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# Evaluation of the dyeing mechanism of an acid dye on protein fibers in supercritical $CO_2$

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## Abstract

The dyeing mechanism of an acid dye on protein fibers in supercritical $CO_2$ has been investigated. The reverse micellar system comprising pentaethylene glycol *n*-octyl ether ($C_8E_5$)/1-pentanol has been applied for the solubilization of an acid dye and the subsequent dyeing of protein fibers in supercritical $CO_2$. Quantitative measurements of the concentrated dye fluid in supercritical $CO_2$ could be achieved by the application of integrated Lambert–Beer method. It has been found that the differences of the pressure in the system have great influence on the molar extinction coefficient ($\varepsilon$) of an acid dye solubilized in the interior of the reverse micelle in supercritical $CO_2$. Adsorption manner of an acid dye on protein fibers in supercritical $CO_2$ was similar to that in an aqueous system and followed a Langmuir manner.

*Keywords:* Dyeing; Protein fiber; Adsorption isotherm; Supercritical $CO_2$; Reverse micelle

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## 1. Introduction

Dyeing in supercritical (SC) $CO_2$ has been identified as an attractive alternative to water-based dyeing and has been investigated in detail [1–5]. Dyeing process in SC-$CO_2$ has the remarkable property of not discharging waste aqueous effluent containing colored compounds and concentrated electrolytes. In addition $CO_2$ is inexpensive, essentially nontoxic, nonflammable, requires relatively mild critical conditions (critical temperature, $T_C = 31.1$ °C and critical pressure, $P_C = 7.38$ MPa) and can easily be recovered and recycled after use. Unfortunately, SC-$CO_2$ is a poor solvent for a wide range of hydrophiles because of its low permittivity [6]. The most current technique to dissolve polar substances such as water-soluble dyes in SC-$CO_2$ is an addition of a small amount of entrainer to increase the polarity and therefore the solvent power. However, water-soluble dyes are insufficiently soluble in this SC-$CO_2$/entrainer medium to function in a dyeing process. Dyeing of textile fibers in SC-$CO_2$, therefore, has been limited to synthetic fibers using SC-$CO_2$-soluble

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disperse dyes but the dyeing of natural fibers in this medium is still under development. In our previous study, we have investigated the application of reverse micellar systems for the solubilization of ionic dyes in SC-$CO_2$ [7,8]. Reverse micelles have the property of enclosing small amounts of water in their interior so providing a stable aqueous micro-environment, the so-called water-pool, in non-aqueous media [9]. Therefore reverse micelles have attracted considerable interest, because of this characteristic solubilization property and the high potential for experimental and industrial applications. In fact, our previous investigations confirmed that conventional ionic dyes were satisfactorily solubilized in the interior of reverse micelles in SC-$CO_2$. Wool and silk fabrics were effectively dyed in deep shade with acid dyes from this system without any pretreatment [10,11]. Cotton fabrics were also dyed with reactive dyes when fabrics were previously cationized.

The purpose of the present study is the elucidation of the dyeing mechanism of an acid dye on protein fibers in SC-$CO_2$. To achieve this purpose, we examined the evaluation of the adsorption isotherm between an acid dye and protein fibers in this system. In this paper, we describe the reliability of the direct quantitative measurements of the concentrated dye fluid in SC-$CO_2$ system and the dyeing mechanism of an acid dye on protein fiber in the same system.

## 2. Experimental

### 2.1. Chemicals

The surfactant used was pentaethylene glycol *n*-octyl ether ($C_8E_5$). The $C_8E_5$ was purchased from Nikko Chemicals Co., Ltd., and was used without further purification. Initial water content of the $C_8E_5$ molecule was found using the Karl Fisher titration method to be 0.3% (w/w). 1-Pentanol, co-surfactant, was purchased from Nacalai Tesque Co., Ltd., and was used after drying with a 3A molecular sieve. Pure carbon dioxide (>99.9%) was purchased from Sumitomo Seika Chemicals Co., Ltd. Fabrics used in this study were silk habutae cloth and 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 1 h before use. The acid dye used was C.I. Acid Red 52. All other chemicals (Kanto Chemical Co., Inc.) used were of reagent grade.

### 2.2. Procedure

The high-pressure reaction apparatus used was the same as described elsewhere [10]. In all experiments, the prescribed amounts of the $C_8E_5$ surfactant, co-surfactant, water and the dye were loaded into the bottom of the cell before commencing. Liquid carbon dioxide from a cylinder was compressed via a pressurising pump and caused to flow to the reaction cell until the pressure reached the desired value. The contents of the cell were stirred using a Teflon-coated bar driven by an exterior magnet. Dyed wool and silk fabrics were washed with ultrasonic washing in water and dried in drying machine. Determination of the amount of the dye on fibers was carried out by the extraction with 25% aqueous pyridine solution. The absorbance of the extracted dye solution was determined using UV–VIS Spectrophotometer UV-1650PC (SHIMADZU Co., Ltd.). The absorbance of the dye in SC-$CO_2$ 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. Quantitative analyses of the concentrated dye fluid were carried out using integrated Lambert–Beer method [12].

## 3. Results and discussion

Fig. 1 shows the variations of absorption spectra of the acid dye from the reverse micellar system in SC-$CO_2$. The absorbance of the dye increases with increasing the concentration of the dye, indicating that the introduced dye is solubilized in the SC-$CO_2$ system. However, the absorbance of the dye in this system saturates in the measurement at comparatively low concentration.

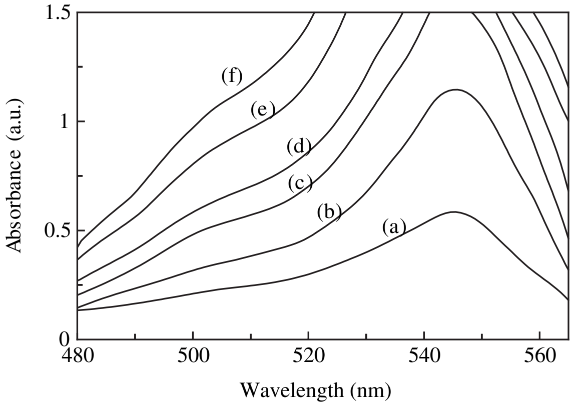

Fig. 1. Absorption spectra of an acid dye solubilized in the $C_8E_5$ reverse micellar system in SC-$CO_2$ at 40 °C. Pressure: 14 MPa, [Dye]; (a) $1.87\times10^{-6}$ M, (b) $9.34\times10^{-6}$ M, (c) $1.26\times10^{-5}$ M, (d) $1.87\times10^{-5}$ M, (e) $4.67\times10^{-5}$ M, (f) $7.00\times10^{-5}$ M.

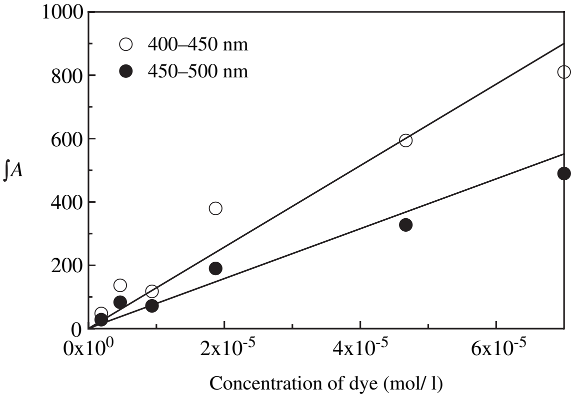

Fig. 2. Relationship between the integral value of absorbance and the concentration of an acid dye in the $C_8E_5$ reverse micellar system in SC-$CO_2$ at 40 °C. Pressure: 14 MPa.

The concentration of the dye that can determine the peak of the absorbance in this system is quite lower than that in the conventional dyeing process. In order to measure the concentration of the dye for the evaluation of the dyeing mechanism in this system, accurate determination of the concentrated dye fluid is necessary. One possibility to overcome this problem may be the application of Lambert–Beer Law at another wavelength that can determine the absorbance. However, preliminary experiments confirmed that the calibration curve obtained at another single wavelength (450 nm or 475 nm) was not a straight line. General Lambert–Beer equation at single wavelength seems to include considerable experimental error in this system. Another possibility to be considered is the application of integrated Lambert–Beer method. Sako et al. [12] reported that the determination of the wide range of the concentration of the silafluofen in *n*-hexane and SC-$CO_2$ can be attained using integrated Lambert–Beer method. If integrated Lambert–Beer Law can be applied in the visible absorption range of the dye, the determination of the concentrated dye fluid in SC-$CO_2$ would be possible. Fig. 2 shows the relationship between integral values of the absorbance and the concentration of the introduced dye in SC-$CO_2$. In this case, the measurements were carried out at the range of shorter wavelength interval compared to that at the peak. In all experiments, we confirmed that spectra at this wavelength interval were not saturated in the measurement. In order to raise the accuracy in the measurement, two different wavelength intervals were also evaluated. As shown in Fig. 2, the integral values of the absorbance of both wavelength intervals have good linear relationship with the concentration of the dye. These results obviously suggest that both calibration curves shown in Fig. 2 can be applied for the quantitative analyses of the dye in this system. Fig. 3 compares integral values of the molar extinction coefficient ($\varepsilon$) of the dye calculated from the calibration curve at different pressures. As shown in Fig. 3, the $\varepsilon$ of the dye decreases monotonously with increasing

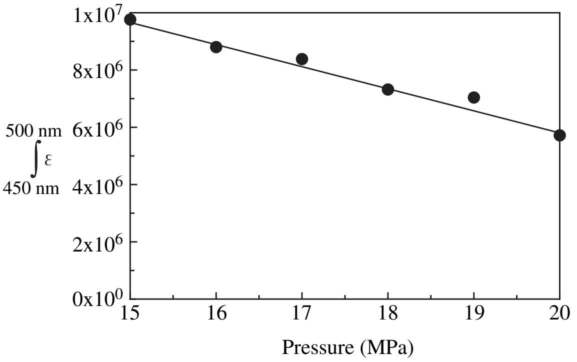

Fig. 3. Influence of the pressure on the integral values of the molar extinction coefficient of an acid dye in the $C_8E_5$ reverse micellar system in SC-$CO_2$ at 40 °C.

the pressure. These results suggest that the characteristic of the $CO_2$ as a solvent varies with the variation of the pressure. These variations of $\varepsilon$ as a function of the pressure may be related to the change of spectral shape or the shift of absorption spectrum. Dealing with the first issue of the change of the absorption spectrum, the dye solubilized in the reverse micellar system may be decomposed by an influence of the high pressure. However, our previous investigation performed in the same system indicated that the dyeing of silk and wool fabrics at the constant dye concentration was not influenced by the dyeing pressure [10]. Dyed wool or silk fabrics had equivalent color depth regardless of the dyeing pressure. Considering the previous results, we can conclude that the decomposition of the dye is ignored in this experimental condition. The second factor to be considered is the shift of the absorption spectrum as reported by Rice et al. [13]. However, previous investigation confirmed that the wavelength at absorption maximum of an acid dye in dilute fluid was not changed even if the pressure of the system was changed [7]. At the present stage, the variation of $\varepsilon$ of the dye cannot be clearly explained with the limited results obtained in this study, but it may be attributable to the aggregation of the dye in the high pressure system. Further investigation is necessary to elucidate the causal relationship between the variation of $\varepsilon$ and the pressure.

Fig. 4 shows the adsorption isotherm of the acid dye on silk and wool fabrics in the reverse micellar system in SC-$CO_2$. Preliminary experiments confirmed that equilibrium adsorption of an acid dye on silk and wool fabrics was attained within 2 h and 16 h, respectively. The amounts of equilibrium adsorption of the dye on silk fabrics are higher than those of wool fabrics. These results may be inconsistent with those in an aqueous system. As is generally known, the wool fiber in the conventional water-based system has high ability to bond with larger number of dye molecules than the silk fiber because the number of the dyeing site in the wool fiber, the amino group, is higher than that in the silk fiber. Low saturation dye uptake of wool fabrics in this system may be explained in terms of the dyeing condition. Different from the conventional water-based dyeing process, the dyeing in this system is performed at low temperature with a small amount of water. Under these conditions, access of dyes into the wool fiber may be restricted at the surfaces of the fiber because of the low swelling of hydrophobic cuticle cells. On the other hand, hydrophilic surfaces of silk fibers would accelerate the access of the dye into the core region. As a result, silk fabrics dyed in this system would have deep color depth compared to those of wool fabrics. In order to dye wool fabrics a deeper shade in this system, an addition of suitable swelling agent or higher dyeing temperature may be necessary. Fig. 4 also shows that adsorption curves of the dye on both wool and silk fabrics are similar to each other. The amount of the dye on fabrics increases with increasing concentration of the dye in the dye bath and levels off at higher concentration of the dye. These results seem to be typical of those in an aqueous system. Fig. 5 shows reciprocal form of the adsorption isotherm. Good linear relationship can be observed in both wool and silk fabrics, indicating that adsorption manners of the acid dye on these fabrics in this system are similar to those in an aqueous system and follow a Langmuir manner. These results suggest that the dyeing of protein fibers in this system progresses between fabrics and small amounts of dye solution in the water-pool. Bulk amounts of $CO_2$ at the outside of the micelle are independent of the series of the dyeing process. This hypothesis may be reasonable with this system. Since the acid dye in the system cannot be dissolved in the $CO_2$

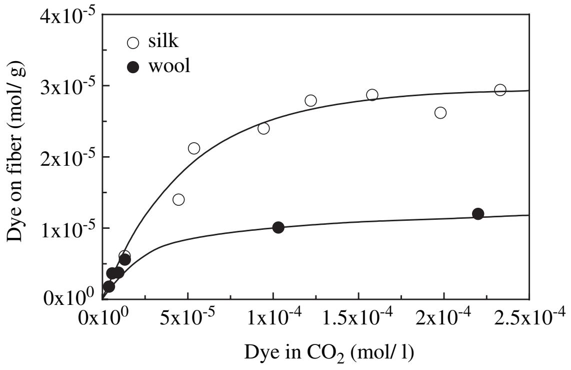

Fig. 4. Adsorption isotherm of an acid dye on protein fabrics in SC-$CO_2$ at 40 °C.

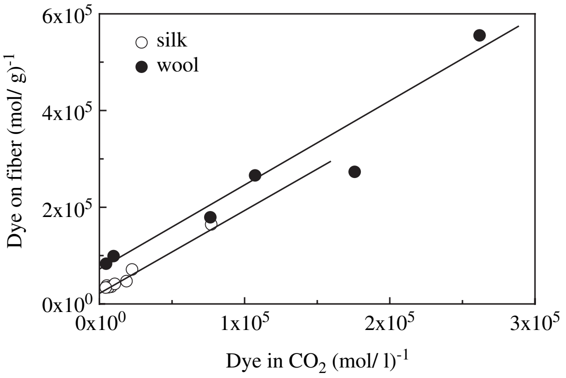

Fig. 5. Adsorption isotherm (reciprocal form) of an acid dye on protein fabrics in SC-$CO_2$ at 40 °C.

but is solubilized in the small amount of water in the water-pool, the dyeing in this system would be regarded as low bath ratio dyeing with highly concentrated dye solution.

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