Interfacial effects and emulsion stabilization by in situ surfactant generation through the saponification of esters

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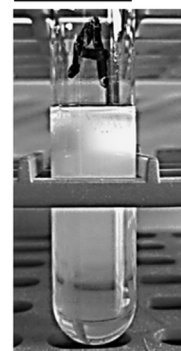
HIGHLIGHTS

- Combined rheology measurements with emulsification for in situ surfactant formation.
- Achieved emulsion stability of a several weeks by in situ generation of surfactant.
- Measured the rates of the interfacial reaction.
- Showed that the interfacial reaction is slowed down by anionic surfactant coverage.
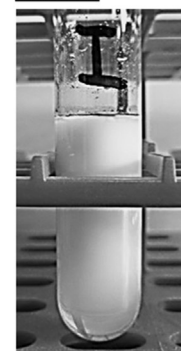
GRAPHICAL ABSTRACT

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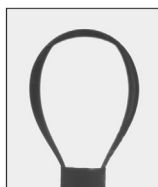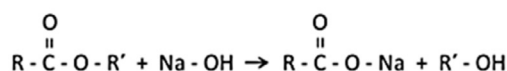
ABSTRACT

The stabilization of oil-in-water emulsions is critical for a wide variety of fields. Here, we explore the reaction dynamics of and emulsion stabilization by in situ surfactant generation through the saponification of esters that are commonly used in cosmetics and drug delivery. We combine measurements of dynamic interfacial tension and surface elasticity with emulsion stability to determine the dynamics of the interfacial reaction and its effect on interfacial properties. The rate of surfactant production through the in situ reaction depends on the surface area and thus the dynamics measured in a pendant drop may not reflect the dynamics in emulsification. To test this, we also measure the dynamics of surfactant production after emulsification. Further, we explore the effect of surfactant chain length and solution pH on the interfacial tension dynamics and the emulsion stability. The results show that the interfacial tension transients in a pendant drop correlate with the in situ reaction dynamics but that there are others factors to consider. The steady state interfacial tension represents a pseudo-steady state between rate of surfactant produced and that desorbing into the aqueous phase. The interfacial tension dynamics and emulsion stability also depend strongly on the charge. The emulsions retain stability after aqueous pH neutralization, suggesting that a portion of the adsorbed surfactant molecules remain ionized at neutral pH. Emulsion stability increases with increasing surfactant chain length, which is the expected trend because a longer chain length reduces aqueous solubility thereby increasing the surfactant surface coverage. Therefore, the approach of emulsion stabilization by in situ surfactant production is more useful

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for surfactants with very low aqueous solubility. Finally, the transients of surfactant concentration in the emulsions show a reduction in the rate of the in situ reaction with increasing coverage of the surface by the adsorbed anionic surfactant most likely due to the buildup of surface charge that reduces the concentration of the hydroxyl ions at the surface.

1. Introduction

Oil-in-water emulsification is critical to several industries including oil and gas, drug delivery, emulsion polymerization, cosmetics, and detergency. Emulsions are typically prepared by homogenization of a mixture of oil, water, and emulsifiers. This homogenization creates small oil drops, which are then stabilized by the adsorption of surfactant to the interface. Large-scale homogenization processes can take tens of minutes and multiple cycles and thus any procedure that could decrease the time and energy requirements would represent a significant step forward for many industries [1]. For these reasons, there has been significant interest since the 1930s in creating surfactant at the oil-water interface instead of adding preformed surfactants to the system. Generation of surfactant at the interface could potentially reduce the amount of time required for emulsification through elimination of the time needed for diffusion and adsorption. The in situ production will, however, only be effective if the reaction dynamics are sufficiently fast. Here we explore the in situ surfactant formation at oil-water interfaces to investigate the feasibility of using this approach to stabilize emulsions for food and cosmetic industries.

Prior studies in this field have focused on measurements of dynamic interfacial tension when the oil containing acidic impurities is exposed to basic aqueous solutions [2–5]. The decrease in interfacial tension was interpreted to reflect the rate of the interfacial reaction between the aqueous base and the acidic components in the oil. However, this decrease in interfacial tension could also be caused by other factors, such as charge adsorption to the interface [6,7]. Thus, the dynamic interfacial tension on its own may not provide a complete understanding of the in situ reaction. Furthermore, in pendant-drop tensiometry, the surface area to volume ratio is relatively small and so the rates of surfactant production are low. Thus the measured dynamics may not reach equilibrium because the surfactant produced at the interface could keep dissolving into the bulk fluid. In another parallel set of studies, oil containing acidic components was emulsified in basic aqueous solutions and the stability of these emulsions were used as an indicator of the in situ reaction [8–10]. Several papers report promising conclusions, including that polymerization of miniemulsions generated by in situ surfactants were successfully performed and that the technique resulted in lower interfacial tension, narrower particle size distributions, a decrease in time to reach a given drop diameter for large scale homogination, and less secondary nucleation sites [1,8–11]. These studies demonstrate improved stability likely due to the formation of surfactant at the interface, but to our knowledge, the relative improvements in stability have only lasted for a few hours and thus not been sufficient to achieve extended stability over months, which is essential for many applications. Since emulsions are commonly used in cosmetic and drug delivery applications, we explore the feasibility of using in situ surfactant generation focusing on such applications. The emulsions for drug delivery applications must remain stable for extended shelf life of approximately two years. The stability requirements for cosmetic emulsions would vary depending on the specific applications, but at least a few months of shelf life would be needed. Additionally, the pH of formulations for both applications must be close to neutral.

To our knowledge, most prior studies on in situ surfactant formations have not achieved extended stability and most researchers have explored stability only under basic solution conditions.

In this paper, we seek to combine interfacial tension and rheology studies at a pendant drop interface with emulsification studies to obtain a more detailed understanding of the in situ surfactant generation. Specifically, we are interested in the rates of the reaction to determine how long the emulsions must be homogenized to achieve the desired concentration. The reaction rates are explored by separating the aqueous and oil phases of emulsions at various times after their formation and then using those separated aqueous phases to measure interfacial tension and viscoelasticity. Another aspect of this work that has not been explored previously is that the oils used here are esters (RCOO-R') that are commonly used in cosmetic, perfume, and transdermal drug delivery fields. Thus, sodium hydroxide in the aqueous phase generates the surfactant (RCOO⁻ Na⁺) through saponification. Most previous studies explored neutralization of the fatty acids to generate the surfactant. This work adds insight into the fundamentals of in situ surfactant generation, has interest in diverse applications, and represents potential for improvements in large-scale processing.

2. Experimental

2.1. Materials

The esters (oil phases) used in this study were isopropyl myristate (IPM, 98 wt.%) purchased from Alfa Aesar, isopropyl palmitate (IPP) purchased from MP Biomedicals, and ethyl stearate (ES, 97 wt.%) purchased from Sigma-Aldrich. Reagent A.C.S. sodium hydroxide (NaOH, 97 wt.%, Acros) was used to modify the aqueous phase pH and generate the in situ surfactant. Concentrated hydrochloric acid (HCl, 37 wt.%), sodium chloride (NaCl, enzyme grade), and HPLC grade submicron filtered water were purchased from Fisher Scientific. HPLC water was used for all experiments.

2.2. Methods

2.2.1. Interfacial tension and viscoelastic modulus

The dynamic interfacial tension was measured with a pendant-drop tensiometer using an oil drop suspended on the tip of an inverted 14 gauge needle and surrounded by aqueous solution in a quartz cuvette 20 mm × 30 mm × 40 mm in size. The pH of the solution was varied by adding base (NaOH) or acid (HCl). The aqueous pH was measured with a Denver Instrument pH meter that was calibrated with buffer solutions prior to measurement. The Young–Laplace equation, assuming hydrodynamic equilibrium, was fit to the digitized drop shapes using the commercial Kruss DSA 100 tensiometer to determine the interfacial tension as a function of time. Separately, the interfacial viscoelastic moduli were examined via oscillatory drop shape analysis, using the same pendant drop system. Surface area and interfacial tension response oscillations were represented by

$$A - A_0 = A_a \sin{(\omega t)} \tag{1}$$

$$\gamma - \gamma_0 = \gamma_a \sin{(\omega t + \theta)} \tag{2}$$