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Coalescence behavior of oil droplets coated in irreversibly-adsorbed surfactant layers

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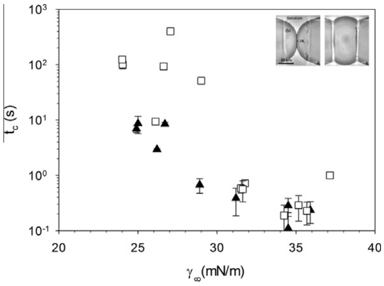
GRAPHICAL ABSTRACT



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ABSTRACT

Coalescence between oil caps with irreversibly adsorbed layers of nonionic surfactant is characterized in deionized water and electrolyte solution. The coalescence is characterized using a modified capillary tensiometer allowing for accurate measurement of the coalescence time. Results suggest two types of coalescence behavior, fast coalescence at low surface coverages that are independent of ionic strength and slow coalescence at high coverage. These slow coalescence events (orders of magnitude slower) are argued to be due to electric double layer forces or more complicated stabilization mechanisms arising from interfacial deformation and surface forces. A simple film drainage model is used in combination with measured values for interfacial properties to quantify the interaction potential between the two interfaces. Since this approach allows the two caps to have the same history, interfacial coverage and curvature, the results offer a tool to better understand a mechanism that is important to emulsion stability.

1. Introduction

The nonionic surfactant Tween 80 has been shown to leave irreversibly adsorbed layers at oil/water and air/water interfaces [1,2]. This nonionic surfactant consists of a branched poly(ethyleneoxide) head group and an oleic acid hydrophobic tail group. The surfactant is of interest as it is used in many applications including as a component in dispersants used in oil spill remediation [3]. The persistence of adsorbed species may impact interactions of droplets with each other and here we present results of coalescence characterization of oil droplets with pre-adsorbed layers of surfactant. The results are relevant to the dispersant design but also to the more general issue of the impact of interfacial properties on coalescence; specifically the initial stage of film drainage. Coalescence is a complex phenomenon that has been studied for decades [4–6]. Here, we focus on a simplified analysis and careful approach to measurement of film drainage between two micro-scale interfaces.

For an emulsion to be stable, suspended oil droplets must resist coalescence. One stage of coalescence is the drainage of the thin film that forms between two approaching interfaces. If their

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interactions are strong enough, the film drains away until the two oil phases come into contact. This is considered a rupturing of the film, after which the combined droplets rapidly coalesce. Many interfacial parameters affect the coalescence rate between pairs of droplets and the bulk stability of an emulsion. Aside from the interfacial tension, the geometry of the interface [7–14], surface charge [15–18], van der Waals interactions [17–21], interfacial rheology and Marangoni stresses have all been observed to hinder or promote film drainage [22–28].

Here, the coalescence time is defined as the time between the initial creation of the film and its subsequent rupture and formation of a single drop pinned between two capillaries. In these experiments, film drainage dominates the total coalescence time [4]. For flat films, the rate of change of the gap between the films, h, is given as [6,26].

$$\frac{dh}{dt} = -\frac{2h^3\Delta P}{3\mu R_f^2}\left(1+\frac{6D_s\mu}{hE_A}\right), \tag{1}$$

where μ is the viscosity of the continuous phase, D_s is the surfactant diffusion coefficient on the interface, R_f is the film radius, E_A is the elasticity of the interface and ΔP is the pressure drop driving the flow. The pressure drop has contributions from the Laplace pressure due to interfacial tension, γ, and curvature of the drop/interface, R, and specific forces between the two interfaces across the gap,

$$\Delta P = \frac{2\gamma}{R} + \Pi_{\text{int}}, \tag{2}$$

where Π_{int} is the sum of various interactions between the two interfaces. At the least, Π_{int} accounts for the van der Waals interactions through an effective Hamaker constant, A_{eff}, to capture the attractive forces that result in coalescence [29,30],

$$\Pi_{\text{int}} = \frac{A_{eff}}{6\pi h^3}. \tag{3}$$

Details of this interaction potential and how adsorbed species at the interface impact it have been the focus of many experimental and theoretical investigations. It is known that while adsorbed surfactants have a minimal effect on the energy of the interface, surfactants may have a substantial effect on the forces between interfaces [18]. Adsorbed C_iE_j surfactants sufficiently alter dipole forces leading to a change in the van der Waals interactions in thin films and charging of the interfaces [17]. Direct measurements of forces using AFM measurements have elucidated the impact of several types of forces affecting droplet and bubble interactions [21,31–38].

The effect of interfacial rheology on the coalescence phenomenon is poorly understood. This is due in part to modelling but also due to difficulties in measuring elasticity, and even in the definition of elasticity [19,22,39–42]. Several authors have noted that elasticity and surface viscosity will hinder the appearance of waves or dimples within coalescing interfaces that tend to speed up film drainage [20,22,24,25]. For many such studies, however, the value of the elasticity is inferred from an isotherm or measured on a separate device (for example, a pendant-drop tensiometer). The dilatational elasticity is affected by curvature of an interface when surfactant transport is a concern [43–45], which makes it difficult or even impossible to establish a correlation when the elasticity of the actual coalescing droplet remains unknown.

In this study, a direct experimental approach is taken toward understanding droplet coalescence and the impact of various interfacial parameters. Using a microtensiometer, a modified capillary tensiometer, irreversibly-adsorbed layers of nonionic surfactant are formed on pairs of oil (squalane)-aqueous interfaces, the elasticity is measured, and coalescence rates are monitored. Because the surfactant is adsorbed irreversibly, these experiments are performed in the absence of bulk surfactant, which simplifies descriptions of the film drainage. Coalescence rates are analyzed in the context of simple film drainage with direct measurement of parameter of the system. The contribution of electrical double layer forces to the stability is also investigated, and it is suggested that oil-aqueous interfaces coated in irreversibly-adsorbed layers generated by adsorption of this nonionic surfactant carry a negative charge.

2. Materials and methods

Liquid Tween 80 (lot # MKBD7486 V) is purchased from Sigma (St. Louis, MO) and used without further purification. Squalane ($C_{30}H_{62}$) is purchased from Sigma at >99.5% purity, and any remaining surface active impurities are removed via gravity filtration through a glass column packed with 1.5 g of basic alumina powder. Filtered squalane is tested for impurities by monitoring the interfacial tension with deionized water prior to each experiment and is considered clean when the interfacial tension remains unchanged within ±0.5 mN/m of the clean value, 52.5 mN/m, for at least one thousand seconds. A partitioning study showed that Tween 80 does not partition into squalane during the timescales of these experiments [2]. Deionized water is prepared with a Barnstead Ultrapure water purification system to 18.2 MΩ cm resistivity. Sodium chloride is purchased from VWR (Batavia, IL) at 99% purity and is baked at 400 °C for 5 h to remove hydrates and impurities. Stock solutions are prepared with deionized water immediately after baking.

The electrophoretic mobility of a series of Tween-80 coated squalane drops in water is measured using a Malvern Zetasizer Nano-ZS. A 5 mL sample of nonionic surfactant is prepared at 0.1 μM in DI water, and sonicated for 3 min with 0.5 mL squalane. A micropipette is used to extract 0.5, 0.25, and 0.1 mL aliquots which are further diluted in DI water to bring each sample volume to 5 mL total. A 1 mL volume of each of these dilutions is pipetted into a disposable cuvette used for electrophoresis measurements. Electrophoretic mobility and drop radius are recorded. The pH is measured for each sample separately on a pH meter.

Interfacial tension dynamics and interfacial mechanics are measured on a microtensiometer designed and built in house [46–49]. Modifications are made to allow for coalescence measurements and a schematic of the modified device is shown in Fig. 1 [2].

Glass capillaries with tip radii ranging from 40 to 50 μm are pulled from 6-inch, 1 mm ID glass capillaries, and treated with siloxane (Sigma, St. Louis, MO). PTFE tubing is connected and a T-junction connects the two PTFE tubes to a single pressure head source and pressure transducer (Omega Model PX409-001GV), allowing for the measurement of the pressure drop over each oil-aqueous interface. The bottom wall of the sample reservoir is a 30 mm circular glass slide (Warner Instruments, Hamden, CT, model CS-30R) affixed using Loctite® marine epoxy. A PTFE ring is fit to the wall of the sample reservoir to prevent contamination. The sample reservoir is fabricated on a 3D prototyping device (Objet Desktop 30 Polyjet printer). The capillary insertion points are tapped to allow for tapered PEEK fittings (Upchurch Scientific, Oak Harbor, WA, model F-331X); each capillary is inserted first through the PEEK ferrule, then screwed into the end of the device such that the tapering seals the contact between the capillary and the device. One of the capillaries is threaded through a micromanipulator to control the location of the tip in the reservoir.

The reservoir is placed on the viewing stage of a Nikon T-300 inverted light microscope and the capillary tips imaged with a Diagnostic Instruments Spot RT Monochrome digital camera and analyzed in-house using LabView® routines. The radius of curvature of the oil cap at the end of the capillary is fit to a circle and