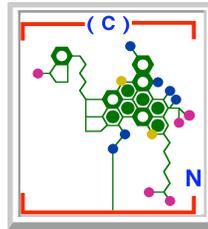# Asphaltene Deposition and its Control

(visit also ASPHALTENE)

(Visit also A Statistical Mechanical Model of Asphaltene Flocculation and Collapse From Petroleum Systems)

UIC/TRL's

ARTERIAL BLOCKAGE in the PETROLEUM and NATURAL GAS INDUSTRIES Project

Abstract

Remediation of the heavy organic deposits in the course of petroleum production has been a costly process and it has hampered the production activities in many parts of the world. In this report the authors study the in situ remediation of heavy organics including asphaltene, resin, paraffin / wax, etc. in oil production and transportation practices and its relation with the laboratory and theoretical simulation experiments. it is demonstrated that while asphaltene is the major compound responsible for various arterial blockage cases in the petroleum industry its interaction with other heavy organics is a major factor whether depositions will occur or not. Various mechanisms of asphaltene flocculation and micelle formation are reviewed and illustrative pathways are presented for each mechanism. The current in situ remediation and laboratory simulation practices in the oil industry to combat these complex systems of problems is reviewed and analysis are made of the cause and effect of each factor influencing them. It is demonstrated that with the development of predictive modelling of heavy organic deposition one can make alterations in the production and transportation schemes to reduce and eliminate the deposition problem. With the development of predictive models one can also screen the candidate dispersants and solvents from the points of view of availability at the site, effectiveness and economy.

Introduction and Background

Arterial blockage in the petroleum industry is mostly due to the deposition of heavy organics from petroleum fluids. Heavy organics such as paraffin / wax, resin, asphaltene, diamondoid, mercaptans, and organometallic compounds may exist in crude oil in various quantities and forms. Such compounds could precipitate out of the crude oil solution due to various forces causing blockage in the oil reservoir, in the well, in the pipelines and in the oil production and processing facilities [Mansoori, 1995, 1996]. Solid particles suspended in the crude oil may stick to the walls of the conduits and reservoirs. The toughness of the precipitate has a lot to do whether there is asphaltene present in the crude oil even in minute quantities. Asphaltene, which is a highly polar compound, could act as glue and mortar in hardening the deposits and, as a result, causing barrier to the flow of oil.

Heavy organics deposition during oil production and processing is a very serious problem in many areas throughout the world [Leontaritis and Mansoori, 1988]. In the Prinos field in North Aegean Sea, there were wells that, especially at the start of production, would completely cease flowing in a matter of a few days after an initial production rate of up to 3,000 BPD. The economic implications of this problem were tremendous considering the fact that a problem well workover cost could get as high as a quarter of a million dollars. In Venezuela the formation of heavy organics (asphaltic sludges) after shutting in a well temporarily and/or after stimulation treatment by acid has resulted in partial or complete plugging of the well [Lichaa, 1977]. At the Hassi Messaoud field, Algeria, deposit of heavy organics in the tubing has been a very serious production problem [Haskett and Tartera, 1965].

Heavy organics have played a significant role in the production history and economics of the deep horizons of the Ventura Avenue field, California [Tuttle, 1983]. Heavy organics deposition problems in this field ranged from deposition during early oil production and deposition resulting from well acidizing and CO2 injection during enhanced oil recovery (EOR). However, the problems were so drastic because of heavy organics (asphalt) deposition at the early history of this field that many wells were redrilled, thus affecting the economics of the project considerably. It was also reported that heavy organics deposits were found in the production tubing in the Little Creek CO2 injection EOR pilot in Mississippi [Tuttle, 1983]. Generally heavy organics deposits could occur during primary, secondary, and enhanced oil recovery stages [Tuttle, 1983]. Heavy organics precipitation, in many instances, carries from the well tubing to the flow lines, production separator, pumps, strainers and other downstream equipment [Katz & Beu, 1945]. Heavy organic materials deposited into the production installations of Mexico's oil fields have caused many operational problems as it is elaborated in reports by Chavez and Lory (1991) and and Escobedo, et al. (1997). For example, in the fields of Tecomonoacan and Jujo depositions in many wells have caused numerous shutdowns and necessity of rather expensive aromatic washes. Heavy organics deposition in the North Sea and in the Gulf of Mexico oil fields in recent years have caused several under-sea pipeline pluggings with substantial economic loss to the oil production operations [Escobedo and Mansoori (1992) and Escobedo, et al. (1997)].

In general, solids in crude oil fall into two classes: "basic sediment" and "filterable solids". These particles have an economic impact on petroleum industry. Carried along in the oil, they can cause fouling, foaming, erosion, corrosion, etc. Depending on the case, coagulants (molecular weight < 10,000.) or flocculents (molecular weight > 10,000.), might provide an indirect aid in solids removal [Schantz and Elliot, 1994]. Coagulants are molecules with strong polar charge which act to disrupt charges on the surface of the oil droplet that would otherwise prevent coalescence. Flocculents, act to coalesce oil droplets, because they are very soluble in oil, but in some cases they can have drastically reduced solids removal, that is to say, solids never die, they just move around.

Depositions of the heavy organics present in oil could happen due to various causes depending on their molecular nature. For instance, by examining each heavy organic compound separately one may argue that mercaptans and organometallics cause deposition due to dissociation or solubility effects. Diamondoids and paraffin / wax may cause deposition due to lowering of the crude oil temperature and formation of crystalline solids [Afanas'ev, et al, 1993]. Resins are not known to deposit on their own, but they deposit with asphaltenes as it will be elaborated later. The reasons for the asphaltene deposition can be many factors including variations of temperature, pressure, composition, flow regime, and wall and electrokinetic effect. When various heavy organic compounds are present in a petroleum fluid their interactive effects must be also considered in order to understand the mechanisms of their collective deposition or lack of it. This is specially important when one of the interacting heavy organic compounds is asphaltene. For example a regular waxy crude containing minute amounts of asphaltene will behave differently at low temperatures (below the wax cloud point) compared with a clean waxy crude with no other heavy organics present in it, an asphaltenic crude containing some paraffin / wax, or a purely asphaltenic crude containing no paraffin / wax. Considering that the major barrier in a profitable deposition-free oil production scheme is the presence of asphaltene in the crude in what follows the in situ role of asphaltene in the petroleum fluids will be discussed.

Asphaltene molecule, asphaltene steric-colloid, asphaltene micelle

The investigation of the chemical constitution of petroleum heavy fractions such as resins and asphaltenes is hindered by their complex nature. The classic definition of asphaltenes is based upon the solution properties of petroleum residuum in various solvents. The word asphaltene was coined in France by J.B. Boussingault in 1837. Boussingault described the constituents of some bitumens (asphalts) found at that time in eastern France and in Peru. He named the alcohol insoluble, essence of turpentine soluble solid obtained from the distillation residue "asphaltene", since it resembled the original asphalt.

Marcusson in1945 classified asphaltene and resin as follows : (i) Neutral resins are defined as the insoluble fraction in alkalies and acids and it is completely miscible with petroleum oils, including light fractions; (ii) Asphaltenes are defined as insoluble fraction in light gasolines and petroleum ether. In contrast to resins, the asphaltenes are precipitated in the presence an excess ether; (iii) Asphaltogenic acid is defined as the soluble fraction in alkaline solutions and in such solvents as benzene.

The asphaltene fraction of a petroleum crude is defined according to Nellensteyn (1924) as the fraction insoluble in low boiling point paraffin hydrocarbons, but soluble in carbon tetrachloride and benzene. According to Pfeiffer (1950) asphaltene is defined as the fraction insoluble in n-heptane but soluble in toluene.

Recently, asphaltene is defined by chemists as the part precipitated by addition of a low-boiling paraffin solvent such as normal-pentane and benzene soluble fraction whether it is derived from carbonaceous sources such as petroleum, coal, or oil shale. Since asphaltogenic compounds are present in petroleum in insignificant quantities, resins and asphaltenes are most important compounds of petroleum. There is a close relationship between asphaltenes, resins, and high molecular weight polycyclic hydrocarbons. In nature, asphaltenes are hypothesized to be formed as a result of oxidation of natural resins. On the contrary, the hydrogenation of asphaltic compound products containing neutral resins and asphaltene produces heavy hydrocarbon oils, i.e., neutral resins and asphaltenes are hydrogenated into polycyclic aromatic or hydroaromatic hydrocarbons. They differ, however, from polycyclic aromatic hydrocarbons by presence of oxygen and sulfur in varied amounts.

On heating above 300-400 oC, asphaltenes are not melted, but decompose, forming carbon and volatile products. They react with sulfuric acid forming sulfonic acids, as might be expected on the basis of the polyaromatic structure of these components. The color of dissolved asphaltenes is deep red at very low concentration in benzene as 0.0003 % makes the solution distinctly yellowish. The color of crude oils and residues is due to the combined effect of neutral resins and asphaltenes. The black color of some crude oils and residues is related to the presence of asphaltenes which are not properly peptized.

Our knowledge of the asphaltenes is very limited. Asphaltenes are not crystallized and cannot be separated into individual components or narrow fractions. Thus, the ultimate analysis is not very significant, particularly taking into consideration that the neutral resins are strongly adsorbed by asphaltenes and probably cannot be quantitatively separated from them. Not much is known of the chemical properties of asphaltenes. Asphaltenes are lyophilic with respect to aromatics, in which they form highly scattered colloidal solutions. Specifically, asphaltenes of low molecular weight are lyophobic with respect to paraffins like pentanes and petroleum crudes. There have been considerable efforts by analytic chemists to characterize the asphaltenes in terms of chemical structure and elemental analysis as well as by the carbonaceous sources. A number of investigators have attempted to postulate a model structure for asphaltenes, resins, and other heavy fractions based on physical and chemical methods. Physical methods include IR, NMR, ESR, mass spectrometry, x-ray, ultracentrifugation, electron microscopy, VPO, GPC, etc. Chemical methods involve oxidation, hydrogenation, etc.

One of representative structure for resin and asphaltene molecules belong to the Athabasca crude [Suzuki, et al., 1982] and includes carbon, hydrogen, oxygen, nitrogen, sulphur as well as polar and
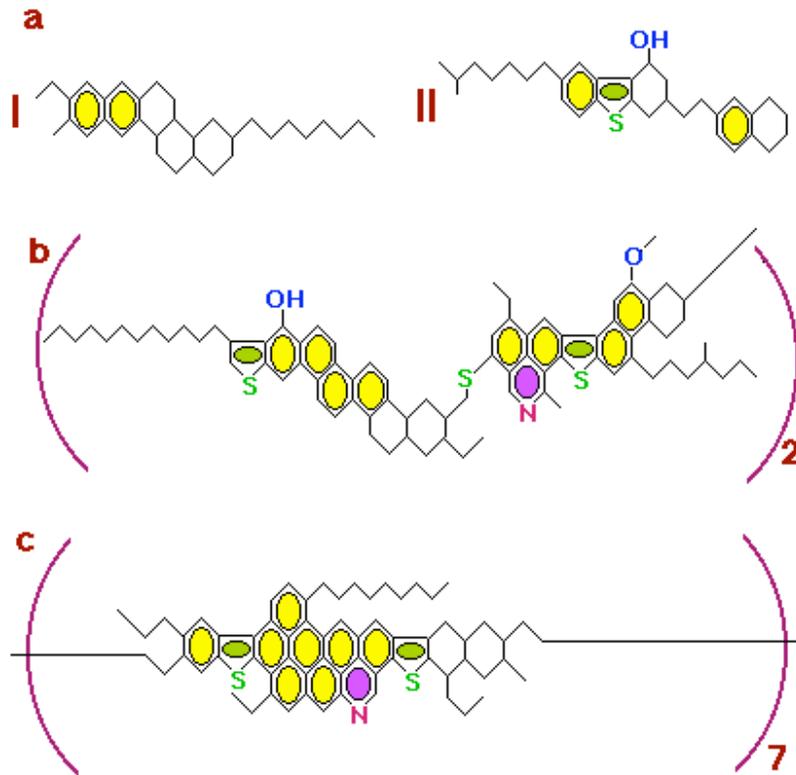
non-polar groups as it is shown by Figure 1.

Figure 1: Average molecular structural models of the fractions of Athabasca tar-sand bitumen and petroleum bitumens; (a) resin fraction, (b) asphaltene fraction of tar-sand bitumen; (c) aspahltene fraction of petroleum bitumen proposed by Suzuki et al. (1982)

Asphaltene particles can assume various forms when mixed with other molecules depending on the relative sizes and polarities of the particles present. It has been shown that asphaltene molecules span a wide range of molecular weights as it is shown in Figure 1. Their structure can vary from source to source as it is studied by Yen et. al. (1994).
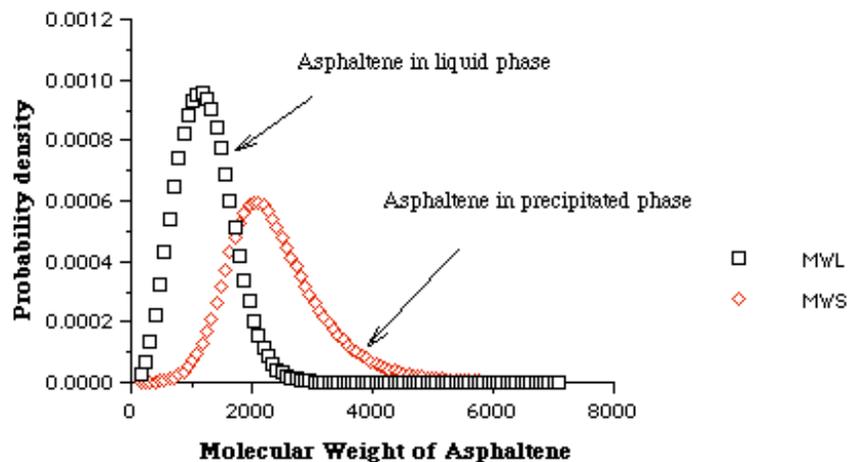
Figure 2: Molecular size distribution of asphaltene of a California crude in solution and after

precipitation by the addition of n-C5

Due to this polydispersivity, entropic effects are important in mixtures containing asphaltenes. In addition, they behave lyophobic and steric, and they posses electrostatic and associative forces.

Thus, asphaltene particles are believed to exist in oil partly dissolved and partly in colloidal and/or micellar form. Whether the asphaltene particles are dissolved in crude oil, in steric colloidal state or in micellar form, depends, to a large extent, on the presence of other particles (paraffins, aromatics, resins, etc.) in the crude oil. The existence of various states of asphaltenes in crude oil has been extensively discussed in numerous other publications [Nellensteyn,1938; Yen, 1974; Mansoori, 1997; Laux and Rahimian, Mansoori, 1996].

Small asphaltene particles can be dissolved in a petroleum fluid, whereas relatively large asphaltene particles may flocculate out of the solution and then can form steric colloids in the presence of excess amounts of resins and paraffin hydrocarbons as it is demonstrated by the following figure:
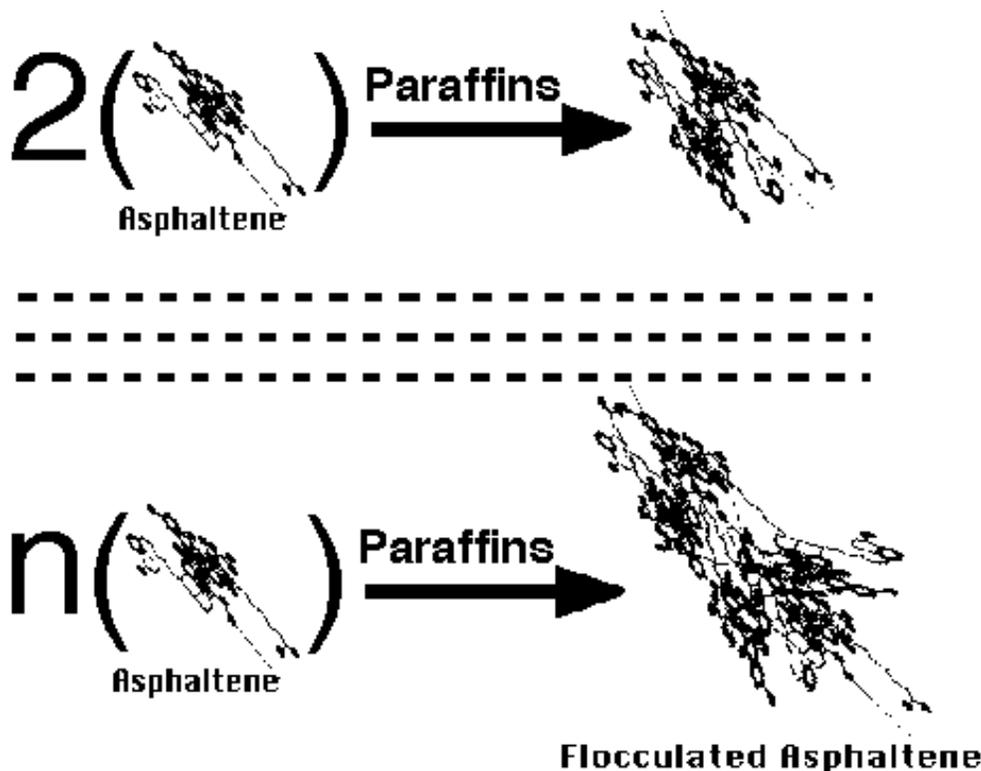

Figure 3: Various stages of asphaltene flocculation due to excess amounts of paraffins in the solution

Flocculation of asphaltene in paraffinic crude oils are known to be irreversible. This is the major cause of unrepairable arterial blockage damage to the flow of petroleum fluids. Due to their large size and their adsorption affinity to solid surfaces flocculated asphaltenes can cause irreversible deposition which may not wash away by current remediation techniques. Asphaltene and its flocculates are known to be surface active agents. This characteristic of asphaltene particles was utilized by L. Vougn in her MSc thesis research at UIC to develop an experimental technique based on the measurement of oil/water interfacial tension, Figure 5, to detect the onset of asphaltene precipitation.
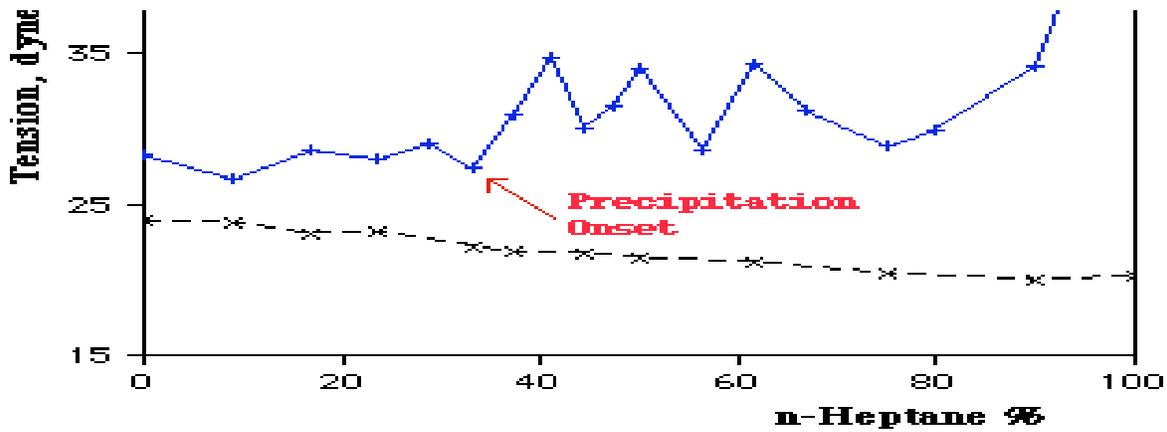
Figure 4. Variation of surface and interfacial tensions due to the addition of n-heptane to Rangley crude and detection of the onset of asphaltene precipitation.

The flocculated asphaltene will precipitate out of the solution unless there is enough resin in the solution so that they can cover the surface of asphaltene particles by adsorption and form steric-colloids as it is shown by Figure 5
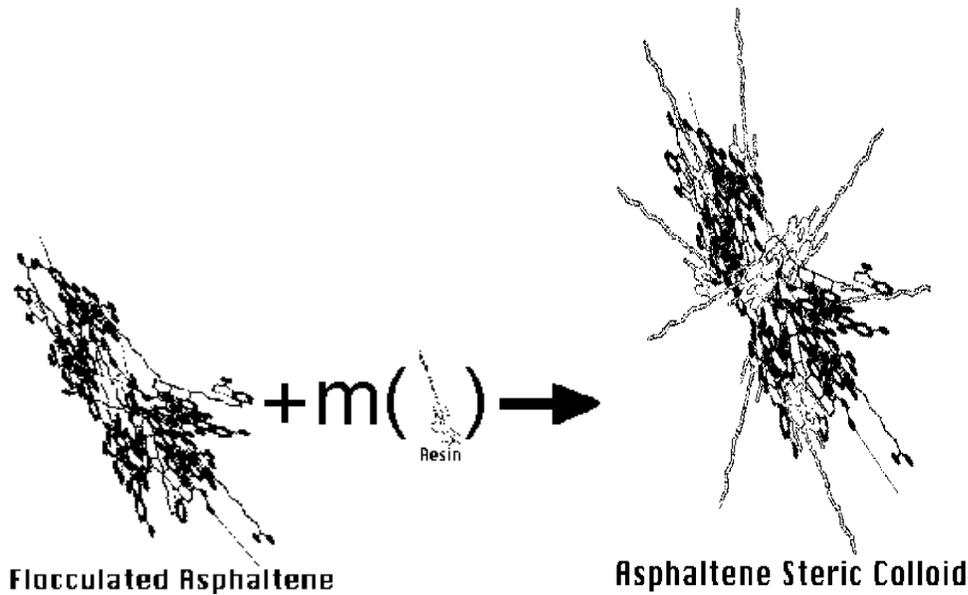

Figure 5: Steric-colloid formation of flocculated asphaltenes with resins

Experimental evidence [Lichaa, 1977; Swanson, 1942] suggests that for an oil mixture there is a critical concentration of resins below which the asphaltene flocculates may precipitate and above which they cannot precipitate regardless of how much the oil mixture is agitated, heated, or pressurized, sort of changing its composition. The onset of steric colloidal formation of asphaltenes in a crude oil can be accurately detected using visometirc techniques as demonstrated by Esocbedo and Mansoori (1995). In Figure 6 we report the detection of the onset of steric colloid formation of flocculated asphaltene
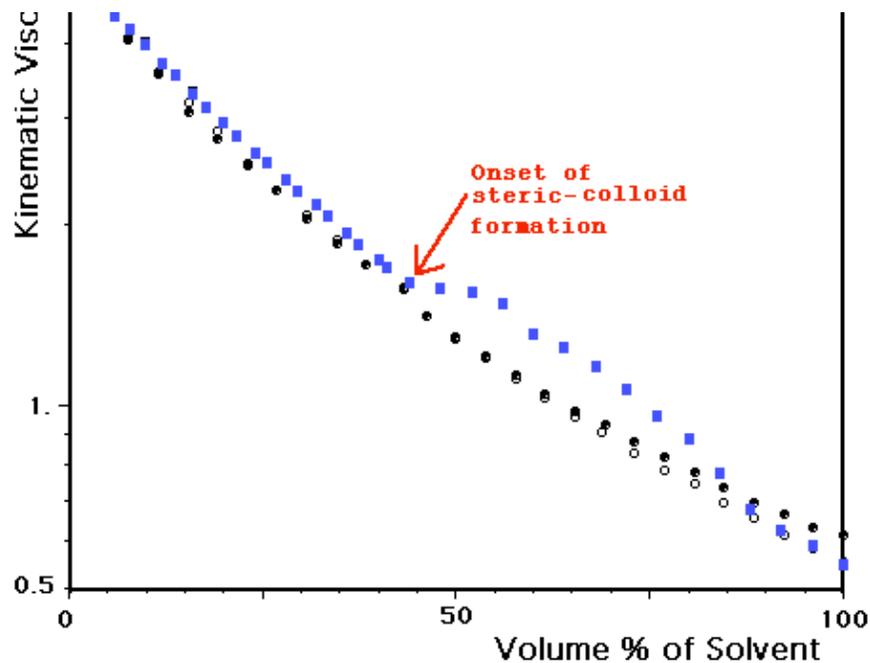
Figure 6: Variation of viscosity of Isthmus crude due to the addition of various solvents and the detection of the onset of steric-colloid formation of asphaltene.

Various investigators have established the existence of asphaltene micelles when an excess of aromatic hydrocarbons is present in a crude oil [Pfeiffer and Saal, 1940; Dickie and Yen, 1967; Galtsev et. al., 1995; Mansoori, 1996]. Several investigators have performed experimental measurements of critical micelle concentration for solutions of asphaltene in aromatics solvents [Sheu, 1996; Andersen and Birdi, 1991; Rogacheva et. al., 1980; Ravey et. al., 1988]. Furthermore, the phenomenon of self-association in asphaltene/toluene systems has been confirmed through measurements of surface tension [Rogacheva et. al., 1980; Sheu, 1996]. Sheu (1996) has shown that at low concentrations, below the critical micelle concentration (CMC), the asphaltenes in solution are in a molecular state, whereas, above the CMC, asphaltene micelle formation occurs in a manner similar to that in surfactant systems where surfactant monomers are much uniform in their structure and less polydisperse. Rogacheva et al. (1980) have also reported experimental data for the phase diagram of asphaltene micelle formation in asphaltene/toluene systems. Espinat and Ravey (1993) with the use of scattering techniques have shown that the best model to describe the morphology of asphaltene micelle in solution is a disk. However, several other experimental investigations have shown that asphaltenes could be of spherical-like, cylindrical-like, or disk-like form [Yen, 1994; Storm and Sheu, 1994; Ravey, et al, 1988]. In Figure 7 we report three possible forms of asphaltene-micelle. All these investigations is indicative of the fact that asphaltene particles may self-associate, but not flocculate, and form micelles in the presence of excess amounts of aromatic hydrocarbons as shown in Figure 7.
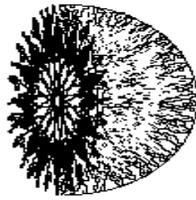
Figure 7: Formation of asphaltene micelles in the presence of excess amounts of aromatic solvents

In some laboratory tests of purified asphaltene in contact with pure toluene, a further increase in the content of asphaltene, after the start of the micelle formation, was shown to lead to the formation of larger micelles in the system, then of coacervate, and, finally, to the separation of asphaltene as a separate phase [Rogacheva, et. al., 1980]. Considering that purified asphaltene and pure toluene was used in this experiment the possibility of its in situ happening in a reservoir fluid is quite remote.

While the mechanisms of asphaltene flocculation and steric colloid formation are well understood and modelled [Mansoori, 1997], the phase behavior of asphaltene micelle formation is not well characterized and in many cases in recent years it is confused with the asphaltene steric colloids. Despite the experimental evidence on the micellization of asphaltenes, little or no theoretical and modelling research has been performed to explain and quantify this phenomenon. Nevertheless, the theories of micellar solutions of oil/surfactant/water are well known. These theory may be used to explain the micellization of asphaltenes in aromatic solvents if it is assumed that the properties of these systems are similar to those of oil/surfactant/water systems.

In the process of steric colloid formation of asphaltenes with resins they follow an irreversible process of flocculation [Leontaritis and Mansoori, 1988; Park and Mansoori, 1988, Kawanaka et. al., 1988, Branco, et al 2001]. When asphaltenes form micelles, a reversible self-association process is recognized similar to surfactant amphiphiles in which resins have no role.

Laboratory Simulation Tests and In Situ Field Remediation Methods

In petroleum production initially it is necessary to take any number of steps necessary to prevent the deposition problem. If the problem of heavy organics precipitation can be eliminated by modification of the production practices, rather than by chemical or mechanical means, the cost of production can be reduced appreciably. This can be achieved by proper laboratory tests, development of deposition prediction models, and design of the oil production and transportation systems accordingly.

Since asphaltenes are amorphic "non-crystalline" in nature and do not uniformly melt in the presence of heat the heavy organic deposits resulting from asphaltene flocculation are quite hard to deal with in petroleum production practices. Asphaltenes are also a common nucleation site for paraffin crystallization and are, therefore, often found within the same deposit. Asphaltenes and resins are responsible for adding most of the color to crude oils. "Black oils" usually contain the highest asphaltene content. As it was mentioned before asphaltene molecule is polar and in purified form it is insoluble in non-polar aliphatic solvents.

Heavy organics deposition due to asphaltene flocculation can be controlled through the better knowledge of the mechanisms that cause the deposition in the first place [Mansoori, 1996]. Processes can be altered to minimize the deposition and chemicals can be used [Borchardt, 1989] to possibly control the deposition when process alterations are not effective.

Asphaltenes may be destabilized in any area of the oil production facility from as far back as the near wellbore area to as far down the system as the refinery feed stock. Flocculation and deposition of asphaltenes can be controlled using various production and chemical treatment techniques.

Production techniques include:

(i) reduction of shear,

(ii) elimination of incompatible materials from asphaltic crude oil streams,

(iii) minimization of pressure-drops in the production facility and

(iv) minimization of mixing of lean feed stock liquids into asphaltic crude streams.

Chemical treatment techniques include: Addition of dispersants, antifoulants, and aromatic solvents which may be used to control asphaltene deposition. Dispersants work by surrounding the asphaltene molecules similar to the natural resin materials. Aromatic solvents for asphaltene deposits need to have a high aromaticity to be effective, and antifoulants have proven effective in condensate stabilization units in gas plants. In order to investigate about asphaltene solubility or precipitation a number of investigators [Borchardt, 1989; De Boer, et. al, 1995] have tested several inhibitors. Their results, indicate that, the activity of inhibitors is not only dependent on the acidic head, but also of the aliphatic or aromatic tail of the inhibitor. Particularly, for the sulfonic acids, when the chain-length of the aliphatic group increased from 13 to 24 carbon atoms, the inhibitor activity increased 5 fold. Substitutions of the hydrocarbon within C18-sulphonic-acids by aromatics like benzene, toluene, ortho or para-xylene gave approximately the same activity. However, when an asphaltenic deposit is in contact with aromatic solvents, such as AROMINA [Garcia-Hernandez, 1989], an interface with a viscosity of up to 1000 Poise was formed, and it was obstructing a greater penetration of the solvent. On the other hand, it was observed that the AROMINA was not able to keep the deposit in suspension when the stirring of the mixture was suspended, causing a settling of asphalt particles [Garcia-Hernandez, 1989]. However, Garcia-Hernandez elaborated an additive dispersant of asphaltenes named IMP-DAS-301, and he observed that an increase of 100% of production, was achieved combining the cleaning system and the stimulation with this dispersant.
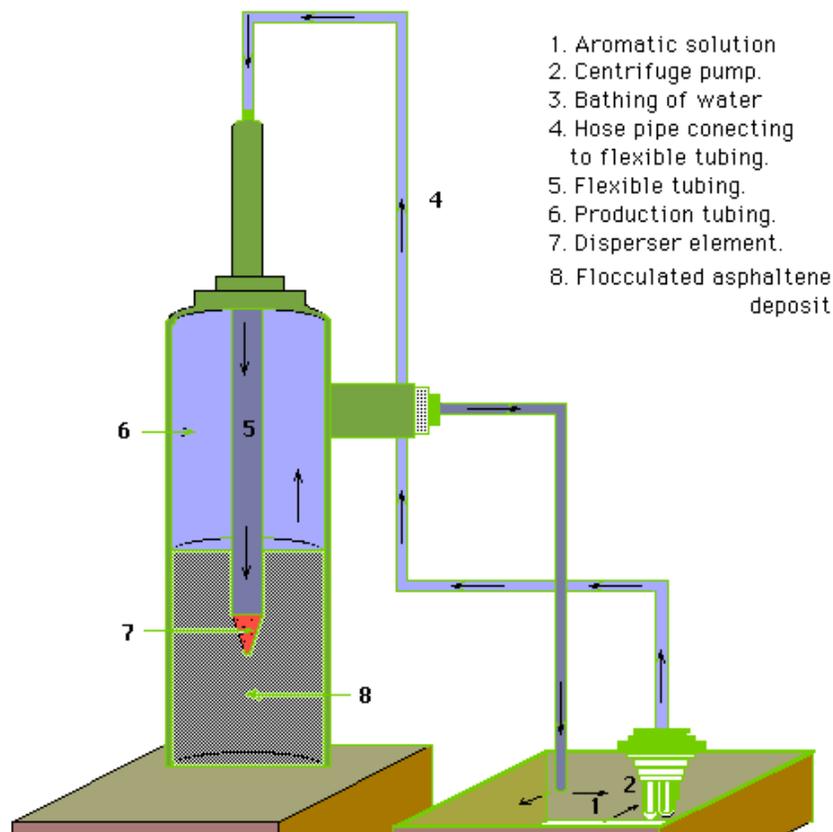

1. Aromatic solution
2. Centrifuge pump.
3. Bathing of water
4. Hose pipe conecting to flexible tubing.
5. Flexible tubing.
6. Production tubing.
7. Disperser element.
8. Flocculated asphaltene deposit

Figure 8: A Laboratory model to simulate the remediation operations of the asphaltene deposits [Garcia-Hernandez, 1989]
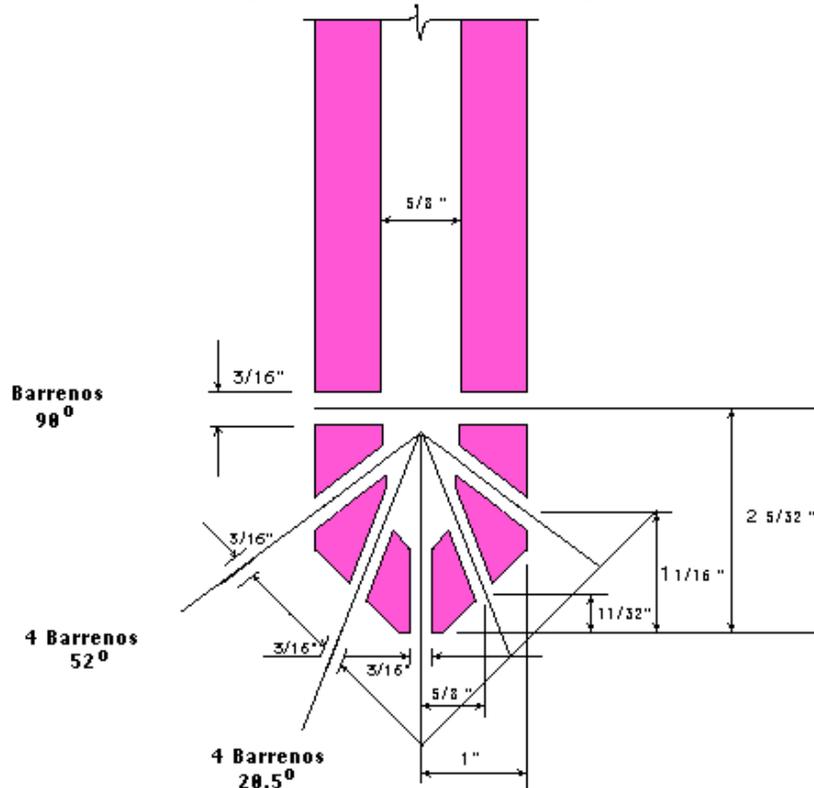

Figure 9. Diagram of the disperser top of the laboratory unit shown by Figure 8 [Garcia-Hernandez, 1989]

Organic material deposited into the production installations of petroleum crude that was causing operational problems, was detected in the study elaborated by Chavez and Lory (1991). They initially tried to dissolve such deposits by means of vapor, diesel and heavy aromatics, without satisfactory results. They estimated that the deposition was caused because of the blending of fluids from two oil well productions and their mixing with acids. They considered to elude the problem using a system of specifically designed additives to stimulate the wells. Their results were then satisfactory despite of the fact that organic deposits persisted into the separation equipment. The chemicals optimally dosificated were a mixture of an inhibitor of asphaltene precipitation (IMP-SIA-301), an asphaltene dispersant (IMP-DAS-301) and an antifoaming agent (IMP-RA-11).

Requirements and / or Recommendations

The steps that appear to have the biggest effect in moderating the severity of the deposition problem are the following:

(a) - Resolution of the heavy organic deposition problem calls for detailed analyses of heavy organic containing oils from the microscopic standpoint and development of molecular models which could describe the behavior of heavy organics in hydrocarbon mixtures. From the available laboratory, field, and refinery data it is proven that the heavy organics which exist in petroleum generally consist of very many particles having molecular weights ranging from a few hundred to several hundred thousands. As a result distribution-function curves are used to report their molecular weight distribution. Most of the heavy organics present in the oil deposit due to the first or second order phase transitions from liquid to

solid state. However, this is not generally the case for asphaltene particles. The high affinity of asphaltene particles to association with one another, their tendency to adsorb resins, and their extensively wide range of size distribution suggest that asphaltenes are partly dissolved and partly in colloidal state (in suspension) in oil peptized (or stabilized) primarily by resin molecules that are adsorbed on asphaltene surface. As a result, a realistic molecular model for the interaction of asphaltene and oil should take into account both the solubility in oil of one segment and suspension characteristic (due to resins) of another segment of the molecular weight distribution curve of asphaltene [Kawanaka, et al, 1989; Escobedo and Mansoori, 1995].

Initially laboratory work may be necessary to quantify and characterize the various families of heavy organics present in a crude and in general shed light on the reasons for such depositions. Laboratory work joined with statistical mechanical modeling may result in the construction of heavy organics deposition envelop (HODE) such as the graph shown in Figures 10 and 11 which would indicate the ranges of temperature and pressure where the crude deposits out heavy organics compounds at various temperatures, pressures, compositions/blending, and electrokinetic effects and flow conditions.

Figure 10: Static (PX) heavy organics deposition envelope (HODE) of a crude oil mixed with a miscible injectant (MI) at 60 oF but at various proportions and pressures. In this figure L stands for liquid phase, L-V is the liquid-vapor two-phase region, L-S is the liquid-solid two-phase region, and L-V-S is the liquid-vapor-solid three-phase region.

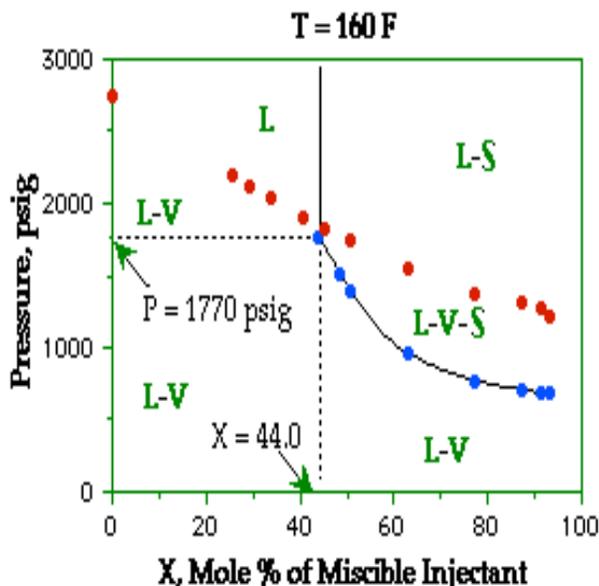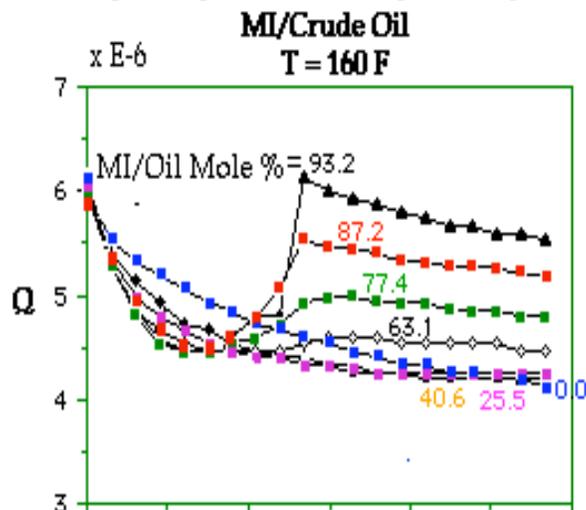0   1000   2000   3000

Pressure, psig

Figure 11: Dynamic (QX) heavy organics deposition envelope (HODE) of a crude oil mixed with a miscible injectant (MI) at 60 oF but at various proportions and pressures. In this figure Q = Uavg1.75 d0.75/k where Uavg stands for crude average velocity in a cylindrical conduit, d is the conduit diameter and k is the crude electrical conductivity. The area above each curve represents the deposition region and under the curve is the flow region with no deposition.

(b) - It is reported (Von Albrecht et al., 1977) that the use of standard well completion techniques when heavy organics deposition is likely has often resulted in costly workovers for deposit removal in those wells. To combat the heavy organics deposit formation the completing wells with a dual completion is necessary. This is with the purpose of: i) using the second tubing string for solvent or dispersant injection or circulation, ii) access for lowering production testing devices. Sometimes the second tubing string is used for production to meet production quotas when the main string is shut-in for maintenance or heavy organics cleaning.

(c) - It is suggested that all well stimulation, injection and enhanced oil recovery (EOR) fluids should be tested for static and dynamic compatibility with the reservoir fluids prior to operations, especially where asphaltenic crudes are present [Tuttle, 1983]. Such experimental compatibility tests may be costly if one needs to study all the possible regions of composition and pressure. However, static and dynamic compatibility modeling using the advanced statistical and fluid dynamic techniques can be quite efficient and economical for shedding light on the problem by constructing heavy organics deposition envelopes (HODE) as shown by Figures 10 and 11.

(d) - It is generally understood that there is a composition gradient of heavy organics in petroleum reservoirs with deeper zones having higher fractions of the heavy organics. The decision to produce first the top zone of the reservoir, which is generally less prone to heavy organics deposition, is always preferred. Actually most of the producing wells must be completed dual commingled. Production surveys would show from which zone most of the oil was being produced.

(e) - In certain circumstances mechanical removal techniques may be effective means of combating the heavy organics problems [Tuttle, 1983]. For example at the Hassi Messaoud field, Algeria, necessitated frequent tubing scrapings and washings to maintain production [Haskett and Tartera, 1965]. Cutting the deposits from the tubing by wireline methods was too time-consuming and some times impractical, so a program of washing the tubing with a solvent was established. An economical study may indicate whether mechanical removal methods of cleaning is preferred over cleaning by using solvents.

(f) - Solvent treatment of the oil is considered to be beneficial in some cases because it dilutes the crude oil and reduces the tendency of the heavy organics to precipitate. Solvent treatments may not be very successful largely because the solvents which can be used are limited to aromatic solvents. Xylene is generally the most common solvent selected to be used in well stimulations, workovers, and heavy organics inhibition and cleaning. In some cases xylene injection through the non-producing string actually may help to minimize the heavy organic deposition problem. In oil fields with frequent need for aromatic wash it may be necessary to design an aromatic solvent with stronger wash power and better economy for the particular deposit in mind [Garcia-Hernandez, 1989]. Laboratory tests may be necessary to blend the most appropriate aromatic solvent and / or dispersant for a given oil field from the points of view of effectiveness, economy, and environmental freindlyness. Then special formulas may be blended to achieve the goal of preventing or cleaning the heavy organics deposits which can be used by the field engineers [Garcia-Hernandez, 1989].

(g) - Circulation with hot oil may be used to avoid or reduce the heavy organics deposition problem. A combination of solvent treatment and reverse and normal circulation with hot oil have been tried in the past in some oil wells with mixed results [Tuttle, 1983].

(h) - Injection of dispersants or antifoulants may be effective in certain crude oils where the ratio of resin to asphaltene is not high enough to prevent asphaltene flocculation and as a result heavy organics deposition. One thing which appears to have universal acceptance is that resins in the crude act as the peptizing agents of the asphaltene particles. It is generally a good practice to analyse a crude oil for its asphaltene and resin content and ratio. In the following table such data for a number of crude oils are reported versus their API gravity.

Table 1: Resin and Asphaltene Content of various Crude Oils

Crude	^{o} API	Resin wt%	Asphaltene wt%	Asph./Resin
Canada, Atabasca	8.3	14.0	15.0	1.07
Venezuela, Boscan	10.2	29.4	17.2	0.58
Canada, Cold Lake	10.2	25.0	13.0	0.52
Mexico, Panucon	11.7	26.0	12.5	0.48
USA, MS, Baxterville	16.0	8.9	17.2	1.93
Russia, Kaluga	16.7	20.0	0.5	0.025
USA, TX, Hould	19.7	12.0	0.5	0.04
Brazil, Campos, Atabasca	19.7	21.55	2.8	0.13
USA, CA, Huntington Beach	26.2	19.0	4.0	0.21
Canada, Alberta	29.0	8.5	5.3	0.62
USA, LA, Brookhaven	30.6	4.6	1.65	0.36
Russia, Balachany	31.7	6.0	0.5	0.08
Russia, Bibi-Eibat	32.1	9.0	0.3	0.03
Russia, Dossor	32.6	2.5	0.0	0.00

Russia, Surachany	35.0	4.0	0.0	0.00
USA, TX, Mexia	36.0	5.0	1.3	0.26
Iraq, Kirkuk	36.1	15.5	1.3	0.08
Mexico, Tecoaminocan	36.7	8.8	1.5	0.17
Mexico, Isthmus	37.8	8.1	1.3	0.16
USA, OK, Ok. City	38.0	5.0	0.1	0.02
USA, OK, Tonkawa	40.8	2.5	0.2	0.08
France, Lagrave	43.	7.5	4.0	0.53
USA, LA, Rodessa	43.8	3.5	0.0	0.00
USA, PA	44.3	1.5	0.0	0.00
Algeria, Hassi Messaoud	45	3.3	0.15	0.05
USA, OK, Davenport	46.3	1.3	0.	0 0.00

[Sachanen, 1945; Lichaa, 1977; Garcia, 1989; Altamiran, et al, 1986]

Crude oils with higher asphaltene to resin ratios are more prone to heavy organics deposition. However, Boscan crude, which is at the top of this list, has had no such problem, while Tecoaminocan crude, which is close to the bottom of the list, is a crude with frequent deposition problems. Considering such severe exceptions to the rule one should not consider this ratio to be the only factor in evaluating the deposition potential of a crude oil. Other factors including the nature of hydrocarbons in the crude, the polydispersivities and polarities of asphaltene and resin, the presence of such compounds as paraffin /wax, organometallics and diamondoids, the nature of conduit, hydrodynamics and electrokinetics have also roles in the deposition. In order to quantify all these factors one has to develop a predictive model in which all these effects are incorporated [Mansoori, 1996].

Figure 12: Deposition and plugging of petroleum flow conduits due to streaming potential generated and sticking of asphaltene particles to the walls.

Conclusions

Insofar as finding a rigorous universal solution to the heavy organics deposition problem is concerned there is still a long way to go. Asphaltene flocculation can be controlled through better knowledge of the mechanisms that cause its flocculation in the first place. Processes can be changed to minimize the asphaltene flocculation and chemical applications can be used effectively to control depositions when process changes are not cost effective.

Since heavy organics deposition takes place during primary, secondary, and tertiary oil recovery, injection of peptizing agents (i.e.: resins) in proper amounts and places may prevent or at least control the heavy organics deposition problem. Furthermore, experiments could be performed (i.e.: of the coreflood type) where peptizing agents are injected to study their effect on inhibition of heavy organics deposition or permeability reductions.

One interesting question posed by previous researchers [Katz and Beu, 1945; Leontaritis and Mansoori, 1988] is why there was asphaltic bitumen deposited at the bottom of the well considering that no phase change or any substantial temperature or pressure changes had taken place. The conclusion was that the question could only be answered after considerable light was thrown upon the nature of the asphaltic bitumen prior to its separation from the crude oil in the well. There were a few efforts to try to determine the size and nature of asphaltene particles while they still are in the original oil [Katz and Beu, 1945; Witherspoon et al., 1957].

Establishing the state of the asphaltene particles in the original crude oil seems to be a basic building block in the scientific quest to find a solution to many irreversible heavy organics deposition problems. Experimental and theoretical modeling work towards this end has been performed [Yen, 1979, Mansoori, 1996], but more is needed. More experiments need to be done to duplicate Witherspoon et al.s' ultracentrifuge work for different oils and possibly utilize other contemporary experimental techniques to establish the state of asphaltenes in crude oils. Meanwhile, it appears, that any modeling effort that describes the phase behavior of asphaltenes in oil should take into account the lack of positive information on the structure of asphaltenes in the original oil and their molecular characteristics. This has been the philosophy followed in our modeling activity [Leontaritis and Mansoori, 1987; Kawanaka et al., 1988; Mansoori, 1997, Escobedo and Mansoori, 1995; Mansoori, 1996] proposed for predicting the deposition behavior of heavy organics in petroleum fluids.

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