

Preparation and Surface Activity of Biodegradable Polymeric Surfactants II: Dyeing Properties of Biodegradable Dextrin Derivatives in Cotton Dyeing

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ABSTRACT: The biodegradability and dyeing properties of a series of dextrin-derivative surfactants in direct-dye cotton-dyeing systems have been studied. It was found that these surfactants have good biodegradability, which is lacking in traditional dyeing auxiliaries. In dye-surfactant systems, the degree of aggregation of direct dyes with surfac-

tants was found to influence the rate of cotton dyeing. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2620–2624, 2007

Key words: biodegradable; surfactants; dye; UV-vis spectroscopy

INTRODUCTION

In the processes of textile dyeing, surfactants, or dyeing auxiliaries, are applied to improve the dyeing properties of natural and synthetic fibers.^{1,2} However, after their use the dyeing auxiliaries are passed quantitatively into wastewater and may appear as a component of water pollutants according to their resistance to bacterial attack. In order to ensure the manifest advantages of traditional surfactants despite this problem, the demand for biodegradability of effluent has become more rigid and the need for biodegradable properties has become more pressing.³

Some carbohydrate-derived surfactants, readily biodegradable and toxicologically safe, were produced and used on an industrial scale. The surfactants contained sorbitan esters, sucrose esters, and, which is rather new, fatty acryl glucamides and alkyl polyglucosides. Strictly speaking, alkyl polyglucosides are not new surfactants. However, this class of surfactants was unearthed again recently, against a background of increasing environmental concern.^{4–6}

Alkyl polyglucosides and their derivatives consist of a hydrophobic alkyl residue and a hydrophilic saccharide structure, similar to traditional surfactants, which exhibit excellent characteristic surface activity. The properties and application of surfactants for use in detergents, personal care, and industrial processes have been recently reported.⁴ However, only limited

information is available with regard to biodegradable alkyl polyglucoside derivatives as dyeing auxiliaries in fabric dyeing systems.

In this article we present the dyeing auxiliary properties of a series of biodegradable dextrin-derivative surfactants containing the biodegradability and dyeing auxiliary properties. The biodegradability of these surfactants was evaluated by the determination of the ratio of biochemical oxygen demand/chemical oxygen demand (BOD/COD),³ and the dyeing properties in the direct-dye cotton-dyeing system were studied using the spectrophotometric method.^{7–10}

EXPERIMENTAL

The dextrin derivatives were prepared according to the technique reported previously^{4–6} in which the propylene glycol polyglucosides is reacted with a hydrophobic oxirane-containing material of the glycidyl ether having decyl, dodecyl, tetradecyl, and octadecyl alkyl groups.⁷ The leveling agent (Ethomid) used to compare the degradability was commercial grade and supplied by the Lion Company (Tokyo, Japan). The structure of these surfactants and commercial leveling agent was shown in Figure 1. All other reagents were reagent grade and were used without further purification.

The dyes used in this study were Everdirect Supra Orange 2GL (C.I. Direct Orange 39), Everdirect Supra Rubine BL (C.I. Direct Red 83), and Solophenyl Turquoise Blue (C.I. Direct Blue 86), as shown in Figure 2. These dyes were commercial grade and supplied by Everlight Company (Taipei, Taiwan). Scoured cotton fabric was used throughout the experiment.

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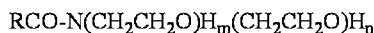
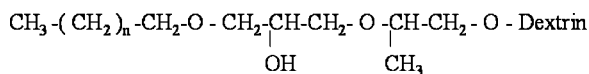


Figure 1 Structure of the dextrin-derivative surfactants and commercial leveling agent (Ethomid).

The biodegradability of was expressed by the ratio of BOD/COD, which was reported for the dates after 5, 10, 20, 25, and 30 days.³

A Shimadzu UV-240 spectrophotometer with a temperature-controlled cell holder was used to measure UV absorption of solution containing either purified dyes alone or the dyes in the presence of surfactants at various concentrations. The dyes were purified by dissolving them in cold *N,N*-dimethylformamide, followed by precipitation with acetone. The concentration of dyes were 1.6×10^{-4} mol/l, 6.4×10^{-5} mol/l, and 1.2×10^{-5} mol/l for C.I. Direct Orange 39, C.I. Direct Red 83, and C.I. Direct Blue 86, respectively. The concentrations of surfactants were varied over a range from 10^{-6} to 10^{-4} mol/l.

A rapid-dyeing machine was used in the laboratory to study the dyeing of cotton with direct dyes. The dyeing recipe included: dye 1% o.w.f., NaCl 20% o.w.f., dyeing auxiliaries 0.4 g/l, liquor ratio 30 : 1, dyeing temperature 90°C, time intervals 10, 20, 40, 60, 80, 120 min. After the dyeing, the reflectance at the wavelength of maximum dye absorption was measured and used to calculate the K/S values using an ACS spectrophotometer.

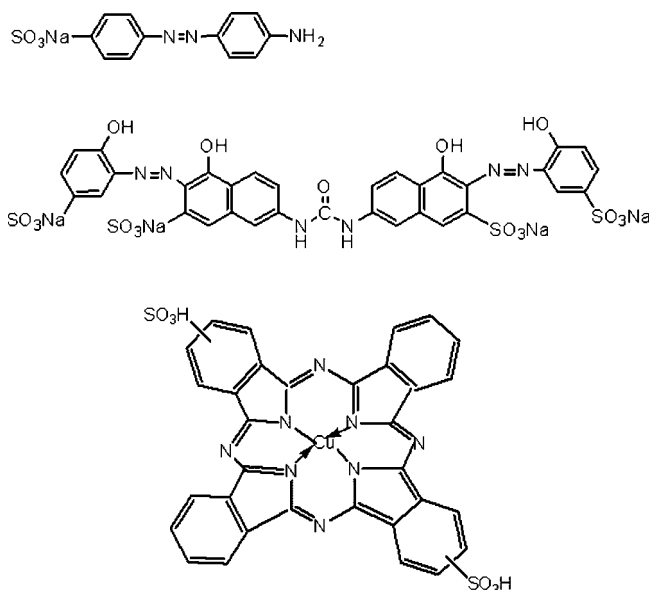


Figure 2 Structure of the direct dyes C.I. Direct Orange 39, C.I. Direct Red 83, and C.I. Direct Blue 86.

RESULTS AND DISCUSSION

Biodegradability of dextrin derivatives

Following their use, all the surfactants which were used as dyeing auxiliaries were passed quantitatively into wastewater. Because of this fact, the constant input of surfactants into the environment requires a particular ecological characterization of this class of compounds. The results of total biodegradation of dextrin derivatives prepared in this study are shown in Figure 3. Apparently, these are considerably more highly biodegradable because they would be the natural foods of bacteria present in sewage or raw river water.

Effect of dextrin derivatives on cotton dyeing

Direct dyes are widely used in dyeing cotton because of their ease of application and low cost. Cotton in water is usually negatively charged through ionization of certain groups in their molecules, and this charge tends to repel the negative anionic direct dyes. Some of the electrolytes are added at later stages of the dyeing process to neutralize the charge and thus allows the direct dyes to enter the cotton fibre faster. However, when the dyes are taken up at a rate by the cotton being dyed, the final dyeing is likely to be uneven. In this case, a technique that consists of adjusting the temperature of the dyeing process and the amount of electrolytes added can be used to produce evenly dyed cotton.⁸ Optimum operation of this technique depends on the equipment, the form of the textile, and the rates of exhaustion of the dyes used in the dyeing process.⁹ Since implementation of this technique is tedious and noneconomical, the use of auxiliaries for retarding or exhausting the dyeing

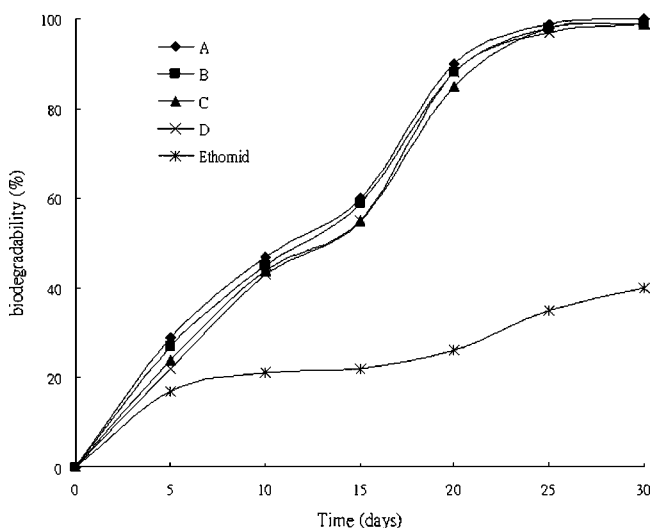


Figure 3 Biodegradability of dextrin-derivative surfactants (A: decyl; B: lauryl; C: myristyl; D: stearyl).

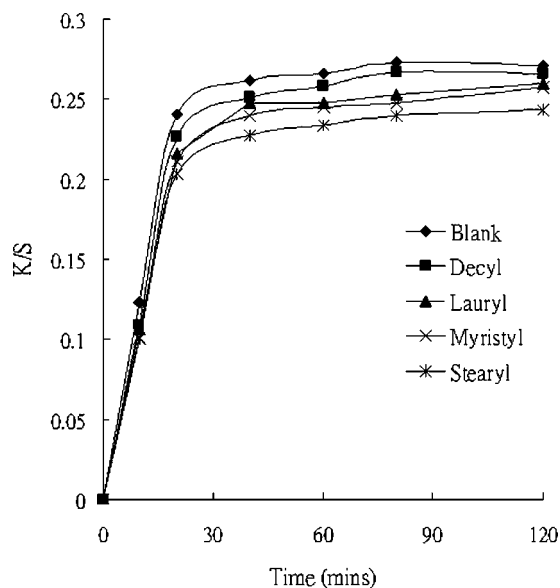


Figure 4 Dyeing dotton with Direct Blue 86.

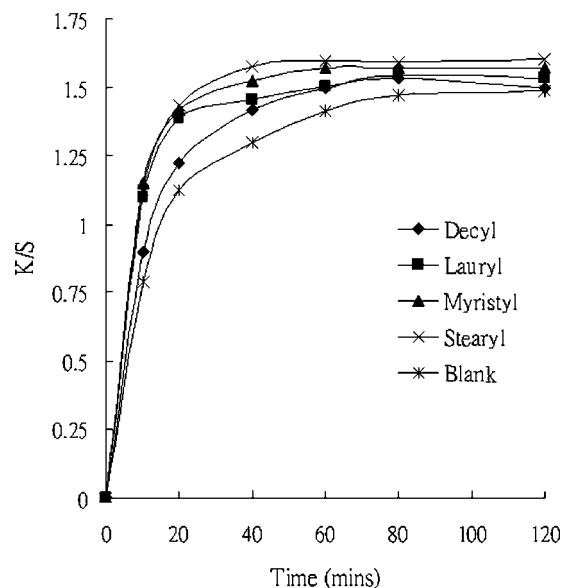


Figure 6 Dyeing dotton with Direct Red 83.

process is indispensable.¹⁰ Figures 4, 5, and 6 depict the rate of dyeing cotton with three direct dyes at 90°C in the presence of the dextrin derivatives. In the case of Blue 86, the presence of the surfactant retards the rate of dyeing. On the other hand, in the cases of Orange 39 and Red 83, the presence of the surfactants increases the rate of dyeing.

Interaction between dextrin derivatives and direct dyes

It is generally accepted that the interactions of dye and surfactant in the dyeing bath is an important factor which affects the rate of dyeing.¹¹⁻¹⁴ The interac-

tion between the direct dye and the dextrin derivative was studied spectrophotometrically. The results of the effect of different derivative concentrations on the absorbance at λ_{\max} in constant concentration of three direct dyes are shown in Figures 7, 8, and 9. In the cases of Orange 39 and Red 83, the absorbance of the direct dyes at λ_{\max} increases without the shift of wavelength when the concentration of the surfactant increased. However, in the case of Blue 86, increase of

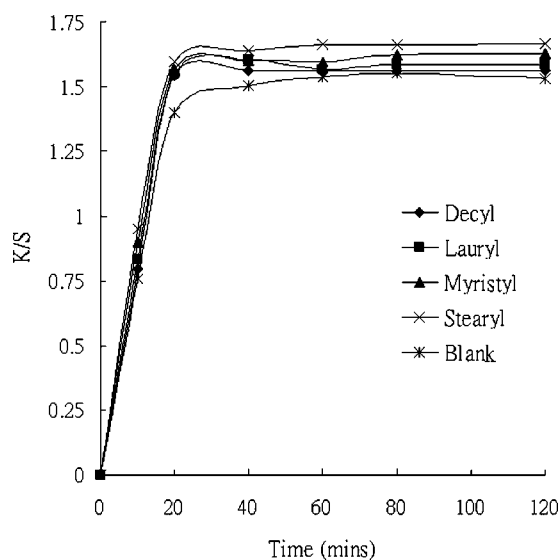


Figure 5 Dyeing dotton with Direct Orange 39.

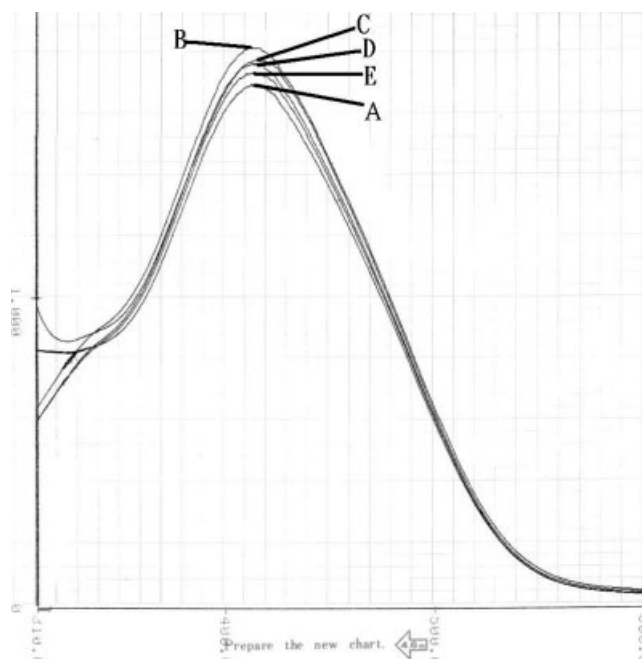


Figure 7 Interaction between Orange 39 and lauryl dextrin derivative: (dye: 2.5×10^{-4} M, A: blank, B: 2.5×10^{-4} , C: 1×10^{-4} , D: 5×10^{-5} , E: 2.5×10^{-5}).

surfactant concentration yielded a decrease of absorbance at λ_{\max} . None of the shift in wavelength in all cases indicate the absence of dye-surfactant complex apparently.

It is generally accepted that the self-association of direct dyes occurs in the dyeing bath and in the pores of cotton fibers.¹³ UV-vis absorption spectra of the dyes in aqueous solution are known to be directly proportional to the number of unassociated molecules.¹³⁻¹⁶ When the dye concentration remains constant, a decrease in absorbance indicates that aggregation of the dye molecules has occurred in the solution. The results shown in Figures 7 and 8 for the Orange 39 and Red 83 dyes, respectively, suggest that the increase of absorbance is probably due to the disaggregation of the dyes in the presence of surfactants. These results are consistent with the observed rate decrease when dyeing cotton in the presence of surfactant, as shown in Figures 5 and 6. Since the disaggregated dye has more affinity toward cotton fiber than the aggregated dye does, addition of the surfactant in the dyeing bath causes the disaggregation of the dyes to occur and, consequently, increases the dyeing rate. On the other hand, the result of the spectrophotometric spectrum shown in Figure 9 reveals that a molecular interaction between the dye and the surfactant has occurred. The decrease at 620 nm in the presence of the surfactants suggests that formation of either dye aggregation or a dye-surfactant complex can effectively decrease the concentration of disaggregated dye in the solution. The formation of dye aggregates would agree with the results shown in Figure 4,

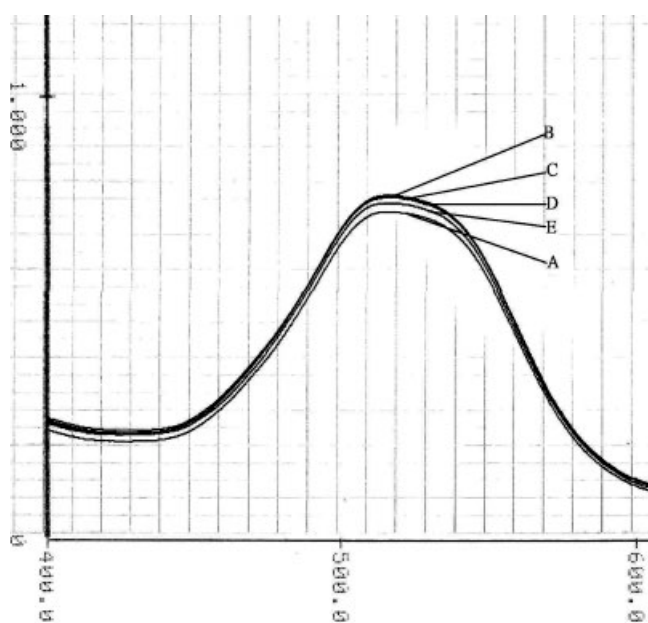


Figure 8 Interaction between Red 83 and lauryl dextrin derivative (dye: 2.5×10^{-4} M, A: blank, B: 2.5×10^{-4} , C: 1×10^{-4} , D: 5×10^{-5} , E: 2.5×10^{-5}).

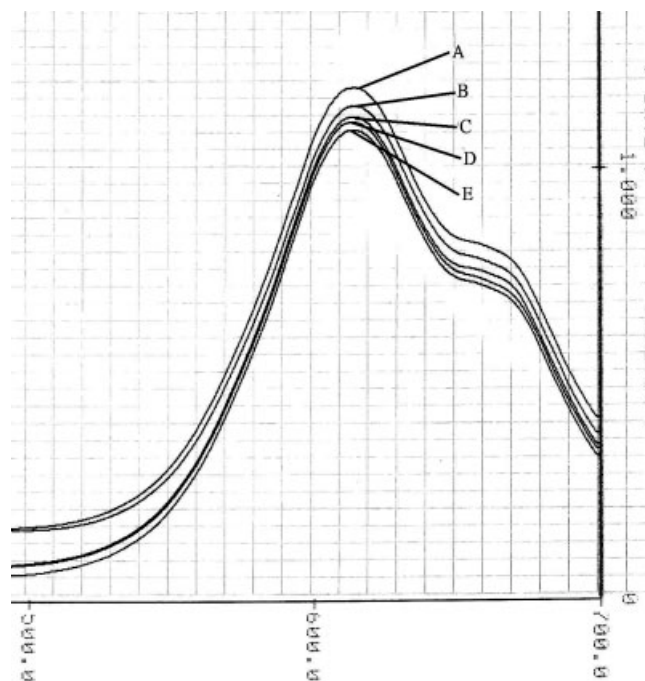


Figure 9 Interaction between Blue 86 and lauryl dextrin derivative: (dye: 2.5×10^{-4} M, A: blank, B: 2.5×10^{-4} , C: 1×10^{-4} , D: 5×10^{-5} , E: 2.5×10^{-5}).

in which the dyeing rate is slower in the dyeing solution containing the surfactant.

CONCLUSIONS

The results of the influence of a series of biodegradable dextrin-derivative surfactants on the direct-dyes cotton-dyeing system have been given. It was found that these surfactants exhibit good biodegradable properties and the presence of these surfactants in direct-dyeing solution can retard or increase the rate of cotton dyeing, depending on the formation of the disaggregated or more aggregated direct dyes in dye-surfactant systems and the degree of aggregation of direct dyes influencing the rate of cotton dyeing.

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