Asphaltenes

Oliver C. Mullins
Science Advisor

Reservoir crude oils consist of dissolved gases, liquids and dissolved solids. Asphaltenes are the dissolved solids components of crude oils and although important in the oil field, they have only recently come to be understood. The definition of asphaltenes differs from the laboratory to the oil field. Fortunately the science of asphaltenes has evolved, enabling a new look at how asphaltenes affect a wide variety of oilfield concerns, such as reservoir plumbing, tar mat and heavy oil formation and surety of fluid flow in pipes.

Asphaltenes negatively impact the economic value of crude oil. As asphaltene content increases from 0% to 40%, the oil's viscosity and density increase dramatically and its color changes from clear to dark brown. Viscosity is a critical rheological property of reservoir fluids; it affects fluid mobility from the reservoir and through production systems. Viscosity depends directly and exponentially on asphaltene content. With a sufficient amount of asphaltenes, hydrocarbons can have flow properties similar to those of coal.

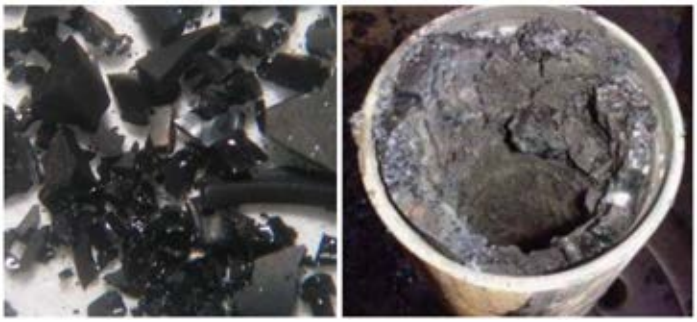

Figure 1. Asphaltenes. A laboratory sample of *n*-heptane asphaltenes (*left*) is derived from crude oil. A field deposit of asphaltenes (*right*) consists largely of *n*-heptane asphaltenes.

Factors Affecting Asphaltene Formation

Generally the gas and liquid components of oil are treated as known chemicals such as normal alkanes, or *n*-alkanes, which are linear chain hydrocarbon compounds that have the chemical formula C_nH_{2n+2}. Examples are methane [CH_4], ethane [C_2H_6], propane [C_3H_8] and *n*-butane [C_4H_{10}]. In contrast, asphaltenes are not defined by their chemical identity. Because they consist of a complex mixture of many compounds, they are defined by their solubility characteristics measured in the laboratory. Asphaltenes are typically defined to be the toluene-soluble and *n*-heptane-insoluble components of crude oil and other carbonaceous materials such as bitumen and coal. The *n*-heptane asphaltenes are solid and powdery (Figure 1). In oilfield applications, solids that are separated from crude oils are generally referred to as asphaltenes if they are largely, but not necessarily entirely, composed of *n*-heptane asphaltenes. In addition, the terms tar and bitumen are loosely used to refer to materials that have a high asphaltene content. Sometimes black oilfield solids, including waxy deposits that have only a small asphaltene content, are incorrectly referred to as asphaltenes.

In chemistry, asphaltenes are defined as a solubility class. They do not dissolve in gases or in alkane liquids such as *n*-heptane [C_7H_{16}], but they do dissolve in aromatic hydrocarbons such as toluene or xylene. Crude oils that have a high gas/oil ratio (GOR) are rich in light hydrocarbons and consequently, have little asphaltene content.

Another important property of asphaltenes is their ability to flocculate. Flocculation refers to a tendency to form, or aggregate in, clumps. Typically asphaltene solubility follows the general rule in solution chemistry that "like dissolves like." Asphaltenes and gas (or high-GOR oil) are not chemically alike and therefore do not dissolve in each other. Also asphaltene solubility increases with temperature. For many reservoir crude oils, asphaltenes are very delicately balanced in the oil; a small change in pressure and temperature can create phase instability, resulting in formation of bulk solids. For instance, oils that have high GOR and are capable of containing more gas in solution—also referred to as undersaturated oils—are particularly prone to asphaltene formation during production in spite of their low asphaltene concentration. These oils are highly compressible. During production they experience a large reduction in pressure, which decreases their density. The asphaltenes may then come out of solution and flocculate. If pressure and temperature decrease below the bubblepoint, dissolved gas evolves out of the oil, thereby increasing the solubility of asphaltenes in the oil. Consequently, the onset of asphaltene development occurs at pressures greater than the bubblepoint pressure.

If oil in a reservoir experiences a gas charge, the GOR of that oil can increase, causing reduction of asphaltene solubility and the onset of asphaltene flocculation, which can result in deposition of asphaltenes. The location of the asphaltene deposit depends on how the reservoir trap fills and how the GOR increases. To describe this and other processes involving asphaltenes in reservoir crude oils, scientists use an equation of state. However, until recently, there was little understanding of the molecular and aggregate sizes of asphaltenes in crude oils or laboratory solvents. Without knowing the size of the aggregate, scientists cannot solve Newton's second law of gravity, $F = m \times g$, where F is force, m is asphaltene mass and g is Earth's gravitational acceleration; therefore, modeling is fruitless. The inability to understand and model asphaltenes in crude oils led to an inordinate focus on asphaltenes as only a problem of flow assurance—the analysis of reservoir fluids to characterize phase behaviors and anticipate associated flow problems within production systems that may interrupt hydrocarbon flow from the reservoir to the refinery. In fact asphaltenes have a much broader impact on the reservoir and can affect evaluation of reservoir connectivity and fault-block migration, as well as cause formation of heavy oil gradients, tar mats and disequilibrium in fluid gradients.

Asphaltene Structures and Sizes

The Yen-Mullins model for asphaltene structures and sizes codifies the nanostructures of asphaltenes into three distinct and separate forms: asphaltene molecules, nanoaggregates of individual asphaltene molecules and clusters of nanoaggregates (Figure 2). The model enables the prediction of asphaltene mass, which is required for modeling the thermodynamic behavior of asphaltenes. Asphaltene molecules are relatively small, and the dominant molecular structure has a single core of aromatic hydrocarbons that have peripheral substituents—side chains or pendant groups—composed of alkanes hanging off them. The typical asphaltene molecule has a mean molecular weight of 750 g/mol.

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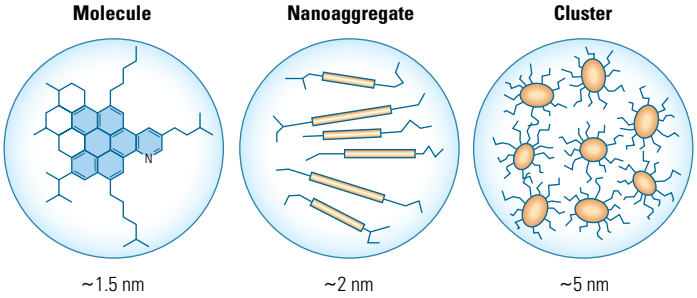

Figure 2. The Yen-Mullins model of asphaltenes. At low concentrations—typical in condensates and volatile oils—asphaltenes are predicted to exist as a solution of dispersed molecules that measure about 1.5 nm (*left*). Asphaltene molecules have a core of aromatic hydrocarbon rings (light blue shading) with side chains of alkanes hanging off them. At higher concentrations—in black oils—asphaltene molecules combine to form nanoaggregates that are about 2 nm in width (*center*). At still higher concentrations, such as those in mobile heavy oils, asphaltene nanoaggregates combine to form clusters that measure about 5 nm wide and are dispersed in the heavy oil (*right*).

Asphaltene molecules readily combine or aggregate. This process originally hindered conventional techniques for determining the molecular weight of asphaltenes. At low concentrations, such as in light oils, asphaltenes are dispersed as molecules. As the asphaltene concentration increases, such as in black oils, nanoaggregates form comprising about six asphaltene molecules each. At high concentrations, such as in heavy oils, clusters form consisting of about eight nanoaggregates each.

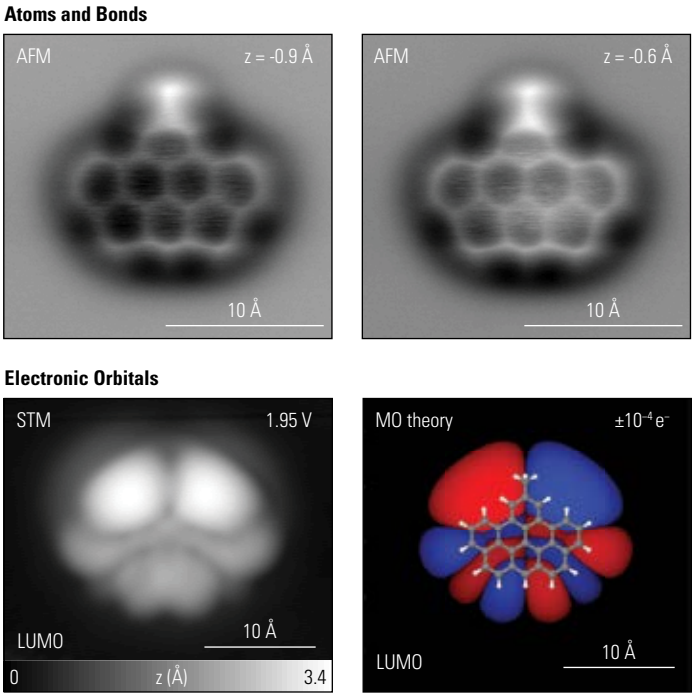

Figure 3. Ultrahigh-resolution molecular imaging of a coal-derived asphaltene molecule. Two atomic force microscopy (AFM) images (*top left and right*) at different levels (z) in an asphaltene molecule show the molecule's atoms and bonds arranged in fused six-membered aromatic rings to form polycyclic aromatic hydrocarbons (PAH). Scanning tunneling microscopy (STM; *bottom*) shows an individual electron orbital, the lowest unoccupied molecular orbit (LUMO; *left*) about the asphaltene molecule. The image supports a calculation of the LUMO using density functional theory of the molecular orbital (MO; *right*). The molecular structure is overlain and consists of carbon (gray) and hydrogen (white) atoms. The red and blue colors represent the opposite phases of the LUMO, a particular molecular orbital. (Images used with permission, courtesy of IBM Research, Zurich, Switzerland. http://dx.doi.org/10.1021/jacs.5b04056.)

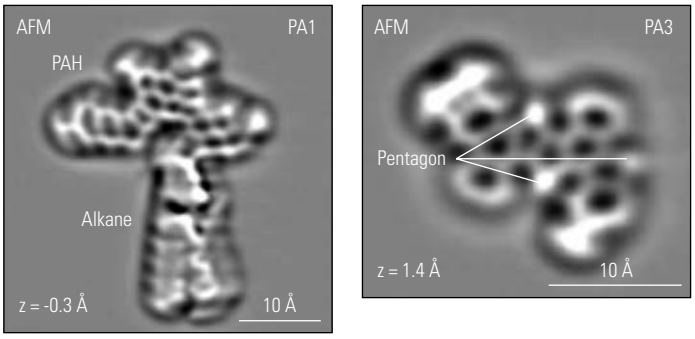

Figure 4. Asphaltenes. Atomic force microscopy (AFM) images of petroleum asphaltene molecules show polycyclic aromatic hydrocarbons (PAH) composed of fused six-membered aromatic rings and some alkane substituents. The pentagons are five-membered rings with some double bonds. These images support the molecular representation in the Yen-Mullins model. (Images used with permission, courtesy of IBM Research, Zurich, Switzerland. http://dx.doi.org/10.1021/jacs.5b04056.)

The Yen-Mullins model delivers a basis for an equation of state for predicting asphaltene concentration gradients in oil reservoirs. From this model, the Flory-Huggins-Zuo equation of state (FHZ EOS) was developed, a simple equation that has few parameters. This EOS model enables analysts to interpret field data using downhole fluid analysis (DFA) from a wireline formation tester.

The Yen-Mullins model has been confirmed by ultrahigh-resolution molecular imaging (Figures 3 and 4). The atoms and bonds of the molecule have been imaged using atomic force microscopy (AFM). Individual electron orbitals have been imaged by scanning tunneling microscopy (STM) and they match theoretical molecular orbital calculations.

Reservoir Fluid Geodynamics

For asphaltenes to reach a state of equilibrium in the reservoir, generally vertical and lateral connectivity must exist; this connectivity has been confirmed in numerous case studies. Disequilibrium gradients of asphaltenes suggest the presence of reservoir fluid geodynamic processes, such as fluid flow within the reservoir and diffusional processes on a geologic timescale.

The combination of asphaltene thermodynamics and DFA measurements has provided a new way to analyze oil reservoirs. The ability to evaluate the connectivity, or interconnectedness, of the plumbing of subreservoir units is important, especially in deepwater reservoirs. Because of the high cost of drilling in these environments, operators seek to produce from deepwater reservoirs using a minimum number of wells. The wells must be optimally placed and reservoir drainage efficiency is economically vital.

Asphaltene gradient equilibration is a strong indicator of reservoir connectivity. Asphaltene gradient disequilibrium, as measured by DFA, indicates that geologic processes have prevented equilibration. Many important reservoir concerns, such as connectivity, baffling, tar mat and heavy oil formation, large GOR gradients, biodegradation and flow assurance have been addressed by combining asphaltene thermodynamics and DFA. Understanding asphaltenes is a key element in helping engineers optimally produce and effectively drain hydrocarbons from the reservoir.