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Petroleum Asphaltenes

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1. Introduction

A crude oil at atmospheric pressure and ambient temperature has three main constituents: (i) oils (that is, saturates and aromatics), (ii) resins, and (iii) asphaltenes. Asphaltenes and resins are believed to be soluble, chemically altered fragments of kerogen, which migrated from the oil source rock during oil catagenesis. However, unlike resins, asphaltenes contain highly polar species that tend to associate. As a result, the interactions of asphaltenes with their environment are very complex. For example, asphaltene precipitation or deposition can occur in wellbores, pipelines, and surface facilities and is undesirable because it reduces well productivity and limits fluid flow (see Figure 1).



Fig. 1. Asphaltenes clogging a pipe. Courtesy of A. Pomerantz, Schlumberger.

The main factors that promote precipitation are pressure, temperature and composition variations due to gas injection, phase separation, mixing of fluid streams. Paradoxically, asphaltene precipitation is often observed in light crude oils that contain very low asphaltene content. This is because light oils contain large amounts of light alkanes in which asphaltenes have limited solubility. Heavy oils, which are usually rich in asphaltenes, contain large amounts of intermediate components that are good asphaltene solvents. However the refining of heavy oils in downstream operations is very challenging because it can lead to coking, fouling, and catalyst deactivation during processing or upgrading, as high temperatures and vacuum conditions are required. In subsurface formations, the adsorption of asphaltenes on mineral rocks can lead to wettability alteration and formation damage.

Asphaltenes impact virtually all aspects of utilization of crude oil and despite this importance; asphaltenes have not been well understood. Fortunately this situation has recently changed rather significantly. The ability to connect asphaltene science performed at different length scales into a single cohesive picture requires establishing structure–function relationships and is the heart of Petroleomics (Mullins et al., 2007). For example, asphaltene molecular weights are now known to be relatively small, ~800 g/mol (Boduszynski, 1981; Groenzin & Mullins, 1999). Compositional variations of the fluid containing asphaltenes directly affect their aggregation state. Under unfavorable conditions, asphaltene molecules tend to associate into small nanoaggregates that can grow into larger clusters and eventually flocculate and precipitate. The connection between molecular architecture and aggregation was not clarified until recently (Akbarzadeh et al., 2007; Mullins, 2010). The role of resins on asphaltene stability has long been controversial and a more unified view is gradually emerging (Goual et al., 2011). This chapter is based upon the author's experience in asphaltene research over the past decade. It focuses on asphaltene separation, characterization, structure, and role of resins.

2. Definition

The term "Asphaltene" originated in 1837 when Boussingault defined them as the distillation residue of bitumen: insoluble in alcohol and soluble in turpentine (Boussingault, 1937). Today, asphaltenes are defined as the heaviest components of petroleum fluids that are insoluble in light n-alkanes such as n-pentane (nC_5) or n-heptane (nC_7) but soluble in aromatics such as toluene. The solubility class definition of asphaltenes generates a broad distribution of molecular structures. These polydisperse molecules consist mostly of polynuclear aromatics (PNA) with different proportions of aliphatic and alicyclic moieties and small amounts of heteroatoms (such as oxygen, nitrogen, sulfur) and heavy metals (such as vanadium and nickel, which occur in porphyrin structures). Heavy resins and waxes can co-precipitate with asphaltenes and their amount is variable depending on the method of separation. Figure 2 shows the separated asphaltenes and resins from a crude oil according to ASTM-D2007 (Goual & Firoozabadi, 2002). Asphaltenes and resins differ in color and texture. Asphaltenes are black, shiny, and friable solids; while resins are dark brown, shiny, and gummy.

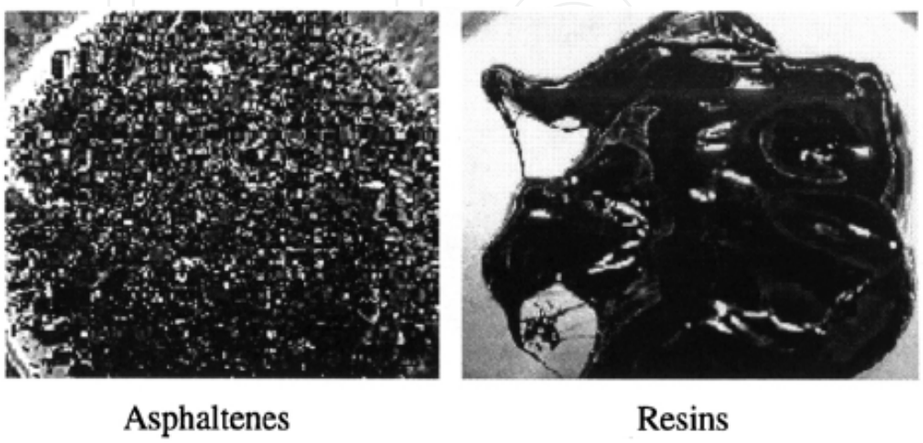


Fig. 2. Asphaltenes and resins separated from crude oils (Goual and Firoozabadi, 2002).

3. Separation

The standard procedures for asphaltene separation consist mainly of precipitation of asphaltenes by excess n-alkanes (typically 40 volumes of n-alkane to 1 volume of oil). In the Institute of Petroleum Standard IP 143 (IP 143/84, 1988), asphaltenes are separated from waxy crude oils with nC_7 then the precipitated phase is washed for 1 h with a reflux of hot heptane to remove waxes. In the ASTM D-3279 method (ASTM D3279-07, 2007), asphaltenes from petroleum residues are precipitated with nC_7 and filtered after 30 min of heating and stirring with a reflux system. In the ASTM D-893 method (ASTM D893-05a, 2010), asphaltenes are precipitated from lubricating oils by centrifugation in nC_7. In the Syncrude analytical method (Bulmer & Starr, 1979), heavy crude oils are mixed with benzene prior to asphaltene precipitation with nC_5; they are then filtered and washed after 2 h of settling in the dark. For each separation method, conditions such as n-alkane, contact time, temperature, filter size, and washing procedure need to be specified. Considering crude oils as a continuum of several thousands of molecules, it is very difficult to define a cut-off between asphaltenes, resins, and oils. The variables introduced in each method may generate different fractions of asphaltenes when using different methods. For example, if nC_7 is used as precipitant for asphaltenes instead of nC_5, then the C_5-C_7 fraction of C_5 asphaltenes will now be part of C_7 resins. A representation of the asphaltenes fractions using molecular weight and polarity/aromaticity is provided in Figure 3 (Long, 1981). In this Figure, the slope of the lines varies with the composition of asphaltene fractions. The concept emphasizes the lower molecular weight and increased polarity of the various asphaltene constituents (Speight, 2007).

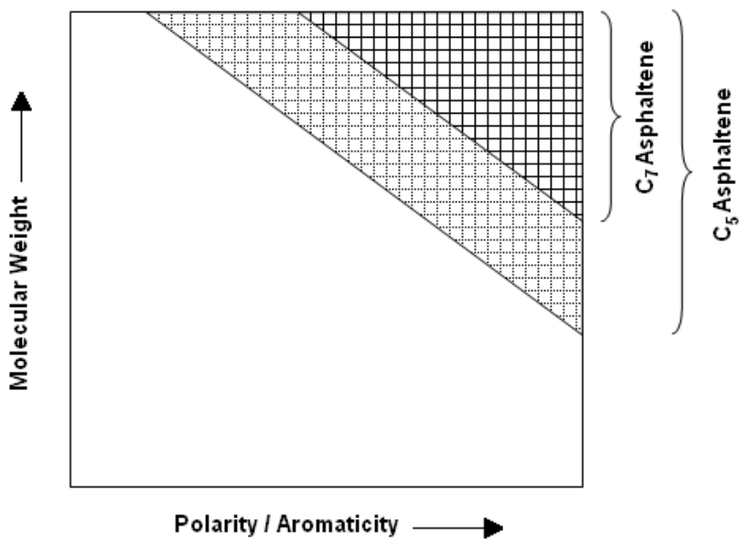
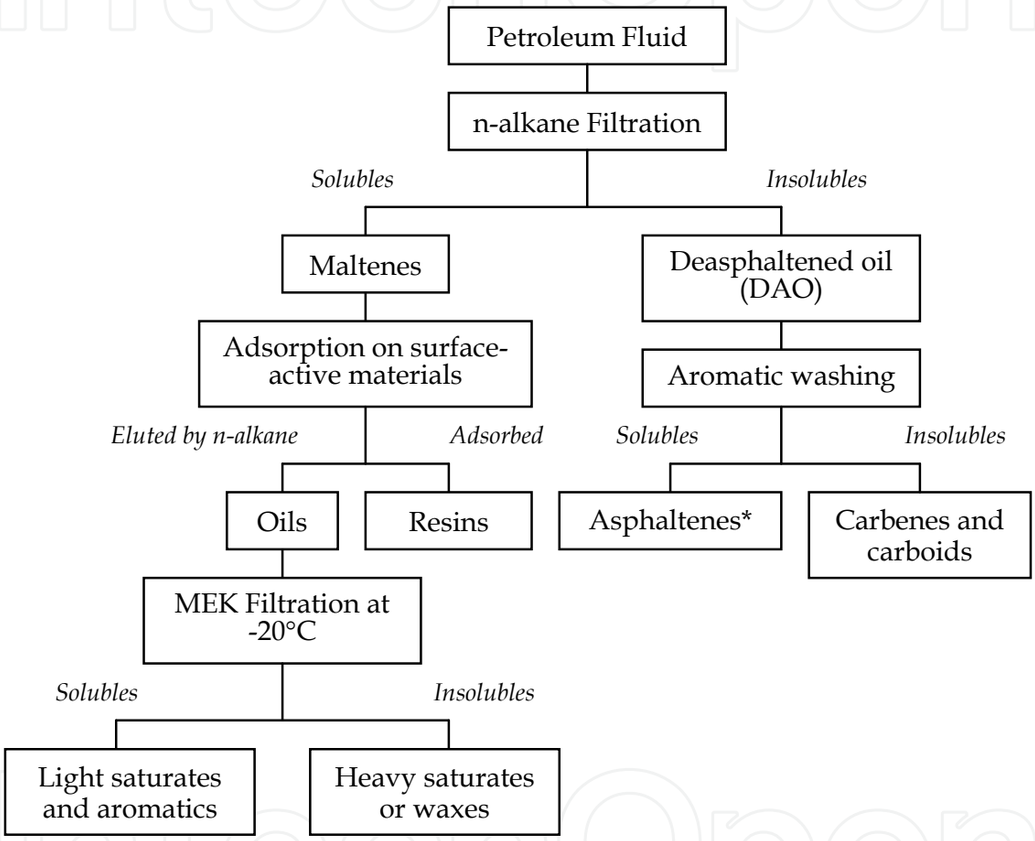


Fig. 3. Representation of n-alkane asphaltenes using molecular weight and polarity/ aromaticity.

Figure 4 depicts the main fractions that can be extracted from a solid-free petroleum fluid. The term "solid" here refers to mineral fines, clays, etc. Asphaltenes extracted from bitumen are very likely to contain solids. In this case, solids can be removed by centrifugation of a 5 wt% solution in toluene at 30,000 g for 3 h (Goual et al., 2006) or by filtration using 0.02 μm

filter size. Resins are usually separated from maltenes by preparative liquid chromatography via adsorption on surface-active materials such as fuller's earths, attapulgus clay, alumina, or silica gel (ASTM-D2007; ASTM-D4124; Syncrude analytical method) then desorption with aromatic/polar solvents such as toluene/acetone mixtures. Other resin separation methods by precipitation in propane or ketones or alcohols also exist in the literature but remove only a fraction of resins, usually the heaviest and more polar. Like asphaltenes, resins are defined according to the solvents used for their separation (Goual & Firoozabadi, 2002). Discrepancies in the amount and chemical composition can be found if adsorbents are different or elution time is varied (Wallace et al., 1987).



* For waxy oils, heavy waxes are removed from asphaltenes by hot-alkane washing (IP 143/84, 1988)

Fig. 4. General fractionation scheme for petroleum fluids.

Analytical methods such as thin layer chromatography with flame ionization detection (TLC-FID) (Karlsen & Larter, 1991) are widely used in the oil industry. These solubility based separation methods allow for the investigation of crude oil components based on polarity. However they can yield very different amounts of Saturates, Aromatics, Resins and Asphaltenes (SARA) depending on the nature of solvents used in the separation. At a panel discussion on standardization of petroleum fractions held at the 2009 Petrophase conference, a need to unify and improve the separation methods for asphaltenes and resins was expressed (Merino-Garcia et al., 2010). The diversity of operating definitions employed and measurement variability affect the ability of researchers to determine whether compound classes are present and to draw cross-comparisons among measurements from different

laboratories. Moreover, the current separation methods create an artificial distinction between resins and asphaltenes yet provide no information on more meaningful distinctions, such as between associating and non-associating species or surface-active versus non-surface-active species. When compared to pressure drop asphaltenes from live oils, heptane-separated asphaltenes from dead oils contained a higher number of rings plus double bonds but exhibited a lower abundance of species containing sulfur (Klein et al., 2006). Thus, the solubility criterion for asphaltenes defines a significantly different chemical composition than the (more field-relevant) pressure-drop criterion.

A new generation of separation methods that permits the extraction of asphaltene nanoaggregates and clusters without solvent use has recently been proposed, namely, ultra- or nanofiltration (Zhao & Shaw, 2007, Marques et al., 2008). Nanofiltration experiments with 5-200 nm mesh show that the composition of filtered asphaltenes closely approximates C_5 asphaltenes over a broad temperature range (Zhao & Shaw, 2007). When used to fractionate small asphaltenic aggregates from larger ones, ultrafiltration tests revealed that small aggregates present lower aromaticity and higher aliphatic composition than larger ones. Their alkyl chains also appear to be shorter and more alkylated. Based on elemental analysis, that smaller aggregates contain a lower metal concentration and are preferentially enriched in vanadium than nickel when compared with larger ones (Marques et al., 2008). The advantage of nanofiltration is that asphaltenes are separated based on their size rather than their solubility, thus nanofiltered-fractions are significantly less polydispersed than alkane-asphaltenes. On the other hand, nanofiltration cannot substitute for solvent standards for routine measurements because of the time as well as the cost involved.

The presence of wax in petroleum fluids renders the separation of asphaltenes even more complex. Figure 4 shows that the heaviest components of wax tend to co-precipitate with asphaltenes and the alkane-soluble wax components can be extracted from oils through precipitation in methyl ethyl ketone (MEK) at -20 °C, then filtration (UOP 46-64). A major drawback of wax and asphaltene separation methods is the fact that they are often time-consuming and require large volumes of solvents. To overcome this limitation, an on-column separation of wax and asphaltenes in petroleum fluids has been proposed (Schabron & Rovani, 2008; Goual et al., 2008) and allows for the detection and separation of these fractions in minutes. The principle of the method is to first precipitate waxes and asphaltenes together on a ground polytetrafluoroethylene (PTFE)-packed column using MEK at -20°C and then re-dissolve the precipitate with solvents of increasing polarity at different temperatures. The development and demonstration of the on-column asphaltene precipitation and re-dissolution technique have been described in detail elsewhere (Schabron & Rovani, 2008). Figure 5 provides an example of separation profile for Dagang waxy crude oil from China using waxphaltene determinator (WAD). The material soluble in MEK elutes as a first peak and consists mostly of aliphatic light oils, including n-alkanes with carbon atoms less than C_{20} and highly branched alkanes. Other functional groups, such as naphthenic or aromatic rings, may be present. The precipitated material is re-dissolved in four steps using solvents of increasing polarity and different temperatures: heptane at -20 °C (for low polarity oils and moderately branched alkanes, possibly containing naphthenic components), heptane at 60 °C (for n-alkanes with carbon atoms higher than C_{20} and slightly branched alkanes), toluene at ~25 °C (for asphaltenes), and then methylene chloride at ~25 °C (for higher polarity asphaltene components).

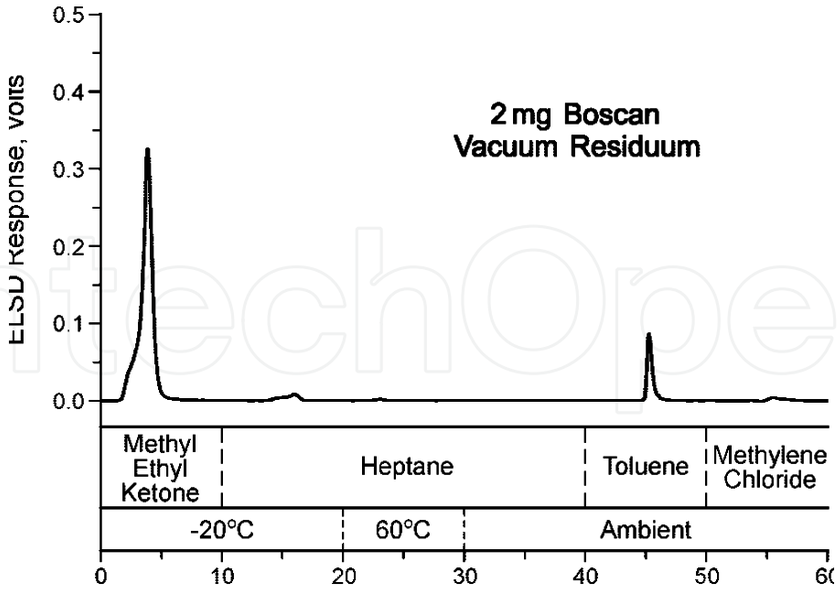


Fig. 5. Separation profile for Dagang crude oil using waxphaltene determinator (Goual et al., 2008).

Note that co-solvency effects have been observed with the WAD method. Co-solvency occurs when individual chemical components that are not soluble in a particular solvent can dissolve readily when they are part of a mixture with other species that impart co- solvency. For example, a significant portion of C_7 asphaltenes from petroleum residua is not soluble in cyclohexane although the whole residua that contain these components dissolve completely in cyclohexane (Schabron et al., 2001). Similar solubility behavior was observed with petroleum resins in *n*-alkanes (Goual and Firoozabadi, 2004). Co-solvency is also observed with wax components. The melting and freezing of *n*-alkane components can also occur in a manner that affects solubility (Goual et al., 2008). The combination of the co-solvency and freezing/melting effects in petroleum systems could be complex. These are also evident when individual chemicals or fractions are isolated from petroleum (Goual & Firoozabadi, 2004; Schabron & Rovani, 2008).

4. Characterization

Asphaltenes have a density between 1.1 and 1.20 g/mL (Speight, 2007), an atomic H/C ratio of 1.0-1.2 (Spieker et al., 2003), and a solubility parameter between 19 and 24 $MPa^{0.5}$ at ambient conditions (Hirschberg et al., 1984; Wiehe, 1996). They strongly affect the rheological behavior of petroleum fluids. Two concentrations regimes have been identified in crude oils: a diluted regime where viscosity increases linearly with asphaltene content, and a concentrated regime where viscosity depends more than exponentially on asphaltene content. Natural heavy oils correspond to the concentrated regime and the high viscosities may be due to the entanglement of solvated asphaltene particles (Argillier et al., 2001).

Studies on asphaltene molecular weight are more controversial. The tendency of asphaltenes to aggregates in toluene at concentrations as low as 50 mg/liter (Goncalves et al., 2004) has led to aggregate weights being misinterpreted as molecular weights with colligative

methods such as vapor pressure osmometry (VPO) or gas exclusion chromatography (GPC). As a result, the molecular architecture of asphaltenes has been the subject of debate for several years. Results from advanced analytical techniques now agree that asphaltene molecular weight distributions are in the 400-1,500 Dalton (Da) range, with a mean mass between 700-800 Da. Examples of these methods are field-ionization mass spectrometry (FIMS) (Boduszynski, 1981), fluorescence correlation spectroscopy (FCS) (Schneider et al., 2007), time resolved florescence depolarization (TRFD) (Groenzin & Mullins, 1999, 2000), electrospray ionization, Fourier transform ion cyclotron resonance mass spectrometry (ESI FTICR MS) (Rodgers & Marshall, 2007; Hsu et al., 2011), atmospheric pressure photoionization mass spectrometry (APPI MS) (Merdrignac et al., 2004), field-desorption/field- ionization mass spectrometry (FDFI MS) (Qian et al., 2007), laser desorption ionization (LDI) (Hortal et al., 2006).

The polar character of asphaltenes impacts their adsorption at interfaces (Abudu & Goual, 2009; Saraji et al., 2010). Figure 6 depicts the adsorption amounts from 5 wt % crude oil in toluene and heptane on different substrates (Abudu & Goual, 2009). The substrates consist of hydrophilic surfaces (gold, silica, and stainless steel) and hydrophobic surfaces (polystyrene). The amount adsorbed from toluene on hydrophilic surfaces varies from 350 to 450 ng/cm^2, with the highest being on silica.

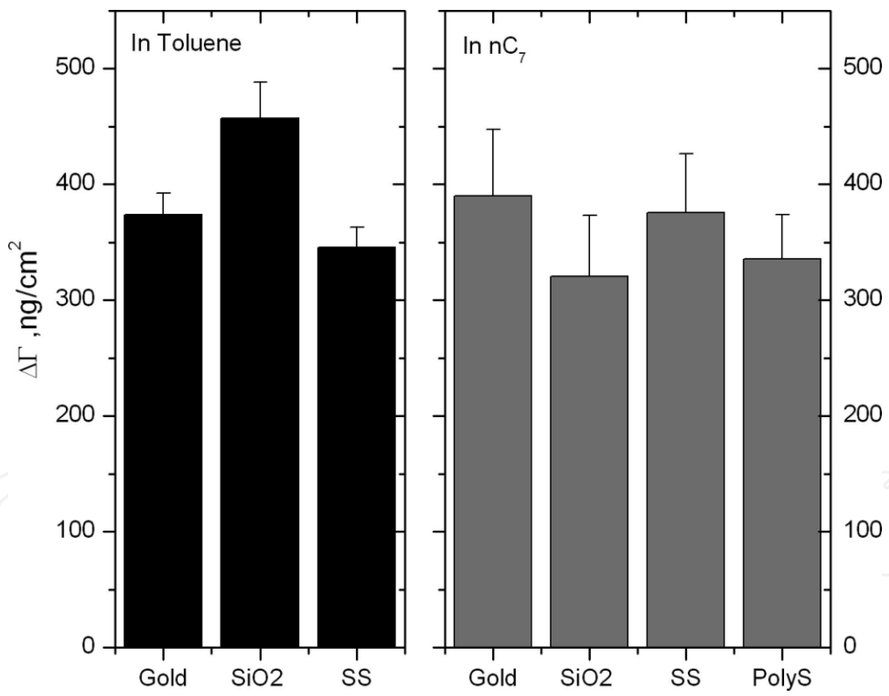


Fig. 6. Adsorption amounts from 5 wt% crude oil in toluene and heptane on different surfaces (gold, silica, alumina, polystyrene, and stainless steel).

Figure 6 also shows that asphaltenes are almost amorphous in heptane, evidenced by almost the same adsorption amounts on hydrophilic and hydrophobic surfaces (~350 ng/cm^2). XPS survey revealed the presence of relatively large percentages of surface heteroatoms (mainly oxygen and sulfur) in adsorbed films from toluene which suggests that asphaltenes are

much more hydrophilic in toluene than in heptane. It is likely that asphaltene polar functions become caged inside clusters because of flocculation in heptane (Sheu & Acevedo, 2006).

What role polarity and/or aromaticity play in aggregation and molecular structure is still largely unknown. On the other hand, non-polar dispersive forces are believed to control the flocculation and precipitation of asphaltene clusters (Buckley et al., 1998). In a recent study of the interactions between asphaltene surfaces in organic solvents using an atomic force microscope (AFM), Wang and co-workers found that the ratio of toluene to heptane in the solvent could significantly change the nature and the magnitude of the interaction forces between asphaltene surfaces. In pure toluene, steric repulsion forces were measured whereas in pure heptane, van der Waals attraction forces were measured (Wang et al., 2010).

The polar character of asphaltenes originates from the presence of permanent dipoles (Goual & Firoozabadi, 2002) and electrical charge carriers (Goual et al., 2006). Measured dipole moments and electrical direct current (DC) conductivities of asphaltene monomers are in the range of 4-7 D (Goual & Firoozabadi, 2002) and 10^{-8} S/m (Goual, 2009), respectively. Electrodeposition studies of solid-free bitumen in organic solvents revealed that asphaltene charge carriers are mainly positively charged in organics solvents such as toluene (Goual et al., 2006). Figure 7 illustrates the contribution of these charge carriers to the DC conductivity.

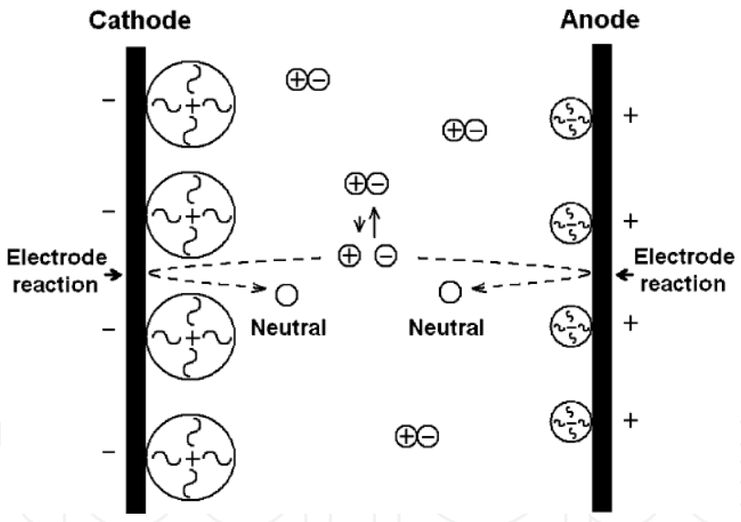


Fig. 7. Schematic of the contribution of charge carriers to the DC conductivity in crude oils

Lewis acids and bases form ion pairs and permanent dipoles. The dissociation of these species produces small-size charge carriers that are involved in charge-transfer reactions at the electrodes and are responsible for the DC conductivity. These acids and bases are also involved in asphaltene association processes leading to high aggregate mass. In these aggregates, the numbers of Lewis acids and bases are not balanced exactly. Electron exchange between the electrodes and these associated acids and bases is hindered (because of steric constrains) so they can only be electrocollected and not electrodeposited at the electrodes; they are quickly released from the electrode surface when the potential is turned off. These species do not contribute to the DC conductivity. The DC conductivity of

asphaltenes increases with their concentration in toluene because of the increased ion mobility or reduced activation energy for charge transfer, as illustrated in Figure 8. Note that less than 10^{-4} mole fraction of asphaltene is charged in toluene. These charge carriers can act as tracers to monitor asphaltene dynamics.

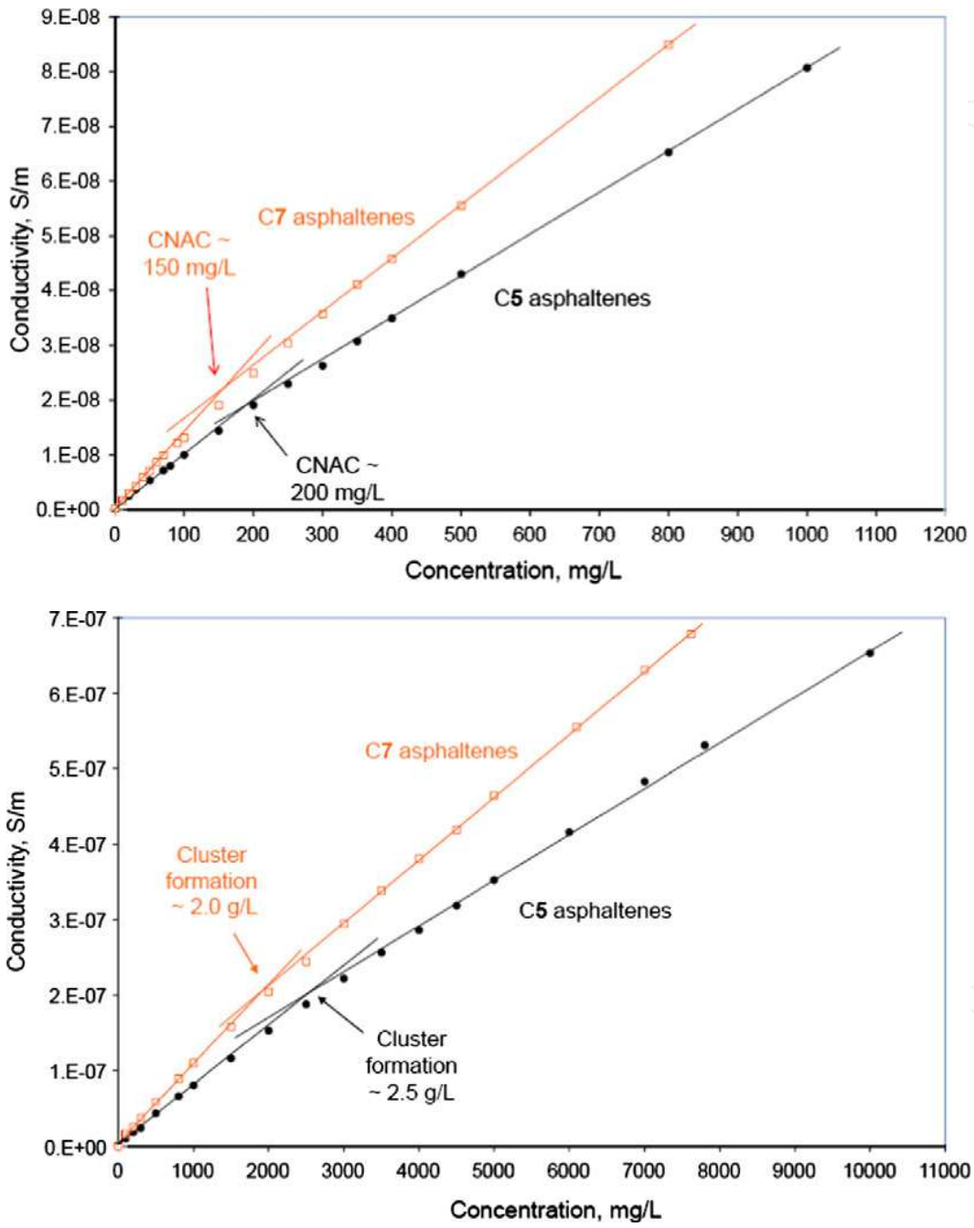


Fig. 8. Critical nanoaggregate concentration (CNAC) and critical cluster concentration (CCC) of C_5 and C_7 asphaltenes (Goual et al., 2011).

The critical nanoaggregate concentration (CNAC), above which nanoaggregates stop growing, can be seen in Figure 8 as a clear breakpoint in the variation of conductivity with concentration. The breakpoint occurs at around 100 mg/L for C_5 asphaltenes and 200 mg/L for C_7 asphaltenes, in agreement with previous work (Andreatta et al., 2005; Freed et al.,

2009; Zeng et al., 2009; Mostowfi et al., 2009). Similarly, the critical cluster concentration (CCC) can be seen at around 2,000 and 2,500 mg/L for C_7 and C_5 asphaltenes, respectively. The CNAC and CCC increase somewhat with the inclusion of the heaviest resins in the C_5 asphaltenes (Goual et al., 2011). A clear demonstration of the formation of asphaltene clusters in toluene was obtained by measurement of the kinetics of asphaltene flocs upon addition of n-heptane to asphaltene-toluene solutions using dynamic light scattering (Yudin & Anisimov, 2007). Below a concentration of ~3 g/liter, the kinetics of floc formation are diffusion limited aggregation; whereas above this concentration the kinetics are reaction limited aggregation. This is consistent with the DC conductivity data in Figure 8.

In low-frequency dielectric relaxation studies (Goual, 2009), DC conductivities were related to the effective diffusion coefficient of asphaltenes via the Nernst-Einstein equation, from which average sizes were calculated assuming asphaltenes are spherical in shape. It was shown that asphaltenes form viscoelastic films at solid interfaces when they are close to the flocculation threshold (Abudu & Goual, 2009) or when their size in toluene is smaller than ~3 nm (Goual & Abudu, 2010), as shown in Figure 9. The topographical features of rigid (d > 3 nm) and viscoelastic (d < 3 nm) asphaltene films obtained by AFM Tapping mode imaging in air are displayed in Figure 10. The viscoelastic films consist of soft multilayers (i.e., toluene-rich) of small aggregates that possibly interact with each other, whereas rigid films consist of a monolayer of particles with few large aggregates scattered on its surface.

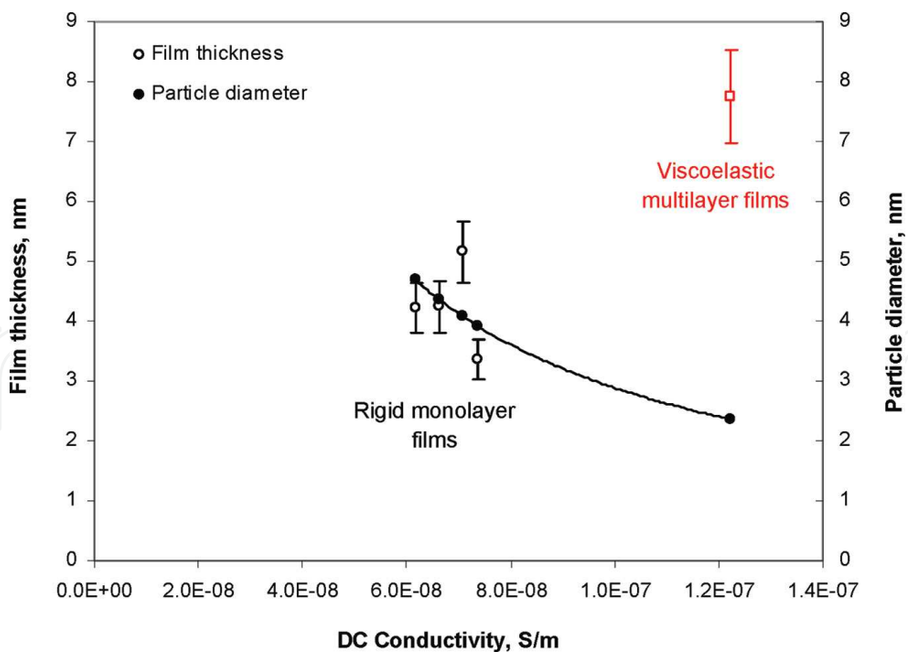
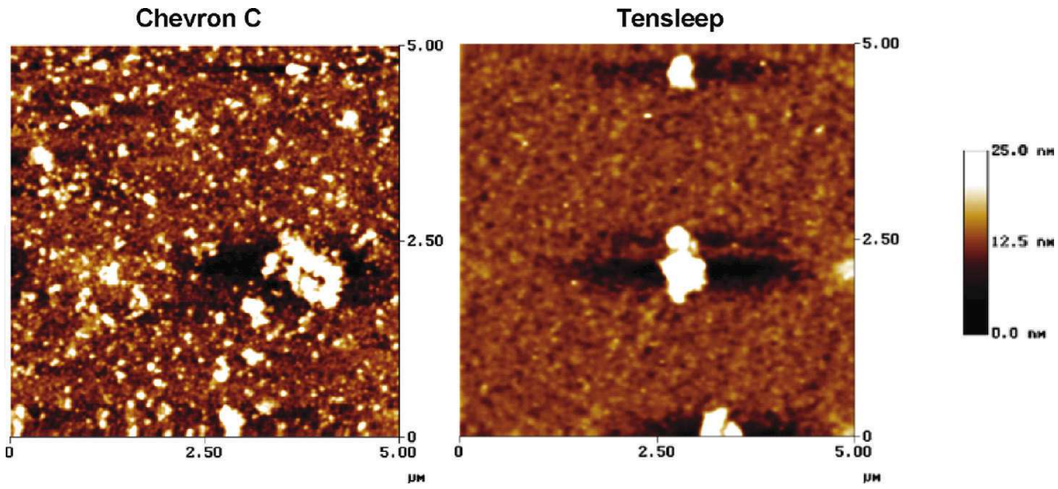


Fig. 9. Relation between film thickness, particle diameter, and DC conductivity of 0.1 wt % asphaltenes in toluene.



Viscoelastic layer (d < 3 nm) Rigid layer (d > 3 nm)

Fig. 10. AFM images of adsorbed particles on gold from 0.5 wt% crude oils in toluene.

Thus, data derived from low-frequency dielectric relaxation are important in predicting asphaltene-associated problems. Low frequency measurements can also produce sensor responses that are sensitive to interactions between asphaltenes and surfactants usually employed in chemical flooding.

5. Structure and role of resins

The chemical structure of asphaltenes is difficult to ascertain due to the complex nature of asphaltenes. Two models have been proposed to describe the molecular architecture in asphaltenes: (i) archipelago models, and (ii) island models. The Archipelago models consider that several aromatic moieties are bridged together via aliphatic chains (Strausz et al., 1992), whereas island models suggest that there is predominantly one fused polycyclic aromatic hydrocarbon (PAH) ring system per asphaltene molecule with pendant aliphatic chains (Dickie & Yen, 1967). New fragmentation studies by two-step laser desorption laser ionization mass spectrometry (L2MS) (Sabbah et al., 2011) and FTICR-MS (Hsu et al., 2011) support the contention that the dominant structural character of asphaltenes is island-like. These results are in accord with other methods such as TRFD (Groenzin & Mullins, 2000), high-Q ultrasonics (Andreatta et al., 2005), and NMR (Freed et al., 2009). Recently, DC conductivity studies showed that resins are unlikely to coat asphaltene nanoaggregates in anhydrous organic solvents (Sedghi & Goual, 2010). Thus, the long-time-standing Nellensteyn hypothetical model (Nellensteyn, 1938), where resins adsorb on asphaltenes to provide a steric stabilizing layer, is not valid. However when water is present in the solvent, the role of resins on asphaltene adsorption at the solvent/water interface becomes important. Resins and natural surfactants tend to diffuse first to the interface before being replaced by asphaltenes (Magual et al., 2006). The amount of adsorbed asphaltenes on water also depends on the resin to asphaltene ratio (Goual et al., 2005).

Based on the previous studies, a new asphaltene model has been codified in the "modified Yen model" and stipulates the dominant structure of asphaltene molecules, nanoaggregates and clusters of nanoaggregates (Mullins, 2010). This model was built upon the Yen Model,

which has been in use for 40 years (Dickie & Yen, 1967). The Yen model has been very useful, particularly for considering bulk properties of phase-separated asphaltenes. Nevertheless, at the time the Yen model was proposed, there were many uncertainties in asphaltene molecular weight, architecture, and colloidal structure. Figure 11 shows the corresponding schematic of the modified Yen model, which incorporates the many substantial advances in asphaltene science particularly over the last ten years (Mullins, 2010). The island architecture exhibits attractive forces in the molecule interior (PAH) and steric repulsion from alkane peripheral groups. These structures were also observed in oil reservoirs with extensive vertical offset, where gravitational effects are evident (Creek et al., 2010; Mullins et al., 2011). Results from analytical methods such as time-resolved fluorescence depolarization (TRFD) (Groenzin & Mullins, 2000), Nuclear magnetic diffusion (Freed et al., 2007); Fluorescence correlation spectroscopy (FCS) (Andrews et al., 2006), DC conductivity (Zeng et al., 2009; Goual et al., 2011) indicate that the size of asphaltene molecules is ~ 1.5 nm.

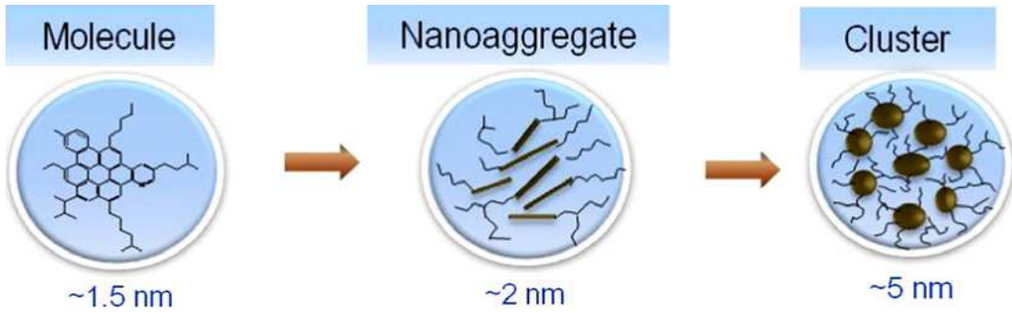


Fig. 11. The modified Yen model. Courtesy of O. Mullins, Schlumberger

With the broad scope and significant applications of the modified Yen model, it is important to validate all aspects of this model. In particular, there are wide ranging studies at many length scales involved in building the modified Yen model. Recently, the cohesiveness of two independent data streams was determined by centrifugation and DC conductivity measurements (Goual et al., 2011). The data indicate that asphaltene nanoaggregates have relatively small aggregation numbers of 4-6, in accord with previous work (Mullins, 2010), and that aggregation is entropically driven (Goual et al., 2011). The relatively small aggregation numbers are consistent with nanoaggregate sizes in the range of 2 nm measured by centrifugation (Mostowfi et al., 2009; Indo et al., 2009) and inferred by small angle X-ray scattering (SAXS) and Neutron scattering (SANS) studies (Eyssautier et al., 2011a). More recent x-ray and neutron scattering analyses confirmed the nanoaggregate architecture in the modified Yen model where PAHs in the aggregate interior are attractive while the alkane substituents act to sterically repel other asphaltene molecules and preclude further aggregate growth (Eyssautier et al., 2011a). The clusters form only at much higher concentration (see Figure 8) because the attractive forces of one nanoaggregate to another are much weaker. Nanofiltration studies indicate that the size of clusters is smaller than 30 nm (Ching et al., 2010). Very recent SAXS and SANS studies revealed that asphaltene clusters consist of ~12 nanoaggregates and, due to their fractal nature, they are very sensitive to temperature variations and solvent type (Eyssautier et al., 2011b). On the other hand, nanoaggregates are insensitive to temperature (Goual et al., 2011; Eyssautier et al., 2011b).

All the latest studies in asphaltene science demonstrate repeated consistency with the modified Yen model proposed in Figure 11. This model provides a foundation that has far reaching implications in many areas associated with the production of crude oil.

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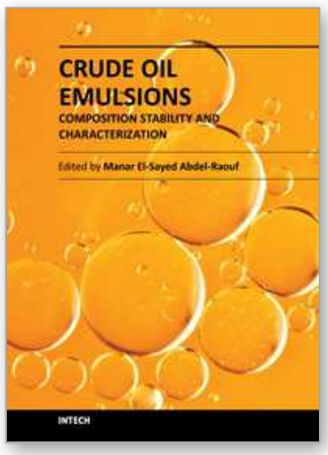
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Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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