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Microemulsion droplets in optical traps

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ABSTRACT

While the optical manipulation of solid particles is increasingly familiar, complex liquids represent a relatively new area of investigation. In this study, microscopic liquid–liquid interfaces are deformed at ultralow interfacial tension using near-infrared optical tweezers. The chosen emulsions, of hydrocarbon oil (heptane and decane) in aqueous solutions of surfactant (AOT, $C_{12}E_4$, $C_{12}E_5$, Brij-L4) and salt, are capable of forming Winsor microemulsions, although the macroscopic phase volumes are unaffected by changes in ambient temperature. The amphiphilic ratio of nonionic ($C_{12}E_{4,5}$) and anionic (AOT) surfactants is chosen to minimise the temperature dependence of the monolayer curvature. These phases and their dispersions are examined, both with and without equilibration of the compositions. Under laser action at powers >0.1 W, a plethora of metastable phases, multiple emulsions and vesicles are produced.

The rates of phase separation of microemulsion increase near the coverglass, which absorbs the laser more strongly. Conversely, substitution with heavy water reduces the absorptive heating, whilst maintaining a similar refractive index contrast. Localised laser heating is found to be the major driving force behind phase separation. The observed changes are rationalised in terms of the phase diagram of the microemulsion and the value of the amphiphilic ratio. The relative importance and origin of the thermal and optical effects on phase separation are discussed.

1. Introduction

Thermodynamically stable mixtures of oil, water and surfactant, known as microemulsions, are of great practical importance for their solubilisation capacity [1], in enhanced oil recovery [2], and as media for enzymatic catalysis [3,4]. Microemulsions exhibit ultralow interfacial tensions (ULIFT) between co-existing aqueous, oleic and middle phases (the latter having a bicontinuous structure composed of interconnected aqueous and oleic phases). ULIFT results in interesting effects including complete wetting or non-wetting of surfaces, stability of jets and threads, and extreme deformability under body or surface forces [5,6].

During the last decade, optical deformations of liquid–liquid interfaces have been explored in bulk [7] and in emulsion microdroplets [8,9]. In [9], we showed how optical tweezing techniques can be used to deform ULIFT emulsion droplets and to create networks of droplets connected by nanometric threads. During the experiments reported in [9], we observed that, under certain conditions, trapped droplets of the microemulsion-forming mixture of brine, heptane and the anionic surfactant, AOT, exhibited unexpected dynamics including the nucleation of new phases, catastrophic phase inversion and spontaneous formation of vesicles. We therefore carried out a more detailed study of the effect of focused lasers on both single microemulsion phases and droplets of microemulsions in an excess phase, the results of which are reported here.

The quaternary system of water, salt, alkane and anionic surfactant of our original observation has a phase diagram and interfacial tensions that are highly temperature-sensitive. Since optical tweezers are known to heat water (owing to the weak absorption by water of the near-IR wavelengths typically used for trapping when tightly focused) this study was carried out with a so-called temperature-insensitive microemulsion containing a mixture of an anionic and a non-ionic surfactant with oil and brine. It is the specific mixture of surfactants which suppresses the temperature dependence of the monolayer curvature [10] that governs observable microemulsion properties. Consequently, these quinary systems form a three-phase (Winsor III) microemulsion over a wide temperature range. We show below that, despite the temperature insensitivity of the macroscopic phase diagram, such microemulsions still show rich dynamics when locally perturbed by focused IR lasers.

This paper is laid out as follows. We first provide some background to optical tweezers and microemulsion phase physics, which is needed to interpret the subsequent observations. We then describe the macroscopic phase behaviour of the temperature-insensitive emulsions, before describing and discussing the effects of a focused laser beam on a continuous sample of the middle phase. Finally, we address the original motivation for this study, namely the effect of focused IR lasers on droplets of oleic or middle phase suspended in the excess aqueous phase.

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1.1. Optical tweezers

Optical tweezers are routinely used to study soft matter, microbiological and related model systems [11–13]. This follows wider recognition of their capability for highly sensitive, non-invasive and responsive measurement and manipulation. Optical tweezers are highly focused lasers, typically of moderately high power (10 mW–1 W), which exert forces on the piconewton scale. They rely on the momentum transfer that occurs on refraction through a microscopic particle, in order to confine that particle's position near the focus of the beam. The laser focus is provided by a microscope objective of high numerical aperture, which also facilitates imaging of the particle.

The scenario in which a solid particle is trapped in liquid continuum allows us to calibrate the imaging quality, trap aberrations and the magnitude of these trap forces [14]. However, we are ultimately concerned with a liquid droplet in place of a solid particle, and thus a liquid–liquid interface. For fluids, the localised response is governed by a more general principle; the majority of the optical force acts along intensity gradients, such that material of high refractive index (oil) tends to displace that of lower index (water) from the regions of highest intensity.

In common emulsions, isolated microdroplets are fixed in spherical shapes. This geometry is dictated by a high interfacial tension (high IFT), which minimises surface area at a fixed, incompressible volume. However, at ultralow interfacial tension (ULIFT), other forces influence the time-averaged and dynamic shapes: these include thermally-excited fluctuations, viscous flows, buoyancy, and the optical forces we impose. Alongside the contrast in refractive index across the interface, ULIFT is therefore an important requirement for optical deformation [9]. We find that these conditions are fulfilled by certain amphiphile/alkane/aqueous systems — those capable of forming efficient microemulsions.

1.2. Curvature in microemulsions

Local minima of IFT occur in parameter space where the preferred mean curvature of the oil–water interface, H_0, becomes zero. For fixed amphiphile concentrations and a fixed ratio of solvents, the phase behaviour is also determined by H_0. When H_0 changes sign under influences such as temperature or ionic strength, emulsions tend to undergo phase inversion [15]. This generates the observable spectrum of Winsor phase equilibria above the critical microemulsion concentration (cμc) [16] of efficient surfactants, that includes the existence of a third, middle-phase microemulsion when $H_0 = 0$.

1.3. Temperature-insensitive microemulsions

If H_0 is insensitive to changes in temperature, both the phase behaviour and IFT are also expected to be temperature-insensitive. In practice, we achieve this condition using a mixture of a nonionic and an ionic surfactant as the amphiphilic component. We also use an electrolyte, NaCl, to control the ionic contribution to the preferred curvature.

The quinary composition is specified by four parameters – χ, γ, S, Ω – in terms of each component's weight fraction m, density ρ and molar mass M:

1. The volumetric water–oil ratio, $\Omega = m_{Aq}/m_{Oil} \cdot \rho_{Oil}/\rho_{Aq}$;
2. The total amphiphile concentration, $\gamma = (m_I + m_{NI})/(\Sigma m)$, expressed either as weight fraction in total (dimensionless percentage), or as an aqueous molarity (units of mM);
3. The amphiphilic ratio, or the weight fraction of ionic surfactant in the amphiphilic mixture, $\chi = m_I/(m_I + m_{NI})$;
4. The aqueous molarity of NaCl, or salinity, $S = (m_{NaCl}/m_{Aq}) \cdot (\rho_{Aq}/M_{NaCl})$.

At a unique value, denoted χ^*, the curvature of the mixed monolayer exhibits the desired low sensitivity to temperature, *i.e.* $\partial H_0/\partial T = 0$. As ionic surfactant is present, the ionic strength alters (decreases) H_0 sensitively and almost independently of temperature. The particular salinity at which $H_0 = 0$ for a given χ is denoted $S^*(\chi)$. The ideal formulation for temperature-insensitive ULIFT is therefore an amphiphilic ratio of χ^* and a salinity of $S^*(\chi^*)$, abbreviated S^{**}. The quinary systems AOT/$C_{12}E_5$/*n*-heptane/NaCl-brine, AOT/Brij-L4/*n*-decane/NaCl-brine and AOT/$C_{12}E_4$/*n*-decane/NaCl-brine are used in this work (Appendix A).

2. Experimental

2.1. Optical tweezer setup and calibrations

A conventional upright microscope (*Leica* DM–LM) was used in brightfield mode with a video camera (*Ximea* xiQ/MQ013MG-E2) at 60 fps, condenser, NA = 1.1 (*Leica*) and oil-immersion objective, NA = 1.25, 100× (*Leica* 506072). Optical tweezers were generated with a 1064 nm TEM_{00} CW Nd:YAG laser, 600 mW (*Forté, LaserQuantum*), a dichroic beamsplitter (*ThorLabs*) and a beam expansion telescope, adjusted to correct chromatic aberration for coincidence of trapping and imaging planes, and to fill the back aperture of the objective for optimal gradient force. A polarising Mach–Zehnder apparatus [17,18] provided two traps of orthogonal linear polarisation, thereby avoiding any optical interference between them. Gimballed mirrors were conjugated with the back aperture to allow independent steering of the beams in the focal plane. A sample chamber of 170 μm depth was formed between a glass microscope slide and #1 coverslip, with a second coverslip as a spacer, sealed together with UV adhesive. All tweezing experiments were performed at 22 ± 2 °C ambient. At very high source powers >0.5 W, air bubbles nucleated in the immersion fluid and were thermally trapped in the field of view. Bubbles form since the solubility of air in liquids decreases with increasing T. Bubble formation was eliminated by replacing the fluorocarbon coupling fluid with water, for which the thermal variation of gas solubility is less.

The tightly-focused laser also causes localised heating of the sample. The increase in temperature, ΔT, is proportional to the optical power P. At fixed power, the temperature increase and distribution are determined by the optical intensity distribution, together with the optical absorption and thermal characteristics of the fluid sample and its enclosing substrates (Appendix C). A typical laser heating in water is of the order 20 K W^{-1}, while in D_2O there is an order of magnitude less heating. The maximum temperature rise predicted in the experiments reported here is 5 K. For middle-phase microemulsions, the water and oil solubilisations are roughly equal; the heating is expected to be close to the average of the bulk phases.

2.2. Formulations

The AOT (sodium di-octylsulfosuccinate, 96%, *Acros Organics*), Brij-L4 and $C_{12}E_{4/5}$ (dodecyl tetra/pentaethyleneglycol ethers, 98%, *Sigma-Aldrich*), NaCl (AR grade, *Fisher*) and D_2O (*Cambridge Isotope Labs.*) were all used as received. UHP H_2O was obtained from a *MilliPore* unit (*MilliQ*). The oils *n*-decane and *n*-heptane (99% and 99.5%, *Fisher*) were purified through silica under N_2.

Each composition forming three-phase equilibrium ($S \approx S^*$), $\gamma \gg$ cμc, typically $\gamma = 1\%$) was allowed to resolve into layers after mixing. Separation took place in 15 mL centrifuge tubes (for formulation scans) or a 100 mL separation funnel (for microscopy samples) for 1 week at 18 ± 2 °C, after which no change in phase volumes was detected. Isolation of each of the three phases in the funnel was confirmed by the persistence of optical clarity on agitation. Where desired, a minority of excess oil or middle-phase was then reintroduced to 5 mL of the excess water phase in a volume ratio $\Omega' = 400$ as shown in Fig. 1. This mixture was agitated manually to form a polydisperse emulsion. A gentle inversion of the phial suffices to shear droplets to the 1–10 μm size needed for optical tweezing.

For temperature insensitivity studies, decane compositions at $\chi =$ 0.66 across 120 mM < S < 220 mM, varying from WI–WIII–WII were included. For samples at temperatures of 20–60 °C, incomplete creaming/