SAVING OF TIME AND ENERGY IN THE LAUNDRY PROCESS: IMPORTANCE OF DYNAMIC SURFACE TENSION, MICELLE STABILITY AND SURFACTANT ADSORPTION

By

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by

Daniel Larry Carter
I would like to thank my parents for their continuing support over the years as well as their guidance through life.
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It has been shown that the residual moisture content of fabrics at the end of a centrifugation cycle is related to the equilibrium surface tension of the residual solution the fabric has soaked in. However, in the case of lowering the surface tension of solution via increasing concentrations of sodium dodecyl sulfate, a peak is observed in the residual moisture content and the residual moisture of fabrics deviates from the predictions of the LaPlace Equation of capillary rise. This is due to adsorption of surfactant on the fabric and the increase of dynamic surface tension. Several other molecular mechanisms have been found to affect the residual moisture content of fabrics such as the following: dynamic surface tension, micellar stability, chain length compatibility, surfactant-vesicle interactions as well as monolayer penetration. In surfactant systems with stable micelles, the dynamic surface tension of solution is high compared to labile micellar solutions and the resulting residual moisture content of fabrics is higher than the residual moisture of labile micellar systems. Similarly, when the chain lengths of multiple surfactants in a two surfactant system are of the same length, the micellar stability of this system is much higher compared to mismatched chain lengths. The residual moisture content of fabrics in same chain length surfactant systems has been shown to be higher compared to mismatched
chains. It has also been established that monolayer penetration can be used to lower the air-liquid surface tension of solution. In this work, we developed a method to lower the air-liquid surface tension values to values much lower than published results (on the order of 7 mN/m). This method was then used to reduce the residual moisture content of fabrics in the laundry process.
1.1 Introduction

- The detergent industry, with a $5.5 billion market, forms a major part of the consumer goods industry. Two large companies, Procter and Gamble and Unilever essentially cover this market, which implies a small percentage gain in the share over its competitor amounts to bulk gains in revenues, thus fuelling a cut-throat competition. To win small competitive ground over its rival, companies are resorting to fierce promotion of brand name by advertisements and sponsorships, matching product for products, saturating shelf space by variations of a brand (Tide has 60 varieties) and investing huge amounts of money on R & D for making “bigger and better” products.

With many of the products already working at their current optimum in terms of efficiency of cleaning fabrics, companies have started to explore newer variables (other than surfactant formulations) to add appeal to their products. In this regard, Procter and Gamble has identified reduction of drying time of fabric as a key variable to add consumer appeal. The Department of Energy (DOE) reports that the cloth dryer is typically the second biggest electricity using appliance after the refrigerator, costing about $2.66 billion to operate annually nationwide. Therefore, a conservative 20% reduction in the drying time of laundry could result in savings of over $500 million per year in the United States alone. It is of great interest to the DOE to conserve energy; however, the cost savings per consumer will not be a key point driving consumer sales (about $16 per year savings per household with an electric dryer). Based on consumer surveys performed by Procter and Gamble, the average consumer desires at least a
30% reduction in drying time which would result in saving time during the drying cycle as well as conserving energy.

The key point in finding ways to reduce water content in fabrics is to understand why the water is being held in the fabric. It is believed that water wicks into fabric because of capillary forces operating between fabric fibers that create capillaries. If capillary forces are indeed the cause of water retention, then the capillary rise in the fabrics should be governed by the LaPlace equation for capillary rise. These forces can be strong or weak depending on the weave of the fabric as well as the composition of the fabric. For example, cotton fiber holds about 75-80% of initial water after the spin cycle of a washing machine. Work has been done to decrease the capillary forces to enhance the water removal from fabrics by the reduction of surface tension between the air-liquid interface (Figure 1-1). This methodology should produce an enhanced laundry product that can significantly reduce the amount of residual water in fabric after the spin cycle thus reducing the drying time.

Figure 1-1: (a) High surface tension, stronger capillary forces and more amount of trapped water (b) lower surface tension, weaker capillary forces and less amount of trapped water (c) adsorbed stable micelles may help in trapping water (d) beading of water on surfaces hydrophobized by de-wetting agents, causing less residual water
1.2 Theory

1.2.1 Surface Tension Reduction

In order to reduce the drying time of fabrics, we have identified the role of surface tension as a key aspect of the laundry process. Our rationale is that if we can reduce the amount of residual water in fabrics during the spin cycle of the washing machine, then that would correspond to a reduction in drying time during the drying cycle. It is assumed that the water is held by capillaries in the fabric structure created by overlapping fabric fibers (Figure 1-2).

As shown in Figure 1-2, the height of rise in a capillary is shown to be a balance of the surface tension forces and the force exerted on the cylinder of water in the capillary by gravity. The basis behind our reasoning is found in the LaPlace Equation for capillary rise (Eqn. 1), where $\gamma$ is surface tension, $\theta$ is the contact angle (which is assumed to be zero for most fabrics), $r$ is the capillary radius and $\rho$ is the solution density. It should be noted that the contact angle and capillary radius are fixed for a given fabric, leading to the idea that the surface tension of solution is the easiest variable to manipulate.

Figure 1-2: A) SEM picture of a woven fabric [1], B) SEM of a scoured cloth [2].
As shown in Equation 1-1, the capillary height is a function of the capillary radius. As the capillary radius is decreased, the capillary height is increased as shown in Figure 1-3. As shown in the figure, as the capillary radius is decreased from 0.50 mm to 0.10 mm the capillary height is approximately tripled. If the LaPlace Equation for capillary rise is can be applied to the removal of water from fabrics then this the same trend would be shown in the residual moisture content of fabrics. If the capillary radii are smaller in a fabric, then there would be a higher capillary rise in the fabric leading to increased residual moisture content.

It has been shown by Preston et al. that water is retained in moist fibers by capillary water held in spaces between fibers and by hydrates of the fiber molecules [3]. They have shown that the amount of retained moisture in viscose and cellulose fibers is proportional to the surface tension of solution. However, their studies only showed the direct relationship between surface tension of solution and the residual moisture content of fiber systems. In our work, we are using a single surfactant in increasing concentration to vary the surface tension and measuring the
RMC of consumer fabrics instead of individual fiber strands. In comparison, Preston used several different surfactants at a single concentration to show the relationship between surface tension and capillary height for fiber bundles.

If by adding proper additives, one can substantially decrease the surface tension of a solution, then with the same centrifugal forces in the rinse cycle of existing machines, we can remove more water. We feel confident about this approach because of our earlier work in enhanced oil recovery, where we had to eliminate or reduce similar capillary forces responsible for trapping oil in fine pores of an oil reservoir by reducing the interfacial tensions [5] (Figure 1-4). (Capillary number is a dimensionless ratio of viscous forces and surface tension forces).

However, the analogy should not be drawn too far as it is relatively easy to achieve low interfacial tensions in oil/water systems (as low as 10-3 dynes/cm) as compared to air/water systems.
1.2.2 Role of Adsorbed Micelles and Micellar Stability

After some of the recent Atomic Force Microscopy (AFM) mapping at solid/water interfaces, where investigators have shown adsorbed surfactant micelles at the interface [6], there is a good possibility that surfactant micelles or other aggregates are also adsorbing at the fiber surfaces in the capillary, hence modifying capillary forces. In systems with high micellar stability, very stable films have been observed. With very stable thin liquid films the RMC should increase due to the higher force required to disrupt these films (Figure 1-8). In this context, micellar stability concepts become important. It is planned to investigate the effect of engineered micelles of low and high stability on water retention in fabric to show their effect on the residual water content.

Over the years, the Shah research group has shown that the micellar relaxation time is a maximum at a concentration of 200 mM SDS [5, 7-11]. This maximum in micellar relaxation time has a dramatic effect on many different properties of SDS solutions (ranging from low foamability, high thin film stability, wetting time, oil solubilization, etc. Figure 1-5 and Figure 1-6). The Shah research group has also shown that micellar kinetics play an important role in detergency. Shah et al. has shown that the efficacy of removing non-polar compounds from
fabrics has been shown to have a strong correlation with the relaxation time of micelles [7-12]. For example, it was shown by Oh and Shah that using 200 mM SDS (which was shown to have the longest micellar relaxation time in the SDS concentration range [8]) provided the most efficient removal of an artificial stain created by the deposition of Orange OT onto fabric samples [11].

Figure 1-6: Liquid/gas phenomena exhibiting minima and maxima at 200 mM SDS concentration [8].

Figure 1-7: Liquid/liquid and solid/liquid phenomena exhibiting minima and maxima at 200 mM SDS concentration [8].
Since the dynamic surface tension is related to the micellar stability (i.e. higher micellar stability leads to higher dynamic surface tension Figure 1-8) and we have proposed that the surface tension of solution (equilibrium and dynamic) can affect the amount of water retained by fabrics, it would be expected that there will be an increase in the RMC around a SDS concentration of 200 mM (the concentration of highest stability for the SDS system). This maximum is believed to be due to the long relaxation time of the SDS micelles at 200 mM. The long relaxation time of the micelles would lead to a decreased monomer flux from the micelles to the bulk. This decrease in monomer flux would then be shown as an increase in the dynamic surface tension this leading to an increase in the RMC (shown in Figure 1-8). Alternatively, another possible explanation to explain the increase in RMC at 200 mM concentrations of SDS could be due to stabilization of thick films on the fabric surface as well as the interfiber spaces due to relatively stable micelles. It has been shown by Shah et al. [13, 14] and Wasan et al. [15-20] that layering of micelles or particles can stabilize thin films (which could possibly explain an increase in the RMC).

Figure 1-8: Effect of micellar stability on dynamic surface tension.
1.2.3 Surfactant Adsorption

It is proposed that sudden adsorption of surfactant onto the fabric surface can effect the residual moisture content of fabrics due to the changes in dynamic surface tension of solution. Since it has been shown that cotton has a negative zeta potential one might think that an anionic surfactant would have minimal adsorption on a negatively charged surface [21-23]. However, there have been several papers showing that ability of sodium dodecyl sulfate (SDS) and other anionic surfactants to adsorb onto negatively charged surfaces such as coal fines, cotton and cellulose [21, 24-27]. Also, it has been shown by Somasundaran et al. that adsorption isotherms can show up to four adsorption regions [28], one of them being a sudden increase of adsorption due to cooperative adsorption of surfactant molecule. If surfactant molecules suddenly adsorb cooperatively on the solid surface at a critical concentration, then it must cause a concomitant decrease in monomer concentration in the bulk solution. Thus, a simple method to determine the monomer concentration below CMC is to measure the surface tension of the residual solution. For a given surfactant below its CMC, the surface tension is a measure of the free monomer concentration of surfactant in solution. However, if the change is surfactant monomer concentration is not very large then the equilibrium surface tension may not change significantly.
However, the dynamic surface tension may reflect it more clearly. If there is a sudden increase in adsorption on the fabric surface then there would be less free monomer available to adsorb on the new air-liquid interface of bubbles created during the dynamic surface tension measurement.

One important aspect in the removal of water from fabrics is the ability of surfactants to adsorb onto the textile fibers. Several researchers have shown that even though most fibers have a negative charge that anionic surfactants are able to adsorb onto the fibers. As shown in Figure 1-10, sodium dodecyl sulfate is able to adsorb onto a cotton fibers. However, the adsorption continues to increase after the solution CMC (8 mM). Rybicki explains that the increase of adsorption after the CMC is due to a competitive adsorption process between surfactant monomers and micelles. Near the CMC, adsorption of monomers and micelles is equally easy, while at higher concentrations micellar adsorption is dominant [21]. Another explanation to this phenomenon may be due to fiber swelling. When the fabric is placed in solutions near the CMC, micellar and monomer adsorption is present. However, due to the lower number of micelles, the monomers are still able to adsorb into micro-pores that are present when the fibers swell. As the concentration is increased, the micellar phase also increases. Due to the increased numbers of micelles, there is a higher probability that these micelles can adsorb and block the micro-pores thus blocking monomers from penetrating into the swollen fibers.
Figure 1-10: Change in adsorption of sodium dodecyl sulfate on cotton as a function of concentration, Temperature 293K, Time of adsorption 42 min [21].

1.3 Textile Chemistry

One of the key important factors is understand the effect of fiber structure and fiber chemistry on water retention. Since there are many different types of fabrics as well as different fabric weaves, it is important to understand their effect on water retention.

1.3.1 Chemical Composition of Cotton Fibers

On average, raw cotton fiber is approximately 95% cellulose which is hydrophilic (Table 1-1). The remainder of the fibers are noncellulosic materials that are mostly hydrophobic (proteins and waxes). However, these noncellulosic materials can be selectively removed by using the proper solvents (chloroform removes waxes; ethanol removes waxes, sugars and ashes, etc.). Also including in the composition of cotton fibers are various metals which can cause several problems in yarn manufacturing (silica and metal oxides can cause friction problems in spinning; peroxide bleaching can be affected by magnesium salts; copper, calcium and magnesium can interfere with dyeing, etc).
Table 1-1: Composition of typical cotton fibers [29].

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Composition (% of dry weight)</th>
<th>Typical</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>95.0</td>
<td>88.0-96.0</td>
<td></td>
</tr>
<tr>
<td>Protein (% N x 6.25)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.3</td>
<td>1.1-1.9</td>
<td></td>
</tr>
<tr>
<td>Pectic Substances</td>
<td>1.2</td>
<td>0.7-1.2</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>1.2</td>
<td>0.7-1.6</td>
<td></td>
</tr>
<tr>
<td>Wax</td>
<td>0.6</td>
<td>0.4-1.0</td>
<td></td>
</tr>
<tr>
<td>Total Sugars</td>
<td>0.3</td>
<td>0.1-1.0</td>
<td></td>
</tr>
<tr>
<td>Pigment</td>
<td>Trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Standard method of estimating percent protein from nitrogen content (% N)

1.3.2 Properties of Cotton

One concern in the treatment of cotton fibers is the effect of solvents on the chemical and mechanical properties of the fibers. The cellulose produced by the bolls in cotton plants is composed mostly of a polysaccharide cellulose. The polymeric backbone for the cellulose is a linear polymerized form of β-D-glucopyranose (Figure 1-11) which is linked at the 1,4-β-glucosidic oxygen bridge [29].

![Figure 1-11: Chemist's drawing of two segments in the cellulose chain.](image)

As briefly discussed, cotton is a hydrophilic fiber as well as porous. It has been shown that when immersed in water, cotton fibers swell and its pores fill with water. Due to the small size of the pores, chemical agents used for modification are not always able to penetrate the pores. These modifications are important in the textile business and can include modifications such as color dyeing, flame resistance, soil release, etc. Therefore, knowledge of these pores is and a chemical’s accessibility to these pores is a necessity. Several methods have been used in the
determination of pore accessibility such as solute exclusion. Using a series of water-soluble molecular probes (increasing in size) that penetrate the cotton fiber and not adsorb onto the fiber surface, the water in pores accessible to a solute dilutes the solution. Then, using chromatographic techniques, the amount of internal volume expansion or contraction can be determined [29]. Another aspect of cotton fabrics is water swelling known as bound water or hydrated water. It has been shown that between 0.1-0.2 g/g of water present in cotton fibers is bound water that can only be removed by thermal methods.

One fabric treatment that is widely used in industry is the swelling of cotton by sodium hydroxide (called mercerization). This process is used to improve fabric properties such as dye affinity, tensile strength, and smoothness. The great improvement in these properties by mercerization is thought to be due to the increase in pore sizes in the cotton fibers. However, another method of fiber swelling, treatment with liquid ammonia, has been shown to have a low level of large pores in the fibers [29].

There are a few other fabric treatments used in industry that can improve fiber properties. Several such methods include etherification (increases wrinkle resistance, water repellency, flame resistance and increases antimicrobial action) esterification and enzyme modification (for fabric softness and colorfastness of dyes).

Fabric dyeing is another important practice in industry that has implication in the removal of water from fabrics. It is general practice to prepare the fabric surface by operations like singeing, desizing, scouring, bleaching and mercerization. As stated previously, these treatments are used in the removal of impurities from the cotton fibers (such as waxes, pectins and ashes). Several dyeing methods exist in industry (such as azoic, direct, reactive, sulfur and vat dyeing) but reactive and direct dyeing are the most common methods. Direct dyeing affixes dyes to the
cellulose by hydrogen bonding and van der Waals forces to attach the dye to the fabric surface. The dyes and pigments used in these processes are mostly of water insoluble inorganic or organic composition [29]. Since some of the dyes are bonded to the surface or reactivity affixed to the fiber structure, changes in the hydrophillicity of the fiber are possible hence the implications into the dewatering of fabrics. These dyes can also influence the affinity of ionic surfactants in the adsorption of these molecules to the fabric surface.

1.3.3 Surface Treatments of Cotton Fabrics

As mentioned, there are many types of surface treatments for fabrics (with a main focus on cotton) that are commonly used for consumer convenience in order to enhance the properties of the fabric. One important cotton treatment is making the cotton fibers flame resistant. Most of the treatments used in this process are inorganic based chemicals that are chemisorbed on the fabric (in the case of using multivalent metallic salts, the surface charge of the fabric will change therefore changing the adsorption kinetics of surfactants onto the fabric) [30].

Another widely used fiber treatment process is treating the fibers for repellency. Several types of treatments are used in the case of different types of repellency (i.e. water, oil, and soil). In the case of water repellency, several different types of hydrophobic compounds can be used to coat the fabric (ranging from waxes, siloxanes, to fluorocarbon treatments) [30]. As mentioned, the contact angle of the solution on the fabric surface is one factor in the water removal from fabrics (based on the Laplace Equation for capillary rise). If the contact angle of the solution is increased, the \( \cos \theta \) term in the Laplace equation is decreased, which would result in a lower capillary rise or lower water retention. Therefore, any fabric that is treated with any of these repellents will show lower residual moisture due to an increased contact angle.
1.4 Scientific Approach

Due to the complex nature of the removal of water from fabrics, several challenges may arise that need to be understood. Technologies ranging from fabric chemistry to the dewatering of coal fines may provide insight to the removal of water from fabrics. There are several things that should be investigated in the process of removing water from fabrics such as surfactant adsorption onto surfaces, the role of vesicle-surfactant interaction in the lowering of surface tension as well as the role of dynamic processes such as dynamic surface tension and transient surface tension by monolayer penetration.

1.4.1 Surface Tension Reduction using Surfactants

For pure surfactants, either anionic or non-ionic, the surface tension (after critical micelle concentration, cmc) is usually in the range of 30 – 40 mN/m. For anionics, the surface tension strongly depends on the counter-ion used [31, 32] (Table 1-2). In the case of non-ionic surfactant system (CiEj), the surface tension changes as a function of the number of ethoxylated groups.

<table>
<thead>
<tr>
<th>Area/molecule (Å²/molecule)</th>
<th>Surface Tension above CMC (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiDS</td>
<td>61.3</td>
</tr>
<tr>
<td>NaDS</td>
<td>51.8</td>
</tr>
<tr>
<td>CsDS</td>
<td>44.8</td>
</tr>
</tbody>
</table>

A host of mixed surfactant systems show synergism in terms of reducing the surface tension, whereby at particular mole ratios of two surfactants, one achieves surface tension values unattainable by an individual surfactant alone. The surface activity is not only enhanced at the gas-liquid interface but also at solid-liquid interface leading to a better wetting of textile fibers and higher detergency [33].

Working with sodium dodecyl sulfate (SDS) system in their chain compatibility study, Sharma and others [34] have shown that the maximum reduction in surface tension of SDS
solution occurs by addition of a small amount of dodecanol, i.e. when the chain length of the alcohol and the surfactant are matching. In a related study, Patist et.al. [35] showed a maximum reduction in surface tension when a small amount of dodecyl trimethyl ammonium bromide (DTAB) is added to the SDS solution.

Shah et.al. [36] has found striking change in properties of various systems (eg. lecithin-cholesterol, stearic acid-stearyl alcohol, decanoic acid-decanol, potassium oleate-hexanol, SDS-cetyl pyridinium chloride) at a 1:3 molecular ratio. Though direct values of surface tension were not reported for these systems, in all cases there is indirect evidence (evaporation rate, foam stability, solubilization in microemulsion) that at this ratio there is a maximum crowding of molecules at the interface and the molecules are tightly packed. Other researchers have reported this synergism for anionic/cationic [37], anionic/zwitterionic [38-40], cationic/zwitterionic [38], non-ionic/zwitterionic [38], anionic/cationic-gemini [41], anionic gemini/zwitterionic [42], cationic-gemini/nonionic [43] and cationic-gemini/sugar surfactants [44]. These investigations suggest that properly engineered synergism can help reduce surface tension values to $\sim 20 \text{ mN/m}$ (Figure 1-12).

![Figure 1-12: Synergism between a cationic Gemini (surfactant 1) and anionic n-dodecane sulfonate (surfactant 2) [40].](image-url)
To further reduce the surface tension, special surfactants (silicone, fluorocarbon surfactant) are needed. Silicone surfactants because of its flexible polymer backbone (Si-O bond) and a preponderance of surface-active methyl groups, which can orient in low energy configurations, are capable of reducing the surface tension to around \( \sim 19 \text{ mN/m} \). Numerous chemistries such as cationic [45, 46], ring based cationic [45], straight chain [47, 48] as well as ring based sulfo and carbo betaines (zwitterionic), siloxanyl phosphinioxides [45] (amphoteric), polyether copolymers (non-ionic) [45], bolaform surfactants [45, 49] (two hydrophilic group and only one hydrophobic group) have been developed to exploit the high surface activity of polydimethyl siloxane (PDMS) backbone some of which we also will be using for the dewetting experiments. Similar chemistries have been developed with the fluorocarbon surfactants and the minimum surface tension possible can be \( \sim 15 \text{ mN/m} \) [50].

So in between pure, mixed, siloxane based and fluorocarbon surfactant, we have a variety of system with surface tensions in the range (15-40 mN/m) to experiment on for surface tension reduction approach.

1.4.2 Effect of Bulk and Adsorbed Micelles

Surfactants are amphiphillic molecules, which tend to adsorb at any possible interface (air-water, fabric-water). In surface tension reduction approach, we dealt only with phenomena occurring at air-water interface. Next we shift our attention to surfactant molecules at the fabric-water interface where the adsorbed molecules may adopt different morphologies such as sparse covering of substrate, monolayer covering, hemimicelles and spherical micelles as shown in Figure 1-13 [51]. These morphologies depend on the concentration, structure of the surface-active molecules and the nature of the substrate (polar/non-polar) [51, 52]. The effect of the underlying substrate can be observed in atomic force microscopy (AFM) images of full cylinders
meandering across mica surface with changes in direction corresponding to changes in mica lattice against spherical micelles on amorphous silica, which lacks these atomic rows [6]. On the other hand, structure of the surfactant itself, because of steric packing constraints (and charge as the case might be), may influence the morphologies. Such is the case for cationic gemini surfactant where curved morphologies are not observed and adsorption proceeds in layer by layer manner [53].

Intuitively, any preference of the surfactant-water-fabric system to form bilayer or spherical morphologies (hydrophilic) should promote capillarity and higher water retention capability. Further the stability of the aggregates as well as the strength with which these aggregates are adsorbed on to the substrate may also heavily influence the amount of water that can be removed from the fabric. Both of these areas are currently the focus of scientific pursuit. Isolated studies exist on the effect of surfactant concentration on wettability of the fabric but there are no definitive studies for the role of adsorbed aggregates or aggregates in bulk and their properties (stability) on the water retention capability or wettability of fabric. A study on scoured (hydrophilic) and unsoured (hydrophobic) cotton with varying concentration of two surfactants, tween 20 and span 20 showed that above their cmc values both surfactants enhanced the wetting irrespective of nature of substrate (hydrophobic/hydrophilic) while the opposite was true for
concentrations below cmc [54], affirming the role of surfactant aggregate morphology. In a related work, we have shown in a SDS surfactant system (above cmc) that wetting time of cotton is entirely dictated by miceller stability. SDS micelles are most stable at a concentration of 200 mM leading to a smaller monomer flux, thus controlling the time for the aggregate morphologies (as in Figure 1-) to build up on the fabric surface.

Figure 1-14: Force required to “puncture” micelles adsorbed on a mica surface [51].

The stability of the aggregates can be measured by: (i) using conductivity detection by pressure-jump method for ionic surfactant micelles in bulk (ii) using stopped flow method for non-ionic surfactants micelles in bulk and (iii) using atomically smooth surfaces (mica, silica, alumina, highly ordered pyrolytic graphite) and AFM for adsorbed surfactant aggregates.

Table 1-3 gives micellar stability for selected surfactants and Figure 1-14 shows the stability of N-alkyl trimethyl ammonium bromide (alkyl chain length: 8, 10, 12, 14, 16) micelles as measured by AFM.

By using additives such as tetra-alkyl ammonium chlorides [55], dodecyl alcohol [56], DTAB [35], 2-ethyl hexanol and tri-butyl phosphate [57], we have also shown that the stability of SDS micelles can be changed both ways as shown in Table 1-4. Thus we have enough systems to study any possible correlation between micellar stabilities and drying time of the fabric.
Table 1-3: Micellar stabilities for pure surfactant systems [58].

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Micellar Stability (τ2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS (200 mM)</td>
<td>7 sec</td>
</tr>
<tr>
<td>Tween 20</td>
<td>6 sec</td>
</tr>
<tr>
<td>Tween 80</td>
<td>8-10 sec</td>
</tr>
<tr>
<td>Pure C12(EO)5</td>
<td>10 sec</td>
</tr>
<tr>
<td>Pure C12(EO)8</td>
<td>4 sec</td>
</tr>
<tr>
<td>Brij 35</td>
<td>80 sec</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>3.5 sec</td>
</tr>
<tr>
<td>Synperionic A50</td>
<td>40 sec</td>
</tr>
<tr>
<td>Synperionic A7</td>
<td>150 sec</td>
</tr>
</tbody>
</table>

Table 1-4: Micellar stabilities for SDS mixed surfactant systems [35, 55-57].

<table>
<thead>
<tr>
<th>Surfactant + additive</th>
<th>Micellar Stability (τ2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS (25 mM)</td>
<td>1 millisec</td>
</tr>
<tr>
<td>SDS (25 mM) + 1.25 mM Dodecanol</td>
<td>230 millisec</td>
</tr>
<tr>
<td>SDS (100 mM)</td>
<td>150 millisec</td>
</tr>
<tr>
<td>SDS (100 mM) + 5 mM DTAB</td>
<td>1350 millisec</td>
</tr>
<tr>
<td>SDS (100 mM) + 5 mM tetra-ethyl ammonium chloride</td>
<td>2500 millisec</td>
</tr>
<tr>
<td>SDS (100 mM) + 5 mM tetra-butyl ammonium chloride</td>
<td>50 millisec</td>
</tr>
</tbody>
</table>

1.4.3 Surfactant Vesicle Interactions

Since the key focus of water removal is during the spinning cycle of a washing machine, an additive that is introduced into the wash cycle before the final spin occurs is desirable. Currently, consumers use products that enhance the fiber softness and are known as fabric conditioners. These products are introduced to the wash cycle during the final rinse before the final spin cycle begins. This implies that the surface tension of this final rinse water is a controlling factor in water removal from fabrics. It has been shown that these fabric conditions contain long chain cationic surfactants (on average 18 carbon chains) in both a monoalkyl form and a dialkyl form. Due to the mixture of the monoalkyl and dialkyl surfactants (known as monoquats and diquats since they are quaternary ammonium salts), they form vesicles. In order to lower the surface tension of this rinse water, the use of an oppositely charged (anionic)
surfactant should be used since it has been shown that a synergism exists between cationic and anionic surfactants. However, it is possible that these added anionic surfactants may interact with the vesicles already formed in these fabric conditioners. Such interactions need to be understood to effectively engineer a system of low surface tension (<20 mN/m).

**1.4.4 Dewatering of Particle Suspensions**

The use of polymers as flocculants for particle suspensions is a widely used practice in the separation and dewatering of solid/liquid systems containing fine particles. Separation by flocculation is appropriate if the desired results are a reduction in sludge volume with rapid separation. However, if it is desired to obtain a dry solid, the sludge is subjected to mechanical forces to aid in the elimination of water. There has been extensive research in the field of flocculation using polymers. However, not much has been done in the area of correlating adsorption phenomena on the effects of filtration and water removal. Several aspects have been investigated in the role of adsorption phenomena on the effect of residual water in porous media and it has been determined that surface tension plays an important role. The use of surfactants has been investigated to determine the effect of surface tension reduction on the amount of residual water. It has been shown that a substantial reduction in the moisture content of porous systems can be achieved by the addition of surfactants.

It has been shown by Singh that there is a direct correlation between the point of zero charge and surface tension reduction in the residual moisture in the dewatering of coal fines [24]. Singh notes that the mechanisms to the reduction of water in the filter cake is complex but that it appears that the reduction of surface tension as well as surface modification in the contact angle by adsorption play an important role. As similar to our study, the Laplace-Young equation for capillary rise is thought to be the controlling mechanism in the retention of water in aqueous slurries. However, Singh points out that there is not always a direct correlation between surface
tension and cake moisture indicating that surfactant adsorption on the liquid-solid interface plays a roll in the dewatering of fine porous media. Using both a cationic and anionic surfactant, Singh showed that when the surfactant is not as strongly attracted to the coal particles (due to a slightly negative surface charge), the cake moisture decreased (Figure 1-15). Since the high affinity of the cationic surfactant to the coal particles, most of the surfactant was adsorbed (~90%) and little surfactant was available to adsorb to the air-liquid interface. Due to lower solid surface adsorption for the SDS system, more of the surfactant could adsorb at the air-liquid interface and thus a lower surface tension could be achieved reducing cake moisture.

![Figure 1-15: Moisture content of filter cake as a function of surfactant concentration used in slurry pretreatment. O, SDS (9.2 x 10^{-6} mole dm^{-3}); Δ, DAB (6.9 x 10^{-6} mole dm^{-3}) [24].](image)

Similar studies of surfactant adsorption on kaolin particles have shown similar results to the earlier work done by Singh. Besra et al. have shown that the equilibrium adsorption isotherm for sodium dodecyl sulfate on kaolin (which is a negatively charged surface) shows a Langmuir type curve (Figure 1-16) with a low amount of surfactant adsorption due to electrostatic repulsion [59].
1.4.5 Interactions at the Solid-Liquid Interface

1.4.5-1 Role of capillarity in the retention of water in fabrics

Since our rationale is that water is retained in the fabric by capillaries formed between fibers, capillarity plays an important role and should be understood to be able to develop novel methods to remove moisture from fabrics. Several studies have been performed on the water transport mechanisms in textiles. It has been shown that water transport is governed mainly by a modified LaPlace-Young equation that takes into account viscous terms in capillary flow [60]. However, it was found that this wicking phenomena was not solely dependant on fabric type (due to hydrophillicity, cotton should show a higher wicking than a hydrophobic material). It was found by Hollies et al. that the fiber roughness as well as weave plays a role in the water transport in fabrics (i.e. the yarn structure is a factor in the transport of liquids in fibers as compared to solely the chemical nature of fibers). It has been suggested that the use of wicking experiments (measuring the height of water in a fabric column as a function of time) can be an indication of fiber arrangement [60]. However, these observations are based on the assumptions of no external gravitational force so extending this information into a dynamic process under centrifugal force may not be appropriate. In the case of centrifugation, the gravitational forces
may be much greater than the forces affected by fabric structure (i.e. viscose forces) thus showing more of a relationship between transport properties (capillarity, etc.) and the composition of the fiber used in experimentation. It should also be noted that these experiments were performed using dry fabrics rather than using fabrics that have been wetted.
CHAPTER 2
THE RELATIONSHIP OF SURFACE TENSION AND THE RESIDUAL MOISTURE CONTENT OF FABRICS

2.1 Experimental Background

In order to reduce the drying time of fabrics, we have identified the role of surface tension as a key aspect of the laundry process. Our rationale is that if we can reduce the amount of residual water in fabrics during the spin cycle of the washing machine, then that would correspond to a reduction in drying time during the drying cycle. It is assumed that the water is held by capillaries in the fabric structure created by overlapping fabric fibers.

The basis behind our reasoning is found in the LaPlace Equation for capillary rise (Figure 2-1 and Eqn 2-1), where $\gamma$ is surface tension, $\theta$ is the contact angle (which is assumed to be zero for hydrophilic fabrics), $r$ is the capillary radius and $\rho$ is the solution density.

\[ h = \frac{2\gamma \cos \theta}{r \rho g} \]  
Eqn. 2-1

The amount of fluid that can wick into a capillary is proportional to the surface tension of the fluid. Equation 2-2 shows that the work required moving a liquid a given distance is proportional to the surface tension.
Based on Equation 2-1, if the surface tension (γ) of the fluid is lowered and the work is held constant (the centrifugal force exerted on the fabric during the spin cycle), then the amount of displacement in the capillary, ΔA, must increase to balance the equation. Therefore, based on these principles, if we can lower the surface tension of the rinse water before the final spin cycle, then more water will be forced out of the fabric. If less water is present in the fabric before placing in it the dryer, then the time required to dry the fabric will be decreased.

It has been shown by Preston et al. that the use of the equation for capillary rise is appropriate for use in examining the capillary rise in fiber assemblies [3, 61, 62]. They have shown that the amount of retained moisture in viscose and cellulose fibers is proportional to the surface tension of solution. However, their studies mainly focused on two different surface tension solutions and a fixed centrifugal time. It was shown that the relative mass of water imbibed in capillaries should be linearly proportional to the surface tension of solution. Therefore it is believed that this is an appropriate method to determine the residual moisture content of different fabric types. However, it should be noted that Preston et al. varied surface tension by using different surfactant types. Our work has expanded on this basis to include surface tension variation by varying the concentrations of a single surfactant. Much of Preston’s work was performed at high gravitational forces (from 1000 – 5000 g), which is much higher than the gravitational forces found in a household washing machine (~100 g). On another note, Preston’s work never mentioned the implications of his work for use in a laundry product.

If by adding proper additives, we can substantially decrease the surface tension of a formulation, then with the same centrifugal forces in the spin cycle of existing machines, we can remove more water. This approach was successfully used in our earlier work in enhanced oil
recovery, where we had to eliminate or reduce similar capillary forces responsible for trapping oil in fine pores of an oil reservoir by reducing the interfacial tensions [5].

Shah et.al. [36] has found striking change in properties of various systems (eg. lecithin-cholestrol, stearic acid-stearyl alcohol, decanoic acid-decanol, potassium oleate-hexanol, SDS-cetyl pyridinium chloride) at a 1:3 molecular ratio. Though direct values of surface tension were not reported for these systems, in all cases there is indirect evidence (evaporation rate, foam stability, solubilization in microemulsion) that at this ratio there is a crowding of molecules at the interface and the molecules are tightly packed. Other researchers have reported this synergism for anionic/cationic [63], anionic/zwitterionic [38-40], cationic/zwitterionic [38], non-ionic/zwitterionic [38], anionic/cationic-gemini [41], anionic gemini/zwitterionic [42], cationic-gemini/nonionic [43] and cationic-gemini/sugar surfactants [44]. These investigations suggest that properly engineered synergism can help reduce surface tension values to ~ 20 mN/m.

2.1.1 Measuring Residual Moisture Content

In order to determine how the system reacts to different variable that could possible affect the residual moisture content (RMC) of fabrics, several experiments were performed to show the effects of centrifugation speed and centrifugation time as well as testing several different types of fabrics. In order to test the effect of surface tension on the residual water content of fabrics several assumptions needed to be made. After several force calculations it was determined that the average household washing machine spins with a force about 90 times the force of gravity. For testing purposes each fabric sample was soaked for ten minutes and then placed in the centrifuge for ten minutes. The experimental apparatus that was used is shown in Figure 2-2. The setup uses a centrifuge tube with a copper insert. The copper insert has a closed end with the other end flared so that it will not fall inside the outer tube. The insert also has small holes drilled
through it to allow water to drain through the insert into the collection tube (much like how a modern washing machine is designed).

Figure 2-2: Experimental apparatus used to determine the RMC of various fabrics. There are holes in the brass insert which holds the fabric samples to allow water to drain from the sample tube during centrifugation.

After the fabric was soaked and centrifuged, the weight was then taken to determine the Residual Moisture Content (RMC) as shown in Equation 2-3. The first sets of experiments were designed to get basic information about how the system acts (such as force and time dependence on the RMC).

\[
RMC = 100 \times \frac{Weight_{\text{centrifuged}} - Weight_{\text{dry}}}{Weight_{\text{dry}}}
\]

Eqn. 2-3

The surface tension measurements were made using the Wilhelmy Plate method. The output from a gram-force sensor holding the plate is sent to a transducer and then output to a voltage readout. The system was calibrated using two known solutions (water at 72.5 mN/m and acetone at 23 mN/m). The platinum plate was heated using a torch between each reading to clean
off anything that may have adsorbed onto the plate. For the experiments that were performed only equilibrium surface tension was correlated with the residual moisture content of fabrics.

After a basic understanding of how the system acts under different forces, it was desired to determine the relationship between RMC and surface tension. Several sets of experiments were performed using various commercial surfactants provided by the manufacturer (DeIonic 100-VLF, DeIonic LF60-MOD, and Dow Corning Q2-5211). All of the commercial surfactants were tested at 1000 ppm (0.1 wt%). Several other surfactant systems were chosen in this study as well. A leading detergent (at 1500 ppm – the normal household dosage in a washing machine) and a leading fabric softener (at 500 ppm – household dosage) were also tested in these experiments.

The first set of experiments was performed using the same surfactant varying the surface tension by using different concentrations. Since a trend was observed, another set of experiments were performed to determine if this relationship holds true for different surfactants with varying surface tensions.

2.1.2 Surface Tension Measurements

The surface tension measurements were made using the Wilhelmy Plate method. The output from a gram-force sensor holding the plate is sent to a transducer and then output to a voltage readout. The system was calibrated using two known solutions (water at 72.5 mN/m and acetone at 23 mN/m). The platinum plate was heated using a torch between each reading to clean off any surfactants or impurities that may have adsorbed onto the platinum plate. For the experiments performed in the basis experiments, only equilibrium surface tension was correlated with the residual moisture content of fabrics.

2.1.3 Materials

The sodium dodecyl sulfate used in these experiments was obtained from the Fisher Scientific Company. Several sets of experiments were performed using various commercial
surfactants provided by the manufacturer (DeIonic 100-VLF, DeIonic LF60-MOD, and Dow Corning Q2-5211). All of the commercial surfactants were tested at 1000 ppm (0.1 wt%). Several other surfactant systems were chosen in this study as well. A leading detergent (Tide at 1500 ppm, the normal household dosage in a washing machine) and a leading fabric softener (Downy at 500 ppm, the household dosage) were also tested in these experiments.

Several different types of fabric were used in the experiments. For the experimental basis, three samples were used. Two fabrics were 100% cotton (the denim fabric and plain cotton fabric) and the last fabric was a 65% polyester-cotton blend. For RMC testing, the first type of fabric that was tested is a Department of Energy (DOE) standard test fabric which is a 50/50 blend of polyester and cotton. A 100% cotton Hanes tee shirt material and an 86/14 cotton polyester terry cloth were also tested.

### 2.2 Experimental Basis

#### 2.2.1 Time Basis

In order to determine the effect of centrifugation time on the residual moisture content (RMC) of fabrics, the centrifugation speed was held constant while the centrifugation time was varied (from 2 minutes to 45 minutes). As shown in Figure 2-3, the RMC decreases as the centrifugation time increases. However, a plateau is observed around 15 minutes. At this RPM (1250 RPM), a point is reached that all of the largest capillaries have released their water (around the 15 minute mark). Water that is trapped in smaller capillaries cannot be forced from the fabric at this centrifugation speed due to the higher force required to expel water in smaller capillaries. Also, as the residence time in the centrifuge increases, the RMC decreases (Figure 2-3). This is due to the fluid overcoming the viscous forces in the capillaries. Since the force is not being increased, the only factors holding the water in the fabric are surface tension and viscous forces.
As the residence time is increased, the system has time to equilibrate and all unbound water can be displaced from the fabric.

![Time variation for different fabrics at 1250 RPM](image)

Figure 2-3: RMC as a function of centrifugation time held constant at 1250 RPM. A plateau is observed at approximately 15 minutes.

### 2.2.2 Centrifugation Speed Basis (Effect of Increasing Gravitational Force)

In order to determine the effect of centrifugation speed on the residual moisture content (RMC) of fabrics, the centrifugation time was held constant while the centrifugation speed was varied (from 1000 RPM to 8000 RPM). It is expected that by the LaPlace Equation for capillary rise, as the gravitational force is increased, the capillary height should decrease leading to lower residual moisture in the fabric. As shown in Figure 2-4, the variation of centrifugation speed held constant at a centrifugation time of 10 minutes is shown to decrease in an exponential decay which is expected due to the increase in gravitational force exerted onto the fabric samples. It should be noticed that at about 4500 RPM, there is another plateau that is observed. It is also shown that the denim and cotton samples (both 100% cotton) show approximately the same RMC as a function of RPM while the polycotton sample is much lower. This is due to the change
in contact angle of the water on the fabric. This is simply due to the face that the polyester samples are much more hydrophobic than their cotton counterparts and thus it is much easier for the hydrophobic fabric to shed water during the centrifugation process. Since the polyester is hydrophobic the contact angle is increased and the capillary height is decreased resulting in a lower RMC.

![RPM variation with various fabrics at 10 minutes centrifugation time](image)

Figure 2-4: RMC as a function of centrifugation speed held constant at a centrifugation time of 10 minutes. A plateau is observed at approximately 4500 RPM.

### 2.3 Lowering of Surface Tension by Surfactant Systems

#### 2.3.1 Simple Surfactant Systems

After we had established a basic understanding of how the system reacted to different forces, we focused attention on determining the relationship between the RMC and surface tension. To determine whether there was a relationship between the surface tension of a solution and the RMC of the fabrics, the RMCs were measured for different solution concentrations of the leading detergent. Figure 2- shows a smooth trend in the relationship between the RMC of fabrics and the surface tension. Since the lowest surface tension achieved using the detergent solutions was ca. 30 mN/m, Dow Corning Q2-5211 was used as a reference point (at 19.9
mN/m) (see Figure 2-5). If one extrapolates these curves to a surface tension of zero, one might assume that the trapped water was simply the water of hydration caused by strong hydrogen bonding between the fabric and water. However, many microcapillaries are present in the fabric structure. Under force, these capillaries may close due to the crushing of the fabric under load, trapping water inside the fabric structure.

Figure 2-5: Relationship between RMC and surface tension for the detergent system for the Hanes and DOE fabrics at 1000 RPM (~92 times the force of gravity) centrifuged for 10 minutes.

Since a clear relationship existed between the surface tension of a solution and the RMC of the fabrics, more experiments were performed using a variety of surfactant types to determine whether a general correlation existed independent of surfactant type. As shown in Figure 2-6, a relationship between the RMC of the fabrics and the solution surface tension existed for various commercial surfactant systems; however, a few discrepancies were present. The range of surfactant types used may account for such disturbances in the trend. Several different types of surfactants (ionic, nonionic, and siloxanes as shown in Table 2-1) were used in this experiment,
and each type may have had some sort of interaction with the fabric surface, causing more or less water to be displaced during centrifugation.

Figure 2-6: Relationship between RMC and surface tension for commercial surfactant systems for Hanes, DOE and Terry Cloth fabrics at 1000 RPM (~92 times the force of gravity) for 10 minutes.

Table 2-1: Surface tensions and corresponding RMC values for Hanes fabric for various commercially available surfactants.

<table>
<thead>
<tr>
<th></th>
<th>Surface Tension, mN/m</th>
<th>RMC, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.5</td>
<td>74</td>
</tr>
<tr>
<td>Fabric Softener (0.1 wt%)</td>
<td>47.2</td>
<td>65.68</td>
</tr>
<tr>
<td>Leading Detergent (0.15 wt%)</td>
<td>30.5</td>
<td>58.53</td>
</tr>
<tr>
<td>DeIONIC 100-VLF (0.1 wt%)(^1)</td>
<td>27.6</td>
<td>57.43</td>
</tr>
<tr>
<td>DeIONIC LF-60MOD (0.1 wt%)(^1)</td>
<td>26.1</td>
<td>55.06</td>
</tr>
<tr>
<td>SDS:C12TAB (3:1 molecular ratio at 0.1 wt%)</td>
<td>21.2</td>
<td>53.84</td>
</tr>
<tr>
<td>Dow Corning Q2-5211 (0.1 wt%)(^2)</td>
<td>19.9</td>
<td>50.3</td>
</tr>
</tbody>
</table>

\(^1\) Manufactured by DeForest Enterprises, Inc.
\(^2\) Manufactured by Dow Corning

2.3.2 Mixed Surfactant Systems – SDS + C\(_{12}\)TAB

Due to the ready availability of sodium dodecyl sulfate (SDS) and dodecyl trimethyl ammonium bromide (C\(_{12}\)TAB) and their opposite charges (anionic and cationic), the surface
tensions and residual moisture contents for various ratios of SDS to C\textsubscript{12}TAB were investigated at a total concentration of 500 parts per million (0.05 wt%, or the typical surfactant concentration during the final rinse cycle of the washing machine). At the 3:1 weight ratio of SDS to C\textsubscript{12}TAB (which is approximately the 3:1 molecular ratio due to similar molecular weights), the lowest RMC of \textasciitilde50\% was achieved at a surface tension of 20.5 mN/m as shown in Figure 2-7 (comparable to results from Dow Q2-5211 Superwetter with a RMC of 50.6\%).

Figure 2-7: Residual moisture content and surface tension of various weight ratios of SDS to C\textsubscript{12}TAB centrifuged at 90g (~1000 RPM in our Sourval Centrifuge) for 10 minutes. Measurements performed at a total surfactant concentration of 500 ppm.
CHAPTER 3
THE EFFECT OF SURFACTANT ADSORPTION ON THE RESIDUAL MOISTURE CONTENT OF FABRICS

3.1 Peak in SDS RMC Curve as a Function of Increasing SDS Concentration

It was shown that the RMC of fabrics depends on several different variables such as centrifugation time, centrifugation speed, and surface tension of solution [64]. However, we have observed that the RMC of fabrics does not completely correlate with the LaPlace equation as expected. Before the CMC of surfactant solution we investigated, there is a sharp peak in the RMC of fabrics. It is proposed that this increase in RMC is due to the sudden adsorption of surfactant onto the fabric surface. Since it has been shown that cotton has a negative zeta potential one might think that an anionic surfactant would have minimal adsorption on a negatively charged surface [21-23]. However, there have been several papers showing that ability of sodium dodecyl sulfate (SDS) and other anionic surfactants to adsorb onto negatively charged surfaces such as coal fines, cotton and cellulose [21, 24-27]. Also, it has been shown by Somasundaran et al. that adsorption isotherms can show up to four adsorption regions [28], one of them being a sudden increase of adsorption due to cooperative adsorption of surfactant molecules, which may explain the peak found in the RMC curves observed in this study. If surfactant molecules suddenly adsorb cooperatively on the solid surface at a critical concentration, then it must cause a concomitant decrease in monomer concentration in the bulk solution. Thus, a simple method to determine the monomer concentration below CMC is to measure the surface tension of the residual solution. For a given surfactant below its CMC, the surface tension is a measure of the free monomer concentration of surfactant in solution. However, if the change is surfactant monomer concentration is not very large then the equilibrium surface tension may not change significantly. However, the dynamic surface tension may reflect it more clearly. If there is a sudden increase in adsorption on the fabric surface then
there would be less free monomer available to adsorb on the new air-liquid interface of bubbles created during the dynamic surface tension measurement. This would thus lead to an increased dynamic surface tension (which should be an amplified measurement of the equilibrium surface tension) that should correspond to the increase in RMC in the same surfactant concentration range.

In these experiments, we have measured the free surfactant monomer concentration by a two phase dye transfer method. This method is commonly used in the determination of anionic surfactants in wastewater. The method that we used was a separation of methylene blue active substances (MBAS) adapted from several different methods [65, 66].

3.1.1 Materials

The sodium dodecyl sulfate used in these experiments was obtained from the Fisher Scientific Company. Experiments were also performed using purified SDS by recrystalization three times in a 50:50 mixture of acetone and ethanol.

Several different types of fabric were used in the experiments for residual moisture testing. The fabrics used were as follows: a Department of Energy (DOE) standard test fabric (a 50/50 blend of polyester and cotton), a 100% cotton Hanes T-shirt fabric and an 86/14 cotton/polyester terry cloth which were supplied by the Procter and Gamble Company.

3.1.2 Residual Moisture Content (RMC) Measurements.

For measuring the residual moisture, each fabric sample was soaked for ten minutes in surfactant solution and then placed in a DuPont Instruments Sorvall RC-5B centrifuge at 1000 RPM (which corresponds to the force of a household washing machine of ~90g) for ten minutes. The experimental apparatus used to hold the fabrics is shown in Figure 3-1. Our setup uses a centrifuge tube with a copper insert that has a closed end with the other end flared so that it will not fall inside the outer tube. The insert also has small holes drilled through it to allow water to
drain through the insert into the collection tube (much like how a modern washing machine is designed).

![Experimental apparatus](image)

**Figure 3-1:** Experimental apparatus used to determine the residual moisture of fabrics.

After the fabric was soaked and centrifuged, the weight was then measured to determine the residual moisture content (RMC) as shown in Equation 3-1.

\[
RMC\% = 100 \times \frac{\text{Weight}_{\text{centrifuged}} - \text{Weight}_{\text{dry}}}{\text{Weight}_{\text{dry}}}
\]

**Eqn. 3-1**

### 3.1.3 Surface Tension Measurements

The equilibrium surface tension measurements were made using the Wilhelmy Plate method. The output from a gram-force sensor holding a platinum plate is sent to a transducer and then output to a voltage readout. The system was calibrated using two known solutions (water and acetone at 72.5 and 23 mN/m respectively). The platinum plate was heated using a flame between each reading to remove surface contamination.

Dynamic surface tension was measured using the maximum bubble pressure technique. The pressure required to form a new bubble in solution is measured by a pressure transducer and the reading is transmitted to an oscilloscope. For these experiments, fabric was soaked in
surfactant solutions for 45 minutes and the dynamic surface tension of the residual solution (in the presence of the fabric) was measured. All dynamic surface tension measurements were taken using an 18 gauge needle tip with a gas flow rate of 7.5 cm$^3$/min (which corresponds to 6-15 bubbles per second or approximately 66 to 166 milliseconds per bubble residence time at the needle tip). We chose this flow rate because at higher flow rates, the nitrogen gas forms a continuous jet in the surfactant solution at the needle tip. At lower flow rates, the results are similar to equilibrium surface tension results.

### 3.1.4 Adsorption Measurements

The actual free concentration of SDS was measured using the MBAS (methylene blue active substance) method. Since this method is accurate in the range of 0-25 μM concentrations of SDS, each sample of SDS that had the cotton fabric soaked in it was diluted by 500 times (i.e. 10 μL in 5 mL of water) and once the concentration was determined we were able to scale back to the original sample size. Using known concentrations of SDS (between 0-8 mM), a calibration curve was measured by dilution and then the revised MBAS method as outlined by Chitikela [66].

### 3.2 Dynamics of Residual SDS Solution and the Effect on RMC

#### 3.2.1 Surface Tensions of Residual Solutions (Dynamic and Equilibrium) and its Correlation to RMC of Fabrics

In our previous work, the residual moisture content has been shown to be a function of surface tension of solution [64]. However, as shown in Figure 3-2, the residual moisture does not completely correlate to the equilibrium surface tension of pure SDS solutions in the range of 5-8 mM. A small dip in the surface tension at ~6 mM SDS concentration suggests that the sample had a small impurity (presumably dodecyl alcohol). Recent work in our laboratory using purified SDS samples have shown the same RMC peak using purified SDS solutions (Figure 3-3).
However, the peak begins to rise at ~5 mM concentrations of SDS with the purified SDS compared to 5.5 mM with the unpurified SDS. There is also no minimum in the purified SDS system compared to the unpurified SDS system which we believe arises from the presence of dodecyl alcohol.

Figure 3-2: RMC of Hanes 100% cotton fabric as a function of SDS concentration plotted with equilibrium surface tension of pure SDS solutions.
Figure 3-3: RMC of Hanes 100% cotton fabric as a function of SDS concentration plotted with equilibrium surface tension of ethanol:acetone purified SDS solutions.

It was shown that the RMC of fabrics did not completely correlate with the equilibrium surface tension of SDS as observed in Figure 3-2 and Figure 3-3. Since it is believed that SDS is adsorbing onto the fabric surface, the equilibrium surface tension of the residual solution should show an increase in the range where SDS is adsorbing onto the fabric. The equilibrium and dynamic surface tensions of residual SDS solution were measured after allowing the fabrics to equilibrate for 45 minutes. The fabrics were soaked in a 20:1 ratio of the weight of fabric to the volume of SDS solution. For each dynamic surface tension measurement, the nitrogen flow rate was held constant at 7.5 cm$^3$/min (approximately 6-15 bubbles per second). It is shown in Figure 3-4 that a small increase was found in the equilibrium surface tension in the concentration range of 5-8 mM. Since there is a small decrease in free monomer in solution due to adsorption onto the fabric, the equilibrium surface tension shows a small increase. It was shown by the dynamic surface tension of the residual SDS solution (Figure 3-4), that the dynamic surface tension
amplifies the small changes seen in the equilibrium surface tension. Since the lowering of surface tension is due to the diffusion of surfactant molecules to the air-liquid interface from the bulk solution (i.e. the lowering of surface tension is a time-dependant process), it is expected that the dynamic surface tension may amplify the changes seen in equilibrium surface tension. As shown in Figure 3-5, the increase in the equilibrium surface tension for the residual SDS solution corresponds with the increase of the RMC of the Hanes fabric presumably due to the adsorption of SDS onto the fabric surface in the range of 5.5 to 6.5 mM SDS concentration.

Figure 3-4: Equilibrium and dynamic surface tension of residual SDS solution after exposure to Hanes fabric.
Figure 3-5: Comparison of the RMC of Hanes fabric and the equilibrium surface tension of residual solution after soaking the fabric.

It has been shown that a peak exists in the RMC curve of Hanes fabric soaked in SDS solutions around approximately 7 mM SDS concentration. This peak has also been observed in the RMC of several other types of test fabrics of varying hydrophobicity as shown in Figure 3-6 (terry cloth and DOE fabrics with 14% polyester and 50% polyester respectively). As the fabric becomes more hydrophobic, the absolute RMC magnitude decreases as well as the magnitude of the RMC peaks as shown in Table 3-1. This decrease in the magnitude of the RMC peak may be due to the mechanism of adsorption onto the fabric surface (i.e. mainly hydrophobic interactions with more hydrophobic fabrics compared to hydrogen bonding with hydrophilic fabrics). The lowering of the RMC may be attributed to the increase in the contact angle of liquid with the fiber surface with more hydrophobic fabrics. During the manufacturing process of fabrics, different chemicals and treatments are used. However, the fabrics that were used in these experiments were thoroughly washed and dried until the surface tension of water after soaking
the fabric remained unchanged from pure water. Thus, adsorbed impurities on the fabric surface cannot account for the observed results.

![Figure 3-6: RMC of Hanes cotton fabric, terry cloth fabric and DOE test fabric as a function of SDS concentration.](image)

Table 3-1: The magnitudes of the RMC peak for various fabrics for I) the absolute different in the maximum and minimum of the RMC peak, II) the difference in the maximum and minimum normalized with respect to the RMC maximum and III) the difference in the maximum and minimum normalized with respect to the RMC minimum.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$RMC_{\text{max}} - RMC_{\text{min}}$</td>
<td>$\frac{RMC_{\text{max}} - RMC_{\text{min}}}{RMC_{\text{max}}}$</td>
<td>$\frac{RMC_{\text{max}} - RMC_{\text{min}}}{RMC_{\text{min}}}$</td>
</tr>
<tr>
<td>Hanes</td>
<td>17.45%</td>
<td>22.72%</td>
<td>29.40%</td>
</tr>
<tr>
<td>Terries</td>
<td>10.23%</td>
<td>16.74%</td>
<td>20.01%</td>
</tr>
<tr>
<td>DOE</td>
<td>4.18%</td>
<td>12.13%</td>
<td>13.89%</td>
</tr>
</tbody>
</table>

We have shown in Figure 3-4 that there is an increase in the dynamic surface tension of the residual solution after the Hanes fabric was soaked. The dynamic surface tension was then measured for the remaining fabrics (DOE and terry cloth). Each fabric was soaked in SDS solutions allowed to equilibrate for 45 minutes. The dynamic surface tension of the residual
solution was then measured (Figure 3-7, Figure 3-8 and Figure 3-9 for the Hanes, DOE and terry cloth fabric respectively). The flow rate was held constant at 7.5 cm³/min (6-15 bubbles per second or approximately 66 to 166 milliseconds per bubble at the needle tip). It is shown in these graphs that a correlation exists between the peaks found in the RMC and the dynamic surface tension of residual solution. Since an increase in surface tension indicates low adsorption of surfactant at the newly created air-liquid interface in the residual solution, the peaks found in the dynamic surface tension measurements are believed to be indicative of decrease in surfactant concentration due to adsorption onto the fabric surface.

Figure 3-7: RMC and DST of the residual solution from the Hanes 100% cotton fabric soaked in SDS solutions.
Figure 3-8: RMC and DST of the residual solution from DOE 50:50 cotton:polyester fabric soaked in SDS solutions.

Figure 3-9: RMC and DST of residual solution from the Terry Cloth 86:14 cotton:polyester fabric soaked in SDS solutions.
An increase in dynamic surface tension is due to the reduced adsorption of surfactant at the air-liquid interface of the new bubble surface created during the measurement. We believe that the decrease in adsorption at the air-liquid interface is due to increased adsorption of SDS on the fabric surface. If there is increased adsorption of SDS onto the fabric surface due to cooperative adsorption, then it is assumed that there would also be a reduction in the free monomer concentration (which has been shown by the increase of equilibrium and dynamic surface tension of residual solution as shown in Figure 3-4).

3.2.2 Molecular Mechanism: Explanation of the Peak in the SDS/RMC Curve

It is shown in Figure 3-10 and Figure 3-11 the 4 regions associated with the increase in residual moisture content and dynamic surface tension. Region A-B is the region of minimal surface adsorption of SDS onto the fabric surface presumably due to a residual negative charge on the fabric surface. The decrease in RMC in this region is due to the increase of free surfactant monomer concentration with low adsorption on the fabric surface. At a concentration of 5.5 mM of SDS, there is a minimum in the RMC and Region B-C begins. This region is due to the sudden increase in adsorption of SDS onto the fabric surface due to a cooperative adsorption phenomenon. Due to electrostatic repulsion between the fabric surface and the SDS monomers, there is a barrier to adsorption. However, once several monomers adsorb onto the fabric surface, it provides a cooperative effect promotes SDS adsorption. This sudden increase in adsorption of the SDS onto the fabric surface reduces the free monomer concentration in the bulk solution thus leading to a reduced amount of free monomer in solution. Hence, less monomer is available to adsorb onto the new air-liquid interface created during the dynamic surface tension measurement which leads to an increased dynamic surface tension. This increase in the dynamic surface tension leads to an increase in the residual moisture. At approximately a concentration of 6.75 mM of SDS, there is a maximum in the RMC where Region B-C ends and Region C-D begins. It
is believed that at this point, complete saturation of the fabric surface by the adsorption of SDS has occurred. Once maximum adsorption has been reached, any additional SDS added into the system will result in an increase in the free monomer concentration. The increased free monomer concentration provides the new air-liquid interface with higher SDS adsorption thus reducing the dynamic surface tension. At approximately 7.5-8.0 mM concentration of SDS, Region C-D ends and Region D-E begins. This region occurs due to the bulk solution reaching the critical micelle concentration (CMC). At this point, the free monomer concentration remains constant. Since the free monomer concentration is now constant, the dynamic surface tension and residual moisture should remain constant as well.

![Graph showing RMC vs SDS concentration](image)

**Figure 3-10:** Indication of the regions associated with the peak in the RMC of Hanes cotton fabric.
Figure 3-11: A-B) High adsorption of surfactant monomer at the air-liquid interface and low adsorption on the fabric-liquid interface resulting in a low dynamic surface tension B-C) Sudden adsorption due to cooperative adsorption on the fabric surface resulting in a decreased monomer concentration in the bulk solution and decreased adsorption at the air-liquid interface C-D) Maximum adsorption is reached at the fabric-liquid interface and increased adsorption is occurring at the air-liquid interface D-E) The CMC is reached and the monomer concentration is stable resulting in a constant dynamic surface tension and RMC.

3.3 Adsorption of SDS onto Cotton Surfaces

It was shown that the RMC of fabrics depends on several different variables such as centrifugation time, centrifugation speed, and surface tension of solution [64]. However, we have observed that the RMC of fabrics does not completely correlate with the reduction of surface tension as predicted by the Laplace equation for capillary rise. We have shown that before the CMC of surfactant solution, there is a sharp peak in the RMC of fabrics as a function of
increasing SDS concentration. It was proposed that this increase in RMC is due to the sudden adsorption of surfactant onto the fabric surface based on secondary data such as the dynamic surface tension of the residual solution after the fabric was soaked [67]. Since it has been shown that cotton has a negative zeta potential one might think that an anionic surfactant would have minimal adsorption on a negatively charged surface [21-23]. However, there have been several papers showing that ability of sodium dodecyl sulfate (SDS) and other anionic surfactants to adsorb onto negatively charged surfaces such as coal fines, cotton and cellulose [21, 24-27]. Also, it has been shown by Somasundaran et al. that adsorption isotherms can show up to four adsorption regions [28], one of them being a sudden increase of adsorption due to cooperative adsorption of surfactant molecules, which may explain the peak found in the RMC curves observed in this study. We have measured the dynamic surface tension of the residual solution after soaking the fabric and we have shown that the increase in RMC does correlate very well with an increase in the dynamic surface tension [67]. Our proposed mechanism indicated that there was a cooperative adsorption of SDS onto the fabric surface thus leading to a decrease in the free monomer concentration. This decrease in the free SDS monomer concentration thus leads to an increase in the dynamic surface tension. If there are less surfactant monomers in the system, there will be less monomer available to adsorb onto a newly created air-water interface (as in the measurement of dynamic surface tension by the maximum bubble pressure technique) which will lead to an increase in the dynamic surface tension.

In these experiments, we have measured the free surfactant monomer concentration by a two phase dye transfer method. This method is commonly used in the determination of anionic surfactants in wastewater. The method that we used was a separation of methylene blue active substances (MBAS) adapted from several different methods [65, 66].
3.3.1 Adsorption Isotherms

We have shown by equilibrium and dynamic surface tension measurements of the residual solution that the fabric samples have soaked in that there is a correlation in the peak found in the RMC as a function of increasing concentration. However, this has been indirect proof suggesting that there is a decrease in the free monomer concentration in the range of the concentrations where the peak exists. Using a two phase dye transfer method (MBAS) we can measure the free monomer concentration of the residual solution after the fabric has soaked in the solution. This measurement will provide a detailed measurement of the actual concentration of SDS left in solution after the adsorption of SDS has occurred onto the fabric surface. If we can show a correlation with the onset of adsorption with the beginning of the RMC peak as well as show a correlation to the fabric surface becoming saturated at the same point at which the RMC peak reaches a maximum, we will have direct proof that surfactant adsorption is the cause of the RMC peak of cotton fabric as a function on increasing SDS concentration.

As shown in Figure 3-12, we have provided a calibration to determine if this method can be applied to diluted SDS solutions in the concentration range that we are interested in. For the concentration range we are interested in, this method appears to be a good selection to determine the free monomer concentration of SDS after the residual solution has equilibrated (after the SDS has adsorbed onto the fabric).
Figure 3-12: Calibration curve for MBAS method in the range of SDS concentrations tested in these experiments.

Now that we have shown the MBAS method can be applied in determining the free concentration of SDS in the bulk solution, we then measured the free concentration of SDS in the residual solution after the SDS adsorption was allowed to equilibrate with the fabric surface. As shown in Figure 3-13, the adsorption of SDS onto the cotton fabric correlated with the peak found in the RMC of cotton as a function on initial SDS concentration. The adsorption begins slightly before the peak starts to increase which we believe is due to impurities in the SDS not adsorbing onto the fabric. These impurities (most likely dodecanol) are available to lower the dynamic surface tension in the bulk solution due to limited adsorption of the dodecanol onto the fabric. Once the fabric has become fully saturated with SDS, the RMC of the cotton fabric begins to decrease. This further strengthens our hypothesis that the peak is due to adsorption of SDS onto the fabric. Once the fabric is saturated, any further SDS added into solution stays in the bulk and thus increases the bulk concentration of SDS. If the bulk concentration of SDS is increased after the point of adsorption saturation on the cotton surface, the dynamic surface tension of the
residual solution then decreases. This maximum in the adsorption isotherm correlates with the peak found in the RMC curve. Once this maximum is reached, the RMC starts to decrease due to the increased amount of SDS in the bulk solution.

![Graph showing adsorption and RMC vs. initial SDS concentration](image)

Figure 3-13: Adsorption of SDS adsorbing onto Hanes cotton fabric. Adsorption was measured from the residual SDS solution after the cotton fabric was soaked for 30 minutes.

We have shown that not only the equilibrium surface tension of solution has an effect on the RMC of fabrics. Therefore, finding a solution with the lowest equilibrium surface tension does not necessarily mean that we have identified a system that will result in the lowest RMC. We have shown that the reduction of RMC has many different aspects. Not only does equilibrium surface tension affects the RMC of fabrics but the dynamic surface tension also plays a very important role on the removal of water from fabrics. We have also recognized that micellar stability plays a very important role in the residual moisture content of fabrics [68]. Therefore, the reduction of RMC is not simply a matter of reducing the surface tension of solution due to the many different aspects of the reduction of RMC.
3.4 RMC Peak in Various Surfactant Systems

3.4.1 Fatty Acids and RMC of Fabrics

We have shown this in fatty acid systems…

Figure 3-14: RMC of Hanes fabric soaked in C8 fatty acid at the first CMC of sodium caprylate (centrifuged for 10 minutes at 1000 RPM).

Figure 3-15: RMC of Hanes fabric soaked in C8 fatty acid at the second CMC of sodium caprylate (centrifuged for 10 minutes at 1000 RPM).
Figure 3-16: RMC of Hanes fabric soaked in C8 fatty acid at the third CMC of sodium caprylate (centrifuged for 10 minutes at 1000 RPM).

Figure 3-17: RMC of Hanes fabric soaked in C10 fatty acid (centrifuged for 10 minutes at 1000 RPM).
3.4.2 Alkyl Quats and RMC of Fabrics

We have shown that in TAB systems....
Figure 3-20: RMC of Hanes fabric in C12TAB solutions (centrifuged for 10 minutes at 1000 RPM).

Figure 3-21: RMC of Hanes fabric in C14TAB solutions (centrifuged for 10 minutes at 1000 RPM).
3.4.3 Technological Impacts (Detergents and Fabric Softeners)

We have shown that this applies in technological systems…

Figure 3-22: RMC of Hanes fabric in C16TAB solutions (centrifuged for 10 minutes at 1000 RPM).

Figure 3-23: RMC of Hanes fabric soaked in solutions of Downy fabric softener (centrifuged for 10 minutes at 1000 RPM).
3.5 Manipulation of RMC Peak

3.5.1 Effect of pH on the RMC of Cotton Fabric

3.5.2 Fabric Pre-Treatment and its Affects on Adsorption of SDS onto Cotton

In order to manipulate the adsorption of SDS onto the fabric, various surfactants and insoluble long chain compounds were coated on the fabric. The fabric was soaked in various solutions of surfactants and polymers which were solubilized in ethanol. The fabric was allowed to equilibrate with the solution for 30 minutes. The fabric was then removed from the solution and allowed to dry. If we can manipulate how much SDS is adsorbed onto the fabric, then the dynamic surface tension of the residual SDS solution can be changed and thus the RMC can be changed. Since we changed from a Hanes tee shirt fabric to the terry cloth fabric, the baseline for the system soaked in increasing amounts of SDS was measured and is shown in Figure 3-25. As shown earlier, the peak in the RMC curve is still present indicating that the SDS is adsorbing on the terry fabric as well.
The first experiments were to soak the fabric in polymers. The fabric was soaked in carboxy methyl cellulose (CMC as shown in Figure 3-26), poly acrylamide (PAA as shown in Figure 3-27) and polyvinylpyrrolidone (PVP as shown in Figure 3-28). It should be pointed out that in each case, the magnitude of the RMC peak is much less compared to the untreated fabric (with the exception of PVP). The adsorption of CMC and PAA both reduced the magnitude of the RMC peak indicating that the amount of SDS adsorbed onto the fabric has been reduced and thus the dynamic surface tension decreases as the concentration of SDS increases.
Figure 3-26: RMC of terry cloth fabric pre-treated with CMC.

Figure 3-27: RMC of terry cloth fabric pre-treated with PAA.
The next set of experiments involved the use of long chain alcohols, fatty acids and insoluble surfactants (C18 fatty acid, C18 alcohol and DODAB). With the use of the octadecanoic acid, the RMC of the terry cloth fabric is a smooth curve and the peak has been almost completely removed (Figure 3-29). When the experiments were repeated with the octadecanol, the RMC peak has been reduced but is still present (Figure 3-30). The last set of experiments involved the fabric being soaked in DODAB. However, the RMC was not reduced near as much with the use of DODAB as compared to the octadecanoic acid (Figure 3-31).
Figure 3-29: RMC of Terry cloth fabric pre-treated with C18 Fatty Acid.

Figure 3-30: RMC of Terry cloth fabric pre-treated with C18OH.
Figure 3-31: RMC of terry cloth fabric pre-treated with DODAB.

It is believed that the adsorption of these various compounds interferes with the adsorption of SDS onto the fabric. In the case of octadecanoic acid, electrostatic repulsion exists which would repel the SDS from adsorbing onto the fabric surface and thus the RMC would then follow the same trend as the equilibrium surface tension. That being said, if one can manipulate the amount of surfactant that is being adsorbed onto the fabric, the RMC can thus be greatly reduced compared to the fabric systems where SDS was allowed to adsorb onto the fabric.
CHAPTER 4
REDISCOVERING MONOLAYER PENETRATION: OBTAINING ULTRA-LOW AIR-LIQUID SURFACE TENSIONS

4.1 Monolayer Penetration

When an insoluble monolayer has a surfactant laden subphase below the monolayer, the surfactant from the subphase can adsorb into the monolayer thus penetrating the monolayer. This adsorption of surfactant penetrating the monolayer thus changes in the surface tension and surface pressure by changing the effective area per molecule in the monolayer (tighter packing in the monolayer results in a decrease in the surface tension). As discussed by Datwani et al., early models for equilibrium monolayer penetration related the surface pressure in the mixed monolayer to the adsorbed amount of the soluble surfactant from the subphase which is a function of the bulk concentration of the surfactant in the subphase [69].

Work has been done by Schulman’s research group which revolutionized the study of monolayers (static monolayers and monolayer penetration). Matalon et al. developed a method in 1949 to measure surface pressures resulting from the interaction of an insoluble monolayer with surfactants adsorbing into the monolayer from the underlying bulk solution [70]. Schulman’s group also researched many other aspects of monolayers and penetration of monolayers such as follows: penetration of monolayers with surfactants [71-73], interactions of monolayers with metal ions [74-76], complex formation and steric effects in monolayers [77, 78], and the ionic structure and the effects of unsaturation on monolayers [79-81].

There has been very many papers published on the various aspects of monolayer penetration such as the effect of charged surfactants penetrating monolayers [69], mathematical evaluations of monolayer penetration [82], the thermodynamics and kinetics monolayer penetration [83-88], and many other papers on monolayer penetration [69, 79, 89-95]. Due to the wide range of papers discussing monolayer penetration, the mathematics governing penetration
will not be discussed. However, based on the similarity of dioctadecyldimethylammonium bromide (DODAB) to the active surfactant in many commercially available fabric softeners [96-98], we chose to use DODAB as the insoluble surfactant to be used in the insoluble monolayer. Several different surfactants, sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate (C$_{14}$SO$_4$), were chosen to use as the penetrating surfactant based on their similarities to the active surfactants in detergents.

We have shown that with the use of monolayer penetration that we can now lower the equilibrium surface tension to values lower than previously achieved with silicone super wetters (lower than 19 mN/m). We have also shown that the ability to lower the surface to low values and maintain that low value depends on the type of insoluble monolayer we spread. When an ionic monolayer is used and penetrated with an oppositely charged surfactant from the subphase, we have shown that this type of system is more effective in lowering surface tension compared to the use of penetrating a nonionic monolayer with an ionic surfactant from the subphase. We believe that this is due to electrostatic attraction between the charged monolayer and the oppositely charged surfactant from the subphase. Another aspect we investigated in monolayer penetration is the use of a mixed monolayer (a mixture of the insoluble surfactant with the penetrating surfactant in the subphase). We have found that the mixed monolayer penetrated with the soluble component of the mixed monolayer provided excellent results in the ability to lower surface tension (to values less than 10 mN/m).

From our previous work, we have shown that there is a correlation between equilibrium surface tension and the residual moisture content (RMC) of fabrics [64, 67]. We have shown that the lower the surface tension the more water can be shed from fabrics during the centrifugation process. Based on this work, we are now trying to reach air-liquid surface tension values of
lower than 10 mN/m using monolayer penetration. Using monolayer penetration, we have been able to measure air-liquid surface tension values as low as 8.5 mN/m and we have determined a method to use monolayer penetration in the reduction of RMC of fabrics.

4.1.1 Experimental Procedure

4.1.1-1 Monolayer Penetration Studies

As discussed by Welzel et al., there are two methods to study monolayer penetration: 1) the penetrant is injected beneath the already spread monolayer and 2) the monolayer film is spread onto the penetrating solution [90]. In these studies, we have used both methods to measure the effects of monolayer penetration. The first method was used in the small scale surface tension measurements and the second method was used in the full scale washing machine experiments.

Penetration studies were done by solubilizing the insoluble monolayer in a mixture of 1:1:3 volume mixture of methanol, chloroform and hexane in a total concentration of 0.5 wt%. The solubilized solution was then 5 μL of this monolayer solution was placed onto the surface of a Petri dish filled with 5 mL of water using a microsyringe (see Figure 4-32). The penetrating surfactant solutions in various concentrations were then injected beneath the monolayer in different volumetric amounts. Meanwhile, the surface tension was monitored using the Wilhelmy plate method. However, unlike previous surface tension methods, the output from the voltage sensor from the Wilhelmy plate was input to a computer using a WinDAQ MODEL. Using this method, the surface tension can be measured as a function of time while the monolayer is being penetrated with the surfactant from the subphase.
Figure 4-32: Diagram demonstrating the spreading and penetration of an insoluble monolayer.

For the washer scale tests, ethanol was used to solubilize the monolayer instead of the methanol, hexane and chloroform solvent due to ethanol being more environmentally friendly and the ethanol is not as corrosive to the washing machine components compared to the other solvent. Also, the penetrating surfactant was already present in the fabric before the monolayer was spread on the fabric due to the difficulty in injecting the subphase surfactant beneath the monolayer in full scale testing (see Figure 4-).

4.1.1-2 Surface Tension Measurement in Monolayer Penetration

The equilibrium surface tension measurements were made using the Wilhelmy Plate method. The output from a gram-force sensor holding a platinum plate is sent to a transducer and then output to a voltage readout. This voltage readout was captured using a computer with a WinDAQ MODEL. The system was calibrated using two known solutions (water and acetone at 72.5 and 23 mN/m respectively). The platinum plate was heated using a flame between each reading to remove surface contamination.
4.1.2 Reduction of Surface Tension – Monolayer Penetration Results

4.1.2-1 Pure Insoluble Monolayers

We first experimented with spreading a monolayer of C\textsubscript{16}TAB dissolved in the universal solvent (1:1:3 volume mixture of methanol, chloroform and hexane) on the Petri dish filled with water. Once the solvent was allowed to evaporate, we began to monitor the surface tension. We then injected solutions of 4 mM C\textsubscript{14}SO\textsubscript{4} beneath the monolayer and continued to measure the surface tension. As shown in Figure 4-2, the surface tension reaches a minimum immediately after the penetrating surfactant solution was injected. Depending on the amount of penetrant injected into the Petri dish, the surface tension stays a low value and then jumps up to higher values (which are a lower value than the surface tension of the pure monolayer). We also repeated the same experiment using stearic acid as the insoluble monolayer penetrated with a subphase surfactant of an opposite charge compared to the stearic acid (C\textsubscript{14}TAB was used at a cationic penetrant). As shown in Figure 4-3, we show the same trend in surface tension as shown in the other monolayer penetration experiments. Immediately after the penetrating surfactant is injected into the system, the equilibrium surface tension drops to a minimum value and then slowly increases to another equilibrium value. When then repeated the same experiment with DDAB as the monolayer with C\textsubscript{14}SO\textsubscript{4} as the penetrating surfactant. As shown in Figure 4-4, the equilibrium surface tension follows the same trend as the C\textsubscript{16}TAB monolayer system. The surface tension goes to a minimum value and then increases. We have called this a transient monolayer and we believe that this phenomenon is due to the solubilization of the monolayer after the penetrating surfactant has penetrated the monolayer. Both C\textsubscript{16}TAB and DDAB have slight solubility in water and with the addition of C\textsubscript{14}SO\textsubscript{4}, we believe that the penetrating surfactant helps solubilize small amounts of the monolayer into the solution and thus increasing the equilibrium surface tension. The low surface tension values are due to the super-saturation of
the air-liquid interface due to the Coulombic interaction between the cationic monolayer and the anionic penetrating surfactant. Then, as shown in Figure 4-5, the monolayer which has been penetrated with the $C_{14}SO_4$ starts to solubilize and dissolves into the solution thus leaving the interface less tightly packed and increasing the equilibrium surface tension.

Figure 4-2: Equilibrium surface tension of a $C_{16}$TAB monolayer penetrated with 4 mM $C_{14}SO_4$. 
Figure 4-3: Equilibrium surface tension of a stearic acid monolayer penetrated with 4 mM C\textsubscript{14}TAB.

Figure 4-4: Equilibrium surface tension of a DDAB monolayer penetrated with 4 mM C\textsubscript{14}SO\textsubscript{4}.
Figure 4-5: Molecular diagram of the transient monolayer phenomena found in slightly soluble monolayers penetrated with a soluble surfactant from the subphase.

Using the monolayer penetration method in these preliminary experiments, we obtained equilibrium surface tension values at the air-liquid interface of ~ 17 mN/m. Previously, values as low as ~18-19 mN/m at the air-liquid interface have been obtained using conventional surfactants.

After we ran the preliminary monolayer penetration studies, we then looked into using a monolayer composed of longer chain surfactants and alcohols that are insoluble in water and would theoretically not exhibit the transient monolayer phenomenon that we observed with slightly soluble monolayers. We first looked at DODAB (the C\textsubscript{18} version of the DDAB used in previous experiments) penetrated with C\textsubscript{14}SO\textsubscript{4}. As shown in Figure 4-6, the equilibrium surface tension of a DODAB monolayer penetrated with C\textsubscript{14}SO\textsubscript{4} reaches a minimum value of approximately 15 mN/m. This value is lower than values obtained at the air-liquid interface for other methods (18-19 mN/m for fluoro-surfactants and siloxanes).
We then chose to use cholesterol and C20OH as the insoluble monolayer and we continued to use C14SO4 to penetrate the monolayer. As shown in Figure 4-7, the surface tension of a C20OH monolayer penetrated with C14SO4 is shown to decrease to a value of about 25 mN/m. However, we were still attempting to achieve surface tensions of much lower values (less than 10 mN/m). We then used cholesterol as the insoluble monolayer penetrated with C14SO4. However, the surface tension was only reduced to about 20 mN/m in this system (Figure 4-8).
Figure 4-7: Equilibrium surface tension of a C_{20}OH monolayer penetrated with 4 mM C_{14}SO_4.

Figure 4-8: Equilibrium surface tension of a Cholesterol monolayer penetrated with 4 mM C_{14}SO_4.

4.1.2-2 Mixed Monolayer Penetration

Using a pure monolayer of DODAB penetrated with 1 mL of 4 mM C_{14}SO_4, a surface tension of 13.5 mN/m was achieved for an indefinite amount of time. It was thought that if a mixed monolayer was formed that tighter packing would be present in the monolayer due to
electrostatic interactions between the headgroups. The system that was investigated was the tetradecyl sodium sulfate (C\textsubscript{14}SO\textsubscript{4}) with dioctyldecyl dimethylammonium bromide (DODAB). Ratios of 1:10, 1:5, 1:3, and 1:2 of the C\textsubscript{14}SO\textsubscript{4}:DODAB were investigated.

The first systems tested were the monolayer compositions that were higher in DODAB concentration (the 1:10, 1:5, 1:3 and 1:2 ratios of C\textsubscript{14}SO\textsubscript{4}:DODAB). As shown in Figure 4-10, the 1:10 ratio of C\textsubscript{14}SO\textsubscript{4}:DODAB monolayer with C\textsubscript{14}SO\textsubscript{4} injected beneath the monolayer resulted in a surface tension as low as 19 mN/m. Increasing the C\textsubscript{14}SO\textsubscript{4} amount to a ratio of 1:5, the surface tension dropped to approximately 8.5 mN/m with 1000 μL of C\textsubscript{14}SO\textsubscript{4} injected beneath the monolayer (Figure 4-9). Since it has been well documented that tightest packing occurs at a 1:3 ratio, the surface tension of a monolayer at this ratio was measured. However, the minimal surface tension for the 1:3 system was not as low as the 1:5 ratio monolayer. It is believed that this is due to molecular packing trying to achieve the 1:3 ratio. At a lower ratio of C\textsubscript{14}SO\textsubscript{4}:DODAB (the 1:5 system), there is somewhat tight packing. This packing can be optimized by the addition of more C\textsubscript{14}SO\textsubscript{4} beneath the monolayer. The addition of the 4 mM C\textsubscript{14}SO\textsubscript{4} results in what we believe is a 1:3 ratio of C\textsubscript{14}SO\textsubscript{4}:DODAB in the monolayer after this addition of C\textsubscript{14}SO\textsubscript{4} beneath the monolayer. However, when the monolayer is already at its tightest packing at a 1:3 ratio of C\textsubscript{14}SO\textsubscript{4}:DODAB, there is not sufficient room for more C\textsubscript{14}SO\textsubscript{4} to penetrate the monolayer resulting in a higher surface tension than the previous system. When higher ratios (1:2) of C\textsubscript{14}SO\textsubscript{4}:DODAB were tested, there was no monolayer present after spreading with universal solvent. Since the C\textsubscript{14}SO\textsubscript{4} is soluble in water, once the monolayer is spread it is being solubilized into solution due to the increased amount of C\textsubscript{14}SO\textsubscript{4} resulting in a higher surface tension (approximately the surface tension of water) that reduces with the addition of C\textsubscript{14}SO\textsubscript{4}.
Figure 4-9: Equilibrium surface tension of a mixed monolayer composed of a 1:5 ratio of C\textsubscript{14}SO\textsubscript{4} to DODAB penetrated with 4 mM solutions of C\textsubscript{14}SO\textsubscript{4}.

Figure 4-10: Equilibrium surface tension of mixed monolayers of various ratios of C\textsubscript{14}SO\textsubscript{4} to DODAB penetrated with 1000 \textmu L of 4 mM solutions of C\textsubscript{14}SO\textsubscript{4}.
4.2 Reduction of RMC via Monolayer Penetration

4.2.1 Experimental Procedure

4.2.1-1 Washer Scale RMC Procedure

Large scale tests were done in a Whirlpool washing machine. Using a strobe-scope, we measured the RPM of the washing machine spin cycle to be 640 RPM or about 90 g’s which is
comparable to the force we tested in the small scale centrifuge. However, the centrifugation time in the washing machine is 6 minutes compared to 10 minutes in the small scale testing. As shown in Figure 4-13, the method we used to test the RMC in the washing machine is as follows: 1) the fabric is soaked in the penetrating surfactant subphase solution, 2) the fabric is placed in the washing machine and the spin cycle is started, 3) once the spin cycle reaches speed, the penetrating solution is poured onto the fabric and the washing machine is allowed to complete the spin cycle.

**Figure 4-13:** A) Fabric soaked in penetrating subphase solution is placed in the washing machine, B) The spin cycle is started and allowed to come to full speed, C) Monolayer solution is poured over the fabric and the spin cycle is allowed to complete and the RMC is measured.

### 4.2.2 Small Scale Monolayer Penetration Results

Several experiments were ran in the lab scale to determine the effectiveness of monolayer penetration in the reduction of RMC. The first experiments were run to determine the baseline of the system. In Table 4-1, the RMC from pure water to 4 mM C$_{14}$SO$_4$ solutions reduced from 82% to 60%. The next experiments were to determine how effective monolayer penetration would be to lower the RMC. The first monolayer penetration experiment was performed by soaking the fabric in 4 mM C$_{14}$SO$_4$ and then spraying the fabric once (with ~2 mL) of the 1:5
C_{14}SO_4:DODAB monolayer solution solubilized in ethanol. The resulting RMC was reduced to 60.7%. However, due to the large amount of bulk solution in the fabric, the RMC wasn’t reduced as much as expected based on the surface tension of that monolayer study. The next experiment was to soak the fabric in the 4 mM C_{14}SO_4 and then centrifuge the sample for 5 minutes to remove most of the bulk water. The fabric was then taken out of the centrifuge and then sprayed with 2 mL of the 1:5 monolayer solution solubilized in ethanol. The resulting RMC was 55% which is comparable to the results from the silicone super wetter (50%) or about a 27% reduction in the RMC from that of pure water.

Table 4-1: RMC of small scale monolayer penetration with C_{14}SO_4:DODAB monolayer.

<table>
<thead>
<tr>
<th></th>
<th>RMC</th>
<th>Abs Change</th>
<th>Rel. Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Water</td>
<td>82.10%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>C_{14}SO_4</td>
<td>60.77%</td>
<td>-21.33%</td>
<td>-25.98%</td>
</tr>
<tr>
<td>C_{14}SO_4 sprayed once with 1:5 C_{14}SO_4:DODAB</td>
<td>60.68%</td>
<td>-21.42%</td>
<td>-26.09%</td>
</tr>
<tr>
<td>C_{14}SO_4 centrifuged for 5 minutes, sprayed with 1:5 C_{14}SO_4:DODAB and centrifuged for 5 more minutes</td>
<td>55.10%</td>
<td>-27.00%</td>
<td>-32.89%</td>
</tr>
<tr>
<td>1 wt% Dow Q2-52-211</td>
<td>50.30%</td>
<td>-31.80%</td>
<td>-38.73%</td>
</tr>
</tbody>
</table>

4.2.3 Washer Scale Monolayer Penetration Results

After showing that monolayer penetration was promising in the reduction of RMC in fabric, we then expanded the experiments into full washing machine scale. The fabric was first soaked in SDS solutions (due to the expense of C_{14}SO_4) and the 1:5 SDS and DODAB monolayer was solubilized in ethanol. The fabric was placed in the washing machine and the spin cycle was started. Once the washing machine reached full speed in the spin cycle, 100 mL of the monolayer penetration solution was poured onto the fabric during the centrifugation process. Once the spin cycle finished, the RMC was determined after weighing the fabric.

In Figure 4-14, we compared the effectiveness of changed the penetrant to SDS as well as changing the monolayer to SDS and DODAB from C_{14}SO_4. As shown in Figure 4-14, the RMC
was reduced to ~68% for both monolayer penetration systems. We then performed the same experiments to determine if the RMC followed the surface tension trend which was observed in the surface tension studies of the mixed monolayers. As shown in Figure 4-15, the RMC of the terry fabrics closely followed the surface tension trend from the 1:10 ratio to the 1:3 ratio of SDS to DODAB with the 1:5 ratio showing the minimum in RMC (and surface tension). This method may prove very valuable in the reduction of RMC and energy in laundry systems.
Figure 4-14: Comparison of RMC values for full scale washing machine experiments (150 ppm of detergent is the standard of comparison) showing the reduction in RMC using monolayer penetration (red bars).

Figure 4-15: Comparison of RMC values for full scale washing machine experiments (150 ppm of detergent is the standard of comparison) showing the reduction in RMC using monolayer penetration (red bars).
CHAPTER 5
MICELLE STABILITY AND ITS AFFECT ON THE RESIDUAL MOISTURE CONTENT OF FABRICS

5.1 Stabilization of Micelles

It has been shown earlier that micellar stability depends on surfactant concentration. The Shah Research group has shown that the micellar stability depends on surfactant concentration. It has been shown that a maximum micellar stability for SDS solutions exists at 200 mM due to the small intermicellar distance, resulting in a strong repulsion between the micelles [5, 7-11]. Therefore, the micelles become more rigid as the surfactant concentration increases. This maximum in micellar relaxation time has a dramatic effect on many different properties of SDS solutions (ranging from low foamability, high thin film stability, wetting time, oil solubilization, etc.). The Shah Research group has also shown that micellar kinetics play an important role in detergency. Shah et al. has shown that the efficacy of removing non-polar compounds from fabrics has been shown to have a strong correlation with the relaxation time of micelles [7-12]. For example, it was shown by Oh and Shah that using 200 mM SDS (which was shown to have the longest micellar relaxation time in the SDS concentration range [8]) provided the most efficient removal of an artificial stain created by the deposition of Orange OT onto fabric samples [11].

However, the micellar stability can also be influenced by the addition of an alcohol [99]. It has been shown that the maximum micellar stability for SDS/alcohol mixtures exists for the system SDS/C12OH, where the chain lengths of the surfactant and the alcohol are the same and thus where the van der Waals interaction between the hydrophobic tails is maximum (hydrophobic-hydrophobic interactions between the tail groups) [100-103].
In this study, we have found that at a concentration of 200 mM of SDS, there is a peak found in the residual moisture content (RMC) of fabrics. As shown by Patist et al. [7], we believe that this correlates to the wetting time of fabrics and is due to the increase in dynamic surface tension resulting from high micelle stability. We have shown that not only the equilibrium surface tension plays a role in the removal of water from fabrics in that the availability of monomer to adsorb onto the air-liquid interface plays a role as well [104]. For systems with high micellar stability, the monomer flux to the air-liquid interface will be less than a system with low micelle stability due to higher availability of surfactant monomers which would lead to a higher dynamic surface tension. At the 200 mM concentration of SDS, there is a maximum in micelle stability which would account for less monomer flux and less monomer to adsorb on the new air-liquid interface of bubbles created during the dynamic surface tension measurement. This would thus lead to an increased dynamic surface tension that should correspond to the increase in RMC in the same surfactant concentration range.

There has been a lot of work from the Shah Research Group showing that the micellar stability of various surfactant systems can be significantly influenced by the addition of co-surfactants[7-9, 55, 58, 103, 105-108]. The increase in micellar stability of mixed surfactant systems is due to synergism shown between oppositely charged headgroups or hydrophobic-hydrophobic interactions between the surfactant tail groups (as shown with a non-ionic co-surfactant). Due to coulombic or hydrophobic interactions, the stability of mixed surfactant systems can be tailored to varying degrees of stability.

It is typically generalized that micelles are often drawn as static structures of spherical nature composed surfactant molecules with polar head groups exposed to the aqueous solution protecting the hydrophobic tails of the surfactant in the micelle core. However, micelles are in
dynamic equilibrium with individual surfactant molecule monomers that are constantly being exchanged between the bulk surfactant solution and the micelles. Additionally, the micelles themselves are continuously disintegrating and re-forming. The kinetics of this process has been evaluated by Aniansson [109-111], and the relevance of micellar relaxation time to various technological processes for single surfactant systems such as sodium dodecyl sulfate (SDS) in water has been extensively studied by Shah and co-workers [112]. The kinetics of micellization has been studied by various techniques such as stopped flow [113], temperature jump [114], pressure jump [115] and ultrasonic absorption [116, 117].

Based on previous RMC work pertaining to the adsorption of SDS onto Hanes fabric, we have shown that an increase in the dynamic surface tension (or a decrease in the free surfactant monomer content in the bulk solution) leads to an increase in the RMC of fabric. This work has continued on to show that phenomena in the bulk surfactant solution that can alter the available free surfactant monomer concentration (i.e. anything that can change the dynamic surface tension of the bulk solution) can influence the RMC of fabric at the end of a laundry spin cycle. Surfactant systems that have a long micellar relaxation time (i.e. micellar systems that are very stable) have been shown to have a high dynamic surface tension and thus a higher RMC. The increase in RMC with stable micellar systems is because micelles must be broken down into monomers to be available to adsorb onto the newly created air-liquid interface and thus reduce the dynamic surface tension (and RMC) [118]. If the micelles are stable, the monomer flux from the micelle is very low and the dynamic surface tension is high resulting in an increase in RMC.

5.1.1 Concentration Dependence on Micelle Stability – 200 mM SDS

In our previous work, the residual moisture content has been shown to be a function of surface tension of solution [64]. However, as shown in Figure 5-1, the residual moisture does not completely correlate to the equilibrium surface tension of pure SDS solutions in the range of 5-8
mM. A small dip in the surface tension at ~6 mM SDS concentration suggests that the sample had a small impurity (presumably dodecyl alcohol). Recent experiments in our laboratory using purified SDS samples have shown the same RMC peak. Due to adsorption of SDS onto the fabric surface, the dynamic surface tension of the residual solution increased thus leading to an increase in the RMC (Figure 5-2).

Figure 5-1: RMC of Hanes 100% cotton fabric as a function of SDS concentration plotted with equilibrium surface tension of pure SDS solutions.
Figure 5-2: RMC and DST of the residual solution from the Hanes 100% cotton fabric soaked in SDS solutions.

We have shown over the past years that stable micelles greatly affect many difference aspects of surfactant systems. For the SDS system at 200 mM (most stable micelles for SDS), we have shown that there is a large increase in bubble volume, single film stability, detergency effectiveness, emulsion droplet size, benzene solubilization etc (Figure 5-3 and Figure 5-4). It has also been shown with there SDS solutions that at 200 mM that there is a decrease in foamability and time to solubilize benzene in solution (Figure 5-3 and Figure 5-4).
Since the relaxation time of surfactants play such a large role in many different properties of surfactant systems, the RMC of Hanes fabric around the concentration range of highest SDS micellar stability was measured (from 125-250 mM concentrations of SDS). Since the dynamic surface tension is related to the micellar stability (i.e. higher micellar stability leads to higher...
dynamic surface tension as shown in Figure 5-7), it would be expected that there will be an increase in the RMC around a SDS concentration of 200 mM. In Figure 5-, we have shown that at 200 mM concentration of SDS that there is peak shown in the RMC of Hanes fabric. This peak is believed to be due to the long relaxation time of the SDS micelles at 200 mM. The long relaxation time of the micelles would lead to a decreased monomer flux from the micelles to the bulk. Since the micellar stability is high for 200 mM SDS, there is less free monomer flux from the micelle to the bulk solution thus causing an increase in the DST. This decrease in monomer flux would then be shown as an increase in the dynamic surface tension this leading to an increase in the RMC. Alternatively, another possible explanation to explain the increase in RMC at 200 mM concentrations of SDS could be due to stabilization of thin films on the fabric surface as well as films in the interfiber spaces due to relatively stable micelles as demonstrated in Figure 5-6. It has been shown by Shah et al. [13, 14] and Wasan et al. [15-20] that layering of micelles or particles can stabilize thin films (which could possibly explain an increase in the RMC). However, it is a possibility that the increase in RMC at 200 mM SDS is due to a combined effect of thin film stability due to layering of micelles as well as the increase in dynamic surface tension from the reduction in monomer flux from the stable micelles.
Figure 5-5: RMC of Hanes fabric around the concentration range of most stable micelles of SDS (200 mM) (i.e. stable micelles can increase the RMC from ~68% to ~76% in SDS solutions).

Figure 5-6: Graphic representation of stable micelles trapped in the interstitial space in between fiber strands. Stable micelles could help stabilize the thin liquid film in this interstitial space leading to an increase in RMC.
5.1.2 Mixed Surfactant Systems

It has been well documented by the Shah Research group that the stability of SDS micelles can be greatly influence by the addition of co-surfactants. For this study, we chose to add C12TAB and C12OH to the SDS solutions in order to increase the stability of the mixed micellar system compared to the stability of the pure SDS system. As shown in Table 5-1, the micellar relaxation times of the systems we chose to test show an increase in micellar relaxation time from ~1 ms to as high as 2,000 ms. Based on our results for the 200 mM SDS system (highest stability over the entire SDS concentration range), we would expect that the RMC of the cotton fabric will show the same trend as the increase in micellar relaxation time shown in Table 5-1.

Table 5-1: Micellar relaxation times ($\tau_2$) for different SDS systems with the addition of co-surfactants [55, 106-108].

<table>
<thead>
<tr>
<th>System</th>
<th>Micelle Stability $\tau_2$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 mM SDS</td>
<td>100</td>
</tr>
<tr>
<td>100 mM SDS + 10 mM C12OH</td>
<td>900</td>
</tr>
<tr>
<td>100 mM SDS + 10 mM C12TAB</td>
<td>2000</td>
</tr>
</tbody>
</table>

As shown in Figure 5-8, we have shown that there is an increase in RMC from the pure SDS system to the mixed system of SDS and C12TAB. The RMC increased from the pure system to the addition of C12OH and then further increased with the SDS and C12TAB system (RMC of
The increase in micellar relaxation time for the SDS and C12OH system arises from the strong ion-dipole interaction between the SDS and the dodecanol. The large increase in relaxation time with the addition of C12TAB to the SDS results from the strong electrostatic (anion-cation) interactions between the head groups of the surfactants resulting in a very tightly packed interface (at the air-liquid and micellar interfaces). These increases in relaxation times also result in an increase in the dynamic surface tension of each solution. Very stable micelles have little monomer flux to the bulk solution and thus for any new air-liquid interface created, there is a small amount of free monomer available to adsorb at the new interface to lower the dynamic surface tension. As we have previously discussed, an increase in the dynamic surface tension will then cause an increase in the RMC of fabrics.

![Figure 5-8: RMC of Hanes cotton fabric for pure SDS and mixed SDS systems (with the addition of either C12OH or C12TAB).](image)

We have shown that many different factors affect the RMC of fabric/surfactant systems. It was shown that adsorption phenomena play an important factor in laundry processes. It should
also be noted that the dynamic surface tension has been shown to play a large role in the manipulation of the RMC of fabrics. Based on the results that have been presented, if the magnitude of adsorption of surfactant onto the fabric or if the micellar kinetics of the surfactant system used can be significantly changed, the magnitude of the RMC can thus be significantly altered (i.e. increased relaxation times for increased RMC or decreased relaxation times for lower RMC).

5.2 Effect of Dodecyl Sulfate Counterions on the RMC of Fabrics

Based on previous RMC work pertaining to the adsorption of SDS onto Hanes fabric, we have shown that an increase in the dynamic surface tension (or a decrease in the free surfactant monomer content in the bulk solution) leads to an increase in the RMC of fabric. This work has continued to show that phenomena in the bulk surfactant solution that can alter the available free surfactant monomer concentration (i.e. anything that can change the dynamic surface tension of the bulk solution) can influence the RMC of fabric at the end of a laundry spin cycle. Surfactant systems that have a long micellar relaxation time (i.e. micellar systems that are very stable) have been shown to have a high dynamic surface tension and thus a higher RMC. The increase in RMC with stable micellar systems is because micelles must be broken down into monomers to be available to adsorb onto the newly created air-liquid interface and thus reduce the dynamic surface tension (and RMC) [118]. If the micelles are stable, the monomer flux from the micelle is very low and the dynamic surface tension is high resulting in an increase in RMC.

For the purpose of the work shown in this article, we have investigated the effects of different counterions for the dodecyl sulfate surfactant. The substitution of one kind of counterion with another counterion has the potential to alter the interactions between both the counterions and the surface-active molecules. By changing the degree of binding of counterions to the surface-active portions of the surfactant molecule can greatly influence the surface active
chemical properties of the surfactant [119]. One key aspect of the solution that is significantly influenced by a change in the counterion is the equilibrium surface tension [32]. In terms of affecting the CMC of the dodecyl sulfate surfactants, the CMCs of LiDS, NaDS, CsDS, and Mg(DS)₂ are reported by Mukerjee (MUKURJEE REFERENCE) to be 8.92, 8.32, 6.09, 0.88 mM, respectively, at 25°C.

5.2.1 Experimental procedure (Surfactant Synthesis)

Lithium dodecyl sulfate (99% purity) is purchased from Acros (Orlando, FL), sodium dodecyl sulfate (99% purity) from MP Biomedicals, Inc. Magnesium dodecyl sulfate (98% purity) from Pfaltz and Bauer (Waterbury, CT). Cesium dodecyl sulfate is prepared in our laboratory with the same procedure as shown by Kim et al. [119]. Chlorosulfonic acid (Aldrich, Milwaukee, WI, 553.5 mM) is added to dodecanol drop by drop with vigorous mixing at 25 °C under a nitrogen atmosphere. The sulfation reaction is performed very slowly (40 min and cooled with ice) since the sulfation process is highly exothermic. After the sulfation process, nitrogen gas is used to purge the reaction mixture to remove HCl produced during the reaction. Aqueous CsOH solution (Aldrich, 50.0 wt%) is added to the reaction mixture in a 1:1 molar ratio to neutralize the acid. The CsDS is recrystallized three times with a 50:50 mixture (by volume) of ethanol and acetone, keeping the solution below 5°C.

5.2.2 Molecular mechanisms

Figure 5-9 shows the equilibrium surface tension values for the dodecyl sulfate surfactants (with Li, Na, Cs and Mg counterions) at both 1 mM and 50 mM molecular concentrations of surfactants. It is well known that the lowering of surface tension is due to efficient molecular packing at the air-liquid interface (tighter packing results in lower surface tension). As shown in Table 5-2, we have indicated the Ionic Radius (Å), Hydrate Radius (Å), Area per Molecule
(Å²/molecule) and the dimensionless dynamic surface tension (θ, as indicated in Equation 5-1). With tighter molecular packing (as shown in Figure 5-10), lower surface tensions can be obtained.

\[
\theta = \frac{\gamma_d - \gamma_{eq}}{\gamma_w - \gamma_{eq}}
\]

Eqn. 5-1

The dimensionless dynamic surface tension (Equation 5-1) is used to show the importance of micellar break up in the measurement of dynamic surface tension where \( \gamma_d \) is the dynamic surface tension, \( \gamma_{eq} \) is the equilibrium surface tension (as measured by the Wilhelmy plate method) and \( \gamma_w \) is the surface tension of pure water [32]. The value of \( \theta = 0 \) (or \( \gamma_d = \gamma_{eq} \)) indicates that the surfactant adsorption under dynamic condition is the same as that under equilibrium conditions and the micelles are labile as well as the monomers are diffusing fast, whereas \( \theta = 1 \) (\( \gamma_d = \gamma_w \)) indicates no surfactant is present at the interface under the dynamic conditions existing during the bubbling process implying either the presence of relatively stable micelles or monomers with high characteristic diffusion time.
Figure 5-9: Equilibrium surface tension for dodecyl sulfate surfactants with various counterions for 1 mM and 50 mM concentrations.

Table 5-2: Physical properties and dimensionless dynamic surface tension ($\theta$) of different counterions of dodecyl sulfate [32].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic Radius (Å)</th>
<th>Hydrated Radius (Å)</th>
<th>Area per Molecule ($\text{Å}^2$/molecule)</th>
<th>$\theta$ Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>0.60</td>
<td>3.82</td>
<td>61.0</td>
<td>0.138</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.94</td>
<td>3.58</td>
<td>51.5</td>
<td>0.131</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>1.69</td>
<td>3.29</td>
<td>44.5</td>
<td>0.202</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.65</td>
<td>4.28</td>
<td>38.7</td>
<td>0.353</td>
</tr>
</tbody>
</table>
Figure 5-10: Effect of counterions on the molecular packing of dodecyl sulfate at the air/liquid interface. Area per molecule (Am) is in the following order for the chosen counterions: $A_m^{Li^+} > A_m^{Na^+} > A_m^{Cs^+} > A_m^{Mg^{++}}$ [32].

Figure 5-11: Foam stability for various dodecyl sulfate counterions at 50 mM total surfactant concentration [32].

Previous work on foam studies by Pandey et al. has shown that at 50 mM concentrations of the dodecyl sulfate surfactants using Li$^+$, Na$^+$, Cs$^+$, and Mg$^{++}$, the foam is most stable using Mg(DS)$_2$ as shown in Figure 5-11 [32]. However, we have shown mixed RMC results with the use of various counterions and cotton fabric. The RMC was measured at 1 mM total surfactant
concentration and as shown in Figure 5-12, the RMC decreases in order of decreasing equilibrium surface tension. Since we are below the CMC of the surfactants (or right at the CMC in the case of Mg(DS)$_2$), micellar kinetics do not play a role in the removal of water from fabrics. However, as shown in Figure 5-13, we have measured the RMC of Hanes cotton fabric at 50 mM total surfactant concentration (which is well above the CMC for each surfactant system) and we have shown that the RMC increases in order of increasing micellar relaxation time, $\tau_2$.

![Figure 5-12: RMC of Hanes cotton fabric for various dodecyl sulfate counterions at 1 mM total surfactant concentration.](image)

Figure 5-12: RMC of Hanes cotton fabric for various dodecyl sulfate counterions at 1 mM total surfactant concentration.
We have already shown that the RMC of fabrics is a function of equilibrium and dynamic surface tension [64, 67, 120]. We have recently shown that the stability of micelles also plays a very important role in the removal of water from laundry [121]. From the data shown here along with the work done on adsorption of SDS onto the fabric surface (causing an increase in the dynamic surface tension [67]), we have identified micellar kinetics to be a very important parameter in the reduction of RMC from fabrics. Micellar kinetics has a huge potential to save millions if not billions of dollars per year (in the US alone) in consumer drying costs. There is a huge potential to save even more money with this information extrapolated into industrial applications.

5.3 Chain Length Compatibility

Sdfsdf

5.3.1 Review of Chain Length Compatibility Work

The Shah Group has shown that chain length compatibility is an important factor in many mixed surfactant systems [55, 103, 106, 107, 122]. As surfactant molecules (or other
hydrocarbon molecules in mixed systems) adsorb at interfaces, the molecular packing at the
interface is influenced by the matching or mismatching of the alkyl chains of the surfactants and
cosurfactants adsorbing at the interface. In general, the chain length of surfactants used in a
given mixture must be the same to maximize lateral molecular interactions. It has been reported
[123] that as the difference in chain lengths of mixed surfactants increases, the spacing between
the adjacent surfactant molecule increases. Although these changes are very small, they have a
very large effect upon the interfacial and bulk properties of the solutions, e.g., foamability, foam
stability, surface tension, surface viscosity, contact angle, bubble size, fluid displacement in
porous media, and microemulsion stability [34, 123-126]. The effect of chain length
compatibility is particularly important to interfacial properties and technologies, such as surface
tension, surface viscosity, foamability, lubrication, contact angle, bubble size, environmental
remediation, enhanced oil recovery, water solubilization in microemulsions, and microemulsion
stability [5, 103, 123].

5.3.2 SDS + Long Chain Alcohols (CₙOH)

The residual moisture content (RMC) of SDS/CₙOH (n = 8, 10, 12, 14, and 16) mixtures
was measured by our established method [64]. Based on the previous work of Patist showing the
micellar stability and the chain length compatibility of SDS/CₙOH systems (where SDS and
C₁₂OH showed the greatest micellar stability, highest foam stability, highest surface viscosity,
etc. [107]) we have shown a correlation of chain length compatibility between SDS and CₙOH
with the RMC of cotton fabrics.

Patist et al. [107] have shown the following conclusions from their work on SDS + long
chain alcohols:

1. Long chain alcohols (CₙOH for n = 8, 10, 12, 14, and 16) stabilize SDS micelles,
up to approximately 150 mM SDS (depending on the carbon chain length of the
alcohol) due to the strong ion-dipole interaction between the negatively charged
SDS head group and the hydroxyl group of the alcohol. Beyond this critical concentration the chain length compatibility starts playing an important role. Therefore, only C12OH will cause a further increase in micellar stability, whereas the mismatch in chain length between the other alcohols and the SDS results in a disruption of the molecular packing in the micelle, thereby decreasing the stability.

2. The effect of adding C12OH is most pronounced when the stability of pure SDS micelles is very low, i.e., at low SDS concentrations (25 mM). At higher SDS concentrations, the micellar stability increases, which makes the effect of C12OH less pronounced.

3. The effect of micellar stability plays an important role in processes involving a rapid increase in surface area. If enough time is allowed for the interface to form, the dynamic surface tension approaches the equilibrium surface tension and thus more foam is generated (more in case of SDS/C12OH mixtures). However, in very high speed processes, the micellar stability, and thus the time it takes for micelles to break up, determines the rate of adsorption of surfactant molecules and therefore higher surface tensions will be attained for SDS/C12OH solutions. In that case less foam is generated, even though the equilibrium surface tension of the SDS/C12OH system is lower. In conclusion, different methods of foaming can produce opposite results as illustrated by the foam-ability measurements in this study.

Based on this work, we measured the RMC of mixed surfactant systems of SDS with the addition of long chain alcohols (C_nOH for n= 8, 10, 12, 14, and 16). As shown in Figure 5-14, there is a maximum in the RMC with the SDS/C12OH system. When the hydrophobic tail groups were of the same chain length, there was a maximum in RMC which corresponds to the maximum found in micellar relaxation time as shown by Patist et al. [107]. We have shown that an increase in the micellar stability results in an increase in the dynamic surface tension of solution due to a reduction in the monomer flux from the stable micelles to the newly created air/liquid interface.
The residual moisture content (RMC) of SDS/CnTAB (n = 8, 10, 12, 14, and 16) mixtures was measured by our established method [64]. Based on the previous work of Patist et al. [55] showing the micellar stability and the chain length compatibility of SDS/CnTAB systems (where SDS and C12TAB showed the greatest micellar stability, highest foam stability, highest surface viscosity, etc.) we have shown a correlation of chain length compatibility between SDS and CnTAB with the RMC of cotton fabrics.

Patist et al. [55] have shown the following conclusions from their work on SDS + alkyltrimethylammonium bromides (CnTAB for n = 8, 10, 12, 14, and 16):

1. For mixed solutions of anionic and cationic surfactants (SDS + CnTAB), the surface properties depend upon the chain length of the individual surfactant molecules.

2. For mixed surfactant systems, minimum surface tension, maximum surface viscosity, highest micellar stability, maximum foam stability, and minimum
foamability were observed when both surfactants in the system had the same chain length (SDS + C₁₂TAB).

3. The chain length compatibility and the Coulombic interaction in SDS/C₁₂TAB mixtures result in a closest packing of molecules in both micelles as well as at the air/water interface.

Based on this work, we measured the RMC of mixed surfactant systems of SDS with the addition of alkyltrimethylammonium bromides (CₙTAB for n= 8, 10, 12, 14, and 16). As shown in Figure 5-15, there is a maximum in the RMC with the SDS/C₁₂TAB system. When the hydrophobic tail groups were of the same chain length, there was a maximum in RMC which corresponds to the maximum found in micellar relaxation time as shown by Patist et al. [55].

These results are relevant to laundry process as consumers often use the fabric softeners which are cationic molecules after washing the laundry with detergents containing negatively charged surfactant molecules. The residual detergent which carries over into the rinse cycle may combine with the fabric softener molecules and produce stable micelles or a tightly packed film at the air–water interface in the fabric. If a stable mixed micelle between the anionic detergent and the cationic fabric softener is formed, the result could be an increase in the RMC of the laundry. This would then lead to an increase in drying time and thus drying energy costs.
Figure 5-15: RMC of cotton fabric (centrifuged for 10 minutes at 1000 RPM) as a function of SDS + CₙOHs (for n = 8, 10, 12, 14, and 16) with a reference to the RMC of cotton fabric at 100 mM pure SDS.

5.4 Labile Micelles

Dsfdfs

5.3.1 Review of Labile Micelles

5.3.2 SDS + Polyvinylpyrrolidone (PVP)

Show relaxation time and corresponding RMC
Figure 5-16: Long relaxation time ($\tau_2$) and RMC of Terry fabric in solutions of PVP.
5.3.3 SDS + Short Chain Alcohols (CₙOH)

Show relaxation time and RMC data.
Figure 5-17: Long relaxation time ($\tau_2$) and RMC of Terry fabric in solutions of 100 mM SDS with the addition of short chain alcohols.
6.1 Various Surfactant Systems in Full Washer Scale

6.1.1 Unconventional Surfactant Systems

We have shown that the reduction of equilibrium and dynamic surface tension and the micellar stability play very important roles in reducing the residual moisture of fabrics [64, 67, 68]. Since the goal is to reduce the RMC of the fabric during the final spin cycle of the washing machine, the use of a fabric softener along with the addition of a co-surfactant to reduce the surface tension of solution may show promise in the reduction of RMC. Our rational was due to the fact that before the final spin cycle of the washing machine, many people add fabric softeners to the final rinse to enhance the properties of the fabric once it has been dried.

Shah et.al. [36] has found striking change in properties of various systems (eg. lecithin-cholestrol, stearic acid-stearyl alcohol, decanoic acid-decanol, potassium oleate-hexanol, SDS-cetyl pyridinium chloride) at a 1:3 molecular ratio. Though direct values of surface tension were not reported for these systems, in all cases there is indirect evidence (evaporation rate, foam stability, solubilization in microemulsion) that at this ratio there is a crowding of molecules at the interface and the molecules are tightly packed. Other researchers have reported this synergism for anionic/cationic [37], anionic/zwiterionic [38-40], cationic/zwiterionic [38], non-ionic/zwiterionic [38], anionic/cationic-gemini [41], anionic gemini/zwiterionic [42], cationic-gemini/nonionic [43] and cationic-gemini/sugar surfactants [44]. These investigations suggest that properly engineered synergism can help reduce surface tension values to ~ 20 mN/m. Since it has been well documented that synergism exists in mixed surfactant systems, anionic co-surfactants were chosen to use in the reduction of surface tension in Downy systems.
6.1.1-1 Small Scale Testing

The surface tension of Downy solutions (500 ppm solutions which is the common household dosage of Downy in the washing machine) with the addition of various co-surfactants was measured to determine if one of the systems would produce a low surface tension value that could significantly decrease the amount of water retained by the fabric at the end of the final spin cycle. With the addition of SDS to Downy solutions, the surface tension initial decreases and then increases once again and then levels off (Figure 6-1). The same trend was observed in the Downy and dioctyl sulfosuccinate (AOT) system (Figure 6-2). This phenomenon is further discussed in this chapter.

![Figure 6-1: Equilibrium surface tension and RMC of Downy systems with the addition of sodium dodecyl sulfate (SDS).](image)

Figure 6-1: Equilibrium surface tension and RMC of Downy systems with the addition of sodium dodecyl sulfate (SDS).
Figure 6-2: Equilibrium surface tension of Downy solutions with the addition of dioctylsulfosuccinate (AOT).

The surface tension of Downy solutions with the addition of a silicone super wetting surfactant was also measured. However, the effectiveness of silicone surfactants has been shown to decrease depending on the pH of solution. At higher pH values, the functionality of silicone surfactants decreases and the surface tension lowering power of silioxanes decreases. In this study, we measured the initial surface tension of solution once the Dow Q2-5211 silicone super wetter was added to the Downy and then once again measured the surface tension after allowing the solution to sit for 4 days. As shown in Figure 6-3, the initial equilibrium surface tension is lowered to ~20 mN/m. After the solution has aged for 4 days, the surface tension has increased from 20 mN/m to as high as 40 mN/m indicating the effectiveness of the silicone surfactant has been altered.
Surface Tension of Dow Q2-5211 added into 500 ppm Downy Solutions

Figure 6-3: Equilibrium surface tension of Downy solutions with the addition of Dow Corning Q2-5211 Silicone Super Wetter.

6.1.1-2 Full Scale Washer Testing

RMC testing was performed at the Procter and Gamble Miami Valley Laboratories in Cincinnati, OH in May of 2004. Based on the research that was performed in small scale at UF, several systems were chosen to measure the RMC in large scale. As shown in Table 6-1, the RMC for the 3:1 molecular ratio of SDS to C12TAC (C12TAB was used in the lab) was on the order of the RMC obtained for the detergent control. Also, the RMC of Downy systems with the addition of SDS and AOT was reduced to values lower than the Tide detergent control. The washing machine used in these studies was a Whirlpool Model LSQ9010LWO with a spin cycle speed of 640 RPM and a drum diameter of 21 inches. The final spin cycle was on average 360 seconds (6 minutes).
Another interested observation that was made while performing experiments at P&G’s labs was the dependence of RMC on the temperature of the rinse water. As shown in Figure 6-4, the RMC decreases from about 94% to about 79% from a temperature change from 60°F to 100°F. This is due to the reduction of surface tension as the temperature increases as well as the swelling of fibers allowing more water to be displaced due to a lessened capillary force from larger capillaries. Also, the drying curve was measured for the same systems as discussed previously (SDS:C12TAC, SDS in Downy and AOT in Downy). In Figure 6-5, the drying rates are shown to be almost superimposed upon each other with no distinguishable differences between the three systems. This is expected since the RMC values for each system are approximately the same.
Figure 6-4: Temperature dependence of the RMC during the final rinse cycle.

Figure 6-5: Drying rate curve for terry fabrics soaked in various solutions.

6.2 Vesicle Surfactant Interactions

As previously discussed, the surface tension values of 500 ppm solutions of Downy with the addition of SDS showed an interesting trend. We believe that this is due to the interaction of the anionic co-surfactant with the vesicles in the Downy system.
6.2.1 SDS and Downy Interactions

As shown in Figure 6-1, the surface tension and RMC of Hane’s fabric was measured for 500 ppm solutions of Downy with the addition of SDS. Several experiments were performed to determine the molecular mechanisms responsible for the changes in surface tension that we observed. Since vesicles compose the Downy system, the turbidity and particle sizing of the interaction between Downy and SDS was measured.

6.2.1-1 Turbidity

The turbidity of Downy solutions with the addition of SDS was measured and shown in Figure 6-6. The initial turbidity was measured immediately after the addition of the SDS to the 500 ppm Downy solutions. The turbidity was then monitored over a period of 7 days. It was noticed that after 24 hours, the turbidity measurements stabilized and were approximately the same from 1 to 7 days. This is an indication that the system has equilibrated. Due to the large increase in turbidity at the 1:1 ratio of SDS to the active surfactant in Downy, it is believed that some sort of agglomeration is occurring due to charge shielding of the vesicles.
Figure 6-6: Turbidity measurements of Downy solutions with the addition of SDS. Solutions were aged up to 7 days. Downy solutions were 500 ppm.

6.2.1-2 Particle Sizing

From the turbidity measurements, we believe that the increase in surface tension and turbidity is due to an agglomeration of the Downy vesicles due to charge shielding at the 1:1 ratio of SDS to the active surfactant in Downy. In Figure 6-7, it is shown that the mean particle size of 500 ppm solutions of Downy increases from 200 nm with no SDS present (which corresponds to data from P&G indicating that the Downy vesicles are 200 nm in size) to over 600 nm at the 1:1 ratio of SDS to the actives in Downy. This validates our assumption that the increase in surface tension and turbidity was due to the agglomeration of Downy vesicles due to charge shielding.
Figure 6-7: Mean particle size of 500 ppm solutions of Downy with the addition of SDS.

6.2.1-3 Molecular Mechanisms between SDS and Downy Vesicles

It has been shown that the surface tension, turbidity and mean particle size of 500 ppm Downy solutions with the addition of SDS show a maximum at the 1:1 ratio of SDS to the active surfactant in Downy (Figure 6-8). It is believed that this is due to charge neutralization of the Downy vesicles allowing the vesicles to agglomerate and cause an increase in turbidity and particle size. A diagram showing the interactions of SDS with the vesicles in Downy at the 1:1 ratio is shown in Figure 6-9.
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Turbidity and Particle Size of 500 ppm Downy Solutions with SDS added

Figure 6-8: Particle size and turbidity of 500 ppm Downy solutions with the addition of SDS.

1:1 SDS-Downy Actives Ratio

1:1 Packing resulting in complete charge neutralization

Agglomeration of Vesicles

Figure 6-9: Molecular diagram describing the interaction of Downy vesicles with SDS at 500 ppm concentrations of Downy at a 1:1 ratio of SDS to the active surfactant in Downy. At the 1:1 ratio, charge neutralization occurs and allows agglomeration of the vesicles.

6.2.2 Verification of Molecular Mechanism: SDS Interactions with DODAB Vesicles

To verify the interactions between SDS and the Downy vesicles, it was desired to experiment with a system without any other additives as in the case with Downy. The use of
DODAB vesicles proved of interest due to the similarities between the active surfactant in Downy to the molecular structure of DODAB.

**6.3 Washer Scale RMC Testing**

In order to reduce the residual moisture content of fabrics at the end of the final spin cycle, several various common surfactant systems were investigated. The use of adding the following common surfactant solutions was investigated: Cascade (Figure 6-10), Dow Q2-5211 (Figure 6-11), Flexiwets (Figure 6-12), Jet Dry (Figure 6-13) and Sylgard 309 (Figure 6-14). As shown in those figures, the RMC was reduced to as low as 60-65% RMC (60% with Jet Dry and 65% with Cascade). The use of the active surfactant in those solutions may prove to be useful in the reduction of RMC at the end of the laundry spin cycle. However, the mechanism behind the lowering of RMC is unknown at this time. As shown in Figure 6-10, the surface tension of the Cascade solutions is in the high 20 mN/m range (about 27-29 mN/m) but the resulting RMC is as low as 65%. This indicates that the surface tension is not playing as an important role in this system. As shown in the LaPlace equation, the contact angle of water with the fabric can be changed and affect the capillary height (and thus the RMC). If the fabric becomes hydrophobic, water is more easily shed from the fabric during the centrifugation process even if the surface tension of solution is higher. This is the mechanism which we believe is responsible for the low RMC values with these commercially available surfactant systems.

As shown in Figure 6-15, the lowest surface tension achieved with monolayer penetration in the washing machine is about 68%. However, using Jet Dry additive in the washing machine, the RMC was reduced to 61%. As shown in Table 6-2, a RMC value of 56% would need to be reached to obtain the ultimate goal of a 30% reduction in the RMC (compared to the RMC reduction of 80% RMC for the 150 ppm carryover of the detergent, Tide, into the rinse water). Table 6-2 lists the various methods used in reducing the RMC and the various RMC values.
obtained for each method. There were several methods used such as monolayer penetration and soaking the fabric in solution. Also, it should be pointed out that the RMC is only reduced to about 70% using the silicone super wetter in the washing machine. Based on these results, monolayer penetration is a promising method to reduce the RMC of laundry using surfactants and monolayer materials that are presently used in the wash cycle.

Figure 6-10: RMC of Terry cloth fabric with the addition of Cascade.

Figure 6-11: RMC of Terry cloth fabric with the addition of Dow Q2-5211.
Figure 6-12: RMC of Terry cloth fabric with the addition of Flexiwet (Q-22, RFD-15A, and NF).

Figure 6-13: RMC of Terry cloth fabric with the addition of Jet Dry.
Figure 6-14: RMC of Terry cloth fabric with the addition of Sylgard 309.

Figure 6-15: Comparison of RMC values for full scale washing machine experiments (150 ppm of detergent is the standard of comparison) showing the reduction in RMC using monolayer penetration (red bars).
Table 6-2: RMC values for large scale washing machine experiments for various surfactant systems.

<table>
<thead>
<tr>
<th>Application</th>
<th>RMC%</th>
<th>SFT, mN/m</th>
<th>Relative RMC Change wrt Detergent %</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimae Goal of 30% RMC Reduction</td>
<td>56.00%</td>
<td>-</td>
<td>-30.17%</td>
<td>-</td>
</tr>
<tr>
<td>Jet Dry (2%)</td>
<td>62.96%</td>
<td>29</td>
<td>-21.49%</td>
<td>Solution</td>
</tr>
<tr>
<td>Cascade Clean and Clear (0.75%)</td>
<td>65.55%</td>
<td>28.5</td>
<td>-18.26%</td>
<td>Solution</td>
</tr>
<tr>
<td>1:5 C14SO4:DODAB Monolayer on 4 mM C14SO4</td>
<td>67.16%</td>
<td>-</td>
<td>-16.25%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>1:5 SDS:DODAB Monolayer on 4 mM SDS</td>
<td>68.53%</td>
<td>-</td>
<td>-14.54%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>Mr. Clean Car Wash (1%)</td>
<td>70.78%</td>
<td>27</td>
<td>-11.73%</td>
<td>Solution</td>
</tr>
<tr>
<td>Dow Q2-5211 SuperWetter (1%)</td>
<td>70.81%</td>
<td>19.9</td>
<td>-11.70%</td>
<td>Solution</td>
</tr>
<tr>
<td>1:7 SDS:DODAB Monolayer on 4 mM SDS</td>
<td>73.66%</td>
<td>-</td>
<td>-8.14%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>4 mM SDS with 100 mL Ethanol Splash</td>
<td>74.73%</td>
<td>-</td>
<td>-6.81%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>1:5 SDS:DODAB Monolayer on 150 ppm Detergent</td>
<td>76.36%</td>
<td>-</td>
<td>-4.78%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>1:10 SDS:DODAB Monolayer on 4 mM SDS</td>
<td>76.68%</td>
<td>-</td>
<td>-4.38%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>500 ppm Fabric Softener + 150 ppm Detergent</td>
<td>77.57%</td>
<td>-</td>
<td>-3.27%</td>
<td>Solution</td>
</tr>
<tr>
<td><strong>1500 ppm Detergent</strong></td>
<td><strong>80.19%</strong></td>
<td><strong>30</strong></td>
<td><strong>0.00%</strong></td>
<td><strong>Solution</strong></td>
</tr>
<tr>
<td>1:3 SDS:DODAB Monolayer on 4 mM SDS</td>
<td>80.45%</td>
<td>-</td>
<td>0.32%</td>
<td>Monolayer</td>
</tr>
<tr>
<td>500 ppm Fabric Softener</td>
<td>85.77%</td>
<td>44</td>
<td>6.96%</td>
<td>Solution</td>
</tr>
<tr>
<td>Pure 4 mM SDS</td>
<td>88.63%</td>
<td>64</td>
<td>10.53%</td>
<td>Solution</td>
</tr>
<tr>
<td>Water</td>
<td>93.55%</td>
<td>72.5</td>
<td>16.66%</td>
<td>Solution</td>
</tr>
</tbody>
</table>
CHAPTER 7
CONCLUSIONS

7.1 UF Contributions to the Lowering of Interfacial Tension and Surface Tension: Saving Energy in the Laundry Process

7.2 Technological Impact of the Reduction of RMC in the Laundry Process

7.3 Suggested Future Experiments
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A.1.2 Equilibrium Surface Tension

A.1.3 Dynamic Surface Tension

A.1.4 Foam Studies

A.1.4-1 Foamability

A.1.4-2 Foam Stability

A.1.5 Dye Solubilization

A.2 Molecular Mechanisms for the Interaction with the Addition of $\text{C}_{12}\text{OH}$ to SDS
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Daniel Carter was born in Hamilton, Alabama and went to high school at Bob Jones High School in Madison, Alabama. Daniel was accepted to Auburn in his junior year of high school as an early admissions student passing over his senior year to attend college. He then completed his bachelors of science in chemical engineering and was then accepted to the University of Florida. In the fall of 2002, Daniel was chosen by Professor Dinesh O. Shah to work on the “Fast Dry” project funded by Procter and Gamble. After four and a half years, Daniel completed the work required for submission of a dissertation for completion of the requirements for receiving his Doctor of Philosophy.