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ARTICLE *in* ENERGY & FUELS · AUGUST 2010

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On the Nanofiltration of Asphaltene Solutions, Crude Oils, and Emulsions

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Received May 26, 2010. Revised Manuscript Received August 2, 2010

It has long been established that crude oils contain a colloidal suspension of asphaltenes where the mass fraction can range from 0 to 15%. The size of the colloidal particles is less well understood. Crude oil properties depend critically on the asphaltene content, yet measurement of these properties can be hindered by emulsified water and inorganic particulates in heavier crude oils. Here we explore the ability to isolate pure and unaltered crude oil samples using Gore-Tex membranes with nominal pore sizes as small as 30 nm where a transmembrane differential pressure no greater than 60 psi is employed. We first demonstrate that conventional crude oils can pass through a Gore-Tex membrane without alteration of their asphaltene content or their transport properties. Second, we demonstrate that the same filtration process can be used to extract crude oil from a water-in-oil emulsion where the extracted crude's properties are not distinguishable from those of the original crude. Third, we show that these experiments put an upper bound on the asphaltene nanoaggregate size in crude oils. For all experiments, visible–near infrared (VIS–NIR) spectroscopy and Karl Fischer titration analysis are used to determine the potential loss of asphaltenes upon filtration and the effectiveness of the removal of water from emulsions. In all cases, negligible asphaltene loss was detected, indicating that asphaltene nanoaggregates and nanoaggregate clusters are smaller than the 30 nm nominal pore size of the membranes used here. While only small sample volumes were used, membrane separation of pure crude oil is an excellent method for isolating pure, representative crude oil samples.

I. Introduction

Asphaltenes¹ have an enormous impact on most properties of crude oils. Worldwide it is observed that their concentration varies from 0 to 15%, giving rise to an associated variation in crude oil properties. For any aspect of petroleum resource utilization, it is essential to determine the properties of the particular crude oil of interest. One of the confounding issues that hinders such analyses is the presence of emulsified water and inorganic solids. Indeed, emulsion stability is particularly problematic for crude oils, especially in the presence of inorganics,² organic acids³ such as tetraacids,⁴ and, of course, high concentrations of asphaltenes.^{5,6} One approach to obtaining pure crude oil

samples could be to perform nano- or ultrafiltration on crude oil emulsions with hydrophobic filters that pass only crude oil.^{7–11} However, the removal of small water droplets may also cause the removal of crude oil components such as asphaltenes; in such a case, the obtained crude oil samples would not be representative. Indeed, in one study, the ultrafiltration of extra heavy oils and bitumens yielded an asphaltene retentate on ceramic filters at elevated temperatures, with the properties of the filtrate (or permeate) strongly altered compared to those of the feed.^{12,13} Nevertheless, for less asphaltic systems, ultrafiltration may be acceptable.

Asphaltenes are known to be colloidal. Indeed, the term colloid is derived from the Greek *kolla*, meaning glue, and originally pertained to species that do not pass through fine filters. Small-angle neutron scattering and small-angle X-ray

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scattering of asphaltenes show particles in the 3–10 nm range.^{14–22} Particles of this size should not be problematic for ultrafiltration. However, the nature of potentially larger particles is not clear from these studies. Indeed, there has been the suggestion that even the smallest nanoaggregates are ephemeral.²³ Recently, there have been significant advances in our understanding of asphaltene colloidal structure both in toluene solutions and in crude oils. The critical nanoaggregate concentration (CNAC) of asphaltenes in toluene is now known to be on the order of 10^{-4} mass fraction in toluene. Many studies converged on this finding, including high-Q ultrasonics,^{24,25} NMR hydrogen index and diffusion,^{26,27} AC conductivity,²⁸ DC conductivity,^{29,30} and centrifugation.³¹ These studies are consistent with the aggregation number being fewer than 10

molecules of the asphaltene nanoaggregates. Centrifugation of live crude oil (containing dissolved hydrocarbon gases)³² and field studies of gravitational gradients^{33,34} show that these small asphaltene nanoaggregates are found in crude oil. In addition, groups of nanoaggregates are known to form nanoaggregate clusters at concentrations of $\geq 10^{-3}$ mass fraction in toluene. Measurement of flocculate formation kinetics^{35,36} and other flocculation properties³⁷ are most compelling with regard to cluster formation. Indeed, the connection of asphaltene molecular structure, nanoaggregate formation, and cluster formation has been placed into the perspective of a first principles approach under the name “modified Yen model.”³⁸ Less is known about the size of the clusters. It appears that the asphaltene nanoaggregate is fixed in size with an aggregation number of fewer than 10 molecules, and the DC conductivity measurements indicate that the clusters in toluene are composed of fewer than 10 nanoaggregates at the clustering concentration.^{29,30} In addition, for some increases in the concentration of asphaltene, there does not appear to be any growth of the cluster. This is consistent with an oilfield asphaltene gradient where clusters of this size are thought to exist.³⁸ Potentially, at much higher concentrations, larger structures are formed.^{12,13} In addition, the enormous increase in the viscosity of asphaltic systems with the eventual viscoelastic behavior being obtained would suggest structures that have a relation to gels.³⁹ Investigation of the asphaltene structure size issue is complicated because oil is often produced in an emulsified state and extraction of the pure oil from the emulsion can be quite challenging. If the asphaltene cluster size in crude oils was micrometer-scale rather than nanoscale, ultrafiltration with a membrane with nanoscale pores would rapidly result in clogging.

In this paper, we demonstrate that ultrafiltration can be used to extract relatively pure crude oil samples from various crude water-in-oil emulsions without removal of asphaltenes where the water concentration is reduced to mere hundreds of parts per million. The black crude oil had a peak asphaltene concentration of 7.6%, but this should not necessarily be taken as the upper limit. Filters with nominal pore sizes of 30, 50, 100, and 200 nm were used. These filtrations were conducted at ambient pressure (no higher than tens of pounds per square inch as opposed to oilfield reservoir pressures) and at ambient temperature (typically 22–23 °C), 50 °C, and 80 °C. The elevated temperatures were employed to preclude difficulties associated with a separated wax phase and to mimic the reservoir

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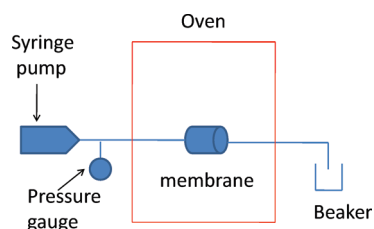
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Table 1. Percentage of Saturates, Aromatics, Resins, and Asphaltenes for the Seven Dead Oils Studied in This Work

dead oil	saturates	aromatics	resins	asphaltenes
North American oil #1	50.1	38	11.7	0.2
North American oil #2	60.8	28.6	10.5	0
Mideast oil #1	46.7	30.2	18.8	4.5
Mideast oil #2	47	27.3	18.7	7.6
South American oil	52.1	27.2	16.1	4.9
Russian oil	45.9	33.9	17.3	3
South Asian oil	63.6	24	12	0.4

**Figure 1.** Schematic of the filtration system employed. The membrane enclosure was able to accept membranes with a range of nominal pore sizes.

temperature. We show that both pure crude oils and crude oil-in-water emulsions were filtered without a decrease in asphaltene concentration. In addition, asphaltene/toluene solutions were also filtered, yielding solutions above and below the CNAC and above and below the clustering concentration.^{24,25} Visible–near infrared (VIS–NIR) spectroscopy was used to monitor the impact of filtration. Density and viscosity measurements of crude oils were taken before and after filtration, and it is shown there is little or no rheological change (no long-term kinetics are seen⁴⁰). Isolation of water-free (or almost free) crude oil samples via ultrafiltration from emulsified crudes revealed little or no change in the transport properties between the original crude and de-emulsified crude.

II. Experimental Section

The crude oils studied here were obtained from the Mideast, South America, Russia, South Asia, and North America. These crude oils were exposed to ambient pressure, thereby removing dissolved gases. In common parlance, the fluids were “flushed” and became “dead” crude oils. These crude oils span a large range of asphaltene content and thus should help identify conditions leading to asphaltene loss with ultrafiltration. However, they would generally be classified as conventional crude oils, though some are highly rich in asphaltenes. The SARA analyses of these crude oils are given in Table 1.

For filtration, oil was pumped through a cartridge containing a Gore-Tex membrane at an upstream pressure no greater than 60 psi (transmembrane differential pressure) with the aid of a K. D. Scientific syringe pump (Figure 1). The temperature of the filter and the upstream tubing was maintained at either ambient temperature, 50 °C, or 80 °C in a forced-air oven (Sigma Systems), but the syringe pump and the collection beaker were kept at ambient temperature. Unless otherwise noted, all filtration took place at 80 °C through a Gore-Tex (GMM-401) membrane with a nominal pore size of 30 nm. In some cases, membranes with pore sizes of 50, 100, and 200 nm were studied as well. The membrane consists of polytetrafluoroethylene which is thermomechanically expanded by the manufacturer for the introduction of pores via a microstructure consisting of nodes connected by fibrils. This material was chosen

because it is currently used in downhole oilfield applications and is not dissolved by known solvents. Section IV discusses characterization of the membrane pore size and geometry by direct imaging and filtration with particles of known diameter to determine the effective pore size. The upstream pressure was monitored with a conventional mechanical pressure gauge, and the downstream pressure was ambient. Because the asphaltene/toluene solutions did not contain waxes, filtration was performed at ambient (22–23 °C) temperature. Samples were transferred from the collection beaker to a cuvette for VIS–NIR spectroscopy measurements, or in some cases, the fluid was directly filtered into a cuvette. A Talboys Bioforce emulsifier was used to emulsify deionized water in crude oil for certain experiments, and the resulting emulsions were stable for at least months because of the surfactant properties of the asphaltenes.

The concentration of asphaltenes is known to linearly impact the coloration of both crude oil and asphaltene/toluene solutions.^{33,41} As such, VIS–NIR spectroscopy is an excellent method for quantifying the potential removal of asphaltenes by ultrafiltration. While some optical properties of crude oils such as fluorescence can be insensitive to emulsion formation, it is well-known that optical transmission measurements in the visible and near infrared are exquisitely sensitive to emulsion formation.⁴² Consequently, isolation of pure crude oil samples from emulsions can be monitored by VIS–NIR spectroscopy with great sensitivity. The predominant effect of emulsions on VIS–NIR spectra is to cause light scattering that is largely wavelength-independent⁴² while the VIS–NIR spectra of asphaltenes are described by the Urbach tail formalism and depend exponentially on photon energy.⁴¹ Thus, the effect of emulsions and of asphaltenes can be separated out for almost all cases.

VIS–NIR spectra of the filtrates (250–2500 nm) were recorded using either a Cary 500 or Cary 5000 optical spectrometer. For these spectrometers, the range of absorbances [or optical densities (OD) for samples exhibiting light scattering in addition to absorption] depends on the wavelength. ODs of >4 are generally not linear, and saturation of the OD value occurs when OD ≈ 5. The baseline consisted of measurements made with an empty optical cell, and all results presented are baseline-subtracted. (A small offset from the Fresnel reflections at two quartz–air interfaces was not corrected for.) Hydrocarbon samples were collected for analysis in cuvettes with a path length of 1 mm. The opacity of the asphaltene-rich crude oils prevented their measurement in cuvettes with longer path lengths.

For experiments with asphaltene/toluene solutions, asphaltenes were extracted from a separate Mideastern black oil using standard procedures. Briefly, an oil sample was diluted 1:40 in *n*-heptane and stirred for 24 h. Asphaltenes were extracted from the solution by vacuum filtration through a nylon filter with a nominal pore size of 1.2 μm and were washed with additional *n*-heptane until the wash solvent was colorless. The extracted asphaltenes were then resuspended in a small volume of toluene to exclude toluene insoluble species such as inorganics. This solution was diluted 1:40 in *n*-heptane, and the asphaltenes were extracted as described above. Finally, the asphaltenes were washed by extensive Soxhlet extraction in *n*-heptane to remove any remaining *n*-heptane soluble compounds.

Viscosity measurements were taken with a Viscolite viscometer manufactured by Hydramotion. Density measurements were taken with an Anton-Paar DMA 35N densitometer or similar device. Measurements were taken at ambient temperature and pressure.

III. Results

A. Filtration of Asphaltene Solutions. Solutions of asphaltenes dissolved in toluene at different concentrations were

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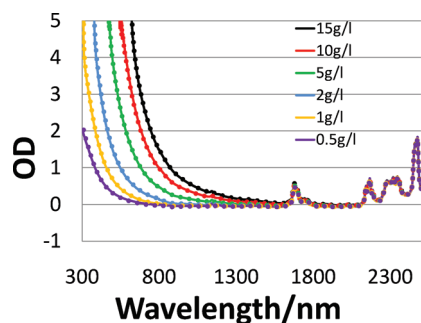


Figure 2. Optical spectra of different concentrations of asphaltenes obtained from a Mideast oil and then redissolved in toluene. The solid lines correspond to the spectra before filtration and the spheres to those after filtration. The two traces of each concentration are color-coded as indicated in the legend. Note that these two traces overlap almost perfectly, indicating that there is little or no difference in asphaltene concentration because of filtration.

filtered at room temperature. For all concentrations studied here, the VIS–NIR spectrum of the filtrate matched the spectrum of the unfiltered solution within experimental error (Figure 2). The dominant experimental error here originates from sample handling. On the basis of experience, we expect an uncertainty consisting of a uniform offset of approximately 0.02–0.03 OD (unitless). This result suggests that essentially all asphaltene passed through the filter for each solution. The solutions of asphaltene in toluene studied here have concentrations ranging from 0.5 to 15 g/L. This range of concentrations was selected to cover both of the asphaltene aggregation states commonly thought to be encountered in black oils: nanoaggregates, which occur at concentrations greater than ~ 0.1 g/L, and clusters, which occur at concentrations greater than ~ 5 g/L.^{28–30,35,36,38,43} The fact that nearly all asphaltene passed through the filter constrains the size of both asphaltene nanoaggregates and asphaltene nanoaggregate clusters to well below the 30 nm nominal pore size of the filter; in general, particles must be 3 times smaller than the pore size to avoid bridging.⁴⁴ This constraint is consistent with previous experiments suggesting that asphaltene nanoaggregates are ~ 2 nm in size and clusters ~ 5 nm.^{29,38,43} Experiments demonstrating that the actual effective pore size is comparable to the nominal pore size are presented in section IV. This result is in agreement with the DC conductivity measurements³⁰ and with field studies.³⁸

B. Filtration of Crude Oils. A wide range of crude oils were filtered with membranes to establish the ability of asphaltene-rich crudes to pass through nanoscale membrane pores. Two examples are shown where the optical spectra of filtered and unfiltered oils agree quite well within experimental error (Mideast oil #2 and South American oil in panels a and b of Figure 3, respectively). The five optical spectra obtained from Mideast oil #2 (7.6% asphaltene) in Figure 3a appear to almost perfectly superimpose. One of these spectra was obtained with the unfiltered crude, and the four others were obtained after filtration with membranes with nominal pore sizes of 30, 50, 100, and 200 nm. This indicates that there are no asphaltene nanoaggregates or nanoaggregate clusters present that are larger than the effective pore size of any of

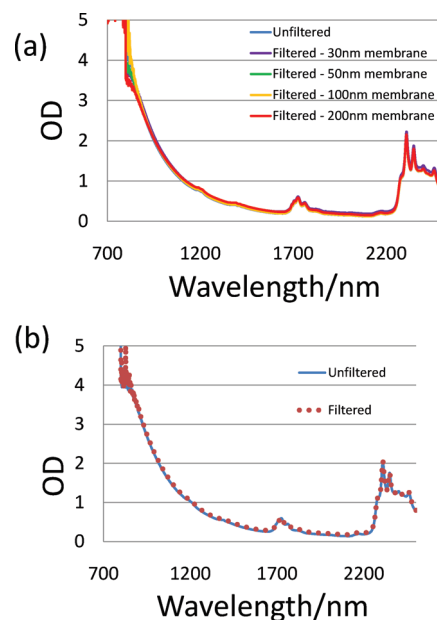


Figure 3. (a) Spectra of Mideast oil #2 before filtration and after passing through filters with nominal pore sizes of 30, 50, 100, and 200 nm. All filtrate spectra overlay very well with the spectrum of the crude oil prior to filtration. (b) Spectra of South American crude oil before and after filtration (nominal pore size of 30 nm) overlay almost perfectly.

these membranes. Presumably, the membrane with a nominal pore size of 30 nm possesses the smallest effective pore size, and its dimensions will be characterized in section IV. Similar agreement between unfiltered and filtered oil is found with South American oil (4.9% asphaltene) in Figure 3b for a membrane with a nominal pore size of 30 nm. Consistent results were obtained for each of the other crude oils listed in Table 1. The very slight spectral differences in absorption barely visible in Figure 3b are seen to be independent of pore size and are attributed to experimental limitations such as sample handling.

An examination of the membrane surface (nominal pore size of 30 nm) after filtration revealed very little retentate to the extent that obtaining a sufficient quantity to analyze proved difficult. Presumably, the retentate could include fines and flocculated molecules with a length scale greater than the nominal pore size of the membrane. Jamaluddin and co-workers have commented on the filtration of live crudes through similarly hydrophobic membranes and observed that there was a significant amount of retentate containing asphaltenes that did not pass through a $0.22\ \mu\text{m}$ pore size membrane.^{45–49} Others have studied similar phenomena for

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Table 2. Viscosities and Densities of Crude Oil Samples before and after Filtration Are in Agreement within Experimental Uncertainty

dead oil	viscosity before (cP)	viscosity after (cP)	% viscosity difference	density before (g/cm ³)	density after (g/cm ³)	% density difference
Mideast oil #1	14	14.7	−5	0.871	0.874	−0.3
Mideast oil #2	43	44	−2	0.896	0.896	0
South American oil	21.8	23.8	−10	0.878	0.88	−0.2

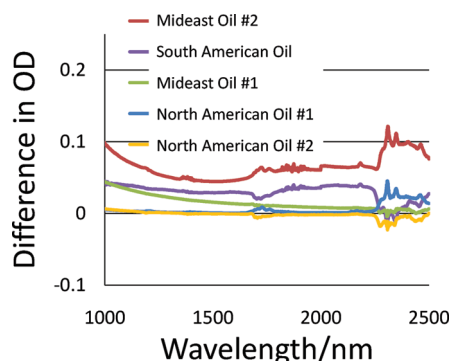


Figure 4. Difference plot of optical spectra obtained after filtration (nominal pore size of 30 nm) less that obtained before filtration for four dead oils. In each case, the optical spectrum has shifted slightly upward due to evaporation of the lighter components. The red, purple, green, blue, and orange curves correspond to Mideast oil #2, South American oil, Mideast oil #1, North American oil #1, and North American oil #2, respectively.

downhole application.⁵⁰ We conclude that the crude oils pass through the membrane unimpeded as long as there is not a significant amount of asphaltene flocculation due to a reduction in pressure or addition of alkane. In our experiments, the quantity of retentate is sufficiently small that its removal does not significantly alter the optical density or transport properties of the filtrate with respect to those of the original oil, as we will show in the following paragraphs.

We point out that filtration of heavy oils with ceramic membranes with a nanoscale pore size has been used to reduce the asphaltene concentration, presumably because of a larger effective size of the asphaltene cluster size in the heavy oil environment.⁵¹ We emphasize that the oils studied here, while rich in asphaltenes, would be generally considered conventional rather than heavy. The configuration of asphaltenes in conventional oils as compared to heavy oils may be what allows them to pass through the 30 nm nominal pore size of the membranes employed here.

The optical density should decrease if molecules in the crude oil were impeded from passing through the membrane. However, we find that the optical density actually increases after filtration, indicative of another process (Figure 4). Optical absorbance differences are no more than 0.1, and this difference most likely arises from evaporation of the more volatile (thus colorless) components from the crude oils. A similar change in the magnitude of the optical density was found for oils that were left exposed to air for a period of time equal to that necessary for filtration. While efforts were made to employ a septum during our filtration experiments to minimize evaporation, this was found to be difficult to implement because of the development of back pressure in the sample collection bottle.

Good agreement was found between the density and viscosity of filtered and unfiltered oils, which is shown in Table 2. Viscosity is extremely sensitive to asphaltene content and increases faster than exponentially with respect to asphaltene concentration.³⁹ Because there is no change in the asphaltene content as determined by optical absorption measurements, no change in viscosity is expected before and after filtration. Nevertheless, if there were a substantial long-lived disruption of the asphaltene colloidal structure, there could be an impact on viscosity. Viscosity measured before and after filtration was the same within measurement error, suggesting there is no colloidal disruption of asphaltenes due to this filtration. The slight increase in viscosity after filtration may be attributed to the same effect as the increase in opacity.

While we mainly report here on filtration performed at 80 °C to simulate the average temperature of the oilfield reservoir formation from which the crudes were extracted, similar studies were performed at 50 °C and ambient temperature. In all but one case, very good agreement was found between the spectra for filtered and unfiltered crude. The exception originated from a simulated crude that consisted of a Central American heavy oil with a taffylike consistency that was diluted 10-fold with hexadecane. This dilution intentionally triggered a flocculation of an asphaltene-like substance that precipitated rapidly and accumulated on the membrane surface. While the size of these flocculates was not measured, it was observed that they did sediment quickly, indicative of structures that are significantly larger than 1 μm in size, with best estimates of $\sim 100 \mu\text{m}$ as they were visible by eye. The spectra of the filtered simulated crude showed a dramatically reduced optical density compared to that of the unfiltered crude because the flocculates could not pass through the membrane. This would not be representative of a live crude oil flowing through an oilfield formation. Finally, we mention that a crude oil that was below its wax onset temperature would cause a similar effect as wax crystals that were larger than the effective pore size of the membrane would not pass through the membrane.

C. Emulsification of Water in Crude Oils. Water was emulsified in several crude oils to test the hydrophobic membrane's ability to extract oil at water concentrations ranging from 0.025 to 25% (v/v). Representative spectra of such emulsions are shown in Figure 5 for the South American crude oil, where the average optical density of the emulsion can be seen to increase with water fraction. The optical absorption of the asphaltenes is exponential in this spectral range,⁴¹ but emulsions can give rise to both wavelength-dependent and wavelength-independent light scattering depending upon the droplet size.⁴² The predominant optical effect from low-water concentration emulsion formation here is strong wavelength-independent light scattering as the emulsified oil contains water droplets equal to or greater than the wavelength of light as verified by optical microscopy. For water concentrations of $< 2.5\%$, the presence of emulsified water merely displaces the spectra vertically by an amount that grows monotonically with water

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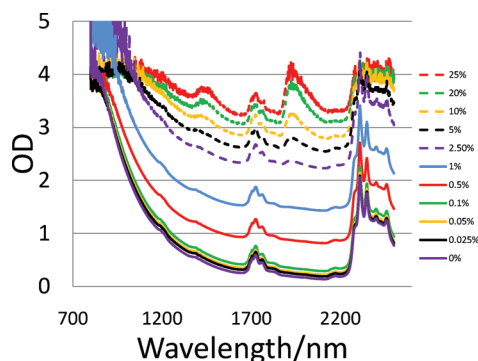


Figure 5. Spectra of water emulsions formed with South American crude oil. The water volume fractions are listed. The average optical density (OD) increases dramatically with an increase in water fraction. At the higher water fractions, the water peak at 1900 nm is evident. Spectrometer nonlinearities start to dominate at OD values of ≥ 4 .

concentration. We note that a slight increase in water concentration over this small range here cannot be readily distinguished from a slight increase in the asphaltene concentration. The well-known water peak at 1445 nm is seen only for water concentrations of $\geq 2.5\%$.

D. Extracting Pure Crude from Emulsified Crude. The hydrophobicity of Gore-Tex membranes and their small nominal pore size (30 nm) create a high capillary pressure for water. If the differential pressure across the membrane is kept below the capillary breakthrough pressure, the hydrocarbon phase passes through the membrane whereas the aqueous phase is blocked.^{52–55} The predominant emulsion formed with crude oil is a water-in-oil emulsion,^{5,6} aiding in separation of the pure oil phase with the membrane. Surfactants in the continuous hydrocarbon phase allow the close approach of water droplets yet add stability by preventing their coalescence. The consequence is that the membrane is always in contact with the continuous crude phase, enabling it to operate acceptably even for high water fractions.

We take advantage of these properties to extract a relatively pure hydrocarbon phase from a 20% (v/v) water-in-oil emulsion. Figure 6a shows three spectra: one from the original crude oil before emulsification, one after emulsification with water, and one after emulsification and subsequent filtration. Note the high optical density of the crude oil with emulsified water as seen earlier in Figure 5. The low optical density of the filtered emulsion recovers the original spectrum, albeit with a slight upward vertical offset. This offset was seen each time after the filtration of an emulsion with a relatively large water fraction. Careful examination reveals that this uniform spectrum offset could not be entirely ascribed to evaporation. Evaporation gives rise to a multiplicative difference for the coloration, but Figure 6a shows an additive, not multiplicative, spectral offset. Because only water droplets significantly smaller than the wavelength of light

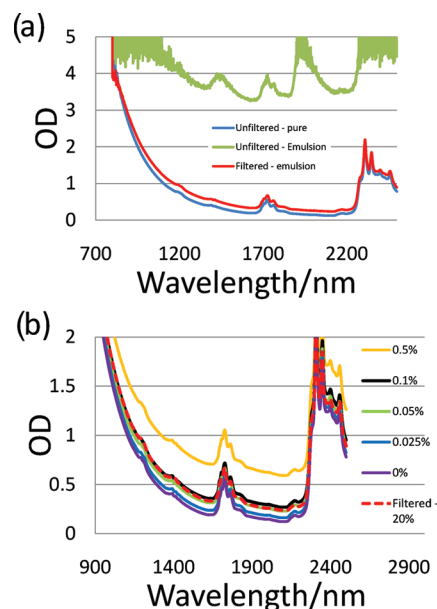


Figure 6. (a) Spectra of pure crude oil (blue), crude oil emulsified with 20% (v/v) water (green), and the filtrate of the emulsion (red) extracted with a membrane with a nominal pore size of 30 nm. The spectrum of the filtered emulsion is very similar to the spectrum of a crude oil emulsion with a water fraction between 0.05 and 0.1% (shown in panel b) and suggests that there may be a small amount of water that passes through the membrane during filtration. (b) Spectra of water emulsified into oil at levels ranging from 0 to 0.5%. The filtrate curve (red) from panel a is replotted here to show that such an absorption spectrum is consistent with a water content of 0.075% (interpolated). The crude used for both panels was Mideast oil #2.

should pass through the membrane, any residual water in the filtrate may lead to Rayleigh scattering. The small length scale of the droplets could then give rise to λ^{-4} Rayleigh scattering and increase the optical absorption at short wavelengths. The weakness of this effect probably prevents our observation of it here, and the spectral offset must originate from a small quantity of well-dispersed water that passes through the membrane.

For the sake of comparison, Figure 6b shows the spectra of emulsions with the same crude oil used in Figures 5 and 6a, but with emulsified water fractions of 0, 0.025, 0.05, 0.1, and 0.5%. The filtered emulsion spectrum of Figure 6a agrees best with the emulsion with a water fraction of 0.075% (interpolated spectrum), suggesting that a similar amount of water passed through the membrane. In general, it was found that the higher the initial concentration of water in the emulsion to be filtered, the higher the concentration of water after filtration through the hydrophobic membrane, consistent with the concept of a small and almost insignificant water flux.

In a separate experiment, Mideast oil #1 crude was emulsified with water fractions ranging from 0 to 25% (v/v). The mixture was then filtered through the membrane with a nominal pore size of 30 nm at 80 °C, and Karl Fischer titration analysis was performed on the filtrate. The water content was determined to be on the order of 100–200 ppm (0.01–0.02%), close to the threshold for detection.

During the filtration of 5–10 mL of emulsion, it was noted that the flow rate decreased. As a dead-end style of filtration was employed here, the water and other components of the crude that did not pass through the membrane necessarily concentrated on the membrane surface. For the sake of comparison, Figure 7a shows the absence of any significant

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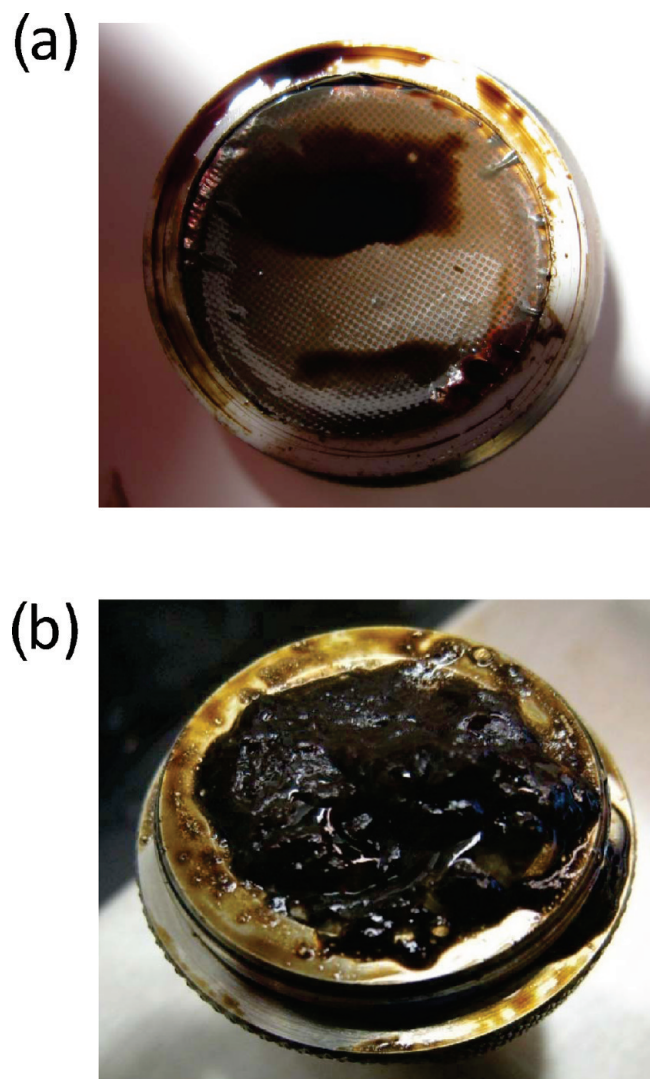


Figure 7. (a) Little or no crude retentate is observed on the membrane surface after filtration of several milliliters of Mideast oil #2. The fluid seen in the image consists of the original oil itself because the membrane has not been cleaned or wiped dry. One could anticipate that fines and particulates would be trapped on the membrane surface for a sample with significant contamination. The periodic structure originates from the metallic mesh that supported the membrane. (b) Water-rich gelatinous mixture that is retained by the filter (retentate) when filtering an emulsion with the hydrophobic membrane. The filtrate consists of nearly pure crude oil.

level of retentate left on the membrane surface from filtering a pure crude (Mideast oil #2). In stark contrast, Figure 7b shows the gel-like dark material that was typically found on the membrane surface after filtration of an emulsion. The figure shows that the quantity of the emulsion retentate is orders of magnitude larger than that found when non-emulsified crudes were filtered. Inspection revealed that this gel contained a large quantity of water. This type of membrane fouling is intrinsic to dead-end filtration which necessarily concentrates on the membrane surface those components (such as water) blocked by the membrane. In contrast, cross-membrane filtration does not suffer nearly as much from this problem as the membrane is continually swept by the fluid flowing tangential to the membrane surface.^{7,8} While cross-membrane filtration is the preferred method, its implementation requires a quantity of fluid much larger than what was available for our laboratory studies.

The emulsification of water in crude oil results in dramatic changes in its transport properties, but the extracted filtrate obtained using the hydrophobic membrane possesses the transport properties of the original crude. In the first example, we present measurements of the viscosity of two crude oils before and after emulsification [20% (v/v) water], where we see a significant increase in viscosity after emulsification (Table 3a, column 4). It is well-known that the viscosity of emulsified crude increases dramatically with water fraction and becomes non-Newtonian, impeding efforts to recover the viscosity of the original Newtonian crude.⁵⁶ For Mideast oil #1 and South American oil, we took viscosity measurements both after emulsification and after subsequent filtration to remove the water and recover the original crude (Table 3a, column 5). The viscosity of the filtered emulsion is significantly higher than the viscosity of the original crude because of the competing effect of evaporation, but similar to that for the crude allowed to evaporate for a similar amount of time (Table 3a, column 6). The percentage difference in viscosities between the filtered emulsion and the original crudes is well within the experimental uncertainty (Table 3a, column 7) and suggests that we have recovered a hydrocarbon with the same viscosity as the original crude.

The interfacial properties of the original crude recovered after filtration of the emulsion were not measured. It is entirely possible that some of the molecules confined to the oil–water interface did not pass through the membrane because they reside in the aqueous phase. Much progress has been recently made on the study of the composition of these molecules by Czarnecki and co-workers.⁵⁷ For a very water-rich emulsion, one could envision a scenario in which the membrane significantly depleted the crude oil of a significant fraction of its asphaltenes and other surface active atoms and molecules. However, for the range of water concentrations used here (0–25%), the asphaltene content of the filtrate does not appear to be greatly changed.

A similar set of experiments was performed to measure the density of two different crude oils after emulsification and subsequent filtration. Results with Mideast oil #1 are presented in Table 3b and those with the South American Oil in Table 3c. Emulsification of water into oil results in a small but significant increase in the emulsion's density because of the greater density of water with respect to oil. This density can be seen to increase with the degree of emulsification in column 2 and is described in terms of percentage in column 3. After filtration, the densities of the filtered crude are significantly reduced (column 4), and they agree well within experimental uncertainty with the densities of the original crudes, after taking evaporation into account. We estimate the experimental uncertainty here of the accuracy to be 0.003 g/cm³ based on long-term use of the laboratory hand-held densitometer with hydrocarbon and aqueous standards of well-known densities.

IV. Characterization of Membrane Pore Size

A. Calculation of the Nominal Pore Size by the Manufacturer. W. L. Gore & Associates provides a nominal pore size for each membrane that they sell. According to documentation provided by the manufacturer, this pore size is calculated from a measurement of the breakthrough pressure of

(56) Kokal, S. Crude Oil Emulsions: A State-Of-The-Art Review. SPE Production & Facilities, February 2005, Vol. 20, Number 1, pp 5–13, 77497-PA.

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Table 3. Viscosities and Densities of Emulsified Crudes before and after Filtration^a

(a) Mideast Oil #1 and South American Oil						
dead oil	% water in oil	viscosity of emulsion (cP)	% increase in emulsion viscosity ^b	viscosity of filtered emulsion (cP)	viscosity ^c of “pure” oil after evaporation (cP)	% change in viscosity ^d
Mideast oil #1	5	14.8	5.71	17.5	19	−7.89
Mideast oil #1	20	22.3	59.29	23	22	4.55
South American oil	10	25.3	29.74	31.5	32.4	−2.78
South American oil	20	35	79.49	39	36.5	6.85
(b) Mideast Oil #1						
% water in oil	density of emulsion (g/cm ³)	% increase in emulsion density ^e		density of emulsion after filtration (g/cm ³)	% increase in density ^f	
5	0.879	0.92		0.881	0.34	
10	0.884	1.49		0.88	0.23	
15	0.89	2.18		0.881	0.34	
25	0.896	2.87		0.881	0.34	
(c) South American Oil						
% water in oil	density of emulsion (g/cm ³)	% increase in emulsion density ^g		density of emulsion after filtration (g/cm ³)	% increase in density ^h	
5	0.886	0.91		0.883	−0.34	
10	0.892	1.59		0.886	0.00	
25	0.905	3.08		0.889	0.34	

^a Results demonstrate the transport properties of the original crude can be recovered after filtration of the emulsified crude through the hydrophobic membrane. ^b The percent increase due to emulsification when compared to the viscosity of the dead oil without evaporation. The viscosity of pure Mideast oil #1 is 14 cP. The viscosity of pure South American oil is 19.5 cP. ^c To most accurately compare viscosities of filtered emulsions and unfiltered crudes, crude samples were allowed to evaporate for the same amount of time required for filtration of emulsions. Filtration took between 4 h and 8 h. ^d The percent increase when compared to the original dead oil sample that was allowed to evaporate for about the same amount of time as required for filtration. ^e The percent increase when compared to the density of the dead oil. The density of pure Mideast oil #1 is 0.871 g/cm³. ^f The percent increase when compared to the density of the dead oil after evaporation for a time similar to that needed for filtration (1 h). The density of pure Mideast oil #1 after evaporation for 1 h is 0.878 g/cm³. ^g The percent increase when compared to the density of the dead oil before evaporation occurs. The density of pure South American oil is 0.878 g/cm³. ^h The percent increase when compared to the density of the dead oil after evaporation was allowed for a time similar to that needed for filtration (1 h). The density of pure South American oil after evaporation for 1 h is 0.886 g/cm³.

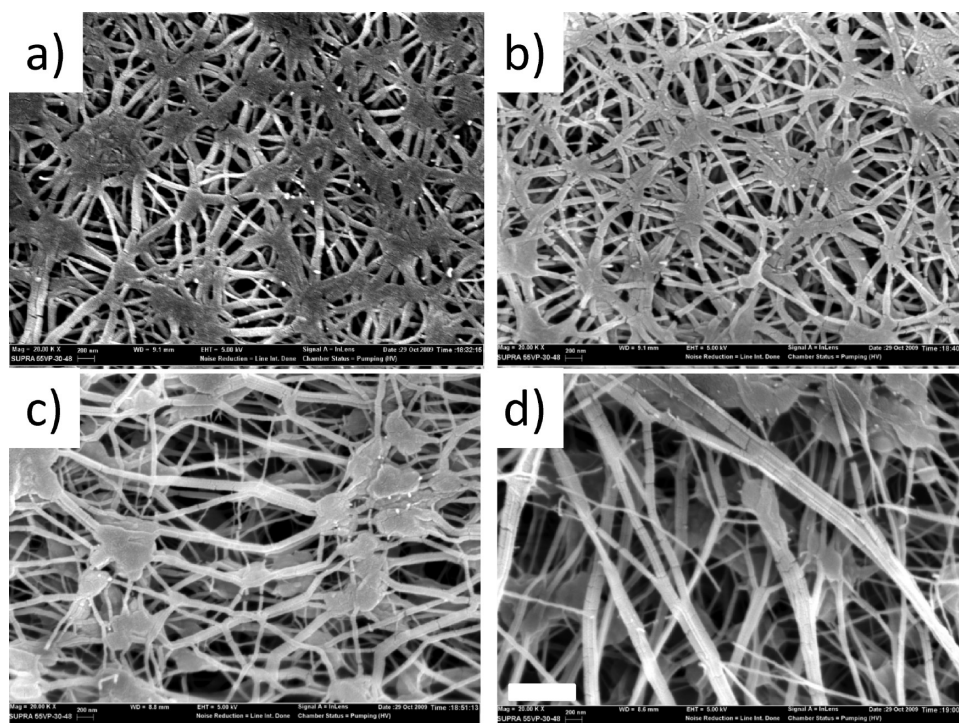


Figure 8. SEM micrographs of Gore-Tex membranes where panels a–d correspond to membranes with nominal pore sizes of 30, 50, 100, and 200 nm, respectively. The torturous path presented by the fibrils and nodes makes direct measurement of an effective pore size impossible by direct imaging; nonetheless, there is a clear trend in panels a–d where the void space between fibrils increases. The scale bar in panel d corresponds to 1000 nm.

2-propanol that is then correlated to a pore size using the Laplace equation (Gore Quality Assurance Test Method 177). However, the manufacturer points out that the pore

size is ill-defined as the torturous path provided by the permeable membrane is not sufficiently regular to generate an estimation of a pore size diameter. Hence, we will use

other more direct methods to characterize the effective pore size in what follows.

B. Direct Imaging via Electron Microscopy. The membranes used here were coated with a 5 nm thick layer of gold and imaged using a Zeiss scanning electron microscope operated at a relatively low beam voltage. Figure 8 shows representative images of the nodes and fibrils of the membranes for reported nominal pore sizes of 30, 50, 100, and 200 nm. While the average distance between fibrils can be seen to increase with the nominal pore size, it is not readily apparent how to assign or measure an effective pore radius for filtration from these images.

C. Determination of Filter Pore Size by Filtration. The effective pore size of the Gore-Tex membrane was measured via a set of filtration experiments with particles of well-defined size. A suspension of fluorescently labeled sulfate polystyrene latex microspheres of known diameter was forced through the membrane with a nominal pore size of 30 nm using the same filtration apparatus employed for all asphaltene studies. The vendor reports that transmission electron microscopy (TEM) is used to measure the microsphere size as well as the standard deviation. The relative concentration of spheres before and after filtration was determined by measurement of their fluorescence intensity. Because the spheres were suspended in water, it was necessary to modify the wettability of the hydrophobic Gore-Tex membrane with ethanol before filtration. The spheres were excited at 490 nm, and their relative concentration was determined by integration of the fluorescence intensity of the solutions in the emission range of 515–750 nm.

Figure 9 shows the results of the microsphere filtration experiments. Spheres with diameters of 19 ± 3 , 60 ± 5 , and 110 ± 5 nm at a concentration of 10^{14} particles/mL of deionized water were filtered. The left panel shows the fraction of spheres of each diameter that passed through the membrane. The right panels show the emission spectra of each solution before and after filtration. The nominal pore size of 30 nm is consistent with these measurements showing that most, but not all, of the 19 nm diameter spheres pass through the membrane while most of the 60 nm spheres do not. Hence, we can determine an effective pore size of the membrane to be between 19 and 60 nm. The fact that all of the asphaltenes are found to pass through this membrane suggests that aggregated asphaltenes in toluene are significantly smaller than 60 nm in diameter, and probably even smaller than 19 nm. We will further discuss the implications for crude oils in the next section.

Figure 9b shows that the fluorescence signal is linearly proportional to the concentration of microspheres over the relevant range here. The point at the top right (relative fluorescence intensity = relative concentration = 1) corresponds to the prefiltration concentration. The concentration can be reduced by a factor of 20 and still be in the linear range.

V. Discussion and Conclusions

Asphaltene nanoaggregates are characterized by aggregation numbers of <10 molecules per nanoaggregate. Clusters of nanoaggregates form at well-documented concentrations in toluene and are believed to exist in crude oils, particularly where asphaltenes have been destabilized. The size of the asphaltene nanoaggregate clusters is less well-known; nevertheless, there are indications in the literature that asphaltene

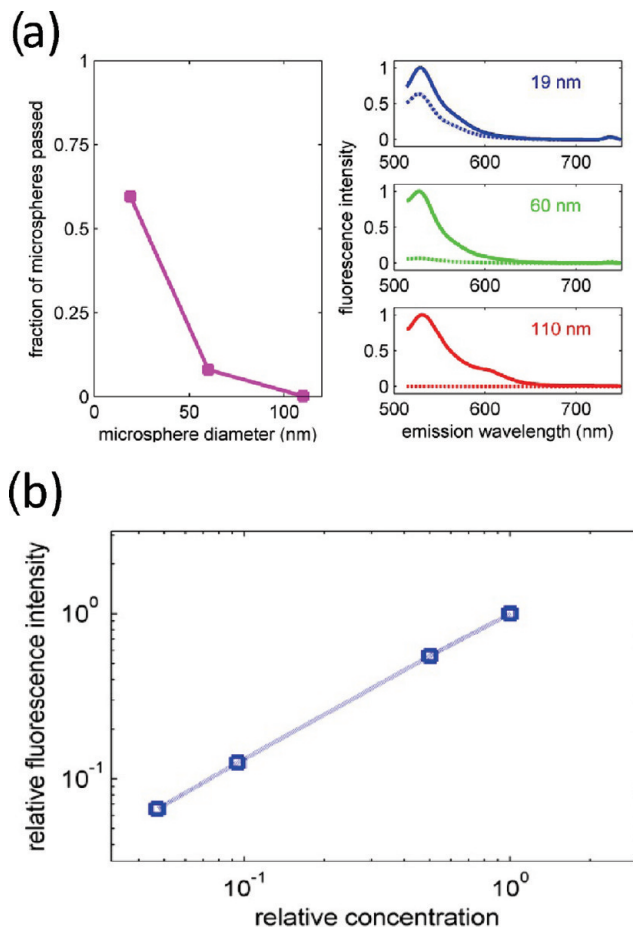


Figure 9. (a) Fraction of microspheres able to pass through the membrane with a nominal pore size of 30 nm as determined by fluorescence intensity for microspheres with diameters of 19, 60, and 110 nm (left). Fluorescence emission spectra of the solutions before (—) and after (···) filtration (right). Spectra are normalized to the peak of the before-filtration spectra. These data suggest that the effective pore size is somewhere between 19 and 60 nm. The same magnification is used for all 4 panels. (b) Graph showing the linearity of fluorescence intensity vs the concentration of fluorescent microspheres.

clusters consist of fewer than 10 nanoaggregates at least in some circumstances, resulting in a structure size significantly smaller than the effective pore size of many hydrophobic membranes. Consequently, the concept of using hydrophobic filters for separation of pure and representative crude oil samples is founded on reasonable expectations.

Our results of filtration of crude oils, emulsions, and asphaltene/toluene solutions establish that ultrafiltration can be used to obtain unaltered crude oils and asphaltene in toluene solutions. For asphaltene in toluene solutions, the CNAC is well-established.^{24,25} These experiments were performed with asphaltene concentrations greater than the CNAC, guaranteeing that the asphaltenes exist in at least nanoaggregates and possibly higher aggregation states. We have measured the effective pore size of the smallest nominal pore size Gore-Tex filters available (manufacturer reported a nominal 30 nm pore size) to be between 19 and 60 nm. Hence, this work suggests that the maximum size of the asphaltene aggregate is significantly below 60 nm, likely even below 19 nm. While this work has included identical filtration tests on crude oils, it is more difficult to establish the existence of asphaltene nanoaggregate clusters in such crudes that would have difficulty traversing the nanoscale pores of a membrane.

However, we have demonstrated that one can pass asphaltene-rich crudes through hydrophobic membranes with essentially no loss of asphaltene content, suggesting that asphaltene structures in crudes are significantly smaller than the effective membrane pore size.

Filtration of crude oil emulsions with a hydrophobic membrane is shown to produce a filtrate that is almost completely water-free. The small quantity of remaining water in the filtrate is estimated by optical measurements to be less than 0.075% (v/v); Karl Fischer titration analysis estimates an even lower value. The optical spectra of the filtered emulsions are

very similar to that of the original crude oil, with the exception of a small vertical offset due to a little residual light scattering. Consequently, all the methods for optical analysis of crude oils can be employed. Finally, the transport properties of the filtered emulsions are shown to be indistinguishable from that of the original crude oils.

Acknowledgment. We cheerfully acknowledge useful conversations with A. K. M. Jamaluddin and the electron microscopy work of Elizabeth Smythe, Totoro, and the Harvard University advanced imaging facility.