

# A high pressure fiber-optic reactor with charge-coupled device array ultraviolet-visible spectrometer for monitoring chemical processes in supercritical fluids

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A versatile spectroscopic reaction monitoring system for high-pressure liquids and supercritical fluids is described. The cell is designed to be attached to a charge-coupled device array ultraviolet-visible spectrometer via fiber optics, and has been shown to be capable of monitoring high speed reactions and rate of dissolution of a variety of compounds. The design is simple, inexpensive, rugged, and self-aligning. The cell has been tested up to 300 atm and 100 °C without failure. © 1999 American Institute of Physics. [S0034-6748(99)05212-0]

## I. INTRODUCTION

Supercritical fluids are currently being used for the extraction of organic and inorganic compounds in both the research and the commercial sector.<sup>1</sup> In addition, an increasing number of research facilities are reporting the use of supercritical fluids as reaction solvents.<sup>2</sup> Supercritical fluids offer several advantages over conventional organic liquids as solvents for separation and for reaction. First, if the supercritical fluid is carbon dioxide, as it usually is, no environmentally unfriendly organic waste is produced. Second, supercritical fluid allows rapid separation of solutes from solvent usually by depressurizing the fluid phase causing precipitation of the products. Third, because of its low viscosity and high diffusivity, rate of transport of solutes in supercritical fluid may be significantly higher than that in conventional solvents. In addition, by changing the pressure and the temperature, the density and solvating power of the supercritical fluid solvent can be changed, thus allowing "tuning" of the solvent to alter the rate of reaction and occasionally the products. This drive to do reactions in supercritical fluids has created a need for the online monitoring of reaction kinetics for the optimization of conditions. Previous spectroscopic experiments in supercritical fluids to determine solubility and monitor reactions has relied on precisely machined view cells with optically transparent windows to enable measurements to be made.<sup>3</sup> These cells are generally difficult and time consuming to clean; the windows are expensive and prone to leakage around the window-cell interface; additionally, the fixed pathlength of this design limits the range of solubilities that can be measured.

To overcome these difficulties, several groups have developed cells based on fiber optics to probe supercritical solutions with a range of spectroscopic techniques. For example, Rhode and Fox reported a high-pressure fiber-optic cell for time-resolved emission and absorbance measure-

ments in near and supercritical solvents.<sup>4</sup> Recently, our laboratory has developed a fiber optic system for the determination of metal chelate solubilities in supercritical CO<sub>2</sub> over several orders of magnitude in concentration.<sup>5</sup> These fiber-optic cells were adapted to standard spectrometers utilizing some form of optical-to-fiber coupling.

In this work, we report the development of a fiber-optic based reactor connected directly to a CCD array ultraviolet (UV)-visible spectrometer for *in situ* determination of reaction rates in supercritical CO<sub>2</sub>. The design of the fiber-optic cell is similar to that described previously in the literature.<sup>4,5</sup> In our design, mounting of optical fibers was accomplished using polyetheretherketone (PEEK) tubing rather than with graphite ferrules as described in the previous report.<sup>4</sup> Our design allows a more precise alignment of smaller fibers, creates a more robust seal, and reduces the damage to the delicate optical fibers. The most drastic difference is the addition of a 9.5 mL reaction cell via a welded flange. The flange/spectroscopic manifold assembly can be connected to different reaction vessels with volumes ranging from 5 to 100 mL, enabling us to investigate a variety of reactions and verify the results using standard analytical techniques; something that is not always possible when working on the micro scale. Additionally, the flange arrangement greatly simplifies the loading of reactants and cleaning the cell between experiments. The flat bottom of the reaction vessel enables the use of a stir bar on an ordinary stirring hot plate, facilitating mixing of reactants and alleviating the problems associated with diffusion in some reaction systems. The fiber-optic reaction cell described in this article was connected to a high speed CCD array UV-visible spectrometer thus facilitating the measurement of reactions of varying rates. To cost effectively build a reaction monitoring spectroscopic cell, we used commonly available materials and commercially obtainable components. The cell can be configured either to study the kinetics of reactions or to determine the rate of dissolution and the solubility of compounds in supercritical fluids. Examples of both of the processes will be presented in this article.

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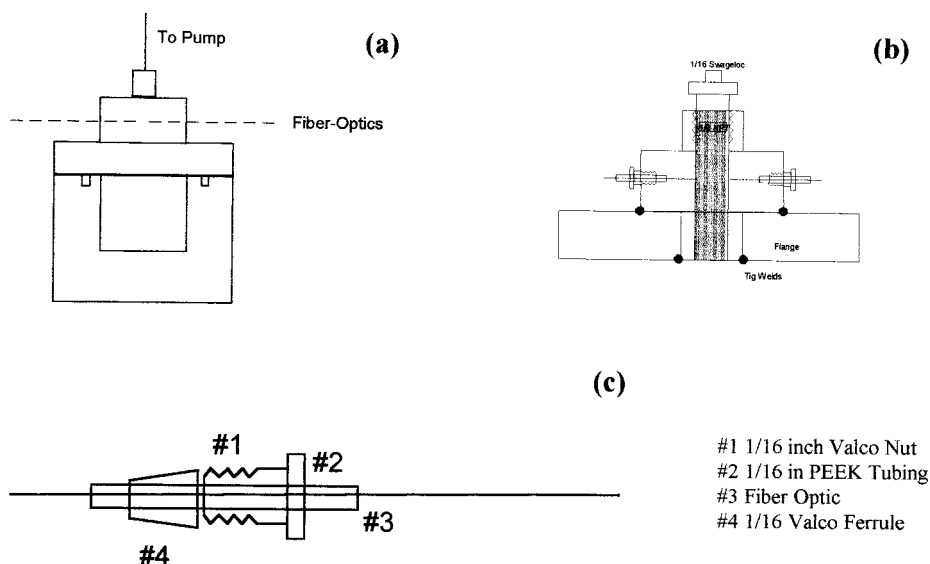


FIG. 1. The high-pressure fiber-optic reactor. (a) Fiber-optic reactor cell, (b) flange and fiber-optic mounting fixture, (c) fiber-optic sealing system.

## II. EXPERIMENTAL

### A. Fiber-optic reactor cell

A schematic of the reaction vessel is shown in Fig. 1. The cell has a single optical path formed by the ends of the two fiber optics and can be configured with path lengths of approximately fifty microns to one cm. In addition, it can be modified to have a perpendicular optical path making it possible to configure for fluorescent measurements. The cell was machined from type 316 stainless steel and has an internal volume of 9.5 ml. The fiber optic holding fixture was constructed from a modified Valco manifold which was Heliarc (Tungsten Inert Gas) welded to the stainless steel flange that functions as the port for introducing solid reactants. The flange is sealed to the cell body with a 3/16 inch Teflon gasket [Figs. 1(b) and 1(c)].

In order to avoid the use of windows and achieve the pathlengths needed, it is necessary for the optical fibers to be immersed in the ScF in an aligned and rigid manner. We have found in our research laboratory that the most satisfactory method for achieving these conditions is to mount the fibers in a manifold using standard high-pressure components, thereby making use of the precisely machined manifolds to achieve alignment. The optical fibers (Polymicro Technologies, Phoenix, AZ) used for this study were 600  $\mu\text{m}$  high OH-silica core surrounded by silica cladding and a polyimide buffer, giving a total outer diameter of 710  $\mu\text{m}$  and a numerical aperture of 0.22. The end of each fiber was fitted with a SMA 906 connector for coupling with the spectrophotometer. The optical path end of the fibers were held in place in the manifold by inserting the distal end through a 2 cm sleeve of PEEK tubing (Fisher Scientific, Pittsburgh, PA) 1/16 in o.d.  $\times$  0.03 in i.d. and inserted into one port of the manifold. The PEEK tubing was compressed by a stainless steel Valco ferrule upon tightening the fitting, thus sealing the fiber into the cell. The output fiber was placed in the opposite port of the manifold and the procedure repeated. Assuming the manifold has the ports milled accurately, the optical components are self-aligning since the threaded nut, ferrule and tubing are concentric and center the fibers. The

#1 1/16 inch Valco Nut  
 #2 1/16 in PEEK Tubing  
 #3 Fiber Optic  
 #4 1/16 Valco Ferrule

high-pressure fiber-optic reactor has been tested up to 300 atm and 100  $^{\circ}\text{C}$  without failure.

### B. High pressure equipment

The fiber optic reaction vessel was connected to the supercritical fluid system by 1/16 in. stainless steel tubing with Swagelok components. High-pressure valves (HIP, Erie, PA) were used on both sides of the cell and to control the injection loop. Figure 2 shows the general plumbing arrangement for these studies. A sample loop of 0.7 ml was used to inject one of the reactants into the reaction vessel. Accurate pressure was accomplished by operating the ISCO Model 260D syringe pump in the constant pressure mode. A 10 cm section of 50  $\mu\text{m}$  fused silica was attached to the outlet end of the system to control the rate of depressurization.

### C. CCD array UV-visible spectrometer

A CCD array UV-vis Spectrophotometer Model SI-440 (Spectral Instruments, Inc. Tucson, AZ) was used for all measurements in this study. The instrument was retro fitted with female SMA fittings, as was the fiber combiner to function with our existing spectroscopic equipment. Spectra were

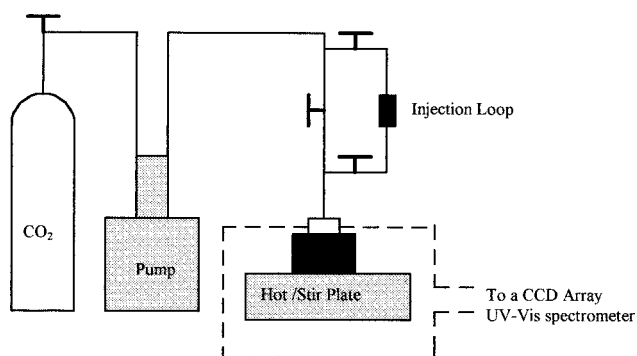


FIG. 2. Schematic of experimental arrangement for high pressure experiments. The injection loop has a volume of 0.7 mL and is controlled by two HIP valves. The fiber optic cell is connected to a CCD array UV-vis spectrometer.

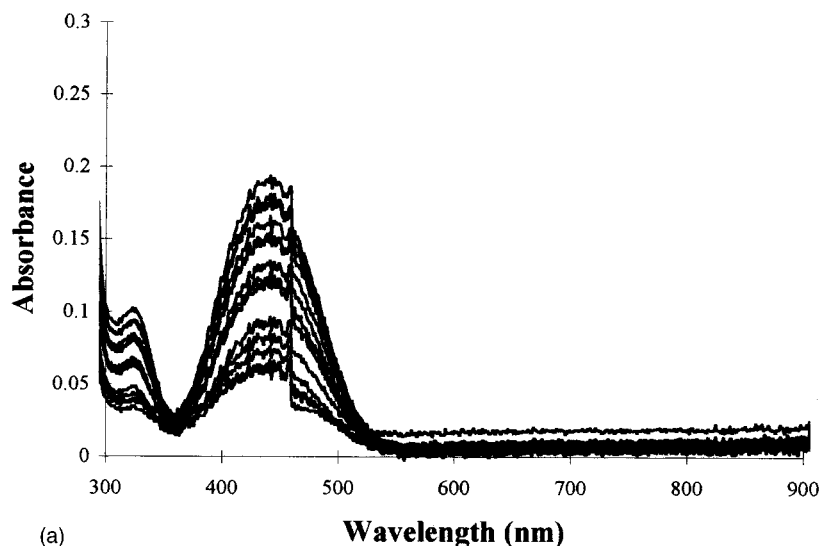
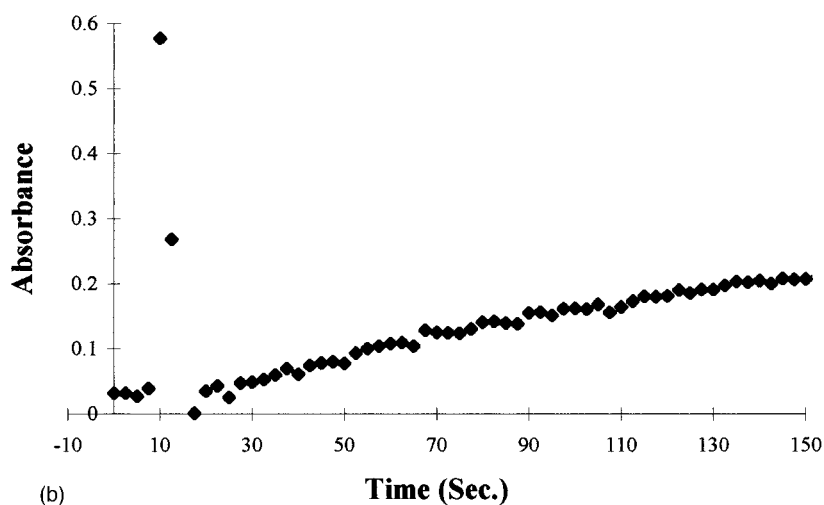


FIG. 3. (a) UV-vis spectra of ferrocene in supercritical  $\text{CO}_2$  at  $38^\circ\text{C}$  and 200 atm, (b) change of absorbance with time (2.5 s intervals) for the 434 nm ferrocene peak.



taken under a variety of conditions with full spectra being taken from 200 to 900 nm to determine the peak absorption and the kinetic spectra taken at a single wavelength at a maximum rate of about one spectrum every 2 s. A blank measurement was taken before every reaction to provide a baseline.

### III. RESULTS AND DISCUSSION

#### A. Measuring dissolution rates

One major application of supercritical fluid technology is extraction of organic compounds from solid materials. The rate of dissolution of organic compounds in supercritical  $\text{CO}_2$  is an important factor in determining the extraction time and the efficiency. Some organic compounds dissolve readily in supercritical  $\text{CO}_2$  with high solubilities; others may be less soluble or slower in dissolution. Modeling solubility and dissolution rate of organic solutes in supercritical fluids requires experimental data. The high-pressure fiber-optic reactor with CCD array UV-vis spectrometer enables us to obtain such information for the compounds which have characteristic absorption bands in the UV-visible region. The pathlength of the optical fiber system for the experiments described in this article was fixed at 0.5 cm. Actually, the pathlength of the

optical fiber in the reactor can be changed to suit the experimental needs. For example, the pathlength can be increased for measuring compounds with low solubilities.

Figure 3 shows the dissolution of ferrocene (m.p.= $174^\circ\text{C}$ ) in supercritical  $\text{CO}_2$  at  $38^\circ\text{C}$  and 200 atm measured by the high pressure fiber-optic reactor. The experiment started by placing 18 mg of ferrocene in the reactor. Supercritical  $\text{CO}_2$  was then introduced and the fiber-optic spectrometer was turned on. Ferrocene has absorption peaks in the UV-visible region at 324 nm and at 440 nm in supercritical  $\text{CO}_2$ . The spectra shown in Fig. 3(a) were taken at 2.5 s intervals. Figure 3(b) shows the increase in intensity of the 440 nm peak with respect to time. In this experiment, recording of the UV-vis spectra started before the introduction of supercritical  $\text{CO}_2$ . Ten seconds after the spectrometer was turned on, supercritical  $\text{CO}_2$  was added to the reactor. An absorbance change at the fifth data point in Fig. 3(b) was caused by the pressure change associated with the introduction of supercritical  $\text{CO}_2$ . The pressure disturbance lasted for about 5 s. After that, the intensity of the 440 nm peak began to increase steadily with time. The peak intensity reached approximately a constant value after about 8 min. The rate of dissolution of ferrocene is slow compared with its dimethyl derivative 1,1'-dimethylferrocene (DMFC) which will be

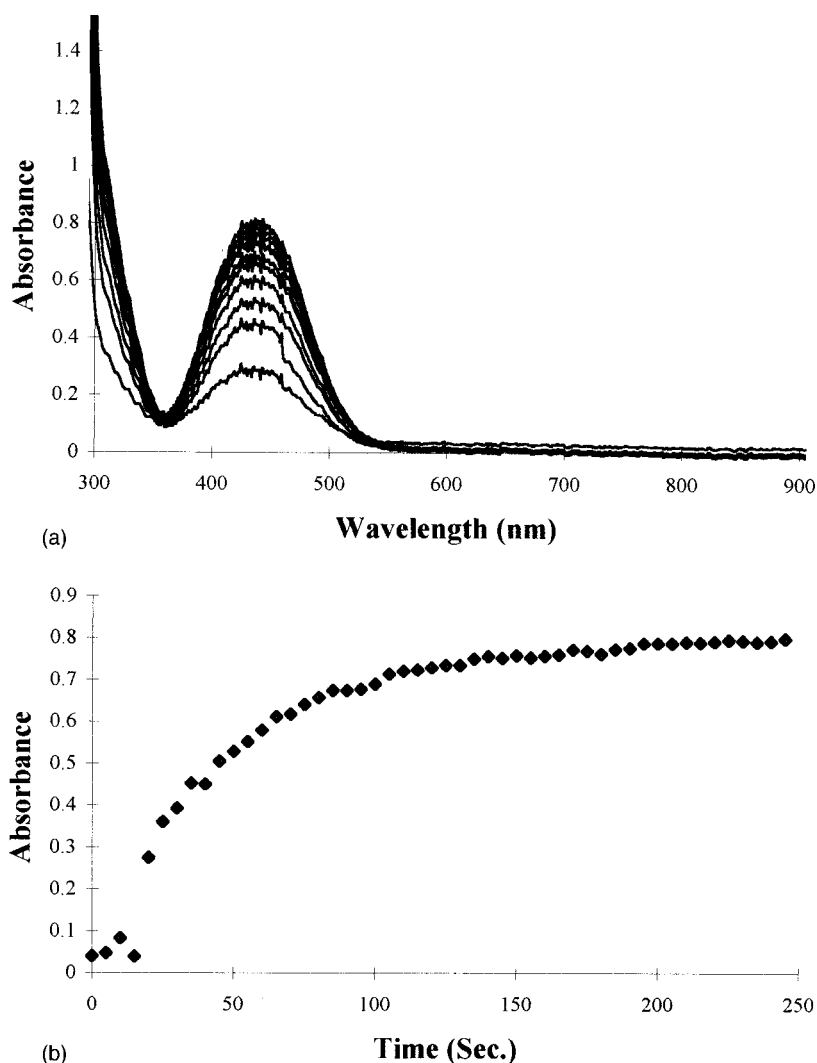


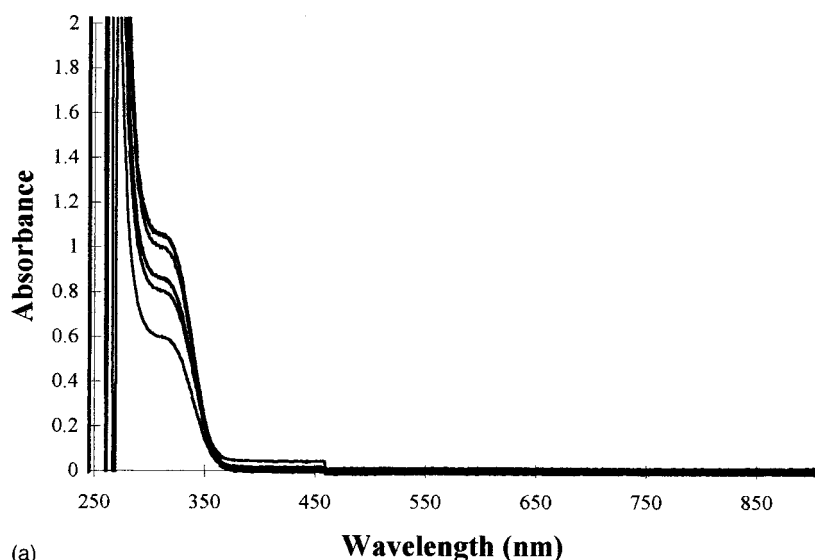
FIG. 4. (a) UV-vis spectra of 1,1'-dimethylferrocene (DMFC) in supercritical CO<sub>2</sub> at 38 °C and 200 atm, (b) change of absorbance with time (5 s intervals) for the 434 nm DMFC peak.

discussed later. The solubility of ferrocene in supercritical CO<sub>2</sub> under the specified conditions can be calculated from the absorbance of the saturation peak at 440 nm with a calibration curve obtained by dissolving known amounts of the compound in the fluid phase. The solubility of ferrocene in supercritical CO<sub>2</sub> at 38 °C and 200 atm determined by this method is 0.055 M (mol/L). Cowey *et al.* measured the solubility of ferrocene in supercritical CO<sub>2</sub> under various temperature and pressure conditions using a chromatographic method.<sup>6</sup> For example, they reported a solubility of 0.042 M for ferrocene in supercritical CO<sub>2</sub> at 40 °C and 183.9 bar. Our measured solubility for ferrocene in CO<sub>2</sub> at 40 °C and 184 atm is 0.046 M, consistent with the value reported by Cowey *et al.* However, these authors did not report the rate of dissolution of ferrocene in supercritical CO<sub>2</sub>.

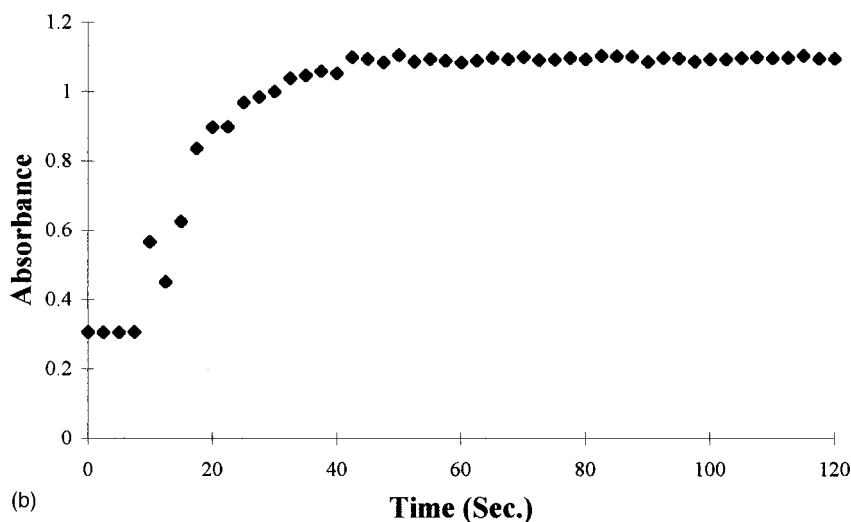
The dissolution of DMFC (1,1'-dimethylferrocene, m.p. 37.4 °C) in supercritical CO<sub>2</sub> is shown in Fig. 4. This compound absorbs strongly at 434 nm in supercritical CO<sub>2</sub>. Figure 4(a) shows the UV-vis spectra of DMFC recorded by the fiber-optic reactor in supercritical CO<sub>2</sub> at 38 °C and 200 atm. The experimental data were obtained by placing 41 mg of DMFC in the reactor and the spectra were taken at 5 s intervals. Figure 4(b) shows the increase in intensity of the 434 nm peak with respect to time. Supercritical CO<sub>2</sub> was intro-

duced to the reactor 15 s after the start of spectra recording. A small absorbance jump at the third data point in Fig. 4(b) was caused by the pressure change associated with the introduction of the fluid. The absorbance of the 434 nm peak increased rapidly after this point indicating a rather fast dissolution of DMFC in the fluid phase. The intensity of the DMFC peak reached a constant value after about two minutes. The constant absorbance value was actually due to the total dissolution of the DMFC initially placed in the reactor. After the experiment, the reactor was opened and no DMFC was found inside. DMFC is extremely soluble in supercritical CO<sub>2</sub>. We performed experiments with very large amounts of DMFC in the reactor and estimated that the solubility of DMFC in supercritical CO<sub>2</sub> at 38 °C and 200 to be >0.5 M.

The rate of dissolution of DMFC in supercritical CO<sub>2</sub> is obviously much faster than that of ferrocene. Analysis of the dissolution data of DMFC indicated that the dissolution is very rapid initially. Nearly 10 mg of the solute was dissolved in supercritical CO<sub>2</sub> in the first 5 s. This was probably caused by the rapid pressure change and stirring of the solute in the high-pressure reactor after the introduction of the fluid. The dissolution rate in general appeared to follow a first order kinetics. At 38 °C, DMFC should be in the liquid state. The



(a)



(b)

FIG. 5. (a) UV-vis spectra of tetramethyl-*para*-phenylenediamine (TMPD) in supercritical CO<sub>2</sub> at 38 °C and 200 atm, (b) change of absorbance at 325 nm with time (5 s intervals).

dissolution of a liquid in supercritical CO<sub>2</sub> is apparently much faster compared with that of a solid as in the case of ferrocene.

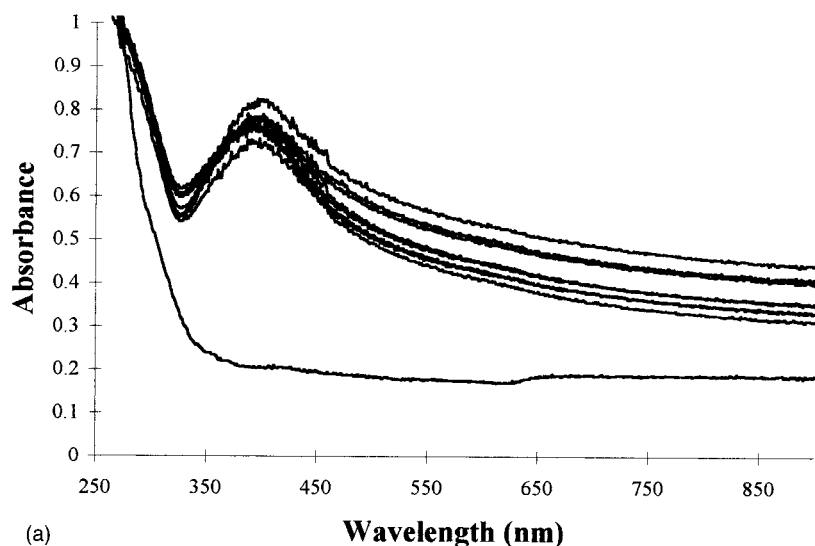
Another example is the dissolution of *N,N,N',N'*-tetramethyl-*para*-phenylenediamine (TMPD) in supercritical fluids. TMPD absorbs in the UV region with a peak maximum at 313 nm [Fig. 5(a)]. The melting point of TMPD at 1 atm is 49.5 °C. Figure 5(b) shows the rate of dissolution of TMPD (1.6 mg) in the high-pressure fiber-optic cell at 38 °C and 200 atm. The UV/vis spectra shown in Fig. 5(a) were recorded every 2.5 s for a total of 125 s. The height of the absorption peak at 313 nm reached a saturation value in about 40 s after the introduction of the supercritical CO<sub>2</sub> [Fig. 5(b)]. This was also due to the total dissolution of the solute placed in the reactor in supercritical CO<sub>2</sub>. The solubility of TMPD in supercritical is also very high, estimated to be >0.5 M at 38 °C and 200 atm.

The three examples shown in Figs. 3–5 illustrate that the dissolution rates of organic compounds in supercritical CO<sub>2</sub> can be quite different, varying from less than a minute to about 10 min. The factors determining rate of dissolution of a solute in supercritical CO<sub>2</sub> is probably complicated and difficult to predict. Direct measurement of dissolution of sol-

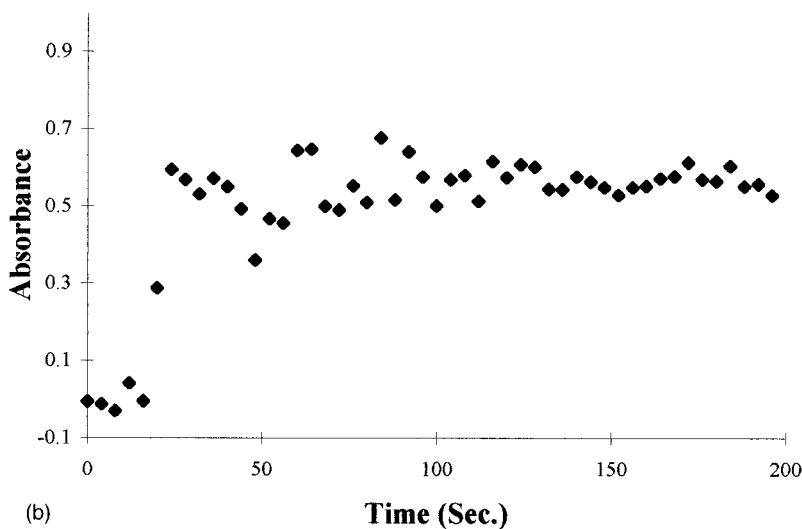
utes in supercritical CO<sub>2</sub> is perhaps the easiest way of obtaining such information at the present time. The high-pressure fiber-optic reactor described in this article provides a convenient method for obtaining such information, which is often needed for designing extraction processes or studying chemical reactions in supercritical fluids.

## B. Studying redox reactions in supercritical carbon dioxide

In a recent report, synthesis of silver nanoparticles in a water-in-supercritical CO<sub>2</sub> microemulsion was reported.<sup>7</sup> The process involved the formation of a water-in-CO<sub>2</sub> microemulsion containing silver nitrate in the water phase, followed by the reduction of Ag<sup>+</sup> to metallic Ag using a reducing agent dissolved in the fluid phase. The water-in-CO<sub>2</sub> microemulsion was formed by mixing an aqueous solution containing silver nitrate and a mixture of two surfactants consisted of bis(2-ethylhexyl)sulfosuccinate (AOT) and a perfluoropolyether-phosphate ether with a general structure of CF<sub>3</sub>O[OCF(CF<sub>3</sub>)CF<sub>2</sub>]<sub>*n*</sub>(OCF<sub>2</sub>)<sub>*m*</sub>OCF<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>-CH<sub>2</sub>OPO(OH)<sub>2</sub> and an average molecular weight of 870.<sup>7</sup> The same surfactants and composition were used in this



(a)



(b)

FIG. 6. (a) UV-vis spectra of Ag nanoparticles in the water-in- $\text{CO}_2$  microemulsion in supercritical  $\text{CO}_2$  at  $38^\circ\text{C}$  and 200 atm. Reduction of  $\text{Ag}^+$  was achieved using sodium cyanoborohydride. (b) Variation of absorbance at 400 nm by Ag nanoparticles with respect to time.

study to make the water-in-supercritical  $\text{CO}_2$  microemulsion. In our experiments, the water phase contained 3.3 mM of  $\text{AgNO}_3$ . Formation of the microemulsion was first investigated in a high-pressure view cell at a W value (water/AOT) of 12 by rapidly mixing the aqueous solution and the surfactants with a magnetic stirrer in supercritical  $\text{CO}_2$ . The optically transparent microemulsion was visually observed after 30 min of mixing. The same conditions were then applied to the formation of the microemulsion in the high-pressure fiber-optic reactor. To ensure the formation of a homogeneous microemulsion, the mixing time for the high-pressure fiber-optic reactor experiments was set at one hour. After that, stirring was stopped and a reducing agent (sodium cyanoborohydride, 1 mM) was injected into the system through a 0.7 ml stainless steel vessel connected to the reactor as shown in Fig. 2. Silver nanoparticles are yellowish in color and exhibit a broad absorption band (due to the surface plasmon resonance absorption) centered around 400 nm.<sup>8</sup> The absorption of Ag nanoparticles made in this system is shown in Fig. 6(a). The absorbance of the broad absorption band characteristic of Ag nanoparticle increases rapidly with time. Bandwidth analysis indicates that the particles have a size of about 4 nm, consistent with that observed in a previous

report.<sup>7</sup> Figure 6(b) shows the increase in absorbance of the Ag nanoparticle peak at 400 nm with respect to time. According to Fig. 6(b), the reduction of  $\text{Ag}^+$  and the formation of silver nanoparticles in this system were essentially complete within 30 s after the injection of the reducing agent.

The rapid reaction rate observed in this system suggests that the microemulsion in supercritical  $\text{CO}_2$  is dynamic in nature and that the reducing agent can easily penetrate the microemulsion membrane to cause reduction of  $\text{Ag}^+$  in the aqueous core. This type of information is very useful for understanding the nature of the microemulsion formed in supercritical fluids. A number of reaction systems utilizing the water-in- $\text{CO}_2$  microemulsion as a “nanoreactor” to synthesize nanoparticles in supercritical  $\text{CO}_2$  are currently in progress. The high-pressure fiber-optic reactor described in this article provides a powerful tool for studying these interesting reactions taking place in supercritical  $\text{CO}_2$ .

Even though only a few examples are given in this article, it is not hard to imagine the usefulness of this instrument for studying rate-related problems in supercritical fluids. The design of this reactor is simple, inexpensive, serviceable, uses conventional materials and is self-aligning.

The best application range of this instrument is probably for the chemical processes occurring in the order of tens of seconds to several minutes. The CCD array spectrometer used in this study is limited to about one spectrum per two seconds. For very rapid reactions, e.g., reactions reaching completion in the order of a few seconds, this type of detector may not be fast enough. However, for many chemical processes in SF CO<sub>2</sub>, diffusion of reactants is often the limiting factor and the time scale of such process is in the range measurable by the high-pressure fiber-optic reactor interfaced with a CCD array spectrometer. The reactor is currently being used for studying a variety of chemical reactions taking place in liquid and in supercritical carbon dioxide.

## ACKNOWLEDGMENT

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