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Solubilization of ionic dyes in supercritical carbon dioxide: a basic study for dyeing fiber in non-aqueous media

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Abstract

Solubilization of ionic dyes in supercntical carbon dioxide has been investigated using the reverse micellar system. The reverse micelle composed of pentaethylene glycol *n*-octyl ether and co-surfactant provided suitable solubilizing space for ionic dyes in supercritical carbon dioxide. The effect of the co-surfactant, alcohol, on the stability of the reverse micelle was also investigated. It was found that stability of the reverse micelle and capacities to dissolve water and ionic dyes in the system are greatly dependent on the chain length of alcohol.

Keywords: Supercritical fluid; Carbon dioxide; Reverse micelle; Ionic dye

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1. Introduction

In recent years, supercritical (SC) fluid has attracted a great deal of interest since it is viewed as a potentially important alternative to environmentally harmful chlorofluorocarbons and other organic solvents for use in chemical extraction, polymer synthesis, and industrial processing [1–4]. In particular, carbon dioxide is a most suitable alternative to both water and organic solvent since it is inexpensive, essentially non-toxic, nonflammable, requires relatively gentle critical conditions ($T_c = 304.1$ K, $P_c = 7.38$ MPa), and can easily be recaptured and recycled after use. Unfortunately, SC–CO_2 is a poor solvent for a wide range of polar molecules because of its low permittivity [5]. In order to overcome this problem, many attempts have been carried out. The most current technique to dissolve polar molecules in SC–CO_2 is to make an addition of a small quantity of entrainer to increase polarity and therefore solvent power. However, an addition of only entrainer does not result in the satisfactory increase of the solubility of polar molecules in this system.

Solubilization of water-soluble dyes in SC–CO_2 is also no exception to this tendency. In the dyeing of fiber in SC–CO_2, therefore, insufficient solubility of water-soluble dyes causes the difficulty of dyeing natural fibers. At the present stage, dyeing of fibers in SC–CO_2 is restricted to hydrophobic fibers with a group of disperse dyes. If ionic dyes such as acid dyes and the reactive

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dyes can be solubilized sufficiently in SC–CO_2, the potential of dyeing natural fibers in this medium would be greatly increased. The aim of this study is the preparation of suitable dye bath that contains conventional ionic dyes in SC–CO_2. Our strategy is to dissolve the ionic dye in a SC–CO_2/reverse micellar system that involves dispersing a small quantity of water in the SC–CO_2. Reverse micelle has a remarkable property for solubilizing large quantity of water in non-aqueous media and hydrophilic microenvironment within the micelle, the water-pool, has high potential to dissolve various kinds of polar substances. Therefore, this system has been used in studies of enzymatic catalysis [6] and separation of biomolecules [7–9]. Unfortunately, investigation of reverse micelles has been carried out mainly in organic solvent and SC-alkanes [10–13] because solubilization behaviors of surfactant and formation of reverse micelles in SC–CO_2 are very complex. In practice, most commercially available surfactants are insoluble or only slightly soluble in SC–CO_2 and neither do they attract and retain significant quantities of water [14]. At present, fluorinated surfactants synthesized by Johnston et al. [15–19], and DeSimone et al. [20–22] seem to have high solubility in SC–CO_2 and have high potential to form thermodynamically stable reverse micelles. However, fluorinated surfactants are not necessarily acceptable from the point of view of environmental problems.

In this study, we have selected pentaethylene glycol *n*-octyl ether (C_8E_5) as a surfactant since it is known to be soluble in liquid and SC–CO_2 [23]. According to the previous report, the C_8E_5/CO_2 system has a potential to enhance the solubility of water remarkably by an addition of co-surfactant, in analogy with a typical reverse micellar system in organic media. In particular, alcohol seems to play a good role as a suitable co-surfactant to accelerate the solubilization of water in SC–CO_2 [23]. However, the relationship between the co-surfactant and the surfactant in SC–CO_2 media is still unclear. In this study, we have investigated the action of co-surfactant on the phase boundaries of the C_8E_5 reverse micelle using various kinds of alcohols. In addition, we have discussed the solubility ionic dyes in the C_8E_5 reverse micellar system when co-surfactant, density of CO_2, and temperature are varied.

2. Experimental

2.1. Materials

Pentaethylene glycol *n*-octyl ether (C_5E_5) was used as a surfactant. C_8E_5 was purchased from Nikko Chemicals Co., Ltd., and was used without further purification. Initial water content of C_8E_5 molecule was found to be 0.3% (w/w) through Karl Fisher titration. Carbon dioxide used was pure grade ($>99.9\%$) and was purchased from Sumitomo Seika Chemicals Co., Ltd. All other chemicals were purchased from Kanto Chemical Co., Inc. and were used after drying with a molecular sieve 3A.

2.2. Procedure

High-pressure reaction apparatus used in this study was the same as descried elsewhere [24]. Phase boundaries of mixtures were confirmed by both visual inspection and optical observation through optical windows. Optical observations were performed using Multichannel Spectrophotometer MCPD-100 (Otsuka Electronics Co., Ltd.) to determine the disappearance of the visible absorption of the system around the cloud point. In each experiment, pressures at cloud point were accumulated by several measurements. Average pressures observed at each cloud point were converted to density through Ely–Haynes–Bain method [25]. In this paper, the quantity of solubilized water in the reverse micellar system is expressed as the molar ratio of water to surfactant, that is, $w=[H_2O]/[C_8E_5]$.

3. Results and discussion

Fig. 1 shows cloud points of the system composed of C_8E_5/*n*-alcohol when chain lengths of *n*-alcohols are varied. In Fig. 1, clear one phase region is given at the upper side of the plot. In this experiment, we have confirmed that measured pressures at cloud point obtained by both visual inspection and optical observation give the same value. As shown in Fig. 1, the lowest pressure is required to obtain clear one phase when 1-pentanol

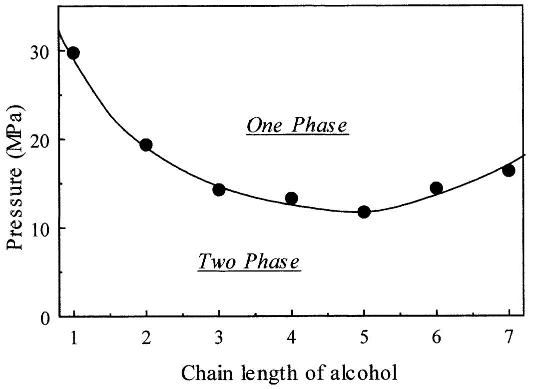

Fig. 1. Effects of co-surfactant on the cloud point of the C_8E_5 reverse micellar system for a constant water content (0.36 M) at 313 K. [C_8E_5]: 62 mM, [*n*-alcohol]: 0.74 M.

is present in the system. These results indicate that solubilization of the solute in the C_8E_5 reverse micellar system can be attained with the mildest condition when 1-pentanol is used as a co-surfactant. In this study, similar results were also obtained when temperature was varied. These results well agree with the fact that 1-pentanol plays a good role for the suitable co-surfactant to accelerate the solubilization of water in SC–CO_2 [23]. The differences in the chain length of alcohol seem to be reflected in the ability as a co-surfactant of C_8E_5 in this system. In order to investigate the effect of alcohols as a co-surfactant of C_8E_5, evaluation of behaviors of alcohols in SC–CO_2 seems to be necessary. This evaluation may be carried out in terms of the solubility of alcohols in SC–CO_2. As is generally known, characteristics of CO_2 as a solvent greatly dependent on the pressure of the system. In other words, solvent power of CO_2 remarkably varies as a function of pressure. Fig. 2 compares the solubility parameter between *n*-alcohols and CO_2. Solubility parameter (δ) was calculated by the following equation reported by Krevelen [26].

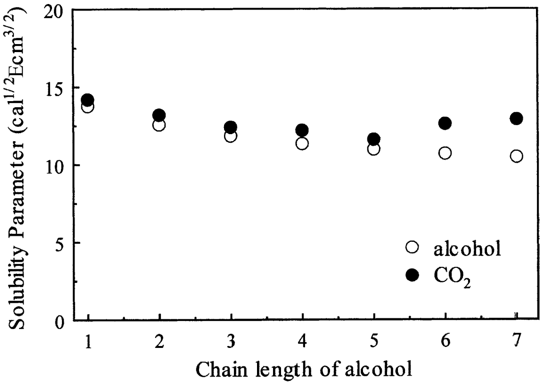

Fig. 2. Comparison of solubility parameters between carbon dioxide and *n*-alcohols.

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$$

$$\delta_{\mathrm{d}} = \frac{\sum F_{\mathrm{di}}}{V} \qquad \delta_p = \frac{\sqrt{\sum F_{\mathrm{pi}}^2}}{V} \qquad \delta_h = \sqrt{\frac{\sum E_{\mathrm{hi}}}{V}}$$

where F_{di} = contribution of dispersion forces F_{pi} = contribution of polar forces F_{hi} = contribution of hydrogen bonding

Each δ of CO_2 in Fig. 2 is the value at each cloud point in Fig. 1. As shown in Fig. 2, solubility parameters of alcohols that have a short chain (< 5 carbons) completely agree with those of CO_2. These results obviously suggest that solubilization of surfactant/alcohol/water mixtures in SC–CO_2 is governed by the solubility of the alcohol. As a result, surfactant/alcohol/water mixtures are not solubilized in CO_2 medium until the δ of CO_2 reaches the same value of that of the alcohol by the compression of the system. On the other hand, alcohols that have middle chain length would be interacted with the surfactant tail more tightly since the surfactant tail also has similar chain length to those of alcohols. As a result, higher solvent power, i.e., higher density of CO_2, is necessary to solubilize the mixtures (surfactant/alcohol complex). From these results, it can be assumed that the alcohol would not be adsorbed on the interface of the micelle but inserted between surfactant tails to exhibit the ability as a co-surfactant in this system. Consequently inserted alcohols can reduce surfactant tail–tail and micelle–micelle interactions and to assist the formation of stable reverse micelles. Among the *n*-alcohols, chain length of 1-pentanol seems to be suitable as a co-surfactant. Fig. 3 shows phase boundaries of the C_8E_5 reverse micellar system in SC–CO_2 as a function of water content. In the following experiment, 1-pentanol has been used as a co-surfactant since 1-pentanol is most suitable

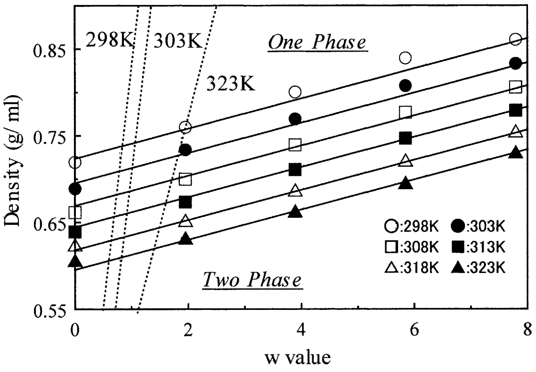

Fig. 3. Phase boundary of the C_8E_5 reverse micellar system. [C_8E_5]: 62 mM, [l-pentanol]: 0.74 M.

for the solubilization of the solute in the lowest pressure. For comparison, the solubility of water in pure CO_2 is presented as dotted line. The solubility of water in the reverse micellar system is significantly higher than that in pure CO_2. These results obviously indicate that introduced water is partially dissolved in bulk CO_2 and the majority is solubilized in the interior of reverse micelles. Under constant temperature, density of CO_2 that requires attaining one phase system is linearly increased with increasing w value. As is generally known, an addition of further quantity of water produces an enlargement of micellar size and an increase of aggregation number [27]. As a result, higher solvent power is necessary to dissolve the grown micelle. In this experimental condition, clear one phase was never obtained over ca. $w = 8$, suggesting that C_8E_5 aggregate was saturated with water around $w = 8$. Fig. 4 shows the shift of phase boundaries of the C_8E_5 reverse micellar system in SC–CO_2 when concentration of 1-pentanol is varied. At the constant density of CO_2, maximal w value without phase separation increases with increasing the concentration of 1-pentanol. In the preliminary experiment, we have confirmed that solubility of water in pure 1-pentanol is quite lower than that in pure CO_2. Therefore, an addition of 1-pentanol provides the stability of the reverse micelle and becomes feasible to solubilize further quantity of water. Fig. 4 also shows that the density of CO_2 that necessary to obtain clear one phase increases with increasing the concentration of 1-pentanol when w value is constant. Reduction of interfacial tension due to an introduction of 1-pentanol would produce the stability of the micelle [28]. Fig. 5 shows the relationship between temperature and w value in the phase boundaries of C_8E_5 reverse micellar systems. As shown in Fig. 5, temperature that necessary to obtain clear one phase increases with increasing w value. These results completely agree with the results in the typical reverse micellar system in organic media [29]. From these results, it can be assumed that the reverse micelle consist of C_8E_5/1-pentanol/CO_2 has a potential to solubilize polar molecules in SC–CO_2 media even in mild conditions when a suitable composition of the system is applied.

In order to evaluate the solubilization of polar molecules in this system, we have examined the solubilization of the ionic dye in the C_8E_5/1-pentanol/CO_2 reverse micellar system. Fig. 6 shows

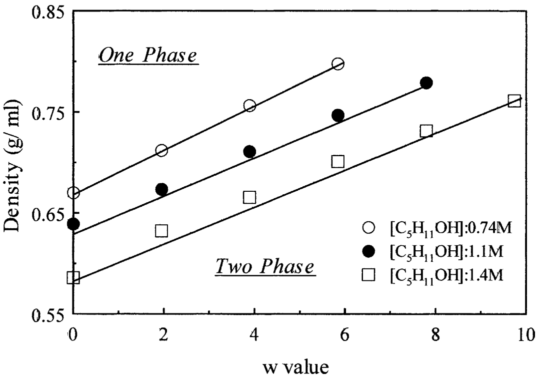

Fig. 4. Phase boundary of C_8E_5 reverse micellar system at 313 K [C_8E_5]: 62 mM.

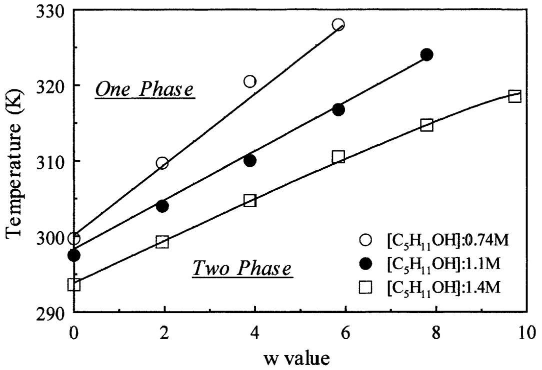

Fig. 5. Phase boundary of C_8E_5 reverse micellar system under constant CO_2 density (0.725 g/ml). [C_8E_5]: 62 mM.

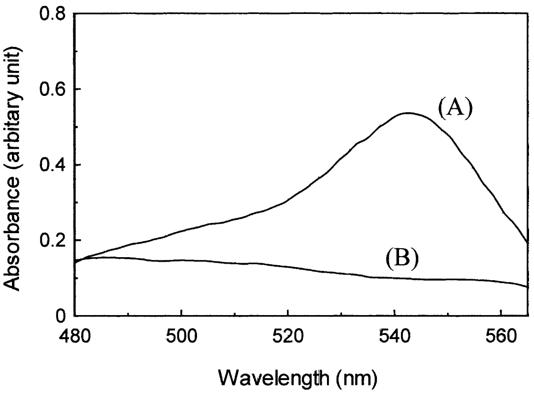

Fig. 6. Absorption spectra of anionic dye (C.I. Acid Red 52) in C_5E_5 reverse micellar system at 313 K. [C_5E_5]: 62 mM, [1-pentanol]: 0.74 M, [dye]: 3.8×10 M, pressure: 12 MPa.

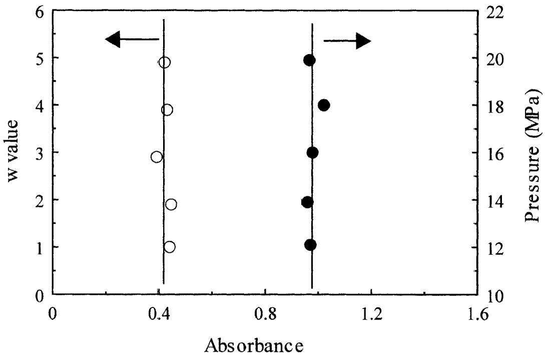

Fig. 7. Effects of water content and pressure on the solubility of anionic dye (C.I. Acid Red 52) in C_8E_5 reverse micellar system at 313 K. [C_8E_5]: 62 mM, [1-pentanol]: 0.74 M.

examples of absorption spectra of the ionic dye observed from SC–CO_2 media (313 K, 12 MPa). In this case, the acid dye (C.I. Acid Red 52) was applied as a model of ionic dyes. Spectra A and B were observed from the system with and without the presence of C_8E_5, respectively. There is no absorption of C.I. Acid Red 52 when C_8E_5 is not present in the system, indicating that CI. Acid Red 52 is not solubilized in SC–CO_2 media at all. Such an insoluble character of C.I. Acid Red 52 in mere CO_2 medium was not improved even if temperature and pressure were raised to 373 K and 25 MPa, respectively. On the other hand, obvious absorption of C.I. Acid Red 52 is observed when C_8E_5 is present in the system. C.I. Acid Red 52 seems to be apparently solubilized in the reverse micellar system even in low pressure and temperature conditions. In this study, we have confirmed that similar solubilization of other ionic dyes into SC–CO_2 media is also observed using several ionic dyes (C.I. Reactive Red 2, C.I. Reactive Blue 74, C.I. Acid Orange 7, C.I. Acid Blue 9 and C.I. Acid Green 25). According to the previous report [30], satisfactory solubilization of dyes in pure SC–CO_2 medium was never observed at less than 400 K and 20 MPa even if low polar dyes were used. It is of interest to note that conventional water-soluble dyes can be solubilized in SC–CO_2 media at mild condition when reverse micellar systems are applied. Fig. 7 shows effects of water content and pressure (density of CO_2) on the solubility of C.I. Acid Red 52 in the C_8E_5 reverse miceilar system. In each experiment, temperature was kept constant. Solubility of dyes was compared with the absorbanee at absorption maxima (543 nm) of the spectrum. Effect of pressure on the solubility of the dye was investigated under the presence of excess quantity of dye and of fixed quantity of water ($w=2$). As shown in filled plots of Fig. 7, the solubiity of the dye is independent of the pressure. These results are quite different from those obtained from SC–CO_2-soluble dyes such as disperse dye or disperse-reactive dye in pure SC–CO_2 [31–33]. According to the report by Hon et al. [34], disperse dyes were hardly soluble in SC–CO_2 at low pressure and temperature ranges. When temperature was raised at more than 373 K, solubility of disperse dyes in SC–CO_2 increased linearly with increasing pressure. In the reverse micellar system, the ionic dye would not be solubilized in bulk CO_2 but solubilized in the water-pool. Therefore further increase of the pressure would not relate to the solubility of the dye in the system when formation of the micelle and subsequent solubilization of the dye into the water-pool is accomplished. In Fig. 7, the effect of water content on the solubility of the dye was also presented, In this case, the concentration of the dye and pressure were kept at 3.74×10^{-6} M and 12 MPa, respectively. As shown in the open plots of Fig. 7, solubility of the dye is independent of the quantity of water in the system. Microquantity of water corresponding to $w=1$ seems to be enough to solubilize the dye introduced in this experiment. Therefore, further addition of water results in the microscopic dilution of the dye solution in the water-pool and is not reflected in the macroscopic variation of the system. If the quantity of the introduced dye increases, apparent solubility of dye in the system may be increased until the water-pool is saturated with the dye.

From these results, solubility of ionic dye in the total system seems to be controlled by the solubility in the water-pool. As far as the water-pool is not saturated with the dye, therefore, a fixed quantity of the dye can be stably soluble in the system regardless of the variation of pressure or further addition of water.

4. Conclusion

Solubilization of water and ionic dyes in the SC–CO_2/C_8E_5 reverse micellar system were investigated. The solubility of water and stability of the reverse micelle were greatly dependent on characteristics of the co-surfactant, i.e., chain length of alcohol. We found that 1-pentanol was the most suitable co-surfactant that assists the formation of stable reverse micelles. Conventional ionic dyes were satisfactorily solubilized in the interior of the micelle even in low temperature and pressure ranges. The solubility of ionic dyes in this system was independent on the working pressure when stable reverse micelles were formed.

It can be concluded that solubilization of water-soluble dyes into SC–CO_2 media at a mild condition is very interesting in energy saving. However, utilization of the co-surfactant may not be necessarily suitable from the viewpoint of the recapture and the recycle after use when this system is applied to a supereritical fluid dyeing process. In order to apply the reverse micellar system in SC–CO_2 for practical use, constructions of suitable apparatus or the development of stable reverse micellar systems without a co-surfactant would be necessary.

References

[1] Cooper AI, DeSimone JM. Polymer synthesis and characterization in liquid/supercritical carbon dioxide. Curr Opin Solid State Mater Sci 1996;1:761–8.

[2] Chang SH, Park SC, Shim JJ. Phase equilibria of supercritical fluid-polymer systems. J Supercrit Fluids 1998;13: 113–9.

[3] Rajagopalan P, McCarthy TJ. Two-step surface modification of chemically resistant polymers: blend formation and subsequent chemistry. Macromolecules 1998;31:4791–7.

[4] Canelas DA, Desimone JM. Polymerizations in liquid and supercritical carbon dioxide. Adv Polym Sci, 133:103-140.

[5] Yee GG, Fluton JL, Smith RD. Aggregation of polyethylene glycol dodecyl ethers in supercritical carbon dioxide and ethane. Langmuir 1992;8(2):377–84.

[6] Lesser ME, Luisi PL, Palmnieri S. Activity of yeast cells solubilized in a water-in-oil microemulsion. Chimia 1989; 43:348–50.

[7] Ichikawa S, Imai M, Urushihara S, Shimizu M. Protein transport between aqueous phase and micellar organic phase using self-assembled amphiphiles. Process Metall 1992;7B:1875–80.

[8] Goklen K, Hatton TA. Protein extraction using reverse micelles. Biotechnol Prog 1985;1:69–74.

[9] Fornay CE, Glatz CE. Reversed micellar extraction of charged fusion proteins. Biotechnol Prog 1994;10:499–502.

[10] Zhang J, Bright FJ. Steady-state and time-resolved fluorescence studies of bis(2-ethylhexyl) sodium succinate (AOT) reverse miceles in supercritical ethane. J Phys Chem 1992;96:5633–41.

[11] Peck DO, Johnston KP. Theory of the pressure effect on the phase behavior of AOT/Propane/Brin water-in-oil microemulsions. J Phys Chem 1991;95:9549–56.

[12] Sheravani Z, Ikushima Y. Micropolarity of sodium bis(2-ethylhexyl sulfosuccinate reverse micelles prepared in supercritical ethane and near-critical propane. Colloid Polym Sci 1999;277:595–600.

[13] Sheravani Z, Ikushima Y. E_T^N values and effective dielectric constants of water/AOT/near-critical propane reverse micelles. Colloid and Surfaces 2000;168:97–9.

[14] Goether ELY, Vorstman MAG, Keurentjes JTF. Opportunities for process intensification using reverse micelles in liquid and supercritical carbon dioxide. Chem Eng Sci 1999;54:1589–96.

[15] Harrison K, Goveas J, Johnston KP. Water-in-carbon dioxide microemulsions with a fluorocarbon–hydrocarbon hybrid surfactant. Langmuir 1994;10:3536–41.

[16] Johnston KP, Harrison KL, Clarkes MJ, Howdle SH, Heitz MP, Bright FV, et al. Water-in-carbon dioxide microemulsions: an environment for hydrophiles including proteins. Science 1996;271:624–6.

[17] Clarke MJ, Harrison KL, Johnston KP, Howdie SM. Water in supercritical carbon dioxide microemulsions: spectroscopic investigation of a new environment for aqueous inorganic chemistry. J Am Chem Soc 1997;119: 6399–406.

[18] Heitz MP, Carlier C, DeGrazia J, Harrison KL, Johnston KP, et al. Water core within perfluoropolyether-based microemulsions formed in supercritical carbon dioxide. J Phys Chem B 1997;101:6707–14.

[19] Lee CT, Psathas PA, Ziegler KJ, Johnston KP, Dai HJ,

Cochran HD, et al. Formation of water-in-carbon dioxide microemulsions with a cationic surfactant: a small-angle neutron scattering study. J Phys Chem B 2000;104:11094–102.

[20] Mawson S, Jhonston KP, Combes JR, DeSimone JM. Formation of poly(1,1,2,2-tetrahydroperfluorodecyl acryl ate) submicron fibers and particles from supercritical carbon dioxide solutions. Macromolecules 1995;28:3182–91.

[21] DeSimone JM, Maury EE, Menculogu YZ, McClain JM, Romack TJ, Combes JR. Dispersion polymerization in supercritical carbon dioxide. Science 1994;265:356–9.

[22] Cooper AC, Londono JD, Wignall O, McClain JB, Samulski ET, Lin JS, et al. Extraction of hydrophilic compound from water into liquid CO_2 using dendritic surfactants. Nature 1997;389:368–71.

[23] McFann GJ, Johnston KP, Howdie SM. Solubilization in nonionic reverse micelles in carbon dioxide. AIChE J 1994;40:543–55.

[24] Sawada K, Takagi T, Jun JH, Ueda M, Lewis DM. Dyeing natural fibers in supercritical carbon dioxide using non ionic surfactant reverse micellar system. Color Tech 2002; 118:233–7.

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

[26] Klevelen DW. Properties of polymers. 2nd ed. New York: Elsevier Science; 1976.

[27] 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.

[28] Mitchell DJ, Ninhâm BW. Micells, vesicles and microemulsions. J Chem Soc Faraday Trans 1981;77:601–29.

[29] Strey R, Jonstromer M. Nonionic bilayer in dilute solutions: effect of additives. J Phys Chem 1992;96:5993–6000.

[30] Joung SN, Shin HY, Park YH, Yoo KP. Measurement and correlation of solubility of disperse anthraquinone and azo dyes in supercritical carbon dioxide. Korean J Chem Eng 1998;15:78–84.

[31] Joung SN, Yoo K. Solubility of disperse anthraquinone and azo dyes in supercritical carbon dioxide at 313.15 to 393.15 K and from 10 to 25 MPa. J Chem Eng Data 1998; 43:9–12.

[32] Wagner B, Kautz CB, Schneider GM. Investigations on the solubility of anthraquinone dyes in supercritical carbon dioxide by a flow method. Fluid Phase Equilib 1999:158–60.

[33] Lee JW, Min SM, Bae HK. Solubility measurement of disperse dyes in supercritical carbon dioxide. J Chem Eng Data 1999;44:684–7.

[34] Hori T, Tabata I. General aspect on dyeing of fibers in supercritical carbon dioxide. Senshoku-Kogyo 1999;47: 310–9.