

Importance of Dynamic Surface Tension to the Residual Water Content of Fabrics[†]

Daniel L. Carter, Matthew C. Draper, Rachel N. Peterson, and Dinesh O. Shah*

*Center for Surface Science and Engineering, Department of Chemical Engineering and
Department of Anesthesiology, University of Florida, Gainesville, Florida 32611*

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At the end of the final spin cycle of the laundry process, the residual moisture content (RMC) of fabric is directly related to the dynamic surface tension of the residual water in the fabric. The LaPlace equation for capillary rise predicts that the capillary rise of solutions in a capillary is proportional to the surface tension at the air–liquid interface. If fabric can be considered to be a large ensemble of capillaries due to interfiber spacing, then the RMC of fabrics will be directly related to the surface tension of residual solution in the fabric. The use of a tailored rinse additive has the potential to decrease the surface tension of solution significantly, thus leading to a decrease in the residual water content of the fabric. It is expected that as the surfactant concentration increases the surface tension decreases. Hence, the RMC of fabrics must decrease with increasing surfactant concentration. However, a peak is observed in the RMC of fabrics before the critical micelle concentration (CMC) is reached. Prior to the CMC, it is proposed that a sudden adsorption of surfactant is occurring on the fabric surface leading to a decrease in bulk monomer concentration. The decrease in free monomer concentration should result in an increase in the equilibrium surface tension of the residual solution leading to a concomitant increase in RMC. Because the dynamic surface tension is measured on a short time scale (on the order of milliseconds), there will be less adsorption of monomer onto the newly created air–liquid interface of the bubbles during the measurement process. This decrease in adsorption should lead to a pronounced increase in the dynamic surface tension. This indeed was observed. The RMC correlates very well with the dynamic surface tension of the residual solution.

I. Introduction

The use of household laundry machines and dryers has become a necessity in the everyday life of most people. Today's society has become rushed, and people have less and less time to spend on everyday household chores such as laundry. Because of this lack of free time, consumer polls have shown that consumers want a significant reduction in the drying time of their laundry. In addition, the energy spent (and hence the time required) in drying fabrics depends on the residual moisture content (RMC) of the fabric after the spin cycle in the washing machine. If we reduce the RMC by 30%, we will spend 30% less energy and 30% less time in drying the fabric. In the US, such a 30% reduction of the RMC has the potential to save over \$900 million per year in energy costs as well as saving time for drying the laundry for the consumer. Because our goal is to reduce the drying time of fabrics, it is important that during the laundry cycle the concentration of the residual detergent from the wash cycle does not fall into the range of concentration where the RMC is increased.

It has been shown that the residual moisture content (RMC) of fabrics depends on the equilibrium surface tension of solution.¹ The LaPlace equation for capillary rise (eq 1, where h is the capillary height, γ is the surface tension, θ is the contact angle, r is the capillary radius, ρ is the solution density, and g is the gravitational constant) predicts that the capillary height (which can be related to RMC) is proportional to the surface tension. Therefore, as the surface tension decreases, the RMC of

the fabric also decreases. As shown in the LaPlace equation, the surface tension and contact angle are parameters that can easily be varied. For cotton fabrics, we assume that the contact angle is zero or that the fabric is completely wettable. It has also been shown by several other researchers that this approach is applicable in porous media (oil recovery, dewatering of coal fines, and dewatering of fabrics).^{2–4}

$$h = \frac{2\gamma \cos \theta}{r\rho g} \quad (1)$$

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.² 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 showed only the direct relationship between the 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 measure 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.

It was shown that the RMC of fabrics depends on several different variables such as centrifugation time, centrifugation speed, and surface tension of solution.¹ However, we have observed that the RMC of fabrics does not

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* Corresponding author. E-mail: shah@che.ufl.edu. Fax: 352-392-0127. Phone: 352-392-0877.

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completely correlate with the LaPlace equation as expected. Before the CMC of the 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. Because it has been shown that cotton has a negative ζ potential, one might think that an anionic surfactant would have minimal adsorption on a negatively charged surface.^{5–7} However, there have been several papers showing the ability of sodium dodecyl sulfate (SDS) and other anionic surfactants to adsorb onto negatively charged surfaces such as coal fines, cotton, and cellulose.^{3,5,8–10} Also, it has been shown by Somasundaran et al. that adsorption isotherms can show up to four adsorption regions,¹¹ one of them being a sudden increase of adsorption due to the 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 in 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.

II. Experimental Section

A. Materials. The sodium dodecyl sulfate used in these experiments was obtained from the Fisher Scientific Company.

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 that was supplied by the Procter and Gamble Company.

B. Residual Moisture Content (RMC) Measurements. For measuring the residual moisture, each fabric sample was soaked for 10 min 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 $\sim 90g$) for 10 min. The experimental apparatus used to hold the fabrics is shown in Figure 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).

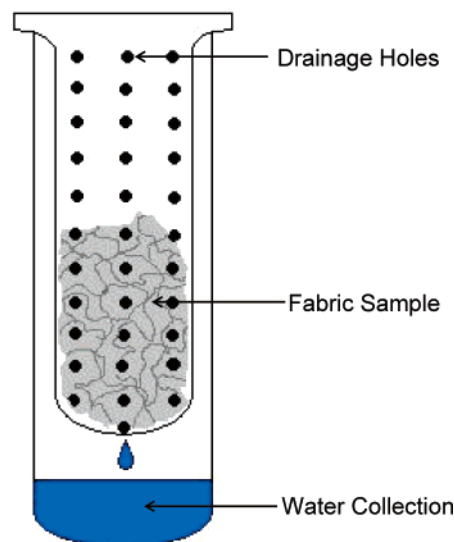


Figure 1. Experimental apparatus used to determine the residual moisture of fabrics.

After the fabric was soaked and centrifuged, the weight was then measured to determine the residual moisture content (RMC) as shown in eq 2.

$$\text{RMC}\% = 100 \frac{\text{weight}_{\text{centrifuged}} - \text{weight}_{\text{dry}}}{\text{weight}_{\text{dry}}} \quad (2)$$

C. 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 min, 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 cm³/min (which corresponds to 6–15 bubbles per second or approximately 66 to 166 ms 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.

III. Results and Discussion

In our previous work, the residual moisture content was shown to be a function of the surface tension of solution.¹ However, as shown in Figure 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 has shown the same RMC peak at a slightly lower SDS concentration.

It was shown that the RMC of fabrics did not completely correlate with the equilibrium surface tension of SDS as observed in Figure 2. Because 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

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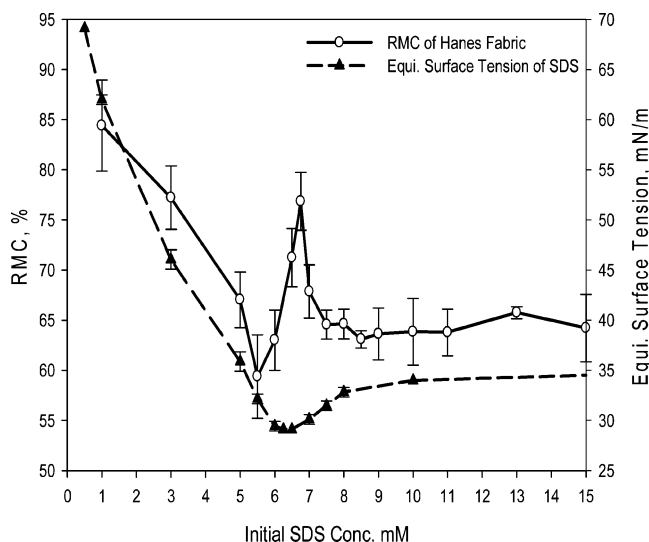


Figure 2. RMC of Hanes 100% cotton fabric as a function of SDS concentration plotted with the equilibrium surface tension of pure SDS solutions.

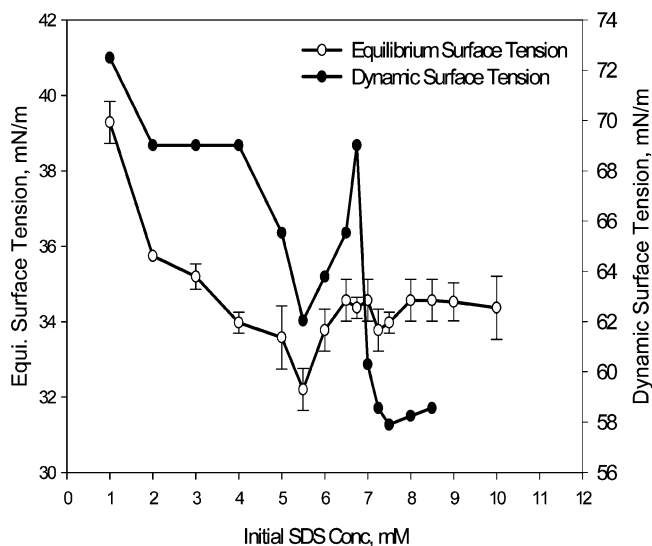


Figure 3. Equilibrium and dynamic surface tension of a residual SDS solution after exposure to Hanes fabric.

solution were measured after allowing the fabrics to equilibrate for 45 min. 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 cm³/min (approximately 6–15 bubbles per second). It is shown in Figure 3 that a small increase was found in the equilibrium surface tension in the concentration range of 5–8 mM. Because 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) that the dynamic surface tension amplifies the small changes seen in the equilibrium surface tension. Because 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-dependent process), it is expected that the dynamic surface tension may amplify the changes seen in the equilibrium surface tension. As shown in Figure 4, the increase in the equilibrium surface tension for the residual SDS solution corresponds to the increase of the RMC of the Hanes fabric presumably because of the

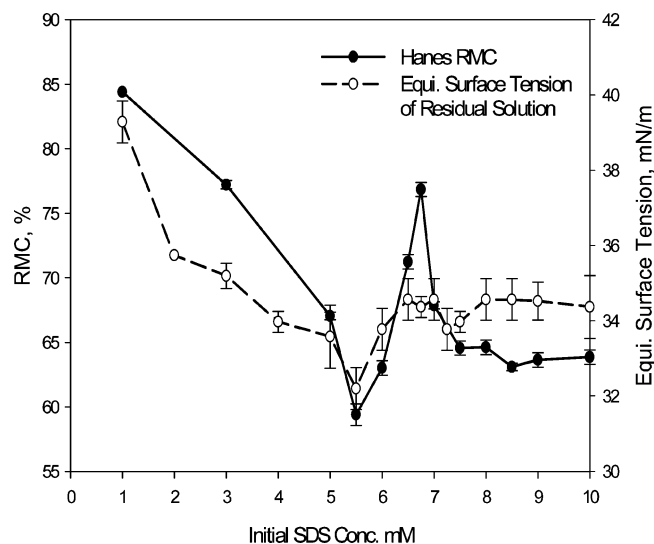


Figure 4. Comparison of the RMC of Hanes fabric and the equilibrium surface tension of residual solution after soaking the fabric.

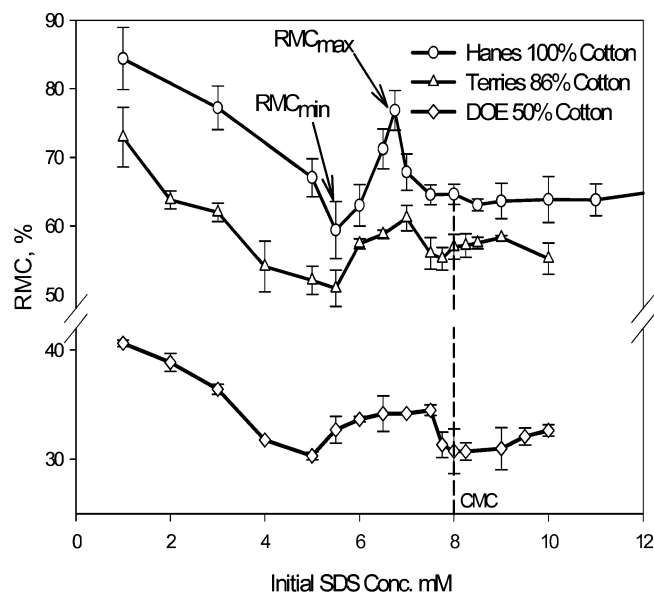


Figure 5. RMC of Hanes cotton fabric, terry cloth fabric, and DOE test fabric as a function of SDS concentration.

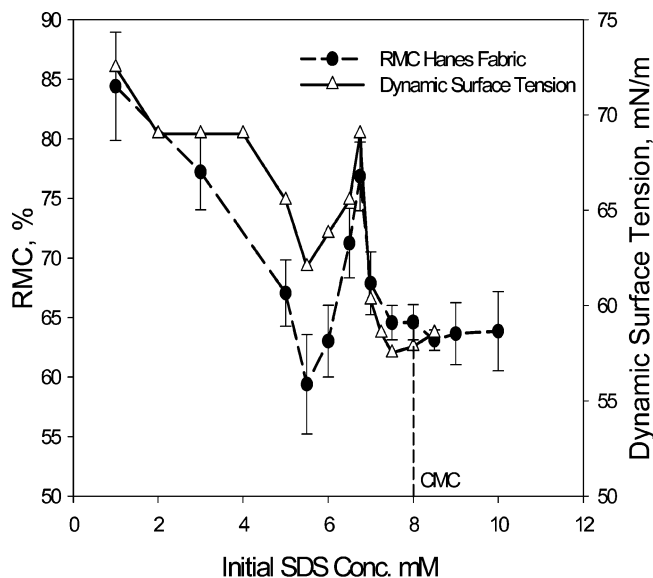
adsorption of SDS onto the fabric surface in the range of 5.5 to 6.5 mM SDS concentration.

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 5 (terry cloth and DOE fabrics with 14 and 50% polyester, respectively). As the fabric becomes more hydrophobic, the absolute RMC magnitude decreases along with the magnitude of the RMC peaks as shown in Table 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

Table 1. Magnitudes of the RMC Peak for Various Fabrics^a

	II		III	
	RMC _{max} - RMC _{min}		RMC _{max} - RMC _{min}	
	RMC _{max} - RMC _{min}	RMC _{max}	RMC _{max}	RMC _{min}
Hanes	17.45%	22.72%	29.40%	
Teries	10.23%	16.74%	20.01%	
DOE	4.18%	12.13%	13.89%	

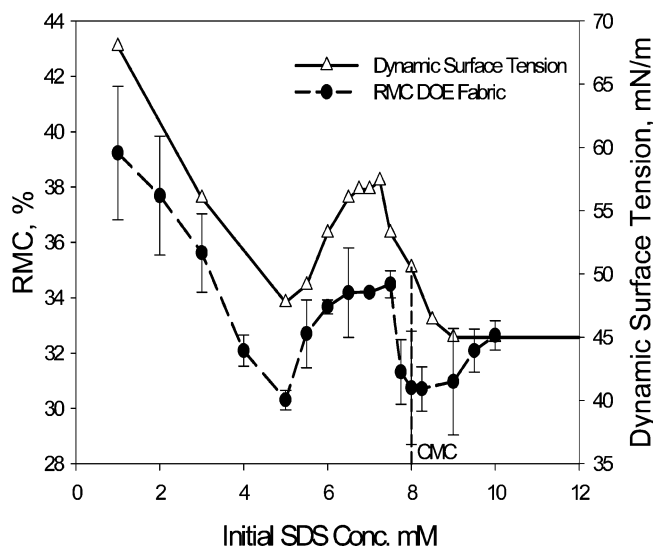
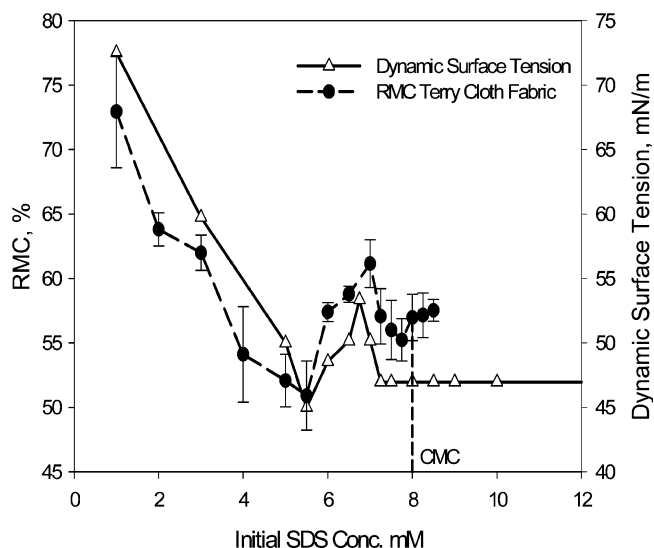
^a (I) Absolute different in the maximum and minimum of the RMC peak, (II) difference in the maximum and minimum normalized with respect to the RMC maximum, and (III) difference in the maximum and minimum normalized with respect to the RMC minimum.

**Figure 6.** RMC and DST of the residual solution from the Hanes 100% cotton fabric soaked in SDS solutions.

soaking the fabric remained unchanged from that of pure water. Thus, adsorbed impurities on the fabric surface cannot account for the observed results.

We have shown in Figure 3 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 solution and allowed to equilibrate for 45 min. The dynamic surface tension of the residual solution was then measured (Figures 6–8 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 ms 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. Because 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 decreased surfactant concentration due to adsorption onto the fabric surface.

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

**Figure 7.** RMC and DST of the residual solution from DOE 50:50 cotton/polyester fabric soaked in SDS solutions.**Figure 8.** RMC and DST of residual solution from the terry cloth 86:14 cotton/polyester fabric soaked in SDS solutions.

been shown by the increase in equilibrium and dynamic surface tension of residual solution as shown in Figure 3).

It is shown in Figures 9 and 10 that there are four 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, which is presumably due to a residual negative charge on the fabric surface. The decrease in RMC in this region is due to the increase in free surfactant monomer concentration with low adsorption on the fabric surface. At a concentration of 5.5 mM 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*. Because of 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 that promotes SDS adsorption. This sudden increase in the 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

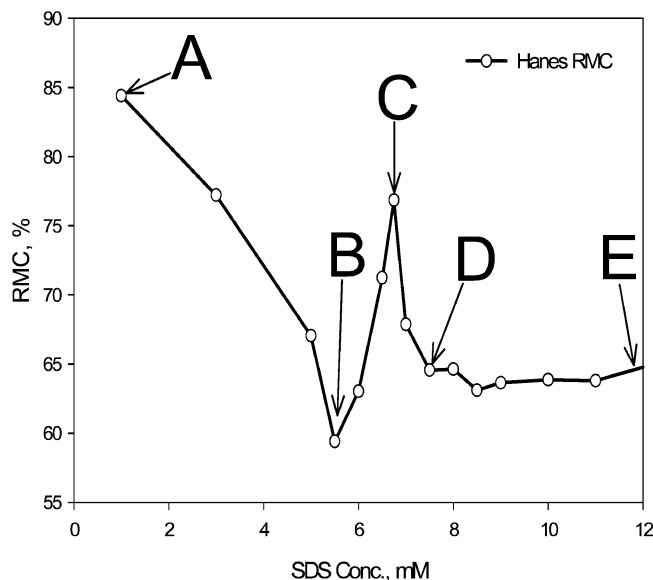


Figure 9. Indication of the regions associated with the peak in the RMC of Hanes cotton fabric.

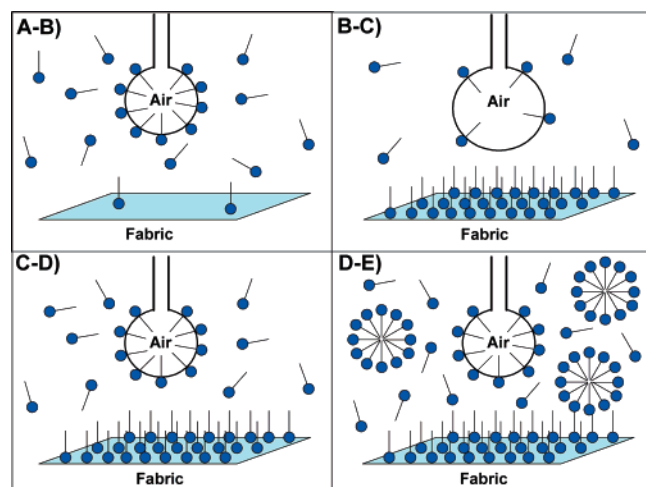


Figure 10. (A-B) High adsorption of surfactant monomer at the air–liquid interface and low adsorption on the fabric–liquid interface resulting in a low dynamic surface tension. (B-C) Sudden adsorption due to cooperative adsorption on the fabric surface resulting in decreased monomer concentration in 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) CMC is reached, and the monomer concentration is stable, resulting in a constant dynamic surface tension and RMC.

tension measurement, which leads to 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 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 to 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 SDS, region C-D ends, and region D-E begins. This region occurs because of the bulk solution reaching the critical micelle concentration (CMC). At this point, the free monomer concentration remains constant. Because the

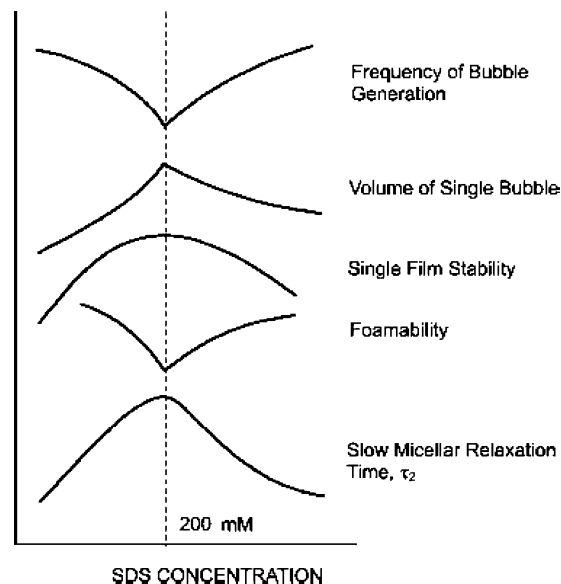


Figure 11. Liquid/gas phenomena exhibiting minima and maxima at 200 mM SDS.¹³

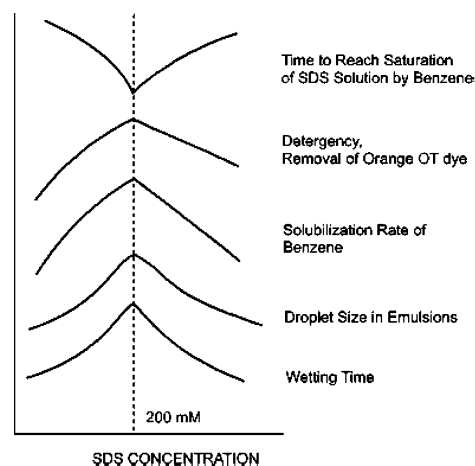


Figure 12. Liquid/liquid and solid/liquid phenomena exhibiting minima and maxima at 200 mM SDS.¹³

free monomer concentration is now constant, the dynamic surface tension and residual moisture should remain constant as well.

Over the years, the Shah research group has shown that the micellar relaxation time is a maximum at a concentration of 200 mM SDS.^{12–17} 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., Figures 11 and 12). The Shah research group has also shown that micellar kinetics plays an important role in detergency. Shah et al. has shown that the efficacy of removing nonpolar compounds from fabrics has been shown to have a strong correlation to the relaxation time of micelles.^{12–14,16–18} For example, it was shown by Oh and Shah that using 200 mM SDS (which was shown to have the longest micellar relaxation time

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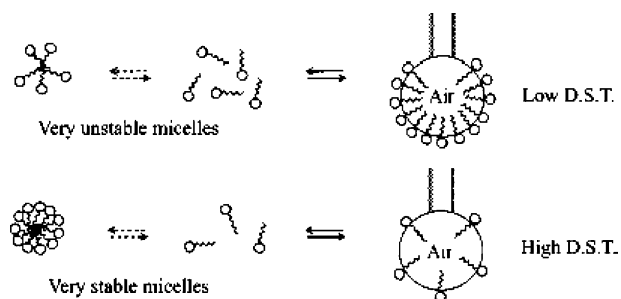


Figure 13. Effect of micellar stability on dynamic surface tension.

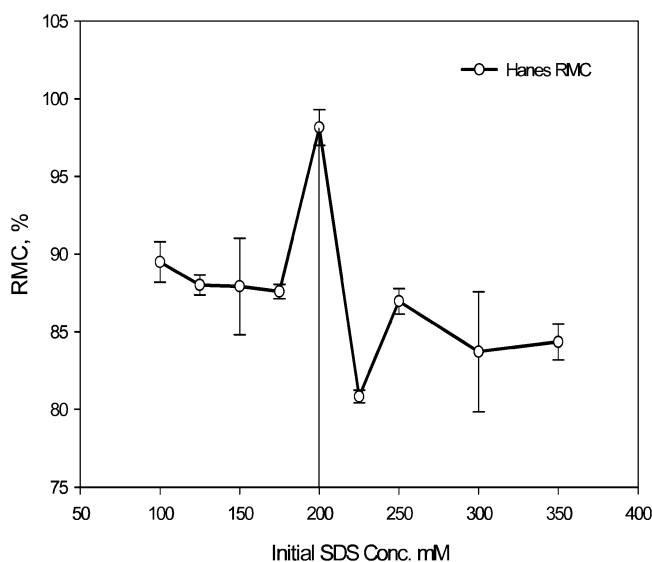


Figure 14. RMC of Hanes fabric around the concentration range of the most stable micelles of SDS (200 mM) (i.e., stable micelles can increase the RMC from ~80 to ~100% in SDS solutions).

in the SDS concentration range¹³) provided the most efficient removal of an artificial stain created by the deposition of orange OT onto fabric samples.¹⁷

Because the relaxation time of surfactants plays such a large role in many different properties of surfactant systems, the RMC of Hanes fabric around the concentration range of highest micellar stability was measured. Because the dynamic surface tension is related to the micellar stability (i.e., higher micellar stability leads to higher dynamic surface tension, Figure 13), it would be expected that there will be an increase in the RMC around an SDS concentration of 200 mM. In Figure 14, we have shown that at 200 mM SDS there is another maximum in the RMC of Hanes fabric. 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, thus leading to an increase in the RMC (shown in Figure 13). Alternatively, another possible explanation to explain the increase in RMC at 200 mM SDS could be due to the 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.^{19,20} and Wasan et al.^{21–26} that the layering of micelles or particles can stabilize thin films (which could possibly explain an increase in the RMC).

We have shown that many different factors affect the RMC of fabric/surfactant systems. It was shown that adsorption phenomena are also an important factor in laundry processes. It should also be noted that the dynamic surface tension seems to play a large role in the reduction of the RMC of fabrics. If the rate of adsorption and micellar kinetics can be controlled, then the magnitude of the RMC can be significantly altered (i.e., increased relaxation times for increased RMC or decreased relaxation times for decreased RMC). To fully understand the increase found in the dynamic surface tension of residual solution and the RMC of fabrics, adsorption studies need to be performed to show a correlation in the increased adsorption of surfactant with respect to the increase in dynamic surface tension and RMC.

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