

Effect of Micellar Lifetime on the Wetting Time of Cotton in Sodium Dodecyl Sulfate Solutions

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Introduction

Textile wetting involves the displacement of air by surfactant solutions in the fiber matrix. The kinetics of surfactant adsorption is more important than the equilibrium properties of surfactant solutions for the textile wetting process because equilibrium conditions are rarely attained during the time allowed for wetting in textile processing.¹ Fowkes observed that the log of the wetting time decreases linearly with the log of the bulk phase concentration of the surfactant below the critical micelle concentration.² Electrolytes that decrease the surface tension of surfactant solutions, such as Na₂SO₄, NaCl, and KCl, increase the wetting power of ionic surfactant solutions.^{3,4} As the temperature of the solution is increased, the chain length for optimum wetting by ionic surfactants generally increases, probably because of the increased solubility of the surfactant at higher temperatures and its decreased tendency to adsorb to the surface.⁵ Fowkes also found that the rate of wetting was determined not by the bulk phase concentration of the surfactant but by the rate of diffusion of the surfactant to the wetting front when adsorption of the surfactant onto the surface is strong.² The surfactants of short alkyl chain length and branched hydrophobic groups are more efficient than the surfactants of long and straight alkyl chains as wetting agents due to their higher diffusion coefficients.^{6,7} This is presumably due to the less efficient molecular packing in the micelles of branched chain surfactants which results in relatively unstable micelles in the solution. The surfactants which cannot be effectively packed in the micelles have strong wetting power due to the higher rate of mass transfer of surfactant monomers to the interface.

The addition of polyoxyethylenated nonionic surfactant increases the wetting efficiency of anionic surfactant solutions but decreases that of cationic surfactant solutions. This is due to the increase in the mobility of anionic surfactant monomers in solution and decrease in the mobility of cationic surfactant monomers by the addition of nonionic surfactants,⁸ resulting in rapid diffusion of anionic and slow diffusion of cationic surfactants.

When a piece of a fabric is placed on the surface of a surfactant solution, the solution penetrates into the interfiber spaces of the fabric (Figure 1). These interfiber spaces can be considered as the cylindrical capillaries of radius r and length l . For the case of thin fabric, where the gravity effect of the liquid inside the capillary can be neglected, the rate of penetration of a liquid into a capillary

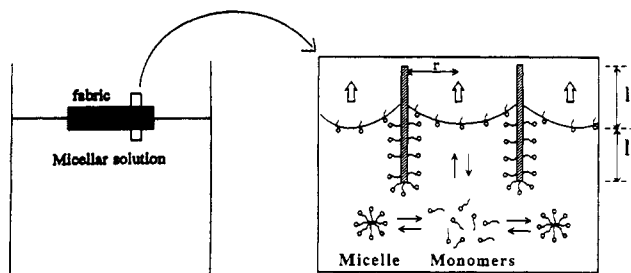


Figure 1. Schematic diagram for the adsorption of surfactant monomers from micellar solution to the textile surface by the disintegration of micelles during the wetting process.

(v) is given by the following equation^{9,10}

$$v = \frac{r\gamma_{L_1L_2} \cos \theta_{SL_1L_2}}{4(\eta_1 l_1 + \eta_2 l_2)} \quad (1)$$

where L_1 is a wetting liquid, L_2 is a displaced fluid (air), l_1 and l_2 are the length of the capillary filled with the corresponding viscosities of η_1 and η_2 of wetting and displaced fluid (air), and S denotes the fiber surface. For textile wetting, the quantity

$$\frac{\gamma_{L_1L_2} \cos \theta}{\eta_1} \quad (2)$$

has the dimension of velocity and thus gives a measure of the penetrating power of surfactant solution into the interfiber spaces of the fabric.¹¹ At high surfactant concentrations, the supply of surfactant monomers depends on the breakdown of micelles to provide additional monomers upon depletion of monomers by the adsorption process on the textile fibers. Thus, micellar stability is expected to influence the wetting time of the fabrics.

We propose that the wetting time of the fabrics should be influenced by the average lifetime of micelles because the micelles must disintegrate into the monomers for adsorption onto the fiber surfaces. If the micelles in the solution are relatively stable, they cannot rapidly breakdown and provide additional surfactant monomers to the fiber surfaces. Therefore, the fabric cannot be quickly wetted by the solution. On the other hand, if the micelles are relatively unstable, their rapid disintegration provides additional surfactant monomers which can rapidly adsorb on the fiber surfaces.

In the present paper, the effect of micellar lifetime on the wetting time of cotton fabric in sodium dodecyl sulfate (SDS) solutions has been studied by measuring the wetting time and relaxation time (τ_2) of micelles by the pressure-jump method as a function of surfactant concentration.

Experimental Procedure

Sodium dodecyl (C₁₂) sulfate, supplied by Sigma Chemical Co. (purity 99%), and double-distilled water were used to make micellar solutions. The surfactant concentration of solutions ranged from 50 to 400 mM of SDS.

The micellar lifetime was measured by the pressure-jump apparatus with conductivity detection from Dia-Log Corp. (Düsseldorf, Germany) as described in the previous paper.¹²

A commercially gained cotton fabric of 1 in.² was placed on the surface of SDS solution at 25 °C. The surfactant solution displaces air in the cotton surface by a wetting process and when sufficient air has been displaced, the cotton starts sinking. The residence time of cotton fabric on the surface of the solution was

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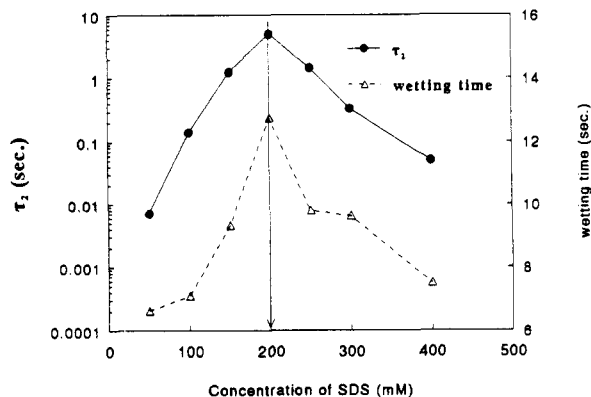


Figure 2. Effects of micellar relaxation time (τ_2) on the wetting time of cotton in SDS solution at 25 °C.

measured as wetting time in this study. This wetting time in each SDS solution was measured 4 times; the average value is shown in Figure 2.

Results and Discussions

All solutions of SDS were prepared above the critical micelle concentration (cmc) which is reported to be 8.2 mM,¹³ since the main objective of this study was to determine the effect of micellar lifetime or stability on the wetting time of cotton.

The micellar lifetime of SDS solution has been reported by several investigators.¹⁴ The micellar lifetime of SDS increases as the surfactant concentration increased up to 200 mM, and then decreases with the surfactant concentration (Figure 2). These data suggest that the most stable micelles are formed at 200 mM SDS concentration at 25 °C. The wetting time of cotton fabric in the SDS solutions was measured at various concentrations.

According to eq 2, the adhesion tension (i.e. $\gamma_{L_1L_2} \cos \theta$) determines the penetrating power of solution into the inter-fiber spaces when the viscosity of solution η_1 is constant.

From Young's equation

$$d(\gamma_{L_1L_2} \cos \theta) = d(\gamma_{SL_2}) - d(\gamma_{SL_1}) \quad (3)$$

If the interfacial tension at the air/cotton interface (γ_{SL_2}) is constant, then

$$\frac{d(\gamma_{L_1L_2} \cos \theta)}{d(\gamma_{SL_1})} = -1 \quad (4)$$

The adhesion tension (i.e. wetting power) increases as the interfacial tension at solution/cotton interface decreases.¹⁵ When the surfactant monomers are supplied rapidly to the wetting front of the solution by the micellar disintegration, the interfacial tensions at air/solution and cotton/solution are decreased. But the adhesion tension of solution increases according to eq 4, because the change in $\cos \theta$ term is dominant as compared to $\gamma_{L_1L_2}$.

The monomers can be supplied rapidly to the wetting front by the micellar breakdown in unstable micellar solution compared to stable micellar solution. Therefore, wetting time is shorter in unstable micellar solution than in stable micellar solution.

The maximum wetting time occurred at 200 mM of SDS concentration at which most stable micelles are formed (Figure 2).

The micellar lifetime or stability influences many dynamic phenomena such as foamability, textile wetting, and ore flotation by surfactant solutions. The correlation of micellar stability with foamability and bubble dynamics was studied and the relative significance of micellar lifetime and the diffusion time surfactant monomer was shown previously.^{16,17}

Textile wetting depends upon effective reduction of the surface tension under dynamic conditions, i.e., as the wetting liquid spreads over the textile, the surface-active molecules must be supplied rapidly to the moving boundary between the liquid and the textile. The interfacial tension of textile/solution interface is determined by the concentration of surfactant monomers in the solution. The average monomer flux is higher when micelles are relatively unstable. The increase in micellar stability (i.e. higher τ_2 value) influences the wetting kinetics by decreasing the flux of surfactant monomers from the bulk solution to the wetting front. This results in the decreased rate of adsorption to the textile surface and, hence, longer wetting time.

In summary, the cotton wetting time in sodium dodecyl sulfate solution was significantly influenced by the micellar lifetime which determines the amount of monomer flux to the wetting front in surfactant solution. The wetting time of cotton and the micellar stability as inferred from the relaxation time were maximum at 200 mM SDS concentration.

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Registry No. Sodium dodecyl sulfate, 151-21-3.

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