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Dyeing of protein fiber in a reverse micellar system

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Abstract

Dyeing of protein fiber in non-aqueous media has been investigated using a reverse micellar solution as a dye bath. Conventional acid dye and direct dye solubilized in the interior of reverse micelle was satisfactorily adsorbed on silk even without the presence of auxiliary. It has become obvious that adsorption manner of anionic dye on silk in this system is similar to that in aqueous system. On the other hand, dyeing property of wool with anionic dye in a reverse micellar system was found to be lower than that of silk because of the low fiber swelling. We have found that reactive dyes also have a high ability to adsorb on fiber in a reverse micellar system. Further, fixation of reactive dye on fiber could be attained in reverse micellar system. Fixing ratio of reactive dye on fiber in this system was almost perfect.

Keywords: Reverse micelle; Silk; Wool; Dyeing

1. Introduction

Conventional dyeing and subsequent washing processes are generally performed in water-based dye bath. However, waste aqueous effluent containing colored compounds and concentrated electrolytes cause serious environmental problems. In recent years, new concepts in the dyeing technology that avoid the use of water are being evaluated. Supercritical fluid dyeing [1] is one of the notable techniques to overcome these problems. According to the previous reports, synthetic fibers such as polyesters, polyamides etc., could be dyed satisfactorily with disperse dyes in supercritical carbon dioxide [2]. Unfortunately, effective dyeing method of natural fibers such as cotton, wool, silk etc., with conventional water-soluble dyes in super-critical fluid has not been established yet.

In our previous study, we have investigated the possibility of dyeing fabrics in reverse micellar system using direct dye and cotton as a simple dyeing model [3]. Reverse micelle has the remarkable property to solubilize a small amount of water at the interior of the micelle and to provide a stable aqueous microenvironment, so-called water-pool, in non-aqueous media. Moreover, reverse micelle has a potential to solubilize a variety of hydrophilic substances such as dye, enzyme etc., in water-pool. If water-soluble dye solubilized in a water-pool could be adsorbed on fiber effectively, this system may be applied to the new dyeing process in non-aqueous media, which would provide one of the possibilities for the replacement of

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the conventional aqueous dyeing system. In fact, our previous study demonstrated that direct dye in a reverse micellar system was satisfactorily adsorbed on cellulose fiber in a similar manner as that in a aqueous system [3]. However, useful knowledge about the dyeing mechanism of protein fiber in this system has not been obtained yet.

In this study, we have investigated the dyeing property of protein fiber, silk and wool, in a reverse micellar system. Acid dye, direct dye, and reactive dye were applied for the evaluation of dyeing protein fiber in a reverse micellar system. In the dyeing with reactive dye, the fixation of dye on fiber in a reverse micellar system was also investigated.

2. Experimental

Surfactant used in this study was sodium bis-2-ethylhexylsulphosuccinate (Aerosol-OT, AOT). AOT was purchased from Nacalai Tesque Co., Ltd. and was used without further purification. Initial water content in AOT was found to be 0.7% (w/w) through Karl Fisher titration. Isooctane (Nacalai Tesque Co., Ltd.,) and all other chemicals used in this study were of reagent grade. Dye liquors were prepared by an injection of prescribed volumes of aqueous dye solution to AOT/isooctane solutions. After an injection of aqueous dye solution, the reverse micellar solutions were gently stirred for few minutes until the solutions became transparent. Unless otherwise noted, aqueous dye solution was prepared with ion-exchange water. The amount of solubilized water in the reverse micellar system was adjusted so that the molar ratio of injected water to AOT should be 30. Dyes used this study were C.I. Acid Orange 7 (Tokyo Kasei Kogyo Co., Ltd.), C.I. Acid Blue 83 (Tokyo Kasei Kogyo Co., Ltd.), C.I. Direct Red 28 (Tokyo Kasei Kogyo Co., Ltd.), and C.I. Reactive red 2 (Nippon Kayaku Co., Ltd.). Fabrics used in this study were silk habutae and wool muslin. Theses fabrics were purchased from Shikisen-sha Co. Ltd., and were further pretreated in boiling water for 1 h before use. Dyeing of fabrics in the reverse micellar system was carried at 313 K for 24 h with bath ratio 100:1 in order to attain equilibrium exhaustion. In the preliminary experiments, we have confirmed that equilibrium exhaustion of dye on the fiber in this system can be attained within 24 h. In the dyeing with reactive dye, subsequent fixation of adsorbed dye on the fiber was attained using another reverse micellar solution that contains lithium hydroxide instead of aqueous dye solution. After the fixing step, unfixed reactive dye on cotton was completely removed by the soaping in boiling water with 1% (w/w) non-anionic surfactant (Triton X-100) and subsequent washing with 25% aqueous pyridine solution. The color depth of dyed fabric was estimated from the reflectance of the dyed fiber mass measured with the Minolta CM-1000 spectrophotometer. The color depth, K/S value, was calculated using the Kubelka–Munk equation. In this paper, dyeability of dye on fiber was evaluated with K/S value because a linear relationship between K/S value and percentage exhaustion of dye on the fiber could be observed in the preliminary experiments.

3. Results and discussion

Fig. 1 shows the color depth of the silk fabric dyed with acid dye (C.I. Acid Orange 7) in reverse micellar system. In order to compare the effect of dyeing in a reverse micellar system, dyeing in an aqueous system was carried out following to the conventional method. In the reverse micellar system, an influence of acid on dyeability was also investigated using acidic reverse micellar solution. Acidic reverse micellar solution that contains acidic aqueous dye

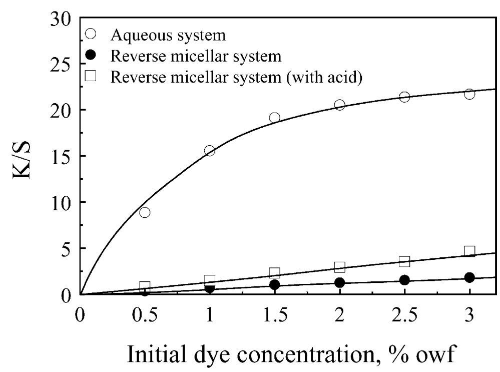

Fig. 1. Dyeability of acid dye (C.I. Acid Orange 7) on silk in an aqueous and a reverse micellar system.

solution was prepared using pH-controlled (pH = 3) buffer solution instead of ion-exchange water. As shown in Fig. 1, color depths of silk fabrics dyed in a reverse micellar system are much shallower than those in an aqueous system. Unfortunately, low dyeability in a reverse micellar system has hardly improved even if acidic reverse micellar solution is applied. These results are quite different from the results in our previous report [3]. In our former study, we have found that adsorption of direct dye on cellulose fiber, cotton, in a reverse micellar system is very excellent compared to that in an aqueous system. In a reverse micellar system, water-soluble dye is not solubilized in bulk organic media but solubilized in a water-pool. Therefore, we assumed that high concentrated dye solution in a water-pool produced high dyeability of direct dye on cotton in this system. The opposite results obtained in this study may be attributed to the competitive adsorption between dye and surfactant molecule on fiber. In general, large molecular direct dye that has substantivity to fiber would have a high affinity to fiber substrate compared to general acid dyes. In particular, C.I. Acid Orange 7 used in this study is well known as a fairly small molecular dye. In fact, the AOT molecule has intermediate molecular weight between C.I. Acid Orange 7 and general direct dyes. If AOT molecule were preferentially adsorbed on silk compared to C.I. Acid Orange 7, adsorption of C.I. Acid Orange 7 would be prevented by previously adsorbed AOT molecule. In order to evaluate the possibility of competitive adsorption between dye and surfactant molecule, a similar dyeing process was carried out using direct dye. Fig. 2 shows the results of dyeing silk fabrics dyed with direct dye (C.I. Direct Red 28) in aqueous and reverse micellar system. Since an effect of acid on dyeability was scarcely observed in Fig. 1, aqueous dye solution prepared with ion-exchange water was applied in the following dyeing. As shown in Fig. 2, dyeability of dye on silk in a reverse micellar system is remarkably improved. The color depth of silk fabrics dyed with direct dye (C.I. Direct Red 28) comes up to the equivalent level to those of acid dye (C.I. Acid Orange 7) in an aqueous system. Direct dye that essentially has low affinity on silk in an aqueous system seems to be effectively adsorbed on silk in a reverse micellar system. Effect of both higher affinity with large dye molecule and highly concentrated dye solution in water-pool would produce high dyeability of direct dye on silk in a reverse micellar system. If competitive adsorption between dye and surfactant molecule is the greatest factor in the dyeing in a reverse micellar system, acid dye that has a larger molecular structure than surfactant may also have suitable affinity on the fiber. Fig. 3 shows the results of dyeing silk with another acid dye in reverse micellar system. In this case, C.I. Acid Blue 83 that has a bulky molecular structure compared to the AOT molecule was applied. As shown in Fig. 3, C.I. Acid Blue 83 is effectively adsorbed on silk even without the presence of acid. Color depth of silk fabric dyed with C.I. Acid Blue 83 is approximately equivalent to that with direct dye, indicating that

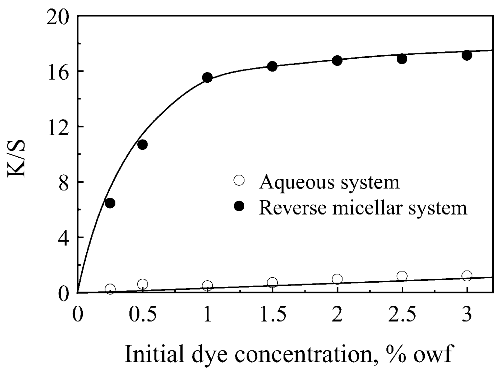

Fig. 2. Dyeability of direct dye (C.I. Direct Red 28) on silk in a reverse micellar system.

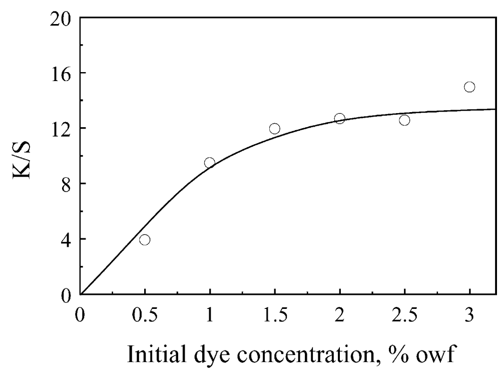

Fig. 3. Dyeability of acid dye (C.I. Acid Blue 83) on silk in a reverse micellar system.

adsorption of a large molecular acid dye proceeds in a similar manner to the adsorption of direct dye. From these results, affinity of dye molecule on fiber must be higher than that of surfactant molecule in order to obtain satisfactory dyeability in a reverse micellar system. Fig. 4 shows adsorption isotherm of direct dye (C.I. Direct Red 28) on silk in a reverse micellar system. In the logarithm form of adsorption isotherm, a linear relationship can be obtained, indicating that adsorption of direct dye on silk in a reverse micellar system proceeds with the substantivity of dye on fiber. As a result, adsorption follows a Freundlich manner just like the relationship between direct dye and cellulose fiber in an aqueous system. Fig. 5 shows adsorption isotherm of acid dye (C.I. Acid Blue 83) on silk in a reverse micellar system. Adsorption manner of acid dye on silk is quite different from that of direct dye.

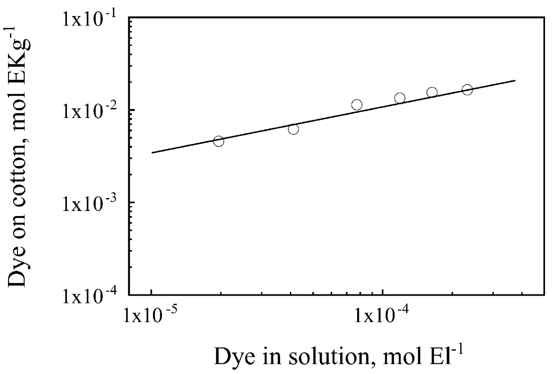

Fig. 4. Adsorption isotherm of acid direct dye (C.I. Direct Red 28) on silk in a reverse micellar system.

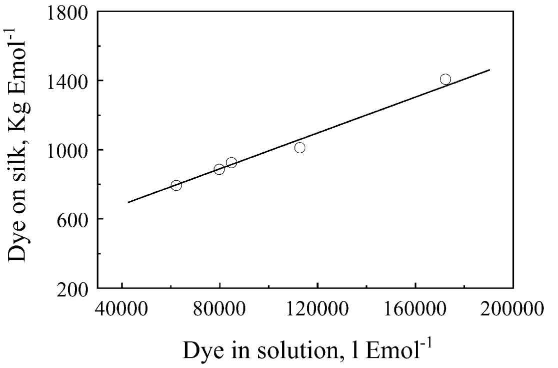

Fig. 5. Adsorption isotherm of acid dye (C.I. Acid Blue 83) on silk in a reverse micellar system.

As shown in Fig. 5, a reciprocal form of adsorption isotherm shows a linear relationship. These results obviously indicate that adsorption of acid dye on silk in a reverse micellar system proceeds at the particular dyeing site on fiber and follows a Langmuir manner. In this way, fundamental adsorption manners of both direct dye and acid dye in a reverse micellar system are similar to those in an aqueous system. Therefore, dyeing in a reverse micellar system can be assumed to proceed between fiber and a small amount of dye solution in a water-pool. Bulk amount of organic solvent present in the system seems to be independent of the dyeing process.

Fig. 6 shows the results of dyeing wool with acid dye in a reverse micellar system. In this case, C.I. Acid Blue 83 has been applied as a large molecular acid dye since it has been found that small dye molecule has little ability to overcome competitive adsorption with a surfactant molecule. As shown in Fig. 6, dyed silk fabrics have comparatively poor color depth compared to those of silk fabrics (Fig. 3). Fig. 7 shows the results of a similar investigation when direct dye (C.I. Direct Red 28) is applied. Dyeability of direct dye on wool in this system is also low, as well as that of C.I. Acid Blue 83. In the dyeing of wool with this system, another factor, other than the competitive adsorption between dye and surfactant molecule, seems to be present. Low dyeing property of wool in a reverse micellar system may be attributable to the characteristic structure of the wool fiber. In contrast to the silk fiber, the surface of the wool fiber is covered

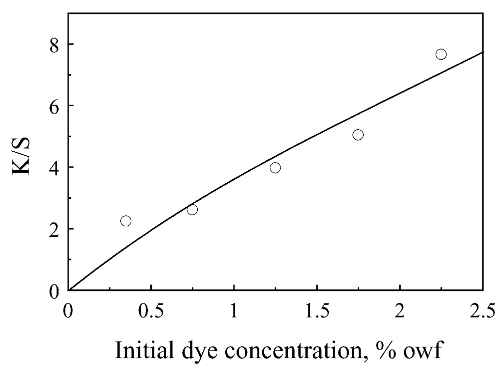

Fig. 6. Dyeability of acid dye (C.I. Acid Blue 83) on wool in a reverse micellar system.

with highly hydrophobic cuticle cells. In the conventional water-based dyeing process, dyeing of wool is performed under high temperature (371 K); under these conditions a large amount of hot water swells the non-keratinous proteins of the cell membrane complex between the cuticle and cortical cells, and also the non-keratinous endocuticle, moving them apart and allowing access of the aqueous dye solution into the bulk of the fiber. On the other hand, the gravimetric ratio of water in a reverse micellar system to fabric can be estimated to be 1:1. Therefore, dyeing under low temperatures (e.g. 313 K) with a small amount of water may not have sufficient effect on the cuticle cells to achieve access into the fiber. Consequently, migration of dye into the fiber would be restricted to surfaces areas of the wool fiber. In order to attain high dyeing property of wool in reverse micellar system, modification of the experimental condition such as the addition of a swelling agent and the treatment at higher temperature may be necessary.

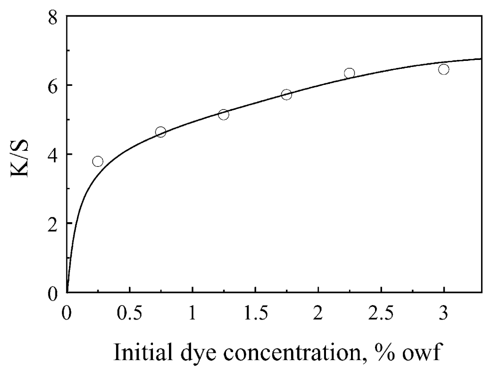

Fig. 7. Dyeability of direct dye (C.I. Direct Red 28) on silk in a reverse micellar system.

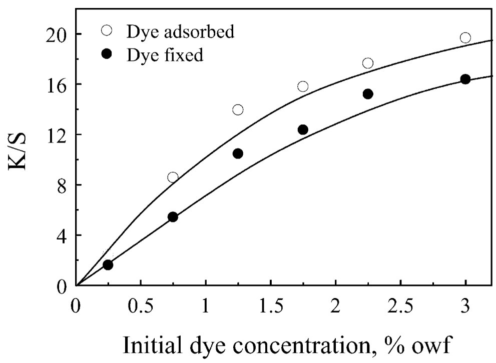

Fig. 8. Adsorption and fixation of reactive dye (C.I. Reactive Red 2) on silk in a reverse micellar system.

Fig. 8 shows the results of dyeing silk with reactive dye in a reverse micellar system. In order to evaluate the effect fixing with this system, color depth of dyed silk fabric before and after the fixing process was presented. As shown in Fig. 8, reactive dye has a high ability to adsorb on silk. Moreover, the fixing ratio of reactive dye on silk reaches an adequate level (80–90%). In general, reactive group in a reactive dye molecule would react with both fiber substrate and water competitively when enough water is present in the system. On the other hand, the amount of water present in a reverse micellar system is less than one hundredth compared to that of a conventional water-based dye bath. As a result, reactive dye in a reverse micellar system would react with fiber effectively compared to aqueous system.

From the results of this study, a reverse micellar system seems to have high potential for the application to dyeing media. The reverse micellar system that does not require special working conditions is of interests considered from the viewpoints of the energy saving, environmental friendliness, safety of working circumstance, etc. In the present industrial dyeing system, organic solvent is not necessarily a suitable media. Nevertheless, the development of a solvent recovery system and the application of supercritical fluid media may overcome this problem. Further accumulation of advanced knowledge based on the results of this investigation would extend the possibilities of the research and the practical application of reverse micelles.

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