Effects of Formulation Conditions on Micellar Interactions and Solution Rheology in Multi-Component Micellar Systems

by

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Abstract

Surfactants are crucial to the personal care industry due to their unique surface activity, cleansing, and self assembly properties. Typically, multi-component systems are used in order to maximize mildness, hard water tolerance, and foaming. System morphology and viscosity are controlled through chemistry and solution conditions. An experimental study was conducted to determine how variations in solution chemistry (surfactant headgroup and blend stoichiometry) and solution conditions (pH and [NaCl]:[anionic + zwitterionic surfactant] ratio) affect the structure and rheology of surfactant solutions. This study examined binary systems of Sodium Laureth Sulfate (SLES) and Lauramidopropyl Betaine (LAPB) or SLES and Lauramidopropyl Hydroxysultaine (LAPHS) as well as ternary systems of SLES/LAPB/PEG-80 Sorbitan Laurate (PEG-80 SL) and SLES/LAPB/Polysorbite-20 (Tween-20). Using dynamic light scattering and rheometric measurements, system morphology was determined.

In the SLES/LAPB system, it was found that there was a break in system viscosity at a critical [NaCl]:[anionic + zwitterionic surfactant] ratio, 0.16:1 (R*). Micelles only had the ability to entangle, thus increasing viscosity, above this ratio. When the system pH decreased such that pH ~ pKa of LAPB, all [NaCl]:[anionic + zwitterionic surfactant] ratios had the ability to entangle, and entanglement began at lower surfactant concentrations. At these pH values, LAPB protonated and created a pseudo-ternary system with SLES, LAPB0, and LAPB.

There was no measured variation in system morphology in the SLES/LAPHS system with [NaCl]:[anionic + zwitterionic surfactant] ratio, most likely because the minimum ratio achievable was above R* due to a high salt content in the raw materials. In addition, there was no measured variation in system morphology in the SLES/LAPHS system with variation in pH, most likely because the system was not tested at pH ~ pKa of LAPHS. The addition of a third surfactant drastically decreased the system viscosity and drove the system towards the formation of spherical micelles because the nonionic surfactant of choice decreased the packing parameter due to its relatively large size as compared to that of SLES and LAPB.

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1. Introduction

1.1 Surfactant overview

Surfactants are unique molecules and are crucial to a number of industries and biological processes. Surfactants are amphiphiles in that they have both hydrophobic and hydrophilic components. The hydrophobic tailgroup is typically a single, straight chain hydrocarbon. The headgroup can either contain charges (anionic, cationic, and zwitterionic surfactants) or contain no charges (nonionic surfactants). It is typically comprised of C, O, N, S, and other hydrophilic elements.\(^1\)

Surfactants display a number of unique phenomena due to their amphiphilic nature. The hydrophobic tailgroups are attracted to each other, causing surfactants to form assemblies of many shapes and sizes. The tailgroups are also able to dissolve oils while the hydrophilic head binds with water, promoting cleansing of surfaces. In addition, surfactant molecules congregate at air-liquid phase boundaries, stabilizing surfaces and foams.\(^1\)

These phenomena are utilized in many industries, including cosmetics, medicine, pharmaceuticals, and petroleum production.\(^1\) In particular, surfactants are common in personal care products because many can increase hard water tolerance, reduce skin irritation, enhance foam properties.\(^2,3\) Typically, mixed surfactant systems will be used as their combination of properties is favorable for the final application.

There are four main classes of surfactant molecules that are distinguished by the electrostatic properties of their hydrophilic headgroups: anionic, cationic, nonionic and zwitterionic. Anionic surfactants have a net negative charge while cationic surfactants have a net positive charge. Collectively, anionic and cationic surfactants are referred to as ionic surfactants. Nonionic
surfactants have no charges, and zwitterionic surfactants (often referred to as amphoteric surfactants) either bear or are capable of bearing both positive and negative charges, usually in an equimolar ratio (see Figure 1a-d). Typical personal care cleansers use multi-component blends of surfactants to give the desired properties (i.e. cleansing, foaming, mildness).

At low surfactant concentrations, surfactant monomers exist independently. However, above a critical concentration (cmc), surfactant monomers will self assemble into ordered aggregate structures whose size and shape is dependent on their composition and solution conditions. These assemblies are called micelles. In a polar solvent, micelles consist of an inner core of hydrophobic tails and an outer shell of hydrophilic heads. Micelles can also interact, thus increasing solution viscosity either through physical entanglements or through charge repulsions.

There is an interest in controlling the rheology, or the flow behavior, of mixed surfactant systems in order to enhance consumer familiarity and satisfaction. \(^4\)

1.2. Single component micelles

1.2.1. Micellar shape

Micellar shape depends on the free energy of formation. This energy can be summarized using the packing parameter\(^5,6\)
\[ P = \frac{V}{LA} \]  

Where \( P \) is the packing parameter, \( V \) is the effective volume of the tailgroup, \( L \) is the length of the tailgroup, and \( A \) is the effective area of the headgroup.

Figure 2 displays the importance of the effective headgroup area relative to the effective tailgroup area. When the headgroup area is much larger than the tailgroup area, the surfactant monomer has a triangular shape, forcing a small radius of curvature in the micelle. This small radius of curvature leads to a spherical micelle. As the effective headgroup size decreases, the surfactant monomer maintains a more trapezoidal shape. This shape creates a larger radius of curvature and allows for cylindrical geometries. In general, \( P < \frac{1}{3} \) corresponds to a spherical shape, \( \frac{1}{3} < P < \frac{1}{2} \) corresponds to a cylindrical shape, and \( P = 1 \) corresponds to a flat bilayer.

Figure 2. Influence of effective headgroup size on micellar shape. a) large effective headgroup size, 2D cross section. b) small effective headgroup size, 2D cross section. c) large effective headgroup size, 3D cross micelle. d) small effective headgroup size, 3D micelle.
Goldsipe and Blankschtein developed a free-energy model to predict the cmc and micellar shape under varying solution conditions. They give the following equation

$$g_{mic} = g_{tr} + g_{int} + g_{pack} + g_{st} + g_{elec} + g_{ent}$$

(2)

where $g_{mic}$ is the free energy of micellization, $g_{tr}$ is the transfer contribution, $g_{int}$ is the interfacial contribution, $g_{pack}$ is the packing contribution, $g_{st}$ is the steric contribution, $g_{elec}$ is the electrostatic contribution, and $g_{ent}$ is the entropic contribution. The first three terms relate to the hydrophobic tail, and the second three terms relate to the hydrophilic head. This work focuses on $g_{st}$ and $g_{elec}$. The steric contribution, $g_{st}$, relates to the bulk of headgroup molecules. The electrostatic contribution, $g_{elec}$, takes into account any headgroup charges as well as any counterions in solution which could mitigate headgroup charges. The micelle will take a shape that minimizes this energy of micellization.

Equation 2 provides a good estimation of the terms influencing the effective headgroup size. Steric bulk plays a large role. The larger the physical size of the headgroup, the larger the effective headgroup size. In addition, electrostatic repulsions increase the effective size of the headgroup whereas electrostatic attractions decrease the effective size. In the case of an ionic surfactant solution, a higher charge density corresponds to a larger effective headgroup size.4, 8, 9

1.2.1.1 Spherical micelles

The two following environments provide favorable conditions for spherical micelles. The first is in circumstances with a low packing parameter. The second is in solutions with a low concentration of surfactant. The first micelles to form at the cmc are spherical due to the low surfactant concentration. As the concentration increases, the packing parameter becomes a
determining factor in micellar shape. In addition, intermicellar repulsion can play a role in micellar shape at higher concentrations.

1.2.1.2 Cylindrical micelles

When \( \frac{1}{3} < P < \frac{1}{2} \) and the surfactant concentration is high enough, the system will begin to form cylindrical micelles. In the literature, this concentration is referred to as the sphere-to-rod transition. The transition concentration is not a material property and depends strongly on solution conditions. In a similar manner to how monomers and micelles coexist in equilibrium above the cmc, monomers, spheres and rods exist in equilibrium past the sphere-to-rod transition (Figure 3). If the system consists of multiple surfactant types, the surfactant with a lower packing parameter will prefer to stay in the spherical micelles whereas the surfactant with the higher packing parameter will gravitate towards the cylindrical micelles.\(^9\) However, all micelles of each shape will tend to have the same composition. That is, all spherical micelles will have the same composition \( A \), and all cylindrical micelles will have the same composition, \( B \).\(^9\)

\[ \text{Figure 3. Possible surfactant assemblies with increasing surfactant concentration. Number and size of monomers and micelles in each region not to scale.} \]

Cylindrical micelles consist of two regions—the body and the endcaps. The body is linear while the endcaps are hemispherical. When the energy of endcap formation is higher than the energy
of lengthening the body, the micelle will maximize its endcap-to-body ratio. However, when the energy of endcap formation is greater than the energy of lengthening the body, the cylindrical micelles will grow. Cylindrical micelles are also referred to as “rodlike”, “wormlike” or “threadlike” micelles in the literature. These terms will be used interchangeably throughout this thesis.

Cylindrical micelles can either form linear or branched structures: a linear structure has no sidechains whereas a branched structure has many branchpoints that give rise to sidechains. At the sphere-to-rod transition, linear cylinders are the first to appear. Branched micelles arise when the energy of forming endcaps is less than the energy of lengthening the micelle. A branched micellar solution exhibits a morphology analogous to that of a solvent-swollen crosslinked polymer system, but has very different rheological behavior as will be discussed later.

Whether the cylinder is a linear or branched micelle, we assume that the persistence length \( (l_p) \) is less than the contour length \( (l_c) \). When this assumption is true, the micelle can be modeled as a long flexible worm. This assumption is usually valid as the persistence length is typically hundreds to thousands of angstroms whereas the contour length is on the order of microns. In the other dimension, typical cylinder diameters are between 5-20 nm. The cylinder diameter depends on the length of the hydrophobic tail; longer tails correspond to larger cylinder diameters.

### 1.2.2 Dilute and semi-dilute regimes

In the dilute regime, micelles tend to exist as non-interacting spheres. As surfactant concentration increases, the system reaches the sphere-to-rod transition at which point cylindrical
micelles begin to form as the most thermodynamically favored structure \((\frac{1}{3} < p < \frac{1}{2})\).

Beyond the sphere-to-rod transition, micelles begin to grow with increasing concentration—first forming elongated spheres, then stiff rods where \(l_p > l_c\), and finally flexible worms where \(l_p < l_c\).

At first, the spheres and ellipsoids are too small to interact with each other in solution. The concentrations corresponding to non-interacting micelles are collectively referred to as the dilute regime. Eventually, the cylinders become long enough and exist in a high enough concentration to begin interacting. The concentrations corresponding to interacting cylinders are collectively referred to as the semi-dilute regime. At very high concentrations, the system becomes concentrated and different stress relaxation parameters apply.

The transition from the dilute to the semi-dilute regime always occurs after the sphere-to-rod transition. It takes place at a concentration \(c^*\) which is the overlap concentration of cylindrical micelles in solution. Both surfactant chemistry and solution conditions have the ability to influence the sphere-to-rod transition. These factors influence the rate of micelle elongation as a function of concentration and its length at \(c^*\). \(c^*\) occurs at a lower concentration for longer micelles. In general, the viscosity of a solution at \(c^*\) is twice the viscosity of the solvent solution.

At concentrations greater than \(c^*\), the cylinders can grow long enough to form network points. There are many possibilities for these network points. Already discussed are branched micelles—cylindrical micelles with side chains of the same composition as the backbone. Also possible are adhesion points. Adhesion points occur in areas where micelles are attracted to each other but do not bond or fuse. Third, and most common, are entanglements. Entangled micelles wrap around each other, much like an entangled polymer. Figure 4 displays an entangled system. A number of length scales are depicted in this image. \(k\) refers to the average distance.
between micelles (also called the mesh size). $l$ and $m$ are the mean distance between entanglements or network points and the persistence length, respectively. If the system has other types of network points (either adhesion or branches), a cryo-TEM image of the system will look very similar to the schematic in Figure 4.

The onset of micellar interaction elicits significant changes in the rheology of a surfactant solution. The network points create a three-dimensional structured morphology that solutions of spherical micelles cannot achieve. The system becomes viscoelastic, where the degree of viscoelasticity is governed by the density of network points. In contrast, dilute solutions of spherical micelles are purely viscous.

![Figure 4. Cylindrical micelles with entanglements and other network points (dashed circles). $k$ is the mesh size, $l$ is the distance between entanglements, and $m$ is the persistence length.](image)

1.2.3 System structure and dynamics

Variations in micellar morphology induce changes in the structural and dynamic properties of the solution. Both of these properties are important in evaluating solution rheology. Structural properties relate only to the moduli and dynamic properties relate to the relaxation time.

When evaluating system flow properties, the plateau modulus, $G^0$ is of primary importance. Rheological measurements can evaluate variations in $G'$, the storage modulus, with frequency.
In some cases, $G'$ will plateau at high frequencies. This plateau value is called $G^0$ (sometimes $G_\infty$) and is a function of the elastic properties of the system. At concentrations greater than $c^*$, $G^0$ increases with increasing viscosity. As the micelles become longer, they interact more and form a tighter network. An increase in $G^0$ corresponds to an increase in the solid-like behavior of the system.8

When a stress is applied to a surfactant system at concentrations above $c^*$, the micelles attempt to relieve that stress through a number of different relaxation mechanisms. The time for the system to relieve this stress is called the relaxation time and is the main factor in the dynamic response of the system.15 Different relaxation mechanisms are dominant at different surfactant concentrations and morphologies.

One common relaxation mechanism is reptation. Micellar reptation is similar to polymeric reptation where the micelle undergoes random motion to extricate itself from entanglements. As $l_p$ increases and micelles become less flexible, reptation becomes more difficult. In addition, as the electrostatic repulsion both within the micelle and between micelles increases, reptation becomes more difficult.

Because wormlike micelles are physical assemblies of individual surfactant monomers, they have additional relaxation mechanisms that are unavailable to polymers of covalently-bound repeat units. In particular, micelles can undergo scission, forming two new micelles from one starting micelle. Fusion can occur at the endcaps, creating one micelle from two starting micelles. In addition, fusion may occur anywhere along the cylindrical micelle, creating a branch point. Finally, surfactant molecules can flow through these branch points, effectively moving the location of the branch point along the length of the micelle. In some circumstances,
micelles can collide, fuse, and break, as an alternative to reptation. To the observer, the micelle would appear to cut through its neighbors.\textsuperscript{16} Collectively, these processes are called “breaking and sliding”.

The energy of scission is summarized in the following equation

$$E_{scission} = E_{endcap} - E_{ionic\ repulsion}$$

where the energies refer to the energy of scission, the energy of endcap formation, and the energy associated with ionic repulsion, respectively.\textsuperscript{8} As ionic repulsion increases, scission becomes more favorable. Similarly, as the energy to form endcaps increases, scission becomes less favorable. These relationships are physically intuitive. When there is a great deal of electrostatic repulsion, micellar breakage is favored in order to decrease the radius of curvature and increase intermicellar distance. However, if the energy of forming endcaps is high, micellar breakage is less favorable due to the energy required to create new endcaps.

When the cylindrical micelles are long, they sometimes display a single relaxation time. This relaxation time can be described by the following equation

$$\tau_r \cong (\tau_{br} \tau_{rep})^{1/2}$$

where $\tau_r$ is the system relaxation time, $\tau_{br}$ is the relaxation time associated with breaking and sliding, and $\tau_{rep}$ is the relaxation time associated with reptation.\textsuperscript{17} $\tau_r$ can be measured via oscillatory rheometry.

Viscosity measurements are useful for understanding micellar growth as well as understanding the effects of additives on system flow.\textsuperscript{18} In a system composed of spherical micelles, the viscosity is governed by Einstein’s law
\[ \eta = \eta_s(1 + 2.5\phi) \]  

(5)

where \( \eta \) is the solution viscosity, \( \eta_s \) is the solvent viscosity, and \( \phi \) is the effective volume fraction of surfactant micelles. It is important to note that \( \phi \) is related to the effective area of the headgroup via the packing parameter.

The zero shear viscosity is an especially valuable measurement as it takes into account both the structural and dynamic properties of the system.\(^4\)\(^{,}\)\(^{16}\)\(^{,}\)\(^{17}\) It can be characterized by the following equation:

\[ \eta_0 = G^0 \tau_r \]  

(6)

where \( \eta_0 \) is the zero shear viscosity, \( G^0 \) is the plateau modulus, and \( \tau_r \) is the system relaxation time from equation 4. With the onset of interacting cylinders, \( \eta_0 \) increases exponentially.\(^{10}\)

1.3 External factors: The effect of salt on micellar systems

Most experiments conducted on surfactant systems with added salt have found a maximum in the viscosity with increasing salt concentration (see Figure 5). At low salt concentrations, viscosity increases with increasing surfactant. However, the viscosity peaks at a certain salt concentration and then decreases with increasing salt. It has been found that the micellar length is highest at the concentration corresponding to the maximum in viscosity.\(^{16}\) General consensus is that the cylindrical micelles transition from a linear to a branched form at this viscosity maximum. More detail on this transition is available in the references.\(^4\)\(^{,}\)\(^{8}\)\(^{,}\)\(^{11}\)\(^{,}\)\(^{12}\)\(^{,}\)\(^{16}\)\(^{,}\)\(^{17}\)\(^{,}\)\(^{19}\)\(^{,}\)\(^{20}\)
Clausen et al. studied the cationic system of cetyltrimethylammonium chloride (CTAC, a cationic surfactant) with NaSal. They evaluated the change in viscosity with increasing surfactant concentration at various salt concentrations and broke the system response into three regions depending on the salt concentrations. In Region 1, the salt concentration was low. As a result, the packing parameter was small and the system consisted of spherical micelles. These micelles did not interact, so the system had no viscoelastic response.

Region 2 had an intermediate salt concentration. This region began after the critical salt concentration enabling the sphere-to-rod transition. As a result, micelles grew and interacted, creating a viscoelastic system. However, the system had no plateau modulus and displayed many different relaxation times depending on salt concentration. This variation in relaxation time and lack of plateau modulus implied that the system exhibited different morphologies throughout this region. However, cryo-TEM imaging did not display any morphological change.

Figure 5. Typical viscosity curve of surfactant system with increasing salt concentration. At low salt concentrations, viscosity increases due to micellar lengthening while at high concentrations, viscosity decreases due to micellar branching.
corresponding to the changes in system rheology. In particular, cryo-TEM did not display any difference in the micellar persistence length. Because imaging techniques displayed similar structures throughout this region, the variation in Region 2 must have been a dynamic response.

High salt concentrations corresponded to Region 3. In this region, the system had a viscoelastic response to applied stress. In addition, the system displayed a plateau modulus and a single relaxation time. Any system with a single relaxation time could be modeled as Maxwellian. Within this region, they used equation 6 to describe the zero shear viscosity. In addition, the loss and storage moduli were modeled with the following equations

\[
G'(\omega) = \frac{G^0\omega^2\tau_r^2}{1+\omega^2\tau_r^2}
\]

(7)

\[
G''(\omega) = \frac{G^0\omega\tau_r}{1+\omega^2\tau_r^2}
\]

(8)

where \(G'\) is the storage modulus, \(G''\) is the loss modulus, and \(\omega\) is the frequency.

Region 3 was modeled with a Cole-Cole plot. While Cole-Cole plots are typically utilized in determining dielectric properties of materials, they can also be of use in rheometric analysis. A Cole-Cole plot graphs \(G''\) against \(G'\). If the system is perfectly Maxwellian, the resulting trace will form a perfect semicircle. Khatory et. al.’s analysis found that entangled micelles exhibited Maxwellian behavior. As a result of this observation, Cole-Cole plots can be used to evaluate entangled micelle systems with an entanglement length much longer than the persistence length. Clausen’s analysis found that at a high salt concentration, micelles were entangled and Cole-Cole analysis was valid. Narayanan et. al. suggest that the depth that the Cole-Cole plot reached before losing its semicircular shape is related to the relative values of \(\tau_{rep}, \tau_{break}\), and entanglement length.
Croce et. al. created a series of cryo-TEM images which display system morphology in each of these three regions. In Region 1, the micrograph displayed spherical micelles. In Region 2, the micrograph displayed long, cylindrical micelles with the ability to entangle and align under shear flow. In Region 3, the micelles branched, as was evident by 3-way connections in the image (a 3-way connection would not be possible with entangled micelles.) These micrographs clearly displayed the effect of salt on system morphology.12

1.4 External factors: The effect of pH on micellar systems

In contrast to changing the salt concentration of a surfactant solution, researchers have varied the $\text{H}^+$ concentration, or the pH. Many surfactant types, in particular ionic, zwitterionic, and semipolar surfactants, have the ability to protonate or deprotonated at a specific pH.22 This protonation event introduces a new species into solution. For example, a neutral zwitterionic element, $Z^0$, can protonate at low pH and become $Z^+$. This thesis will only discuss the protonation of a zwitterionic surfactant.

Protonation has a large effect on system interactions. When $Z^0$ protonates, pure solutions become binary, binary solutions become ternary, etc. The additional surfactant type will impact the effective headgroup size, the effect of counterions in solution, and the micellar geometry. Its presence also alters the equilibrium of surfactant elements in both monomeric and micellar form.

Typically, we use the Henderson-Hasselbalch equation to model the $pK_a$, or the pH at which half of the pH sensitive surfactant has protonated.

$$pK_a = \text{pH} + \log \frac{x_1}{1-x_1}$$  \hspace{1cm} (9)
where $x_j$ is the fraction of protonated monomers. However, this equation assumes an ideal solution, and can only be used to characterize the pK$_a$ of surfactant in monomer form.$^{22,23}$

To evaluate the protonation of surfactant in micellar form, we evaluate the pK$_m$

$$pK_m = pH + \log \frac{x_{mic}}{1-x_{mic}} \tag{10}$$

where $x_{mic}$ is the fraction of protonated surfactant in the micelle.$^{22}$ The pK$_a$ and pK$_m$ are always equal when $x_{mic} = 0$.\textsuperscript{24} While equations 9 and 10 look similar, the main difference lies in the nature of the pK. pK$_a$ is a constant and is governed by the fraction of protonated monomer, $x_j$. In contrast, pK$_m$ is not a constant. The fraction of protonated surfactant in the micelle, $x_{mic}$, depends on a number of external factors, to be discussed below. $x_{mic}$ constantly changes in order to maintain the equilibrium of all solution elements in monomeric and micellar form. As a result, $x_{mic}$, as well as the micellar composition (for multi-component systems) depends strongly on the pH.$^{22,24}$

A purely electrostatic argument states that pK$_m = pK_a$.\textsuperscript{24} However, these values are typically not equal. This difference stems from both short range interactions and the image force contribution. Short range interactions (primarily hydrogen bonds) increase the favorability of protonation within the micelle. In contrast, the image force contribution (a low dielectric constant in the micellar core), makes protonation unfavorable within the micelle. Both of these contributions lend to the difference between pK$_a$ and pK$_a$.\textsuperscript{22,24}

The effect of solution pH on surfactants is extremely complicated. It depends on the salt concentration, system geometry, and other surfactants in solution, to name a few contributing factors. The salt (or counterion) concentration screens positive and negative micellar charges,
thus increasing the amount of charge allowable in a micelle of a particular geometry.\textsuperscript{25}

Geometry itself plays an important role—spheres will titrate differently than rods due to the change in effective headgroup area from short-range interactions.\textsuperscript{24,25}

Because this thesis is primarily concerned with understanding general trends, we use a simple, first order approximation and only consider the pK\textsubscript{a} of the zwitterionic surfactant in solution.

Both Regular Solution Theory (RST) and Molecular Thermodynamic (MT) theories exist to explain micellization with variations in pH. More detail on these theories is available in the listed references.\textsuperscript{22,24,25}

1.5 Binary systems

1.5.1 Synergistic effects of mixing

As previously mentioned, personal care cleansers are generally comprised of multiple surfactants (as well as many other types of additives) to achieve the optimum properties.\textsuperscript{25,26} Most of these additives and surfactants enhance consumer satisfaction and improve system stability.\textsuperscript{21} Mixed surfactant systems mitigate problems of receiving polydisperse samples from suppliers and also help dilute the effects of impurities in the raw materials.\textsuperscript{2} This section will primarily focus on binary mixtures of zwitterionic and anionic surfactants as that system is most applicable to this thesis. However, parts of this section will refer to experimental results from other types of binary systems if those results are applicable to the zwitterionic/anionic system.

In many cases, synergistic effects arise from mixing different types of surfactants (for example, anionic and zwitterionic, anionic and cationic, cationic and nonionic, etc). This section will only discuss surfactant combinations in which synergistic effects occur (not anionic-anionic or
cationic-cationic). These effects can be modeled using the Molecular Interaction Parameter (MIP). This parameter describes how well two different surfactants interact with each other.

\[ \beta = \frac{\ln \left( \frac{c_{cmc}^\alpha}{c_1 x} \right)}{(1-x)^2} \]  

(11)

where \( \beta \) is the MIP, \( c_{cmc} \) is the cmc of the mixed system, \( \alpha \) is the mole fraction of surfactant 1 in solution, \( c_1 \) is the cmc of surfactant 1, and \( x \) is the mole fraction of surfactant 1 in the micelle. Larger values of \(|\beta|\) correspond to more favorable interactions. Traditionally, \(-\beta\) is reported in order to compare positive magnitudes.\(^{26}\)

These experimental results can be translated into simple physical explanations. The addition of a second surfactant decreases the effective headgroup size and therefore increases the packing parameter.\(^{10,27}\) For example, adding zwitterionic surfactant to a solution of anionic surfactant introduces spacer molecules to push the negative charges farther apart. In addition, the negative charge in the anionic surfactant can interact with the positive charge in the zwitterionic surfactant, mitigating some charge repulsion. This effect is even more dramatic when anionic and cationic surfactants are mixed.

Rheological measurements have found that in mixed micelles, smaller effective headgroup sizes correspond to larger relaxation times and larger plateau moduli. Mixed micelles with large \( \beta \) have high viscoelastic character.\(^{17}\) Because the smaller effective headgroup size corresponds to a larger packing parameter, surfactant combinations with a large \( \beta \) are more likely to be cylindrical instead of spherical. This conclusion was verified in Nagarajan et. al.'s model where they found that the size of a mixed micelle composed of surfactants A and B is larger than the size of a micelle composed only of component A or B.\(^9\)
1.5.2 Effect of salt and pH on a binary system

Because most commercial products are comprised of mixed surfactant systems, there is an interest in understanding the effect of additives in mixed systems. Abe et. al. conducted a thorough study of adding NaCl to a binary system and found that increasing the salt concentration decreases the cmc. This finding indicates that increasing the concentration of counterions makes mixing even more favorable. They found that the cmc of a mixed system with salt was less than both the cmc of an unmixed system with salt and the cmc of a mixed system without salt.\(^2\,^{26}\)

Adding salt to a mixed system produces a similar effect as adding salt to an unmixed system. At a constant mole fraction of zwitterionic surfactant, increasing the salt concentration corresponds to a maximum in the system viscosity. This maximum is attributed to variation in the system relaxation time and not variation in the plateau modulus.\(^17\) Penfield conducted a number of experiments on binary zwitterionic/anionic systems which showed that the number of entanglements undergoes a maximum at the same salt concentration as the viscosity and relaxation time maxima. Entanglement is inversely proportional to the mesh size. Therefore, with increasing salt, the mesh size decreases up to a critical salt concentration, then increases with added salt.\(^17\)

Little research has examined the effect of solution pH on mixed solution surfactant morphology. Abe et. al. conducted a series of experiments on a zwitterionic/anionic system with added NaOH or HCl to determine pH effects. The particular zwitterionic surfactant they chose, DMLL, becomes anionic at high pH and cationic at low pH. They found that in a basic solution, DMLL no longer had an attractive interaction with the anionic surfactant (SDS). The MIP for this
system was less than the MIP of the neutral system. In addition, mixing did not have a synergistic effect on the DMLL/SDS system. The cmc increased linearly with increasing zwitterionic molar ratio. Viscosity also increased linearly with increasing zwitterionic molar ratio. They believe that the anionic charge on the DMLL is the cause of this behavior. At high pH, both surfactants experience electrostatic repulsions, so the effective headgroup size does not change with added zwitterion.26

In contrast, making the solution acidic through the addition of HCl made DMLL cationic. It had a very strong interaction with the SDS, resulting in a high MIP. The cmc of this system was significantly lower than the cmc of a system with no additives or a system with NaCl. The cationic DMLL interacted very closely with the anionic SDS, reducing the electrostatic repulsion between SDS molecules and decreasing the effective headgroup size. In evaluating the additives in terms of their effect on the MIP and cmc, they found the following: NaOH < no salt < NaCl < HCl.26

1.6 Ternary systems

Commercially available surfactant systems are typically composed of many elements due to maximization of solution properties, impurities in the starting materials, and pH effects. These systems often have at least 3 different surfactant components. However, very little research has been conducted on ternary systems, especially on combinations of anionic, nonionic, and zwitterionic surfactants.23,28

The majority of the research in this field has been aimed at developing a model to predict the cmc. As previously discussed, the cmc is the easiest solution property to measure, and trends in
the cmc often mimic trends in other solution properties. There are two opposing models for cmc characterization.

The first of these models is called “regular solution theory” (RST). It requires the pseudophase approximation, where the cmc is assumed to be a phase transition, and micelles are infinitely large. This theory also requires a number of inputs including the cmc of each pure surfactant component as well as $\beta$ for each surfactant pairing. Many of the inputs do not have specific physical translations and are typically used as fitting parameters. RST can predict the cmc of a mixed solution.

The second model is called “molecular-thermodynamic theory” (MT). It does not require as many assumptions, and the inputs are macroscopic solution properties (temperature, salt concentration, molecular surfactant structure, and surfactant composition). This model can predict the cmc, micellar shape, and micellar size. It is most useful when a solution is composed of complex mixtures where the individual components are not easily isolated.\textsuperscript{23}

Goldsipe and Blankschtein conducted a series of experiments to test the validity of their MT theory. Most applicable to this thesis, they examined a cationic/anionic/nonionic ternary system. As expected, this surfactant combination exhibited synergistic effects, and the cmc of the ternary system was lower than the cmc of each individual pure solution. They found that their model correctly predicted the cmc, shape, and size of the resulting ternary micelles.\textsuperscript{23}

In addition, Dar et. al. compared RST to MT through a series of experiments involving two cationic and one nonionic surfactant in a ternary mixture. They found that decreasing the fraction of nonionic surfactant increased the system cmc due to the increased repulsions between the cationic headgroups. In addition, they found that the aggregation number increased and the
effective headgroup size decreased with increasing fraction of nonionic surfactant. Again, because the nonionic surfactant mitigates cationic-cationic repulsion, the monomers pack tighter with increased nonionic surfactant. In comparing these two models, Dar et al. found that both theories adequately describe system behavior, but RST works slightly better as long as all system parameters are known. \(^{28}\)

### 1.7 Investigative aims

While there is a great deal of literature on pure and mixed surfactant systems, the majority examines either cationic or cationic/zwitterionic surfactant systems. Relatively little research has been conducted on anionic/zwitterionic systems. These systems are important to the personal care industry as most shampoos are composed of anionic/zwitterionic surfactant combinations.

In addition, most of this cationic-focused research has been conducted in academic settings. Such research is extremely valuable for elucidating the mechanisms by which surfactants act and interact. However, academic research is not always fully applicable to industrial uses. In these studies, the surfactant type, complexity, or concentration is often significantly different than that found in a bottle of shampoo. This thesis targeted the following questions in order to bridge the gap between academic pursuits and industrial applications.

- How does a weak salt (NaCl) impact the morphology of an anionic/zwitterionic surfactant system?

- How does variation in the pH affect the morphology of an anionic/zwitterionic surfactant system?
• How does headgroup identity (both size and chemical make-up) affect the morphology of an anionic/zwitterionic system?

• How does the addition of a third surfactant type (nonionic) affect the morphology of an anionic zwitterionic system?

To answer these questions, I conducted an extensive study targeted towards the personal care industry. In this study, I used comparable surfactant types and salt types to those found in manufactured products. In addition, I examined comparable surfactant concentrations, salt concentrations, and pH values to those found in industry.

Personal care products will continue to evolve in response to consumer demands. However, all new formulations must meet current consumer standards in foam generation, cleansing capabilities, and rheological properties. This thesis developed a comprehensive picture of means to alter system rheology in the face of new design parameters.
2. Materials and Methods

2.1 Rheometry

2.1.1 TA Instruments AR 2000

Viscosities were measured using two instruments. Samples with viscosities above 1.5 cP were tested on an AR 2000 rheometer manufactured by TA Instruments. This rheometer could apply torques between 0.1 μN-m and 200 mN-m. The minimum angular displacement was 40 nano-rad and the angular velocity ranged from 10^-8 to 300 rad/s. The rheometer also contained a Peltier Plate to control temperature with an accuracy of ±0.1°C. Standard error on the rheometer was approximately 3%.

The rheometer was recalibrated using the following procedure. First, the system recalibrated the instrument inertia and the total system inertia. Then, the system reset the geometry inertia, depending on the geometry in use. Third was an instrument rotational mapping step using one iteration of either a standard or precision bearing mapping. Finally, the gap was zeroed. The rheometer underwent this recalibration procedure each morning as well as each time the geometry was changed.

Two different geometries were utilized with the AR 2000 for the experiments presented in this thesis. The first was a stainless steel cone and plate geometry with a 1°, 40mm diameter cone and a gap height of 30 μm. This geometry was used for any sample of high viscosity (above approximately 8000 cP). In loading, excess sample was wiped from the region surrounding the cone such that the sample was “correctly loaded” as specified in Figure 6.
Figure 6. Illustration of correct loading configurations for cone and plate geometry. a) sample overloaded, b) sample underloaded, and c) sample correctly loaded.

The second geometry was a stainless steel concentric cylinder geometry using a 40.76mm inner diameter/43.92mm outer diameter cylinder and a gap height of 500µm. This geometry was used for samples of lower viscosity (between approximately 1.5cP and 8000cP). In loading, 6 mL of sample were injected into the cylinders. In both geometries, all components were washed with tap and DI water, then rinsed with ethanol and thoroughly dried between sample reloading.

All samples in the AR 2000 rheometer, regardless of geometry, underwent the following testing procedure. First, a Conditioning Step was performed to ensure all samples had identical history. This step consisted of setting the temperature to 25°C, preshearing the sample for 30 seconds at a shear rate of 20 Hz, and allowing the sample to equilibrate for 5 minutes. After equilibration, samples underwent a Stress Sweep Step with oscillatory stresses ranging from 0.01 Pa to 10 Pa at a controlled angular frequency of 1 Hz. Samples then equilibrated for 5 minutes before beginning the Flow Step. In the Flow Step the shear stress was ramped from 0.01 Pa to 10 Pa with a 5 second sampling period. The step required 3 consecutive points within 5% tolerance with a maximum point time of 1 minute. The instrument was then cleaned of the old sample and loaded with fresh sample for the final step of the testing. The cleaning procedure on the cone
and plate geometry consisted of simply wiping down both components. The concentric cylinder geometry was rinsed with tap and DI water and then thoroughly dried before continuing. Samples were reloaded according to the procedure previously outlined.

After reloading, samples underwent a Conditioning Step identical to the original Conditioning Step, with a controlled temperature of 25°C, a 30 second preshear at a shear rate of 20 Hz, and a 5 minute equilibration period. The final testing step was a Frequency Sweep, with the angular frequency ramping down from 100 rad/s to 0.03 rad/s. The oscillatory stress was held constant at a stress determined to be in the linear elastic regime as found from the Stress Sweep Step. The determination of this controlled stress is discussed below.

The three tests on the AR 2000, the Stress Sweep, the Flow Step, and the Frequency Sweep all collected data on different aspects of the sample. Stress Sweep data were plotted as modulus against oscillatory stress (Figure 7). The sample was linear elastic at all stresses where both G' and G” were linear on said plot. A stress from this linear elastic regime was then used as the controlled stress in the Frequency Sweep Step. All testing within this thesis was conducted in the linear elastic regime.
Figure 7. Typical Stress Sweep Step data from the AR 2000 rheometer. Black squares represent $G'$ and red circles represent $G''$. The sample is linear elastic at all stresses where both $G'$ and $G''$ are linear.

Data from the Flow Step were plotted as viscosity vs. shear stress (Figure 8) and were used to determine zero shear viscosity. These data were analyzed by the TA Instruments Data Analysis software using a Newtonian fit. The error from this fit was not the error in the viscosity of the sample, but instead was the error in linearity. As a result, the error from Newtonian measurements has not been included as error in this research. Typical error between zero shear viscosity measurements on the same sample was 3%. Further viscosity analysis plotted the zero shear viscosity (as determined from the Data Analysis software) against surfactant concentration. All plots were either semi-log (viscosity axis) or log-log (both axes). Consequences of this plot will be discussed in section 2.1.2.
Figure 8. Typical Flow Step data from the AR 2000 rheometer. Extrapolating the linear portion of the curve to the y-axis provides the zero shear viscosity.

Data from the Frequency Sweep test were plotted as modulus vs. angular frequency (Figure 9). The TA Instruments Data Analysis software calculated the modulus and angular frequency at the crossover point (ω*). The inverse of the crossover angular frequency is the characteristic relaxation time of the sample. Above this frequency the sample behaves as a viscoelastic solid (G’ > G”), whereas below this frequency the material behaves as a viscoelastic liquid (G” > G’).
Cole-Cole plots were used to further analyze Frequency Sweep data (see Figure 10). As discussed in Section 1.3.3, these plots are perfectly semicircular in a Maxwellian system. Deviations from that curve indicate loss of Maxwellian behavior. Entangled micelles exhibit Maxwellian behavior; therefore, if a plot of $G''$ against $G'$ follows a semi-circular path, the sample contains entangled micelles. Plots were determined to be semi-circular if they passed the apex of the semi-circle (see Figure 11).
Figure 10. Typical Cole-Cole plot. The semi-circular shape indicates Maxwellian behavior and an entangled system.

Figure 11. Possible behaviors of the Cole-Cole plot. a) plot is semi-circular and the sample is entangled. b) plot is not semi-circular, and the sample is not entangled.

2.1.2 Capillary Viscometry

Samples of extremely low viscosity (less than 1.5 cP) were tested using a size 75 Cannon-Fenske capillary viscometer for heightened accuracy. 10 mL of sample were loaded into the viscometer, and then placed in a water bath at 25°C ±0.7°C for at least 30 minutes. Tests were timed using a
stopwatch accurate to 0.1s. Samples were tested a minimum of three times, or until three measurements were acquired with error of less than 0.2s. Between tests, the viscometer was thoroughly cleaned with DI water then rinsed with ethanol and allowed to dry.

Viscosity was determined using the following equation

\[ \eta = k \rho t \]  

Where \( \eta \) is the kinematic viscosity in cP, \( k \) is a constant depending on the viscometer size (0.008 for a size 75 Cannon-Fenske capillary viscometer), \( \rho \) is the density of water at the experimental temperature, and \( t \) is the average experiment time. Typical measurement error was 0.006 cP.

While capillary viscometry measured the kinematic viscosity and the AR 2000 rheometer measured the zero shear viscosity, no distinction was made between these two values and all viscosity measurements were assumed to be the zero shear measurement. Discrepancies between viscosities measured on the AR 20000 and the capillary viscometer were approximately 10%. However, because the data were plotted on a log scale, this 10% difference was negligible in overall trend analysis.

Complied viscosity data (from both the AR 2000 rheometer and the capillary viscometer) were plotted against [anionic + zwitterionic surfactant] ([A+Z]) to determine transition points in micellar interactions. As reported by Holland, the relationship between viscosity and [A+Z] is dependent on micellar interactions in the system. Introducing new interactions creates an easily measured slope change.\(^{21} \) Within this thesis, the slope change indicated the onset of interacting micelles. The slope change was unrelated to micellar entanglement.

2.2 Dynamic Light Scattering
Dynamic light scattering experiments were conducted on a Malvern Zetasizer Nano Series instrument equipped with a 22 mW He-Ne laser operating at $\lambda=632.8$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 tau digital correlator electronics system. Light scattering experiments were only performed on samples with viscosities less than 3 cP so as to ensure all diffusion in the sample was caused by Brownian motion. Samples were loaded in 4.5 mL disposable cuvettes which were wiped with a Kimwipe before loading. Samples were run at 25°C with a 2 minute equilibration time. While the measurement position was fixed to 4.65 mm, automatic attenuation selection, as well as automatic measurement duration was enabled. Each run was 10 seconds long, but the instrument chose the number of runs per measurement to maximize measurement quality. Each sample underwent 6 measurements with a 30 second delay between measurements. The Malvern used the default 173° backscatter angle.

Program analysis assumed a refractive index of 1.334 and an absorption of 0.01. These are the refractive index and absorption values for Sodium Dodecyl Sulfate, a surfactant similar in size, shape, and structure to the surfactants used in these experiments. All analysis used DI water as the dispersant at a temperature of 25°C with a viscosity of 0.8872 cP and a refractive index of 1.330. For completeness, NaCl solution was also tested as a dispersant in the analysis, producing no significant difference in the measured diffusivities.

In addition to size measurements, the Malvern was also equipped with autotitration capabilities. Autotitrations were performed using a standard quartz flow cell and 0.106M Citric Acid and 0.519M NaOH as titrants. Samples were run at 25°C with a 2 minute equilibration time. Sample volume was 10 mL. Tests lowered the pH from pH 8.0 to pH 4.0 with a tolerance of 0.10. Pump speed, attenuator position, measurement position, stir speed, and the number of runs per
measurement where automatically chosen by the instrument. Three measurements were taken at each pH. The apparatus underwent a thorough cleaning procedure before any data were collected. The cell was first flushed with DI water and then air. The cell was then filled with sample in both the forward and reverse pump directions in order to eliminate all air from the system. Titrant tube placement was designed to minimize bubbles in the bulk sample.

For analysis, the data were exported out of the Malvern Zetasizer software into Microsoft Excel. The 1st, 2nd, and 3rd Intensity, Volume, and Diffusion peaks, as well as the diffusion coefficient and the diffusion trace were all extracted from the program. In autotitration experiments, the measured pH was also calculated. In analysis, only the diffusion data were used as it underwent the least number of analytical transformations. Typical standard deviations in the diffusion data were less than 1 μm²/s. All analysis examined the diffusivity corresponding to a peak in intensity (Figure 12) and plotted that diffusivity in relation to the variable in question ([NaCl], pH, [surfactant], etc).

![Graph showing peak diffusivity](image-url)
It is important to remember that DLS only measures the average properties of systems with Brownian-motion type diffusion. Static Light Scattering (SLS) can be used to determine the diffusivity of more viscous systems.\textsuperscript{14}

2.3 Solutions

All anionic and zwitterionic surfactants used in this study were generously donated by Rhodia, Inc. This includes Sodium Laureth Sulfate (SLES), trade name Rhodapex ES/2K, Lauramodipropyl Betaine (LAPB), trade name Mackam ULS-DAB, and Lauramidopropyl Hydroxysultaine (LAPHS), trade name Mackam LSB-50. PEG-80 Sorbitan Laurate (PEG-80 SL), trade name ATLAS G-4280, and Polyoxyethylene (20) Sorbitan Monolaurate (Tween-20) were gifted by Croda, Inc. Sodium Chloride (NaCl) was purchased from Spectrum. Molecular structures of LAPB, LAPHS, SLES, PEG-80 SL, and Tween-20 are displayed in Figures 19, 69, 59, 21, and 25, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure13.png}
\caption{Molecular structure and 3D molecular model of Lauramidopropyl Betaine (LAPB).}
\end{figure}
Figure 14. Molecular structure and 3D molecular model of Lauramidopropyl Hydroxysultaine (LAPHS).

Figure 15. Molecular structure and 3D molecular model of Sodium Laureth Sulfate (SLES).

Figure 16. Molecular structure of PEG-80 Sorbitan Laurate (PEG-80 SL).

Figure 17. Molecular structure of Polysorbate-20 (Tween-20).
All solutions were made using an identical procedure. A stock solution at the highest necessary [A+Z] was made for each [NaCl]:[A+Z] ratio. This stock solution was then diluted using DI water to all desired [A+Z]. In ternary solutions, the nonionic surfactant was mixed with DI water and allowed to dissolve for 10 minutes. 15-20g of water were kept out of solution to allow for later quality control adjustment. SLES was then added slowly to either DI water (in the binary systems) or the nonionic surfactant solution (in ternary systems) and mixed for 20 minutes. At this point, the solution pH was lowered with a 1.18M Citric Acid solution. The zwitterionic surfactant (either LAPB or LAPHS) was then slowly mixed into the solution. The solution was heated to 50°C, and then cooled to room temperature. The solution pH was measured again and readjusted with either 1.18M Citric Acid or 6.11M NaOH as necessary. Solution pH was typically equal to the target pH ± 0.2, but on occasion could be off by ±0.3 in extremely viscous solutions. The additional 15-20g of water were added to the solution, and stirred for 20 minutes. All solutions sat overnight and were completely deaerated before a final pH reading and rheometric testing. All stirring was done by a mechanical mixer at 175 rpm. If the sample was to have a controlled [NaCl]:[A+Z], a salt solution was added instead of DI water.

Dilutions were made in a similar manner. The stock solution was added to all but 15-20g of the necessary amount of DI water and mixed at 175 rpm for 20 minutes. The pH of the solution was then adjusted using 1.18M Citric Acid or 6.11M NaOH and mixed for another 20 minutes. All solutions sat overnight and deaerated before a final pH reading and rheometric testing.
3. Results and Discussion

The effects of intrinsic and extrinsic variables on system morphology and micellar interactions were investigated experimentally, focusing on the effects of surfactant concentration, ionic concentration, pH, surfactant headgroup, and addition of a nonionic surfactant. We characterized the properties of model surfactant systems through rheometry, capillary viscometry, and dynamic light scattering. All model solutions were comprised of a 1.0:1.7 molar ratio of anionic (A) to zwitterionic (Z) surfactant. This molar ratio is frequently used in mild cleansing personal care products.

3.1 Effect of ionic strength and surfactant concentration on solution morphology in a binary system

Initial experiments examined the effect of increasing concentrations of NaCl on the morphology of binary surfactant systems. Several studies have found that system viscosity varies parabolically with increasing salt concentration and peaks at a critical salt concentration. These studies hypothesized that this trend is a result of micellar lengthening and eventually branching. Increasing salt concentration increases the number of counterions in solutions. At low concentrations, these counterions bind with the anionic surfactant and lower the energy such that the system surpasses the sphere-to-rod transition. As the salt concentration increases, solution viscosity also increases due to the lengthening of micelles. However, at a certain salt concentration, the viscosity peaks and begins decreasing, most likely due to the formation of branched micelles. Croce et. al. captured a number of cryo-TEM images verifying the onset of micellar branching.
To test this hypothesis, our experiments examined the effect of salt on system morphology. These experiments characterized an initial binary system comprised of SLES (A) and LAPB (Z) (pH=6.3) at various concentrations of total surfactant [A+Z]. While commercial formulations often use CAPB instead of LAPB, for the current experiments LAPB was the preferred surfactant due to its homogeneous tail length in comparison to CAPB. All solutions had a pH of 6.3 because this pH closely mimics the conditions of current commercial shampoo formulations.

We probed the effect of ionic strength on system morphology by varying the molar ratio of [NaCl] to [A+Z]. By controlling the ratio of [NaCl]:[A+Z], the effect of surfactant headgroup screening was independent of surfactant concentration. While each sample had a different [NaCl], the ratio of Na\(^+\) ions to negatively charged SLES molecules remained constant within each ratio.

Figure 18 displays the range of [A+Z] and [NaCl]:[A+Z] probed in the initial studies. Surfactant concentration varied from 0.044M to 0.30M, providing data in both the dilute and concentrated regimes. [NaCl]:[A+Z] ratios varied from 0:1 to 0.30:1. All samples used the procedure described in the Methods section.
Figure 18. Solution set of SLES/LAPB samples, pH 6.3. Solutions ranged from [NaCl]:[A+Z] of 0:1 to 0.30:1 and [A+Z] of 0.044M to 0.666M.

3.1.1 Rheology

Figures 19 and 20 display the viscosity trends of all samples. Lines are added to guide the eye. At high [A+Z], the solutions cluster into two groups, where samples with higher [NaCl]:[A+Z] ratios (0.16:1 – 0.30:1) have a viscosity over an order of magnitude greater than the viscosity of samples with lower [NaCl]:[A+Z] ratios (0:1 – 0.093:1). This break is noticeable in Figure 19, the two dimensional display of viscosity with [A+Z]. Figure 20 displays these same data in three dimensions. The same shoulder exists, grouping the viscosities of samples with high vs. low [NaCl]:[A+Z]. In addition, Figure 20 shows an increase in viscosity with increasing [A+Z].
Figure 19. Zero shear viscosity of SLES/LAPB system, pH 6.3 at various [A+Z]. Sample groupings have been labeled and lines have been added to guide the eye.

Figure 20. 3D plot of zero shear viscosity of SLES/LAPB system, pH 6.3 at various [NaCl]:[A+Z] ratios and [A+Z].
Subsequent experiments examining the viscoelastic properties produced this same grouping, with a clear distinction in moduli between samples with high and low [NaCl]:[A+Z] ratios. Figures 21a and 21b, and 22a and 22b display these viscoelastic properties. As seen in Figures 21a and 21b, the storage and loss moduli at high [NaCl]:[A+Z] follow the same groupings as observed in the viscosity data (low ratio: 0:1 – 0.093:1, high ratio: 0.16 – 0.30:1). The Cole-Cole plots in Figure 22 display different shapes depending on [NaCl]:[A+Z] ratio. Samples with higher ratios maintain a semi-circular shape while samples with lower ratios do not exhibit a semi-circular shape. Again, the same samples fall into each grouping.

Figure 21. a) storage modulus, b) loss modulus of SLES/LAPB systems, pH 6.3 at various [NaCl]:[A+Z] ratios.
Additional analysis evaluated the relaxation times of the samples (Figure 23). The relaxation time is the inverse of $\omega^*$, the angular frequency corresponding to the crossover of $G'$ and $G''$ in a frequency sweep. Above this frequency the sample behaves as a viscoelastic solid, whereas below this frequency the material behaves as a viscoelastic liquid. Samples with high [NaCl]:[A+Z] ratios (0.16:1 – 0.30:1) have a relaxation time at least 0.5 seconds longer than samples with low [NaCl]:[A+Z] ratios (0:1 – 0.093:1).
Figures 19 – 23 display the same sample set in each cluster. The cutoff for this grouping is a [NaCl]:[A+Z] ratio of 0.16:1. All samples with ratios ≥ 0.16:1 have different rheological behavior than those samples with ratios < 0.16:1. In particular, samples at and above this ratio display the semi-circular shape indicative of an entangled micelle with a single relaxation mechanism (Figure 22). This ratio of 0.16:1 is $R^*$, the critical ratio of [NaCl]:[A+Z] needed for entanglement between micelles at a specific surfactant concentration and pH. Clausen et. al.’s analysis of CTAC and NaSal found a similar trend, where below a critical salt ratio, Cole-Cole plots were not semi-circular. At $R < R^*$, their solutions displayed a number of relaxation times and could not be classified as “entangled”\(^\text{19}\).

Figure 24 displays an overlay of multiple rheological traces. Called a Penfield Plot, it displays relationships between many viscoelastic properties of the system. In particular, it relates viscosity, relaxation time, crossover modulus, and maximum storage modulus. Due to its
comprehensive nature, the Penfield plot shows how changes in morphology (entanglement) affect the aforementioned system properties. As seen in Figure 24, all four parameters increase dramatically upon reaching $R^*$. The viscosity of the system increases due to the increased challenges to flow presented by entangled micelles. The relaxation time also increases, as new relaxation mechanisms are necessary for micellar motion in an entangled system. Entanglement creates a network which leads to a system with more solid-like properties, boosting both the crossover modulus and the maximum storage modulus. Entanglement is a phenomenon that affects all parts of the system.

Experiments conducted by Penfield and others found a decrease in viscosity at high [salt]:[surfactant] due to micellar branching. Our systems did not undergo this viscosity decrease. Therefore, we believe that at all tested [NaCl]:[A+Z] ratios, micelles were either spherical or linear. However, only Cryo-TEM has the capacity to visually verify system morphology.
Figure 25 is a phase diagram, plotting system interactions as a function of [NaCl]:[A+Z] ratio and [A+Z]. Red squares designate entangled micelles, blue squares designate interacting micelles, black squares designate non-interacting micelles, and green squares designate samples which could not be classified. We determined the type of system interaction by examining both the Cole-Cole plot shape as well as sample viscosity. This phase diagram breaks into three distinct regions. Region I contains only non-interacting micelles and is commonly referred to in the literature as the “dilute region”. In this region, the [A+Z] is too low for micelles to grow larger than elongated spheres. Region I extends to 0.253M at [NaCl]:[A+Z] < R* because there is too little charge shielding at these ratios to support micellar growth. This region is similar to that found by Croce et. al. where salt had no effect at low surfactant concentration. Region II marks the beginning of the “semi-dilute region” and contains elongated, interacting micelles. This region includes all [NaCl]:[A+Z] ratios and ranges from 0.253M to 0.666M A+Z. At [NaCl]:[A+Z] ≥ R*, Region II only extends to 0.450M A+Z. Samples at high [A+Z] (greater than 0.450M) and [NaCl]:[A+Z] ≥ R* are in Region III. In this region, the concentration of surfactant is sufficient to allow micellar elongation, and enough [NaCl] is present to shield the negatively charged SLES molecules from each other. As seen in Figure 25, entanglement only occurs within Region III.
3.1.2 Diffusivity

Figure 26 is a two dimensional plot displaying diffusivity vs. [NaCl]:[A+Z]. There is a close linear relationship between the diffusivity and [NaCl]:[A+Z] with an $R^2$ value of 0.98. Figure 27 adds a third dimension, [A+Z]. These charts show that as [A+Z] increases, diffusivity decreases. In addition, as [NaCl]:[A+Z] increases, diffusivity decreases.
Figure 26. Diffusivity of SLES/LAPB system, pH 6.3. A linear regression line for the 0.169M A+Z sample is included, R²=0.98.

Figure 27. 3D diffusivity of SLES/LAPB system, pH 6.3 with [NaCl]:[A+Z] and [A+Z].

Diffusivity is inversely proportional to the size of the micelle. Therefore, increasing [A+Z] corresponds to increasing micelle size as the spheres begin elongating into rods. In addition, increasing [NaCl]:[A+Z] corresponds to increasing micelle size. Here, increasing the number of
Na\textsuperscript{+} ions neutralizes additional negatively charged SLES molecules. These neutral molecules have a smaller effective headgroup size and can better form cylindrical micelles\textsuperscript{11}. Rods are larger than spheres and therefore diffuse more slowly than spheres, explaining these trends. Unfortunately, without access to Cryo-TEM, these results could not be visually verified.

### 3.2 Effect of pH and surfactant concentration on system morphology in a binary system

As discussed in Section 1.4, the pH of a surfactant solution can influence the charge of the zwitterionic surfactant. At the pK\textsubscript{a}, the zwitterionic monomer will protonate and introduce a new surfactant element into solution. The fraction of protonated surfactant in micellar form governs the pK\textsubscript{m}.\textsuperscript{22,24,25} Once the pH nears the pK\textsubscript{m}, the protonated surfactant begins influencing micellar interactions. This thesis assumes that the pK\textsubscript{m} and the pK\textsubscript{a} are similar and only considers the pK\textsubscript{a} in analysis.

Additional testing examined the effect of pH on the SLES/LAPB system. All samples had the same SLES:LAPB ratio of 1.0:1.7 as in the previous salt dilution studies. We tested a range of [NaCl]:[A+Z] ratios and pH values. Samples with a [NaCl]:[A+Z] ratio of 0.16:1 had pH values of 3.0, 4.0, 6.3, 8.0, and 10.0. Samples with a [NaCl]:[A+Z] ratio of 0.093:1 had pH values of 4.0, 6.3, and 8.0 while samples with a [NaCl]:[A+Z] ratio of 0.053:1 had pH values of 4.0 and 6.3. Figures 28a-28c display the sample space of these experiments.
Figure 28. Solution set of SLES/LAPB samples. Solutions ranged from [A+Z] of 0.044M to 0.666M and a) pH 3.0 to 10.0 at a [NaCl]:[A+Z] ratio of 0.16:1, b) pH 4.0 to 8.0 at a [NaCl]:[A+Z] ratio of 0.093:1, c) pH 4.0 to 6.3 at a [NaCl]:[A+Z] ratio of 0.053:1.

3.2.1 Rheology

Figure 29a displays four Cole-Cole plots at a constant [NaCl]:[A+Z] ratio of 0.16:1, a constant pH of 4.0, and varying [A+Z] from 0.338M to 0.666M. As [A+Z] decreases, the plots lose their characteristic semi-circular shape. In addition, the maximum $G'$ and $G''$ decreased with decreasing [A+Z]. Figures 29b and 29c each display an overlay of five Cole-Cole plots. All samples in these plots have a constant [NaCl]:[A+Z] ratio of 0.16:1 and a constant [A+Z] of 0.450M but have varying pH values from 3.0 to 10.0. Figure 29c is a zoomed in depiction of
Figure 29b. In these two plots, the samples lose their semi-circular shape as pH increases.

Figures 29a, 29b, and 29c are representative samples of all Cole-Cole plots generated for these pH experiments. Combined, the Cole-Cole plots for each sample displayed in Figures 28a-28c, as well additional Frequency Sweep data provide a comprehensive analysis of system entanglement at all [NaCl]:[A+Z] ratios, [A+Z], and pH values.

![Cole-Cole plots](image)

**Figure 29.** Representative Cole-Cole plots of SLES/LAPB system at a constant [NaCl]:[A+Z] ratio of 0.16:1 and various pH values and [A+Z]. a) pH 4.0. b) 0.45M A+Z. c) 0.45M (magnified 29b).

Figure 30 displays the combined viscosity traces for each sample. Lines are added to guide the eye. All samples at pH 4.0, 6.3, 8.0, and 10.0 behave similarly while the samples at pH 3.0
follow a different pattern. For this reason, the following discussion will address those samples not at pH 3.0, and the pH 3.0 samples will be addressed separately.

![Graph showing zero shear viscosity of SLES/LAPB system at various pH and [NaCl]:[A+Z] ratios with increasing [A+Z].](image)

**Figure 30.** Zero shear viscosity of SLES/LAPB system at various pH and [NaCl]:[A+Z] ratios with increasing [A+Z]. Lines have been added to guide the eye. Data of the same color have the same pH, and data of the same line type and symbol have the same [NaCl]:[A+Z] ratio. The plot has been divided into three regions for further discussion.

Figure 30 is divided into three distinct regions. Each region corresponds to a different micellar morphology. Region I ranges from [A+Z] of 0.044M to 0.084M. Within this region, all samples have similar viscosities (see Figure 31). Region II ranges from [A+Z] of 0.084M to 0.563M. Within this region, there is a division between those samples at pH 4.0 and samples at pH > 4.0. The [NaCl]:[A+Z] ratio does not appear to influence the viscosity grouping of these samples. All samples track together; viscosity increases as [A+Z] increases. Region III ranges from [A+Z] of 0.563M to 0.666M. In Region III, the viscosities of the samples again form groups, but
the clustering in Region III is different than the clustering in Region II. In Region III, all samples at pH 4.0 and all samples at a [NaCl]:[A+Z] ratio \( \geq 0.16:1 \) (the aforementioned R*) achieve a viscosity over an order of magnitude greater than samples at both a [NaCl]:[A+Z] ratio < 0.16:1 and a pH > 4.0.

Figure 31. Magnified Region I of Figure 30.

In Region I, micelles are small (less than 4 nm). They consist mostly of spheres, elongated spheres, or short rods. \(^{19}\) [A+Z] is too low to support significant growth of the micelles. As a result, micelles are still too small to interact with each other. Region II begins just past the slope change on the viscosity vs. [A+Z] plot. This slope change indicates elongated, interacting micelles. The adjusted viscosity grouping in Region III is similar to the grouping seen in Figure 19. Samples at either the lower pH and/or higher [NaCl]:[A+Z] ratio have the ability to entangle,
thus increasing their final viscosity. Samples at both a higher pH and lower [NaCl]:[A+Z] ratio do not have the ability to entangle, so their viscosity is relatively lower.

This research examined how external factors ([Na⁺], [H⁺], etc) influence the surfactant molecules, and how those molecules then alter their interactions with each other, thus affecting overall system properties. Decreasing the pH of the system increases the concentration of H⁺ in solution. At some point the pH of the solution approaches the pKₐ of LAPB (approximately pH 3.2), thus drastically changing the makeup of the solution (see Figure 32). At a pH of 3.2, the ratio of protonated LAPB⁺:deprotonated LAPB⁰ is 1:1, resulting in a 1:1 ratio of cation:zwitterion. Table 1 and Figure 33 display the [zwitterion]:[anion]:[cation] ratio at each tested pH value. As seen from both the table and the figure, samples at pH 3.0 and pH 4.0 have a considerable fraction of LAPB in cationic form. The cationic LAPB⁺ has the ability to both neutralize the negatively charged SLES and to create new packing configurations with LAPB⁰ and SLES. These changes in interactions are quantified through bulk viscosity differences, as viewed in Figure 30.

![Figure 32. Protonation of LAPB⁰ to LAPB⁺ with decreasing pH.](image)
Figure 33. Titration curve of solution with pK_a = 3.2 (pK_a of LAPB) governed by the Henderson-Hasselbalch equation.

Table 1. Relative amounts of zwitterion, anion, and cation at various pH values assuming pK_a = 3.2.

<table>
<thead>
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<th>C/A</th>
<th>C/Z</th>
</tr>
</thead>
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<td>0.64</td>
<td>1.01</td>
<td>1.58</td>
</tr>
<tr>
<td>4.0</td>
<td>1.42</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td>6.3</td>
<td>1.65</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>8.0</td>
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<td>0.00</td>
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</tr>
<tr>
<td>10.0</td>
<td>1.65</td>
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</table>

The presence of LAPB^+ explains both the grouping in Region II of Figure 30 as well as the anomalous behavior of the pH 3.0 sample in the same figure. The ratio of LAPB^+ to SLES in a pH 4.0 solution is 0.2:1—a small but significant ratio. Because this ratio is small, the viscosities of the pH 4 solutions follow a similar pattern to the viscosities of the pH > 4.0 solutions. However, because this ratio is significant, the pH 4.0 samples group together with a higher
viscosity than the pH > 4.0 solutions. This ratio of LAPB\(^+\) to SLES explains the trend described in Region II.

These results are supported by Abe et. al. in their analysis of SDS/DMLL and HCl. They found that the addition of acid protonated the DMLL, increasing the molecular interaction parameter and decreasing the effective headgroup size. In their system, DMLL acted like a cationic surfactant and increased the favorable electrostatic interactions with SDS. While they did not conduct viscosity measurements, we anticipate that their trends would have mirrored ours.\(^{26}\)

The ratio of LAPB\(^+\):SLES in a pH 3.0 solution, 1:1, is significantly larger than that of a pH 4.0 solution. In a pH 3.0 solution, there is an equal concentration of cation and anion. Due to this high ratio, the system behaves drastically differently at pH 3.0 than at pH > 3.0.

In both Figures 19 and 30, there is little variation between viscosity traces of solutions above R\(^*\). It is possible that at these higher NaCl levels, the system is saturated. Additional Na\(^+\) ions do not further neutralize the micelles.

To test this hypothesis, we made LAPB solutions at a [NaCl]:[A+Z] ratio of 0.68:1 and at a pH of both 4.0 and 6.3. In the SLES/LAPB system, pH 4.0 resulted in the highest final viscosity, and pH 6.3 is commonly found in current shampoo formulations. Analysis compared samples with a [NaCl]:[A+Z] ratio of 0.68:1 to those with a ratio of 0.16:1.

Figure 34 and 35 display the comparative viscosities of these two sample sets. At pH 4.0, there is almost an order of magnitude difference between the viscosities of the 0.16:1 and 0.68:1 samples at all [A+Z]. On average, the viscosities are closer together at pH 6.3. However, there is a power of $10^{1.5}$ shift in viscosity between the two [NaCl]:[A+Z] ratios at 0.450M A+Z. This large difference could come from a transition in system interactions at this [A+Z], but we did not
explore this idea further. In both cases, increasing the [NaCl]:[A+Z] ratio changes the viscous properties of the solution.

Figure 34. Comparative zero shear viscosity of SLES/LAPB system at various [NaCl]:[A+Z]. a) pH 4.0, b) pH 6.3.

Figures 35a-d show the comparative Cole-Cole plots at each [A+Z] and pH. Increasing the [NaCl]:[A+Z] ratio drastically changes the viscoelastic properties of the solution. Unfortunately, we were not able to investigate this phenomenon further due to time constraints.
Figure 35. Cole-Cole plots of SLES/LAPB system at various [NaCl]:[A+Z] ratios. a) pH 4.0, 0.450M A+Z. b) pH 4.0, 0.666M A+Z. c) pH 6.3, 0.450M A+Z. d) pH 6.3, 0.666M A+Z.

Figures 36 and 37 both display compiled three-dimensional phase diagrams, plotting [A+Z], [NaCl]:[A+Z], and pH. The figures are identical and examine the same data from different perspectives. These diagrams display the onsets of micellar interaction and micellar entanglement as determined by Cole-Cole plots. In summary, low pH enables entanglement, regardless of [NaCl]:[A+Z] ratio. Also, at tested pH values where no LAPB$^+$ is present (pH > 4.0), R$^*$ is 0.16:1.
Figure 36. 3D phase diagram of SLES/LAPB system at various [NaCl]:[A+Z], [A+Z], and pH. Fading colors indicate lower [NaCl]:[A+Z] ratios. All black/grey symbols designate non-interacting samples, all blue/light blue symbols designate interacting samples, and all red/pink symbols designate entangled samples. ■ 0.16:1 [NaCl]:[A+Z], ■ 0.093:1 [NaCl]:[A+Z], ■ 0.053:1 [NaCl]:[A+Z]. □ designates an undetermined sample.
Figure 37. 3D phase diagram of SLES/LAPB system at various [NaCl]:[A+Z], [A+Z], and pH. Fading colors indicate lower [NaCl]:[A+Z] ratios. All black/grey symbols designate non-interacting samples, all blue/light blue symbols designate interacting samples, and all red/pink symbols designate entangled samples. 0.093:1 [NaCl]:[A+Z], 0.053:1 [NaCl]:[A+Z]. Red designates an undetermined sample.

3.2.2 Diffusivity

Figure 38 displays the trend of diffusivity vs. pH. This figure plots the results from samples at 0.180M A+Z, [NaCl]:[A+Z] ratios of 0.093:1 and 0.16:1 within a pH range of 4.0 to 8.0. Samples at pH 3.0 were too viscous for dynamic light scattering testing. We extracted the additional data points on this plot from autotitration experiments. The diffusivity increases dramatically between pH 4.0 and pH 5.0 and then plateaus at higher pH values.
Figure 38. Diffusivity of SLES/LAPB system, 0.169M A+Z at various [NaCl]:[A+Z] ratios with increasing pH. Data from autotitration experiments in DLS.

3D plots of diffusivity with respect to both pH and [A+Z] are on display in Figures 39a and 39b. These plots display the trends previously discussed. Decreasing pH corresponds to decreasing diffusivity. Increasing [A+Z] corresponds to decreasing diffusivity at low pH but does not have as significant an impact at higher pH.

Figure 39. 3D diffusivity plot of SLES/LAPB system, [NaCl]:[A+Z] a) 0.16:1, b) 0.093:1.
As previously discussed, the LAPB\(^+\) is present in solutions at pH 4.0. This pseudo-ternary system of SLES, LAPB\(^+\), and LAPB\(^0\) explains the behavior of samples at pH 4.0 as seen in Figure 38. Both this diffusivity plot (Figure 38) and the LAPB titration curve (Figure 33) align; decreasing LAPB\(^0\) concentration corresponds to decreasing diffusivity.

### 3.3 Effect of headgroup identity, ionic strength, and surfactant concentration on system morphology in a binary system

While electrostatic effects play an important role in determining micellar shape, steric interactions also impact the effective headgroup size and thusly, micellar morphology.\(^2\)\(^,\)\(^5\)\(^,\)\(^9\) Christov et. al. observed that the sphere-to-rod transition occurred at higher surfactant concentrations with bulkier surfactant headgroups. Steric effects and electrostatic repulsion work together to determine whether micelles can elongate.

This next investigation examined how zwitterion identity affected the morphology of the system. We substituted LAPHS for LAPB and tested the new system at multiple [NaCl]:[A+Z] ratios as well as at multiple pH values. The hydrophobic tailgroup of LAPHS is identical to that of LAPB, but the headgroup has both a sulfate unit and a hydroxyl unit instead of a carboxylic acid (see Figure 13). Through this investigation, we explored how headgroup substitution (in particular, the substitution of a sulfate unit) changed the interactions between SLES and the zwitterionic surfactant.

As mentioned previously, LAPHS arrived from the supplier with 1.1M NaCl. Dialysis was impractical for the scope of this study, so all solutions had a [NaCl]:[A+Z] ratio ranging from 0.68:1 to 0.79:1 at various [A+Z]. In addition, solutions had a constant pH of 6.3 (see Figure 40). All samples had a constant SLES:LAPHS ratio of 1.0:1.7.
3.3.1 Rheology

We tested both the viscous and viscoelastic properties of the SLES/LAPHS system using the methods outlined above. Figure 41 displays the viscosity traces of this system, plotting the zero shear viscosity against [A+Z] at each tested [NaCl]:[A+Z] ratio. Unlike the SLES/LAPB system, the viscosity of this system does not appear to change with increasing salt. There is no significant difference between the viscosity traces of the three tested salt ratios. Figure 42 displays these same data in a 3-D plot. The colored striations are mostly parallel to the [NaCl]:[A+Z] axis, showing no change in viscosity with changing ratio.
Figure 41. Zero shear viscosity of SLES/LAPHS system, pH 6.3 at varying [NaCl]:[A+Z] ratios with increasing [A+Z].

Figure 42. 3D plot of zero shear viscosity with [NaCl]:[A+Z] and [A+Z].

Figure 43 displays an overlay series of Cole-Cole plots at 0.644M A+Z and all three tested [NaCl]:[A+Z] ratios. While there is a slight variation between the curves, they are almost
identical. Figures 41 and 43 show that neither the viscous nor the viscoelastic properties of the SLES/LAPHS system change with varying [NaCl]:[A+Z] ratio.

![Figure 43. Cole-Cole plots of SLES/LAPHS system, pH 6.3, 0.644M A+Z with varying [NaCl]:[A+Z] ratios.](image)

This lack of response indicates that the system is saturated. Additional salt does not interact with the negatively charged SLES molecules or the negative charges in the LAPHS molecules. At higher [NaCl]:[A+Z] ratios, the viscous and viscoelastic properties of the SLES/LAPHS system may change. However, we did not test this system at higher ratios. In addition, because the viscosity is constant at all [NaCl]:[A+Z] ratios, we do not know whether this system consists of linear or branched micelles. Cryo-TEM could visually confirm the morphology of these micelles.

The Cole-Cole plot (Figure 43) displays a semicircular shape, indicating entangled micelles. Because the system is entangled at the lowest possible [NaCl]:[A+Z] ratio (0.68:1), we assume
that the LAPHS received from the supplier is above the $R^*$ of this system at pH 6.3. $R^*$ for a binary system at a ratio of 1.0:1.7 SLES:LAPHS and pH 6.3 is less than 0.68:1.

Figure 45 is the phase diagram for the SLES/LAPHS system at varying [NaCl]:[A+Z] ratios. Black symbols represent noninteracting spheres, blue symbols represent elongated, interacting rods, and red symbols represent entangled rods. Unlike in the SLES/LAPB system (Figure 25), SLES/LAPHS system morphology does not appear to depend on [NaCl]:[A+Z].

![Figure 45. Phase diagram of SLES/LAPHS system, pH 6.3. ▢ designates non interacting micelles, □ designates interacting micelles, and ▣ designates entangled micelles.](image)

3.3.2 Diffusivity

Figure 44 displays the diffusivity of the SLES/LAPHS system at each [NaCl]:[A+Z] ratio for various [A+Z]. The diffusivity is within instrumental error and consequently, does not change with [NaCl]:[A+Z] ratio. These findings in the SLES/LAPHS system contrast the findings in the LAPB system (Figure 26). In the SLES/LAPB system, [NaCl]:[A+Z] is linearly dependent on
diffusivity. In the SLES/LAPHS system, [NaCl]:[A+Z] has no dependence on diffusivity. It is possible that the SLES/LAPHS systems we tested were so far above $R^*$ that additional salt has no effect. However, additional research is needed to further explain this discrepancy.

![Graph showing diffusivity vs. [NaCl]:[A+Z] ratio](image)

**Figure 44.** Diffusivity of SLES/LAPHS system, pH 6.3 at various [A+Z] with increasing [NaCl]:[A+Z] ratios.

### 3.4. Effect of headgroup identity, pH, and surfactant concentration on system morphology in a binary system

Subsequent experiments examined the effect of pH changes on the morphology of the SLES/LAPHS system. Solutions had a constant [NaCl]:[A+Z] ratio of 0.68:1, various pH values of 3.0, 4.0, 6.3, and 8.0, and [A+Z] ranging from 0.044M to 0.644M (see Figure 46). The LAPHS from the supplier appeared to contain a buffer system, preventing the solutions from reaching and maintaining a pH of 8.0. While the data presented below are recorded at pH 8.0, the true pH fell between pH 7.6 and pH 8.0.
3.4.1 Rheology

We probed both the viscous and viscoelastic properties of this system to understand how pH affects the morphology and system behavior. Figure 47 displays the trace of viscosity vs. [A+Z] at each tested pH. These traces overlap and show no significant difference in viscosity with pH. Figure 48 shows these same data displayed in a 3-D plot. The colored striations are mostly parallel to the [NaCl]:[A+Z] axis, showing no change in viscosity with changing ratio.

Figure 49 displays an overlaid series of Cole-Cole plots for 0.644M [A+Z] and all tested pH values. While there is a slight variation in the shape of the pH 8.0 curve, these pH curves are almost identical. Figures 47-49 do not show any significant change in either the viscous or viscoelastic properties of the SLES/LAPHS system with changing pH.
Figure 47. Zero shear viscosity of SLES/LAPHS system, 0.68:1 [NaCl]:[A+Z] at varying pH values with increasing [A+Z].

Figure 48. 3D plot of zero shear viscosity with pH and [A+Z].
As concluded in the LAPB/SLES system, the pH must be approaching the pKₐ of the system in order to have an effect on system morphology. The pKₐ of the sulfate group in the LAPHΣ has not been measured, but is expected to be comparable to the pKₐ of taurine (pKₐ = 1.5). This pKₐ is well below the lowest tested pH of 3.0. At pH values so far above the pKₐ, the additional H⁺ ions in solution have no significant effect on the surfactant molecules (see Figure 50 and Table 2). Though we changed the pH of the solution, the molecules themselves remained identical and so the rheological properties of the solution were unaffected.
Figure 50. Titration curve of solution with \( pK_a = 1.5 \) (approximate \( pK_a \) of LAPHS) governed by the Henderson-Hasselbalch equation.

Table 2. Relative amounts of zwitterion, anion, and cation at various pH values assuming \( pK_a = 1.5 \).

<table>
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<td>0.00</td>
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<td>10.0</td>
<td>1.65</td>
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</table>

Figure 51 displays the phase diagram of the SLES/LAPHS system with varying pH. Black symbols represent noninteracting spheres, blue symbols represent elongated, interacting rods, and red symbols represent entangled rods. Unlike in the SLES/LAPB system where pH plays a
role in the system interactions (Figures 36 and 37), pH does not appear to affect the morphology of the SLES/LAPHS system.

![Figure 51. Phase diagram of SLES/LAPHS system, 0.68:1 [NaCl]:[A+Z]. ■ designates non interacting micelles, ■ designates interacting micelles, and ■ designates entangled micelles.]

3.4.2 Diffusivity

Figure 52 displays the diffusivity as a function of pH. The diffusivity traces in Figure 52 are within error of each other. Diffusivity is constant at all tested pH values. Figure 53 is the three-dimensional depiction of Figure 52. While this plot was only generated from 8 data points, the diffusivity is unchanging with pH. As discussed above, changes in pH do not affect the structure of either the LAPHS or the SLES. Therefore, the diffusivity remains constant as each sample is structurally identical.
Figure 52. Diffusivity of SLES/LAPHS system, 0.68:1 [NaCl]:[A+Z] at various [A+Z] with increasing pH.

Figure 53. 3D diffusivity plot of SLES/LAPHS system, 0.68:1 [NaCl]:[A+Z] with increasing [A+Z] and pH.

While the tested SLES/LAPB and SLES/LAPHS solutions had similar pH values (3.0-10.0 and 3.0-8.0, respectively), they had different [NaCl]:[A+Z] ratios. The highest [NaCl]:[A+Z] ratio in
the SLES/LAPB system was 0.30:1, and the lowest [NaCl]:[A+Z] ratio in the SLES/LAPHS system was 0.68:1. Because the LAPHS received from the supplier contained 1.1M NaCl, the smallest possible [NaCl]:[A+Z] ratio (at a 1.0:1.7 ratio of SLES:LAPHS) was above the maximum ratio tested in the LAPB system.

To reconcile this difference, we made LAPB solutions at a [NaCl]:[A+Z] ratio of 0.68:1 and at pH values of 4.0 and 6.3. In this set of experiments, we expected viscosity to increase with increasing [NaCl]:[A+Z]. If these experiments proved that the increase in viscosity with added salt was insignificant, the SLES/LAPB and SLES/LAPHS systems would be comparable even at different [NaCl]:[A+Z].

Figures 34 and 35 compare the 0.68:1 and the 0.16:1 ratios. There is a dramatic difference in both the viscous and viscoelastic properties of these two ratios. As a result, we cannot directly compare the behavior of the SLES/LAPB system to the behavior of the SLES/LAPHS system.

3.5 Effect of ionic strength and surfactant concentration on system morphology in a ternary system

Current baby shampoo formulations include three types of surfactant—anionic, zwitterionic, and nonionic—in a fixed ratio. These three components optimize mildness, cleansing, and consumer aesthetics (i.e. rheology). In addition to analyzing the binary system of anionic and zwitterionic surfactant, we also tested a series of ternary systems to understand how the addition of a nonionic surfactant affects system morphology. Unfortunately, there has been very little investigation of ternary surfactant systems in the literature, so we cannot make any quantitative comparisons at this time.
There were two nonionic surfactants of interest: PEG-80 Sorbitan Laurate (PEG-80 SL) and Polyoxyethylene (20) Sorbitan Monolaurate (Tween-20). Past and present baby shampoo formulations use both of these nonionic surfactants. Figure 16 displays the molecular structures of these molecules. They are both significantly larger and bulkier than the other surfactants in the system (SLES and LAPB). Initial experiments examined the PEG-80 SL system. Tween-20 experiments will be discussed in the next section.

These experiments used a ratio of SLES:LAPB:PEG-80 SL of 1.0:1.7:x and a constant pH of 4.0. Solutions contained 2.6, 5.2, 10.3, and 20.6 mM PEG-80 SL. Because the water content changed as the PEG-80 SL concentration changed, each solution had a slightly different [A+Z] and [NaCl]:[A+Z] ratio. These solutions compared average [A+Z] of 0.39M and 0.55M in order to understand how the addition of a nonionic surfactant influences both the bulk properties and the morphology of the system. The 0.39M A+Z and 0.55M A+Z solutions had an average [NaCl]:[A+Z] ratio of 0.49:1 and 0.79:1, respectively. Table 3 displays the actual [NaCl]:[A+Z] ratio and [A+Z] in each sample.

Table 3. Values of [A+Z] and [NaCl]:[A+Z] for each [PEG-80 SL] sample.

<table>
<thead>
<tr>
<th>[PEG-80 SL] (mM)</th>
<th>[A+Z] (M)</th>
<th>[NaCl]:[A+Z]</th>
<th>[PEG-80 SL] (mM)</th>
<th>[A+Z] (M)</th>
<th>[NaCl]:[A+Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>0.53</td>
<td>0.50:1</td>
<td>2.6</td>
<td>0.38</td>
<td>0.84:1</td>
</tr>
<tr>
<td>5.2</td>
<td>0.54</td>
<td>0.48:1</td>
<td>5.2</td>
<td>0.39</td>
<td>0.83:1</td>
</tr>
<tr>
<td>10.3</td>
<td>0.55</td>
<td>0.46:1</td>
<td>10.3</td>
<td>0.40</td>
<td>0.79:1</td>
</tr>
<tr>
<td>20.6</td>
<td>0.58</td>
<td>0.40:1</td>
<td>20.6</td>
<td>0.42</td>
<td>0.71:1</td>
</tr>
</tbody>
</table>
3.5.1 Rheology

Previous, binary experiments examined system rheology and diffusivity by altering one variable at a time: either $[\text{NaCl}]:[\text{A+Z}]$ or pH. The ternary systems in these experiments varied both $[\text{NaCl}]:[\text{A+Z}]$ and nonionic surfactant concentration. Initial experiments compared the rheological properties of a sample with constant nonionic surfactant concentration at both the highest and lowest $[\text{NaCl}]:[\text{A+Z}]$ ratios to ensure that the salt ratio variation would not change the overall conclusions. Figures 54 and 55 display the comparative viscosity traces and Cole-Cole plots of these two samples. In Figure 54, the zero shear viscosity of the 0.84:1 $[\text{NaCl}]:[\text{A+Z}]$ sample is less than 1 cP greater than the zero shear viscosity of the 0.40:1 $[\text{NaCl}]:[\text{A+Z}]$ sample. This is not a significant enough viscosity difference to significantly alter our findings. Similarly, the Cole-Cole plots of the 0.84:1 and 0.40:1 $[\text{NaCl}]:[\text{A+Z}]$ samples in Figure 55 are almost identical. Because the viscous and viscoelastic properties are the same, the $[\text{NaCl}]:[\text{A+Z}]$ ratio has little impact on system behavior. As a result, we approximated all samples in the SLES/LAPB/PEG-80 SL system to have a constant $[\text{NaCl}]:[\text{A+Z}]$ of 0.63:1.
Figure 54. Flow step trace for SLES/LAPB/PEG-80 SL samples, pH 4.0, 0.58M A+Z at highest and lowest [NaCl]:[A+Z] ratios.

Figure 55. Cole-Cole plots of SLES/LAPB/PEG-80 SL system, pH 4.0, 0.58M A+Z at highest and lowest tested [NaCl]:[A+Z] ratios.

Figure 56 displays viscosity vs. PEG-80 SL concentration at both tested A+Z concentrations. Increased amounts of PEG-80 SL correspond to decreased system viscosity. There is a larger
gap between the viscosities of the 0mM and 2.6mM PEG-80 SL samples in the 0.39M A+Z system than in the 0.55M A+Z system; This is likely because 2.6mM PEG-80 SL in a 0.39M A+Z system has a higher molar ratio of [PEG-80 SL]:[A+Z] than the same PEG-80 SL concentration in a 0.55M A+Z system. Figures 57a and 57b display all of the Cole-Cole plots for the SLES/LAPB/PEG-80 SL system. Figure 57a shows the Cole-Cole plots for 0.39M A+Z, and Figure 57b shows the Cole-Cole plots for 0.55M A+Z. Figure 57b displays a semicircular shape at 0mM and 2.6mM PEG-80 SL, indicating entanglement at both those concentrations. There does not appear to be entanglement at higher PEG-80 SL concentration or at any PEG-80 SL concentration in the 0.39M A+Z system.

![Graph showing zero shear viscosity of SLES/LAPB/PEG-80 SL system, pH 4.0, 0.63:1 [NaCl]:[A+Z] at various [A+Z] with increasing [PEG-80 SL].](image)

Figure 56. Zero shear viscosity of SLES/LAPB/PEG-80 SL system, pH 4.0, 0.63:1 [NaCl]:[A+Z] at various [A+Z] with increasing [PEG-80 SL].
By comparing the data from Figures 56 and 57, we conclude that the "entanglement" in the ternary SLES/LAPB/PEG-80 SL system is a different type of interaction than the "entanglement" in the binary SLES/LAPB or SLES/LAPHS system. In the SLES/LAPB system, there is a large viscosity gap (over an order of magnitude) between those solutions which could entangle and those which could not (Figure 19). There is no corresponding order of magnitude gap between any two concentrations in this ternary system.

PEG-80 SL is significantly larger and "hairier" than either LAPB or SLES (Figures 13, 15, 16). It has many ethylene oxide units which have the ability to hydrogen bond with LAPB and SLES. In addition, it has the ability to both hydrogen bond and to physically entangle with itself. In a binary system, the elongated rod-like micelles would entangle around each other. This type of entanglement requires either reptation or a breaking & sliding mechanism to enable disentanglement. However, in the ternary system, the PEG-80 SL molecules join the micelles and interact with each other. No longer are the micelles themselves tangling, instead there are specific interactions between PEG-80 SL molecules. The lack of a viscosity gap indicates a new
mechanism of "entanglement". Unfortunately, ternary systems have not been fully investigated in the literature, so there is little to support this conclusion.

At low concentrations of PEG-80 SL and high concentrations of [A+Z], the system can still form rod-like micelles. However, increasing concentrations of PEG-80 SL increases the effective size of the headgroup, driving the system from elongated rod-like micelles back towards spherical micelles. The viscosity of the ternary system with spherical micelles remains significantly higher than the viscosity of the binary system with spherical micelles, due to the PEG-80 SL molecules maintaining the viscosity through self-interaction (Figure 56). However, the Cole-Cole plots (Figure 57) lose their semi-circular shape as the system is no longer entangled and Maxwellian.

3.5.2 Diffusivity

Figure 58 displays a three dimensional diffusivity plot at an average [NaCl]:[A+Z] of 0.63:1. This figure plots [A+Z], [PEG-80 SL], and diffusivity. At higher [A+Z] (0.092M), the addition of PEG-80 SL affects the diffusivity in a somewhat linear fashion. More PEG-80 SL corresponds to higher diffusivity. This finding is consistent with conclusions from system rheology. We believe that additional PEG-80 SL forces micellar shape towards a spherical system, thus increasing the diffusivity.
PEG-80 SL addition at low [A+Z] (0.044M) does not follow a predictable path. The diffusivity initially decreases with increasing PEG-80 SL concentration, and then begins increasing back to its initial value. It is worth noting that there are only five data points at an [A+Z] of 0.044M. However, there is a similarly unpredictable pattern of PEG-80 SL displayed below in Figure 60. Additional research is needed to determine why PEG-80 SL does not have the same influence on diffusivity at low [A+Z]. Unfortunately, commercial products do not tend to use such low [A+Z], so there is little industrial interest in understanding PEG-80 SL behavior at these [A+Z].

To test this hypothesis, we examined a second ternary system. This system incorporated Polysorbate-20 (Tween-20), a nonionic surfactant used in older baby shampoo formulations. Formulators found that Tween-20, as seen in Figure 17, significantly decreased the viscosity of the shampoo system. It was later replaced with PEG-80 SL which had less of an effect on system viscosity.
The system in these experiments consisted of a 1.0:1.7:x ratio of SLES:LAPB:Tween-20 at a constant pH of 4.0. Solutions contained 6.0 and 16.8 mM Tween-20. Because the water content changed as the [Tween-20] changed, each solution had a slightly different [A+Z] and [NaCl]:[A+Z]. However, the difference between the highest and lowest [A+Z] was only 0.04M, so we did not do any additional experiments to ensure the properties of the highest and lowest [A+Z] and [NaCl]:[A+Z] were the same. The average [A+Z] was 0.51M, and the average [NaCl]:[A+Z] was 0.50:1.

Figure 59 displays the viscosity plot comparing PEG-80 SL to Tween-20. As expected, the viscosity of Tween-20 solutions is lower than the viscosity of PEG-80 SL solutions. The Tween-20 behaves similarly to the PEG-80 SL; as additive concentration increases, viscosity decreases. Like PEG-80 SL, Tween-20 is a large, “hairy” molecule. When it inserts itself into the rod-like micelles, those micelles are driven towards a spherical shape. The viscosity of a spherical micelle system is lower than that of a rod-like micelle system.
As discussed previously, the PEG-80 SL decreases the viscosity by forcing the system towards spherical micelles. However, it self-entangles, maintaining a higher system viscosity than a spherical micellar system might otherwise have. While Tween-20 is significantly larger than SLES and LAPB, it is significantly smaller than PEG-80 SL. It does not have the same ability to self-entangle. As a result, the viscosity of the Tween-20 system is lower than the corresponding viscosity of the PEG-80 SL system.

Figure 60 displays the light scattering data comparing PEG-80 SL to Tween-20. Black symbols represent solutions with 0.044M A+Z, and red symbols represent solutions with average 0.095M A+Z. Solid squares represent PEG-80 SL solutions, and open circles represent Tween-20 solutions. In this figure, both Tween-20 solutions and the PEG-80 SL solution at 0.092M A+Z increase in diffusivity with increasing additive concentration. This trend matches the viscosity trends discussed above. However, the PEG-80 SL solution at 0.044M A+Z decreases in diffusivity with increasing additive concentration. We developed a number of hypotheses, none of which adequately explains this trend. Additional research is necessary to understand the deviant behavior of PEG-80 SL at low [A+Z].
Figure 60. Diffusivity of SLES/LAPB/Additive systems, pH 4.0, comparing PEG-80 SL to Tween-20 at different [A+Z].

It is important to note that these experiments were performed at pH 4.0. Section 3.2 clearly determined that LAPB$^0$ and LAPB$^+$ exist in equilibrium at this low pH. Therefore, our ternary system is actually a pseudo-quaternary system with SLES, LAPB$^0$, LAPB$^+$, and nonionic (either PEG-80 SL or Tween-20). The equilibrium concentration of each of these components in the micelle will change with changing concentration of nonionic surfactant. The unexplained trends in Figure 60 may depend on the addition of LAPB$^+$ into the system.
4. Conclusions

This thesis endeavored to address the following questions:

4.1 How does a weak salt (NaCl) impact the morphology of an anionic/zwitterionic surfactant system?

We found that system morphology with increasing salt concentration divided into three regimes, dependant on surfactant concentration. Low surfactant concentrations correspond to the “dilute regime” (Region I) where there is not enough surfactant to form interacting micelles. This regime exists at all tested salt concentrations, from [NaCl]:[A+Z] of 0:1 to 0.30:1 and [A+Z] from 0.044M to 0.253M. The next regime (Region II) spans from [NaCl]:[A+Z] of 0:1 to 0.30:1 and [A+Z] from 0.253M to 0.666M. Within Region II, the micelles have elongated and are interacting, but display multiple relaxation times. Cole-Cole analysis determined that these samples are not entangled. Region III spans from [NaCl]:[A+Z] of 0.16:1 to 0.30:1 and [A+Z] from 0.450M to 0.666M. Cole-Cole analysis determined that samples within this region are both interacting and entangled. A [NaCl]:[A+Z] ratio of 0.16:1 is R*, the critical ratio enabling entanglement in a LAPB/SLES system at pH 6.3. Because the viscosity never peaked with increasing salt concentration, we determined that all micelles were either spherical or cylindrical and linear.

4.2 How does variation in the pH affect the morphology of an anionic/zwitterionic surfactant system?

As the pH approached the pKₐ of the zwitterionic LAPB, system interactions and entanglements began at lower [A+Z]. At the highest tested [NaCl]:[A+Z] ratio, 0.16:1, system interactions
began at 0.253M A+Z for pH ≥ 6.3, 0.169M A+Z for pH 4.0, and < 0.044M A+Z for pH 3.0. Entanglement began at 0.563M A+Z for pH 6.3, 0.450M A+Z for pH 4.0 and 0.169M A+Z for pH 3.0. Similar trends were encountered at lower [NaCl]:[A+Z] ratios. We concluded that at low pH, LAPB protonated and became LAPB+. This pseudo-ternary system of SLES/LAPB0/LAPB+ reached the sphere-to-rod transition at much lower concentrations than the binary SLES/LAPB0 system due to the decreased effective headgroup size from the anionic/cationic surfactant interactions. The increase in viscosity with increasing [A+Z] at pH 3.0 follows a different path than the corresponding increase at pH ≥ 4.0. This difference is due to the drastically different interactions stemming from approximately equal proportions of SLES and LAPB+.

4.3 How does headgroup identity (both size and chemical make-up) affect the morphology of an anionic/zwitterionic surfactant system?

While we could not directly compare the SLES/LAPB system to the SLES/LAPHS system due to different [NaCl]:[A+Z] ratios, we did find that changing the headgroup did affect system properties. The viscous and viscoelastic properties did not depend on either salt concentration or pH in the tested ranges. We believe that the salt concentration in the LAPHS from the supplier was above $R^*$ for the SLES/LAPHS system, resulting in no change in effective headgroup area and therefore, packing parameter. In addition, the pKa of LAPHS is similar to that of taurine (pK = 1.5) and is much lower than the lowest tested pH, 3.0. As a result, changes in H+ concentration did not have any measurable effect on LAPHS.

4.4 How does the addition of a third surfactant type (nonionic) affect the morphology of an anionic/zwitterionic surfactant system?
Adding a nonionic surfactant drastically changed the viscous and viscoelastic system properties. Increasing concentration of either PEG-80 SL or Tween-20 decreased the system viscosity. Cole-Cole analysis indicated that increasing amounts of PEG-80 SL and Tween-20 drove the system towards disentanglement. Because the nonionic surfactant was significantly larger than both the anionic and zwitterionic surfactants, it increased the effective headgroup size and therefore, decreased the average micelle size. Increasing nonionic surfactant concentration corresponded to an increase in diffusivity, and a general shortening of the cylindrical micelles. However, these ternary systems had a surprisingly large viscosity, which we believe stems from self-entanglement of the nonionic surfactant molecules between micelles.
5. Future Work

There is still a great deal of work to be done in order to fully understand how to control the rheological properties of Johnson & Johnson shampoo formulations. First and most importantly, many of the systems presented here must be examined with cryo-TEM in order to visually verify our results. Imaging micellar morphology, micellar interactions, and the types of network points in these systems (entanglement, branching, or adhesion) will further elucidate how concentrations of additives and surfactants affect system rheology and consumer satisfaction.

Within this same topic, many of these systems should be tested with Static Light Scattering (SLS) to evaluate changes in aggregation number with changing concentrations of additives and surfactants. SLS does not require samples to undergo Brownian motion enabled diffusion; it would allow us to take measurements on our more viscous samples. Understanding how additives affect the aggregation number will give us more insight into how the surfactant monomers assemble and how these assemblies change at higher surfactant concentrations.

Additional experimentation should examine the SLES/LAPB system at [NaCl]:[A+Z] ratios above 0.30:1. Preliminary experiments conducted at a ratio of 0.68:1 found that the viscosity continues to increase with increasing salt concentration. Further increasing the salt concentration in this system would allow formulators to work in a larger sample space. In addition, characterizing the SLES/LAPB system at higher [NaCl]:[A+Z] ratios would allow for comparison to the SLES/LAPHS system. This comparison would create a better understanding of how headgroup bulk influences surfactant morphology.

In order to transition from these model surfactant systems to common commercial formulations, we must further investigate the ternary SLES/LAPB/PEG-80 SL system. Current diffusion data
are inconclusive in explaining how increasing concentration of PEG-80 SL affects solution morphology. Cryo-TEM would help clarify how a nonionic surfactant changes the geometry of the system. In particular, further research should examine how PEG-80 SL integrates into the micelles—whether it preferentially sits on the endcaps or the cylindrical body—and how that affects the evolution of the cylindrical micelles back into spherical micelles. There is also an interest in varying the nonionic and zwitterionic components to see how surfactant bulk affects micelle formation in a ternary system.

Future experimentation could examine the addition of multivalent salts or multivalent surfactants. Little research has been conducted on multivalent systems. Alargova et. al. found that a multivalent salt increases the micellar size relative to the same concentration of monovalent salt. Johnson & Johnson currently only uses monovalent salts in their formulations. Further exploration of multivalent salts could allow them to develop shampoos with lower concentrations of surfactant, leading to a less expensive, more sustainable product.

Once these model systems have been fully characterized, it is imperative that we also study the effects of salt concentration, pH, and headgroup size on a non-idealized system. Commercial shampoo formulations contain a number of additives, including dyes, fragrances, thickeners, and preservatives. Each of these components has the potential to alter micelle formation and system rheology. While understanding generic micelle behavior is important for developing models and predicting trends, industrial applications demand the manipulation of complex systems.
References


