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Chemical fixation of disperse dyes on protein fibers

K. Sawada [a,*], M. Ueda [b]

[a] *Department of Integrated Life, Osaka-Seikei College, 3-10-62 Aikawa Higashiyodogawa-ku, Osaka 533-0007, Japan*
[b] *Department of Home Economics, Kobe Women's University, 2-1 Aoyama, Higashisuma, Suma-ku, Kobe 654-8585, Japan*

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Abstract

Chemical fixation of disperse dyes on protein fibers has been examined in non-aqueous dyeing media. Disperse dyes that contained amino group within a molecule had high potential to react with protein fibers. Selection of dyeing medium gave marked influence on the dyeability of dyes on fibers. 4-(Dimethylamino)-pyridine (DMAP) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were also examined as auxiliaries for acylation and dehydration, respectively. Effects of DMAP on the reaction between disperse dyes and protein fibers were higher than that of DCC.

Keywords: Disperse dye; Dyeing; Protein fiber; Peptide bond; Non-aqueous system

1. Introduction

In recent years, new concepts in dyeing technology which avoid the use of water have been investigated. In particular, dyeing in supercritical carbon dioxide [1] has been identified as an attractive alternative to water-based dyeing. For example, it has become clear that synthetic fibers such as polyesters and polyamide can be dyed satisfactorily with disperse dyes in such a medium [2,3]. Unfortunately dyeing of natural fibers such as cotton, wool and silk in this system is very difficult since conventional water-soluble dyes cannot be dissolved in supercritical carbon dioxide. In order to overcome this problem, a number of investigations have been undertaken. For example, prior modifications of dyes or fibers make the dyeing of natural fibers practicable [4–6]. However, poor handle, prolonged dyeing time and high energy consumption seem to be major problems even if the dyeing is attained. Of course, these problems make the industrial application of this system unsuitable.

In our previous study, we have also proposed the new method for dyeing natural fibers in non-aqueous media utilizing reverse micellar systems. Fundamental investigations of dyeing natural fibers from reverse micellar systems were carried out in organic media [7–9]. Cotton, silk and wool fabrics were satisfactorily dyed in deep shade with conventional reactive dyes and acid dyes even in organic solvents. Further, utilization of reverse micellar systems was applied to supercritical carbon dioxide medium [10–15]. Natural fibers in supercritical carbon dioxide were also satisfactorily dyed with conventional water-soluble dyes in a similar manner to organic media. Unfortunately, some problems are still left. Removal of surfactant molecules that adsorbed on fabrics is difficult. In addition, color fastness is not necessarily excellent compared to fabrics dyed in water-based media. In order to overcome these problems, further modification of dyeing method is necessary.

In this study, we investigated new method for dyeing natural fibers in non-aqueous media using conventional disperse dyes. Wool fibers (protein fibers) were used as representative example of natural fibers. Our strategy of dyeing protein fibers in non-aqueous media is the formation of covalent bond between fibers and dyes. Then, we examined the possibility for peptide bond or ester bond formation between protein fibers and disperse dyes. The purpose of this study is an accumulation of fundamental knowledge of chemical reactions between

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[*] Corresponding author. Tel.: +81 6 6829 2561.
E-mail address: sawada-k@osaka-seikei.ac.jp (K. Sawada).

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fibers and dyes in non-aqueous media. In order to simplify the system, dyeing was carried out in organic media. We believe that this system is a good model for the future application in supercritical carbon dioxide medium. In the first half of this paper, screening of the suitable solvent for dyeing medium was discussed. In the latter half of this paper, effects of auxiliaries, 4-(dimethylamino)-pyridine (DMAP) and *N*, *N*′-dicyclohexylcarbodiimide (DCC), on the dyeability of dyes were evaluated.

2. Experimental

2.1. Chemicals

Fabrics used in this study were wool muslin and ware obtained from Shikisen-sha Co., Ltd. Disperse dyes used were C.I. Disperse Violet 26, C.I. Disperse Blue 3 and C.I. Disperse Blue 14. These dyes were all obtained from Aldrich Chemical Co., Ltd. Disperse dyes were all purified by recrystallization before use. 4-(Dimethylamino)-pyridine (DMAP) was used as an auxiliary for acylation and was obtained from Kanto Chemical Co., Inc. *N*,*N*′-Dicyclohexylcarbodiimide (DCC) was used as a promoter of dehydration and was obtained from Merck Ltd. All other chemicals used were obtained from Kanto Chemical Co., Inc. and were used as received.

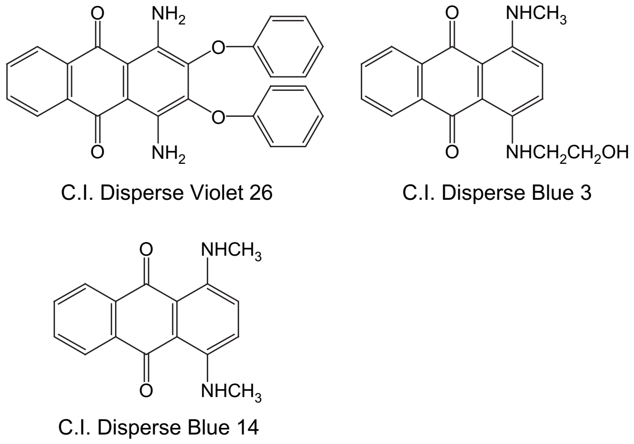
2.2. Procedure

All fabrics used were pretreated in boiling water for 1 h before dyeing. Dyeing was carried out in a closed stainless steel vessel using Mini-colour 12E (Texam Co., Ltd.) dyeing machine under definite time and temperature. Bath ratio was all adjusted to 1:50. Unfixed dyes on fabrics were completely removed by soaping in boiling water with 1% (w/w) nonionic surfactant (Triton X-100) followed by washing with 25% aqueous pyridine solution. Dyeability of dyes on fabrics was evaluated as surface reflectance of the fabric. Surface reflectance of fabrics was measured with the Minolta CM-1000 spectrophotometer (illumination diameter: 12 mm) under illuminant D65 using 10° observer.

3. Results and discussion

3.1. Determination of dyeing medium

Chemical structures of used dyes are shown in Fig. 1. As shown in Fig. 1, each dye has anthraquinone skeleton in a molecule. These dyes were selected as a representative example which has a possibility to form different chemical bond with fibers. C.I. Disperse Violet 26 has a possibility to form peptide bond from amino group in dye molecules and carboxyl group in fibers. On the other hand, C.I. Disperse Blue 3 has a possibility to form ester bond from hydroxy group in dye molecules and carboxyl group in fibers. C.I. Disperse Blue 14 is a reference standard which has little possibility to form covalent bond.



C.I. Disperse Violet 26

C.I. Disperse Blue 3

C.I. Disperse Blue 14

Fig. 1. Chemical structure of disperse dyes.

Table 1 shows experimental data of the solubility of these dyes in various kinds of organic solvents. In order to screen suitable dyeing media, organic solvents shown in Table 1 were restricted to the data that showed common solubility for three dyes. In Table 1, solubility of DMAP and DCC in these solvents was also summarized. As shown in Table 1, organic solvents that dissolve DMAP have an ability to dissolve DCC. In addition, organic solvents that can dissolve both DMAP and DCC were found to be good solvents for the used disperse dyes. This experimental result is a good advantage in the selection of suitable organic solvents, because solubility of dyes in a medium (organic solvent) is one of the important factors to characterize dyeability. In order to narrow down the suitable solvent more detail, preliminary dyeing test was carried out without using DMAP and DCC.

Fig. 2 compares surface reflectances of wool fabrics dyed with C.I. Disperse Violet 26 in various kinds of organic solvents. The purpose of this preliminary dyeing test was the determination of the organic solvents that had a potential to give high yield without auxiliaries. In Fig. 2, experimental data that showed more than 40% reflectance were omitted. Each organic solvent shown in Fig. 2 completely agreed with organic solvents which had high ability to dissolve disperse dyes. In

Table 1
Solubility of disperse dyes, DMAP and DCC in various kinds of organic solvents

	DMAP	DCC	Dye
Benzene	+	+	+
Dichloromethane	++	++	++
Chlorobenzene	+	+	+
n-Hexane	−	−	+
Chloroform	++	++	++
Cyclohexane	−	−	+
Toluene	−	+	+
Diethyl ether	+	−	−
Cyclohexanone	−	−	+
DMSO	++	++	++
THF	++	++	++
DMF	++	++	++

++: Very soluble; +: soluble; −: insoluble or slightly soluble.

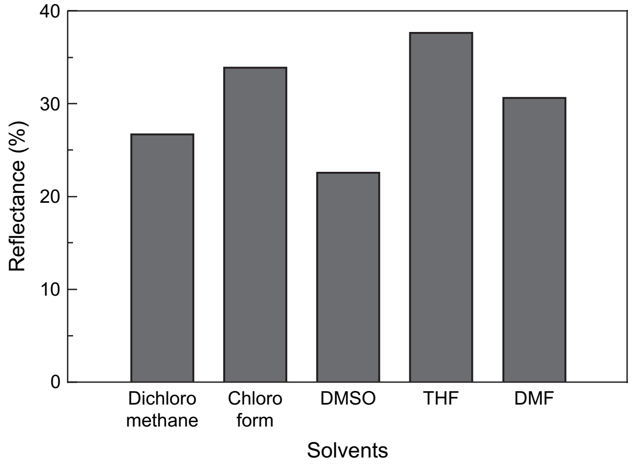


Fig. 2. Comparison of surface reflectance of wool fabrics dyed with C.I. Disperse Violet 26 at 100 °C for 1 h.

particular, surface reflectance of wool fabrics dyed in DMSO is significantly low compared to those in other organic solvents. From these data, DMSO seems to be a suitable dyeing media in this dyeing method.

3.2. Chemical fixation of disperse dye on protein fiber

Based on those data, investigations for raising the reactivity between disperse dyes and fibers have been carried out using DMSO as a dyeing medium. Fig. 3 shows effects of DCC on the dyeability of dyes. In this case, DMAP was not present in the system. Dyeing temperature and time were adjusted to 100 °C and 1 h, respectively. As shown in Fig. 3, surface reflectances of wool fabrics dyed with C.I. Disperse Blue 14 were not varied for all range of concentrations of DCC. C.I. Disperse Blue 14 that has not contained reactive functional group within a molecule seems to have no ability to react with fibers. Slight coloration of fibers would be derived from soiling. Similar results were also observed when C.I. Disperse Blue 3 was used, indicating that DCC had little effect to accelerate chemical reaction between dye molecules and fibers. However, surface reflectance of wool fabrics dyed with C.I. Disperse Blue 3 was lower than those with C.I. Disperse Blue 14. These differences would be attributed to the differences of the chemical structure of the dye molecule. The hydroxy group in the C.I. Disperse Blue 3 molecule would react with a carboxyl group in a fiber without the help of an auxiliary. Unfortunately, reactivity of dyes on fibers seems not to be excellent judging from the value of surface reflectance. On the other hand, variations of surface reflectance of wool fabrics dyed with the C.I. Disperse Violet 26 were different from those with others. Surface reflectance was decreased with increasing the concentration of DCC and reached plateau. However, those values are also insufficient as deep color dyeing.

Fig. 4 shows effects of DMAP on the dyeing of wool fabrics in this system. In this case, DCC was not present in the system. Dyeing temperature and time were adjusted to 100 °C and 1 h, respectively. The data are similar to those in Fig. 3. Surface reflectance of wool fabrics dyed with C.I. Disperse Blue 3 and C.I. Disperse Blue 14 is nearly constant at higher value. DMAP as an auxiliary for acylation seems to have little effect for the reactivity between these dyes and fibers. On the other hand, the data from the dyeing with C.I. Disperse Violet 26 were different. An increase in the concentration of DMAP gave a decrease in the surface reflectance of dyed wool fabrics. More remarkable are the degree of the drop of surface reflectance and the low concentration of DMAP. Surface reflectance of wool fabrics falls to equal or less than 1/2 compared to that of the control. Further, minimum concentration of DMAP to make the surface reflectance fall to the constant value is ca. 1×10^{-4} mM. This concentration is 1000 times lower than that of DCC. In this way, DMAP seems to have high potential to form covalent bond (peptide bond) between amino group in a dye molecule and carboxyl group in a fiber.

In order to find optimal dyeing condition, further investigation has been carried out. Based on the above shown data, the auxiliary and the dye were restricted to DMAP and C.I. Disperse Violet 26, respectively. Fig. 5 shows the effect of dyeing

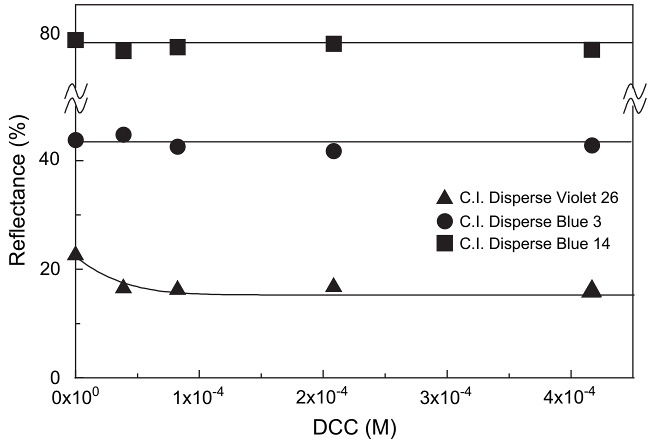


Fig. 3. Variations of surface reflectance of dyed wool fabrics as a function of the concentration of DCC.

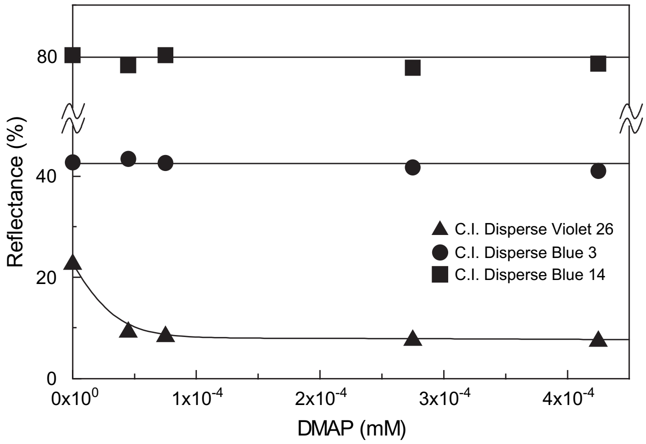


Fig. 4. Variations of surface reflectance of dyed wool fabrics as a function of the concentration of DMAP.

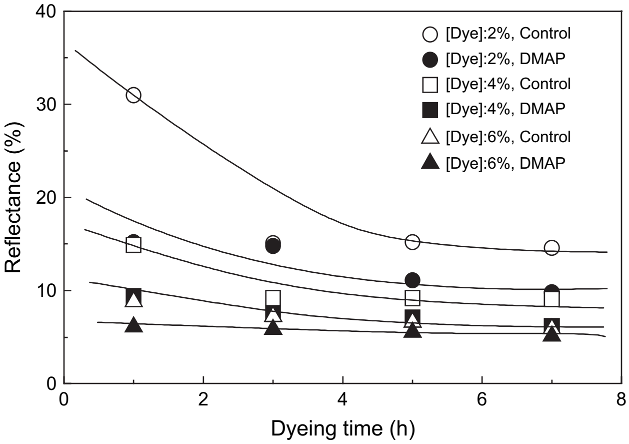


Fig. 5. Effects of dyeing time on the reactivity between fibers and C.I. Disperse Violet 26.

time on the dyeability of dyes on fabrics. In this case, three different concentrations of the dye were examined. As shown in Fig. 5, surface reflectance of wool fabrics dyed in the system with DMAP is lower than those without DMAP. Effect of DMAP on the color depth of dyed fabrics seems to become low with increasing dyeing time. In addition, positive effects of DMAP are not necessarily significant in the range of higher concentration of dyes. From these data, we can conclude that remarkable acceleration of peptide bond formation by DMAP is attained in the range of low concentration of dyes and short dyeing time. This result is a good advantage from the viewpoints of energy saving and the reduction of waste fluid.

Fig. 6 shows the effect of dyeing temperature on the dyeability of dyes on fabrics. In this case, DMAP and C.I. Disperse Violet 26 were used along with the previous experiment. As shown in Fig. 6, higher dyeing temperatures gave excellent dyeability of dyes. This result is the same as conventional dyeing with disperse dyes. Effect of DMAP on the dyeability of dyes was also observed. However, the differences between solid plot and open plot at the same temperature become narrow at the range of higher temperature. This means that spontaneous acylation reaction between dye molecules and protein fiber are accelerated by an increase of temperature. At the dyeing with 120 °C, effects of the thermal factor for acylation reaction are nearly equal to that of DMAP. In order to improve acylation by an effect of DMAP, lower dyeing temperature seems to be better. This dyeing condition is also a good advantage from the viewpoint of energy saving. Further, dyeing at low temperature would prevent the drop of handle of fabrics. Unfortunately, dyeability of dyes at the range of lower temperature is not excellent with this limited investigation. Further investigations for the improvement of reaction ratio at lower temperatures are necessary.

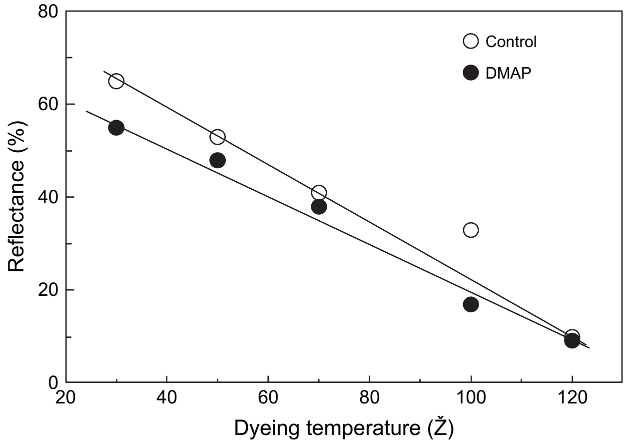


Fig. 6. Effects of dyeing temperature on the reactivity between fibers and C.I. Disperse Violet 26.

4. Conclusions

Dyeing of the wool fibers with conventional disperse dyes in non-aqueous media has been investigated using DMAP and DCC as auxiliaries for acylation and dehydration, respectively. A disperse dye that did not contain reactive functional group in a molecule had no ability to react with fiber even if auxiliary was present in the system. A disperse dye that contained hydroxy group in a molecule could be reacted with carboxyl group in a fiber, although the reactivity was low. On the other hand, a disperse dye that contained amino group in a molecule was effectively reacted with carboxyl group in a fiber with the help of DMAP. Effect of DMAP for acceleration of peptide bond formation was superior to that of DCC. Significant effect of DMAP was found at the range of low concentration of dyes, short dyeing time and low dyeing temperature. These dyeing conditions are favorable from the viewpoints of environmental protection.

In this study, organic solvents were used as a model of non-aqueous medium. Unfortunately, application of organic solvents would not be acceptable in the future industrial process. However, if organic solvents as a dyeing medium could be replaced with the supercritical fluid, the potential for industrial application of this technique would be greatly raised.

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