

Background

What is a surfactant? What is a foam?

Surfactants are used in many industries from consumer care products and cleaning to oil recovery, food, and medicine. A *surfactant* is a molecule composed of a hydrophilic head group and a hydrophobic tail group. This duality in surfactant structure allows for their adsorption onto gas-liquid interfaces, which, in turn, decreases the molecular forces within the liquid phase and lowers the surface tension [1]. The reduction in surface tension in presence of surfactants promotes foaming, i.e., formation of gas bubbles dispersed in a liquid phase (see Fig. 1). Foam stability is governed by three processes as follows, *liquid drainage*, *coalescence*, and *Oswald ripening*. Liquid drainage is caused by the gravitational field acting on the foam due to density difference between the gas bubbles and the liquid phase, which results in thinning of the foam lamellae. The *lamellae* are the thin walls of liquid between foam bubbles. The thinning of the foam lamellae, followed by its rupture, results in merging of two gas bubbles in a process called coalescence (see Fig. 1) [2]. In Oswald ripening, the gas diffuses from smaller bubbles into larger bubbles due to the pressure differential across the gas bubble-liquid interface, i.e., the Laplace pressure. All of these processes lower the stability of foam over time; however, properties of the surfactants used in the formulation can affect these processes to retard or even arrest foam destabilization.

How do surfactants impact foam stability?

Surfactant bind to the fluid interface with their hydrophobic tail in the gas phase and their hydrophilic head residing in the liquid phase [1]. The presence of surfactants at the interface interrupts the intermolecular forces between liquid molecules thereby lowering the surface tension, which allows the interface to stretch without rupturing. The *Laplace* pressure, which is the pressure difference between the inside and the outside of the bubble, is a function of surface tension. Foam systems, with surfactants that have a strong impact on surface tension reduction, can withstand a greater Laplace pressure because the lower surface tension allows the bubble to expand to the size needed to balance the outside pressure (also known as the *capillary* pressure). The *Marangoni effect* is a restorative force that occurs in the presence of surfactants. When a bubble surface is stretched in vicinity of a plateau border (see Fig. 2), the density of surfactants is lowered in that region, raising the surface tension locally. The generated surface tension gradient gives rise to the flow of surfactants from high concentration to low concentration creating the Marangoni flow, which, in the process, drags water back into the thin film between the bubbles [3]. As a result, the foam remains wet and stable for a longer time. Lastly, the interaction of surfactant molecules and the elasticity of the resulting interfacial film can impact bubble stability. For example, hydrogen bonding, which is a strong intermolecular force, results in the formation of a more elastic surface by keeping the surfactants bound to the interface.

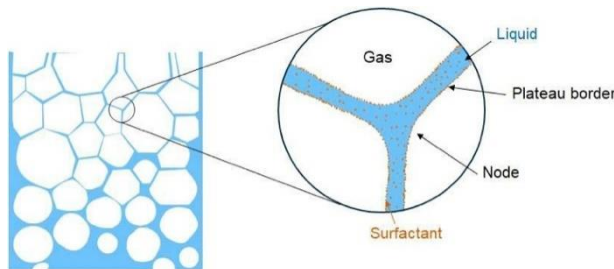


Fig. 2. Schematic of a foam microstructure (adapted from Hjelt et al. [4]).

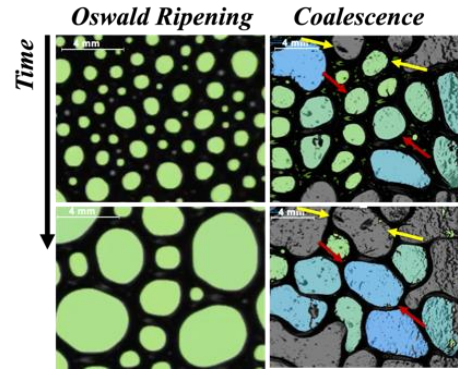


Fig 1. Aging of foam bubbles stabilized by SDS surfactant undergoing Oswald ripening (left) and coalescence (right).

How are surfactant-laden interfaces characterized?

The impact of surfactants on the resulting surface tension can be studied using a Wilhelmy plate partially submerged in the liquid. The liquid wets the surface of the plate and the surface tension, which acts on the plate and pulls it down, can be measured using a force balance. In presence of surfactants at the interface, the measured surface tension is reduced. Increasing the surfactant concentration leads to a lower surface tension reading. The critical micelle concentration (CMC) is the surfactant concentration at which the interface is fully saturated with surfactant molecules. Increasing the concentration of surfactant beyond the CMC leads to the formation of surfactant micelles in the solution. Therefore, by measuring the surface tension value as the surfactant concentration is increased, the CMC for a given surfactant can be evaluated [5]. In addition, studying the dynamic properties of the gas-liquid interface (i.e., *rheology*), in presence of surfactant molecules and under flow conditions, is important in tuning the properties of surfactant-stabilized foams. Pendant bubble tensiometry can be used to study the interfacial rheological properties by applying a change in the bubble surface area and tracking its effect on the corresponding surface tension. The elastic modulus represents the solid-like character of the interface, whereas the viscous modulus is a measure of the liquid-like tendencies of the interface [6]. Understanding the viscoelastic properties of an interface provides insight into how surfactant-stabilized bubbles will respond to applied stresses, which determines the foam stability.

Why APG-stabilized interfaces are of interest?

The majority of feedstock used to synthesize conventional surfactants are derived from fossil fuels; most of the rest from seed oils (e.g., palm kernel oil, linked to deforestation in Southeast Asia) [7]. Therefore, achieving sustainability demands novel sustainable surfactants that are obtained from renewable feedstock, without relying on fossil fuels or competing with food. For example, a common synthetic surfactant is sodium dodecyl sulfate (SDS), which is found in many household products used in cleaning and detergency. SDS is used because it is inexpensive and very effective; however, it is known to be environmentally unfriendly, toxic to microbiota, and harmful to plants roots [8,9]. Many synthetic surfactants do not degrade in the environment well [10]. A possible green alternative to conventional petroleum-based surfactants is alkyl polyglycoside (APG). The sources that APG is made from makes APG an environmentally friendly alternative to petroleum

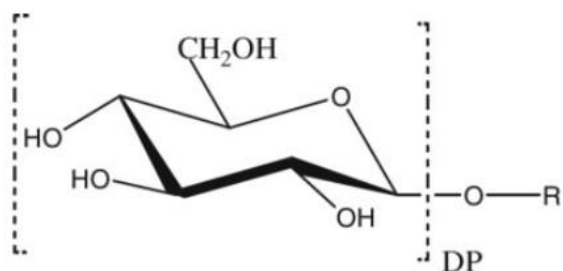


Fig 3. Generalized molecular structure of APG. (adapted from Sulek et al. [15]).

derived surfactants. APG is composed of a carbohydrate head and a fatty alcohol which are biocompatible. APG has a low toxicity and can degrade into the biofriendly components that it is composed of [9,11,12,] (See Fig. 3). As well, due to APG's nonionic head group it has a resistance to salts [13]. APG can be modified by using different fatty acids in its production to alter the length and shape of APG's tail. Research conducted with other surfactants has found that longer chained and branched surfactants lower the air-water surface

tension more effectively compared to their shorter chained analogs [14]. Furthermore, increasing the chain length of APG is shown to increase the hydrophobicity of the tail in accordance with Traube's rule, which will help APG to lower the air-water surface tension more effectively [12,15]. While the tail length of surfactants is known to impact the surface tension, **the effect of APG's tail shape and length on its performance as a foaming agent is an outstanding scientific question that needs to be addressed.**

Research Question

Due to its environmental friendliness, APG is currently being studied as a candidate to reduce or replace more harmful surfactants in areas such as cosmetics, enhanced oil recovery, and detergents. **While APG is showing a remarkable promise as a green surfactant, there is a lack of understanding on how fundamental physiochemical properties of APG affect its ability to perform as a quality surfactant.** One area that contains a gap in knowledge pertains the impact of APG's tail chain length on the resulting interfacial properties such as its ability to lower the surface tension, the rheological properties of the APG-laden interface, and the impact of these properties on the foam stability. **We hypothesize that the tail length of APG molecules will impact their configuration and interaction at the interface, which, in turn affect the resulting interfacial properties and foaming performance.**

Objectives

The overarching goal of this project is to advance our fundamental understanding of the role APG structure plays in its behavior as a surfactant to establish the knowledge base needed to move towards sustainable formulations using green surfactants. This goal will be accomplished by pursuing the following research objectives.

1. Study the impact of APG chain length on interfacial properties (e.g., surface tension and critical micelle concentration).
2. Examine the rheological properties of APG-laden interfaces using APGs with different chain lengths.
3. Investigate the effectiveness of APGs of different chain length in foaming.
4. Establish Structure-Property-Function relationship for APGs with different chain lengths.

Materials and Methods

The following materials will be used in the proposed research activities:

- ***Deionized (DI) water*** - DI water (18.2 MΩ.cm) that will be used throughout the study is generated via Milli-Q® IQ 7000 Ultrapure Lab Water System (Millipore Sigma).
- ***APG Surfactant*** - APG surfactant of varying tail length - AC6 (6C-Tail), APG0810 (10C-Tail), AC1200 (12C-Tail) - will be obtained from Prime Surfactants.

The following methods and analysis will be used in the proposed research activities:

- ***Wilhelmy Plate*** - The Wilhelmy plate works by measuring the surface tension of a monolayer of surfactants at the surface of the bulk liquid phase. Solutions of APG surfactant at different concentrations will be used to measure the surface tension as a function of surfactant concentration. From the obtained data, the CMC value of APG surfactant will be determined. APGs of different tail length will be used to study the impact of tail length on surface tension reduction and CMC values. These experiments will also inform the choice of surfactant concentration that will be used for foaming studies.
- ***Oscillating Pendant Bubble Tensiometry*** - Oscillating pendant bubble tensiometry works by expanding and contracting a bubble that is submerged in an aqueous solution containing water and APG surfactant. This form of

tensiometry measures the change in surface tension in response to the applied changes in surface area of the bubble. The obtained phase shift (δ) between the applied changes in the surface area and the resulting surface tension will be used to determine the surface elastic modulus (i.e., $\delta = 0$) and viscous modulus (i.e., $\delta = 90^\circ$). The surface tension measurements detailed above will guide the choice of surfactant concentration and wait period in tensiometry experiments.

- **Dynamic Foam Analysis-** Dynamic Foam Analysis (DFA) is a technique to visually measure and quantify the destabilization of foam over time. It works by foaming a surfactant solution in a column placed in front of camera and light. A computer then can analyze the change in bubble diameter and bubble count as a function of time. Using this information foam stability can be characterized by studying the liquid drainage and bubble coarsening. The results of surface tension and surface rheology measurements will guide the choice of surfactant concentration used in foaming experiments.

Proposed Timeline

The proposal objectives will be pursued based on the following timeline as shown in table 1.

- April 22** – Suply List finalized.
- May 29** – Research experiments Start.
- Aug 7** – Research experiments Conclude. Begin Drafting Report and Poster.
- Aug 26** – Report is Completed.
- Sept 2** – Report is Due.
- Sept 27** – Poster is Completed.
- Oct 4** – UReCA Showcase.

Expected Outcomes

Successful completion of the proposed research will **advance the knowledge on how altering the APG’s tail length can be used in tuning the properties of APG-stabilized foam**. This fundamental understanding will enable the design of sustainable formulations with properties tuned to a specific application in a variety of fields, i.e., oil recovery, consumer care products, and food and agriculture.

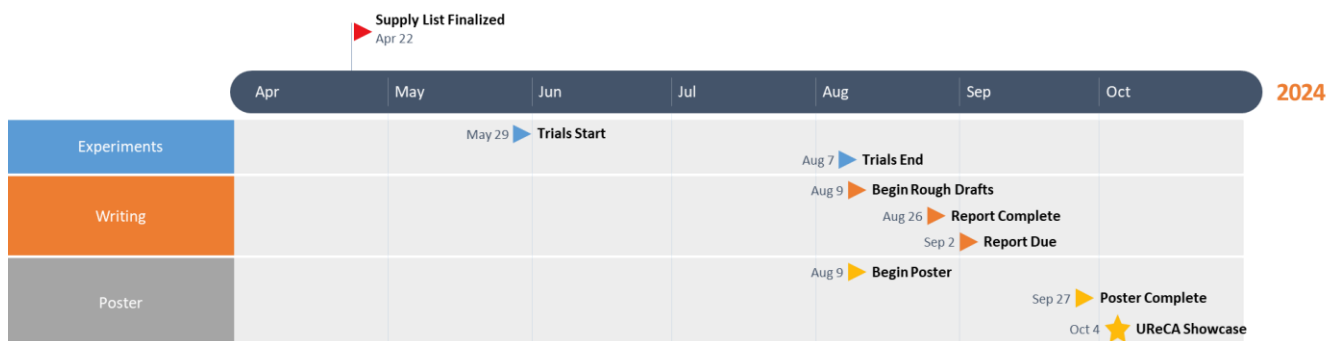


Table 1. Proposed Timeline for Project

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