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Mechanical Characterization of Ultralow Interfacial Tension Oil-in-Water Droplets by Thermal Capillary Wave Analysis in a Microfluidic Device

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ABSTRACT: Measurements of the ultralow interfacial tension and surfactant film bending rigidity for micron-sized heptane droplets in bis(2-ethylhexyl) sodium sulfosuccinate—NaCl aqueous solutions were performed in a microfluidic device through the analysis of thermally driven droplet interface fluctuations. The Fourier spectrum of the stochastic droplet interface displacement was measured through bright-field video microscopy and a contour analysis technique. The droplet interfacial tension, together with the surfactant film bending rigidity, was obtained by fitting the experimental results to the prediction of a capillary wave model. Compared to existing methods for ultralow interfacial tension measurements, this contactless, nondestructive, all-optical approach has several advantages, such as fast measurement, easy implementation, cost-effectiveness, reduced amount of liquids, and integration into lab-on-a-chip devices.

INTRODUCTION

Immiscible liquids with ultralow interfacial tensions (ULIFT), such as oil−water microemulsions and aqueous two-phase systems, are ubiquitous in a number of important applications in the oil industry (e.g., enhanced oil recovery) and environmental protection (e.g., oil pollution remediation), as well as the food and pharmaceutical industries. When the interfacial tension reaches values lower than 1 μN/m, classical techniques, such as the Wilhelmy plate and the pendant sessile drop, are very difficult to apply. For those systems, the commonly used techniques are based on the analysis of either the steady-state deformation of droplets caused by external forces (e.g., spinning droplet tensiometry)1 or droplet relaxation dynamics after cessation of the rotational flow field (e.g., relaxation time method).2 Similarly, the interfacial tension can also be estimated by following the early breakup dynamics of elongated droplets subject to rotational flow fields (the so-called breaking-thread method).3 Alternatively, the profile analysis of flat interfaces deformed either by the presence of single walls4 or by continuous laser sources5 can be used to measure such ultralow values of interfacial tension. Unfortunately, these methods require dedicated apparatus, and hence, they cannot be integrated into a lab-on-a-chip device with multiple functionalities. To this end, Tsai et al.6 have recently introduced a microfluidic device for ultralow interfacial tensiometry where the interfacial tension is estimated by analyzing the dynamics of magnetic particles crossing a flat liquid interface. Although this microfluidic technique can effectively measure interfacial tension on the order of 0.1−1 μN/m, the precalibration of the particle magnetic susceptibility, the risk of interface contamination caused by these magnetic probes, and the requirements of low viscosity contrast between the liquid phases limit the applicability of this method. Furthermore, none of the mentioned methods can measure the bending rigidity of the fluid−fluid interface.

Microfluidic manipulation of ULIFT oil−water interfaces within a microfluidic environment has recently attracted growing interest both experimentally7−10 and theoretically.11 Carefully chosen surfactant−oil−water systems can be used to lower the interfacial tension down to 1 μN/m or less. Under this condition, optical fields allow one to sculpt oil droplets into more complex shapes for manufacturing asymmetric solid particles,7,8,12 to actuate flows in micron-sized liquid channels created by light7 as well as to create user-defined three-dimensional nanofluidic networks.10,13 In order to characterize and optimize emulsion systems for such applications, a simple and fast method for ULIFT measurements is highly desirable. A microfluidic approach offers the possibility of integrating the mechanical characterization of the ULIFT interfaces directly into the lab-on-a-chip devices, where these interfaces are optically manipulated, hence avoiding the need for a dedicated tensiometry apparatus (e.g., spinning droplet tensiometry).

At equilibrium, thermal motion causes stochastic fluctuations of the local position of the interface between two fluid phases.14 The typical amplitude of this thermally driven capillary waves is on the order of (kBT/γ)1/2, where kBT is the Boltzmann constant, T is the absolute temperature, and γ is the interfacial tension. When γ is in the range from 0.1 to 1 μN/m, the fluctuation amplitudes are on the order of 100 nm, so conventional digital video microscopy can be used to detect the capillary waves at...
the interface between two phases. Such a direct visual observation of capillary waves for a phase-separated colloid–polymer system was performed through confocal microscopy by Aarts et al., thereby enabling the measurement of ultralow tension values. However, this approach required the use of a horizontally placed microscope in order to image the horizontal interface profile, and such a configuration is not suitable for lab-on-a-chip applications. Conversely, the analysis of the equilibrium thermal fluctuations, measured at the equatorial plane of lipid vesicles and cell membranes, enables the simultaneous measurements of the membrane interfacial tension and bending rigidity within a microfluidic environment by standard microscopy techniques. Despite these advantages, this method has never been used to characterize the interfacial properties of oil/water emulsion droplets.

In this work, we combined our microfluidic technique for the generation of monodisperse ultralow interfacial tension oil-in-water droplets with the analysis of thermal capillary waves, observed at the droplet equatorial plane through bright-field microscopy. By fitting the static fluctuation spectrum to the prediction of a capillary wave model, both the droplet interfacial tension and the surfactant film bending rigidity were measured. Although this method was validated for an oil–water–surfactant system close to the microemulsion phase transition, it could also be applied to other ULIFT systems, provided that such a suitable capillary wave model is used (e.g., phase-separated colloid–polymer solutions, aqueous two-phase systems). Easy implementation, cost-effectiveness, fast measurement, absence of external probes, reduced amounts of liquid samples, and integration into microfluidic devices are the advantages of our approach with respect to other existing methods.

**EXPERIMENTAL SECTION**

**Experimental Setup.** The generation, transport, and storage of monodisperse ULIFT droplets were performed using a microfluidic platform described in our previous work and briefly summarized here. Heptane (VWR, 99%) and an aqueous solution of bis(2-ethylhexyl) sodium sulfosuccinate (AOT) (Sigma-Aldrich, 98%) and sodium chloride (VWR, 99.6%) were used as dispersed and continuous phases, respectively. Droplets were generated in a glass flow-focusing junction device at room temperature (T ≈ 21 °C) and subsequently collected in a separate microfluidic chamber (Figure 1a). The latter was manufactured by plasma bonding a microscope glass slide to a 24 × 60 mm coverslip coated with a PDMS film 30 μm in thickness. The flow-focusing junction device (Dolomite 3200136) was fed with the aqueous (continuous) and oil (dispersed) phases by means of syringe pumps (WPI-Aladdin2-220). The flow rates of the aqueous and oil phases were 20 and 0.5 μL/min, respectively, and the resulting average droplet diameter was 15.5 ± 0.4 μm. After formation, droplets were transferred in the observation chamber, which was pre-equilibrated at the desired temperature through the thermal control unit. This was consisting of a 2 × 5 mm resistance thermometer (PT100 Class A) and a Peltier cell (Ferrotec) attached to the glass slide and coverslip of the observation chamber chip, respectively. The bottom wall of the chip was covered with a 2-mm-thick PDMS layer to be thermally isolated from the external environment. A 5 mm diameter hole was punched in the PDMS layer to avoid any optical aberration caused by the latter. The Peltier cell had a central 5 mm diameter hole to allow optical access to the chamber. A finite element analysis was performed with Comsol Multiphysics (COMSOL Ltd.) to estimate the temperature field in the observation chamber by assuming that heat enters the system from the Peltier module and leaves it through the external walls by natural convection. For a typical room temperature of 22 °C and an average chip temperature of 30 °C, the standard deviation of the temperature field in the observation chamber is about 0.3 °C. This value is a quantitative estimate for the uncertainty of the emulsion temperature measurements. Droplets were imaged using an inverted microscope (Olympus IX81) in bright-field mode, equipped with a 60× 0.7 NA objective and a 12-bit CCD camera (QImaging Retiga EXi fast). The camera frame rate was varied between 1 and 10 fps. The scale factor m of the optical system was 0.109 μm per pixel.
Capillary Wave Model. The thermally driven fluctuations of a liquid–liquid interface about a reference plane \( z = 0 \) can be described through the normal displacement field \( h(x,y) \). The Fourier transform of the static correlation function, defined as \( g(x,y) = \langle h(x',y') h(x+x',y+y') \rangle \), gives the static fluctuation spectrum, which can be written as

\[
\langle h(k_x,k_y) \rangle^2 = \frac{1}{k_T} \frac{k_x T}{\gamma k_x^2 + k_y^2}
\]

where \( h(k_x,k_y) \) is the Fourier transform of \( h(x,y) \), defined as \( \frac{1}{\pi} \int h(x,y) e^{i(k_x x + k_y y)} dk_x dk_y \), \( k_2 \) is the amplitude of the wave vector \( (k_x,k_y) \) corresponding to the position vector \( (x,y) \), \( T \) is the temperature, \( \gamma \) the interfacial tension, \( \kappa \) the interface bending rigidity, \( A \) the interface area projected to the reference plane, and angled brackets denote the ensemble average. Since eq 1 describes the static character of the capillary waves, it does not contain any dynamic quantities (e.g., the liquid viscosities). Bright-field microscopy allows us to measure the interface deformation at the droplet equatorial plane only, so the observable fluctuation spectrum is

\[
\langle h(k_x,k_y) \rangle^2 = \frac{k_x T}{2L_x \gamma} \left( \frac{1}{k_x^2} - \frac{1}{\sqrt{k_x^2 + k_y^2}} \right)
\]

where \( L_x \) is the droplet equatorial circumference. The lifetime \( \tau \) of the fluctuations decreases as the wavenumber increases. If at the higher wavenumbers \( \tau \) is comparable to the camera exposure time, the corresponding interface deformations are averaged by the camera over the time \( \tau \). As a result, the fluctuation spectrum, measured at the higher modes, is no longer accurate. To correct the dynamic error caused by the camera, Fécreaux et al.\textsuperscript{16} calculated the average of the static correlation function over the camera exposure time, thereby obtaining the following corrected prediction for the measured fluctuation spectrum

\[
\langle \hat{h}(k_x,k_y) \rangle^2 = \frac{k_x T}{4L_x \eta} \int_{-\infty}^{\infty} \left[ \frac{\tau}{\tau_m + \exp\left( \frac{\tau}{\tau_m} \right)} - 1 \right] dk_y
\]

where the fluctuation lifetime is given by

\[
\tau_m = \frac{4\eta}{k_y^2 + k_x^2}
\]

Equation 3 holds when the dispersed and continuous phases have the same dynamic viscosity \( \eta \). In our system, the two phases have different viscosities, so we replaced the parameter \( \eta \) with an effective viscosity \( \eta_{df} \) equal to \( \eta_{df} = (19\mu + 6/2\mu + 3/80\mu + 80\mu)^{-1} \), where \( \mu \) is the ratio between the continuous and dispersed phase dynamic viscosities \( \eta_c \) and \( \eta_d \) respectively. The detailed derivation of \( \eta_{df} \) is available in the Supporting Information (SI). To avoid any artifact caused by the camera dynamic error, we fitted the experimental data to eq 3 instead of eq 2. To ease the notation, in the following we will denote \( \hat{h}(k_x,k_y=0) \), \( L_x \), and \( k_x \) as \( h(k), L, \) and \( k \) respectively.

Interfacial Tension and Bending Rigidity Measurements. As the droplets reached the observation chamber chip, the flow was stopped and the droplets, at rest, were allowed to equilibrate at the chip temperature for a few minutes. The droplet interface profile was measured via image-processing analysis implemented in Python. The oil–water interface position was detected with subpixel precision on \( N = L_m/3 \) equally spaced points along the droplet interface, where \( L_m = L/m \) is the droplet circumference in pixels. The following interface detection algorithm was adopted. After selecting an initial guess for the droplet center, the radial pixel intensity profile \( I(r) \), averaged over the azimuthal angles from \( \theta = 2\pi/N \) to \( \theta_{1} = 2\pi(i + 1)/N \), was calculated. The indiction point \( r \) of the pixel intensity distribution \( I(x,y) \) was determined (Figure 1c) and assumed as the radial coordinate of the interface point at the angle \( \theta \). The same operations were repeated for \( i \) from 0 to \( N - 1 \). An example of the detected interface profile is shown in Figure 1b as a solid line overlapping the micrograph of a deforming droplet. The corresponding plot of the polar coordinates \((\theta, r)\) is reported in Figure 1d. Subsequently, the droplet interface profile was fitted to a circle. The center of the best-fitting circle was used as the new origin of the polar coordinate system, and the pixel intensity profiles \( I(r) \), as well as the inflection points \( r_p \) were calculated again with respect to this new center. Such an operation is required to avoid artifacts due to slight displacement of the droplet between two consecutive frames. The center of the best-fitting circle of one frame is used as an initial guess for the droplet center in the consecutive frame.

The interface fluctuation amplitude at the angle \( \theta \) was defined as \( u_i = r_i - R \), where \( R \) denotes the radius of the best-fitting circle. The discrete Fourier transform of the fluctuation displacements \( u_i \) was calculated and denoted as \( U(k) \). The wavenumbers \( k_i \) are defined as \( k_i = n N/R \) with \( n \in [-N/2, N/2 - 1] \) if \( N \) is even or \( n \in \{-(N - 1)/2, (N - 1)/2 \} \) if \( N \) is odd. The experimental fluctuation spectrum \( \langle \hat{h}(k_i) \rangle^2 \) was obtained by averaging the expression \( I(U(k_i))^2/N^2 \) over 200 frames. Finally, both the interfacial tension and the bending rigidity were obtained by fitting the experimental spectrum \( \langle \hat{h}(k_i) \rangle^2 \) to eq 3.

The absolute errors of the measured interfacial tension and bending rigidity were calculated as 3 times the corresponding fit parameter uncertainties. To confirm the reproducibility of the results, we verified that three consecutive measurements for the same droplet at constant temperature returned interfacial tension and bending rigidity values within the corresponding absolute errors.

To conclude, it is worth reporting that, even though a third surfactant-rich microemulsion phase should coexist with the excess oil and water phases between the critical end point temperatures, such a third phase could not be observed in our experiments.

Fitting Procedure. The first five modes (i.e., \( k_0 \), \( k_1 \), \( k_2 \), \( k_3 \), \( k_4 \)) were not included in the fit, since at these wavenumbers the assumption of a planar interface is no longer valid.\textsuperscript{13} The higher modes must also be excluded from the fit because of artifacts caused by the image pixelization and the finite lateral spatial resolution of the microscope. Due to the pixelization of the interface position in the direction parallel to the interface, we ignored any fluctuations wavelengths shorter than 5 pixels. Artifacts due to the microscope lateral spatial resolution \( d_{pxy} \) are avoided by disregarding fluctuations wavelengths smaller than \( 5d_{pxy} \). Consequently, the experimental fluctuation spectrum \( \langle \hat{h}(k_i) \rangle^2 \) was fitted to eq 3 in the range \([k_5, k_{max}]\), where \( k_{max} = \frac{2\pi}{5 \max(m d_{pxy})} \). The validity of the arbitrarily defined threshold \( k_{max} \) was confirmed by the experimental results, as discussed later.

The resolution of the interface position measurement in the direction orthogonal to the interface depends on several parameters, such as the image pixelization, the noise level of the camera, the exposure time, the microscope lamp intensity, and the objective numerical aperture. This resolution was experimentally measured by tracking the interface of a rigid droplet whose interfacial fluctuation amplitudes are on the order of nanometers or lower, thereby inaccessible to a bright-field microscope. The resulting fluctuation spectrum is a constant value \( \varepsilon \), which defines the level of the random background noise in the Fourier domain. As a result, the experimental fluctuation spectra \( \langle \hat{h}(k_i) \rangle^2 \) are fitted to eq 3 only in the range of wavenumbers where \( \langle \hat{h}(k_i) \rangle^2 > \varepsilon \).

RESULTS AND DISCUSSION

Figure 2 shows the fluctuation spectra, excluding the first five modes, for heptane droplets in (i) 4 mM AOT aqueous solution at 21.0 °C (squares), (ii) 2 mM AOT and 50 mM NaCl aqueous solution at 26.6 °C (triangles), and (iii) 2 mM AOT and 50 mM NaCl aqueous solution at 26.3 °C (circles). The camera exposure time was 0.01 ms. The inset in the figure shows the normalized distributions of the fluctuation amplitudes for the three droplets together with the best-fitting Gaussian curves. For case i, the droplet interfacial tension is about 1 mN/m. Consequently, the expected fluctuation amplitudes were well below the localization precision, and...
any measured interface displacement was just due to random noise. The droplet was hence rigid with a perfectly spherical shape. The corresponding standard deviation of the fluctuation distribution, which is about 36 nm (see inset Figure 2), provides a quantitative estimate for the resolution of our interface tracking method. Such a resolution can be reduced to 11 nm (that is $1/10$ of the pixel size) if the exposure time is increased to 0.1 ms. The spectrum of the rigid droplet is almost flat with a mean value of $\langle \varepsilon \rangle \approx 1.2 \times 10^{-17}$ m$^2$ (horizontal dashed line in figure). This spectrum represents the signal of the random background noise in the Fourier domain. The noise level $\varepsilon$ is reduced to $1.1 \times 10^{-18}$ m$^2$ when the camera exposure time is increased to 0.1 ms. As already mentioned, the experimental fluctuation spectra are fitted to eq 3 only in the range of wavenumbers where the squared amplitude of the fluctuations is higher than $\varepsilon$. This condition sets the upper limit of the range of interfacial tension that can be measured by our system to a few $\mu$N/m (see the SI). It is worth noting that, according to eqs 2 and 3, $\varepsilon$ depends on the droplet radius. However, the microfluidic approach allowed us to generate a monodisperse droplet population, so such a dependence can be neglected. In cases ii and iii, 50 mM NaCl was added to 2 mM AOT aqueous solution under varying temperature conditions. The resulting interfacial tension values varied over a range of a few tens of $\mathrm{mN/m}$ to a few $\mu\mathrm{N/m}$. The standard deviation $\sigma_\varepsilon$ of the interface fluctuation distribution (see inset of Figure 2) is a measure of the typical fluctuation amplitude, and as such, it is expected to scale linearly with $\sqrt{k_0 T/\gamma}$. Figure 3 shows the correlation between $\sigma_\varepsilon$ and $\sqrt{k_0 T/\gamma}$ for our measurements. This plot is well fitted by a linear relation $\sqrt{k_0 T/\gamma} = a \sigma_\varepsilon$ with fitting parameter $a = 1.21 \pm 0.06$. Our measurements of interfacial tensions and interface fluctuation amplitudes thus follow the expected scaling law. It is also worth highlighting the correlation between the interfacial tension and the droplet equatorial radii. The droplet deformations are greatly exaggerated for illustration purpose.
of 15 μm and interfacial tensions ranging from 0.1 to 1 μN/m, Bo varies between 0.2 and 2. As a result, the average droplet shapes only slightly deviate from a sphere, and hence, the buoyancy-induced droplet deformations have no effect on the interface fluctuation analysis.

Let us now consider the measurements of bending rigidity of the monolayer surfactant film coating the oil droplets. In Figure 4 the values of bending rigidity are plotted against those of interfacial tension. This plot shows two unexpected results: (i) at the higher interfacial tensions, the fitted values of κ are outside the range of (0.5—5)k0T (gray area in the figure) in which literature data of AOT film bending rigidity previously reported in the literature.20,21 The inset shows the fluctuation spectra (obtained with a 0.7 NA objective) and the corresponding best-fitting curves for three droplets with increasing κ: 2.0k0T (circles), 11.7k0T (triangles), and 29.8k0T (squares). The camera exposure times were 0.01 ms (circles and triangles) and 0.1 ms (squares). These spectra show a crossover from a scaling law k−4 at low wavenumbers, where the amplitude mainly depends on γ, to a scaling law k−3 at the high wavenumbers, where the amplitude mainly depends on κ.

Figure 4. Correlation between the droplet interfacial tension γ and the AOT film bending rigidity κ. The droplet interface motion was tracked by using inverted microscopes equipped with 0.7 NA (white circles) and 1.4 NA (black circles) objectives. The gray area represents the range of values for the AOT film bending rigidity previously reported in the literature.20,21 The inset shows the fluctuation spectra (obtained with a 0.7 NA objective) and the corresponding best-fitting curves for three droplets with increasing κ: 2.0k0T (circles), 11.7k0T (triangles), and 29.8k0T (squares). The camera exposure times were 0.01 ms (circles and triangles) and 0.1 ms (squares). These spectra show a crossover from a scaling law k−4 at low wavenumbers, where the amplitude mainly depends on γ, to a scaling law k−3 at the high wavenumbers, where the amplitude mainly depends on κ.

### Equation 3

\[
(k_{\parallel}k_{\perp})^2 = \frac{1}{A} (\gamma_0 + \gamma_1(k_{\perp})) k_{\perp}^2 + \kappa_0 k_{\perp}^4
\]

with \(\kappa_0\) being the actual film bending rigidity. So, the high values of the fitting parameter κ could be due to the term \(\gamma_1(k_{\perp})k_{\perp}^{-2}\) instead of \(\kappa_0\), which is on the order of \(k_0 T\). Such a mechanism could also explain the positive correlation between γ and κ. As the interfacial tension increases, the measured interface fluctuations are of lower amplitude but are faster, thereby possibly limiting the amount of surfactant diffused to the interface. For a given wavenumber, this could lead to the increase of the local interfacial tension and, thus, of the term \(\gamma_1\).

Finally, we validated our method by measuring the interfacial tensions of heptane droplets in 51.2 mM NaCl and 2 mM AOT aqueous solution at varying temperatures. Figure 5 shows the comparison between our interfacial tension measurements (gray circles) and those obtained by Aveyard et al. under the same conditions through spinning droplet tensiometry20 (white circles). The good agreement between these two sets of data demonstrates that our method is capable of reproducing the expected trend of the interfacial tension against temperature. At a given salt concentration, the droplet interfacial tension reaches a minimum at the so-called phase inversion temperature (PIT). Spinning droplet tensiometry measurements near the PIT are difficult to perform because the ULIFT leads to the onset of artifacts (e.g., dumbbell- and dog-bone-shaped droplets) as well as hydrodynamic instabilities that eventually cause the droplet breakup. Our microfluidic method has no such disadvantages, but instead, its sensitivity and precision increase as temperature approaches the PIT, since lower...
interfacial tensions correspond to larger fluctuation amplitudes and, hence, higher signal-to-noise ratios. Furthermore, in spinning droplet tensiometry the density ratio between the dispersed and the continuous phases has to be lower than unity, whereas our microfluidic approach can measure the interfacial properties of droplets either lighter or heavier than the surrounding medium. Finally, the time required for the droplet shape to equilibrate during spinning droplet measurements can be quite long (up to 1 h) due to the slow droplet dynamics in the ULIFT regime. Conversely, micron-sized droplets, enclosed in a temperature-controlled microfluidic environment, rapidly reach the thermal equilibrium, and data acquisition for thermal capillary wave analysis is hence very fast (i.e., a few minutes).

Since our platform allows for the rapid evaluation of the droplet interfacial properties under varying conditions of temperature and salinity level, the proposed method is particularly useful for the characterization of those microemulsion systems for which the phase behavior is unknown and for which the physical conditions for the phase inversion have to be determined. Our technique should also allow for the characterization of the interfacial properties of other ULIFT systems (e.g., phase-separated colloid–polymer solutions, all-aqueous polymer solutions) as long as the interface fluctuation amplitudes are larger than the optical resolution of the microscope (namely, γ lower than a few μN/m) and an appropriate capillary wave model is used.

**SUMMARY**

In conclusion, in this paper we have presented a microfluidic technique for the measurement of the interfacial tension of oil-in-water droplets over a range from a few tens of nN/m to a few μN/m. The bending rigidity of the surfactant film, formed at the oil–water interface, was also determined. The Fourier spectrum of the droplet interface displacements was measured via bright-field digital video microscopy and fitted to the theoretical prediction for the thermal-driven fluctuations of a fluid membrane with the interfacial tension γ and the bending rigidity κ as the fitting parameters. The standard deviation of the fluctuation amplitudes was also measured and demonstrated to scale linearly with \((k_B T/\gamma)^{1/2}\). The fitting parameter κ was found to be positively correlated to γ. We hypothesize that at the higher wavenumbers the equilibrium surfactant surface coverage might not be reached on the time scale of the interface expansion. As a consequence, the dynamic interfacial tension depends on the fluctuation wavenumber, thereby leading to an additional term in the model parameter κ. Artifacts in the experimental method were ruled out by comparing the measurements obtained through optical setups with different spatial resolutions. The bending rigidity of DOPC giant unilamellar vesicles was also measured and compared to literature data. Our microfluidic technique was finally validated by measuring the interfacial tension for a heptane–AOT–NaCl–water system at varying temperatures and comparing our results with the corresponding spinning droplet tensiometry data available in the literature.

Compared to existing techniques for ULIFT measurements, our method has several advantages, including fast measurement, absence of external probes, easy implementation, reduced amount of liquids, and integration into lab-on-a-chip devices. As a consequence, this technique will prove very useful for the rapid characterization and optimization of ULIFT emulsion systems for both traditional applications, such as surfactant-enhanced oil recovery, and more recent applications, such as flow actuation in micron-sized liquid channels created by light, optical sculpting of micron-sized droplets for the synthesis of asymmetric solid particles, and optical generation and manipulation of nanofluidic networks.

**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b04702.

Further details on the microfluidic tensiometry technique and the results of control experiments (PDF)

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**Notes**

The authors declare no competing financial interest.

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![Figure 5. Variation of interfacial tension with temperature. The results from microfluidic tensiometry (gray circles) are in good agreement with those obtained through spinning droplet tensiometry (white circles). The error bars are ±0.2 °C for the spinning droplet tensiometry data and ±0.3 °C for the microfluidic tensiometry data.](image-url)


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