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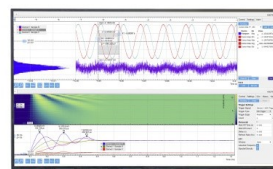
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ABSTRACT

In this work, we provide a comparison between the stability and the interfacial structure of micrometer-sized and nanometer-sized droplets by employing a multi-instrumental approach comprised of the surface-sensitive technique of sum frequency scattering as well as dynamic light scattering and microscopy. We monitor the stability of oil-in-water and water-in-oil emulsions and the structure of surfactants at the oil/water nano-interface, when stabilized with an oil-soluble neutral surfactant (Span80), a water-soluble anionic surfactant (sodium dodecyl sulfate, SDS), or with a combination of the two. Micron-sized droplets are found to be stabilized only when a surfactant soluble in the continuous phase is present in the system, in agreement with what is traditionally observed empirically. Surprisingly, the nanodroplets behave differently. Both oil and water nanodroplets can be stabilized by the same (neutral Span80) surfactant but with different surface structures. A combination of SDS and Span80 also suffices, but for the case of water droplets, the strongly amphiphilic SDS molecules are not detected at the interface. For the case of oil droplets, both surfactants are at the interface but do not structurally affect one another. Thus, it appears that, in this study, empirical rules such as the Bancroft rule, the hydrophile–lipophile–balance scale, and the surfactant affinity difference predict the stability of the micrometer-sized droplets better than the nanometer-sized ones, probably due to a different balance of interactions on different length scales.

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I. INTRODUCTION

Emulsions are extensively used in a variety of industrial products, including food, cosmetic, and pharmaceutical goods. In addition, they are employed as miniature reaction vessels, for example to conduct biochemical reactions or to perform high throughput screening assays.^{1,2} A basic requirement for their efficient use is the preparation of stable emulsions. There are two different views on emulsion stability within the materials science research field: For the physical chemistry community, the identity of the two liquid

phases, and their interface, including the mechanism by which surfactants impart stability to emulsion drops, is of highest importance. Therefore, special attention is given to the interfacial properties of droplets. By contrast, the community studying colloids considers emulsion droplets as one homogeneous entity and attributes a crucial role to their arrangement and interactions.

Emulsion droplets are often stabilized with surfactants to prevent their coalescence by increasing the repulsive barrier between the droplets.³ To impart good stability to emulsion drops, appropriate surfactants are selected according to empirical criteria; this

choice depends on the composition of the fluids, if oil-in-water or water-in-oil emulsions are needed, the ratio of water-to-oil,⁴ and the temperature and pressure.^{3,5–11} The choice of the appropriate surfactant is often based on empirical rules such as the Bancroft rule⁵ or the surfactant affinity difference (SAD), the difference in surfactant chemical potentials between the oil and water phase. The Bancroft rule states that surfactants should be dispersed in the continuous phase, in agreement with the Hydrophile–Lipophile–Balance (HLB) scale.¹² The SAD depends on a number of experimental observables as well as structural information, such as the interfacial tension, the computed surfactant curvature, the cloud points of the surfactant in either solution, the electrolyte concentration, the amount of carbon in the surfactant, and the temperature.¹³ Accordingly, water-soluble, hydrophilic surfactants are expected to stabilize oil-in-water emulsions, while oil-soluble, hydrophobic surfactants stabilize water-in-oil emulsions. The basic idea behind these three empirical classifications is that when two emulsion droplets come in close proximity, a thin film of the continuous phase forms between them, which prevents merging of the droplets.¹¹ Extensive studies have shown that such films are more stable if they comprise surfactants, which is the case if surfactants are dissolved in the continuous phase.³ Indeed, stability data dating back to the 1940s^{14,15} demonstrate the incapability of water-soluble or charged surfactants to stabilize water droplets in oil.

Even though emulsion stability is recognized to critically depend on the structural properties of the interfacial region and the interfacial interactions, the underlying mechanisms are still elusive on the molecular level. Emulsion stability is typically characterized by phase inversion studies, phase separation, gravitational/centrifugal sedimentation, size distribution, nuclear magnetic resonance, ultrasound, optical microscopy, and similar techniques.^{3,16–18} These techniques provide information on a macroscopic level; for example, they allow determining the number of phases present in the system, or the partitioning of surfactants in each phase. The necessary knowledge about the interfacial regions is inferred from studies on extended planar interfaces^{19–23} or molecular dynamics simulations. However, if studies on planar systems could be used to characterize the interface of both water-in-oil and oil-in-water systems, then the empirical rules regarding emulsion stability should not hold. Indeed, recent studies employing advanced experimental spectroscopic techniques²⁴ reveal previously unexpected discrepancies between planar and droplet interfaces,^{25,26} demonstrating the need to link stability to droplet interfacial structure.

Here, we study the effect of reversing the dispersed phase with the continuous phase on the stability of emulsions stabilized with the same surfactants. In particular, we focus on the structure of surfactants adsorbed on droplet surfaces. We study oil-in-water and water-in-oil emulsions with droplets whose radius is on the order of several micrometers ($\sim 5\text{--}20\ \mu\text{m}$) and several tens of nanometers ($\sim 65\text{--}100\ \text{nm}$). These droplets are stabilized with either a neutral oil-soluble surfactant (Span80), a negatively charged water-soluble surfactant (sodium dodecyl sulfate, SDS), or a combination of the two. We characterize the surfactants at the liquid-liquid interface using a multi-instrumental approach that combines macroscopic data, from microscope images, with molecular level information, obtained with vibrational Sum Frequency Scattering (SFS).^{24,27} SFS is a coherent surface spectroscopy that directly probes the structure of the

surfactants present at the interface of the droplets. We find that the micrometer-sized droplets can be stabilized only with a surfactant that is dissolved in the continuous phase (SDS or Span80, respectively), in agreement with expectations based on empirical rules. For nanometer-sized droplets, the situation is different. The neutral surfactant (Span80) stabilizes the interface of nanodroplet samples, irrespective of whether the surfactant is dissolved in the continuous or dispersed phase. The surface structures in the two cases are different, however. If the two surfactants coexist, the tendency of one to approach the interface is not altered by the presence of the other.

II. MATERIALS AND METHODS

A. Chemicals

Hexadecane (Sigma Aldrich, analytical standard), deuterated (d_{34})-hexadecane (Cambridge Isotope Laboratories, 98% deuteration), SDS (ReagentPlus®, $\geq 98.5\%$, GC quality), deuterated (d_{25} -) SDS (Cambridge Isotope Laboratories, 98% deuteration), Span80 (Sigma Aldrich, GC quality), and D_2O (99.8%, Armar, $>2\ \text{M}\Omega\ \text{cm}$) were used as received. The structure of each surfactant is shown in Fig. 1(a).

B. Production of nanometer-sized droplets

Extra care was taken to minimize any possible contamination during the preparation of nanometer-sized oil droplets in water and water droplets in oil, according to a specific protocol. As a first step, all glassware used to prepare and store solutions and samples was cleaned prior to use according to one of the three different cleaning methods: (a) glassware was soaked in a freshly prepared piranha solution [3:1 H_2SO_4 (95%–98%, Sigma-Aldrich) and H_2O_2 (30%, Macron Fine Chemicals)] for a minimum of 30 min and subsequently rinsed with copious amounts of ultrapure water prior to use; (b) glassware was soaked in a freshly prepared NoChromix®: H_2SO_4 (Sigma Aldrich) mixture that is mixed based on the provided instructions, followed by thoroughly washing and rinsing with MilliQ water to remove acidic components from the glass surface; and (c) glassware was cleaned with a Deconex® (Sigma-Aldrich) solution prepared by 1:20 dilution with MilliQ water, then sonicated for an hour, and subsequently washed and rinsed at least 10 times with MilliQ water. Each of these glass cleaning methods gives rise to identical emulsion samples [size, polydispersity index (PDI), zeta-potential, second harmonic scattering (SHS), and SFS]. Using these procedures, the amount of organic impurities in the aqueous solution is $<3\ \text{nM}$.⁴⁰ Apart from the cleaning process, the choice of employed chemicals is another possible way to minimize impurities. Hence, the chemicals with highest commercially available purity were always used. The purity of alkanes was verified with a Zisman test.^{28,29} We also tested if further purification of the hexadecane phase had any effect on emulsion quality. For these tests, hexadecane was purified by running it through an activated alumina (Sigma-Aldrich) column, which is preprocessed by heating to $500\ ^\circ\text{C}$ for 2 h. Such processed hexadecane gives rise to identical emulsion samples with the samples using the commercially available pure hexadecane.

The dispersions of nanometer-sized oil droplets in D_2O and nanometer-sized D_2O droplets in oil were prepared with

1 vol. % of the dispersed phase in the continuous phase. Before the mixing of the two phases, Span80 was added to the oil phase and/or SDS to the water phase. The dispersions were mixed for 2 min with a hand-held homogenizer (TH, OMNI International) with an angular velocity of 300 rpm and then placed in an ultrasonic bath (35 kHz, 400 W, Bandelin) until a monodisperse sample was formed. The size distribution of the droplets was measured with dynamic light scattering (DLS, Malvern ZS nanosizer) and, for stable samples, was consistently found to have a mean radius in the range of 65–100 nm with a polydispersity index (PDI) of less than 0.3. The final sample was achieved by monitoring the dynamic light scattering (DLS) results every few minutes of the sonication process, typically lasts for less than 10 min for a generic sample preparation. The hydrodynamic radii were calculated from the intensity autocorrelation function, using the optical properties of the liquids. The samples were stored and measured in sealed (glass) cuvettes. All measurements were performed at 24 °C.

C. Production of micrometer-sized droplets

Emulsion droplets with radius between 5 and 20 μm were produced with microfluidic devices. These devices were made of polydimethylsiloxane (PDMS) using soft lithography.³⁰ To produce oil-in-water emulsions, the channel walls were made hydrophilic by exposing them for 30 min to an aqueous solution containing 2 wt. % poly(diallyldimethylammonium chloride) and 1M NaCl. To produce water-in-oil emulsions, the channel walls were made hydrophobic by exposing them for 10 min to a dodecane-based solution (Abcr) containing 2 vol. % of trichlorododecylsilane (Sigma-Aldrich). Fluids were injected into the microfluidic device using volume-controlled syringe pumps (Cronus Sigma 1000, Labhut, UK). Oil in water emulsion droplets were produced by injecting the outer phase at rates between 600 and 800 $\mu\text{l/h}$ and the inner phase at 10–60 $\mu\text{l/h}$. Water in oil emulsion droplets were made by injecting the outer phase at rates between 100 and 200 $\mu\text{l/h}$ and the inner phase at rates between 80 and 400 $\mu\text{l/h}$. The droplet formation was recorded using a high-speed camera operated at 506 frames per second (Mikrotron EoSens CL, Germany) and attached to an inverted microscope (Nikon, Eclipse TS100, Japan). Alternatively, we also prepared micrometer-sized droplets by vortexing a solution composed of 10% of the oil phase and 90% of the water phase, each one containing the appropriate surfactant. This rapid preparation is to visually test the stability of micrometer-sized droplets by imaging the resulting droplets over a period of 8 h.

D. Sum frequency scattering

The vibrational sum frequency scattering setup has been previously described in detail.^{31,32} Briefly, an infrared (IR) laser beam and a visible (VIS) laser beam were temporally and spatially overlapped under an angle of 20° (measured in air) in a sample cuvette with a path length of 200 μm . The IR pulses were centered at 2900 cm^{-1} (FWHM = 160 cm^{-1}) for the measurement of C–H stretch vibrational modes and at 1040 cm^{-1} (FWHM = 120 cm^{-1}), for the measurement of S–O vibrational mode, and the VIS pulses at 12 500 cm^{-1} (FWHM = 12 cm^{-1}) at a repetition rate of 1 kHz. The polarization of the IR beam was controlled by two BaF₂ wire

grid polarizers (Thorlabs, WP25H-B) while that of the VIS beam was controlled by a polarizing beam splitter cube (CVI, PBS-800-050) and a half-wave plate (EKSMA, 460-4215). The SFS light was measured at a scattering angle of 57°, collected and collimated by a planoconvex lens ($f = 15$ mm, Thorlabs LA1540-B). The polarization state of the SFS light was controlled by a Glan-Taylor prism (Thorlabs, GT15-B), and it was filtered by two short wave pass filters (3rd Millennium, 3RD770SP). Finally, the SFS signal was spectrally dispersed with a monochromator (Acton, SpectraPro 2300i) and detected with an intensified and gated CCD camera (Princeton Instruments, PI-Max3). The gate width is set to 5 ns and the acquisition time for a single spectrum to 300 or 600 s. All SFS spectra shown were normalized to a SFS spectrum obtained from a dispersion of potassium niobate (KNbO₃) nanoparticles (Sigma-Aldrich) in D₂O.

III. RESULTS

To investigate the structure of surfactants at the surface of dispersed droplets, we employ oil droplets in water and water droplets in oil. Droplets are stabilized with 8 mM of the anionic water-soluble surfactant sodium dodecyl sulfate (SDS, cmc, of 8.25 mM at $T = 293$ K³³), with 5 mM of the neutral oil-soluble surfactant Span80 (HLB value of 4.3), or with a combination of the two with the same concentrations. We compare the stability of nanometer-sized droplets with that of micrometer-sized ones. During the preparation of the nanodroplet emulsions, SDS is dissolved in the water phase and Span80 in the hexadecane oil phase. Nanoemulsions contain ~1 vol. % of the dispersed phase that is constituted of droplets with radii of ~65–100 nm. To evaluate their stability, the droplet size distribution of nanoemulsions is measured with Dynamic Light Scattering (DLS). A sample is considered stable when the size distribution consists of a single peak with a polydispersity index (PDI) below 0.3.³⁴ Stable nanoemulsions were investigated with SFS. Emulsions with micrometer-sized droplets contain ~9 vol. % of dispersed phase that is composed of droplets with radii of ~5–20 μm . The stability of these emulsions is characterized by comparing microscopy images of the microemulsions immediately after formation in a flow focusing microfluidic device with images taken within 0.2 ms after the droplets are getting in contact with each other. If droplets coalesce within such a short amount of time, we consider them to be unstable. The stability of micrometer-sized droplets was also tested by mixing the two phases containing the appropriate surfactant(s) by vortexing them for 30 s. If we observe a macroscopic phase separation within 8 h of storage, we consider the emulsions with micrometer-sized droplets as unstable.³ If neither coalescence is microscopically detected, nor phase separation is macroscopically observed, the emulsions are considered stable.

A. Nanometer-sized oil-in-water droplets

We performed SFS measurements on stable hexadecane nanometer-sized droplets in water to study the interfacial structure of surfactants adsorbed on the surface of nanodroplets. To determine if surfactants are present at the interface and to obtain information about their conformation, we make use of deuterated d₃₄-hexadecane as oil and monitor the vibrational modes of the surfactants only. Figure 1 shows SFS spectra for a range of samples and

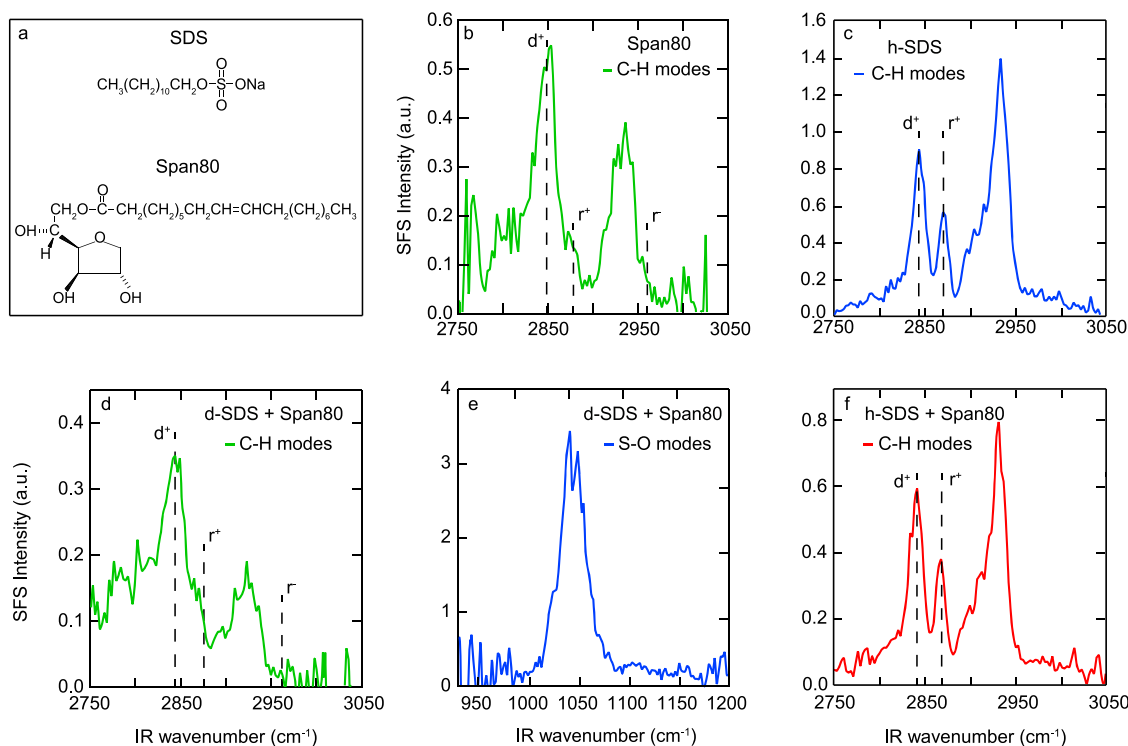


FIG. 1. Surface structure of surfactants stabilizing nanometer-sized oil droplets in water. (a) Molecular structure of SDS (top) and Span80 (bottom). [(b)–(f)] Normalized SFS intensity spectra of the vibrational modes of surfactant molecules adsorbed at nanometer-sized droplets of d_{34} -hexadecane (1 vol. %) in D_2O . The surfactant(s) used to stabilize the system are shown at the top right corner of each panel and also indicate whether hydrogenated (h-) or deuterated (d-) SDS was employed. CH stretch modes (~ 2845 – 2965 cm^{-1}) of the methyl and methylene groups of the alkyl chains of the interfacial (b) Span80 molecules on droplets stabilized with 5 mM Span80, (c) DS^- anions on droplets stabilized with 8 mM SDS, (d) Span80 molecules on droplets stabilized with a combination of 5 mM Span80 and 8 mM d_{25} -SDS, and (f) both Span80 and DS^- anions on droplets stabilized with a combination of 5 mM Span80 and 8 mM SDS. (e) Symmetric S–O stretch mode of the sulfate head group of interfacial d_{25} - DS^- (~ 1045 cm^{-1}) molecules on droplets stabilized with a combination of 5 mM Span80 and 8 mM SDS. Deuterated (d_{25} -) instead of hydrogenated (h-) SDS is used for (d) and (e) to isolate the CH modes of Span80 when combined with SDS. All SFS spectra were collected with the IR (VIS, SF) beam polarized parallel (perpendicular) to the scattering plane (SSP). The radius of the nanoemulsion and its PDI are (b) 83 nm and 0.29, (c) 75 nm and 0.16, (d) and (e) 78 nm and 0.21, and (f) 71 nm and 0.17.

vibrational modes. For Span80 molecules and/or hydrogenated (h-) DS^- anions, Figs. 1(b)–1(f) demonstrate SFS spectra of the methyl (CH_3) and methylene (CH_2) stretch modes of the alkyl chains. Figure 1(e) reports the S–O symmetric stretch mode (~ 1045 cm^{-1}) of the deuterated (d_{25} -) DS^- anions sulfate head group. Note that the spectral response of SDS stabilized nanodroplet emulsion samples has been previously controlled for the presence of dodecanol that could result from progressive hydrolysis of SDS.³¹ Given that dodecanol is practically insoluble in water with a solubility of 0.004 g/l or 20 μM at $T = 298$ K,³⁵ we expect it to display a higher interfacial activity than the charged SDS (cmc, of 8.25 mM at $T = 293$ K). However, no change in the spectra for the C–H region was detected, confirming the absence of interfacial dodecanol.^{31,36,37} The significant SFS intensity of Span80 in Fig. 1(b) shows that the neutral oil-soluble Span80 molecules populate the nanometer-sized droplet interface and stabilize the emulsion despite being dissolved in the aqueous dispersed phase. To test whether charged surfactants are also located at the oil droplet interface, we prepared nanoemulsions with SDS (8 mM) and measured

the SFS intensity, as shown in Fig. 1(c). The CH modes of the alkyl chains of the hydrogenated interfacial DS^- anions are clearly observed, indicating that SDS indeed adsorbs at the droplet interface. To test if one of the surfactants preferentially adsorbs at the interface, we stabilized d_{34} -hexadecane nanometer-sized droplets with a combination of 8 mM d_{25} -SDS and 5 mM Span80 and used the S–O stretch mode and C–H stretch modes to track each surfactant separately. Figures 1(d) and 1(e) show the presence of CH stretch vibrational modes and S–O symmetric stretch modes, respectively, indicating the presence of both interfacial Span80 and SDS molecules. To obtain more information about the interfacial structure, we measure the SFS intensity of the CH modes from both d_{34} -hexadecane droplets that are stabilized with Span80 molecules and h- DS^- anions. The resulting SFS spectrum [Fig. 1(f)] shows a striking similarity to the spectrum in Fig. 1(c). This similarity suggests that the SFS response is dominated by the alkyl chains of the interfacial DS^- anions, with Span80 molecules contributing considerably less. To test if Span80 influences the SDS structure, we measured the S–O stretch mode with SSP and PPP polarizations, in the

presence and absence of Span80. Figure S1 in the [supplementary material](#) shows different SSP/PPP ratios, indicating that the configuration of the sulfate headgroup of the DS^- anions is affected by the presence of Span80 at the interface (see Sec. S1 and Fig. S1 for more information).

For the CH spectra, the positions of the symmetric CH_2 (d^+ , $\sim 2850\text{ cm}^{-1}$), the symmetric CH_3 (r^+ , $\sim 2875\text{ cm}^{-1}$), and the anti-symmetric CH_3 (r^- , $\sim 2965\text{ cm}^{-1}$) stretch modes are indicated with dashed lines. The value of the amplitude ratio d^+/r^+ is a common empirical indicator for the conformation of alkyl chains. When $d^+/r^+ \sim 0$, the alkyl chains adopt an all-trans conformation, while a value of $d^+/r^+ > 1$ is an indicator of the presence of gauche defects.³⁶ We also note that for all observed SFS spectra obtained in the CH stretch mode region, a value of $d^+/r^+ > 1$ is observed, indicating that in all cases, the surfactant alkyl tails exhibit a conformation dominated by the presence of gauche defects.

B. Micrometer-sized oil droplets in water

To test whether the droplet size influences the adsorption of surfactants, therefore droplet stability, we study hexadecane-in-water microemulsions stabilized with the same combinations of surfactants. Droplets of radii (R) ranging from $5\ \mu\text{m}$ to $20\ \mu\text{m}$ are prepared in a microfluidic flow focusing device (see Sec. II). To characterize the stability of microemulsions, we visualize droplets immediately after they entered the analysis chamber and $0.2\ \text{ms}$ thereafter, when they have come in contact with each other, as shown in Fig. 2. Note that inside the observation chamber, drops are slowed down significantly such that we do not expect their flow to influence their stability. Hence, we assign observed differences in drop stabilities to differences in the interfacial composition and/or structure.

Unstable droplets coalesce when they come in contact with each other; this results in changes in their number and size. Microscopy images suggest that droplets stabilized with SDS [Fig. 2(a)] or a combination of SDS and Span80 [Fig. 2(c)] are stable. By contrast, droplets stabilized with Span80 coalesce, as shown in Fig. 2(b). To test this finding further, we vortexed a solution composed of 10%

of the oil phase and 90% of the water phase, each one containing the appropriate surfactant, and observed the resulting emulsion over 8 h. The microemulsions are considered to be stable when the lighter oil droplets gather at the top of the cuvette, forming a horizontal layer of droplets which covers the meniscus and scatters light, leaving the heavier water phase at the bottom, as can be seen for emulsions stabilized with SDS or a combination of SDS and Span80, shown in movies S1 and S2, respectively. By contrast, when emulsions are unstable, the two fluid phases separate and a clear meniscus forms between the two phases, as observed for emulsions stabilized with Span80, as shown in movie S3. The presence of both surfactants at the micro-interface is verified with SFS measurements, as discussed in Sec. S2 in the [supplementary material](#). These results are in good agreement with our molecular-level observation and confirm that micrometer-sized droplets stabilized with SDS [Fig. 2(a)] or a combination of SDS and Span80 [Fig. 2(c)] are stable, whereas microdroplets stabilized only with Span80 [Fig. 2(b)] are unstable.

The results shown in Fig. 2 indicate that the stabilization of micrometer-sized droplets requires the presence of a surfactant soluble in the continuous phase, in agreement with expectations from empirical rules. However, in all cases, micrometer-sized droplets are more difficult to stabilize than nanometer-sized droplets.³⁸ Moreover, the microfluidic formation of emulsion droplets depends on the presence of the surfactants that affect the interfacial tension. As a result, the size of the micrometer-sized droplets produced in microfluidic devices strongly depends on the type of surfactant employed. Thus, the interaction of the surfactants with the hexadecane/water interface does not seem to be a simple matter of adding the effects of both surfactants, which is different from the results obtained from the nanometer-sized droplets.

C. Nanometer-sized water droplets in oil

If the surface curvature influences emulsion properties, we expect the interfacial surfactant structure of nanometer-sized water-in-oil emulsions to be different from that of oil-in-water emulsions. To test this expectation, we measured the adsorption of

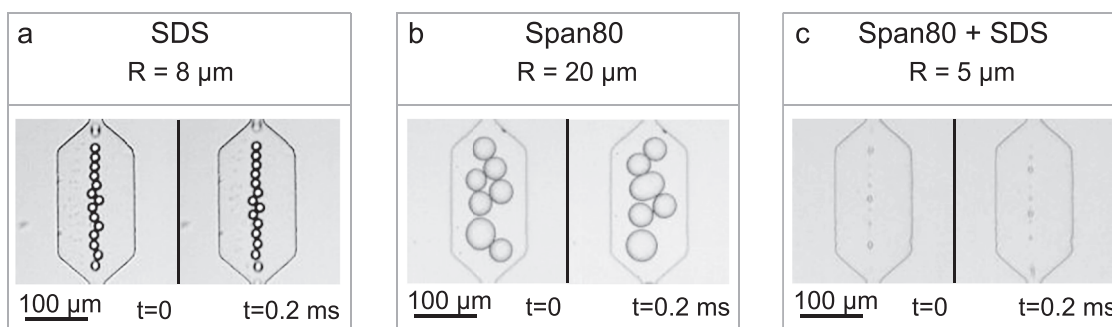


FIG. 2. Stability of micrometer-sized oil droplets in water. Microscopy images of hexadecane micrometer-sized droplets in water (radius $R = 5\text{--}20\ \mu\text{m}$) at $t = 0$ (left panels) and $t = 0.2\ \text{ms}$ (right panel) after the injection of droplets into the analysis chamber. Within the analysis chamber, which is incorporated into the main channel downstream the flow focusing junction, droplets are slowed down and forced to contact each other. The systems are stabilized with (a) 8 mM SDS, (b) 5 mM Span80, or (c) a combination of 8 mM SDS and 5 mM Span80.

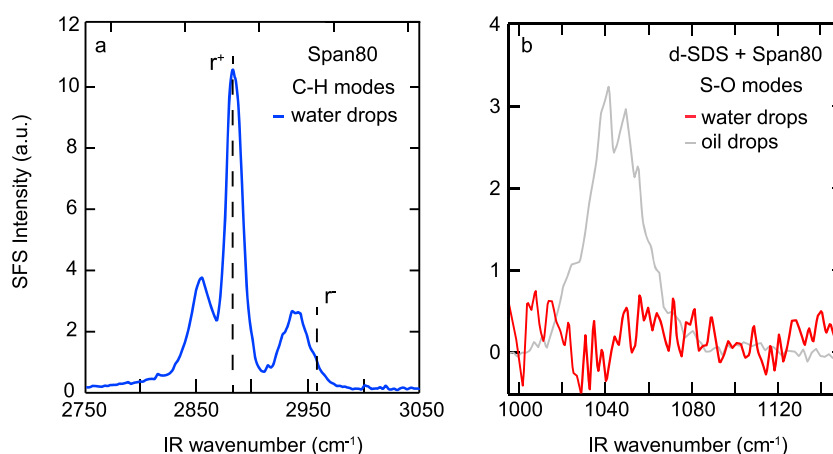


FIG. 3. Surface structure of surfactant stabilizing nanometer-sized water droplets in oil. Normalized SFS intensity spectra of interfacial surfactant molecules adsorbed at nanometer-sized droplets of D_2O (1 vol. %) in (a) d_{34} -hexadecane stabilized with 5 mM Span80 or (b) h_{34} -hexadecane stabilized with a combination of 8 mM d_{25} -SDS and 5 mM Span80. (a) CH stretch modes of the methyl and methylene groups of the interfacial Span80 molecules. Symmetric and antisymmetric stretches of the CH_3 groups are indicated with dashed lines at 2845 cm^{-1} (r^+) and 2965 cm^{-1} (r^-). (b) Spectra of the symmetric S–O stretch mode of the sulfate head group (with a resonance frequency of 1045 cm^{-1}) of interfacial d_{25} - DS^- molecules. All SFS spectra were collected with the IR (VIS, SF) beam polarized parallel (perpendicular) to the scattering plane (SSP). The radius of the nanoemulsion and its PDI are (a) 75 nm and 0.16 and (b) 100 nm and 0.2.

surfactants at the interface of nanometer-sized water droplets dispersed in hexadecane with SFS. The results are shown in Fig. 3.

Droplets are stabilized with 5 mM Span80 [Fig. 3(a)], or with a combination of 8 mM SDS and 5 mM Span80 [Fig. 3(b)]. As expected, it was impossible to stabilize water droplets in oil by using only SDS. By contrast, water droplets in oil were stabilized when Span80 was added to the oil phase. Indeed, in this case, the observation of CH stretch surface vibrational modes ($\sim 2850\text{--}2970\text{ cm}^{-1}$) in Fig. 3(a) shows that Span80 is adsorbed at the droplet interface. The value of the amplitude ratio r^-/r^+ can be used to calculate the average tilt angle of the CH_3 group with respect to the droplet surface, as discussed in Ref. 26. A ratio of $r^-/r^+ \sim 0.27$ indicates that the CH_3 groups of the interfacial Span80 molecules are approximately parallel to the surface normal, as detailed in Ref. 26. By contrast, if nanometer-sized water droplets are formed with SDS only,

they immediately coalesce. Interestingly, when droplets are stabilized with a combination of surfactants, SFS spectra of the S–O symmetric stretch mode displayed in Fig. 3(b) show a complete absence of SDS molecules at the interface. The response of the S–O symmetric stretch mode of the sulfate head group of d_{25} - DS^- when both SDS and Span80 are used to stabilize nanometer-sized oil droplets is repeated in Fig. 3(b) for comparison.

D. Micrometer-sized water droplets in oil

To test the stability of micrometer-sized water droplets in oil, we prepare water droplets in oil with Span80, SDS, or a combination of the two surfactants using our microfluidic device. Micrometer-sized droplets of radii between ~ 7 and $15\ \mu\text{m}$ are prepared. The results are shown in Fig. 4. Droplets stabilized with SDS coalesce, as can be seen by the increase in the size of droplets after they

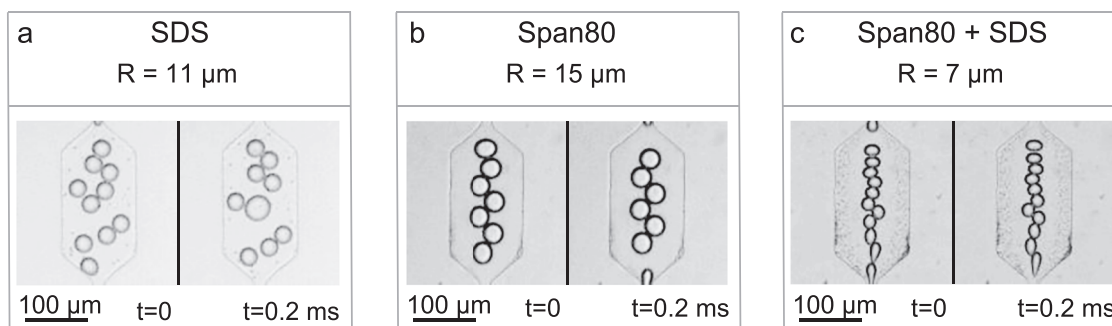


FIG. 4. Stability of micrometer-sized water droplets in oil. Microscopy images of micrometer-sized water droplets in oil (radius $\sim 7\text{--}15\ \mu\text{m}$) when they entered the analysis chamber at $t = 0$ (left panels) and $t = 0.2\text{ ms}$ thereafter (right panels). The systems are stabilized with (a) 8 mM SDS, (b) 5 mM Span80, or (c) a combination of 8 mM SDS and 5 mM Span80.

have been in the analysis chamber for 0.2 ms, as shown in Fig. 4(a). By contrast, Figs. 4(b) and 4(c) show that droplets stabilized with Span80 or a combination of SDS and Span80 are stable, as can be found by comparing the size of droplets immediately after they entered the analysis chamber and those that have been there for 0.2 ms.

To confirm these results, we vortexed a solution containing 10% of the water phase and 90% of the oil phase, each containing the surfactant soluble in the respective phase and observed the resulting emulsion over 8 h. Macroscopic phase separation cannot be observed within 8 h if microemulsions are stabilized with Span80 or a combination of SDS and Span80, indicating that these microemulsions are stable, as shown in movies S4 and S5, respectively. By contrast, emulsions stabilized only with the SDS phase separate within 30 s, indicating that these emulsions are unstable, as shown in movie S6. These macroscopic data support the microscopic observation that water micrometer-sized droplets stabilized with Span80 or a combination of SDS and Span80 are stable, in contrast to micrometer-sized droplets stabilized with SDS only.

IV. DISCUSSION

Empirical rules that govern emulsion stability, such as the Bancroft rule, the HLB scale, and SAD, predict that (kinetically stable) emulsions will be stable if surfactants are mainly present in the continuous phase. However, such rules are based on macroscopic observations and the molecular mechanisms behind them are still not understood. Interestingly, recent experimental studies have shown that charged surfactants stabilize the nanoscopic interface of oil in water nanometer-sized emulsions with a different structure and surface density than surfactants at the respective flat oil/water interface.^{31,39} To further explore whether size-dependent effects/differences appear in the stability and surface structure with the inversion of the two phases (oil in water vs water in oil emulsions), we compared nanometer-sized emulsions with micrometer-sized ones stabilized with Span80, SDS, or the combination of the two. Again, the mean field approach predicts no difference between these two systems of different size. Instead,

our results, summarized in Table I, show that the latter does not hold and differences are observed in the stability of the two systems.

In terms of stability, we find that nanodroplets of both oil and water can be stabilized with the neutral hydrophobic surfactant Span80. For nanodroplets, there are a few other notable findings that are unexpected, based on the empirical Bancroft rule, the HLB scale, or the SAD. Figure 1 shows that hexadecane-in-water nanoemulsions can be stabilized by SDS and Span80, as well as by a combination of the two surfactants. The water-soluble DS⁻ anions populate the interface [Figs. 1(c), 1(e), and 1(f)] and stabilize it by forming a dilute layer of charges²⁵ with surfactant areas of >4.25 nm².²⁵ Since the density of SDS at the interface of these small droplets is considerably lower than that measured for macroscopic interfaces,³⁹ there is enough room for Span80 molecules to co-adsorb. Furthermore, the very different SFS intensity spectra measured for oil [Fig. 1(b)] and water [Fig. 3(a)] nanometer-sized droplets indicate that Span80 attains a very different interfacial configuration in the two systems (oil-in-water or water-in-oil). The SFS intensity, which differs by a factor of 20 between the two systems [max. of ~0.55 in Fig. 1(b) vs ~11 in Fig. 3(a)], indicates that the density of Span80 at the surface of oil nanodroplets in water is much lower than at the surface of water nanodroplets in oil, even when their sizes are similar. Another interesting feature is that there is no signature of SDS on the water nanodroplet surface, even when it is present in the aqueous phase, as displayed in Fig. 3(b). This suggests that SDS stays essentially in the dispersed water phase (within the detection limit of SFS), while Span80 adsorbs at the liquid-liquid interface and imparts stability to the system. Given that SDS is an amphiphilic molecule and that the water/hexadecane interface is a water/oil interface, this may be considered surprising from a surface chemistry point of view.

By contrast, micrometer-sized droplet behavior is in agreement with empirical expectations. Stability arises only when a surfactant is added that is soluble in the main phase. The difference between both behaviors may have something to do with the size of the droplets compared to the length scale over which interactions occur. For nanometer-sized droplets, the droplet size is on the

TABLE I. Summary of findings regarding stability and droplets' interfacial structure for nanodroplets and micrometer-sized droplets.

	Surfactant(s) used to stabilize the system		
	SDS	Span80	SDS + Span80
Formation of stable nanometer-sized:			
Oil droplets	Yes	Yes	Yes
Water droplets	No	Yes	Yes
Surfactants at the interface of the nanometer-sized:			
Oil droplets	Yes	Yes	Yes + Yes
Water droplets	No ^a	Yes	No + Yes
Formation of stable micrometer-sized:			
Oil droplets	Yes	No	Yes
Water droplets	No	Yes	Yes

^aThe absence of surfactant from the nanointerface is postulated from the instability of the respective system. Here, SFS measurements could not be conducted as they require stable droplets.

order of, or below, the electrostatic interaction length scale,³⁹ which impacts the interfacial structure. If this is also true for other types of interactions remains an open question although recent measurements of the hydrogen bond network structure on the surface of a water droplet suggest that hydrogen bonds rearrange differently over different length scales.²⁶

V. CONCLUSIONS

In this work, we provided a comparison between the stability and the interfacial structure of micrometer-sized and nanometer-sized droplets by employing a multi-instrumental approach comprised of the surface-sensitive technique of sum frequency scattering as well as dynamic light scattering and microscopy. We monitored the stability of oil-in-water and water-in-oil emulsions and the presence of surfactants at the oil/water nano-interface, when stabilized with an oil-soluble neutral surfactant (Span80), a water-soluble anionic surfactant (sodium dodecyl sulfate, SDS), or with a combination of the two. Micrometer-sized droplets are found to be stabilized only when a surfactant soluble in the continuous phase is present in the system, in agreement with what is traditionally observed empirically. Surprisingly, the nanodroplets behave differently. Both oil and water nanodroplets can be stabilized by the same neutral Span80 surfactant but with different surface structures. A combination of SDS and Span80 also suffices, but for the case of water droplets, the strongly amphiphilic SDS molecules are not detected at the interface. For the case of oil droplets, both surfactants are at the interface but do not structurally affect one another. Thus, it appears that empirical rules such as the Bancroft rule, the HLB scale, and the SAD Difference work best when emulsion droplets exceed a certain size, probably due to a different balance of interactions on different length scales. This outcome is of great interest to a large community of researchers working in chemistry, soft matter science, and biological sciences.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for sections on surface structure of SDS with and without the addition of Span80 in a system of nanometer-sized oil droplets in water (S1), surface structure of SDS and Span80 in a system of micrometer-sized oil droplets in water (S2), and size distributions measured by dynamic light scattering (DLS) for the nanometer-sized oil droplets in water and water droplets in oil (S3), as well as for Figs. S1-S3 and microscopy movies S1-S6.

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