

APPLIED SCIENCES AND ENGINEERING

Ablation of water drops suspended in asphaltene/heptol solutions due to spontaneous emulsification

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Complex molecules from crude oil, such as asphaltenes, can adsorb onto oil/water interfaces. This creates a viscoelastic network that may cause difficulties in oil recovery and oil spills. In addition to stabilization of oil/water emulsions, they may also cause the spontaneous formation of micron-sized droplets. Here, we investigate spontaneous emulsification in the presence of asphaltenes, probing parameters that may affect this phenomenon by observing isolated drops of water immersed in asphaltene/hydrocarbon solutions within a co-flow microfluidic device. The results indicate that the initial internal pressure of the drop strongly influences the rate at which the drop will shrink due to spontaneous emulsification. In addition, the viscoelastic skin formation by the asphaltenes inhibits increases in this pressure that normally accompanies a decrease in drop radius. Understanding this spontaneous emulsification has implications not only for the oil industry, but also to the cosmetics, foods, medical, and pharmaceutical industries.

INTRODUCTION

Water-in-oil emulsions are frequently encountered in the production and refining of crude oils. For example, the desalting process is one of the first steps performed in an oil refinery and has the purpose of removing corrosive salts from the crude oil. This is accomplished by a liquid-liquid extraction process where water is mixed with the crude oil. Later, this mixture undergoes a separation process, where after the oil enters the refining process and the water, after being treated, is discharged into the environment. The efficacy of the separation process between oil and water during the desalting process has economic and environmental impacts.

Complex molecules from crude oil, such as asphaltenes, are well known to adsorb on oil/water interfaces where they form a viscoelastic layer and stabilize oil/water emulsions, causing difficulties in the separation process (1–3). These surface-active poly-aromatic hydrocarbon molecules are defined by solubility—they are the fraction of crude oil soluble in toluene and insoluble in *n*-heptane (4, 5)—which is the source of complexity. Moreover, it has been recently found that asphaltenes may cause a spontaneous emulsification at the oil/water interface, where micron-sized droplets spontaneously appear at the oil/water interface (6). As shown in that work (6), most of the spontaneously emulsified droplets consist of water droplets in the oil phase; however, oil droplets in the aqueous phase are also present. Although that was the first report on spontaneous emulsification in the presence of asphaltenes, bulk experiments from the literature also report that asphaltenes increase the solubility of water in organic solvents (7, 8). Andersen *et al.* (7) did suggest that this increase in solubility could be achieved by a micro-emulsion zone at the oil/water interface, although they did not investigate it further.

The spontaneous creation of oil and water droplets is harmful to oil/water separation processes. For instance, it may cause difficulties during cleanup processes of oil spills by creating micron-sized oil droplets that could disperse in the ocean. On the other hand, the spontaneous creation of water droplets in spilled oil could be beneficial. For instance,

Meckenstock *et al.* (9) identified the presence of oil-degrading bacteria inside water droplets that were dispersed in an oil spill in Pitch Lake, Trinidad, and Tobago. The droplets inside the oil created a larger surface area of oil to be degraded by the bacteria, accelerating the degradation process. Spontaneous emulsification may explain the origin of these water droplets in the crude oil.

To better understand this spontaneous emulsification phenomenon in the presence of asphaltenes, we examine this phenomenon at the micron scale by using a co-flow microfluidic device (10). Instead of creating several drops at a time (11, 12), we observe a single and stationary water drop immersed in oil. Since the majority of the spontaneously formed droplets are water droplets in the oil phase, the larger “parent” water drop will shrink as a function of time while small droplets are spontaneously created in its vicinity. Throughout this paper, the term drop refers to the initial parent drop formed by the microfluidic device, and the term droplets refers to the spontaneously emulsified droplets. The initial size of the water drops and the solvents used in the oil phase are varied in our study. The solvents used for the oil solution are toluene and heptane and the following two different compositions are studied: (i) pure toluene and (ii) a heptane/toluene mixture (heptol). By adding heptane in the oil phase, we systematically diminish the solvent quality with respect to asphaltene solubility (4, 5).

RESULTS

Influence of spontaneous emulsification on the interfacial mechanics of asphaltene solutions

The mechanics of fluid-fluid interfaces are captured through a combination of surface energy and surface rheological measurements. In this work, all three are reported. Interfacial tension measurements were conducted using a Wilhelmy plate. Interfacial rheology measurements are classified in one of two ways: surface shear rheometry where the interface is deformed as a simple shear deformation at a constant surface area or dilatational rheometry where the interfacial area is subjected to either (or both) dilatation or compression. As described in Materials and Methods, the double wall ring method was used for surface shear rheometry, whereas the internal drop pressure method was used to measure surface compressive stresses.

The shear interfacial rheology at an oil/water interface, where the aqueous phase consists of deionized water and the oil phase consists of different heptol mixtures, are studied. The oil solutions consist of

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asphaltene molecules (1 mg/ml) dissolved in two different solvent compositions: pure toluene and a 40/60 heptane/toluene (heptol) mixture by volume.

Results for the shear interfacial rheology are shown in Fig. 1A. In the linear regime, where the interfacial viscoelastic moduli are independent of strain (strain amplitudes $\gamma_0 < 0.2\%$ and $\gamma_0 < 0.16\%$ for pure toluene and 40/60 heptol, respectively), the asphaltene layer is solid-like for both cases (storage modulus, G'_s , greater than loss modulus, G''_s). Moreover, the storage modulus is slightly higher in the heptol case compared to the pure toluene case, which indicates that more asphaltene aggregates adsorb at the oil/water interface, creating a stronger network.

For higher strain values, the interface strain-softens and the interface eventually transitions from a solid-like behavior to a liquid-like behavior (G''_s greater than G'_s). This transition occurs through a yielding phenomenon, where the elastic modulus equals the loss modulus. Moreover, this transition is characterized by an overshoot in G''_s , which means that the interfacial layer yields plastically [a similar behavior is seen in other systems such as in globular protein-surfactant mixtures (13)]. The yield point is reached at higher strains as the ratio of toluene increases in the oil phase ($\gamma_0 \approx 0.4\%$ for 40/60 heptol and $\gamma_0 \approx 0.9\%$ for pure toluene). Last, in the nonlinear regime, the slopes of G'_s and G''_s with strain amplitude have a ratio of about 2, which is consistent with the value reported in the literature for materials that yield (14, 15).

Effect of solvent quality on interfacial tension

Interfacial tension values as a function of time for both systems are shown in Fig. 1B. In both cases, the interfacial tension decreases very rapidly for the first 20 min (the interfacial tension in the absence of asphaltene is 36 mN/m for a toluene/water interface and 39 mN/m for a 40/60 heptane-toluene/water interface). Following this rapid decrease, the interfacial tension continues to decrease but at a much slower rate. At the end of our experiments, the values of interfacial tension are approximately 16 mN/m for pure toluene and 14.5 mN/m for 40/60 heptol mixture. The lower interfacial tension value in the presence of heptane indicates a higher adsorption of asphaltenes when heptane is present in the oil solution. Similar to our results, Tsamantakis *et al.* (16) also found a decrease in interfacial tension when heptane is present for a concentration of 0.1 (v/v) of bitumen in the hydrocarbon phase.

As previously discussed in the literature (17, 18), the initial interfacial tension decay is a rapid process and it is due to a diffusion-

controlled adsorption. This is followed by a long reorganization of the interface that slows down the interfacial tension decay. Furthermore, Yarranton *et al.* (19) found that the surface activity of a given asphaltene molecule is inversely related to its solubility. In general, fewer asphaltene molecules adsorb onto the oil/water interface in better solvents. This agrees with our findings where interfacial tension is larger in the case of pure toluene.

Ablation of parent drops by spontaneous emulsification

A previous work in our laboratory investigated the spontaneous creation of water droplets at a largely planar hydrocarbon/water interface in the presence of asphaltenes (6). The present study considers the influence of interface curvature by analyzing this phenomenon occurring on the surface of water drops of various diameters. For this purpose, we used a co-flow microfluidic device to create single water drops immersed in hydrocarbon solutions. Figure 2A presents a schematic drawing of the microfluidic device used. As shown in Fig. 2 (B to D), the initially formed water drop decreases in size as spontaneously created water droplets are formed at its interface. This process was recorded using video microscopy to determine the volume of the water drop as a function of time. These measurements were repeated for drops of various diameters. Four different compositions of the oil phase are studied: (i) pure toluene (shown in Fig. 3A), (ii) 40/60 heptol mixture (Fig. 3B), (iii) asphaltenes (1 mg/ml) in toluene (Fig. 3C), and (iv) asphaltenes (1 mg/ml) in 40/60 heptol mixture (Fig. 3D).

The results in Fig. 3 (A and B) show that in the absence of asphaltenes, the drop volume remains approximately constant during the duration of our experiments (approximately 6 hours). Moreover, the behavior is independent of the initial drop size and oil composition.

In the presence of asphaltenes, however, a different behavior is observed. In pure toluene (Fig. 3C), the drop volume decreases with time due to the spontaneous emulsification process occurring at the oil/water interface. The presence of asphaltenes in the oil solution not only creates a viscoelastic skin at the interface, as previously discussed, but also causes the spontaneous emulsification phenomenon to occur. For large drops (initial drop diameter, $D_0 > 200 \mu\text{m}$), the volume decreases only slightly with time. As the initial drop size decreases, the rate of volume shrinkage progressively increases.

For the 40/60 heptol mixture in the presence of asphaltenes (Fig. 3D), the results show trends that are similar to those observed for pure

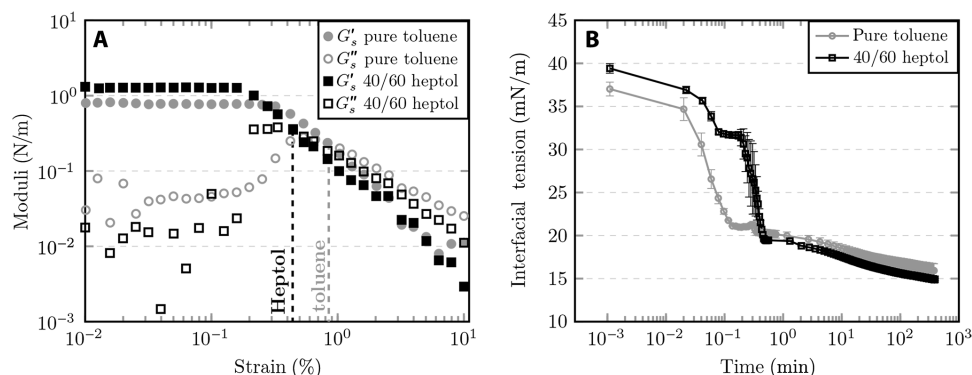


Fig. 1. Interfacial properties at the oil/water interface. Aqueous phase consists of deionized water. Oil phase consists of asphaltene (1 mg/ml) molecules dissolved in two solutions: pure toluene and 40/60 heptane/toluene mixture in volume. (A) Results for interfacial moduli as a function of strain are shown. The storage modulus, G'_s , is represented by closed symbols, whereas the loss modulus, G''_s , is represented by open symbols. Experiments performed with toluene only as a solvent are identified by gray circles; black squares identify the experiments performed with a 40/60 heptol mixture. (B) Interfacial tension as a function of time. For both cases, the surface tension initially decreases rapidly followed by a very slow decreasing process.

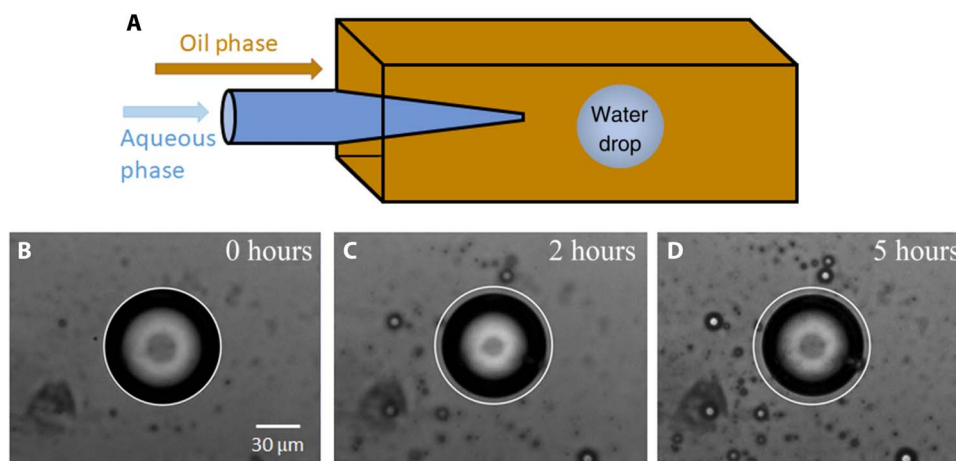


Fig. 2. Microfluidic device used for experiments. (A) Schematic drawing of the co-flow microfluidic device used. Pictures of the drop are taken at time intervals. Because of spontaneous emulsification, the initially formed water drop (B) reduces in size (C and D) as a function of time, while micron-sized droplets appear in the drop's vicinity. The white circles in (B) to (D) represent the initial size of the drop. The oil phase consists of asphaltenes (1 mg/ml) in toluene.

toluene with asphaltenes: The drop volume decreases faster as the initial drop size decreases. The optical contrast presented by the heptol solutions produced lower-quality images, and this placed a lower limit on the size of drops studied for that case. Overall, results in the presence or absence of heptane were found to be fairly similar, indicating that heptane does not have a strong influence on spontaneous emulsification over the concentration range studied. This is unexpected since diminishing the solvent quality was demonstrated in Fig. 1 to produce changes in interfacial properties. This suggests that the spontaneous emulsification may be affected by interactions between asphaltene nanoaggregates and the aqueous phase rather than interactions between asphaltenes and the solvents in the oil phase.

The rate at which the drop volume decreases is related to the rate at which spontaneously emulsified droplets are created, and evidence shows that this is a function of interface curvature. The data in Fig. 3C for drops smaller than 100 μm in radius are replotted as drop radius (in microns) as a function of time (in hours), and the results are shown in Fig. 4A. This plot indicates that the drop radius decreases linearly as a function of time for all drop sizes analyzed. In other words

$$R(t) - R_0 = \Delta R = -\alpha t$$

where R is the drop radius, R_0 is the initial drop radius, α is the coefficient at which the radius decreases, and t is the time. This linear decrease in drop radius with time was observed to remain constant for long periods, and the results obtained for a 50- μm drop in radius over a period greater than 2 days can be seen in fig. S1. This indicates that a drop once formed will always shrink at the same rate, independent of its current size. This is evident by the horizontal dashed lines in Fig. 4A where drops of the same radius are shrinking with different rates. For example, a drop of initial radius $R_0 = 32.5 \mu\text{m}$ (blue curve) will keep its linear slope even after the drop shrinks to $R = 25 \mu\text{m}$. On the other hand, a fresh drop with an initial radius $R_0 = 25 \mu\text{m}$ is seen to shrink at a much faster rate (dark blue curve). Other works that investigated the diminish of water drops in oil due to spontaneous emulsification in the presence of a simpler surfactant, Span 80, also found a constant decrease in radius as a function of time (20–22). This result indicates that the rate of ablation of water drops is controlled by the rates of interfacial processes as opposed to diffusional processes (20).

Interface curvature is known to strongly influence coarsening phenomena in foams and emulsions (23, 24). Differences in drop and bubble radii directly lead to a distribution in the internal Laplace pressures of the disperse phase, causing large drops in an emulsion to grow at the expense of smaller drops. In systems lacking interfacial viscoelasticity, this process drives itself since the diminution of the radii of smaller drops increases their Laplace pressure, thereby increasing this driving force. However, if the drop interface is laden with species that render it viscoelastic, then the rate of process can be diminished, and several studies have reported on this possibility (25, 26). Presumably, this will occur as spontaneous emulsification proceeds in the presence of asphaltene molecules that serve the dual roles of initiating the creation of droplets at the surface of the parent drop, thereby diminishing its volume and surface area while simultaneously rendering the interface viscoelastic. Whereas the reduction in volume would normally increase the internal Laplace pressure, arming the interface with a viscoelastic skin of adsorbed asphaltene molecules should suppress that increase.

On the one hand, if the Laplace pressure of the parent drops serves as one driving force for spontaneous emulsification, then this would explain the increase in the rate of volume reduction as the drop diameter is decreased as reported in Fig. 3 (C and D). However, the rate of decay, α , of the drop radius is measured to be constant over time once a fresh drop is introduced and allowed to interact with asphaltene solutions. This suggests that the internal pressures within the drop are not following a simple Laplace pressure relationship as time proceeds. For this reason, we have tracked the internal pressure within water drops of different sizes using the experimental setup presented in fig. S2, and the results are shown in Fig. 4B. In this plot, the internal pressure of drops is presented as a function of time. The internal pressure is determined as the difference between the inside and the outside of the drop due to its curvature. Instead of increasing as the drop slowly decreases in size, the pressure remains relatively constant as the surface area is diminished and the viscoelastic interface is compressed. In addition, as the initial drop size increases, the initial internal pressure decreases.

As previously mentioned, the slope α presents a strong dependence on the initial drop radius, R_0 , rather than the drop current radius, $R(t)$. We found that α is exponentially proportional to $1/R_0^2$ as shown in Fig. 4C. These results indicate that the spontaneous emulsification is

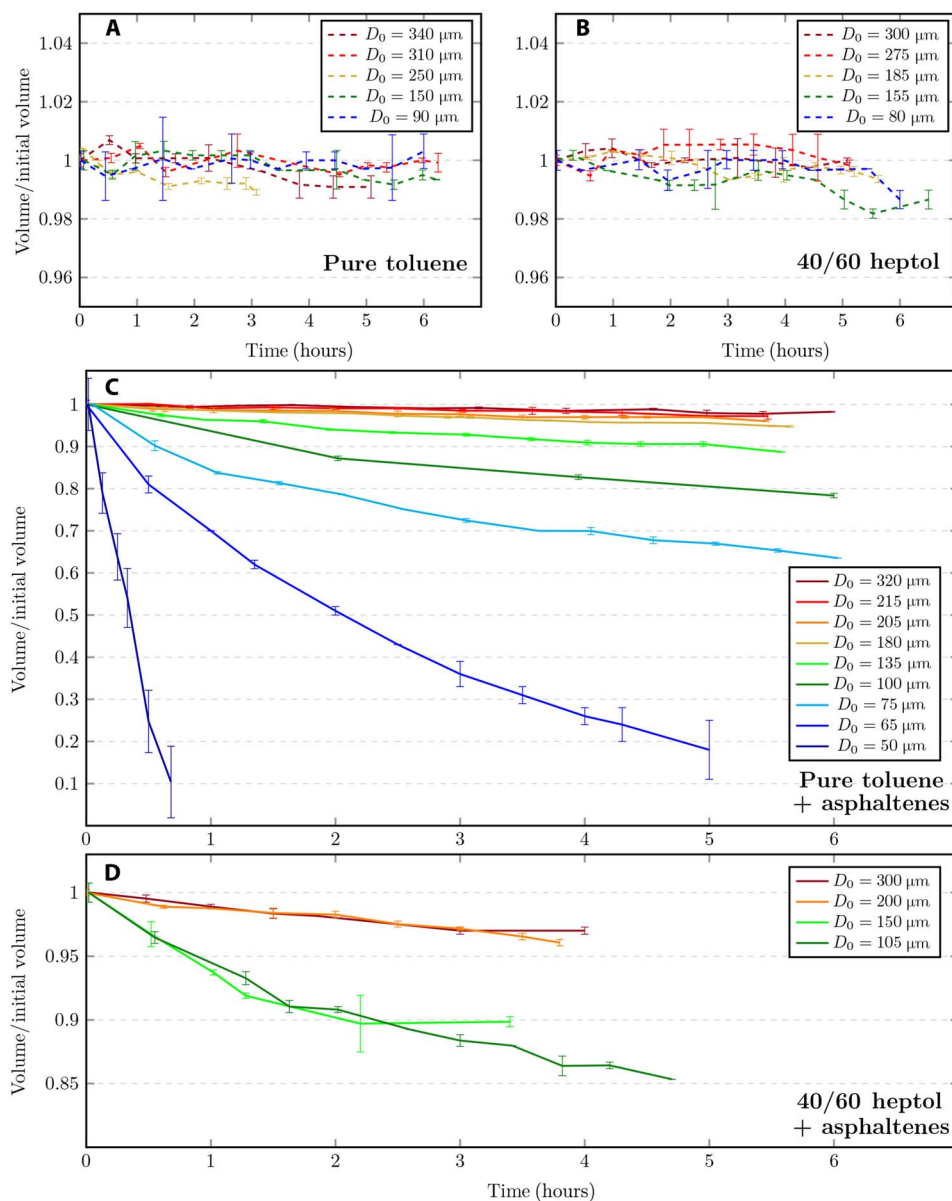


Fig. 3. Normalized water drop's volume as a function of time for different initial drop sizes. The oil phase are (A) toluene only, (B) 40/60 heptane/toluene mixture by volume, (C) asphaltenes (1 mg/ml) dissolved in toluene, and (D) asphaltenes (1 mg/ml) dissolved in a 40/60 heptol mixture by volume.

a surface phenomenon as it is strongly affected by the oil/water initial interfacial area, and it has a strong dependence on the drop's initial internal pressure. Similarly, the internal pressure also presents an exponential dependence on the inverse of the drop's initial area, as presented in Fig. 4D, which suggests, once again, that the internal pressure of the drop does not simply follow a Laplace pressure relationship and it could be one driving force for spontaneous emulsification.

The interfacial stress, τ , can be calculated from a simple force balance once the interfacial pressure drop, ΔP , and the drop radius are known using the simple relationship $\tau = R \cdot \Delta P / 2$. These stresses are calculated and shown in fig. S3. Because the radii for the drops are decreasing slowly, the qualitative appearance of the interfacial stress traces is similar to the pressure drop traces and does not vary much with time. This interfacial stress seems to be imposed by the initial size of the drop.

DISCUSSION

We investigated the spontaneous emulsification phenomenon in the presence of asphaltenes by observing the evolution of isolated parent water droplets immersed in hydrocarbons containing asphaltenes in a microfluidic device. Results show that a water/heptol interface will only spontaneously emulsify if asphaltene molecules are present in the oil phase. In addition, interfacial rheological properties due to the presence of asphaltenes seem to present a strong effect on spontaneous emulsification. This process slowly removes water droplets from the parent drop, causing it to slowly diminish in volume.

We found that the spontaneous emulsification phenomenon is a function of the drop's initial internal pressure since smaller drops (with higher internal pressure) shrink faster than large ones. Moreover, as the drop shrinks, the internal pressure of the drop remains constant. We

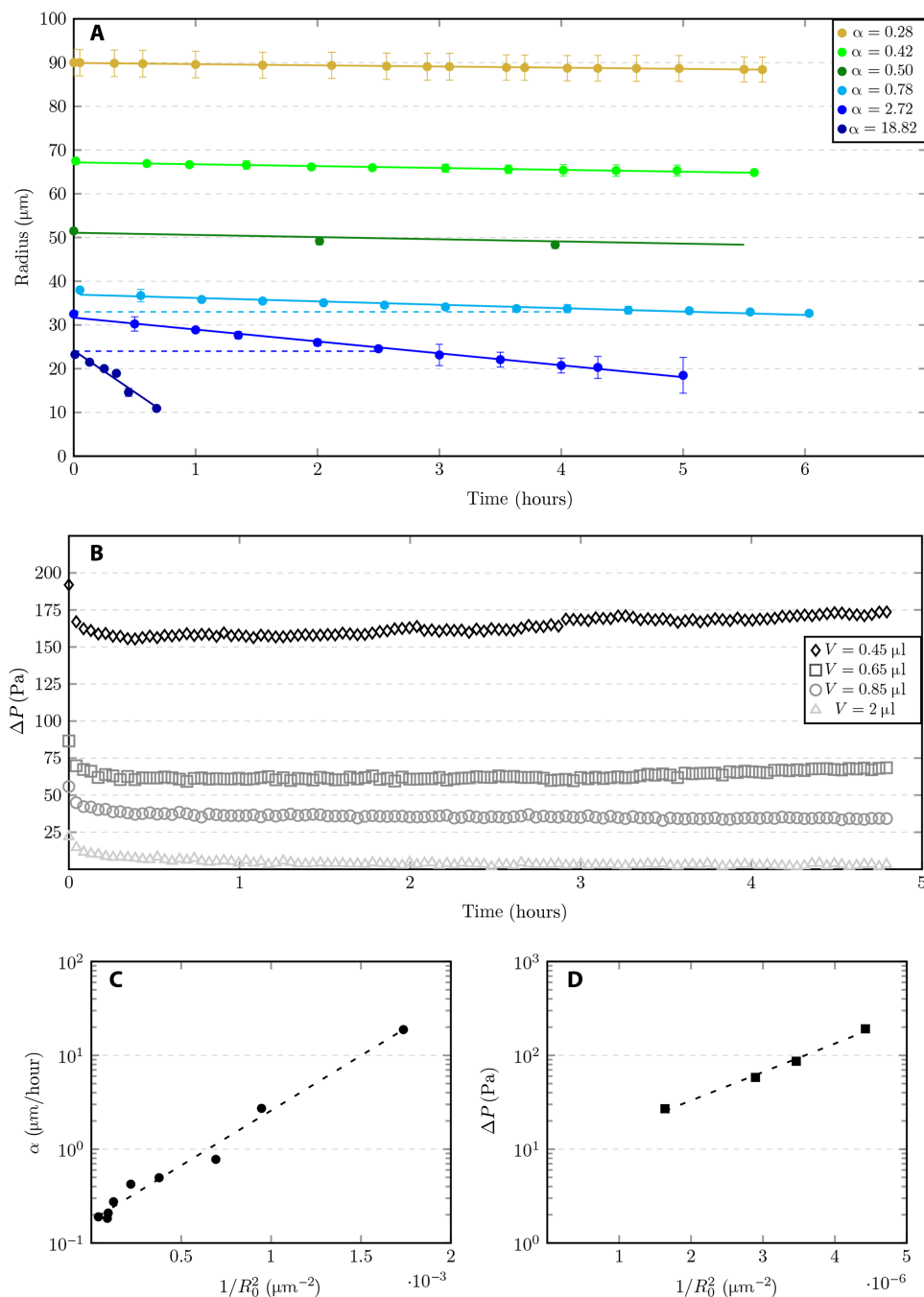


Fig. 4. Drop size effect on spontaneous emulsification behavior. (A) Radius as a function of time for drops at different initial sizes immersed in asphaltenes (1 mg/ml) in toluene. The rate at which the drops shrink, α , depends on the initial drop size rather than its current size. In addition, the rate increases as the initial drop size decreases. (B) Internal pressure of drops as a function of time. ΔP is the pressure difference between the inside and the outside of the drop due to its curvature. The internal pressure remains relatively constant although the drop is slowly shrinking due to spontaneous emulsification. (C) The slope α increases exponentially with the inverse of the drop's initial area ($1/R_0^2$). (D) Internal pressure of drops also increases exponentially with the inverse of the drop's initial area ($1/R_0^2$).

believe that this is due to the viscoelastic skin of adsorbed asphaltenes that is formed at the drop's interface. Since the drop's internal pressure, which seems to be the driving force for spontaneous emulsification, does not change as a function of time, the drop's radius decreases at a constant rate. This constant rate indicates that interfacial processes are driving the shrinkage of the drops. Similar results with a constant diminishing rate have been reported in the literature

but in the presence of a simpler surfactant, such as Span 80 (20–22). Hence, drops of the same size may have different internal pressure depending on their initial size and, as a consequence, they will shrink at different rates as found in our experiments. Last, our results indicate a strong dependence on the initial interfacial area of the rate at which drops shrink, once more confirming that this is an interfacial phenomenon.

The addition of heptane on toluene diminishes the solvent quality with respect to the asphaltenes since they are not soluble in this nonpolar solvent, which mimics more closely crude oil characteristics. The presence of heptane does affect interfacial rheological properties and interfacial tension behavior, indicating a higher adsorption of asphaltene molecules at the oil/water interface in comparison to the pure toluene case. However, it did not strongly affect the spontaneous emulsification behavior. This suggests that the spontaneous emulsification phenomenon is related to interactions between asphaltene and water molecules rather than asphaltene and oil molecules. It is known that the presence of water in organic solvents can affect asphaltene characteristics and drive agglomeration (7, 27–29). One hypothesis is that asphaltenes will interact with water molecules through hydrogen bonds as presented by Aslan and Firoozabadi (8).

The full understanding of this thermodynamic phenomenon of spontaneous emulsification is still unknown, but possible mechanisms and driving forces have been previously discussed in the literature (30, 31). A common assumption used in past works suggests that spontaneous emulsification occurs when interfacial tension reaches zero or negative values at the liquid-liquid interface, which does not appear to have occurred in the present study. Here, we find that interfacial rheology affects the spontaneous emulsification phenomenon and the rate at which it occurs. However, similar to our results, Cates *et al.* (31) found that when the system is far from a steady state, the radius of a drop decreases linearly with respect to time. Although these theories were developed for simpler systems (e.g., systems with homogeneous surfactants that have short hydrophobic tails and small hydrophilic heads) than the present case, it gives some insight on possible dynamics of spontaneous emulsification.

An important characteristic of the spontaneous emulsification phenomenon is its “inverse Ostwald ripening” behavior, since the number of small droplets grows at the expense of a large drop that diminishes in size. Both phenomena seem to be related to the internal pressure of the drops; however, the Ostwald ripening theory assumes that the system will obey the Young-Laplace equation (32–34), and it is usually applied to simple interfaces in the absence of viscoelasticity (25, 26). Our results in the presence of asphaltenes, which causes a strong viscoelastic interface to be formed, indicate that the internal pressure of the drops does not follow a simple Laplacian relationship, but instead, the internal pressure is an exponential function of the inverse of the initial area and it remains constant as a function of time, although the drop is expected to shrink due to spontaneous emulsification. Nevertheless, the rate of shrinkage of the drop due to spontaneous emulsification is related to the internal pressure of the drop, but unlike Ostwald ripening, the pressure remains constant. As the results show, the rate α at which the drops shrink in radius is also exponentially proportional to the inverse of the initial area. Therefore, the results indicate a strong dependence on the drop’s initial size and on interfacial rheological properties on the spontaneous emulsification behavior.

Because asphaltene samples are influenced by the extraction method used to separate them from crude oil (e.g., the relative solubilities of the solvents used), and by the original location of the crude oil from which they were extracted, the results on spontaneous emulsification may vary with the asphaltene sample used. The asphaltene sample used in the present study originated from Eni, and the extraction method used is described in Materials and Methods. We have not conducted an extensive survey of different asphaltene sources but obtained qualitatively similar results using a sample of asphaltenes donated from the Shanghai Research Institute of Petrochemical Technology.

The conversion of water drops residing within asphaltenic crude oils into a dispersion of simultaneously generated water droplets is expected to be of paramount importance to the extraction of oil from reservoirs, refining processes, and oil spill cleanups. Reservoir water in contact with such crudes can become incorporated within the oil in the form of micron-sized droplets, and dehydration of such oil will be difficult. If the water contains salts, this would lead to corrosive oil that must be treated by desalting processes. Those desalting processes, which deliberately create water-in-oil emulsions for the purpose of liquid-liquid extraction, will also be affected by ablation of those water drops and the creation of micron-sized water droplets.

Besides the oil industry, emulsions are encountered in several other applications such as in cosmetics, foods, medical, and pharmaceutical industries. To manufacture those products, several emulsification techniques have been proposed to produce monodisperse emulsions with low energy requirements (35). Spontaneous emulsification, however, consists on forming emulsions without external energy supply. The fundamental understanding of the importance and effects of interfacial rheology on the spontaneous emulsification phenomenon may greatly affect the production of emulsions and the industries cited above.

MATERIALS AND METHODS

Materials used

Asphaltenes represent the toluene-soluble fraction of crude oils. The materials used in this study are extracted from a heavy crude oil with a density of $988 \text{ kg}\cdot\text{m}^{-3}$ at 20°C , which corresponds to 11.6° API gravity (American Petroleum Institute gravity). The ASTM (American Society for Testing and Materials) method D-3279-97, 2001 (“Asphaltene preparation method” or standard ASTM D4312 or D4072 test methods) was used for the asphaltene extraction, as reported in Merola *et al.* (36). The asphaltene content is approximately 22 wt % (weight %) of the raw crude oil.

The aqueous phase used is filtered deionized water. For the oil phase, we used two different solvents: toluene and heptane. The oil phase consisted of asphaltene molecules at a concentration of 1 mg/ml dissolved in pure toluene and 40/60 heptane/toluene (heptol) in volume mixture. The heptol mixture was made before the addition of asphaltenes in the solution. The toluene used is from Fisher Chemicals (purity, 99.9%; water, $<0.001\%$). The heptane used is from Sigma-Aldrich (purity, 99%; water, $<0.01\%$). The solvents were used as purchased. The glass vial containing the oil solution was closed with a lid and sealed with parafilm. The solution was sonicated for 30 min before each experiment.

Interfacial rheology experiments

The viscoelastic properties of the asphaltene layer are measured at the oil/water interface. We used the stress-controlled Discovery Hybrid Rheometer (DHR-3) from TA Instruments (USA) equipped with a du Noüy ring and the double-wall Couette flow-cell geometry (37). The latter is made of a glass external cylinder and a Teflon internal cylinder. The rheological study consists of an amplitude sweep at $\omega = 1 \text{ rad/s}$, exploring the strain range from 0.01 to 10%. The experiments were performed in the following way. First, the aqueous phase was added to the inner region between the glass and Teflon cylinders. Then, the du Noüy ring was placed at the air/water interface. Last, the oil phase was added on top of the aqueous phase, and the ring was slightly displaced to be located at the oil/water interface.

Interfacial tension measurements

To measure the interfacial tension properties at the oil/water interface as a function of time, a platinum Wilhelmy plate connected to a balance (KSV NIMA Ltd., Helsinki, Finland) was used. The oil/water interface was created inside a 40-mm-diameter glass vial, and the experiments were performed in the following way. First, the beaker was filled with deionized water, then the Wilhelmy plate was placed in contact with the water/air interface, and its interfacial tension was measured to confirm the accuracy of the measurements. Then, the oil solution was gently added on top of the aqueous phase until the Wilhelmy plate was completely submerged. The beaker was covered with microscope slides to reduce evaporation. Experiments were performed at room temperature. The time zero is defined as the moment at which the measured interfacial tension corresponds to a clean oil/water interface (in the absence of asphaltenes). This value corresponds to 36 and 39 mN/m for a toluene/water interface and 40/60 heptane-toluene/water interface, respectively.

Spontaneous emulsification in a microfluidic device

To study the evolution of spontaneous emulsification in the presence of asphaltenes, a coaxial flow (co-flow) microfluidic device was used (10). The device was fabricated in the following way: a tapered cylindrical glass capillary (outer diameter, 300 μm) was inserted into a glass square tube (inside diameter, 400 μm). A schematic drawing of the experimental setup is presented in Fig. 2. The aqueous phase was inserted through the inner cylindrical capillary, whereas the outer square tube was filled with the oil phase. Both fluids flowed in the same direction, resulting in a coaxial flow. The pressure at both channels was controlled by a compact microfluidic controller from Fluigent, which permits the creation of a single water drop and its detachment from the inner capillary. After the drop was created, a valve located at the end of the system was closed for the complete isolation of the system. The microfluidic device sits on top of a Leica DMI6000 B inverted microscope. Images of the drop were taken at intervals of a couple of minutes (≈ 5 min) using a complementary metal-oxide semiconductor camera. The images were analyzed using the software ImageJ.

Drop's internal pressure experiments

To understand how the internal pressure of water drops changes due to spontaneous emulsification, we performed the following experiment. A squared glass chamber (25.4 mm by 25.4 mm by 38 mm) was filled with asphaltenes (1 mg/ml) in toluene. A capillary was connected to a syringe pump and a pressure transducer by Teflon tubing that was filled with deionized water, as shown in the schematic drawing in fig. S2. The capillary was placed inside the oil phase, then a water drop was formed at the tip of the capillary, the drop was aged inside the oil solution, and its pressure was recorded as a function of time. Measurements from the pressure transducer of the internal pressure of the drop were recorded by a code developed in MATLAB.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/10/eaax8227/DC1>

Fig. S1. Linear behavior of radius as a function of time.

Fig. S2. Experimental setup for internal pressure measurements.

Fig. S3. Interfacial stress, τ , at the oil/water interface.

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