Effects of pressure and temperature on dyeing acrylic fibres with basic dyes in supercritical carbon dioxide

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The dyeing of acrylic fibre with CI Basic Blue 47 has been investigated using an ammonium carboxylate perfluoropolyether as an auxiliary in order to perform the reverse micellar system in supercritical carbon dioxide media. The basic dye was satisfactorily solubilised in the interior of the reverse micelle in the system, and dyeability in the supercritical carbon dioxide media was excellent, even in the absence of a retardant and/or an acid. The optimum proton-rich condition for dyeing of acrylic fabric is performed without the presence of additives. Changes in glass transition temperature of acrylic fibre in the carbon dioxide media also influence the dyeing behaviour of acrylic fabric.

Introduction

In recent years, the use of supercritical fluids as a reaction medium has been extensively investigated in order to take advantage of their unique properties. For example, the density and diffusion coefficient of supercritical fluids can be modified continuously by changing the pressure applied [1]. In particular, supercritical carbon dioxide (SC-CO2) can be used as an alternative to conventional solvents in a variety of applications due to its unusual characteristics, for example relatively low critical properties (critical temperature, 304 K; critical pressure, 7.38 MPa). It also has the advantages of being non-toxic and non-flammable, and it is inexpensive, readily available and environmentally benign [2,3]. For these reasons, SC-CO2 has now become widely accepted as a medium for extraction [4], for materials processing [5] and in the synthesis of novel organometallics [6]. On the other hand, SC-CO2 has the drawback of being unable to dissolve a wide range of hydrophiles, particularly ionic species, due to its low dielectric constant and non-polarity. This has tended to limit its application as an alternative to conventional solvents.

In the field of dyeing, it has been found that disperse dyes can be dispersed or solubilised in SC-CO2 as a consequence of their low polarity and small molecular size. In the 1990s Schollmeyer and co-workers demonstrated for the first time that polyester could be successfully dyed in this solvent [7]. The dyeing of natural fibres using water-soluble dyes in SC-CO2 has not however been successful, since dyes such as reactive, acid and basic dyes have very poor solubility in SC-CO2 due to their high polarity. To overcome this problem the present authors have focused on the use of a reverse micellar system in SC-CO2. This has the ability to solubilise a large proportion of water, and consequently a variety of hydrophiles [8–10]. If a reverse micellar system may be successfully prepared in SC-CO2 using as surfactant an ammonium carboxylate perfluoropolyether (PFPE), which contains a nonpolar fluorocarbon chain and a hydrophilic carboxylate header group [13]. In addition, Heitz et al. confirmed that a water pool ('bulk-like water') could be formed in the core of a PFPE reverse micelle [14].

The authors have previously demonstrated that natural fibres such as cotton, silk and wool can be successfully dyed with conventional anionic dyes in a PFPE/water/CO2 system [15–17]. This depends on the successful solubilisation of the dye in the interior of the reverse micelle. It was thought interesting to investigate whether this could be extended to the dyeing of acrylic fabric with basic dyes, which has led to the present study. A conventional basic dye, CI Basic Blue 47 (8), was chosen.

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Experimental

Materials

PPFE surfactant (2) (molecular weight, 845.15) was prepared by chemical modification of perfluoro-(2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoyl) fluoride (Daikin Chemical Co. Ltd) using Zielinski's method [18]. The initial water content of the PPFE was found to be 2.24% by Karl Fischer titration.

The dye (CI Basic Blue 47, 1) was obtained from Sumitomo Chemical Co. Ltd, and was used without further purification. Carbon dioxide was purchased from Sumitomo Seika Chemicals Co. Ltd (purity > 99.9%). The acrylic fabric was jersey knit provided by Shikisensha Co. Ltd.

Dyeing procedure

The dyeing of acrylic fabric with basic dye was carried out both in SC-CO2 and by the conventional aqueous method. The dyeing process was conducted at a fixed dye concentration, chosen to give medium colour depth and dyed fabric evaluated by optical measurement.

Dyeing in SC-CO2 was carried out using a high-pressure experimental apparatus as described in earlier studies [15–17]. The dyeing cell was stainless steel (total volume 4.6 ml) and provided with two windows (3 cm diameter, 1.5 cm thick) for optical measurement. The supercritical state was obtained by compressing the CO2 by means of a pressure pump. PFPE surfactant (0.003 g, 7.5 × 10⁻⁶ µl), and aqueous dye solution (30 µl) were loaded into the bottom of dyeing cell, followed by the SC-CO2. A sample of the fabric (0.07 g) was loaded into the upper portion of the dyeing cell to avoid contact with the other contents before starting the dyeing process. After reaching the experimental temperature and CO2 density, the contents were stirred using a magnetic stirrer. Homogeneous mixing of the SC-CO2 and other contents was confirmed visually. The solubility of dye 1 in PPFE/water/SC-CO2 systems has previously been determined experimentally and found to be less than 5.78 × 10⁻⁶. (d) 8.24 × 10⁻⁶ µl; density of CO2, 0.72 g/ml; PFPE conc., (a) 0 M and (b–d) 7.5 × 10⁻⁶ M
d

The dyeability of acrylic fabric in SC-CO2 with dye 1

Figure 2 shows the plot of colour yield at various initial dye concentrations, both in aqueous and SC-CO2 media. Other experimental conditions, for example temperature, dyeing time and CO2 density, were kept constant. The results show that the colour yield increased with increasing dye concentration, confirming that acrylic fabrics may be satisfactorily dyed in a PFPE/dye/SC-CO2 system therefore appears to provide a satisfactory medium for dyeing acrylic fabric.

Results and Discussion

Effect of dye concentration

Figure 1 shows the absorption spectra at various concentrations of dye 1 in the PPFE/SC-CO2 system. The absorption spectrum of a similar system without PPFE is also shown in plot (a) for comparison. The amount of water (30 µl) in this system is significantly higher than the maximum water solubility in pure CO2 [16].

It is clear from the results in Figure 1 that the absorption of the dye solution in the presence of PPFE increased linearly with increasing dye concentration. On the other hand, there was no absorption whatever in the absence of PPFE. In preliminary experiments, it had been confirmed that PPFE was able to form stable micellar aggregates in SC-CO2 and that the dye could be satisfactorily accommodated [16]. These results confirm that dye 1 was satisfactorily solubilised in the interior of the micellar aggregate containing a small amount of water, and that the PPFE/dye/SC-CO2 system therefore appears to provide a satisfactory medium for dyeing acrylic fabric.

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systems. In aqueous media the dye molecules are uniformly solubilised throughout the aqueous phase (4.6 ml water). On the other hand, in the PFPE/dye/SC-CO2 system the dye molecules are solubilised only in the interior of the reverse micellar aggregates, each containing a very small amount of water (30 µl); the dye is completely insoluble in the outer SC-CO2 medium. Even for dyeings carried out in a similar dyebath size (4.6 ml), the effective concentration of dye in SC-CO2 is therefore much higher than in the aqueous system.

Effect of temperature
Figure 3 illustrates the absorption of dye 1 on acrylic fabric in a PFPE/water/SC-CO2 system at various temperatures. The uptake in aqueous medium under similar conditions is shown for comparison. It is seen that a marked increase in colour yield occurs above 60 °C in the PFPE/water/SC-CO2 system. In the aqueous system, on the other hand, there was a sudden increase in uptake above 75 °C, corresponding to the glass transition temperature \( T_g \) of the acrylic polymer [20].

Effect of CO2 density
From the results in Figure 3, the dye uptake in the SC-CO2 system appears to be a function of CO2 density. To investigate this, a series of dyeings was carried out in which all experimental conditions except CO2 density were kept constant. Figure 4 shows the effect of CO2 density on dye absorption on acrylic fabric and indicates that higher colour yields were obtained as the CO2 density increased.

At this stage the difference in dyeability at different CO2 densities and in the aqueous medium cannot be fully explained owing to the limited number of results. It does, however, seem likely that a plasticisation effect may partly account for the variation in dye absorption by polymers in SC-CO2, since this would cause a reduction in \( T_g \). According to Shieh et al. [21,22] and Kwak et al. [23], crystalline as well as amorphous polymers are able to absorb carbon dioxide, giving changes in weight and in thermal and mechanical properties. For this reason, polymers undergo a reduction in glass transition temperature when treated with SC-CO2. For example, Chiu et al. have reported that the \( T_g \) of polyester was depressed from 74 to 52 °C in a SC-CO2 medium at 35 °C and 20 Mpa [24]. Hori and Tabata have investigated the influence of CO2 density on the dyeability of polyester fibre and have shown that, as the density increases, the dye molecule is able to penetrate more easily into the amorphous phase of the fibre owing to swelling of the fibre by SC-CO2 [25]. The results in Figures 3 and 4 similarly suggest that the amorphous phase of acrylic fibres becomes plasticised and swollen in the presence of SC-CO2. Since the degree of crystallinity of acrylic is much lower than that of polyester, the effect is more pronounced in the case of acrylic fibre.

Effect on dyeing kinetics
The dyeing kinetics of both systems at dyeing temperatures similar to those encountered in conventional dyeing are shown in Figure 5. The dyeing kinetics of the aqueous systems are such that equilibrium is reached very quickly (ca. 15 min), this rapidity of dyeing giving rise to the characteristic unevenness in dyeing this fibre. For this reason, a retardant or acid is often used to reduce the speed of dyeing. In the PFPE/dye/SC-CO2 system, on the other hand, a milder and more controllable dyeing behaviour is observed.
These results may be attributed to the acidic conditions present in the reverse micellar system. Niemeyer and Frank have demonstrated that the pH of the water pool in the reverse micelle is acidic (3.1–3.5) due to dissolution of CO2 in the water pool, forming carbonic acid [26]. These acidic conditions in the water pool have the effect of restraining dye uptake to give a more level dyeing.

Conclusions

The application of a basic dye on acrylic fabric in aqueous and SC-CO2 media has been investigated and compared. A more acceptable dyeing behaviour was obtained in a PFPE/dye/SC-CO2 system due to the presence of proton-rich conditions in the reverse micellar aggregates. Moreover, a higher dye uptake was achieved in SC-CO2 than in a conventional aqueous system at relatively low temperatures. This appears to be the result of changes in the glass transition temperature of the acrylic fibre in the SC-CO2 system. However, the experimental data obtained in this study require further amplification to permit a more complete quantitative assessment of the dyeing mechanism in SC-CO2 media.

Figure 5  Comparison of colour depth of dyed acrylic fabric at high temperature (dyebath conc., 1.29 × 10−4 M; temp. (aqueous), 100 °C; temp. (SC-CO2), 95 °C; density of CO2, 0.55 g/ml; water, 30 µl)

References