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The Colloidal Structure of Crude Oil and the Structure of Oil Reservoirs

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Received February 16, 2007. Revised Manuscript Received May 14, 2007

Large sand bodies in the subsurface are shown to provide a unique laboratory for understanding both reservoirs and crude oils. Here, we treat the discovery by downhole fluid analysis of a gravitational concentration gradient of asphaltenes, the most dense component of crude oil, in a 2500-ft column of crude oil in the reservoir. The continuous trend of crude oil properties across the field implies flow connectivity of this giant sand body, addressing the single largest uncertainty in the development of deepwater oil fields today—drainage area that can be achieved by each one of the extremely expensive wells. Consequently, downhole fluid analysis provides a new way to identify flow connectivity and to achieve significantly improved efficiency in oil production in high-cost arenas. In addition, detailed downhole and laboratory analyses of the asphaltene gravitational gradient show that asphaltenes are dispersed in crude oils of this weight as nanoaggregates. This observation agrees with the recently reported asphaltene nanoaggregates in toluene by high-Q ultrasonics and by NMR diffusion measurements. Finally, this case study suggests that resins are predominantly not associated with these asphaltene nanoaggregates, implying that the 70-year-old asphaltene–resin micelle model is in error. This asphaltene–resin micelle model, which has virtually no supporting data, appears to be substantially misleading in treating asphaltene colloidal structure.

Introduction

Oil production costs in fields located under deep water are huge, often exceeding many billions of dollars. Deepwater is an extremely important arena for the production of oil; the United States Geologic Survey has estimated that one-half of the world's undiscovered oil is offshore.^{2,3} The largest uncertainty in these projects is the size of individual oil-bearing compartments;⁴ a compartment must be penetrated by a well to drain, and selecting the most optimal drainage locations for a deepwater reservoir drives economic return. However, compartment size has been most difficult to assess. Seismic methods cannot determine sealing barriers, nor can near well-bore measurements. Pressure communication, which can occur on geologic time (10⁷ years), does not prove flow communication in a production time frame (10 years). Variations in the reservoir hydrocarbons are useful for delineating reservoir structure and continuity because reservoir filling (which is often ongoing as a result of active fluid movement in the subsurface) reflects this structure and continuity.

Traditional geochemical analysis has been performed routinely to identify compartments. That is, oil samples can be acquired by specialized sampling tools introduced into oil wells. These samples can then be brought to the well site surface and shipped to a laboratory for subsequent analysis, usually weeks or months after the sampling event. However, it is far more powerful to analyze the oil samples in real time with the downhole sample acquisition tool. For example, the measurement of unexpected fluid properties can be checked in real time, and the data collection program can be optimized as it progresses.^{5–7} These novel chemical analysis methods of subsurface fluids performed in situ in oil wells accentuate compositional gradients of hydrocarbon fluid.^{5–7} These downhole chemical analysis methods rely extensively on the comparison of light-end to heavy-end content of the crude oil. As has recently been pointed out, this type of analysis is more sensitive than traditional geochemical analyses for detecting crude oil variations.⁸ Discovery of a continuous hydrocarbon gradient across a field implies flow connectivity; discrete fluid changes and higher density fluids higher in the column (fluid

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density inversions) imply flow barriers and compartmentalization.^{5–7} Petroleomics methods^{1,9} (detailed chemical analysis of all petroleum chemical constituents) coupled with downhole fluid analysis^{5–7} are now being utilized to identify compartments in reservoirs.¹⁰ In addition, advanced gas chromatography methods are being linked with downhole fluid analysis again to understand reservoir structure and fluid variations.¹¹

A variety of different physical processes can give rise to reservoir fluid variations, and these variations in turn can speak to compartmentalization. Convection and diffusion cause the hydrocarbon column to approach equilibrium.¹² In geologic terms, convection is fast while diffusion is slow.¹² Convection of fluids, if it occurs, can dominate other processes keeping an oil column at equilibrium. However, diffusion is often much slower than other processes precluding equilibrium in some cases. Processes that can cause disequilibrium in a hydrocarbon column include steady-state hydrocarbon and/or CO₂ charging into the reservoir (very common) and biodegradation.¹³ For example, Lake Nios of Cameroon requires continuous venting to prevent deadly CO₂ plumes from erupting from the lake. Likewise, reservoirs close to the corresponding tectonic fault contain CO₂.¹⁴

This paper treats the discovery of a gravitational concentration gradient of asphaltenes,¹ the most dense component of crude oil, in a unique laboratory, a 2500-ft column of crude oil in the reservoir. In situ optical absorption measurements versus height delineate a large concentration gradient of asphaltenes. Corresponding analysis shows that the asphaltenes are present in crude oils as nanoaggregates, a result previously unknown but in accord with recent determinations of asphaltene colloidal structure in toluene by high-Q ultrasonic spectroscopy,^{15,16} NMR diffusion measurements,¹⁷ and conductivity measurements.¹⁸ In addition, this paper addresses a 70-year-old paradigm of

petroleum science which conjectures with virtually no supporting data^{19,20} that resins are associated with previously uncharacterized asphaltene aggregates.^{21,22} That is, resins had been conjectured to stabilize asphaltene as a natural surfactant. However, laboratory analysis of samples from different heights in the oil column shows little concentration gradient for resins, in contrast to the huge asphaltene gradient. This long-standing resin–asphaltene association paradigm does not apply to the crude oils analyzed here. Asphaltene colloidal stability is fundamentally different than standard oil–water surfactant systems. With this improved understanding of petroleum science, we establish new methods to identify hydraulic connectivity within large reservoirs. Furthermore, the dramatically altered picture of petroleum interfacial chemistry impacts all areas of resource utilization.

Experimental Section

Downhole fluid analysis measurements have been performed with a custom visible–near-infrared (vis-NIR) spectrometer.⁵ The spectrometer consists of a 10 W W–I₂ bulb, custom fiber optics, a high-pressure cell with sapphire windows, and 10-way bifurcated fiber optics fitted with individual optical filters to select wavelengths. A total of 10 different optical detectors are used for light detection; the detectors are Si, InGaAs, and various extended InGaAs detectors, depending on the wavelength of the optical channel. A second set of fiber optics bypasses the optical cell to enable I₀ measurements. This custom spectrometer is capable of working up to temperatures of 175 °C with sample pressures up to 20 000 psi. The spectrometer is placed on a downhole sampling tool (cf. Figure 1). The sampling tool has a probe module that forces a stout steel tube against the wall of a permeable zone (cf. the picture in Figure 1). A pump drops the pressure in the flowline; formation fluids flow into the probe, through the flowline and through the high-pressure cell of the spectrometer where the optical measurements are made. Figure 1 schematically shows the downhole sampling tool with two different spectrometers at different locations on the sample flowline. The fluid flow can be directed into the borehole or into a sample bottle depending on need. Subsequently, in the chain of custody process, laboratory measurements confirmed the validity of the laboratory samples by comparing the vis-NIR spectra acquired at the point of sample acquisition versus the same measurement in the lab under downhole conditions of pressure and temperature.²³

For comparison, two crude oils were obtained from different depths; the live (gas-containing) samples were flashed at one atmosphere to obtain the dead oils. The gas–oil ratios of these oils are small [ca. 500 scf/bbl (standard cubic feet of gas/barrel of dead crude oil)] and nearly the same, so there is little dilution effect of the live oils by gas. For each sample, 70 mg of oil was placed in a 5 cm³ volumetric flask brought to volume with CCl₄. A 2-mm-path-length cell was used for optical absorption measurements of the diluted whole crude oils with a Cary 500 UV–vis-NIR spectrometer. Dilution with CCl₄ was used for several purposes: this process obviates any problem associated with light scattering from colloidal wax; this dilution enabled comparison in the same

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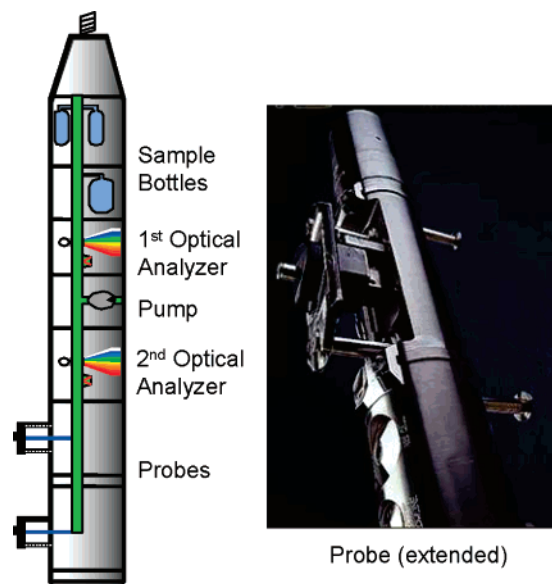


Figure 1. Schematic depiction of a sampling tool which descends into an oil well (on a wireline), establishes flow communication with permeable formations through the probe (photograph shown), pumps formation fluids into the flowline, and performs spectral analysis of these fluids.

spectral range of the whole oil and the deasphalted oil (which was diluted ca. 100:1), and this dilution enabled facile acquisition of spectra in the visible range where the asphaltene molecular volumes have been measured.^{24,25} To obtain deasphalted oils, a 60 mg crude oil sample was placed in a 5 cm³ volumetric flask which was brought to volume with *n*-heptane. The asphaltenes were readily observed to have settled on the bottom of the flask. After 24 h, the supernatant was used to acquire an optical spectrum in a 10-mm-path-length cell. No scattering was detected in the spectra, indicating that there was no detectable suspension of asphaltene flocs. Repeat runs were performed to ensure consistency.

Time-resolved fluorescence depolarization data are shown. As explained elsewhere,^{24,25} time-dependent fluorescence depolarization data were collected with the PTI C-72 system, which employs a PTI GL-3300 nitrogen laser source along with a PTI GL-302 high-resolution dye laser with a fiber optic coupling to the measurement cell to excite the fluorescence. The directions of the excitation and emission light from the cell are oriented 90° from each other with vertical polarization defined to be perpendicular to this plane. Typical concentrations of asphaltenes in the 10 mm measurement cell are 6 mg/L.

For depolarization measurements, the wavelength of the PTI model 101M emission monochromator is fixed while two Glan-Thompson polarizers are used to select the polarizations. One polarizer is placed at the output of the fiber optic, immediately before the measurement cell, and the other polarizer is placed at the entrance to the emission monochromator. Fluorescence time decay curves are collected for four polarizations: vertical on the source side, vertical on the emission side (*v-v*); vertical–horizontal (*v-h*); horizontal–vertical (*h-v*); and horizontal–horizontal (*h-h*). The laser firing triggers a box car delay gate which then triggers a high-voltage pulse at a known delay to the photomultiplier (PMT). The short duration of the high-voltage pulse “turns on” the PMT for a short time interval. The integrated current over this time interval from the PMT is detected. The delay time is sequentially scanned over the desired time range, providing the fluorescence decay curve. The time resolution of the system is about 80 ps. A complete data set for one excitation and emission wavelength pair

corresponds to acquisition of the four polarization combinations mentioned above. Typically, the total acquisition time for the four curves is 2 h. Reproducibility of the signal levels was checked periodically during the acquisition time to validate the data. In addition, the *v-h* and *h-h* curves should overlay again, allowing for excellent quality control. Duplicate (or more) runs were performed for all wavelength pairs to ensure precision. Typically, ϕ^2 values of 1.2 or less were obtained for a good run.

Results and Discussions

Figure 2 shows a map of a very large, world-class reservoir, the Tahiti field, which is located under 4000 ft of water and at a depth of 27 000 ft in the Gulf of Mexico.^{26,27} The total expenditures for all phases of the Tahiti field development are expected to run as high as \$3.5 billion;²⁶ econometric modeling of this and other reservoirs is critically dependent on understanding reservoir connectivity. Three main oil wells with several subsidiary penetrations are indicated in this figure. The upper and lower surfaces of the primary reservoirs, the reservoir horizons, are depicted in this figure—the embedding formation structures have been stripped away in this image to allow the reader to “see” the reservoir. The Tahiti field contains two large reservoirs in two laterally extensive, stacked sands which are not in flow communication with each other, the M21A Sand and the M21B Sand. Downhole fluid analysis of contained hydrocarbons was performed at several depths in each of the wells. Figure 3 shows NIR spectra that were recorded in situ in several oil wells on fluids in one of the reservoirs. The NIR spectra consist of both electronic absorption bands of polycyclic aromatic hydrocarbons and vibrational overtone and combination bands primarily of alkanes.⁵

Figure 4 shows that the coloration measured by downhole fluid analysis closely matches the asphaltene content of the crude oils as determined by laboratory measurements. The spectral data were recorded in the oil well. The asphaltene content was determined by *n*-heptane addition (40:1 dilution) in the laboratory on the dead oil samples. This figure shows that the measurement of crude oil coloration is a proxy for determining relative asphaltene concentration, particularly within a single oil field. The asphaltenes are by far the most strongly “colored” component in the crude oils. The intercept of the straight line fit to the data in Figure 4 shows that there is a little color that remains at zero asphaltene concentration. This color corresponds primarily to the crude oil component “the resins”, which are the second most aromatic component in crude oil after the asphaltenes. The one outlier (at 4% asphaltenes, OD = 2) has been shown by chain of custody methods to be an invalid laboratory sample; thus, this point can be discounted.

Figure 5 shows the crude oil coloration plotted for the two sand layers as a function of depth. Deeper crude oils show increased coloration, reflecting an increased asphaltene content. Asphaltenes are more dense than the surrounding liquid hydrocarbon; their negative buoyancy is given by Archimedes’ principle $V\Delta\rho$, where V is the volume of the asphaltene colloidal particle and $\Delta\rho$ is the density contrast of asphaltenes versus the bulk liquid. (Below we address whether this asphaltene distribution is molecular or colloidal.) We use the Boltzmann distribution, eq 1, to describe the concentration of asphaltene

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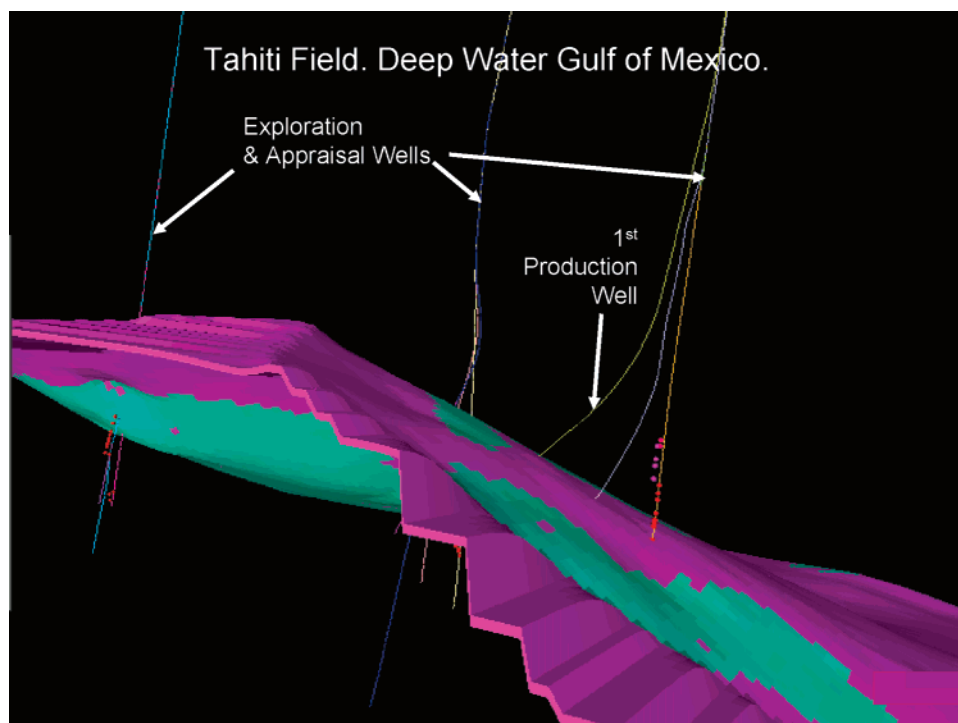


Figure 2. A world class reservoir. The reservoir depicted is under 4000 feet of water (Gulf of Mexico) and at a depth of 27 000 feet. Embedding formation layers have been stripped away to allow the reader to “see” the reservoir. Three main wells, along with subsidiary wells, were drilled for evaluation purposes. Recently, the first production well was drilled. Fluids in the production well matched trending discovered in the exploration/appraisal wells indicating flow connectivity.

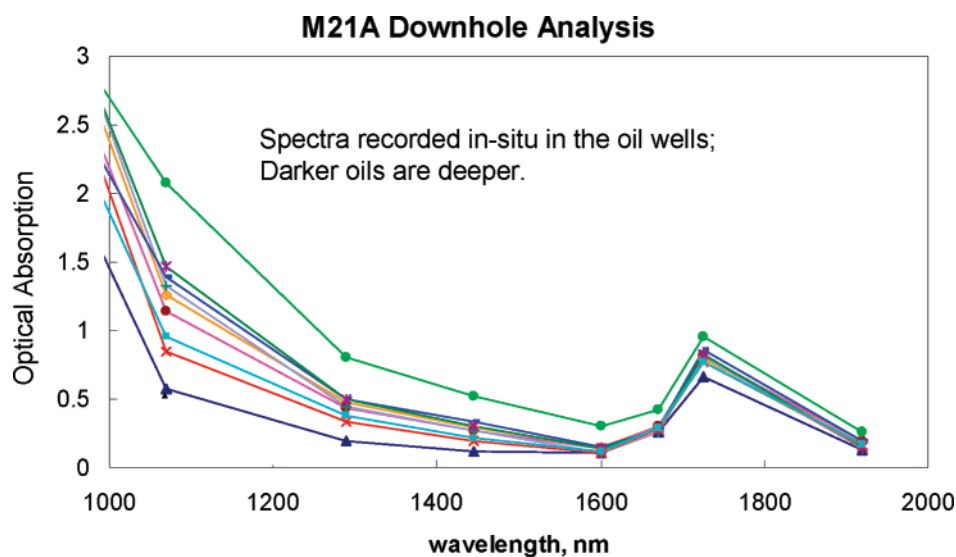


Figure 3. Near-infrared spectra acquired in situ in the oil wells for crude oils in one reservoir at various depths in the different oil wells. The sloping absorption due to electronic transitions of aromatic molecules is quite variable for these different oils, indicating very different asphaltene concentrations.

as a function of height h in the oil column above reference 0, the lowest point with a measured oil color in the oil column.

$$\frac{OD(h)}{OD(0)} = \exp\left\{-\frac{V\Delta\rho gh}{kT}\right\} \quad (1)$$

where $OD(h)$ is the optical density in a particular wavelength channel at height h above the reference 0, g is earth's gravitational acceleration, k is Boltzmann's constant, and T is the reservoir temperature. To fit the data in Figure 5, the only adjustable parameter is V . To use eq 1 to treat the reservoir fluids, we assume the reservoir fluids are in thermodynamic equilibrium. The very high horizontal permeability (600

mDarcy), the very high ratio of vertical to horizontal permeability (0.6 on core data), the high reservoir dip angle (30–40°), the fact that the Tahiti field consists of tilted sheet reservoirs, and the great height of the oil column all contribute to enabling the reservoir fluids to attain thermodynamic equilibrium.²⁸ The fact that the light ends are evenly distributed in this field is an indication that the oil column is in equilibrium. That is, a highly undersaturated, black oil as found

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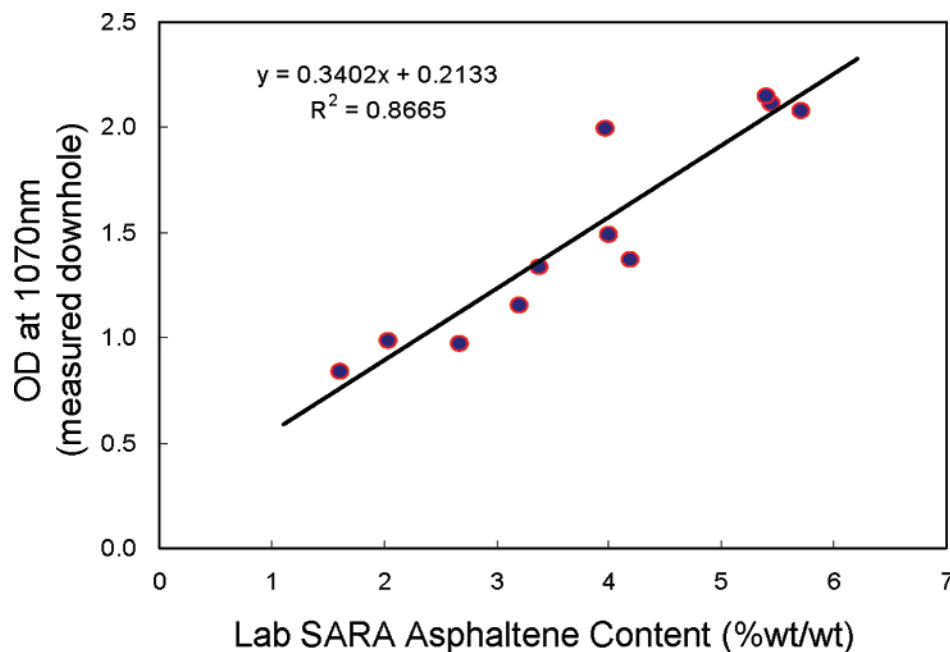


Figure 4. The scaling of the coloration of the crude oils with the asphaltene content. Asphaltenes are known to be strong absorbers of visible and near-infrared radiation.

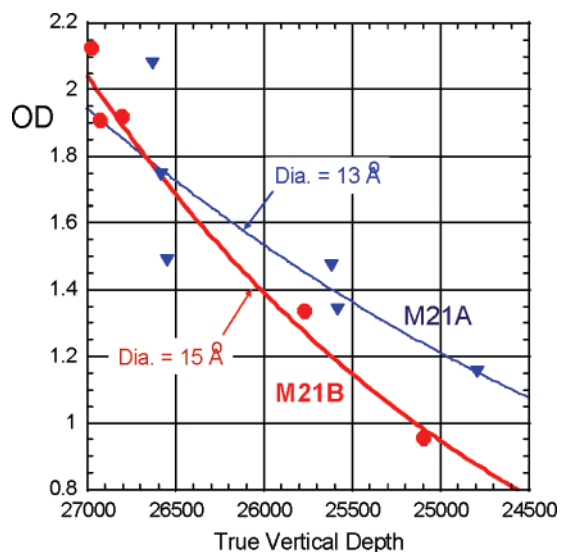


Figure 5. The crude oil coloration versus depth. This relationship shows a large asphaltene gradient in each of the two reservoirs, M21B and M21A Sands. With eq 1, the asphaltene colloidal particle diameter is found to be about 15 Å, thus nanocolloidal.

in the Tahiti field is expected to have a homogeneous distribution of light ends if the oil is in equilibrium.²⁹

Figure 5 plots the coloration versus the depth for crude oils in each of the two primary reservoir sands. The crude oils in the M21B Sand exhibit a much closer fit to eq 1 than those of the M21A Sand. Nevertheless, M21A does exhibit the same overall trend. Furthermore, the trend predicted by eq 1 (see Figure 5) for the fluids was matched in the last well drilled (the first production well in Figure 2), reinforcing the model of laterally connected reservoirs and indicating a high probability that the production well will in fact efficiently drain the intended target. This powerful new method of mapping fluid connectivity (the opposite of compartmentalization) is gaining rapid ac-

ceptance worldwide, addressing at small marginal cost the biggest problem in the deepwater production of oil.

Asphaltenes¹ are the most aromatic component of crude oil and are defined by a solubility classification, for example, soluble in toluene, insoluble in *n*-heptane. Asphaltenes are deeply colored dark brown, which is related to electronic transitions of their polycyclic aromatic hydrocarbons.³⁰ Asphaltenes and their nature in crude oil have been enshrouded in controversy. For example, the molecular weight of asphaltenes is now known to be rather small;^{24,25,31,32} previous estimates, mostly much larger, varied by orders of magnitude.

The colloidal nature of crude oils has proved notoriously difficult to delineate. For a long time,^{21,22} asphaltenes have been thought to be colloiddally suspended in crude oil. By definition, they are insoluble (and flocculate) in alkanes, the dominant constituent of crude oil. Figure 5 shows that asphaltenes are present in this crude oil as 15 Å colloidal particles. To obtain this, we used a continuous (live) fluid density of 0.8 g/cm³, an asphaltene density of 1.2 g/cc, and $T = 100$ °C, the reservoir temperature. We show below that these asphaltene particles cannot be a molecular dispersion (a true molecular solution).

Two crude oils separated by 1800 ft in vertical depth were obtained in a single oil column. The spectra of equally diluted shallow and deep crude oil samples show that the coloration is roughly twice for the deeper crude oil, and this matches the much higher asphaltene content of the deeper crude oil. In addition, Figure 6 shows that these two spectra scale. That is, the spectrum of the shallow crude oil multiplied times a constant equals the spectrum of the deeper crude oil. Also plotted is the

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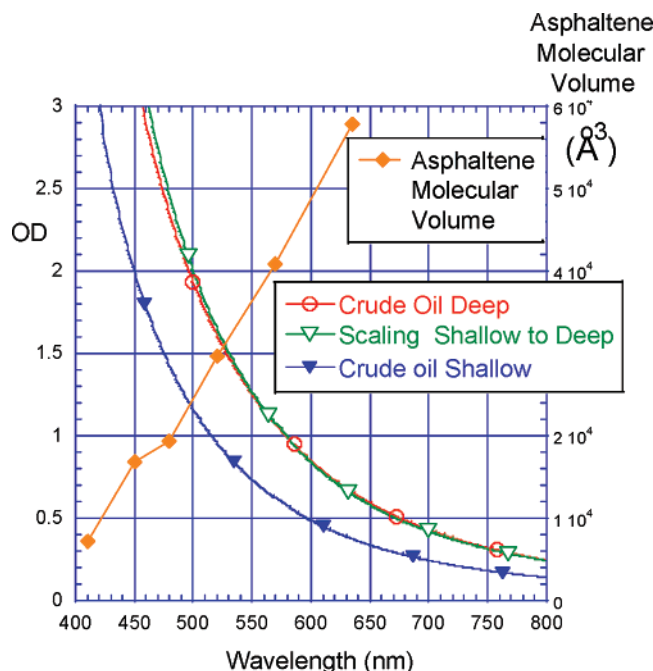


Figure 6. Laboratory spectra of a deep and a shallow crude oil. The large color (optical density) contrast between the deep and shallow oil is due to the difference in asphaltene concentration. By multiplying the spectrum of the shallow oil by a single scale factor, one obtains a “scaled spectrum” that is almost identical to the spectrum of the deep oil. There is no dispersion to the asphaltene gradient (the scaled spectrum of the shallow oil overlays the spectrum of the deep oil). Yet, the asphaltene molecular volume (in cubic angstroms) shows a huge dispersion. Thus, the little and big asphaltene molecules are bound together—in nanoaggregates.

molecular volume of asphaltenes (in cubic angstroms) as determined by rotational diffusion measurements using time-resolved fluorescence depolarization (TRFD) of typical virgin petroleum asphaltene molecules.^{24,25,31} These molecular volumes are obtained by the Stokes–Einstein equation:

$$\tau_r = \frac{\eta V}{kT} \quad (2)$$

where η is viscosity and V is molecular volume. Figure 6 shows that there is near-spectral invariance of the asphaltene gravitational gradient while the asphaltene molecular volumes exhibit a factor of 10 variation with wavelength.^{24,25,31} That is, by multiplying the spectrum of the shallow oil by a single scale factor, one obtains a “scaled spectrum” that is almost identical to the spectrum of the deep oil. There is no dispersion to the asphaltene gradient (the scaled spectrum of the shallow oil overlays the spectrum of the deep oil). Yet, the asphaltene molecular volume shows a huge ($\times 10$) dispersion. If the asphaltenes were molecularly dispersed, this factor of 10 difference in volume would enter the argument of the exponential in eq 1, giving enormous wavelength dependence to the asphaltene concentration gradient. This is not seen; the spectra scale. Thus, the little and big asphaltene molecules are bound together—in nanoaggregates. In any event, it is not surprising that asphaltenes are not molecularly dispersed in crude oil, which is a rather poor solvent for asphaltenes because asphaltenes form nanoaggregates in toluene, a good solvent at a 10^{-4} mass fraction.^{15–18}

To clarify, in asphaltenes, the molecular size correlates with spectral properties due primarily to quantum particle-in-a-box considerations; large polycyclic aromatic hydrocarbons (PAHs)

absorb long wavelengths (graphite is an extreme), while small PAHs absorb only blue or UV light (consider naphthalene or benzene).³³ These divergent volumes versus the wavelength would produce a large dispersion in the gravitational grading if the asphaltenes were molecularly dispersed (V enters into the exponential argument of eq 1). Consequently, the small and big asphaltene molecules must be associated to show the same gravitational gradient. The small aggregate size determined from eq 1 means these asphaltene particles in crude oil are nanoaggregates.

In Figure 6, the visible wavelength range is used (dilute samples), whereas downhole we used the near-infrared. The crude oils with more asphaltene possess higher optical density both in the visible and in the near-infrared (cf. Figure 4).³³ This result is expected given the broad scaling properties of asphaltene spectra.^{33,34} We use the visible range in Figure 6 because the molecular sizes of asphaltene molecules have been made in the visible range—this is valuable to understand the nature of asphaltene dispersion in crude oil.

Neutron and X-ray scattering show nanoaggregate particles in asphaltenes among particles of other length scales.^{35,36} Recently, high-Q ultrasonic spectroscopy (measuring accurate compressibility)^{15,16} and NMR diffusion measurements¹⁷ have shown the formation of asphaltene nanoaggregates at a roughly 10^{-4} mass fraction in toluene. Clusters of nanoaggregates can form at much higher concentrations³⁷ but are weakly bound and can dissociate at modest temperatures such as those found in oil reservoirs. Very recent laser-desorption, mass spectral measurements have found nanoaggregates in the same range.^{38,39} The asphaltene nanoaggregates found in reservoir crude oil herein are consistent with laboratory measurements.

The nanoaggregates found by use of eq 1 are about 15 Å. But this size is comparable to the asphaltene molecular size determined by rotational diffusion measurements^{24,25} as well as recent translational diffusion measurements.^{40,41} How can this be? The diffusion measurements are sensitive to the hydrodynamic radius. The gravitational gradient is a hard-sphere, static model of asphaltene nanoaggregates. For example, solvent entrainment would affect the hydrodynamic radius but not gravitational gradient radius because Archimedes buoyancy is a product of volume and density. We view that the factor of 2

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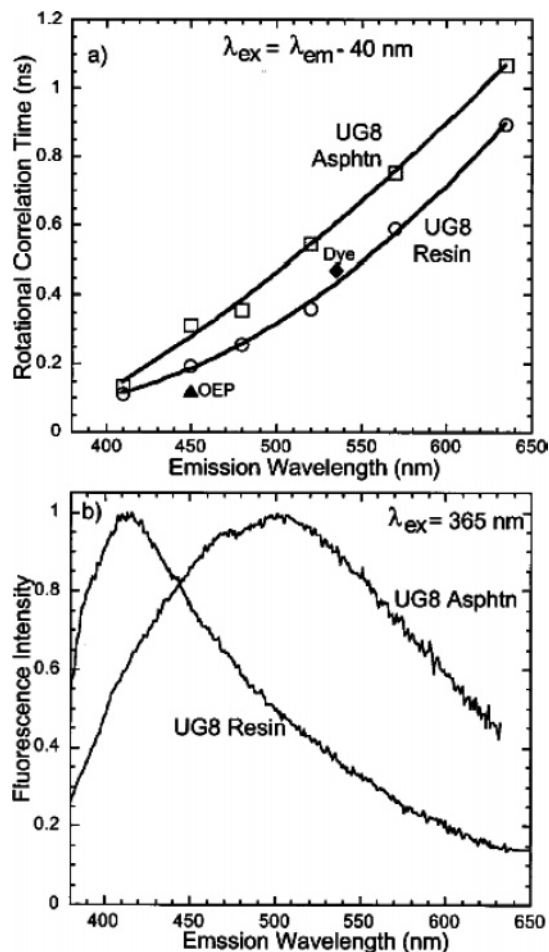


Figure 7. (a) Both resins (the colored portion of the maltenes) and the asphaltenes showing a large variation of molecular size in the visible wavelength range. Large polycyclic aromatic hydrocarbons absorb and emit red light; small PAHs absorb and emit blue light. The huge dependence of asphaltene molecular size on the rotational diffusion of a single PAH shows that there is only one PAH for the bulk of asphaltene molecules. (b) The fluorescence emission spectra of resins and asphaltenes. Most resins are small molecules; the asphaltene population is shifted to a larger molecular size than the resins.

disagreement likely results from a comparison of different physical parameters.

We now examine a foundation of petroleum science. For 70 years, it has been conjectured that petroleum “resins” are surfactant to asphaltenes and stabilize colloidal asphaltene particles;^{21,22} resins are the next most aromatic component of crude oils next to asphaltenes. However, as Buckley states “This model [of resin-asphaltene association] has been adopted by succeeding generations of asphaltene researchers with little further examination and its influence on subsequent research is difficult to overstate.”²⁰ This model has also been seriously questioned by Lockhart and co-workers.¹⁹ The standard laboratory analyses of the samples from the Tahiti field exhibit a large asphaltene gradient but do not exhibit any resin gradient. However, standard analyses of resin mass fractions are somewhat uncertain.

Here, we analyze two samples in detail to determine whether the resins are associated with the asphaltene nanoaggregates. We note that there is always uncertainty whether the two sampling points in the reservoir are, in fact, connected; thus, the following is suggestive. As shown in Figure 7, the largest molecular weight resins are known to absorb light; the redder

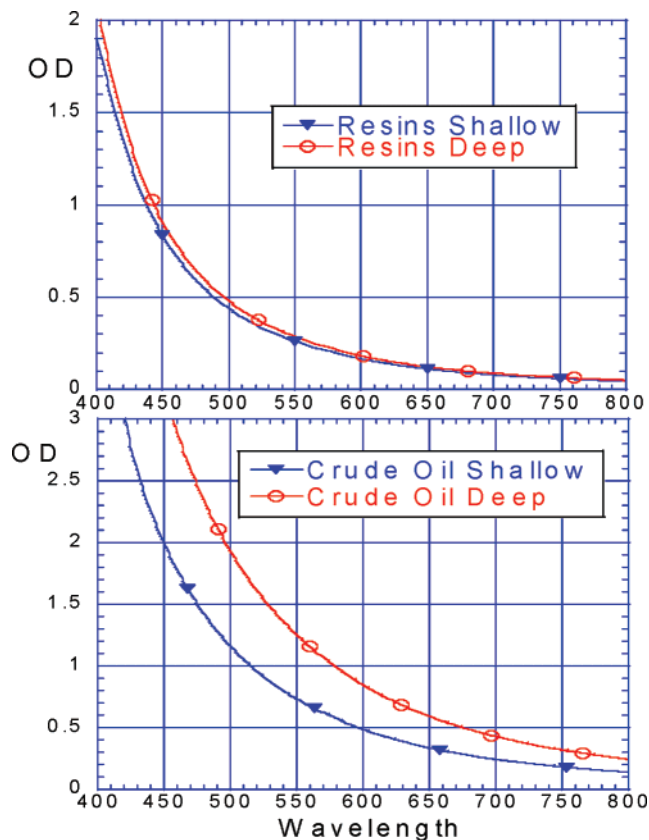


Figure 8. Crude oils in the Tahiti field exhibiting a large asphaltene concentration grading but little resin concentration grading. The asphaltene grading is due to asphaltenes being in nanoaggregates. The lack of a resin concentration gradient shows that the resins are not associated with the asphaltenes in the nanoaggregates.

the light absorption, the larger the molecule.²⁴ Comparison of the rotational diffusion constants of resins and asphaltenes in Figure 7a and the fluorescence emission spectra plotted in Figure 7b show that the resins are mostly smaller molecules than the asphaltenes, as expected. (The heaviest resins are the predominant visible light absorbers in maltenes.) We compare original crude oils where the color is dominated by asphaltenes and those oils lacking asphaltenes due to intentional flocculation where the color is dominated by the heaviest resins. Figure 8 shows for these two samples that the gravitational grading of the heaviest resins is approximately 8%, while the asphaltene grading is a factor of 2. This 8% heaviest resin grading can be represented as a sum of 8% of the heaviest resins exhibiting a factor of 2 grading (in nanoaggregates) and 92% of the heaviest resins showing no grading (molecularly dispersed). This indicates that most of even the heaviest resins are not associated with asphaltene. If we assume the chromophores of the resins and asphaltenes have comparable oscillator strengths, then by knowing measured optical absorption strengths of the crude oil and deasphaltened crude oil, and knowing that only 8% of the colored resins are associated with asphaltene, we obtain that the nanoaggregates consist of 1 part resin per 40 parts asphaltene. The nanoaggregates consist of roughly eight molecules.^{15–17} Thus, out of five nanoaggregates, four have no resin and the fifth only a single resin molecule. The 70-year-old paradigm of petroleum science does not apply to the oils here and likely not to crude oils of similar asphaltene concentration. This 70-year-old paradigm may not apply to any crude oils.

In the course of this work, we have learned of a separate experimental study that also concludes that resins are not

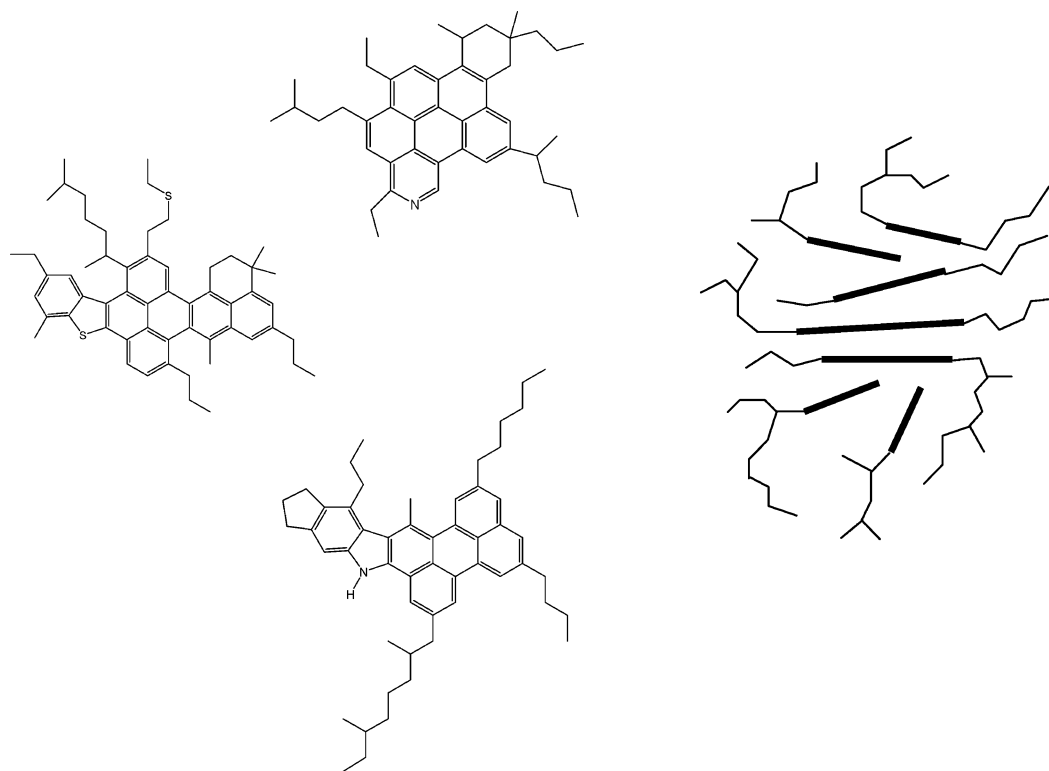


Figure 9. Three asphaltene molecules. The bulk of asphaltenes possess a single fused aromatic ring system. The interior fused ring system of the molecule accounts for intermolecular attraction; the peripheral alkane chains engage in steric repulsion. A two-dimensional cross section of a nanoaggregate is shown on the right. The solid straight lines represent the single fused aromatic ring system per asphaltene molecule; the branched thin lines represent peripheral alkane substituents. The interior of the aggregate concentrates the attractive fused aromatic ring systems. The alkane chains project out, repelling additional asphaltene (or resin) molecules.

associated with asphaltenes, this time in Athabasca bitumen (18.6% asphaltenes) and Maya crude oil (15% asphaltene).⁴² Shaw and Zhao have performed ultrafiltration experiments to learn about the nanocolloidal structure of heavy oil and extra heavy oil. They observe that asphaltenes and undifferentiated oil hang up on filters of various pore sizes. That is, the filters preferentially hold back asphaltenes but not resins. Furthermore, the filtrate is depleted in asphaltenes but not in resins. The obvious conclusion from these studies is that resins are not associated with asphaltenes. We note that these experiments are performed on the heaviest oils, whereas our experiments are performed on medium-weight crude oils. One might complain that the process of filtration could strip resins from asphaltenes. But in our experiments, there is absolutely no energy imparted to the system to perform the measurement. It is an extraordinary and fortuitous occurrence that, after 70 years of no data, we have two complementary studies of a very different nature on very different crude oils with exactly the same conclusion: asphaltenes are predominantly *not* associated with resins. We further note that the nanocolloidal sizes that were determined to exist in the ultrafiltration study are somewhat larger than what we measure here. It is known that asphaltene nanoaggregates cluster at sufficient concentrations.³⁷ It would be no surprise if highly asphaltic systems contain primarily nanoaggregate clusters. Second, filtration can be perturbed by blockages forming in filter pores (flow assurance) or by smaller effective pores created by filtered solids so the ultrafiltration may assess upper limits on size.

All these results are consistent with the measured lack of any resin deposition onto an asphaltene surface (on gold) from a

resin–toluene solution.⁴³ If resins did have a strong association with asphaltenes, one would have expected resin deposition on the asphaltene surface. It is important to note that at an oil/water interface there could easily be some resin and asphaltene species present. The work presented herein treats bulk properties.

Why Little Resin–Asphaltene Interaction? This reservoir study herein and the ultrafiltration study⁴² indicate that there is little resin–asphaltene association. We further note that many studies have shown the existence of asphaltene nanoaggregates in toluene. This reservoir study finds nanoaggregates in crude oil. If resins “did something” to asphaltene nanoaggregates, then we would not find identical nanoaggregates in crude oil, which contains resins, and toluene, which does not contain resins.

The structure of asphaltene nanoaggregates provides a strong indication why resins are not associated with asphaltenes. Asphaltene nanoaggregate structure is dictated by asphaltene molecular structure. Asphaltene molecules predominantly possess a single fused-ring system per molecule (cf. Figure 9). This has been shown in a series of molecular rotational diffusion measurements by TRFD.^{24,25,31} The diffusion of a single PAH of a petroleum asphaltene is consistently found to represent about $1/2$ of the molecular size. Petroleum asphaltenes are about $1/2$ aromatic carbon. Thus, there is roughly one PAH per molecule. Pendant groups containing one or two ring aromatics would have little effect on diffusion constant measurements and are plausible contributors to asphaltene molecular structures. This asphaltene molecular structure has been termed “like you hand” or the “island” model. The “island” model is further supported by known asphaltene molecular weights coupled with

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their optical data.³⁰ Asphaltenes are deeply colored, a canonical property of asphaltene; thus they must have large PAHs.^{30,44} One large PAH per molecule consumes all aromatic carbon in the known small molecular weight of asphaltenes.^{24,25,31,32,38–41} Again, occasional pendant groups containing one or two ring aromatics would not alter these conclusions. Thus, asphaltenes have their attractive forces in their interior (the PAH) and the repulsive part on the outside (steric repulsion of alkanes).⁴⁵

After several asphaltene molecules self-assemble (cf. Figure 9), the high-energy molecular interior is enshrouded in alkanes.^{15,16} This is why the asphaltene nanoaggregates do not grow in size with the addition of more asphaltene in solution;^{15–18} there is no high-energy molecular surface available to stabilize additional asphaltene molecules. We know that the asphaltene nanoaggregates once formed do not grow in size. The NMR diffusion constant of the nanoaggregates remains fixed independent of the asphaltene concentration.¹⁷ In addition, the nanoaggregate compressibility (from ultrasonic velocity) remains fixed independent of the concentration unlike the compressibility of micelles of other surfactants in organic solvents with variable micelle sizes.^{15,16} Thus, the additional asphaltene molecules form additional nanoaggregates. Furthermore, the governing steric repulsion of the asphaltene alkane substituents⁴⁵ is shown by the fact that the asphaltene alkanes undergo restricted diffusion upon formation of the nanoaggregates.¹⁷ Consequently, increasing asphaltene concentration does *not* change the size of the asphaltene nanoaggregates, only their number.^{15–18} Since the high-energy asphaltene molecules cannot bind to the nanoaggregates, then lower-energy resin molecules do not bind. That is, the loss of entropy for a resin molecule binding cannot be overcome by the small resin–nanoaggregate binding. There is no role for resins in this nanoaggregate structure; resins do not act as surfactants to the asphaltene nanoaggregates—the 70-year-old conjecture is probably incorrect. Figure 9 shows representative asphaltene molecules and a cross section of a nanoaggregate. Structures very similar to this nanoaggregate with comparable stacking have been seen with direct molecular imaging in high-resolution transmission electron microscopy of asphaltenes.^{46,47}

It is important to note that an asphaltene nanoaggregate projects predominantly alkanes to the exterior. Consequently, the interfacial tension is very low between the bulk crude oil—predominantly alkane—and the asphaltene nanoaggregate with its exterior alkanes. There have been several literature reports of the lowering of toluene surface tension with increasing asphaltene concentration. As was pointed out, the critical micelle concentration interpretation of these reports was in error;^{15,16,48} the reports were most likely observing nanoaggregate loading on the surface with corresponding surface tension reduction.⁴⁸ The reported concentrations of interest in these misinterpreted

studies match clustering of the nanoaggregates.³⁷ These studies were not observing asphaltene molecules at the surface lowering surface tension;⁴⁸ they were observing the lowering of surface tension due to nanoaggregate loading on the surface.^{15–18,48} The low interfacial tension at the surface of an asphaltene nanoaggregate is in sharp contrast to colloidal oil–water systems which are marked by very high interfacial tension—here, surfactants are required to stabilize colloidal oil–water systems. Such an expectation was incorrectly presumed for asphaltene–organic-solvent and asphaltene–crude-oil systems.

One might change the nature of the asphaltene–resin debate. One might now say that, since the resins are not found on the periphery of asphaltene nanoaggregates, then maybe they are found in the interior of the nanoaggregate. Indeed, such a shift would disclaim the 70-year-old conjecture of surfactant resin. Still, we can consider this “new” conjecture. This discussion immediately becomes embedded in semantics. One would note that single-ring aromatics do not have a tendency to aggregate at room temperature nor at the reservoir temperature. One would then have a cutoff of PAH which does or does not aggregate. Large PAH systems would tend to aggregate; small-enough PAH systems would not.

The definitions of resin and asphaltenes are somewhat arbitrary. Both are defined by an operational definition, not a chemical classification. Here, we have used the definition that asphaltenes are *n*-heptane insolubles. That is, the asphaltenes flocculate in *n*-heptane, but not the resins. Of course, this definition distinguishes those molecular components which tend to flocculate—the asphaltenes—from those that tend not to—the resins. This mirrors the observation that only asphaltenes form nanoaggregates. If we were to use a broader definition of the classification of asphaltenes, say *n*-pentane insolubles, then the asphaltene–resin ratio we obtain for the nanoaggregates of 40:1 would increase. Perhaps with this definition, there would be 0% resin in the asphaltene nanoaggregates instead of 2.5%. But this does not change our thinking regarding the structure of the nanoaggregate, nor its stability in crude oil or toluene.

In addition, we also note that, if we had used multiple flocculations to obtain the asphaltenes, some little lighter mass material would have separated and now be defined as ‘resin’. This would change our asphaltene–resin ratio in the nanoaggregates, but this would have no impact on our conclusions. That is, at the border between asphaltenes and resins, there is some material which participates in nanoaggregates. Nevertheless, by far the bulk of resins do not participate in nanoaggregates and for the most part the (aggregated) asphaltenes do not participate with resins. The *n*-heptane insoluble definition for asphaltenes turns out to be a rather good one. This definition not only captures the most aromatic component of crude oils; this definition also captures those crude oil components that form nanoaggregates.

Conclusions

The new methods of downhole fluid analysis presented here coupled with new insights in petroleum science provide an excellent means to address the largest uncertainty associated with the cost-efficient development of these reservoirs—compartmentalization. In addition, the unusual laboratory of the reservoirs has provided direct evidence that asphaltenes form nanocolloids in crude oils which are quite similar to asphaltene nanoaggregates which form in toluene. Furthermore, the 70-year-old conjecture that resins are surfactant to asphaltenes (in crude oils) appears to be in error. Asphaltene nanoaggregates

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are not a standard micelle system. The resulting new insights on the colloidal and interfacial properties of petroleum promise to have a significant impact on many important economic aspects of oil production including enhanced oil recovery, flow assurance, and wettability.

Acknowledgment. The authors are indebted to Christopher Scott for performing log playbacks to initiate this project.

EF0700883