

Supercritical Fluid Dyeing of PMMA Films with Azo-Dyes

BARRY L. WEST, SERGEI G. KAZARIAN, MICHAEL F. VINCENT, NOEL H. BRANTLEY, CHARLES A. ECKERT

Georgia Institute of Technology, School of Chemical Engineering, and Specialty Separation Center, Atlanta, Georgia 30332-0100

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ABSTRACT: *In situ* ultraviolet–visible spectroscopy has been used to study diffusion of two azo-dyes in a CO₂-swollen matrix of poly(methyl methacrylate) (PMMA). The diffusivity of both dyes can be tuned simply by changing the system pressure. Higher pressure of CO₂ enhances diffusion of a dye in PMMA. The diffusion of dyes in CO₂-swollen PMMA can also be influenced by specific interactions. The partitioning of the dyes between the polymer phase and the fluid phase was measured, and the partition coefficients are large (10⁴–10⁵). Thus, supercritical fluid dyeing is possible, although the solubility of the dyes in the fluid phase is low. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 911–919, 1998

Key words: dye diffusion; dye partitioning; dye solubility; ultraviolet–visible spectroscopy

INTRODUCTION

Supercritical fluids (SCFs) have been widely used in the synthesis and processing of polymers.¹ Supercritical CO₂ is known to reduce the T_g for many glassy polymers. Furthermore, it is possible to change the degree of swelling simply by changing the system pressure, and the polymer free volume can easily be tuned. Thus, it seems feasible that CO₂ dissolved with a glassy polymer could significantly influence mass transfer properties of solutes in the polymer matrix. Indeed, researchers have exploited this increase in solute mass transfer rate in polymeric matrices for supercritical fluid extraction^{2–4} and, to a lesser extent, supercritical fluid impregnation processes.^{5–8}

Supercritical dyeing of polymeric matrices is a particular case of impregnation with several potentially encouraging applications. The replacement of aqueous dyeing solvents with a benign supercritical fluid solvent can reduce waste streams in the textile industries significantly.

Further, after the supercritical fluid dyeing process is complete, there is virtually no residual CO₂ in the polymer. Volatile components, such as residual monomer or organic solvents used in the polymer production process, are effectively removed with supercritical CO₂. Thus, after the process, the polymeric matrix is very clean. There has been significant effort to commercialize SCF poly(ethylene terephthalate) (PET) dyeing in other countries due to these environmental advantages.⁹

Another application of SCF impregnation of dyes into glassy polymers is the production of advanced optical components. Recently, CO₂-plasticized poly(methyl methacrylate) (PMMA) doped with an azo-dye was poled with an electric field near room temperature.¹⁰ The poling aligns the dipoles of the dye molecules, and depressurization freezes the aligned molecules in the matrix (that is, the polymer is returned to its glassy state). The resulting polymeric matrix exhibits nonlinear optical properties, which are important in the communication industry.¹¹ Traditional methods for poling dye-polymer systems include heating the polymer above its T_g and then applying an electric field to the plasticized system. Poling CO₂-

Correspondence to: C. A. Eckert.

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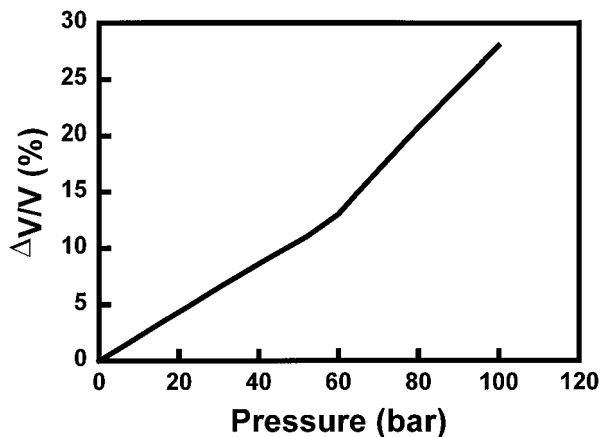


Figure 1 Volume change (%) of PMMA with CO₂ pressure at 42°C taken from Wissinger and Paulaitis.¹⁶

plasticized materials at lower temperatures will allow the use of thermally labile dyes and also will reduce Brownian motion of the dye molecules while the polymer is being returned to the glassy state, resulting in a more efficient dipolar alignment.

While there has been interest in exploiting supercritical fluids as a dyeing solvent, most researchers have concentrated on the solubility of the dyes in the fluid phase.^{12–14} Very little research has concentrated on partitioning of dyes between the polymeric phase and the fluid phase. The objective of this work is to measure both the thermodynamic partitioning of dyes between the fluid and polymer phase and also the mass transport properties of dyes in CO₂-swollen PMMA. We report how the density of CO₂, and consequently, swelling of the polymer, influences the partition coefficient and the diffusion process. Also we show how the molecular structure of the dye molecules may affect these two processes.

We chose to study PMMA because of its many practical applications. It is known that CO₂ acts as a Lewis acid when interacting with PMMA and, thus, is an effective plasticizer.¹⁵ The polymer can uptake over 20 wt % of CO₂ at high pressures, resulting in significant swelling of the matrix.¹⁶ Figure 1 shows the swelling behavior of PMMA subjected to CO₂. The two azo-dyes chosen are shown in Figure 2. Disperse Red 1 (DR1) and the similar 4-4'-(diethylamino) nitroazobenzene (DENAB) were chosen because they are common chromophores for nonlinear optic (NLO) materials.

EXPERIMENTAL

We studied the diffusion of dyes into the polymer matrix by an *in situ* spectroscopic technique, per-

mitting observation of kinetic processes within the polymer film without disturbing the polymer.^{6,17} While most of the previous work has been with Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy is ideal for PMMA–disperse dye system. First, PMMA is transparent in the UV–vis spectral regions that dyes absorb, making background subtraction facile. Next, the dyes studied here are solvatochromic (that is, the wavelength of the absorption bands of the dye will change depending on their environment). The solvatochromic behavior and the fact that solubility of these dyes is low in CO₂ allows us to separate spectral contributions of the dye in the fluid phase from the dye in the polymer phase.

A thin film of PMMA is placed in the optical path of the cell, as shown schematically in Figure 3. The path length of the cell was approximately 2.0 cm. The reviews on high-pressure optical cells for supercritical fluid solutions have recently been published.^{2,17} The cell is placed in a diode array spectrometer, where all wavelengths of the spectra are acquired simultaneously. Spectra of the dye in the fluid phase and polymer phase are acquired with this configuration.

Materials

SCF-grade carbon dioxide (99.99% purity) was purchased from Matheson (Montgomeryville, PA) and was passed over a 13× molecular sieve supplied by the vendor to remove trace water and

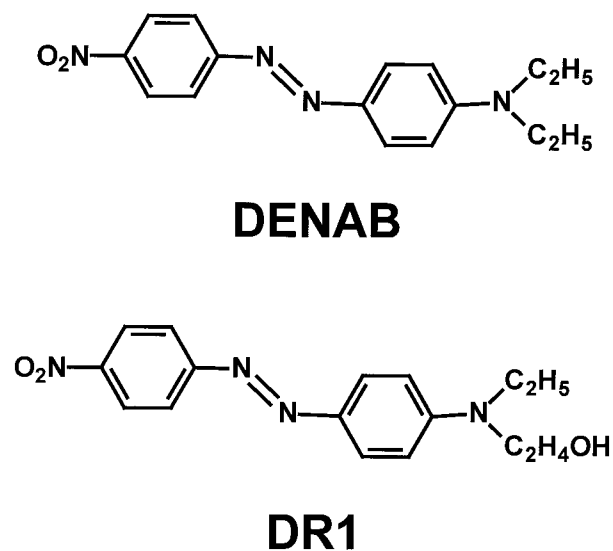


Figure 2 Structure of the two azo-dyes used in this study.

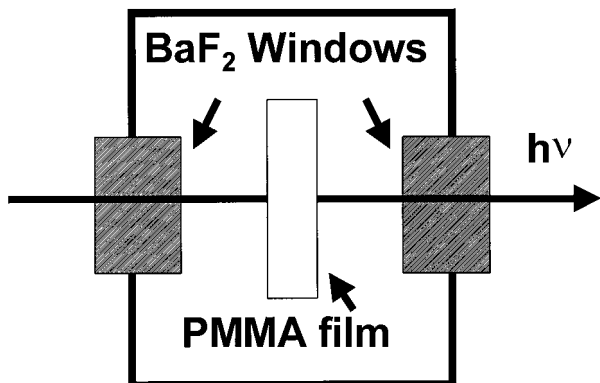


Figure 3 Schematic diagram of *in situ* spectroscopic monitoring of polymers subjected to supercritical fluids. The polymer film is placed between the two windows of a high-pressure vessel, and the cell is placed in the light path of the spectrometer.

hydrocarbons. PMMA (average M_w 100,000) was purchased as cylindrical pellets from Polyscience, Inc. (Warrington, PA). Disperse Red 1 (95% dye content, Aldrich, Milwaukee, WI) was used as received, and 4-4'-(diethylamino) nitroazobenzene (DENAB) was synthesized as described elsewhere.¹⁸

Equipment

All spectra were taken on a HP 8452A diode array UV-vis spectrometer (Hewlett-Packard Co., Palo Alto, CA). The optical cell was pressurized using an ISCO 260D syringe pump. Temperature was controlled with an Omega CN9000a temperature controller, and system pressure was measured with a Heise DPI 260 3000 psi pressure gauge. PMMA films were hot-pressed to the desired thickness using a Universal Film Maker (Spectra Tech, Shelton, CT). Care was taken to ensure identical thermal history of the polymer films by the method described in the literature.⁷ The film thickness was typically 0.005 cm, but films of varying thickness were used in some cases to verify the diffusion mechanism. The pathlength of the CO₂-swollen PPMA film was adjusted by the swelling factor for PMMA taken from Wissinger and Paulaitis¹⁶; the assumption of the isotropic swelling was used in this case.

Molar Absorptivity of Dyes in CO₂

To determine the solubility of the dyes in supercritical CO₂, the optical cell given in Figure 3 was used without the polymer film in place. Solute

concentrations are determined from the intensities of the primary UV-vis spectral band by the Beer-Lambert law given below.

$$A = \epsilon cl$$

where A is the absorbance, ϵ is the molar absorptivity, c is the concentration (M) of the dye, and l is the pathlength.

Since the pathlength is known, only the molar absorptivity is required. However, evidence exists that the molar absorptivity may vary significantly in compressible solutions.^{19,20} The addition of co-solvents or changes in the fluid density can lead to changes in the molar absorptivity. Table I shows the molar absorptivities and maximum absorption wavelengths of the two dyes used in this study in a variety of solvents. The ethyl acetate value compares well with data in the literature.²¹ Both dyes are solvatochromic with a saturated solution appearing pale yellow in cyclohexane and deep red in methylene chloride. Additionally, the molar absorptivity does change, although not very much, depending on the liquid solvent.

The molar absorptivity of the dyes was determined in the CO₂. A representative example of the data is given in Figure 4. The absorbance of DENAB is shown as a function of concentration at 40°C. At each concentration, the absorbance was recorded at 90, 100, 110, 120, and 150 bar (11.0 to 17.7 mol/L). The good linear fit of the data shows that Beer's Law is indeed obeyed, and the molar absorptivity is only a very weak function of the CO₂ pressure (or density) for the pressure range we studied. Similar results were obtained for DR1. These results, along with the data in Table I, show the molar absorptivity is a weak function of the solvent environment for a given dye. There is evidence that the molar absorptivity can be a strong function of density, particularly in very close proximity to the critical point of the solvent.¹⁹ The assumption that the molar absorptivity is constant at our experimental conditions is valid because we are operating at temperatures and pressures removed from the critical point of the carbon dioxide. Other studies have also concluded that the molar absorptivities of dye molecules in UV-vis and near-IR spectral regions are not a strong function of CO₂ density.^{14,22}

Solubility of Dyes in CO₂

Once the molar absorptivity of the dyes in CO₂ is known, the solubility of DR1 and DENAB could be

Table I Molar Absorptivities of Dyes in Various Solvents at the Absorption Maximum (λ_{\max})

Solvent	DENAB		Disperse Red 1	
	ϵ ($M^{-1} \text{ cm}^{-1}$)	λ_{\max} (nm)	ϵ ($M^{-1} \text{ cm}^{-1}$)	λ_{\max} (nm)
Toluene			34,700	470
Ethyl acetate			36,500	480
Methylene chloride	35,800	480	34,300	480
Cyclohexane	33,800	430	29,600	430
CO ₂	46,000	430	34,600	426
CO ₂	6,300*	500 ^a		

^a The molar absorptivity for DENAB is also given at 500 nm.

measured at 40°C. Other researchers have used similar techniques to measure the solubility of solids in supercritical fluids.²³ Excess solid was placed in the bottom of the cell, and the spectra were recorded as a function of pressure. The maximum wavelength of absorption (λ_{\max}) was used in Beer's law for DR1. However, the intensity of the spectral band of DENAB at higher CO₂ pressures (above 88 bar) was too large to guarantee the linearity of Beer's Law. For this reason, 500 nm was chosen to measure the concentration of DENAB at CO₂ pressures above 88 bar. The value of the molar absorptivity of DENAB at 500 nm is given in Table I.

Dye Partitioning

The partition coefficient (K_c) is defined as the saturation concentration of dye (M) in the polymer

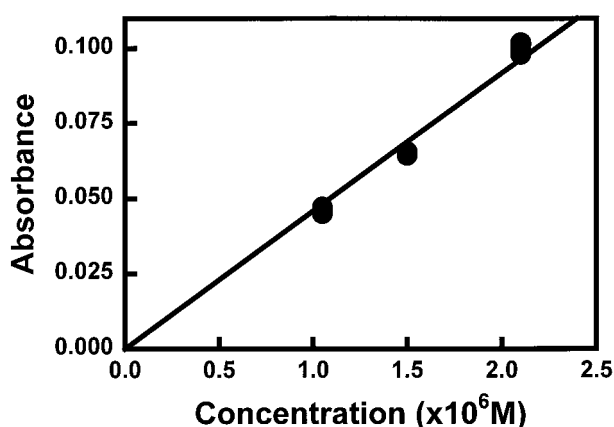


Figure 4 Absorbance at $\lambda_{\max} = 431$ nm as a function of solute concentration of DENAB dissolved in supercritical CO₂. Linearity indicates the validity of the Beer-Lambert law.

phase divided by the saturation concentration of dye (M) in the fluid phase. The saturation concentration of dye in the polymer phase was determined by placing polymer films in small (10 cm³) batch vessels with excess solid dye. The vessels were pressurized slowly and placed in a temperature bath ($40.0 \pm 0.2^\circ\text{C}$) for a period of several h to several days, depending of the CO₂ pressure. When saturation was achieved, the vessels were depressurized slowly to eliminate turbulence within the vessel that could entrain solid dye particles in the fluid phase and possibly deposit solid on the polymer surface. The dyed polymer films were recovered, and the film surface was wiped clean. A small sample of the dyed polymer (~ 50 mg) was removed and dissolved in methylene chloride (10 mL) and analyzed via UV-vis. To report concentration in molar terms (that is, mol/L) at pressurized conditions, the PMMA swelling data of Wissinger and Paulaitis¹⁶ are utilized.

Dye Diffusion

The relative mass uptake of dye into the polymer was measured by placing a thin PMMA film in the optical path, as shown in Figure 3, with excess dye in the bottom of the optical cell. The cell was slowly pressurized to 75 bar and maintained at that pressure for 3 h. This pretreatment allows the PMMA to uptake approximately $\frac{2}{3}$ of the CO₂ that will be present during the actual diffusion experiment. The dyes are not soluble in CO₂ in at these conditions, so no diffusion of the dye into the polymer phase occurs. After the pretreatment, the cell is pressurized to operating conditions in about 5 min. The diffusivity of CO₂ in PMMA²⁴ is much higher than the dye molecules, so it is assumed that the PMMA film is at its equilibrium

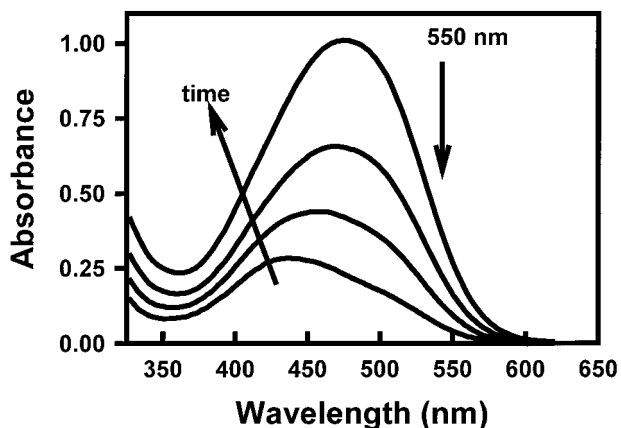


Figure 5 *In situ* UV-vis spectroscopic monitoring of DENAB diffusion in CO₂-plasticized PMMA at 87 bar. The dye uptake in the polymer is measured at 550 nm to prevent spectral contributions of the dye in the fluid phase.

state very quickly, compared to the mass transfer rate of the dyes.

The UV-vis spectra of the dye are then recorded with time. Figure 5 shows the early stages of a diffusion experiment (DENAB; film thickness is 0.005 cm unswollen, pressure is 90 bar, and temperature is 40°C). The diffusion profile is constructed at 550 nm for the following reasons. First, the dye is solvatochromic, and the solubility of the dye in the fluid phase is low, so there is no spectral contribution of the dye from the fluid phase. The spectral bands presented Figure 5 are a result of two separate contributions. The dye band in the fluid phase is centered at 430 nm, and the dye band in the polymer phase is centered at 480 nm. The band of the dye dissolved in the fluid phase remains constant throughout the experiment because the fluid phase remains saturated with dye. Second, the polymer will eventually uptake so much dye that the linearity of Beer's Law will no longer be valid. Monitoring dye diffusion at 550 nm prevents deviation from Beer's Law.

It should be noted that the molar absorptivity of the dyes in the CO₂-swollen PMMA phase is not necessary to measure the diffusion profile. The ratio of dye absorbance at any time to the dye absorbance at saturation is proportional to the relative mass uptake of dye at the time to the final equilibrium mass uptake. The relative mass uptake measurement provides a description of mechanism of diffusion,²⁵ as will be shown later.

RESULTS AND DISCUSSION

Dye Solubility in CO₂

Figure 6 presents the solubility of DR1 and DENAB as a function of pressure at 40°C as measured spectroscopically. There are advantages to measuring solid solubilities with spectroscopy compared to other techniques. The flow technique²⁶ takes much longer, and the detection limits at the ppm level shown in Figure 6 are very difficult to achieve. The sampling technique²⁷ also cannot achieve the same detection limits. Further, with a spectroscopic technique, the approach to equilibrium can be observed in essentially real time.

Partitioning of Dyes

The partitioning process is illustrated in Figure 7. Solid dye in the base of the vessel is dissolved in the CO₂ phase and then begins to diffuse in the swollen polymer phase. Because there is an excess of solid dye, any dye that is impregnated into the polymer phase from the fluid phase is quickly replaced, keeping the fluid phase saturated with dye. Eventually, an equilibrium concentration will be achieved in the polymer phase. The partitioning coefficient, K_c , we report here is the ratio of the saturated concentration of dye in the polymer phase to the saturated concentration of dye in the fluid phase.

Initial experiments with the DR1-PMMA system were conducted to measure possible dye loading in the polymer. The magnitude of this K_c was approximately 10⁵; thus, despite the relatively low solubility of the dye in the fluid phase, appre-

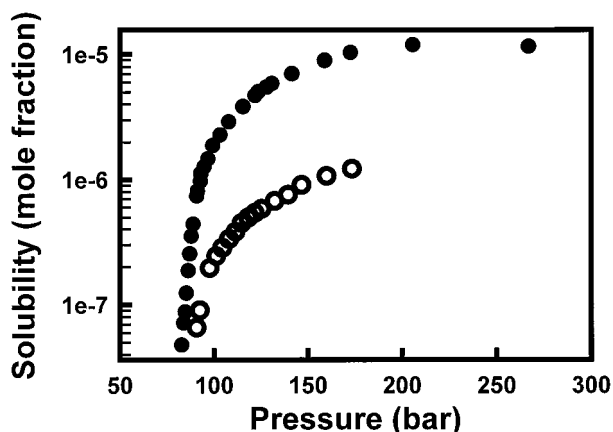


Figure 6 Pressure dependence of the solubility of (●) DENAB and (○) DR1 in supercritical CO₂ at 40°C.

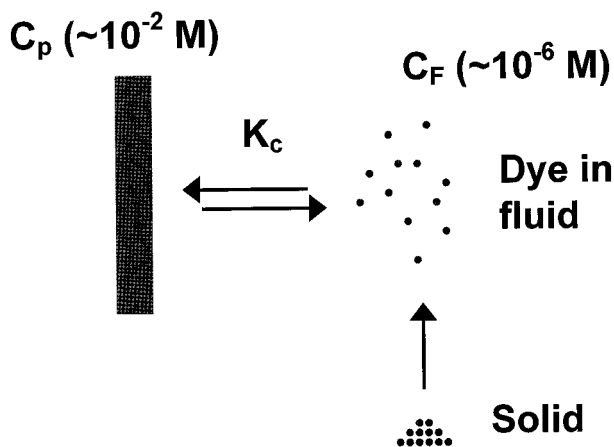


Figure 7 Supercritical fluid dyeing experiment. Excess solid dye is in equilibrium with dye dissolved in the fluid phase. The dye then diffuses into the polymer phase, where saturation is eventually reached.

able quantities of dye could be loaded into the polymer phase. The strong affinity of the dye for the polymer phase led us to hypothesize hydrogen bonding of the dye to the carbonyl group in the repeating unit of PMMA and to study the partitioning of the DENAB–PMMA system because DENAB is incapable of the same kind of specific interaction.

Figure 8 shows the partition coefficient K_c of DENAB and DR1 and a function of pressure at 40°C. There is a distinct difference in the partition coefficient; however, there is also a considerable difference between the saturated concentration of the two dyes in the fluid phase. Table II compares the saturated concentration of the two dyes in the polymer phase as a function of pressure. Each da-

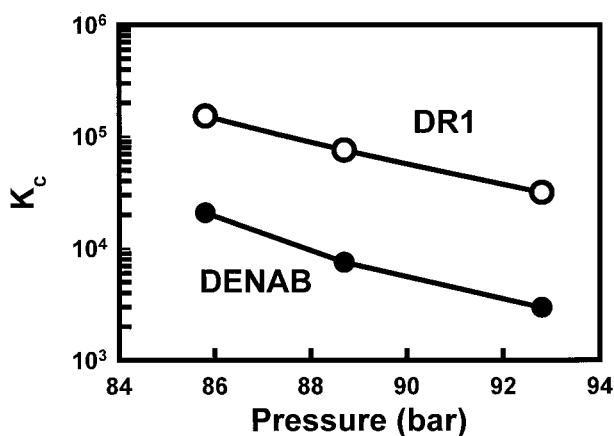


Figure 8 Pressure dependence of the partition coefficient of (●) DENAB and (○) DR1 in supercritical CO_2 at 40°C.

tum in the table represents an average of at least 3 experiments.

It is clear that the concentration of dye in the polymer phase is not a function of the system pressure in the pressure range studied (in all cases, the polymer dissolves about 0.5 wt %). However, the time required to reach saturation is a strong function of pressure (see below). This limited pressure range is a result of two factors. At slightly lower pressures, the diffusion rate may be too slow to achieve saturation in the polymer phase. At higher pressures, the polymer becomes too soft and no longer maintains its structure (that is, it flows in the vessel and makes contact with solid dye).

From the dye saturation data in the polymer phase (Table II), we conclude that hydrogen bonding of DR1 to the carbonyl groups in PMMA has little influence on the equilibrium concentration of dye in the polymer for these experimental conditions. Rather, since both dyes have very similar dipole moments and PMMA is a polar environment, dipole–dipole forces are involved in the affinity of the dye for the polymer phase. The difference in the partitioning coefficient is a result only of differences of solubility of the dyes in the fluid phase. Over a wider pressure range, this may not be the case, as pointed out by other researchers.²⁸

Comparison with Other Polymers

We dyed several other polymers with DR1 using CO_2 (40°C and 91 bar) for comparison. We report here the qualitative information. Polystyrene (PS) and polycarbonate (PC) all were colored slightly pink (as opposed to PMMA's dark red color). Considerably less DR1 dissolved in nylon and PET. Both PS and PC are significantly swollen by high pressure CO_2 ,^{16,29} but because of the relatively nonpolar environment, they uptake less polar dye. Nylon and PET do not absorb much CO_2 and have significant crystalline structure, so the supercritical dyeing process is restricted.

Table II Saturated Concentration (C_s) of Dye in the Polymer Phase at 40°C

P (bar)	DR1 C_s (wt %)	DENAB C_s (wt %)
88	0.54 ± 0.05	0.48 ± 0.05
91	0.51 ± 0.05	0.49 ± 0.05
95	0.52 ± 0.05	0.51 ± 0.05

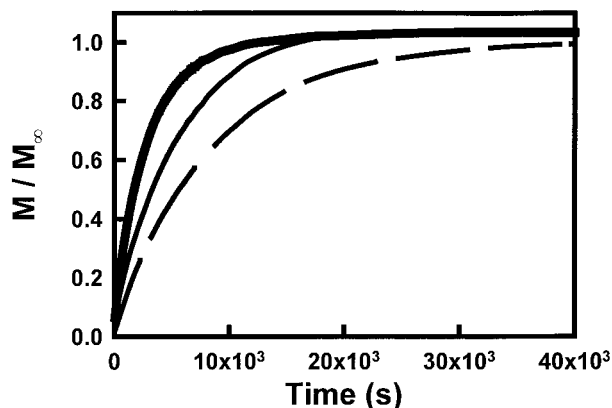


Figure 9 Relative mass uptake of DENAB into CO_2 -swollen PMMA at 40°C . The dashed, thin, and thick lines represent 88, 91, and 95 bar, respectively. Increasing the CO_2 pressure leads to higher diffusion rates in the swollen polymer.

Dyeing of PMMA with Ferrocene

We also dyed PMMA with ferrocene using supercritical CO_2 (40°C , 91 bar).³⁰ Ferrocene is quite soluble in CO_2 (up to several wt %), in contrast to the disperse dyes.^{1,31} We were able to achieve 5.0 ± 0.1 wt % ferrocene impregnated in PMMA using CO_2 . Ferrocene is a nonpolar compound, so there presumably is not a high degree of affinity for the PMMA matrix. We attribute the loading of ferrocene to two factors.^{30,32} First, the thermodynamic partition coefficient is much smaller than that of the disperse dyes because of its higher solubility in the fluid phase. Second, the high solubility of ferrocene in the CO_2 phase may cause an appreciable amount of the solid to be deposited within the polymer matrix when the system is depressurized, and CO_2 leaves the polymer phase.

Diffusion of Dyes in CO_2 -Swollen PMMA

This next stage in this investigation was to study the mass transfer of the dye molecules into CO_2 -swollen PMMA. We found that, in all cases, the mechanism of uptake of solute into the polymer follows a Fickian model for diffusion. We modeled the data with a relationship that describes one-dimensional diffusion of a component through a finite plate, as follows²⁵:

$$\frac{A}{A_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{l^2}\right\}$$

where A is the absorbance at a given time, A_∞ is the equilibrium absorbance, D is the diffusivity,

l is the thickness of the film, and t is time. We found that truncating the series at $n = 8$ provided sufficient detail to fit the diffusion profile accurately.

Figure 9 shows the diffusion of DENAB (40°C) at 3 pressures. The diffusivity of DENAB increases as CO_2 pressure is increased, presumably, due to additional free volume available in the polymer caused by the swelling. Thus, the rate of dye uptake can be tuned simply by changing the pressure of CO_2 surrounding the polymer film.^{6-8,33}

It appears that the rate of mass transfer differs for the two dyes. Figure 10 shows the diffusion profile of DENAB and DR1 at 40°C and 91 bar. DR1 diffuses through the polymer at a much slower rate. This suggests that specific interactions between the DR1 and the polymer matrix may play a role in the diffusion process, unlike the thermodynamic partitioning process. In a dielectric study,³⁴ it has been suggested that there is hydrogen bonding between the hydroxyl group of DR1 and the ester repeating unit in PMMA. The evidence for such hydrogen bonding has been obtained via FTIR spectroscopy between DR1 and PMMA.⁶ Figure 11 shows there is consistently about an order of magnitude difference in the diffusivity of DR1 and DENAB in the polymer matrix at all pressures studied. We suggest that the molecular friction⁶ between the DR1 molecule and the swollen-polymer matrix may be due to the hydrogen bonding.

Figure 12 shows the same data plotted versus the degree of swelling taken from Wissinger and Paulaitis.¹⁶ The data appear to be consistent with a free volume theory of mass transfer.³⁵ The diffusion of azo-dyes in a swollen gelatin matrix³⁶ and the diffusion of phenylalanine in swollen poly(2-

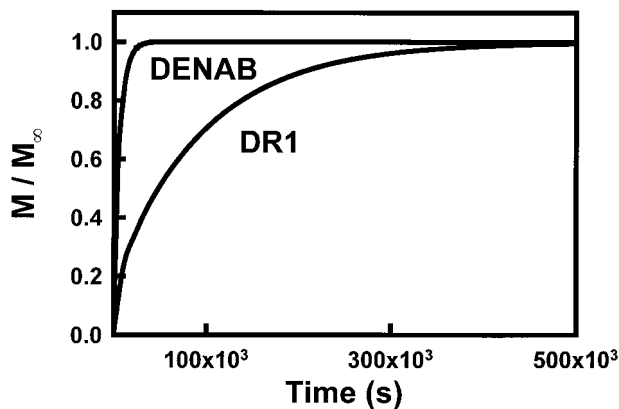


Figure 10 Relative mass uptake of DENAB and DR1 in CO_2 -swollen PMMA at 40°C and 91 bar.

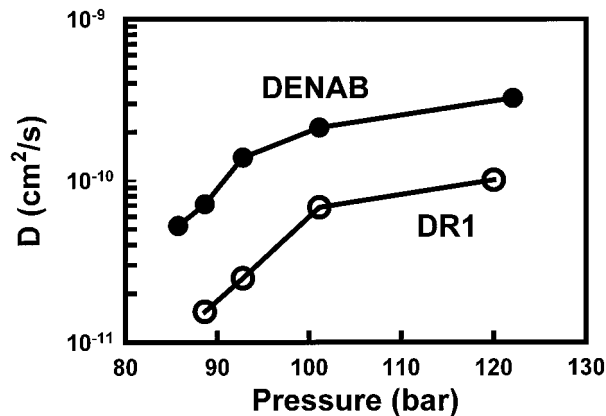


Figure 11 Pressure dependence of the diffusivities of (●) DENAB and (○) DR1 in supercritical CO₂ at 40°C.

hydroxyethyl methacrylate)³⁷ also agree with the free volume theory.

In a final experiment, we compare the diffusivity of DENAB in CO₂-swollen PMMA to that of heat-plasticized PMMA. Here, we placed DENAB in the base of an optical cell heated to 120°C in a N₂ environment (1 bar). DENAB under these conditions has a sufficient sublimation pressure to be transported into the polymer phase. We followed the diffusion of the dye into the polymer matrix using the same spectroscopic approach. The diffusion is much slower than that in CO₂-plasticized PMMA, despite the considerably higher temperature. Although we have not reached saturation of the dye in the polymer film in this case, we estimate the diffusivity to be approximately 9×10^{-12} cm²/s. This value indicates that swelling the polymer with CO₂ facilitates the mass transfer of dyes into the polymers considerably.

However, it has been shown that the presence of CO₂ in the polymer matrix can enhance significantly the diffusivity of solutes in polymers. Vincent et al.⁷ compared the diffusion of water in CO₂-swollen PMMA with that of lyophilically swollen PMMA.³⁸ They concluded that free volume theory alone cannot describe the difference in the two systems. Chapman et al.⁸ studied diffusion of azobenzene in CO₂-swollen polystyrene and the diffusion of the same dye in tricresyl phosphate (TCP) plasticized polystyrene. The CO₂-swollen matrix showed an enhanced diffusivity over a matrix with similar free volume. The presence of CO₂ in a swollen matrix seems to play a role in the mass transport process, possibly by solvating the dyes and, thus, facilitating the diffusion.^{6,8} This phenomenon is analogous to the effect of liquid organic solvents, which

can also plasticize polymers and increase impregnation rates of dyes in polymers.³⁹

CONCLUSIONS

We have measured the partition coefficient of two azo-dyes between a swollen PMMA phase and a supercritical CO₂ phase. The solubility of the dyes was very low in the supercritical fluid, but appreciable mass uptake was achieved in the PMMA phase. Thus, the partition coefficients were very high. There is about an order of magnitude difference in the partition coefficient of DENAB and DR1. However, this difference is a result only of differences of solubility in the fluid phase. Both dyes seem to have the same affinity for the polymer matrix at the conditions studied. In both cases, the high partition coefficient demonstrates that in a supercritical fluid impregnation process, the solubility of the penetrant in the fluid phase is not the only governing factor. Rather, the relative affinity of the molecule by both the fluid phase and the matrix should be considered.⁴⁰

This is quite different than a supercritical fluid extraction process, where the solubility of the extractant in the fluid phase should be as high as possible. Thus, for example, addition of cosolvents can indeed help an extraction process by the affinity of the molecule to the fluid phase. In a supercritical fluid dyeing process, the addition of cosolvents might increase the solubility of dyes in the fluid phase but also might cause a decrease of the partition coefficient. This increase of solubility in the fluid phase would thus decrease the dye loading in the polymer. Moreover, the low sol-

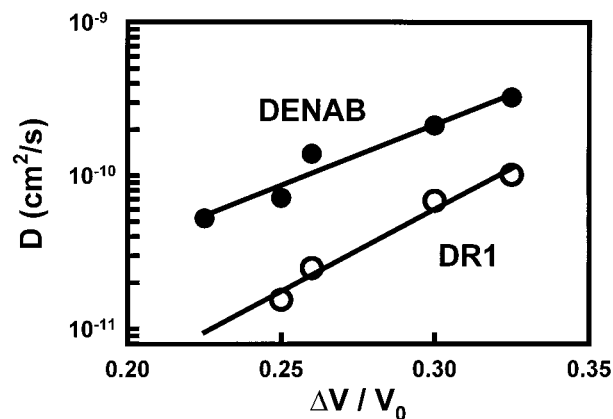


Figure 12 Diffusivity of (●) DENAB and (○) DR1 in CO₂-swollen PMMA at 40°C as a function of the degree of swelling of PMMA caused by the incorporation of CO₂.

ubility in the fluid constitutes a great advantage in minimizing dye losses (and, thus, environmental burdens) in loading and unloading dyeing apparatus on an industrial scale.

The diffusivities of these dyes were also measured in CO₂-swollen PMMA by an *in situ* spectroscopic approach that measures the mass uptake of dye as a function of time without disturbing the pressurized system. The presence of CO₂ as a plasticizer facilitates the mass transport process, and the diffusivity can be tuned by simply changing the pressure of the system. Additionally, we found the ability of DR1 to form hydrogen bonds with polymer matrix results in a considerable decrease in the diffusivity of the dyes in the polymer.

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