

Adsorption behavior of direct dye on cotton in non-aqueous media

K. Sawada^{a,*}, M. Ueda^b

^a*Department of Chemistry and Material Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*

^b*Department of Design Engineering and Management, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*

Received 12 October 2002; received in revised form 23 December 2002; accepted 21 January 2003

Abstract

Solubilization and adsorption behavior of direct dye on cotton in Aerosol-OT (AOT) reverse micellar system has been investigated. Cotton fabrics could be dyed in deep shade with direct dye from reverse micellar system without adding auxiliaries. Exhaustion of dye was almost perfect and was very superior to that in aqueous system. High exhaustion of the dye in reverse micellar system was attributed to the very low bath-ratio (water–fabric ratio) compared to the conventional aqueous dyeing process. It has become obvious that adsorption of direct dye on cotton in reverse micellar system is similar to that in aqueous system and follows a Freundlich manner.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Reverse micelle; Non-aqueous dyeing; Cotton; Direct dye

1. Introduction

Dyeing of textiles is generally performed in water-based media. Dyeing of the water-based methods and subsequent aqueous washing process, however, has undesirable environmental impact such as the discharge of chemical pollutant and of large amount of colored wastewater. In recent years, new concepts in the dyeing technologies that avoid the use of water as a solvent are being under investigation. Supercritical fluid dyeing is one of the representative examples for the alternative-dyeing technique [1]. According to the previous

reports, it has become obvious that synthetic fibers such as polyesters, polyamides, etc. could be dyed satisfactorily with disperse dyes [2]. On the other hand, dyeing of natural fibers such as cotton, wool, silk etc. with conventional hydrophilic dyes in the super critical fluid has not been established yet.

In our previous study, we have investigated the possibility of the application of non-aqueous media, i.e., reverse micellar system, to textile processing [3,4]. Reverse micelle has a 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 [5]. In some cases, hydrophilic substances such as enzyme can be solubilized

* Corresponding author. Tel./fax: +81-75-724-7563.
E-mail address: sawada@kk.chem.kit.ac.jp (K. Sawada).

in the water-pool without losing their activities [6]. Our previous investigation also demonstrates that the enzymes in the reverse micellar solution showed their activities and satisfied enzymatic textile processing could be achieved in the reverse micellar solution as well as in the conventional aqueous media. If the hydrophilic dye, similar to the case of the enzyme processing, can be solubilized in the water-pool of reverse micelle, this system may have high potential for the new dyeing process in non-aqueous media, which would provide one of the possibilities for the replacement of the conventional aqueous dyeing system.

In the present study, we have investigated the possibility of dyeing cotton in non-aqueous system, reverse micellar system, using direct dye as a simple dyeing model. In this paper, we report the solubilization and adsorption behavior of direct dye in reverse micellar system in detail.

2. Experimental

Surfactant used in this study was sodium bis-2-ethylhexylsulpho-succinate (Aerosol-OT, AOT). AOT was obtained 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. The quantity of solubilized water in the reverse micellar system was shown by the molar ratio of injected water to AOT, that is, $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$. Maximal w value without phase separation of AOT reverse micellar system attained in this study was ca. 60. 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. Dyeing of cotton fabrics were carried out with direct dye (CI Direct Red 28, Tokyo Chemical Industry Co., Ltd.) under the conditions at 313 K for 24 h with bath ratio 50:1.

3. Results and discussion

Fig. 1 shows the solubility limit of direct dye in reverse micellar system. As shown in Fig. 1,

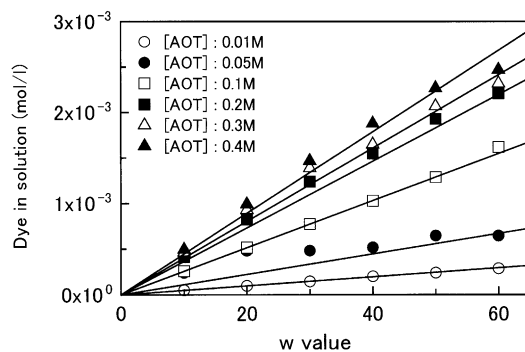


Fig. 1. Solubility limit of direct dye in reverse micellar system.

concentration of dye in the system increases with increasing w value. Since the size of micelle is known to enlarge with increasing quantities of added water [7], higher amounts of dye could be stably solubilized in the swollen water-pool. An increase of AOT concentration also brings about an increase of maximum solubility of dye in the system. These results would be related to an increase of total number of micelle in the system. In these experimental conditions, direct dye seems to be solubilized satisfactorily in the system even in organic media.

Fig. 2 shows the results of dyeing of cotton fabric with direct dye in reverse micellar system when w value is varied. In this study, we have confirmed that variation of the amount of injected water due to the variation of w value has negligible influence to the total bath ratio (50:1) because the amount of injected water is very small compared with that

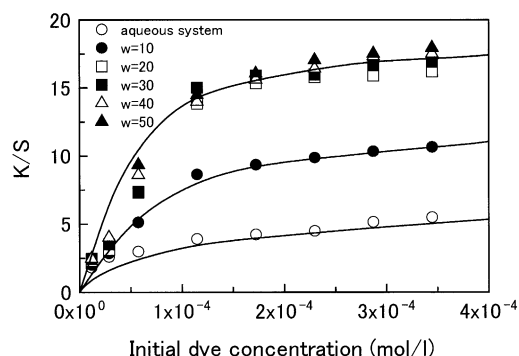


Fig. 2. Dyeability of direct dye in aqueous and reverse micellar system.

of organic solvent. In order to compare the effect of dyeing in reverse micellar system, the results of dyeing in aqueous system without an addition of electrolyte were presented. In Fig. 2, the color depth of dyed fabric was estimated from the reflectance of the dyed fiber measured with the Minolta CM-1000 spectrophotometer. The color depth, K/S value, was calculated using the Kubelka–Munk equation. As shown in Fig. 2, color depths of cotton fabrics dyed in reverse micellar system with low water content ($w=10$) are comparatively lower than those with higher w ranges ($w=20$ –50). In the low w range, cotton fiber may not be swollen satisfactorily due to a lack of free water. As a result, insufficient formation of pore in the fiber would prevent the diffusion of dye. Judging from the results in Fig. 2, surplus water present in the system did not seem to affect the dyeability of dye when the fiber is swollen with suitable amount of water. Another meaningful knowledge obtained from Fig. 2 is high dyeing property in reverse micellar system. As shown in Fig. 2, color depths of cotton fabrics dyed in reverse micellar system are much deeper than those in an aqueous system even without an addition of electrolyte. Aqueous dyeing media without the presence of electrolyte seems to have a low ability to reduce electrostatic repulsion between dye and the cotton substrate. In the reverse micellar system, on the other hand, ionic head-group of surfactant molecule may play a role of dyeing auxiliary. In order to elucidate adsorption mechanism and high dyeability of dye in the reverse micellar system, more detailed investigation is necessary.

Fig. 3 shows an adsorption isotherm of direct dye on cotton in aqueous and reverse micellar systems. In order to prevent insufficient swelling of fiber due to a lack of free water, the following investigations were performed at $w > 20$ ranges. As shown in Fig. 3, a logarithmic form of adsorption isotherm shows a linear relationship in both systems. Furthermore, the slope of linear plots obtained from reverse micellar system is the same as that from the aqueous system. These results obviously suggest that adsorption of direct dye on cotton in the reverse micellar system is similar to that in the aqueous system and follows a Freundlich

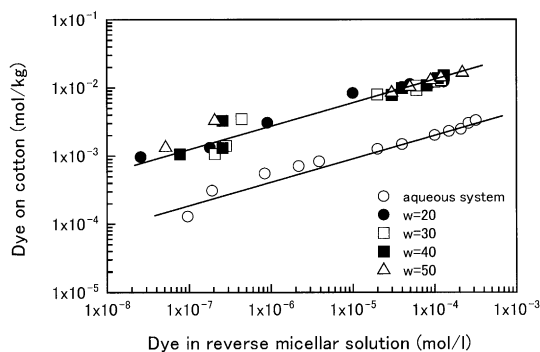


Fig. 3. Adsorption isotherm of direct dye on cotton in aqueous and reverse micellar system.

manner. It is very interesting that the adsorption manner of water-soluble dye (direct dye) in organic media is similar to that in the aqueous media. This interesting result may be explained in terms of the solubilizing condition of direct dye in the system. In the reverse micellar system, direct dye would not be solubilized in bulk organic media but in the water-pool. Bulk organic solvent in the system, therefore, can be considered not to act in any role to the adsorption of direct dye. In order to evaluate this hypothesis, a concentration of dye in reverse micellar system, i.e. overall system, is converted to that in water-pool. As shown in the converted adsorption isotherm of Fig. 4, linear plot obtained in the reverse micellar system completely fits on the extrapolated line of that in the aqueous system. These results obviously indicate an apparent high dyeability of dye in the reverse micellar system is produced by highly

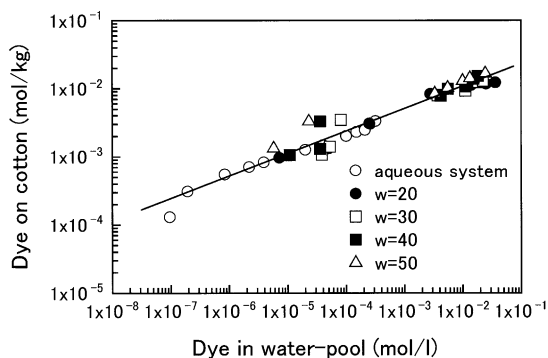


Fig. 4. Converted adsorption isotherm of direct dye on cotton in aqueous and reverse micellar system.

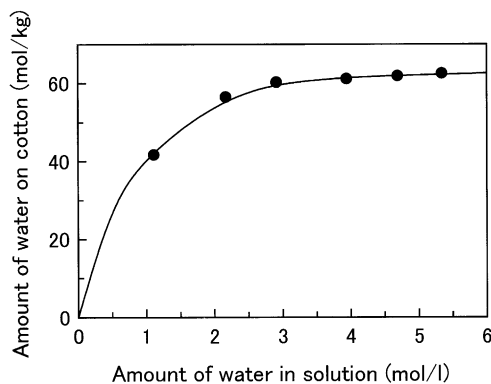


Fig. 5. Adsorption of water on cotton in reverse micellar system.

concentrated dye solution in the water-pool. Thus, dyeing of cotton with direct dye in the reverse micellar system can be regarded as a very low bath-ratio dyeing with highly concentrated dye solution.

Different from general water-based dyeing process, transport phenomenon of dye into the fiber in such a unique system would be accomplished together with the transport of a small amount of water in the water-pool. Therefore, mass transfer phenomenon of water in the system may also be an important factor to characterize the dyeing in the reverse micellar system. Fig. 5 shows adsorption isotherm of water on cotton in the reverse micellar system. The amount of equilibrium adsorption of water in the system was evaluated with Karl–Fisher titration. As shown in Fig. 5, the amount of water adsorbed on cotton significantly increases with increasing amounts of water in the

system and levels off at higher water content. The most striking result is the high amount of adsorbed water on cotton fabric, which reaches ca. 60 mol/kg, although left water in the system is no more than a few mol/l. These results obviously demonstrate that the adsorption property of water on cotton in the reverse micellar system is excellent. In the reverse micellar system, excellent transport phenomenon of a small amount of water in the system would cause remarkable augmentation of the chemical potential of dye in the water-pool. Consequently, apparent high dyeability of direct dye on cotton is attained.

References

- [1] Saus W, Knittel D, Schollmeyer E. Dyeing with supercritical carbon dioxide—an alternative to high-temperature dyeing of polyester. *Text Prax Int* 1992;47:1052–4.
- [2] Knittel D, Saus W, Schollmeyer E. Application of supercritical carbon dioxide in finishing process. *J Text Inst* 1993;84:534–52.
- [3] Sawada K, Tokino S, Ueda M. Bioscouring of cotton with pectinase enzyme in a non-aqueous system. *J Soc Dyers Color* 1998;114:355–9.
- [4] Sawada K, Ueda M. Effect of protease activity on a non-aqueous detergent system. *Txt Res J* 2000;70:166–71.
- [5] Fendler JH. *Membrane mimetic chemistry*. New York (USA): John Wiley & Sons; 1982.
- [6] Matinek K, Levashov AV, Klyachko N, Khmel'nitski YL, Berezin IV. Micellar enzymology. *Eur J Biochem* 1986; 155:453–68.
- [7] Zulauf M, Eicke HF. Inverted micelles and microemulsions in the ternary system H_2O /aerosol-OT/isooctane as studied by photon correlation spectroscopy. *J Phys Chem* 1979;83:480–6.