Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Dyes and Pigments 76 (2008) 1–6
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Complexation of ionic substances with surfactants for solubilisation in supercritical carbon dioxide

K. Sawada [a,*], M. Oshima [b], M. Sugimoto [b], H. Urakawa [c], M. Ueda [d]

[a] *Department of Integrated Life, Osaka-Seikei College, 3-10-62, Aikawa Higashiyodogawa-ku, Osaka 533-0007, Japan*
[b] *Department of Design Engineering and Management, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
[c] *Department of Material Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
[d] *Department of Home Economics, Kobe Women's University, 2-1, Aoyama, Higashisuma, Suma-ku, Kobe 654-8585, Japan*

Received 18 July 2006; received in revised form 31 July 2006; accepted 2 August 2006

Abstract

Solubilisation of ionic substances in supercritical carbon dioxide has been investigated by making complexes of the ionic substances with specific surfactants that have an affinity for carbon dioxide. Three kinds of water-soluble dyes were used as examples of ionic substances; for the complexation of water-soluble dyes, two kinds of fluorinated surfactants and one kind of polyethyleneglycol surfactant were used. Water-soluble dyes that had been complexed with a suitable surfactant were each solubilised in supercritical carbon dioxide although their solubility was quite different. The contents of dyes and surfactants in complexes also had a significant influence on their solubility in supercritical carbon dioxide.

Keywords: Supercritical carbon dioxide; Ionic substance; Surfactant; Solubilisation; Complexation

---

1. Introduction

The use of supercritical fluid for industrial applications has been investigated widely. Recent applications of supercritical fluid technology may be divided into two areas:

1. The degradation of chemical substances in which fluids that have high critical conditions are generally used to obtain high-energy potential. Supercritical water is a substance that satisfies and represents these properties. Indeed, toxic organic substances such as PCBs and dioxin are easily degraded into non-toxic substances under the presence of supercritical water [1–5].
2. As an extraction medium [6–10]: in contrast to the former case, fluids that have gentle critical conditions can be used as solvents. In addition, the diffusion coefficient of supercritical fluids is higher than that of liquids. As a result, the extraction effects of supercritical fluids can be expected to be higher than those of liquids. Moreover, the permittivity of supercritical fluid can be controlled by variation in pressure. This means that the solubility of extracts into a medium can be controlled by variation in pressure. Currently, the fluid that would be represented as an extraction medium would be carbon dioxide. It has attractive characteristics, for example, less expensive, non-toxic and non-flammable that have advantages of energy saving, work safety and environmental friendliness. In the recent years, supercritical carbon dioxide has been used for many other purposes. For example, carbon dioxide can be used as a medium in dry cleaning [11]. Waste substances in the textiles are dissolved in supercritical carbon dioxide and removed. Organic solvents that are used in current dry cleaning processes may be replaced by carbon dioxide in the near future.

---

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

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.08.004

Another example of the application of supercritical carbon dioxide is its use as a dyeing medium. In 1991, Schollmeyer et al. proposed a new method for dyeing polyester in supercritical carbon dioxide [12,13]. In this method, dyes dissolved in supercritical carbon dioxide were effectively transported inside the fibers. Because extraction and dyeing methods are opposite from mass transfer, a high diffusion coefficient of supercritical fluid may bring about excellent results in each of the methods.

Unfortunately, supercritical carbon dioxide as a dyeing vehicle has a serious restriction because carbon dioxide is a poor solvent for water-soluble dyes. Therefore, in this system, only hydrophobic dyes such as disperse dyes can be applied. As a result, hydrophilic natural fibers such as cotton, wool and silk cannot be dyed with conventional water-soluble dyes in this system. Various attempts to overcome this problem have been examined. Furthermore, the addition of an entrainer such as ethanol or methanol is a representative technique to raise the polarity of the medium [14,15]. However, no significant improvement in the solubility of water-soluble dyes is observed with this technique. In our previous study, we investigated the dyeing of natural fibers in supercritical carbon dioxide. The previous strategy of dyeing natural fibers included the use of reverse micellar systems. Reverse micelles have the property of incorporating polar substances inside the aggregates. In fact, water-soluble dyes can be solubilised in carbon dioxide with the help of reverse micelles [16–18]. Cotton, silk and wool fabrics were satisfactorily dyed to a deep shade with conventional reactive dyes and acid dyes. However, our previous dyeing method had a problem. Not all kinds of water-soluble dyes were solubilised in the interior of reverse micelles because the size of the micellar aggregates was not enough to incorporate bulky dyes.

In this study, we have examined another method to solubilise ionic dyes in supercritical carbon dioxide. Our strategy included complexation of ionic dyes with specific surfactants that have a high affinity to carbon dioxide. In order to raise the potential for solubilisation of dye–surfactant complexes, two kinds of fluorinated surfactants and one kind of polyethyleneglycol surfactant were applied.

2. Experimental

2.1. Materials

Two kinds of fluorinated surfactants (CFa, CFc) and one kind of polyethyleneglycol dialkylglycerol ($C_{13}E_5$) were used. Chemical structures of surfactants are shown in Fig. 1 as the estimated structures of dye–surfactant complexes. Fluorinated surfactants were specially synthesized by NEOS Co., Ltd. $C_{13}E_5$ was synthesized in our laboratory following the method described previously [19]. Dyes used for complexation with fluorinated surfactants were CI Basic Blue 47 (Sumika Chemtex Co., Ltd.) and CI Acid Orange 7 (Nacalai Tesque, Inc.). The dye used for complexation with $C_{13}E_5$ was Alizarin Red S (Kanto Chemical Co., Ltd.). These dyes were used as received. The solvent used for preparing the dye–surfactant complexes was a mixture of $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$. The commercial name of this mixed solvent is ASAHIKLIN AK-225 (Asahi Glass Co., Ltd.). The carbon dioxide used was pure grade (>99.9%) (Sumitomo Seika Chemicals Co., Ltd.). All other chemicals were obtained from Kanto Chemical Co., Inc. and were used as received.

2.2. Sample preparation

In this experiment, CFa and CFc were used for complexation with CI Basic Blue 47 and CI Acid Orange 7, respectively. Similarly, $C_{13}E_5$ was used for complexation with Alizarin Red S. The surfactant and the dye were dissolved in AK-225 and distilled water, respectively. These solutions were mixed and vigorously agitated for 1 h. In this process, dye molecules were complexed with surfactant molecules. As a result, dyes in aqueous phase were extracted in AK-225 phase as a dye–surfactant complex. After separation in AK-225 phase, the aqueous phase was washed twice with fresh AK-225 to extract the dye–surfactant complexes. Collected AK-225 fractions were dried over Na_2SO_4 and evaporated.

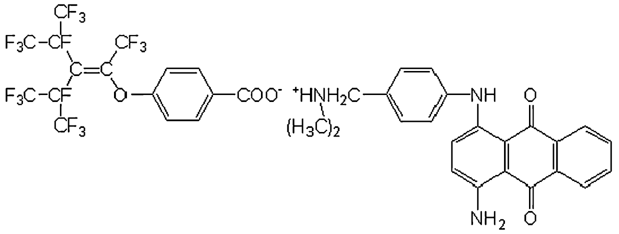
2.3. Procedures

Solubilisation of dye–surfactant complexes in supercritical carbon dioxide was evaluated using a high-pressure reaction apparatus as described in a previous study [20]. The main component of the apparatus was a stainless steel viewing cell (total volume 4.6 cm^3) containing a 3 cm diameter optical window, which was 1.5 cm thick. In all experiments, prescribed amounts of dye–surfactant complexes were loaded into the bottom of the cell before commencing solubilisation. Liquid carbon dioxide from a cylinder was compressed via a pressurizing pump and was made 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. Solubilisation of dye–surfactant complexes were confirmed by both visual and optical observations through optical windows. Optical observations were carried out using the Multichannel Spectrophotometer MCPD-100 (Otsuka Electronics Co., Ltd.) to determine the visible absorption of the system. When dye–surfactant complexes completely dissolve in the medium, then the turbid phase in the cell becomes clear. Therefore, absorbance of the system becomes zero. In this experiment, measurements of the pressure at this cloud point were repeated several times. Average pressures at cloud points were converted to density through the Ely–Haynes–Bain method [21].

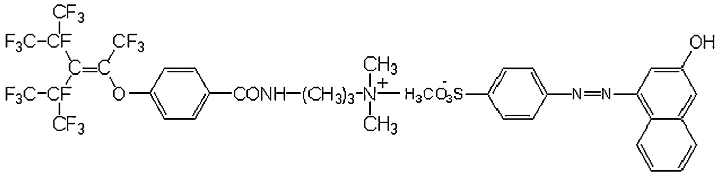
3. Results and discussion

The estimated structures of dye–surfactant complexes shown in Fig. 1 indicate that complexation was attained by ionic interaction between the dye and the surfactant. In addition, poly(ethylene oxide) units in the $C_{13}E_5$ molecule may have the potential to form a hydrogen bond with Alizarin Red S molecules. In the complexation process, we confirmed

CFa / C.I. Basic Blue 47 (CFa-complex)



CFc / C.I. Acid Orange 7 (CFc-complex)



$C_{13}E_5$ / Alizarin Red S ($C_{13}E_5$-complex)

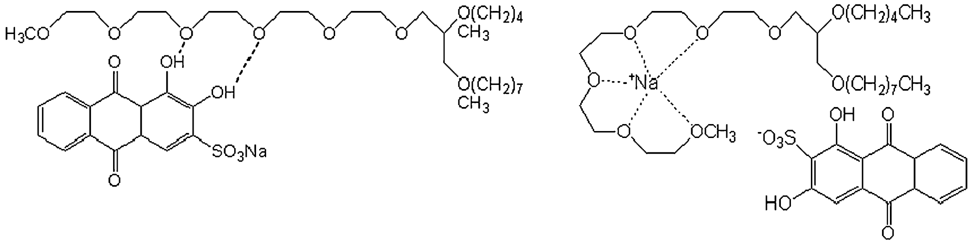


Fig. 1. Chemical structures of dye–surfactant complexes.

that the color depth of the aqueous phase in aqueous solution/AK-225 mixture became pale with increasing agitation time. As a result, the absorbance of dyes in the aqueous phase became zero. On the other hand, the color depth of the AK-225 phase became deeper with the elapse of agitation time. This means that all dyes introduced in the reaction vessel were completely complexed with the correspondent surfactant.

3.1. Dyes complexed with fluorinated surfactants

Fig. 2 shows the solubility of CFa alone in supercritical carbon dioxide at different temperatures. A clear one-phase region is given at the upper side of each plot. The visual and optical observations showed similar data. As shown in Fig. 2, the solubility of CFa is increased with increasing density of carbon dioxide. An increase in the number of carbon dioxide molecules seems to raise the opportunity for the solvation of surfactant molecules. However, relationships between the concentration of CFa and the density of carbon dioxide were not linear at each temperature. The slope of the plot became gentler with increasing concentrations of CFa. This means that the number of carbon dioxide molecules solvated with one CFa molecule decreases. Generally, variation in permittivity of carbon dioxide by an increase in the density of the system is small. Therefore, at high concentrations of CFa, solvation of CFa may be attained with smaller number of carbon dioxide molecules. Fig. 2 also shows the influence of temperature on the solubility of CFa. At the definite density of carbon dioxide, the solubility of CFa in the system decreased with the decreasing temperature. These results well agree with the solubilisation behaviors of solutes in a liquid solvent.

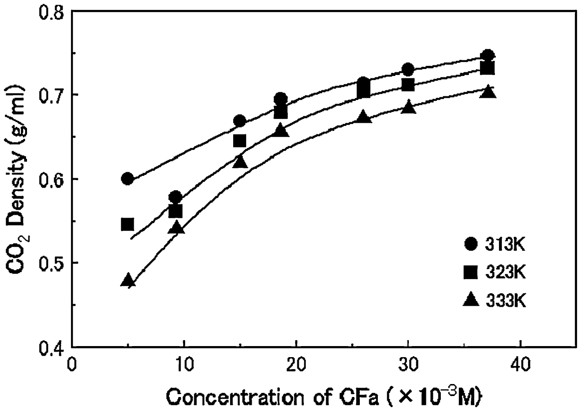


Fig. 2. Phase boundary of CFa/carbon dioxide system at different temperatures.

Fig. 3 shows the solubility of CFc in supercritical carbon dioxide and compares the solubility of CFa . In this case, the data were collected at 313 K in each surfactant. As expected, Fig. 3 shows the low solubility of CFc. The solubility of CFc was reduced to about 1/1000 as compared to the solubility of CFa. Similar results were observed at other temperatures. The low solubility of CFc may be related to the differences in the chemical structure of molecules. As shown in the chemical structure, CFc molecule contains an amido

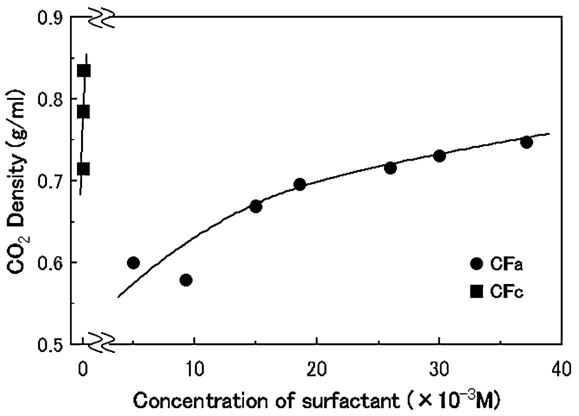


Fig. 3. Phase boundary of CFc/carbon dioxide system.

group. This suggests that CFc molecules have the opportunity to form a hydrogen bond between molecules and produce strong intermolecular interactions. As a result, strong cohesive forces would prevent access of carbon dioxide molecules to the CFc molecules.

Fig. 4 shows the solubility of CFa-complexes in supercritical carbon dioxide. In this experiment, CFc complexes were found to show little solubility in supercritical carbon dioxide even if the temperature and density of the carbon dioxide were changed. On the other hand, CFa-complexes showed obvious solubility in the same medium. The ionic dye, CI Basic Blue 47, may be solubilised in the system by complexation with a suitable surfactant. Solubility curves of CFa-complexes shown in Fig. 4 are similar to the data for CFa. However, the solubility of CFa-complexes at the definite density of carbon dioxide was quite lower than that of CFa alone. This result would also relate to the enlargement of intermolecular interaction between CFa-complexes.

In order to evaluate solubilisation behaviors of CFa-complexes in more detail, similar investigations have been carried out by changing the molar ratio of the dye to CFa. The data are shown in Fig. 5. In this case, the density of carbon dioxide was fixed at 0.83 g/ml. Fig. 5 shows that excess quantities of CFa in complexes have a negative effect on their solubility. These results may be related to the cluster structures formed around complexes. Generally, the density of carbon dioxide around the solute is higher than densities in a bulk system because solute–solvent interactions in supercritical conditions are superior to thermal motions. This means that the fluctuation of the density of carbon dioxide molecules becomes remarkable in the supercritical state. In this condition, carbon dioxide molecules would preferably solvate with surplus CFa molecules. As a result, the ratio of CFa-complexes that have solvated with carbon dioxide would decrease. Consequently, the solubility of CFa-complexes in supercritical carbon dioxide would also be decreased.

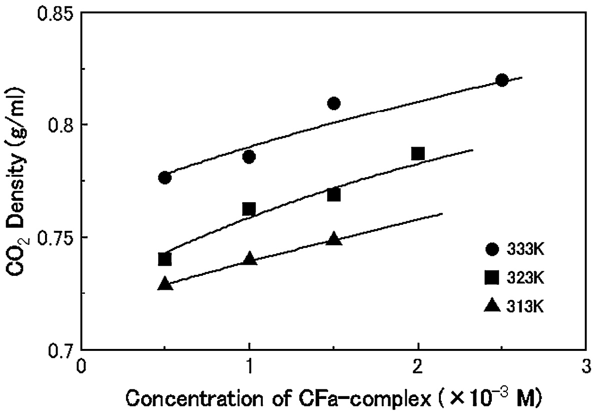


Fig. 4. Phase boundary of CFa-complexes/carbon dioxide system at different temperatures.

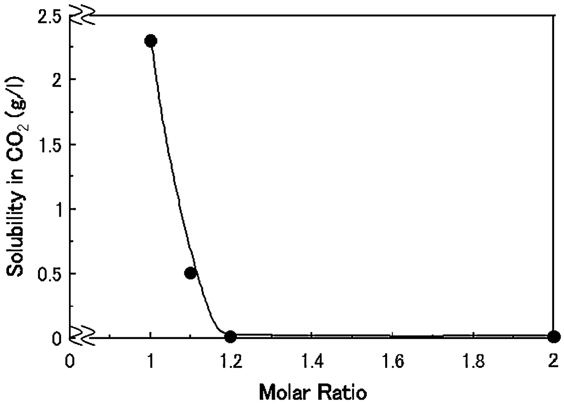


Fig. 5. Effects of molar ratio of the dye to CFa on the solubility on CFa-complexes in supercritical carbon dioxide.

3.2. Dyes complexed with polyethyleneglycol dialkylglycerol

From these results, it has been found that the solubility of dye–surfactant complexes greatly depends on the solubility of the surfactant in carbon dioxide. In addition, the solubility of complexes was controlled by the molar ratio of the dye to the surfactant. Based on these results, further examinations using $C_{13}E_5$ surfactant were investigated. In our previous study, $C_{13}E_5$ showed high solubility in carbon dioxide [19].

Fig. 6 shows variations in the absorbance (λ_{max}: 422 nm) of $C_{13}E_5$-complex in supercritical carbon dioxide. Experimental data were collected at 313 K under 20 MPa. The concentration of $C_{13}E_5$ was fixed at 5×10^{-2} M. As shown in Fig. 6, absorbance of $C_{13}E_5$-complex linearly increased with the increasing dye contents. The dyes contained in $C_{13}E_5$-complexes appeared to be completely solubilised in supercritical carbon dioxide. Furthermore, we found that $C_{13}E_5$-complexes that contained higher concentrations of dyes were not solubilised in the system. As shown in Fig. 6, the concentration of the dye that dissolves in carbon dioxide in the $C_{13}E_5$-complexes was low as compared to that of $C_{13}E_5$. In addition, maximum dye contents in $C_{13}E_5$-complexes were also lower than those of CFa-complexes. Because the solubility of $C_{13}E_5$ in supercritical carbon dioxide was higher than that of CFc [19], the low solubility of $C_{13}E_5$-complexes would not relate to the solubility of $C_{13}E_5$. This result may be related to the method of

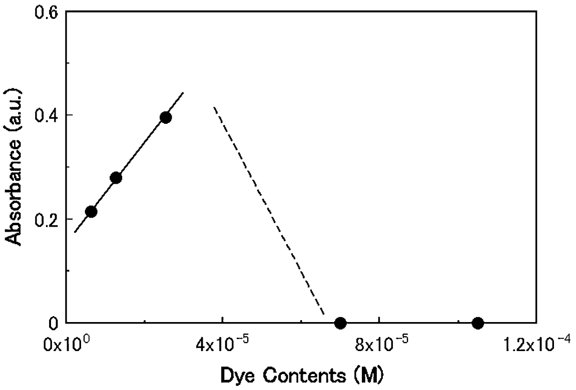


Fig. 6. Variations of absorbance of $C_{13}E_5$-complexes in supercritical carbon dioxide.

complexation between $C_{13}E_5$ and Alizarin Red S. As described above, CFa-complexes can be formed by ionic interactions between the dye and the surfactant. On the other hand, a hydrogen bond formation between $C_{13}E_5$ and Alizarin Red S may be stronger than the ionic force in $C_{13}E_5$-complexes. Solvation of $C_{13}E_5$ molecule with carbon dioxide is attained at the poly(ethylene oxide) units in $C_{13}E_5$ molecules. In this case, most of the poly(ethylene oxide) units in $C_{13}E_5$ molecules are previously occupied by Alizarin Red S molecules with a hydrogen bond. As a result, solvation of $C_{13}E_5$-complexes with carbon dioxide molecules may be hard to achieve.

Fig. 7 shows the effect of pressure on the solubility of $C_{13}E_5$-complexes in supercritical carbon dioxide. The dye content in $C_{13}E_5$-complexes was fixed at 3.8×10^{-5} M at 313 K. As shown in Fig. 7, an increase in the solubility of $C_{13}E_5$-complexes was quite small until the pressure reached about 11 MPa. However, their solubility markedly increased with an increase of pressure and later reached a plateau. Carbon dioxide molecules could be solvated with poly(ethylene oxide) units that are left after conjugation with dye molecules. As expected from the data in Fig. 7, $C_{13}E_5$-complexes dissolved when remaining poly(ethylene oxide) units are combined with a definite number of carbon dioxide molecules. In this case, solvation of the remaining poly(ethylene oxide) units that is required for dissolution is attained at about 13 MPa. As a result, the introduced $C_{13}E_5$-complexes were completely solubilised at this pressure.

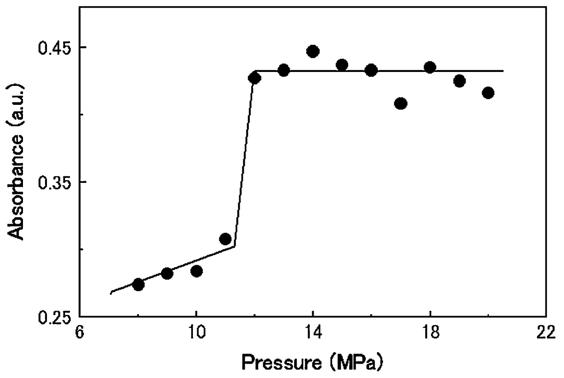


Fig. 7. Effects of pressure on the solubility of $C_{13}E_5$-complexes.

4. Conclusion

Solubilisation of ionic dyes in supercritical carbon dioxide was investigated by making their complexes with fluorinated surfactants or polyethyleneglycol surfactant. The solubility of dye–surfactant complexes in supercritical carbon dioxide greatly depends on the solubility of the surfactant. In addition, the method of conjugation between dyes and surfactants had an important role in the solubilisation of complexes. From the data obtained in this study, we conclude that complexation of dyes and surfactants by ionic interactions is favorable for solubilising them in supercritical carbon dioxide.

References

[1] O'Brien CP, Thies MC, Bruce DA. Supercritical water oxidation of the PCB congener 2-chlorobiphenyl in methanol solutions: a kinetic analysis. Environ Sci Technol 2005;39(17):6839–44.

[2] Del RG, Di GG. Removal and destruction of toxic micropolluting organic compounds from waste waters by a combined NF and SCWO process. Desalination 2001;138(1, 3):61–4.

[3] Sako T, Sugeta T, Otake K, Kamizawa C. Dechlorination of PCBs with supercritical water hydrolysis. J Chem Eng Jpn 1999;32(6):830–2.

[4] Sako T, Sugeta T, Otake K, Sato M. Decomposition of dioxins in fly ash with supercritical water oxidation. J Chem Eng Jpn 1997;30(4):744–7.

[5] Crain N, Gloyna E. Supercritical water oxidation of sludges contaminated with toxic organic chemicals. Water Sci Technol 2000;42(7, 8):363–8.

[6] Khosravi-Darani K, Vasheghani-Farahani E, Khosravi-Darani K. Application of supercritical fluid extraction in biotechnology. Crit Rev Biotechnol 2005;25(4):231–42.

[7] Zhao H, Xia S, Ma P. Use of ionic liquids as 'green' solvents for extractions. J Chem Technol Biotechnol 2005;80(10):1089–96.

[8] Cole-Hamilton DJ. Homogeneous catalysis – new approaches to catalyst separation, recovery, and recycling. Science 2003;299(5613):1702–6.

[9] Marr R, Gamse T. Use of supercritical fluids for different processes including new developments – a review. Chem Eng Process 2000;39(1):19–28.

[10] Salgin S, Salgin U. Supercritical fluid extraction of walnut kernel oil. Eur J Lipid Sci Technol 2006;108(7):577–82.

[11] Wentz M. Textilreiniger wollen Klarheit ueber die Zukunft existierender und innovativer Technologien. Reiniger Waescher 1997;50(9):24–6.

[12] Poulakis K, Spee M, Scheider GM, Knittel D, Buschmann HJ, Schollmeyer E. Faerbung von polyester in ueberkritischem CO_2. Chemiefasern 1991;41(2):142–7.

[13] Saus W, Knittel D, Schollmeyer E. Faerben aus ueberkritischem Kohlendioxid-physikalischchemische Grundlagen. Tex Praxis Int 1993;48(1):32–6.

[14] Ikushima Y, Saito N, Goto T. Selective extraction of oleic, linoleic, and linolenic acid methyl esters from their mixture with supercritical carbon dioxide–entrainer systems and a correlation of the extraction efficiency with a solubility parameter. Ind Eng Chem Res 1989;28(9):1364–9.

[15] Schleussinger A, Reiss I, Schulz S. The influence of entrainers on the extraction of polycyclic aromatic hydrocarbons from contaminated soils. ACS Symp Ser 1997;670:171–87.

[16] Sawada K, Takagi T, Ueda M. Solubilization of ionic dyestuff in supercritical carbon dioxide: a basic study for dyeing natural fiber in supercritical fluid. Dyes Pigments 2004;60(2):129–35.

[17] Jun KH, Sawada K, Ueda M. Perfluoropolyether reverse micelle in supercritical CO_2 to dyeing process. Dyes Pigments 2004;61(1):17–22.

[18] Sawada K, Ueda M. Evaluation of the dyeing mechanism of an acid dye on protein fibers in supercritical CO_2. Dyes Pigments 2004;63(1):77–81.

[19] Sawada K, Oshima M, Sugimito M, Ueda M. Microemulsions in supercritical CO_2 utilizing the polyethyleneglycol dialkylglycerol and their use for the solubilization of hydrophiles. Dyes Pigments 2005;65(1):67–74.

[20] Sawada K, Jun JH, Ueda M. Phase behavior of perfluoropolyether microemulsion in supercritical CO_2 and their use for the solubilization of ionic dye. Dyes Pigments 2004;60(3):197–203.

[21] Ely JF, Haynes WM, Bain BC. Isochoric (p, Vm, T) measurements on CO_2 and on ($0.982\ CO_2 + 0.018\ N_2$) from 250 to 330 K at pressures to 35 MPa. J Chem Thermodyn 1989;21(8):879–94.