field crude oil mixtures.

Solubilization of asphaltenes (microscopic viewpoint)

Although Hirschberg and Hermans [2] and Burke et al. [8] were able to correlate observed macroscopic effects of asphaltenes precipitation from crude oils and hydrocarbon fluids, the concept of asphaltenes solubility in crude oils may have been over-extended and/or obscured in the cause-and-effect relationship assumed in the correlation model. There is no doubt that asphaltenes can precipitate as a result of changing the composition of the fluid. Such change in the composition is the basis for the well-established laboratory method for determining the asphaltenes content of petroleum fluids, e.g., addition of *n*-pentane or *n*-heptane to a sample of petroleum fluid. Asphaltenes precipitate as a result of such changes in the composition of crude oil. It does not necessarily follow, however, that asphaltenes precipitate from petroleum fluid due to a decrease in their solubility in the petroleum fluid, as a result of the addition of lower molecular weight alkanes. The key question is: are asphaltenes soluble in crude oil or do asphaltenes exist in a colloidal state in crude oil? A preponderance of experimental evidence and field observations indicate that asphaltenes exist in a colloidal state in crude petroleum.

It is, indeed, tempting to conclude that precipitation of asphaltenes results from a significant difference between the solubility parameter of the fluid mixture and the solubility parameter of the asphaltenes. On the macroscopic scale, one can certainly develop such an argument. However, such a conclusion appears at odds with considerable evidence indicating the colloidal nature of asphaltenes in petroleum fluids [21–23]. Waxman et al. [7] and Hotier [24] indicate that asphaltenes precipitation may not be fully reversible.

From the microscopic point of view, however, asphaltenes are assumed to have little or no solubility in crude oil. Asphaltenes are assumed to be an insoluble or immiscible material that is solubilized in the crude oil in the form of colloidal particles or similar amphiphilic structures, with the help of naturally-occurring resins and similar amphiphilic components of the crude oil.

Using a microscopic model, it is obvious that a key factor in the stability of asphaltenes in petroleum fluids is the integrity of the protective film of the amphiphilic material that surrounds the core of asphaltenes. Anything that damages or removes the amphiphilic film allows the aggregation of asphaltene particles that can result in precipitation or deposition. Likewise, anything which enhances the amphiphilic film would stabilize the system. Experiments have shown that addition of resins or amphiphiles can increase the stability of asphaltenes in certain crude oils [36,38–42]. According to established models of phase behavior involving reverse micelles (*so called, because the oil is on the outside and the 'non-oil' is on the inside of the micelle*), it is acceptable to characterize the phase behavior of asphaltenes using classical solubility theory. However, in this case, the solute is the amphiphilic substance(s) and the solvent

is the asphaltenes-free petroleum fluid. Asphaltenes are assumed to be, for all practical purposes, totally immiscible and/or insoluble in the asphaltenes-free petroleum fluid.

As a consequence of the microscopic model, then, existing precipitation data for asphaltenes suggest that the mutual compatibility of resins and petroleum fluid increases as the average molecular weight of the petroleum fluid decreases. Thus, the effective solubility parameter value for amphiphilic resins must be similar to that of the lower carbon number alkanes, i.e., about 5–6 hildebrands.

The microscopic point of view also indicates that asphaltenes are not soluble in the higher molecular weight petroleum fluids, but remain suspended in them, as stable colloidal particles. Likewise, asphaltenes precipitate when low carbon number alkanes are added to petroleum fluid, due to the destabilization of the colloidal particles, with resultant coalescence, agglomeration and precipitation. This viewpoint is quite the opposite of that which Hirschberg [14] and Burke et al. [8] assumed. The experimental picture, on the macroscopic scale, is indefinite with regard to the true mechanism leading to precipitation of asphaltenes. Evidence from the microscopic scale must be used to distinguish among competing mechanisms, only two very simplified versions of which are presented here.

One also has to include in such a microscopic model a definition of the interfacial adsorption effects, between the resins and the asphaltenes. There is a competition between the asphaltenes and the asphaltenes-free petroleum for the resins and other naturally occurring amphiphiles. When temperature, pressure or composition changes such that the asphaltenes-free petroleum fluid exhibits greater compatibility with the resins, a certain amount of the resins are solvated away from their protective role surrounding the reverse micelles. As a result, some micelles become unstable, coalesce or agglomerate to form larger micelles, and may precipitate from the fluid or deposit on solid surfaces.

The previously described entropy-modified regular solution theory model for the fluid phase can be combined with a suitable model of adsorption of amphiphilic substances, such as resins, at the asphaltenes–petroleum fluid interface. The resulting model, including fluid–fluid equilibrium and fluid–nonfluid interfacial effects, indicates that simultaneous solution of both types of equilibrium equations is necessary in order to correlate and/or predict the phase behavior of systems such as oil + resins + asphaltenes.

Microscopic vs. macroscopic models

Interestingly, phase equilibrium of asphaltenes in crude oil can be correlated with reasonable success using either the macroscopic or the microscopic point of view. The fundamental picture strongly favors the microscopic model as a true representation of the physical phenomenon. From the macroscopic viewpoint, one observes an apparent inverse relationship between precipitation of asphaltenes and the effective solubility parameter of the crude oil. Asphaltenes appear to have a solubility parameter of about 10 hildebrands and tend to precipitate in increasing amounts as the effective solubility parameter of the petroleum fluid decreases below approximately 9 hildebrands. This observation is based upon, among other factors, the assumed relationship between solubility of asphaltenes and the magnitude of the difference in solubility parameters of the solvent and the asphaltenes, i.e., $(\delta_A - \delta_{CO})^2$.

On the microscopic scale, the solubility relation between resins and petroleum fluid is assumed to be modeled by similar physics, e.g., $(\delta_R - \delta_{CO})^2$.

In this scenario, however, resins appear to be increasingly soluble in the petroleum fluid as the solubility parameter of the petroleum fluid decreases from about 9–10 hildebrands toward about 5–6 hildebrands. Thus, one is led to observe that the apparent solubility parameter of petroleum resins is in the range of about 5–6 hildebrands. Asphaltenes are assumed to be negligibly soluble in petroleum fluid. Interfacial adsorption effects, between resins and asphaltenes can be described in terms of Langmuir-type models using parameter values determined from experiments.

Ionic and/or electrochemically induced asphaltene precipitation

Changes in the ionic and/or electrochemical environment of asphaltenes in crude oil can cause flocculation of microscopic asphaltenes particles in the crude oil. Reports of asphaltenes deposition following acidizing procedures are common. The nature of asphaltenes particles in crude oil is such that they exhibit polarity and/or induced polarity. Although a resinous skin usually protects and stabilizes asphaltenes aggregates, the polar resins can be affected by changes in pH and/or mineral ion environment. Contact with acids and with mineral ions favor flocculation and deposition of asphaltenic solids.

Consider resins to have a net charge that is electrically opposite to that of asphaltenes, such that the resins are attracted to the asphaltenes globule and tend to render the resins + asphaltenes particle electrically neutral. Indeed, this is a possible mechanism whereby resins can be attracted to the asphaltenes–resins interface. Upon contact with a strong solution of acid and/or ionic solution of minerals, especially iron, calcium and magnesium, the resins may be attracted away from the asphaltenes, such that unprotected asphaltenes particles agglomerate and precipitate as a sludge, together with coagulated resins and minerals.

Asphaltene deposits are frequently encountered following acidizing procedures downhole, even when asphaltene deposits had not been a problem before the acidizing procedure. Such deposition seems to result from interaction between ions and the polar asphaltenes globules, resembling a process of coagulation or flocculation. Chemical analysis of such deposits commonly shows the presence of minerals such as iron, calcium and magnesium.

Models for correlating and predicting this ion-related mechanism for asphaltenes deposition need to account for the association effect between the ‘monomers’ and the ‘monomer complexes’. Heidemann and Prausnitz [18], Jackson et al. [20], and Suresh and Elliott [25] present models useful for describing phase equilibrium, chemical equilibrium and PVT behavior of associating substances. For example, consider the reversible interaction



If ‘A’ represents an individual asphaltene particle or globule, such that two such globules associate to form a ‘2A’ dimer, then the computation of equilibrium composition of coexisting phases must also involve the simultaneous solution of the association

equilibrium, which can be viewed either as a chemical reaction or a physical combination. In nature, the combination mechanism of asphaltene particles is quite complex, involving a distribution of particles and groups of particles. The general problem of particle association is well suited to statistical mechanical analysis, and has been studied by Wertheim [26], Chapman et al. [27], and others.

Empirical methods for predicting and correlating the association of asphaltene particles and their precipitation due to ionic effects involve application of equations of state for associating substances. To date, researchers using these methods have not extensively studied the problem of asphaltene. This area of research should be of interest to companies that experience costly production problems due to asphaltene.

Mechanical shear-induced asphaltene precipitation

The concept of asphaltene as adhesive colloidal particles encased in a thin non-adhesive resinous skin, well dispersed in crude oil, lends itself to the interpretation of shear-induced deposition of asphaltene solids. Damage or rupture of the resinous skin, by mechanical shear effects and/or solvent action, can result in agglomeration of asphaltene and precipitation of solids from crude oil.

Shear effects occur when the fluid is subjected to high-energy shear fields, such as in turbulent flow through porous media, perforations and screens, sudden acceleration in production tubing, surface and downhole pumps and chokes. Such effects may also result from injection of gas into crude oil, as in gas lift production systems.

The literature contains very little reliable experimental data pertaining to mechanical shear-induced deposition of asphaltene, although numerous studies of shear-induced alteration of similar colloidal systems have been described. Field experience indicates that such deposition may occur; however, reported data are insufficient for development of useful correlations and/or predictive methods.

DISCUSSION

What is the principal mechanism of asphaltene precipitation?

The principal mechanism of asphaltene deposition seems to be desolubilization, nucleation, agglomeration and precipitation of solid material due to changes in solvent power of crude oil and dissolved light ends. Such phenomenon may result from physical changes in the environment to which crude oil is subjected, such as reduction in pressure from an initially high reservoir pressure toward bubble point pressure of the system. Such phenomenon may also result from the admixture of light ends with a heavy crude. McHugh and Krukoni [28] discuss nucleation phenomena. Andersen and Birdi [29] and Sheu et al. [30] report critical micelle concentrations (CMCs) of asphaltene. Such studies support the concept of colloidal nature of asphaltene complexes in petroleum fluids.

The apparent solubility parameter for asphaltene seems to be about 9.54–10.00 hildebrands. The basic principle of solvent action is that 'like dissolves like'. Hildebrand and Scott [31] discuss the regular solution theory, which describes the compatibility

TABLE 12-3

Effect of solvent carbon number on solubility of asphaltenes in tank oil [14]

Solvent	Asphaltenes deposited (wt.%)	δ_{CO}	$(\delta_A - \delta_{CO})^2$
<i>n</i> -C ₅	3.61	7.05	8.7
<i>n</i> -C ₇	1.82	7.45	6.5
<i>n</i> -C ₁₀	1.45	7.75	5.0

between solute and solvent via a functional relation between their respective solubility parameters, i.e.,

$$\text{Solvent power of crude oil} \propto (\delta_A - \delta_{CO})^2 \quad (12-10)$$

Burke et al. [8] found that the solubility parameter of crude oil, including the effect of dissolved light ends, changes with pressure and temperature, such that $|\delta_A - \delta_{CO}|$ reaches a maximum. Hirschberg [14] reports asphaltenes solubility in relation to the effective solubility parameter of *n*-alkane solvents. Table 12-3 shows a qualitative forecast of the expected solubility of asphaltenes in three solvents, in terms of the similarity or dissimilarity of their solubility parameters. Agreement between measured and predicted solubility is qualitatively correct, although such measurements are very difficult, often nonrepeatable, and may be of questionable statistical accuracy.

Hirschberg [14,17], Burke et al. [8], and others have found that asphaltenes precipitation can be predicted using a modified version of the regular solution theory, together with established principles of solubility. Mansoori and Jiang [15] and Kawanaka et al. [10] present a method based on the Scott and Magat [32] theory of polymer solutions, using a polydisperse mixture concept of the asphaltenes fraction.

Sufficient evidence shows that precipitation and deposition of asphaltenes can be correlated and predicted using solution theory models such as a Flory-Huggins Modified Regular Solution Theory. Using a macroscopic approach, one can correlate asphaltenes phase separation in terms of the solubility parameter of the solvent. However, a more fundamentally correct approach should account for effects observed on the microscopic scale, i.e., solubility of naturally-occurring amphiphilic resins in the solvent phase, and to model the aggregation of asphaltenes resulting from distribution of resins between the continuous solvent phase and the asphaltenes-rich phase. In order to develop such models and to test theories of solution for asphaltenes, additional reliable experimental data need to be available to theoreticians. Data reported in the literature are useful, although very limited at this time.

Other mechanisms which influence precipitation of asphaltenes

Solution theory, as reviewed herein, accounts for a very substantial portion of asphaltenes problems experienced in industry. Other mechanisms can also have an effect on solubility of asphaltenes in reservoirs and in deep wells.

Supercritical fluids, such as methane, ethane and propane, act as supercritical solvents at typical reservoir pressures and temperatures, but lose some of their solvent capability

when pressures are reduced. In deep reservoirs in which the reservoir fluid contains a substantial amount of light ends and dissolved gases, supercritical effects can be significant in terms of deposition of asphaltenes and other heavy substances dissolved in or suspended in reservoir fluids. Several mechanisms of supercritical solution phenomena in reservoir fluids have been previously reported [33,34,37].

SUMMARY AND CONCLUSIONS

This review of fundamentals of the oil + resins + asphaltenes phenomenon in heavy oils and tar sands presents a rational framework for reservoir engineers to use in evaluating the benefits and consequences of proposed production methods and/or operations involving asphaltenic crudes.

(1) Asphaltenes phase behavior is predictable using classical solution theory models of solid-liquid and liquid-liquid phase equilibrium, together with appropriate adsorption equilibrium models for interactions between asphaltenes and resins. Development of improved models requires additional reliable experimental data, including measurements of asphaltenes nucleation, agglomeration and precipitation, and additional phase equilibrium data for well-defined compositions. Precipitation and deposition of asphaltenes in heavy crudes and tar sands is inhibited by transport processes, but may be significant in high-temperature reservoirs. Reliable experimental data for such systems in the literature are very limited at the present time.

(2) Asphaltenes precipitation due to electrochemical effects is not yet well defined. Equations of state for associating fluids have appeared in the literature, but have found few applications relating to asphaltenes precipitation phenomena. Such applications are certainly warranted. Experimental measurements are needed, in order to provide necessary data for development of models for the interaction between asphaltenes and ionic species, and for modeling the behavior of asphaltenes in contact with ionic solutions.

(3) Asphaltenes precipitation and deposition data due to mechanical shear effects have not been reported in the literature; however, the phenomenon is herein described in terms of field experiences. This mechanism should be experimentally investigated in order to define its importance, related to field-experienced problems and problems which may occur in-situ during production of asphaltenic hydrocarbon fluids.

In summary, the state of our knowledge of asphaltenes deposition mechanisms is certainly improved from a decade ago; however, the development of fundamentally correct solution models of asphaltenes behavior is just beginning. With additional reliable experimental data, theoreticians should be able to accurately define the mechanisms and establish interaction parameters between components of the fluid-fluid and fluid-solid systems. Electrochemical effects and mechanical shear effects are not yet sufficiently well defined. Accurate and precise experimental data are needed in order to determine these mechanisms and their practical importance.

In heavy oils and tar sands, although phase separation can be predicted according to rigorous thermodynamic phase equilibrium principles, transport mechanisms interfere with aggregation, precipitation and deposition of asphaltenes from the petroleum fluid. In viscous fluids that experience a quantitative imbalance between asphaltenes and their

associated resins, mechanisms of micelle destabilization, aggregation and precipitation operate on a much slower time scale than for less viscous fluids. Thus, the physical properties of heavy oils and tar sands can ameliorate the problem of asphaltenes drop out, by maintaining such particles in suspension within the fluid phase. Furthermore, due to the dissimilarity between the solubility parameter values for resins and for heavy crudes, resins + asphaltenes micelles tend to remain relatively stable in heavy crudes and tar sands.

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