Effect of Water on Deposition, Aggregate Size, and Viscosity of Asphaltenes

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Ⓢ *Supporting Information*

ABSTRACT: The aggregation and structure of polar molecules in nonpolar media may have a profound effect on bulk phase properties and transport. In this study, we investigate the aggregation and deposition of water and asphaltenes, the most polar fraction in petroleum fluids. In flow-line experiments, we vary the concentration of water from 500 up to 175 000 ppm and provide the evidence for clear changes in asphaltene deposition. Differential interference contrast (DIC) microscopy and dynamic light scattering (DLS) are used to measure the size of the aggregates. Rheological measurements are performed to get fixed ideas on the structural changes that water induces at different concentrations. This study demonstrates the significant effect of water on asphaltene aggregation and deposition and explores the molecular basis of water–asphaltene interaction. Our aggregate size measurements show that while asphaltene molecules increase the solubilization of water, there is no increase in the aggregate size. Our aggregation size measurements are different from the reports in the literature.
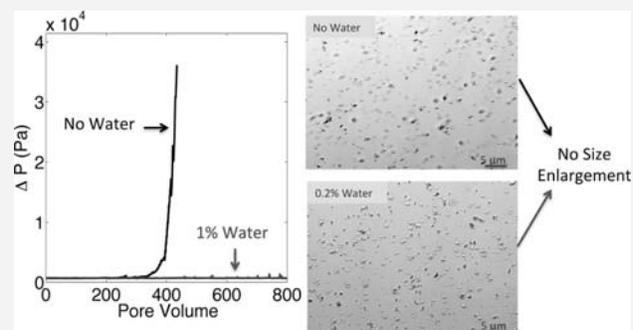
INTRODUCTION

Asphaltene deposition is a serious problem in petroleum production caused from either gas injection or depressurization of the petroleum fluid, resulting in slowdown in production and operational shutdowns for removal of the deposited aggregates.[1]

Asphaltenes are the most polar aromatic components of petroleum fluids. They are operationally defined as part of crude oil that is insoluble in light alkanes such as heptane and pentane and soluble in aromatic solvents such as toluene and xylene.[1] They are charged entities with metals and heteroatoms (i.e., nitrogen, oxygen, sulfur, etc.).

Crude oil is often coproduced with formation water. There is limited and controversial data on the effect of low water concentrations (solubilized) on asphaltene aggregation and deposition. Water can appear in three different forms in oil systems: solubilized, emulsified, or free water. Nonpolar oils dissolve very small amounts of water depending on the saturation limit of the type of oil. Beyond the saturation limit, water becomes either emulsified when surfactants are added or separates as a free water phase. Water-in-oil (w/o) emulsions have been studied extensively in the literature; such emulsions are highly undesirable in crude oil production.[2] The w/o emulsions can form to a high volume ratio of water to oil. In this work, we investigate the effect of small amounts of water.

Andersen et al. have tested the effect of solubilized water in trace amounts (ranging from 0 to 470 ppm on a mass basis) on the aggregation behavior of asphaltenes in toluene.[3] They have performed calorimetric measurements of asphaltene association and reported that the heat absorption data indicates asphaltenes interact with water. They have also studied the effect of water on association of asphaltenes—what they called micellization of asphaltenes—and observed a stepwise association rather than showing a classical micelle formation mechanism. They have measured the heat of titration with and without water and discovered that water increases the heat of titration significantly in the mixture of asphaltenes and toluene. Andersen et al. have employed a Karl Fischer titration coulometer to determine water solubility in a mixture of asphaltene particles and toluene. Without asphaltenes, the solubilized water content in toluene is around 0.04%, 400 ppm (w/w), and when 20 g/L asphaltene is added to toluene, the water content increases to 0.1%, 1000 ppm (w/w). From their limited data, they approximated a linear relation between the uptake of water and asphaltene concentration. Their calculation shows that an asphaltene molecule interacts with 1.2 water molecules. They speculated two possible explanations for the increase of water solubility in the presence of asphaltenes: one explanation is that water molecules in the organic solvent act as a bridge between asphaltene molecules, and another possibility is that water molecules can form microdroplets that make up the center of the aggregates of asphaltenes, forming a w/o microemulsion.

However, they hesitated drawing any conclusion due to their limited experimental data. From the solubility results, they calculated the Gibbs free energy transfer of a free water molecule to the asphaltene aggregate and concluded the presence of hydrogen bonding either between water and oxygen/nitrogen-containing groups in asphaltenes or between water and aromatic rings.

Tharanivasan et al. have studied emulsified water in the Athabasca bitumen and a Gulf of Mexico crude oil with various dilutions of *n*-heptane.[4] They have measured the asphaltene precipitation yields and compared the results for oil–heptane solutions with and without emulsified water (water-in-oil emulsion) up to 50 wt %. Their results indicated that asphaltene precipitation yields are the same for the samples with and without emulsified water. They also characterized the composition of precipitated asphaltenes and observed no difference between the samples with and without emulsified water.[4]

Khvostichenko et al. employed infrared spectroscopy and the Flory–Huggins model to study water molecules in an asphaltene–toluene solution and found that the solubility of water in the organic phase (toluene) increases with increasing asphaltene concentration—water concentration is around 0.04% (w/w, 400 ppm) in pure toluene as mentioned above and increases steadily with concentration of asphaltenes up to 0.09% (900 ppm) at 20 g of asphaltenes in 1 L of the organic solution. The solubility result is consistent with Andersen et al.[3] From IR spectroscopy data, they determined the state of water molecules both as free and bound molecules via hydrogen bonding to monomeric and aggregated asphaltenes.[5] They did not measure asphaltene aggregate size in their mixtures.

In a molecular mechanics simulation study, Murgich et al. analyzed the effect of water on asphaltene aggregation in toluene.[6] Molecular mechanics calculation is based on determining the most stable configuration of molecules or aggregates in a solution by employing analytic functions to represent bond stretching, bending, and nonbonded energies of molecules such as electrostatic interactions, dispersion attraction, and exchange repulsion. Their calculations showed that water increased the association of asphaltene monomers to form dimers due to H bonding created by water molecules between the heteroatoms of asphaltenes. Murgich et al. only studied asphaltene monomers and dimers; their result was qualitative rather than quantitative in terms of aggregate size of asphaltenes. They confirmed their results with experimental studies by comparing enthalpy of association performed by titration calorimetry. Their results indicate H bonding to be important for asphaltene aggregation.

A molecular simulation study using density functional theory (DFT) was performed by da Costa et al. to determine the effect of π–π stacking and hydrogen bonding interactions of one, two, three, and four water molecules to the aggregation of asphaltene dimers.[7] Their analysis showed the formation of two water bridges composed of one, two, or three water molecules per bridge between two asphaltene monomers, which provided additional stabilization of asphaltene aggregates due to hydrogen bonding. Their enthalpy and Gibbs free energy calculations proved hydrogen bonding to be as important as π–π interactions in asphaltene aggregation.

The literature reviewed above provides the evidence of increased solubility of water in toluene when asphaltene molecules are added to the mixture. There is suggestion that water and asphaltene molecules form hydrogen bonds. There

are no reports of aggregate size measurements. There are also no reports of increased water solubility in petroleum fluids. In flow-lines asphaltene aggregates and may deposit. There are no reports of the effect of water on deposition. The main goal of this work is to investigate the interaction between water and asphaltene molecules in petroleum fluids. In this work, we present results from an extensive set of flow experiments in 1 mm diameter stainless steel tubing to examine the effect of water on deposition. We then report the effect of water at the ppm level (1000 and 7000 ppm) on aggregate size in petroleum fluids. Next we discuss the viscosity measurements of three petroleum fluids mixed with water to shed light on the structure of the aggregates.

■ MATERIALS AND METHODS

We obtain our petroleum fluids, BAB and MN-133, from two different regions in the Middle East: BAB from Abu Dhabi and MN-133 from Kuwait. Bitumen is from an Athabasca field in Canada. A summary of the relevant fluid properties is provided in Table 1. "*f*" denotes the

Table 1. Material Properties of MN-133, BAB, and Bitumen

petroleum fluid	f (g/g)	μ (Pa·s)	ρ (g/mL)	nitrogen content (mass %)	water content (ppm)
MN-133	0.0088	0.0043	0.8193	0.20	10
BAB	0.0156	0.0055	0.8394	0.16	120
bitumen	0.17	244.63	1.0061	0.51	N/A

asphaltene content of the oil in grams of asphaltene/grams of oil. The asphaltene content is measured by mixing 1 g of oil with 40 mL of *n*-heptane. Then the solution is sonicated and filtered through 0.2 μm pore size cellulose nitrate membrane filters (Whatman). Viscosity measurements are conducted using a stress-controlled rheometer with parallel and two-degree cone–plate geometry (Anton Paar, MCR 302). The density (ρ) is measured with densitometer from Anton Paar (DMA 5000). A coulometer is employed to measure the water content of the petroleum fluids in parts per million (Karl Fischer 331 coulometer). In order to measure the total dissolved solids (TDS) and conductivity of water samples, we employ SevenGO conductivity meter from Mettler Toledo.

Pressure drop measurements are performed in a pipe-flow setup, which consists of three syringe pumps (KD Scientific), two manifolds (Cole Parmer), steel and brass T-junctions, a pressure transducer, and a pipe. We employ a 30 cm long stainless steel pipe with 1 mm i.d. The schematic of the setup is shown in Figure S1 (see Supporting Information). Heptane, crude oil, and water flow from different pumps at different flow rates and mix in the stainless steel pipe. When the water syringe is deactivated, mixing of heptane and crude oil results in asphaltene deposition in the pipe; hence, pressure drop increases with time. The water syringe pump is activated for the runs with DI water or brine. Prior to flow experiments, DI water is deaired with a vacuum pump for 20 min to eliminate pressure changes caused by air bubbles. All flow-line experiments are repeated at least three times and are performed at room temperature (Figures 1 and 2, Figures S2–S4). When DI water concentration is reported for each test, we use volume percentage to indicate the DI water concentration to compare to the total volume of solution, including the volume of *n*-heptane, and the ppm values are given as the mass of DI water when compared to the mass of crude oil.

A contact angle goniometer (VCA-2500 from AST Products, Inc.) is used to measure DI water and petroleum fluid contact angles (Figure 3) on the surface of stainless steel.

Asphaltene aggregate images are obtained by differential interference contrast (DIC) microscopy (Biorad Model 1024) and aggregate sizes are counted by ImageJ to analyze the number of aggregates of different sizes per area of 1000 μm^2 (Figures 4–6). Samples are prepared by mixing *n*-heptane and MN-133 oil (2 v/v), and images are
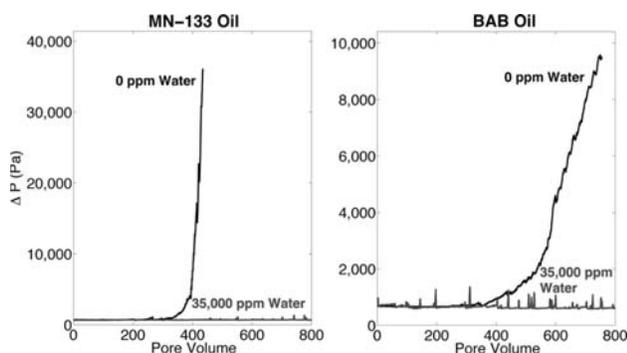
Figure 1. Panel on the left shows the pressure drop versus pore volume of *n*-heptane and MN-133 oil (2 v/v) with 0 and 35 000 ppm DI water. Panel on the right shows the pressure drop versus pore volume for *n*-heptane and BAB oil (3 v/v) with 0 and 35 000 ppm DI water.
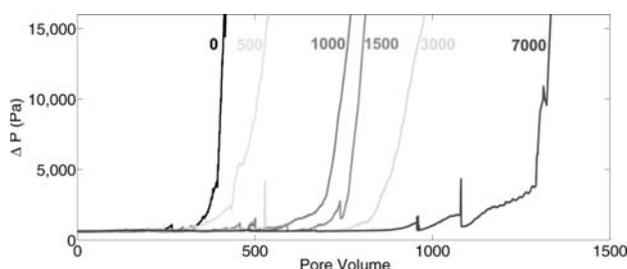
Figure 2. Pressure drop versus pore volume for *n*-heptane and MN-133 oil with 2 v/v ratio. The number for each line indicates the amount of water in ppm.
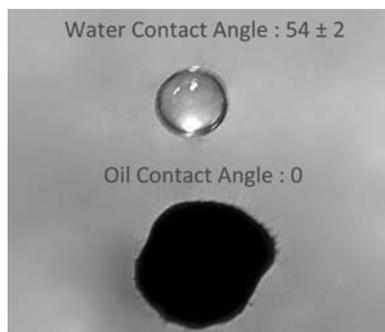
Figure 3. Image of water and oil (MN-133) droplets on stainless steel surface and their respective contact angle measurements.

Figure 4. Images of asphaltene particles with and without water (7000 ppm) in a mixture of *n*-heptane and MN-133 oil (2 v/v). The size measurements are performed 45 min and 24 h after mixing.

Table 2. Dynamic Light Scattering (DLS) Results of *n*-Heptane with MN-133 Oil at 100 v/v and 120 v/v Ratio[a]

sample	mean aggregate diam (μm)
heptane + MN-133 (100 v/v)	1.7 ± 0.1
heptane + MN-133 (100 v/v) + 7000 ppm DI water	1.5 ± 0.1
heptane + MN-133 (120 v/v)	1.4 ± 0.1
heptane + MN-133 (120 v/v) + 7000 ppm DI water	1.6 ± 0.3

[a]7000 ppm DI water by volume is added to each sample, and aggregate diameter is measured.

Table 3. Viscosity Data of Various DI Water Concentrations in *n*-Heptane and MN-133 Samples Mixed at 2 v/v Ratio (Same Ratio Used in Pipe-Flow Experiments)[a]

sample	viscosity (mPa·s)	viscosity change (%)
0 ppm DI water in MN-133 oil	0.93 ± 0.04	
500 ppm DI water in MN-133 oil	0.71 ± 0.03	−24
1000 ppm DI water in MN-133 oil	0.74 ± 0.03	−21
1500 ppm DI water in MN-133 oil	0.78 ± 0.03	−17
2000 ppm DI water in MN-133 oil	0.76 ± 0.03	−18
5000 ppm DI water in MN-133 oil	1.11 ± 0.06	19
10 000 ppm DI water in MN-133 oil	1.09 ± 0.05	17

[a]Below 2000 ppm, the water containing samples have average of 20% less viscosity. Above 5000 ppm the viscosity increases around 20%.

Table 4. Viscosity Data of Various DI Water Concentrations in Bitumen Samples[a]

sample	viscosity (Pa·s)	viscosity change (%)
0 ppm DI water in bitumen	245 ± 1	
1000 ppm DI water in bitumen	229 ± 1	−6
4000 ppm DI water in bitumen	252 ± 2	+3
6000 ppm DI water in bitumen	261 ± 2	+7
10 000 ppm DI water in bitumen	271 ± 2	+11

[a]Above 4000 ppm, viscosity increases with increasing water concentrations.

taken at two different time points: 45 min and 24 h after mixing. The samples with water have 1000 and 7000 ppm DI water in the solution. We also investigate the aggregate size in toluene dilution by mixing 50% by volume toluene with MN-133 oil overnight. Then the solution is mixed with 50% by volume *n*-heptane. For samples with water, DI water is mixed at the time of *n*-heptane addition, and images are taken at 45 min and 24 h after mixing. All samples are mixed in a bath sonicator for 2 min before measurements.

Dynamic light scattering is performed with a compact goniometer system from ALV, at a scattering angle $\theta = 90°$ and wavelength $\lambda = 532$ nm (Table 2). Samples are bath-sonicated for 2 min right before the measurements are made.

Viscosity data of petroleum fluid samples with DI water (Tables 3 and 4, Table S1) is obtained with the rheometer mentioned above (Anton Paar). Sample preparation for MN-133 and BAB oil (light crudes) is as follows: DI water is added to the oil at different water contents and mixed in a bath sonicator for 1 h. After the sonication, *n*-

heptane is mixed with the solution at 2 v/v for MN-133 and 3 v/v for BAB oil, and then the mixture is bath-sonicated for another 2 min. Bitumen is mixed with DI water in a bath sonicator for 1 h before the measurements.

■ RESULTS AND DISCUSSION

Table 1 summarizes the characteristics of the three petroleum fluids investigated in this study: MN-133, BAB, and bitumen. The first two fluids have low asphaltene content (0.9% for MN-133 and 1.6% for BAB, weight basis) and water content (10 and 120 ppm, for MN-133 and BAB oil, respectively). Bitumen has high asphaltene concentration of 17 wt %. Nitrogen contents of MN-133 and BAB oil are close (0.2% and 0.16%), whereas bitumen has higher nitrogen content (0.51%) and this may be due to the fact that bitumen has considerably higher asphaltene content than the two light crudes (MN-133 and BAB). Asphaltenes contain nitrogen and other heteroatoms such as oxygen and sulfur (not quantified in this work), which may provide hydrogen bonds that are discussed in the literature mentioned above. Bulk rheology measurements reveal MN-133 and BAB oil to be a Newtonian fluid with viscosity of μ = 0.0043 Pa·s and μ = 0.0055 Pa·s, respectively, at the shear rates between 10 and 100 s^{-1}. Bitumen is a viscous Newtonian oil with viscosity of 244.6 Pa·s at the shear rates between 0.1 and 10 s^{-1}.

We present the results from extensive sets of flow-line measurements to examine the effect of water on deposition. There are no reports of such data in the literature to the best of our knowledge. The schematic of the flow-line setup is presented in Figure S1 (see Supporting Information); the details have been provided in the previous section. In Figures 1 and 2 and Figures S2–S4, we present pressure drop versus pore volume for different pipe-flow experiments. Pore volume is defined as the total fluid volume that a pipe can hold. When we plot the pore volume in the x-axis, it represents the number of pore volumes injected in the tube. We perform tests with n-heptane and oil in different ratios and measure the pressure drop as asphaltene particles deposit on the walls of the pipe. In the field conditions, the problem of asphaltene deposition occurs as a result of depressurization or by injection of gases. In depressurization thousands of pore volumes pass through the flow-line prior to asphaltene deposition buildup. However, we induce aggregation by mixing the petroleum fluid with n-heptane for lab scale studies.

In Figure 1, the left panel shows the pressure drop versus pore volume for n-heptane and MN-133 oil at 2 v/v ratio in 1 mm pipe with flow rate of 42 pore volumes/hour (0.165 mL/min) in 0 and 35 000 ppm DI water. At 35 000 ppm, water is not soluble in oil in vial observations; however, we do not observe any separation during the pipe-flow experiments, which may be due to mixing effect of flow. A gradual pressure buildup is detected for 0 ppm, and at around 400 pore volumes the pressure drop is as high as 34 000 Pa. When 35 000 ppm DI water by mass in crude oil (1% by total volume) is run through the third syringe pump, the pressure drop stays steady around 700 Pa—the base pressure during the entire test. The plot on the right shows similar results for BAB oil. The asphaltene deposition is observed with n-heptane and BAB oil at 3 v/v ratio in 1 mm pipe with flow rate of 22 pore volumes/hour (0.11 mL/min) with 0 ppm DI water. While cleaning the pipe, one can clearly see the asphaltene aggregates coming out of the pipe when there is no water used. MN-133 and BAB present different clogging patterns—experiment with MN-133 clogs

suddenly at around 400 PV whereas the BAB oil run goes through gradual asphaltene deposition between 400 and 800 PV. This could be due to the fact that crude oils are from different sources and asphaltene concentration and compositions are different. However, when 35 000 ppm DI water by mass in crude oil (1% by total volume) is introduced to the system, asphaltene deposition is not observed for the duration of the tests. When cleaning the pipe, we observe almost no asphaltene deposition on the walls of the pipe for the runs with DI water. The effect of water in preventing or delaying the asphaltene deposition is observed for both MN-133 and BAB oil; we conclude that the effect is not specific for only one type of oil.

In Figure S2 (see Supporting Information), we vary the water concentration from 7000 ppm by mass in the crude oil. This concentration is obtained with the lowest flow rate of the syringe pump and corresponds to 0.2% by total volume—to 175 000 ppm DI water by mass in crude oil (5% by total volume). The ratio of n-heptane to MN-133 oil is 2 v/v in the 1 mm pipe with flow rate of 42 pore volumes/hour (0.165 mL/min). Note that in the inset graph the pressure drops are zoomed from 0 to 2000 Pa for clarification to see if there is variation in pressure drop behavior with changing water concentration. We observe no significant difference among the tests and conclude that 7000 ppm DI water by mass in crude oil (0.2% by total volume) is adequate to observe the effect of water on eliminating the asphaltene deposition for the pore volumes tested. In all pipe-flow tests, note that the fluctuations are higher in higher concentrations of water—maximum absolute fluctuation reaching 1000 Pa, starting from 800 Pa up to 1800 Pa—possibly due to structural changes induced by water molecules in asphaltene aggregates. Air bubbles cannot cause these fluctuations as we deair all water samples prior to our experiments.

In Figure 2, we examine the effect of low concentrations of DI water in MN-133 oil and observe the effect of water in ppm levels—in these runs; the water is mixed with oil and sonicated for an hour before injecting the solution into the pipe. We notice that MN-133 oil without water clogs around 400 pore volumes whereas the tests with DI water delay the clogging up to 1300 pore volumes. Evidently, the delay is strongly dependent on the concentration of DI water.

In Figure S3 (see Supporting Information), we double the test duration to 1600 pore volumes with total flow rate of 42 pore volumes/hour (0.165 mL/min) for MN-133 and 28 pore volumes/hour (0.11 mL/min) for BAB oil and observe no asphaltene buildup during the experiment for both crudes with 35 000 ppm DI water by mass (1% by total volume).

In Figure S4 (see Supporting Information), the results of pressure drop from 35 000 ppm DI water and 35 000 ppm brine by mass (1% of total volume) in n-heptane and MN-133 oil with 2 v/v ratio are presented in the 1 mm pipe with flow rate of 42 pore volumes/hour (0.165 mL/min). The brine solution has 144.89 g/L NaCl in DI water, compatible with the water in MN-133 wells. Both runs, brine and DI water, have the same effect on delaying the asphaltene deposition for the duration of our experiments; therefore, we conclude that brine is also effective in delaying the aggregation/deposition of asphaltenes. In future studies, this topic could be further explored to investigate the effect of brine in asphaltene aggregation and deposition.

Evidently, water delays the deposition of asphaltene aggregates. There are two possible explanations for this drastic
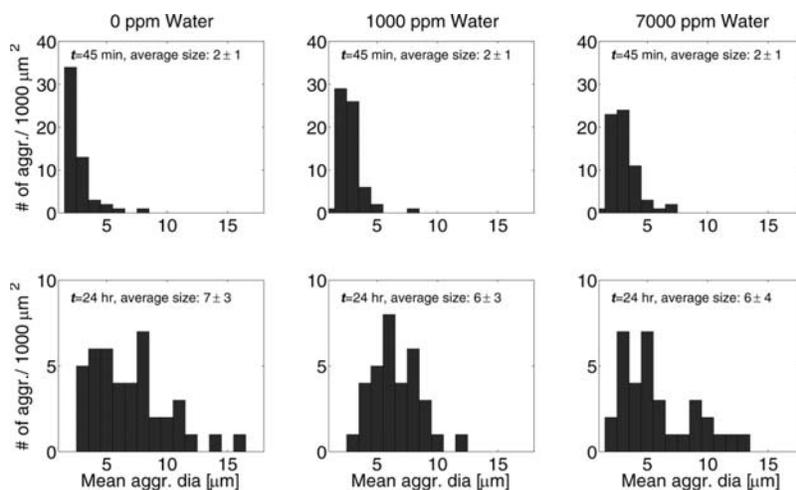
Figure 5. Size distribution of asphaltene aggregates with various concentrations of water (0, 1000, and 7000 ppm) in a mixture of *n*-heptane and MN-133 oil (2 v/v). The size measurements are performed 45 min and 24 h after mixing as indicated in the legend. Aggregate sizes are counted with ImageJ.

effect of water on pipe-flow experiments. One hypothesis is that water forms a layer around the steel pipe and prevents asphaltene from depositing. Another possibility is that water molecules interact with asphaltene molecules and decrease the size of aggregates or change the aggregates from hydrophobic to hydrophilic states. In order to determine if the effect is due to the formation of water layer around the pipe, we measure the contact angle of DI water and oil on stainless steel (SS) surface. Figure 3 shows the image of DI water and oil droplets and their respective contact angle measurements. Visibly, water droplets form beads and oil spreads over the surface denoting that oil is more surface-wetting than water. The contact angle of water on SS surface is $54 \pm 2°$, and when the surface is immersed into oil and then oil is removed, the water contact angle increases to $82 \pm 1°$. Crude oil and *n*-heptane spread over the SS surface immediately after placement; hence, contact angles are reported as 0. These results indicate that the first hypothesis may not be valid. Our contact angle results are in agreement with previously published data. Roero studied the contact angle of water on stainless steel surface with different drop volumes and reported the values between $50°$ and $70°$.[10] Starkweather reported the contact angle of quench oil on stainless steel surface to be between $3°$ and $6°$.[11]

We measure the size of asphaltene aggregates by differential interference contrast (DIC) imaging in order to determine the effect of water. Figure 4 shows DIC imaging results. The panels on the right have 7000 ppm DI water. The images are taken 45 min and 24 h after preparation of samples. There is no discernible difference in aggregate size when comparing the images from the effect of water. As expected, the size of the asphaltene aggregates increase over time. We quantify the number of aggregates at each image by ImageJ and present them in Figures 5 and 6.

Figure 5 shows the size distribution of asphaltene aggregates with and without water. For the samples without water at 45 min, the aggregate sizes average around 2 μm—the aggregates are mostly concentrated around 2 μm although the range is between 2 and 8 μm. In the presence of water at 45 min, the sizes range from 1 to 8 μm averaging around 2 μm. The measurements at 24 h after mixing have larger asphaltene aggregate sizes and have slightly lower number of aggregates as
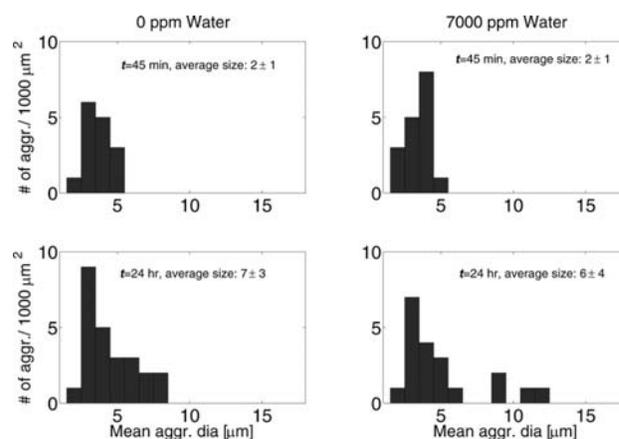
Figure 6. Size distribution of asphaltene aggregates with and without water when MN-133 oil is diluted with toluene (50% by volume) and then *n*-heptane is added at 1−2 (volume of MN-133 + toluene/ volume of *n*-heptane) ratio. The size measurements are performed 45 min and 24 h after mixing. Aggregate sizes are counted with ImageJ.

expected since with time, the smaller aggregates coalesce and form larger particles. There is no noticeable difference at both times among the samples with and without water. The size distribution of aggregates are different for 0, 1000, and 7000 ppm DI water, but the average aggregate sizes are the same. We also perform experiments with toluene dilution (50% by volume) and observe similar results in Figure 6. The literature reports the effect of water on size of asphaltene particles in organic solvents, specifically in toluene.[3,5] These studies discuss the interaction of water with asphaltenes and speculate that water increases the size of asphaltene particles (see Supporting Information for details of these studies) .[3,6,8] Our results provide, for the first time, direct measurements on the effect of water in asphaltene aggregate size. We show that there is no measurable size change from the effect of water at 1000 and 7000 ppm.

To confirm our DIC imaging results, we also employ dynamic light scattering (DLS) to measure the aggregate size of asphaltenes (Table 2). The light scattering techniques require very dilute solutions to minimize the effect of multiple

scattering. We measure the size of aggregates at two different dilutions of *n*-heptane and MN-133 (100 and 120 v/v) at 45 min after mixing. The DIC imaging shows no size difference in samples with and without water. Note that DIC measurements inherently have larger errors than DLS (DIC results in 2 ± 1 for 0 ppm water after 1 h, whereas DLS provides 1.7 ± 0.1); they both indicate the same size range.

In Table 3, we show the viscosity of mixture of *n*-heptane and MN-133 samples (2 v/v—note that this is the same ratio as in pipe-flow measurements which will be discussed shortly) containing various DI water concentrations (in ppm). MN-133 oil behaves as a Newtonian fluid in the range of shear rates that the experiments have been performed ($10-100$ s^{-1}). Up to 2000 ppm DI water concentration, the viscosity reduces around 20% compared to the sample without the addition of water. Above 5000 ppm, the viscosity increases about 20%. The reduction in the viscosity can be indicative of smaller asphaltene aggregates.[9] The increase in the viscosity may be also explained as the structural changes induced by the excess of water molecules. There may be also emulsion formation, which could cause larger asphaltene aggregates. Our sizing results by DIC and DLS measurements do not reflect the increase in asphaltene aggregate size. The same trend in viscosity change is also observed for BAB oil as seen in Table S1 (see Supporting Information). Below 2000 ppm, there is not much change in viscosity from the sample without added water. Above 5000 ppm, the viscosity increases ∼30%. BAB oil has more initial water than MN-133 oil (120 ppm vs 10 ppm), and this may be the reason for the different trend below 2000 ppm. BAB oil viscosity measurements are also performed between 10 and 100 s^{-1} shear rate and show constant viscosity, indicating the samples to be Newtonian. In Table 4, we examine bitumen between the shear rates of $0.1-10$ s^{-1} (higher shear rates may disturb the sample). Bitumen has higher asphaltene content (17%) than MN-133 and BAB (1% and 2%, respectively). In bitumen, 1000 ppm DI water reduces viscosity by 6%. Above 4000 ppm, the viscosity increases with increasing water concentration. All viscosity measurements are performed at least three times for each sample for which the standard deviations are provided in Tables 3 and 4. The trend for the three oils is consistent although their composition and asphaltene content is different.

Pipe-flow measurements and the viscosity data provide strong evidence for interaction of asphaltenes with water molecules. Water solubility decreases as the number of carbon atoms in *n*-alkanes and aromatics increase.[12,13] Schatzberg et al. report that the number of carbon chains is indirectly proportional to the solubility limit of water. For instance, solubility of water in C_7 is 91 ppm, C_{10} is 72 ppm, C_{12} is 65 ppm, and C_{16} is 64 ppm.[12] Wing et al. showed the solubility of water in aromatics to decrease with the number of carbon atoms; solubility limit of water in benzene (C5) is 554 ppm whereas in toluene (C7) it is 334 ppm.[13] The systems, which include heteroatoms with alkyl chains and aromatics, show high water solubility. Stephenson et al. studied the water solubility in pyridine samples and reported the solubility of water to be around 10% by mass.[14] Therefore, asphaltenes through the heteroatoms are the components of crude oil that interact with water. Asphaltenes are composed of fused benzene rings with aliphatic chains, heteroatoms (O, N, S), and metals (Fe, V, Ni).[15] Water molecules most likely interact with heteroatoms oxygen, sulfur, and nitrogen on the surface of asphaltene aggregates via hydrogen bonding, therefore delaying the

deposition of aggregates. The presence of hydrogen bonding may change the hydrophobic state of asphaltenes to hydrophilic. Arunan et al. give a clear description of hydrogen bonding as "The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X−H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation".[16] In asphaltenes, oxygen exists mostly in OH groups and can be found in peripheral aromatics or in aliphatic chains.[17] Nitrogen can be found in pyrolic (5-member ring) or pyridinic (6-member ring) form. Sulfur mostly exists as thiophene (5-member ring), sulfide type groups (R−S−R), or sulfoxide (R−S(=O)−R).[18] These heteroatoms (O, N, S) in asphaltenes can form hydrogen bonds with water molecules.[8] Generally, the hydrogen bond between O and N is stronger than the S atom.[19] Further studies are needed to determine the number of O, OH, and NH heteroatoms in an asphaltene molecule to decipher where the hydrogen bonding mostly occurs. The techniques may include Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analysis in order to firmly establish this hypothesis.[8,20]

■ CONCLUDING REMARKS

This study centers on assessing the effect of small amounts of water on deposition behavior of asphaltenes in flow-lines, their aggregate size, and viscosity. We present flow-line experiments to elucidate the effect of water on deposition of asphaltenes. Our data show that water delays the deposition of asphaltenes most likely due to hydrogen bonds between the water molecules and heteroatoms (N, O, S) in asphaltenes. As a result of the hydrogen bonding, the aggregates will be less likely to adsorb onto the metal pipe surface. We have demonstrated that the size of the asphaltene aggregates is independent of water molecules. Our findings reveal the viscosity to decrease up to about 2000 ppm water concentration and then increase in higher concentrations due to structural changes that water induces in the asphaltene aggregates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S4 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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