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Dyes and Pigments 61 (2004) 17–22

DYES and PIGMENTS

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Application of perfluoropolyether reverse micelles in supercritical CO_2 to dyeing process

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Received 12 April 2003; received in revised form 21 July 2003; accepted 11 August 2003

Abstract

Dyeing of wool fabrics with conventional acid dyes in a supercritical CO_2 has been investigated using a reverse micellar system. A reverse micelle composed of perfluoro 2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoic acid ammonium salt/CO_2/water had a high potential to solubilize conventional acid dyes and to dye wool fabrics in this system. It has found that dyeability of the acid dye on wool in this system take no influence of the density of CO_2. On the other hand, variation of dyeing temperature resulted in the remarkable differences of the dyeability of the acid dye on wool even though the solubility of dye in the system was not varied by the variation of temperature.

Keywords: Reverse micelle; Dyeing; Wool; Supercritical CO_2; Acid dye

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1. Introduction

Owing to environmental advantages of supercritical fluid, dyeing of fabrics in a supercritical fluid is recently noticed as an alternative dyeing method of the conventional water-based one. In particular, supercritical CO_2 (SC–CO_2) is an attractive alternative to both water and organic solvent since it is inexpensive, essentially nontoxic, nonflammable, requires relatively gentle critical conditions ($T_C = 31.1$ °C, $P_C = 7.38$ MPa), and can easily be recaptured and recycled after use. Unfortunately, SC–CO_2 is a poor solvent for a wide range of hydrophiles because of its low permittivity [1]. Dyeing of textile fibers in SC–CO_2, therefore, has been limited to synthetic fibers using SC–CO_2-soluble disperse dyes but the dyeing of natural fibers from this medium is still under development [2,3]. In order to dye natural fibers in a SC–CO_2, satisfactory solubilization of water-soluble dyes such as the acid dye and the reactive dye must be attained.

In our previous study, we have also examined the solubilization of water-soluble dyes in a non-aqueous media [4,5]. Our strategy is to solubilize the water-soluble dye in a SC–CO_2/reverse micellar system that involves dispersing a small amount of water in SC–CO_2. Reverse micelles have remarkable property to solubilize small amount of water at the interior of the micelle and to provide

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0143-7208/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2003.08.003

stable aqueous microenvironment, the so-called water-pool, in a non-aqueous media [6]. Therefore, reverse micelle has a potential to solubilize water-soluble dyes in a non-aqueous media. In fact, our previous study investigated the possibility of dyeing natural fibers from a reverse micellar system in SC–CO_2 using ethyleneglycol derivatives as a surfactant [7,8]. In that study, we found that wool and silk fabrics were effectively dyed with the conventional acid dye from a reverse micellar system in SC–CO_2 when significant amount of suitable co-surfactant was present in the system. However, we also pointed out that the necessity of the co-surfactant made it difficult to understand the characteristics of the system. In order to raise the potential of dyeing fibers from a reverse micellar system in SC–CO_2, simplification of the system is necessary. At the present stage, another promising surfactant that can apply to our purpose may be a group of perfluoropolyether (PFPE) derivatives. Since surfactant's that contains fluorocarbon tail within a molecule have low intermolecular interaction and surface tension compared with that contains hydrocarbon tail, the PFPE surfactant has a potential to dissolve in SC–CO_2 and to form thermodynamically stable reverse micelles [9–13]. Unfortunately, PFPE surfactants so far proposed are not commercially available at present, making it difficult for the practical applications. Based on these backgrounds, we have prepared suitable PFPE surfactant by the simple modification from the commercially available surfactant precursor.

In this paper, we report the possibility of dyeing wool with conventional acid dyes from a reverse micellar system in SC–CO_2 using the PFPE surfactant. An influence of the density of CO_2 and temperature on the dyeability of acid dyes has also been investigated.

2. Experimental

2.1. Chemicals

The surfactant used in this study was perfluoro 2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoic acid ammonium salt and was prepared by the same way as described before [14]. Carbon dioxide used was pure grade ($>99.9\%$) and was purchased from Sumitomo Seika Chemicals Co., Ltd. The dye used in this study was C.I. Acid Red 52 and was purchased from Tokyo Chemical Industry Co., Ltd. Fabrics used in this study were wool muslin cloth, which had been properly desized and scoured with conventional methods. These were purchased from Shikisen-sha Co. Ltd., and were further pretreated in boiling water for one hour before use. All other chemicals were purchased from Kanto Chemical Co., Inc. and were used after drying with molecular sieve 3A.

2.2. Procedure

High-pressure reaction apparatus used in this study was the same as the previous study [14]. Prescribed amounts of the surfactant, water and the dye were previously loaded into the bottom of the cell (inner volume: 4.6 cm^3). Unless otherwise noted, maximum amount of water without phase separation, i.e., 30 μl, was introduced in order to solubilize the dye stably. Fabrics to be dyed were also fixed at the upper side of the cell in order to prevent advance staining of the fabrics due to direct contact with dye. After the temperature and pressure reached the chosen operating conditions, dyeing was started by the starring with a Teflon-coated bar driven by an outside magnet. The liqor ratio was adjusted to be 1:100 in all experiments. In order to evaluate the effect of dyeing in a reverse micellar system, dyeing in an aqueous system was also carried out following to the conventional method. The color depth of the dyed fabric was estimated from the reflectance of the dyed fiber mass measured with the Minolta CM-1000 spectrophotometer under illuminant D65 using 10° observer. The color depth, K/S value, was calculated using the Kubelka–Munk equation. In this study, dyeability of the dye on the fiber was evaluated with K/S value because liner relationship between K/S value and percentage exhaustion of dye on fiber could be observed in the preliminary experiments. The absorbance of the dye in a supercritical CO_2 was measured using the Multichannel Spectrophotometer MCPD-100 (Otsuka Electronics Co., Ltd.) and a similar stainless steel viewing cell. Before recording the spectrum, the contents were stirred and equilibrated for 15 min each.

3. Results and discussion

Fig. 1 shows the results of dyeing wool with the acid dye from a reverse micellar system in SC–CO_2. In order to compare the effect of reverse micellar system on dyeing, the results of dyeing in an aqueous system were also presented. As shown in Fig. 1, the acid dye in an aqueous system is scarcely adsorbed on the wool when acidic solution is not present in the system. In contrast, adsorption of the acid dye on the wool in an aqueous system with acidic solution gradually increases with increasing dyeing time and attains equilibrium at about 150 min. These results well agree with the general adsorption behavior of dyes in an aqueous system. As shown in Fig. 1, further excellent dyeability is observed from a reverse micellar system in SC–CO_2 media. The dyeing rate of the wool in a reverse micellar system is remarkably faster than that in an aqueous system. Equilibrium adsorption of the dye seems to accomplish within initial 30 min. High diffusion coefficient of SC–CO_2 would support the rapid diffusion of the dye into the fiber even in mild temperature. Fig. 1 also shows that saturation dye uptake in a reverse micellar system is also higher than that in an aqueous system. Since dyeing conditions such as dye concentration, temperature, liqor ratio etc., are the same in both systems, positive effects of reverse micelles on the dyeability seem to be obvious. In a reverse micellar system, the acid dye would not be dissolved in the bulk CO_2 media but solubilized in the water-pool. Therefore, apparent high concentration of the dye in the water-pool may provide higher dye uptake. In Fig. 1, we can appreciate further advantage of the reverse micellar system. Excellent dyeability of the acid dye on wool in a reverse micellar system can be attained without an addition of additives, i.e., acidic solution. In general, an addition of acidic solution in an aqueous dyeing system is indispensable for the positive charging of amino group in wool fiber and subsequent formation of electrostatic bond between acid dyes and fibers. Niemeyer et al. reported that the water-pool of the PFPE surfactant reverse micelle in SC–CO_2 is in the acidic condition because of the dissolution of CO_2 into the water-pool and subsequent ionization of carbonic acid [15]. Therefore, proton rich conditions of the water-pool may be suitable for the series of adsorption behavior of dyes on the fiber even without an addition of additives.

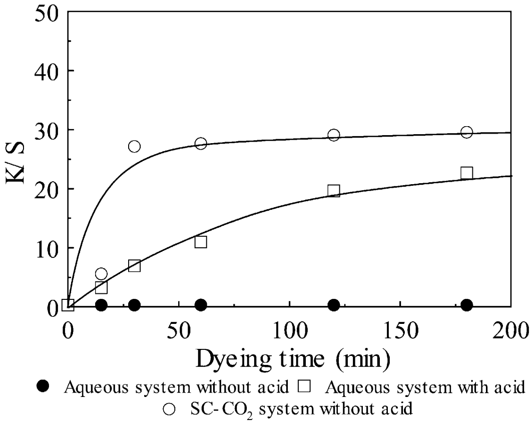

Fig. 1. Dyeability of acid dyes on the wool from the reverse micellar system in SC–CO_2. [dye]: 3.09×10^{-7} mol/l, [surfactant]: 7.5×10^{-4} mol/l, density of CO_2: 0.782 g/ml, water content: 30 μl, temperature: 55 °C.

Fig. 2 compares an influence of the density of CO_2 on the dyeability of the acid dye on wool in a reverse micellar system. In this paper, results are all discussed with the density of CO_2 instead of pressure because the density is suitable for the evaluation of the solvent power under constant volume. As shown in Fig. 2, the variation of the density of CO_2 has no influences on the color depth on dyed wool fabrics. These results are quite

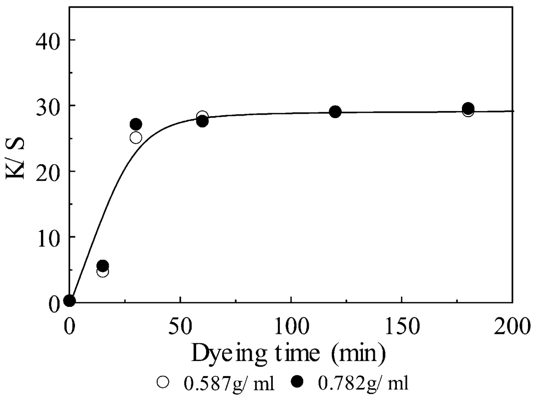

Fig. 2. Comparison of the color depth of wool fabrics dyed at different density of CO_2. [dye]: 3.09×10^{-7} mol/l, [surfactant]: 7.5×10^{-4} mol/l, water content: 30 μl, temperature: 55 °C.

different from the dyeing of synthetic fabrics with disperse dyes and disperse-reactive dyes in SC–CO_2 [16–18]. As is generally known, the disperse dye in a SC–CO_2 is scarcely adsorbed on polyester when temperature and pressure are less than 100 °C and 12 MPa, respectively [19,20]. Moreover, dyeability of the disperse dye on the polyester in SC–CO_2 remarkably improves with increasing temperature and pressure. These characteristics are supposed to be governed by the solubility of the disperse dye in an SC–CO_2. In a reverse micellar system, however, dissolution of the acid dye to the system is different from that of the disperse dye. As described above, the acid dye would not be dissolved in the bulk CO_2 but solubilize in the water-pool. Therefore, dyeability of the acid dye on wool fibers would not be influenced by the density of CO_2 when the acid dye is satisfactory solubilized in the water-pool. Fig. 3 compares the solubility of the acid dye into a reverse micellar system at various densities of CO_2. In this experiment, water content was reduced compared to that in the dyeing process in order to prevent the optical saturation in the measurement. Since excess amount of the dye is present in the system, experimental data imply saturated concentration of the dye at the individual density of CO_2. For comparison, results from the similar system without surfactant are also presented. As shown in Fig. 3, the acid dye is not solubilized in the SC–CO_2 when the surfactant is not present in the system. On the other hand, the acid dye in a reverse micellar system has constant absorption regardless of the density of CO_2, indicating that the water-pool is already saturated with the dye at the lowest density of CO_2 examined in this study. From these results, excessive density of CO_2 seems to unnecessary for the dyeing with this system when solubilization of the acid dye into the water-pool is accomplished.

Fig. 4 compares an influence of the dyeing temperature on the dyeability of the acid dye on the wool in a reverse micellar system. As shown in Fig. 4, the color depth of dyed wool fabrics is remarkably influenced by the temperature even though the concentration of dye is constant in both systems. At the equilibrium exhaustion, color depths of wool fabrics dyed at 55 °C are twice of those at 45 °C. These results may also be related to the solubility of the acid dye in the system. Fig. 5 compares the solubility of the acid dye in a reverse micellar system at various temperatures. The measurement was carried out at the condition of low water content in a similar manner as above. For comparison, results from the similar system without surfactants were also presented. As shown in Fig. 5, the system without surfactants has no ability to dissolve acid dye even if the temperature is raised. In contrast, absorption of the acid dye in this system with the surfactant keeps constant at all temperature ranges. Stable reverse micelles

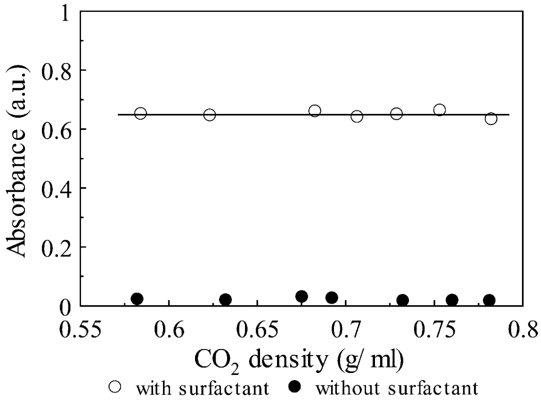

Fig. 3. Variation of the absorbance of the acid dye in a reverse micellar system at various density of CO_2. [dye]: excess, [surfactant]: 7.5×10^{-4} mol/l, water content: 3 µl, temperature: 55 °C.

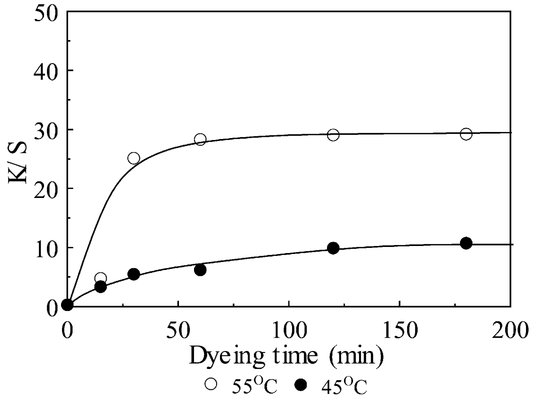

Fig. 4. Comparison of the color depth of wool fabrics dyed at different temperature. [dye]: 3.09×10^{-7} mol/l, [surfactant]: 7.5×10^{-4} mol/l, density of CO_2: 0.578 g/ml, water content: 30 µl.

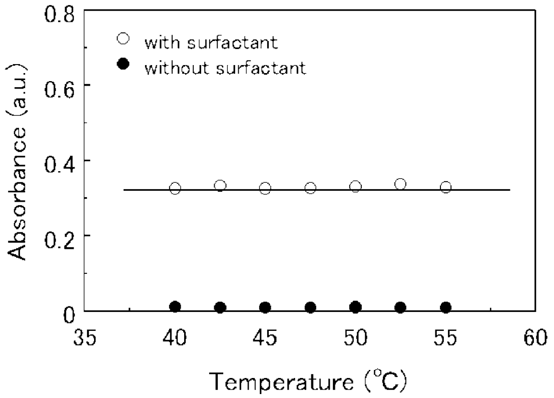

Fig. 5. Variation of the absorbance of the acid dye in a reverse micellar system at various temperatures. [dye]: excess, [surfactant]: 7.5×10^{-4} mol/l, water content: 3 µl, density of CO_2: 0.782 g/ml.

seem to be formed even in low temperature ranges. Consequently the water-pool is already saturated with the dye at the lowest temperature examined in this study. From these results, the differences in the color depth of dyed wool fabrics shown in Fig. 4 seem to be independent of the solubility of the dye in the system. Another factor to be considered may be the differences of the swelling of the fiber due to the characteristic structure of the wool. As is generally known, the surface of the wool fiber is covered with highly hydrophobic cuticle cells. In the conventional water-based dyeing process, dyeing of the wool is performed under high temperature (98 °C); under these conditions the 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. In the dyeing under low temperature with small amount of water, slight differences of the dyeing temperature may relate the differences of the degree of the fiber swelling. Dyeing at 45 °C with this system may not have sufficient effects on the cuticle cells to achieve access into the fiber. Consequently, migration of the dye into the low swelling fiber would be restricted to surfaces areas of the wool fiber.

4. Conclusions

Dyeing of wool fabrics from the PFPE surfactant reverse micellar system in SC–CO_2 has been investigated. The conventional acid dye could be effectively adsorbed on wool fibers in a short time dyeing from this system without an addition of auxiliary. Exhaustion of the acid dye was almost perfect. We also found that dyeability of the acid dye on wool fibers in this system were scarcely influenced on the differences of the density of CO_2 when the dye was satisfactory solubilized in the interior of reverse micelle. On the other hand, the difference of temperature of the system had significant influence on the dyeability of the dye. Nevertheless, effective dyeing could be attained under mild temperature (55 °C) compared with the conventional water-based dyeing process.

In order to apply this system to the practical application, further detail investigation such as an evaluation of the fastness and the recycling of CO_2, surfactant and dyes must be necessary.

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