

# Water in Supercritical Carbon Dioxide Microemulsions: Spectroscopic Investigation of a New Environment for Aqueous Inorganic Chemistry

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**Abstract:** In this paper, we present spectroscopic evidence for the formation of water in supercritical carbon dioxide (scCO<sub>2</sub>) microemulsions stabilized by an ammonium carboxylate perfluoro polyether (PFPE) surfactant. FTIR spectroscopy has been employed to determine the existence of “bulk” (hydrogen-bonded) water (H<sub>2</sub>O and D<sub>2</sub>O) at the core of the microemulsions, and to distinguish between this and the presence of “free” (monomeric) water dissolved in the scCO<sub>2</sub> and builds on preliminary results described elsewhere (Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph, T. W. *Science* **1996**, *271*, 624). Cloud point studies confirm that optically transparent and thermodynamically stable microemulsion solutions are formed. We have investigated the utility of these microemulsions as novel environments for reaction chemistry. In particular, we have shown that, using the PFPE surfactant, an aqueous solution of potassium permanganate (KMnO<sub>4</sub>) may be dispersed in scCO<sub>2</sub>, leading to a purple-colored solution with concentration on the order of  $5 \times 10^{-4}$  M, as detected by UV–vis absorption spectroscopy. Moreover, aqueous sodium nitroprusside (Na<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)]) and potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) are also shown to be soluble in the water/PFPE/scCO<sub>2</sub> microemulsions and to undergo simple aqueous inorganic reactions with gaseous reactants such as H<sub>2</sub>S and SO<sub>2</sub>. Methyl orange has been used to investigate the presence of a carbonic acid microenvironment in the water/PFPE/scCO<sub>2</sub> microemulsions.

## Introduction

Supercritical carbon dioxide (scCO<sub>2</sub>) shows promise as an environmentally acceptable solvent for a wide range of chemical, analytical, and materials processes including extraction and materials processing,<sup>1</sup> supercritical fluid chromatography,<sup>2</sup> polymerization,<sup>3</sup> catalytic reactions,<sup>4</sup> and synthesis of novel organometallics.<sup>5</sup> Each of these applications has drawn upon the unique combination of properties found in supercritical fluids, namely low viscosity, high diffusivity, rapid product recovery, and complete miscibility of added reactant gases.<sup>1,6</sup>

One major limitation to the broader use of scCO<sub>2</sub> is its inability to dissolve a wide range of hydrophiles, in particular

ionic species. Recent work<sup>3b,7</sup> has shown that chelating ligands may be employed to extract toxic heavy metal species and to solubilize them in scCO<sub>2</sub>. These chelating ligands act in much the same way as the crown ethers and cryptands that have been used for many years to dissolve metal ions in conventional organic media.<sup>8</sup> The chelating ligands for scCO<sub>2</sub> are fluorinated, because the weak intermolecular van der Waals' forces between the fluorinated molecules are similar to those found in CO<sub>2</sub>,<sup>9</sup> thus leading to high solubility in scCO<sub>2</sub>.

An alternative methodology is the use of surfactants to stabilize microemulsions of water, so called water-in-oil (w/o) microemulsions. These surfactants are amphiphilic molecules, which contain a hydrophilic head group and a hydrophobic tail, where the molecular size and shape of the head and tail are designed to favor aggregation. When such molecules aggregate in oil solution, a reverse micelle is formed, with the hydrophilic head groups forming a core and the hydrophobic tails interacting with the oil phase (Figure 1). When water is added, it partitions into the hydrophilic core, forming microscopic water pools which swell the reverse micelles, leading to w/o microemulsions. Such systems are characterized by the ratio of water-to-surfactant molecules in the solution ( $W_0$ ). In general, systems with  $W_0 < 15$  are referred to as reverse micelles, whereas  $W_0 > 15$  indicates larger water droplets and are labeled as microemulsions.<sup>10</sup>

Over the past decade, there has been intense research into the development of such surfactants for supercritical fluid applications. Elegant studies by several groups<sup>11–15</sup> have shown that surfactants such as bis(2-ethylhexyl) sodium sulfosuccinate

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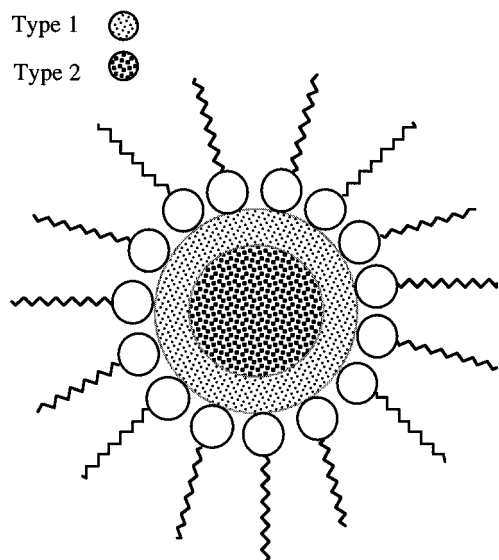
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**Figure 1.** Schematic representation of the water environments in reverse micelles or microemulsions showing the possible environments in which water may be found.<sup>21</sup> Bound or interfacial water (type 1) is closely associated with the ionic head groups (represented by the white circles) of the PFPE surfactant molecules. Bulk water (type 2) is located at the core, forming a water pool or droplet. (A third environment is that of free water which is dissolved in the “oil” or scCO<sub>2</sub> phase and is not associated with the microemulsion environment.)

(AOT) can form thermodynamically stable microemulsions of water in supercritical alkanes and in supercritical xenon. However, dispersion of water in scCO<sub>2</sub> has proved to be elusive, despite attempts with more than 150 surfactants during the last decade.<sup>16</sup> Block copolymer systems in scCO<sub>2</sub> have also been investigated,<sup>17</sup> and show formation of very large micelles, with a hydrated poly(ethylene oxide) core. Recently, preliminary results of four different spectroscopic studies (FTIR, UV-vis, fluorescence, and EPR) provided the first conclusive evidence for formation of water in carbon dioxide microemulsions.<sup>18</sup>

Scattering techniques provide the most definitive proof of the formation of micellar aggregates and have been applied successfully by a number of groups to various high-pressure

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solutions including scCO<sub>2</sub> (small angle neutron scattering (SANS),<sup>11i,12b,19</sup> small angle X-ray scattering (SAXS),<sup>17</sup> and dynamic light scattering<sup>11e,11h,12</sup>). However, these techniques alone cannot demonstrate the formation of bulk water environments at the micelle core. Extensive phase behavior and cloud point measurements of scCO<sub>2</sub> solutions have shown conclusively that water is solubilized by various surfactant and cosurfactant materials, to significantly greater concentrations than that observed in the absence of surfactant. Again however, these methods are unable to show conclusively the presence of bulk water. Moreover, there is the added complication that a significant quantity of free (monomeric) water is soluble in dense CO<sub>2</sub>.<sup>20</sup>

Thus, the key problem is to identify the presence of bulk hydrogen-bonded water in the ammonium carboxylate perfluoro polyether (PFPE) microemulsions and to distinguish this from free monomeric water dissolved in the continuous scCO<sub>2</sub> phase. The focus of this paper is to demonstrate that FTIR spectroscopy can provide a direct insight into the formation of water-containing reverse micelles and microemulsions in scCO<sub>2</sub>.

Although the intense infrared absorptions of CO<sub>2</sub> itself actually mask a significant portion of the mid-infrared spectral region, we show that spectroscopic measurements of stretching and bending modes of both H<sub>2</sub>O and D<sub>2</sub>O microemulsions allow this difficulty to be overcome. Moreover, the spectroscopic data provide evidence for the presence of a further water environment, at the interface of surfactant and scCO<sub>2</sub>, in accordance with the model proposed by Zinsili<sup>21</sup> (Figure 1). We show that ionic complexes can be solubilized by water-in-scCO<sub>2</sub> microemulsions. These species are totally insoluble in pure scCO<sub>2</sub>, but will dissolve when both PFPE and added water are present, and our observations confirm that water pools with the properties of bulk water do exist in the microemulsions.

The local environment within a microemulsion droplet can be characterized with UV-vis solvatochromic probes. Methyl orange, [(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na], has been used to investigate the microenvironment in non ionic Triton-X100 reverse micelles in cyclohexane,<sup>22</sup> pentaethylene glycol *n*-octyl ether reverse micelles in CO<sub>2</sub>,<sup>23</sup> and large (25 nm) poly-(fluoroacrylate)-*g*-poly(ethylene oxide) reverse micelles in CO<sub>2</sub>.<sup>24</sup> The ethylene oxide core of the poly(fluoroacrylate)-*g*-poly(ethylene oxide) micelles was hydrated with approximately two water molecules per ethylene oxide group, and the absorption maximum ( $\lambda_{\max}$  = 418 nm) of the methyl orange probe was identical to that of water-free reverse micelles containing ethoxylated head groups, thus indicating that no bulk water was present. Recently, our experiments with methyl orange indicate that the polarity in PFPE water-in-CO<sub>2</sub> microemulsions begins to approach that of pure water ( $\lambda_{\max}$  = 460 nm).<sup>18</sup> In this paper, we show that methyl orange can be used to probe the acidity of these PFPE microemulsion water droplets and to investigate the possibility of the presence of carbonic acid.

Finally, using a combination of FTIR and UV-vis measurements, we test the nature of the aqueous environment by demonstrating that common ionic species undergo simple inorganic chemical reactions that are well-known in conventional aqueous solution.

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## Experimental Section

**Infrared and UV–Vis Studies.** The internal volume of the Nottingham high-pressure spectroscopic cell<sup>25</sup> was of the order of 0.5 mL with a spectroscopic path length of 2.8 mm, unless otherwise stated. The surfactant, ammonium carboxylate perfluoropolyether (PFPE), a waxy material at room temperature, has the general formula  $F_3C-[(OCF_2CF(CF_3))_n(OCF_2)_m]OCF_2COO-NH_4^+$   $\{n \approx 3, m \approx 2\}$  and an average molecular weight<sup>26</sup> of 740. The surfactant was stored in a dry, air-tight environment, but FTIR spectroscopy indicates the surfactant has a low but non-zero concentration of associated water which is very difficult to remove, a characteristic similar to other well-known surfactants.

The mass of  $CO_2$  used in these experiments was calculated to be 0.46 g (150 bar and 32 °C,  $\rho = 0.92 \text{ g cm}^{-3}$ ), PFPE (1.4 wt % with respect to  $CO_2$ ) was placed in the high-pressure cell, and the required quantity of water (deionized  $H_2O$  or 99.9 atom %  $D_2O$  (Aldrich)) was added via syringe. The cell was then sealed, and  $CO_2$  was added from a high-pressure pump (NWA PM101). The contents of the cell were stirred for a minimum of 2 h using a miniature magnetic flea, ensuring that no water droplets or film appeared on the cell windows; a single-phase, optically transparent solution was observed to form. In our experiments, water saturated solutions of  $scCO_2$  were formed in the absence of PFPE surfactant by addition of excess water to create a two phase system. Great care was taken to ensure that the excess water phase remains below the line of sight of the FTIR beam. A series of experiments showed that the concentration of water detected in the  $scCO_2$  in these two-phase systems was found to be independent of the amount of excess water added to the vessel, under the same conditions of temperature and pressure. Experiments in which excess water was deliberately deposited on the spectroscopic windows, by inverting or shaking the cell, confirmed that the presence of droplets/films of water was immediately detectable in the FTIR spectrum. For the studies of inorganic reactants, a measured volume of an aqueous solution of the inorganic species and solid PFPE were added directly to the cell. Carbon dioxide (32 °C/164 bar) was added, and the mixture was stirred to ensure formation of a homogeneous, optically clear solution.

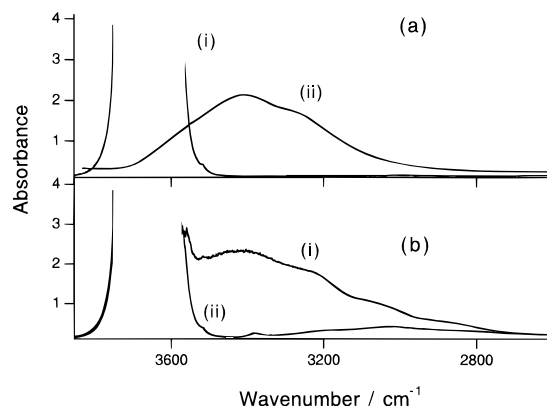
The solution temperature was measured *in situ* (RS K-Type probe, diameter = 1.6 mm) and was controlled from ambient temperature through to a maximum of ca. 100 °C ( $\pm 0.5$  °C) by means of a thermostatically controlled aluminium heating block encasing the cell. FTIR spectra were obtained at a nominal resolution of  $2 \text{ cm}^{-1}$  (16K data points, 32K transform points) on a Nicolet 730 spectrometer with liquid nitrogen cooled MCT detector and 680D data station. UV–vis measurements were performed in the same spectroscopic cell using a Perkin Elmer Lambda-5 spectrometer.

Potassium permanganate (East Anglia Chemicals), potassium dichromate (BDH), sodium nitroprusside (BDH), hydrogen sulfide (Aldrich 99.5+%), and sulfur dioxide (Aldrich 99.9%) were used as received.  $CO_2$  (99.99% Air Products, SFC Grade) was dried where necessary by passing through a molecular sieve in a 2 m column.

**UV–Vis Studies of Methyl Orange Probe.** A concentrated solution of the solvatochromic probe methyl orange,  $[(CH_3)_2NC_6H_4N=NC_6H_4SO_3Na]$ , was added to a 2.5 mL constant volume stainless steel cell fitted with two 1 in. diameter  $\times$  5/8 in. thick sapphire windows (1 cm path length). The solvent was evaporated to produce a methyl orange concentration on the order of  $5 \times 10^{-5} \text{ M}$ . The surfactant was added to the cell, along with a known volume of  $CO_2$ . The temperature was controlled to within  $\pm 0.1$  °C, and the pressure to  $\pm 0.2$  bar. The contents of the cell were equilibrated using a 7 mm long  $\times$  2 mm diameter magnetic stir bar for 15–20 min at a given temperature and pressure. Experiments were conducted in the order of increasing pressure by adding  $CO_2$  to maintain constant molarities of surfactant, water, and probe. Spectra were obtained with a Varian Cary 3E UV–vis spectrophotometer and were deconvoluted with the Peaksolve program, which uses a Levenberg–Marquardt nonlinear optimization algorithm to determine peak parameters based on initial estimates. The spectra were fitted with sums of Gaussian and Lorentzian line shapes. There are four parameters for each peak: peak height and wavelength

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**Figure 2.** FTIR spectra in the  $\nu(O-H)$  region of water. Traces are marked as follows: (a) (i) pure  $scCO_2$  (at 152 bar and 32 °C) shows only the strong overtone/combination band of  $CO_2$  centered at ca.  $3600 \text{ cm}^{-1}$ ; (ii) a thin film of liquid water comprising the broad  $\nu(O-H)$  band showing multiple hydrogen-bonding environments. (b) (i) optically clear microemulsions of  $H_2O$ /PFPE (uncorrected  $W_o = 32$ ) in  $scCO_2$  (152 bar and 32 °C) (a strong absorption centered at ca.  $3420 \text{ cm}^{-1}$  indicates the presence of bulk water); (ii) PFPE surfactant (1.4 wt %) in  $scCO_2$  (152 bar and 32 °C) in the absence of added  $H_2O$ . The vibrational features observed in the region of  $2700-3300 \text{ cm}^{-1}$  may be assigned to the ammonium ion<sup>29</sup> and to residual “bound” water associated with the surfactant head groups. Comparison with the infrared spectrum of the commercially available nonionic precursor (carboxylic acid end group) confirms the presence of the ammonium ion.

at the maximum, peak width at half peak height, and percent Lorentzian character. The correlation coefficients were always greater than 0.99, and the average percent deviation between the measured absorbance and the fitted value was  $\sim 6\%$  or  $< 0.03$  absorbance units. In these experiments, the value of  $W_o$  (corrected) is quoted, that is, the value obtained after correction for the presence of free water dissolved in  $scCO_2$ .

## Results and Discussion

Several features of FTIR spectroscopy make it a particularly suitable technique for the study of microemulsions; it is noninvasive and is sensitive to the environment of the species under study, particularly for the detection and characterization of water.<sup>27</sup> FTIR spectroscopy has been used in several detailed studies of water-in-oil microemulsions using AOT surfactant<sup>28,29</sup> and recently to study perfluoropolyether/water systems.<sup>30</sup>

Moreover, others<sup>11,31</sup> have made extensive use of FTIR spectroscopy to characterize reverse micelles and aggregates in supercritical alkanes and the rare gases krypton and xenon. All of these studies have focused on a detailed examination of the vibrational features associated with water, both dispersed in microemulsions and dissolved in the continuous (oil) phase. It is clearly important to take great care to ensure that no water droplets or surfactant-supported films are present upon the inner surfaces of the spectroscopic windows; situations which could of course lead to erroneous detection of bulk water in the FTIR spectra.

The FTIR spectrum of liquid water is characterized by a broad O–H stretching absorption ( $\nu(O-H)$ ) in the region of  $3750-3200 \text{ cm}^{-1}$  (Figure 2a) where the width of the band indicates

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the presence of many different hydrogen-bonded environments. The FTIR spectrum of scCO<sub>2</sub> in this same region reveals a broad overtone/combination feature centered at ca. 3650 cm<sup>-1</sup>. Using the data obtained from cloud point measurements (i.e. pressure, temperature, and concentrations of surfactant and water),<sup>18</sup> a solution was prepared in our high-pressure cell. The FTIR spectrum obtained (Figure 2b) appears as the superposition of the two spectra in Figure 2a, and most importantly, the broad feature centered at ca. 3500 cm<sup>-1</sup> corresponds to the  $\nu(\text{O-H})$  mode of bulk water solubilized in a microemulsion environment.<sup>11,28,30</sup> Closer examination reveals that the tail of this band contains some unexpected weak absorptions and extends to lower wavenumber than might be expected. These features can be assigned to the infrared absorptions of the PFPE surfactant itself (Figure 2b). The absorption maximum of the band of bulk water has been shown<sup>11</sup> to be strongly dependent upon the amount of water ( $W_o$ ) present.

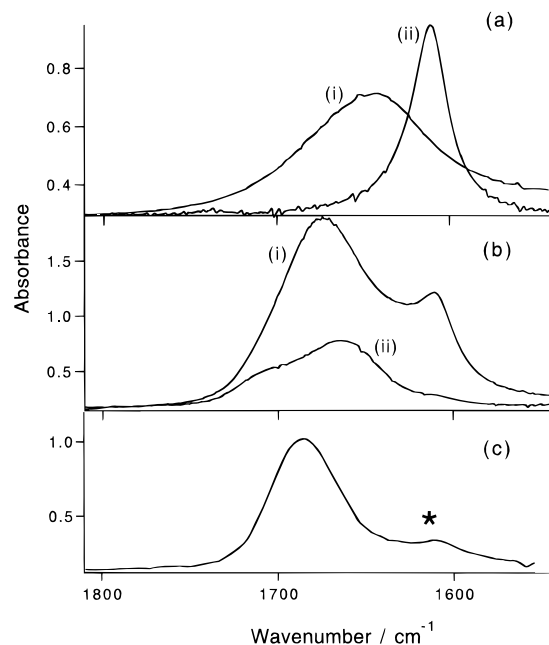
Water is known to have limited solubility in dense CO<sub>2</sub>.<sup>20</sup> The saturated concentration in scCO<sub>2</sub> at 31°C and 150 bar is of the order of  $2 \times 10^{-4}$  M and varies only modestly with density over the range of 0.75–1.00 g/cm<sup>3</sup> at a given temperature, but increases with temperature.<sup>20</sup> The presence of dissolved water in other solvents (e.g. carbon tetrachloride)<sup>28</sup> has been determined by FTIR spectroscopy, by observation of two sharp bands, the symmetric  $\nu_1$  and antisymmetric  $\nu_3$   $\nu(\text{O-H})$  modes at 3630 and 3700 cm<sup>-1</sup>. These bands are found at *higher* frequency than those of bulk-like water, reflecting the absence of intermolecular hydrogen bonding; hence, described as “free” or “monomeric” water. For scCO<sub>2</sub> totally saturated with water, these bands, if present, are completely obscured by the overtone/combination vibrational absorptions of scCO<sub>2</sub>.

In the region of 1800–1500 cm<sup>-1</sup>, liquid water is characterized by a strong  $\delta(\text{O-H})$  ( $\nu_2$ ) bending mode at 1640 cm<sup>-1</sup>, and there are no infrared absorptions of CO<sub>2</sub> (Figure 3a). The FTIR spectrum of scCO<sub>2</sub> saturated with water shows a much sharper  $\delta(\text{O-H})$  band at *lower* wavenumber (1609 cm<sup>-1</sup>, Figure 3a) indicating the presence of free, monomeric water dissolved in the scCO<sub>2</sub> solution. When this saturated solution was warmed, we found that the  $\delta(\text{O-H})$  band at 1609 cm<sup>-1</sup> rises in intensity, indicating increasing solubility of water in CO<sub>2</sub> as observed in earlier studies.<sup>20</sup>

The presence of bulk water within the microemulsions should be indicated by a strong  $\delta(\text{O-H})$  mode at 1640 cm<sup>-1</sup>. However, the spectrum is complicated by overlap with the intense carbonyl stretching vibration  $\nu(\text{C=O})$  of the carboxylate PFPE headgroup (Figure 3b). Even in the absence of added water, this  $\nu(\text{C=O})$  band is broader than might be expected (Figure 3b), indicating the presence of residual water as indicated by the shoulder to *higher* wavenumber.

Residual water, even in apparently dry surfactants is a perennial problem.<sup>28,30</sup> Examination of the FTIR spectra of thin films of the waxy PFPE surfactant reveal the same shoulder to the high wavenumber side of the  $\nu(\text{C=O})$  band. These films were dried to some extent at higher temperatures (ca. 80 °C) under vacuum. We monitored the drying process in a sealed spectroscopic cell, and observed concomitant decrease (but not total removal) of features at ca. 3400 and 1680 cm<sup>-1</sup> in the FTIR spectrum. We assign these modes to that water which remains tightly bound to the surfactant head groups. Hence, it seems reasonable to assign the high-frequency shoulder (1687 cm<sup>-1</sup>) of the  $\nu(\text{C=O})$  band (Figure 3b) to the presence of H<sub>2</sub>O tightly bound to the head group. Other infrared bands (e.g.,  $\nu(\text{C=O})$ ,  $\nu(\text{N-H})$ ) remained constant in intensity, indicating little or no decomposition or vaporization of the PFPE surfactant.

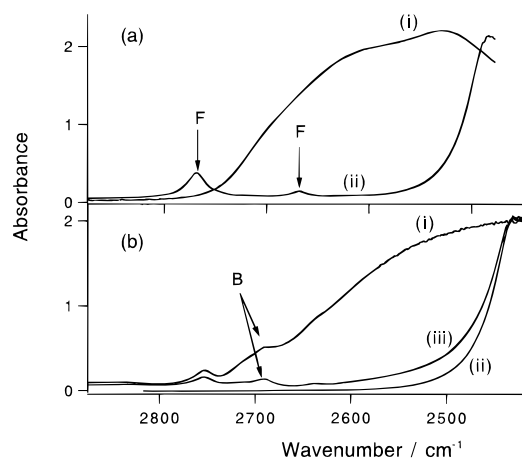
It was not possible to remove all of the residual water, even after a significant period of time. Hence, we used deuterated



**Figure 3.** FTIR spectra in the  $\delta(\text{O-H})$  region of water. Traces are marked as follows; (a) (i) liquid film of pure water showing the broad  $\delta(\text{O-H})$  feature centered at 1640 cm<sup>-1</sup>; (ii) by contrast, for a saturated scCO<sub>2</sub> solution of H<sub>2</sub>O, a much sharper band is observed at a lower wavenumber of 1609 cm<sup>-1</sup>, indicating the presence of free, monomeric water (pure dried scCO<sub>2</sub> shows no absorptions in this region); (b) (i) the overlapping  $\nu(\text{C=O})$  and  $\delta(\text{O-H})$  bands of the same PFPE and H<sub>2</sub>O solution as Figure 2b (uncorrected  $W_o = 32$ ) in scCO<sub>2</sub>. Note that the infrared band at 1609 cm<sup>-1</sup> still clearly shows the presence of “free” H<sub>2</sub>O. When  $W_o$  is decreased from 32 to 5 (not shown), the intensity of this band of free water remains constant, indicating that the scCO<sub>2</sub> phase is saturated with dissolved water, while that of the complex band decreases dramatically, indicating a decrease in the presence of bulk water in the microemulsions. Trace b ii represents the  $\nu(\text{C=O})$  band of the PFPE surfactant in the absence of added water. A shoulder at higher wavenumber (ca. 1687 cm<sup>-1</sup>) indicates the presence of residual water in the PFPE material. Trace c represents D<sub>2</sub>O in scCO<sub>2</sub> PFPE microemulsions (uncorrected  $W_o = 15$ ). Unlike the complex absorption observed in the H<sub>2</sub>O systems, a single, sharp band was observed at 1683 cm<sup>-1</sup> and assigned to the  $\nu(\text{C=O})$  mode of the PFPE-carboxylate head group. A small feature at 1609 cm<sup>-1</sup> (marked with an asterisk), indicates the presence of some residual H<sub>2</sub>O in solution, presumably arising from the surfactant, from the CO<sub>2</sub>, or from the source of D<sub>2</sub>O.

water (D<sub>2</sub>O) to exchange for H<sub>2</sub>O. The increase in mass from H to D causes the bands associated with D<sub>2</sub>O to shift to lower wavenumber (e.g. the  $\delta(\text{O-D})$  bending mode is now shifted to the region of ca. 1200 cm<sup>-1</sup>). This region of the FTIR spectrum is obscured by absorptions of the Fermi resonance doublet of CO<sub>2</sub>,  $\nu(\text{C-F})$  of the PFPE surfactant, and the “cut-off” of the CaF<sub>2</sub> windows of the high pressure spectroscopic cell. Hence, only one band, the  $\nu(\text{C=O})$  mode of the surfactant headgroup found in the D<sub>2</sub>O/scCO<sub>2</sub> microemulsions is now observed (Figure 3c). On comparing a number of different D<sub>2</sub>O/scCO<sub>2</sub> microemulsions, we found no significant changes in the position of this mode with  $W_o$ . Similar observations were reported by Yarwood and colleagues<sup>30</sup> for the  $\nu(\text{C=O})$  mode of AOT in conventional solvents.

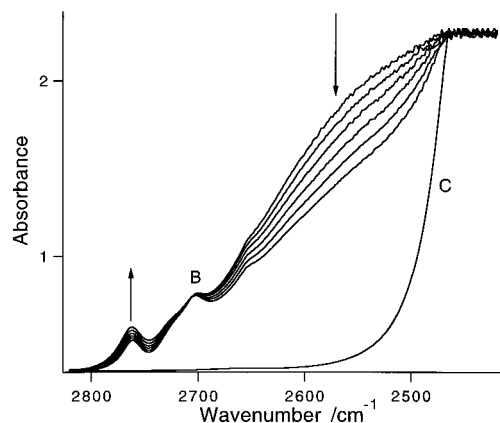
When H is substituted for D, the *stretching* modes of water also shift to lower wavenumber. For a saturated solution of D<sub>2</sub>O in scCO<sub>2</sub>, the FTIR spectrum in the region of 3000–2400 cm<sup>-1</sup> shows two sharp and strong bands (ca. 2761 and 2653 cm<sup>-1</sup>): the antisymmetric and symmetric  $\nu(\text{O-D})$  vibrations of free D<sub>2</sub>O dissolved in scCO<sub>2</sub> (Figure 4a). This spectrum, along with that of H<sub>2</sub>O-saturated scCO<sub>2</sub> (Figures 2a and 3a), shows no evidence for the presence of “bulk” water, thus



**Figure 4.** (a) (i) FTIR spectrum of a liquid film of pure D<sub>2</sub>O showing the broad  $\nu(\text{O}-\text{D})$  feature centered at 2500  $\text{cm}^{-1}$ . (ii) A saturated solution of D<sub>2</sub>O dissolved in scCO<sub>2</sub> (at 156 bar and 32 °C) shows only the antisymmetric and symmetric vibrations of free D<sub>2</sub>O (labeled F) at 2761 and 2653  $\text{cm}^{-1}$ . (b) (i) A single-phase solution of PFPE and D<sub>2</sub>O (uncorrected  $W_0 = 15$ ) in scCO<sub>2</sub> (156 bar and 32 °C) shows the broad  $\nu(\text{O}-\text{D})$  band of bulk D<sub>2</sub>O. (ii) At lower wavenumber this band overlaps with the fundamental ( $\nu_3$ ) mode of pure scCO<sub>2</sub>. At higher wavenumber, the presence of free D<sub>2</sub>O may still be detected by the two bands at 2761 and 2653  $\text{cm}^{-1}$ . Another shoulder at 2697  $\text{cm}^{-1}$  (labeled B) on the broad  $\nu(\text{O}-\text{D})$  band is also detected. (iii) A single-phase microemulsion solution containing less D<sub>2</sub>O (uncorrected  $W_0 = 5$ ) in scCO<sub>2</sub> (156 bar and 32 °C) showing that the bulk water content is much lower, but that free and "interfacial" water are still present.

confirming that no splashes or droplets of water were forming on the spectroscopic windows of our cells throughout these studies. The corresponding bands for H<sub>2</sub>O in scCO<sub>2</sub> were obscured by intense bands associated with CO<sub>2</sub> (see Figure 2b). In the presence of PFPE and added water (Figure 4b), an intense broad band appears at lower wavenumber: the  $\nu(\text{O}-\text{D})$  of D<sub>2</sub>O<sup>11,28-30</sup> in a microemulsion environment. The width of the band is attributed to the large number of environments in which the D<sub>2</sub>O molecules are found in the microemulsions, with more strongly coordinated molecules absorbing at lower wavenumber. As with the H<sub>2</sub>O in scCO<sub>2</sub> microemulsions, the infrared spectrum depends strongly on the amount of added water present. A comparison of the two spectra of the D<sub>2</sub>O microemulsion solutions, one with a low  $W_0$  and one with a high  $W_0$ , shows significant differences in intensity of the  $\nu(\text{O}-\text{D})$  vibrational band (Figure 4b). The lower wavenumber tail of this broad band is obscured by the fundamental vibration of the CO<sub>2</sub> solvent, and hence, a detailed study of the precise band shape is precluded.

Varying the temperature of the microemulsion at constant density leads to significant changes in the FTIR spectrum (Figure 5). As the temperature is raised from 31 to 60 °C, the two sharp features associated with free D<sub>2</sub>O increase in intensity, and the broad band of bulk D<sub>2</sub>O decreases in intensity. The solubility of free water in carbon dioxide is known to increase with temperature, and these spectra show that as the temperature increases, D<sub>2</sub>O is preferentially absorbed from the bulk water into the scCO<sub>2</sub> phase, although the microemulsions containing bulk water do clearly persist at the higher temperature. When cooled, the process is reversed reproducibly as D<sub>2</sub>O migrates back into the microemulsion environment. These spectroscopic data correlate well with the cloud point data<sup>32</sup> which show a decrease in the corrected  $W_0$  with increasing temperature. The observation of a well-defined isobestic point confirms the



**Figure 5.** FTIR spectra in the  $\nu(\text{O}-\text{D})$  region showing the effects of temperature on the D<sub>2</sub>O/PFPE microemulsions (uncorrected  $W_0 = 15$ ) in scCO<sub>2</sub>, recorded at intervals of 15 °C, as the temperature of the solution is increased slowly from 31 to 60 °C. The pressure increases from 156 to 300 bar, but the density remains constant. The concentration of bulk D<sub>2</sub>O in the micelle cores is seen to fall, with concomitant increase in the intensity of the  $\nu(\text{O}-\text{D})$  band assigned to free D<sub>2</sub>O. When the temperature is lowered, the observed changes proved to be totally reversible. The intensity of the high wavenumber shoulder (labeled B) is invariant over the temperature range measured, thus supporting the assignment as "interfacial" D<sub>2</sub>O.<sup>42</sup> The spectrum of pure CO<sub>2</sub> (labeled C) is shown for reference.

presence of an equilibrium between water in the scCO<sub>2</sub> phase and that in microemulsions. Intriguingly, the isobestic point is coincident with a distinct "shoulder" at 2697  $\text{cm}^{-1}$  which appears only in the presence of PFPE and D<sub>2</sub>O. This band must be associated with another environment of D<sub>2</sub>O, and because of its invariant nature, we assign it to D<sub>2</sub>O which is associated with the polar head groups of the PFPE surfactant, so called "bound" or "interfacial" water. Although this assignment is at odds with conclusions drawn from recent work on PFPE/water/oil systems,<sup>29</sup> which suggests that the bound species should show a vibrational band at wavenumbers somewhat lower than those observed for the bulk water in the microemulsions, it agrees with earlier results<sup>28</sup> for microemulsions of AOT in CCl<sub>4</sub> which suggest that water bound to the surfactant head group should appear at a higher wavenumber.

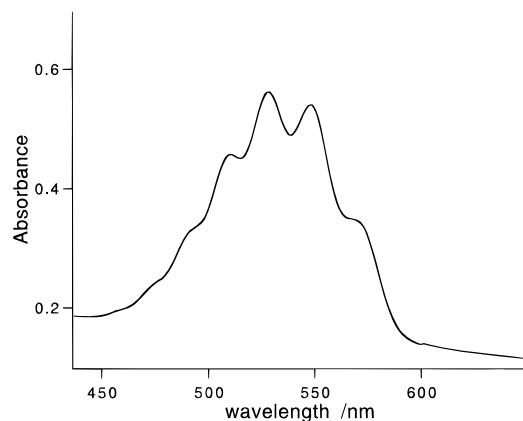
Pressure variable studies at constant temperature show little change in the FTIR spectra of the water in scCO<sub>2</sub> microemulsions above 110 bar, a result in agreement with previous observations for AOT water in propane microemulsions.<sup>11</sup> Below 110 bar, the infrared bands corresponding to the PFPE and bulk water decrease dramatically, while those of free (monomeric) water dissolved in the scCO<sub>2</sub> change very little. Below 100 bar, a distinct cloudiness/turbidity is observed, along with precipitation of water droplets onto the surface of the spectroscopic windows which is easily detectable via FTIR. These pressures correspond well with the observed cloud point data.<sup>18,32</sup>

**Dissolving Ionic Species.** The use of AOT water-in-oil reverse micelles and microemulsions as a microreactor environment is well established. Several different processes have been investigated including enzymatic reactions and synthesis of metallic and semiconductor nanocrystallites.<sup>33</sup> Others have investigated electron transfer and other kinetic processes in the same environment.<sup>34</sup> Our interest in the study of reverse micelles and microemulsions of PFPE/water in scCO<sub>2</sub> has been to investigate the possibility of supporting aqueous solutions

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(33) Lisiecki, I.; Pileni, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 3887.

(34) Fletcher, P. D. I.; Howe, A. M.; Robinson, B. H. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 985.



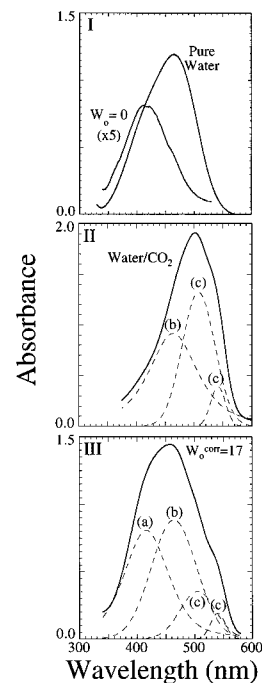
**Figure 6.** UV-vis absorption spectrum of purple-colored single-phase solution of  $\text{KMnO}_4$  dissolved in water in  $\text{scCO}_2$  microemulsions. The broad band has a series of sharper bands superimposed ( $\lambda = 546, 525,$  and  $507$  nm) which represent coupling with vibrational modes. The spectrum is essentially identical to that of  $\text{KMnO}_4$  dissolved in conventional aqueous solution ( $\lambda = 546, 526,$  and  $508$  nm). The concentration of  $\text{KMnO}_4$  in the  $\text{scCO}_2$  solution can be estimated to be on the order of  $7 \times 10^{-4}$  M, from the known UV-vis extinction coefficient in aqueous solution.

of metal ionic species. Solubility of such species in  $\text{scCO}_2$  can only occur in bulk-like water with solvating properties which approach those of pure water. Our aim in this section is to show using a combination of FTIR and UV-vis spectroscopies that complex metal ions can be solubilized.

Potassium permanganate ( $\text{KMnO}_4$ ) has powerful, yet controllable, oxidizing properties which have long been recognized by organic chemists. However, the complete insolubility of  $\text{KMnO}_4$  in most organic solvents has limited its utility. The first reports of methods to overcome this insolubility centered around the use of crown ether systems leading to "purple-benzene",<sup>8</sup> in which controlled oxidation reactions of a range of organic substrates in good yield was demonstrated.

We have found  $\text{KMnO}_4$ , as both a solid and in a concentrated aqueous solution, to be completely insoluble in  $\text{scCO}_2$  even after prolonged stirring of the mixture. However, in the presence of the PFPE surfactant and aqueous  $\text{KMnO}_4$ , the  $\text{scCO}_2$  solvent takes on a distinct purple coloration. The UV-vis spectrum of the supercritical solution was recorded (Figure 6), revealing features which are essentially identical to those of  $\text{KMnO}_4$  in conventional aqueous solution. The FTIR spectrum of the purple  $\text{scCO}_2$  solution showed the presence of water-in- $\text{CO}_2$  microemulsions exactly as observed previously, thus confirming that microemulsions containing  $\text{KMnO}_4$  solubilized in a bulk-like water pool had been formed.  $\text{KMnO}_4$  has no strong absorptions in the FTIR spectrum which could be observed in our experiment.

In the absence of  $\text{KMnO}_4$ , the water-in- $\text{CO}_2$  microemulsions described above were found to be stable indefinitely. Therefore, it was at first sight rather surprising to observe decolorization of the solution over a period of ca. 4 h, indicating reaction of  $\text{KMnO}_4$ . An FTIR spectrum of the decomposed (colorless) supercritical solution clearly showed the continued presence of bulk water in  $\text{scCO}_2$  microemulsions, at the same water concentration as that recorded prior to decomposition. After the high pressure vessel was vented, we noted the presence of a black/brown powdery material indicating formation of  $\text{MnO}_2$ , the product of  $\text{KMnO}_4$  oxidative action. We have demonstrated that there is no oxidative action of the permanganate upon the PFPE surfactant. However, permanganate is known to be



**Figure 7.** UV-vis absorption spectra (solid lines) of methyl orange probe: (I) pure water ( $\lambda_{\text{max}} = 464$  nm) and "dry" micelles in  $\text{scCO}_2$  (1.4 wt % PFPE, 241 bar, 35 °C;  $\lambda_{\text{max}} = 416$  nm); (II) water saturated with  $\text{CO}_2$  (241 bar, 35 °C) (dashed traces are simulations (see Table 1) showing relative amounts of water (b) and carbonic acid environments (c)); (III) water in  $\text{scCO}_2$  microemulsions (1.4 wt % PFPE,  $W_o$  (corrected) = 17) (dashed traces are simulations showing (a) a significant fraction of the probe resides in the interfacial region of the microemulsion droplet away from the polar water; (b) a similar fraction also resides in a bulk water environment; (c) a substantial presence of carbonic acid in the microemulsions). Although the acidic microenvironment is significant, it occupies a smaller volume fraction of the aqueous droplet phase relative to that observed in bulk aqueous carbonic acid (compare II and III). The spectra in panels II and III could be fit more accurately with two acid peaks than one. However, additional spectroscopic techniques would be required to further describe the structure of acidic microenvironments at various locations in the microemulsion droplet.

unstable under acidic conditions, decomposing<sup>35</sup> to  $\text{MnO}_2$  and  $\text{O}_2$ , and the process is known to be accelerated by light. Exposure of our  $\text{scCO}_2$  solution to a visible light source resulted in rapid decolorization and decomposition ( $t_{1/2}$  ca. 15 min). Furthermore, an acidic environment is present, as shown by the methyl orange probe experiments below.

**Determination of Acidity via UV-Vis Spectroscopy.** Methyl orange is a sensitive solvatochromic probe of aqueous and microemulsion environments. We have already shown<sup>18</sup> that as increasing amounts of water are added to the microemulsions, the visible absorption maximum of methyl orange shifts to higher wavelength indicating greater polarity. To probe the acidity of PFPE reverse micelles with methyl orange, it was first necessary to understand and calibrate the spectral shifts for the relevant solutions. Spectra were obtained for methyl orange dissolved in pure water, liquid water saturated with  $\text{CO}_2$ , and "dry" PFPE reverse micelles with no added water (Figure 7). The spectrum of methyl orange in PFPE/water in  $\text{scCO}_2$  microemulsions is also shown, and it is clear that this spectrum is a composite of the three individual spectra described above. Most noticeable is the presence of a long wavelength tail which indicates the presence of carbonic acid in the microemulsions. We have used spectroscopic deconvolution (see Table 1 and

(35) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience Publishers: New York, 1980.

**Table 1.** Curves for Spectral Fits for Methyl Orange Absorbance in Various Environments

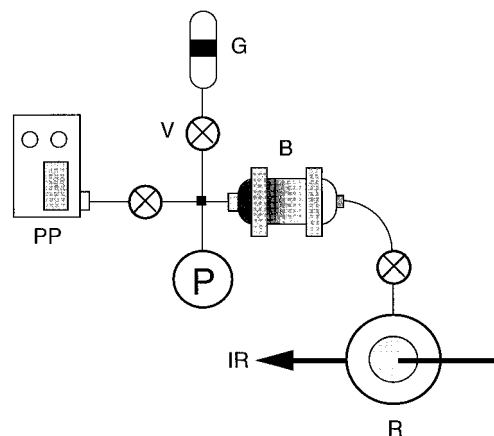
system	wavelength (nm) of band maximum	peak height	peak width (nm) (at half height)	area (%)	Lorentzian (%)
water	464.2	0.917	87.31		0.0
CO <sub>2</sub> in water	464.2	0.768	73.11	36	0.0
	507.0	1.340	62.51	54	0.0054
	539.9	0.488	32.22	10	0.0
CO <sub>2</sub> + 1.4 wt % PFPE	415.8	0.167	99.05		43.9
CO <sub>2</sub> + 1.4 wt % PFPE	416	0.808	91.15	40	43.9
+ 0.5 wt % water	464	0.885	92.25	43	0.0
(W <sub>0</sub> = 17)	505	0.353	72.31	14	0.0
	540	0.192	29.29	3	0.0

Figure 7) to determine that a significant fraction of the methyl orange probe resides in the interfacial region of the microemulsion droplet away from the polar water and a large fraction of the probe also resides in a bulk-water-like environment. The acidic environment was briefly mentioned in our earlier work, based on the shoulder at higher wavelength. In the present study, it was possible to resolve the acid peaks and demonstrate clearly an acidic environment within a microemulsion in CO<sub>2</sub>. The pH of aqueous solutions saturated with CO<sub>2</sub> at elevated pressures<sup>36</sup> is on the order of 3.

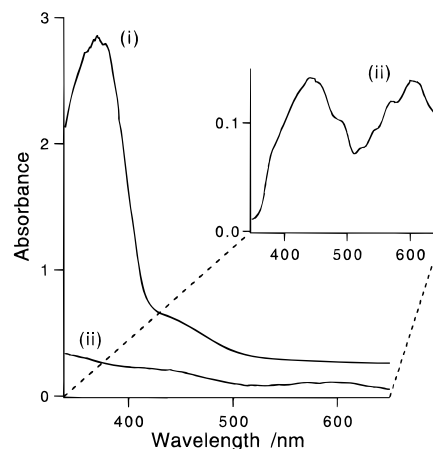
Carbonic acid exists in equilibrium with the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) which, in aqueous solution, has a broad but strong infrared absorption centered at ca. 1360 cm<sup>-1</sup>. In the FTIR spectra of PFPE/water in scCO<sub>2</sub> microemulsions, we detect a feature at this position, although the band overlaps slightly with weak bands of the PFPE surfactant and the Fermi resonance diad of the scCO<sub>2</sub> solvent. Moreover, the FTIR spectrum of the "dry" PFPE micelles in scCO<sub>2</sub> shows only a minimal absorption in this region. In order to test the validity of this observation, we recorded the FTIR spectrum of a concentrated aqueous sodium bicarbonate solution in the microemulsions. This spectrum showed a clear increase in the band at ca. 1360 cm<sup>-1</sup>, thus confirming our assignment of this feature to bicarbonate and, hence, carbonic acid within the bulk water of the microemulsions.

**Reactions in Water-in-scCO<sub>2</sub> Microemulsions.** In this section, we show that well-known inorganic reactions can occur in the aqueous environment of the microemulsions. Below, we illustrate the possibilities for reactions in the aqueous microenvironment, in particular reactions with gases which are, in general, totally miscible with scCO<sub>2</sub>.<sup>6</sup>

Aqueous acidified potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) solution (sulfuric acid, pH ≈ 4) is commonly used as an oxidant. An acidified aqueous solution of dichromate showed no solubility in scCO<sub>2</sub>. However, in the presence of the PFPE surfactant and after the solution was stirred, an optically clear orange scCO<sub>2</sub> solution was obtained and a strong absorption was detected in the UV-vis spectrum corresponding to the intense ligand-to-metal charge transfer absorption of dichromate in aqueous solution. Acidified dichromate is used as a common test for the presence of sulfur dioxide gas (SO<sub>2</sub>); a color change from orange to blue/green is observed. A method for addition of SO<sub>2</sub> to a high-pressure solution of aqueous dichromate in scCO<sub>2</sub> micelles was needed. Briefly, this was achieved by use of a high-pressure CO<sub>2</sub> source to sweep a fixed volume of reactant gas into the FTIR cell (Figure 8). On addition of SO<sub>2</sub>, we were able to observe the orange color disappearing over a period of 30 min, to be replaced by a clear blue/green solution. UV-vis spectroscopy (Figure 9) reveals this color to be due to



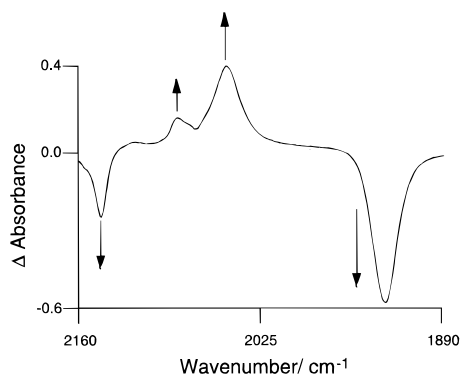
**Figure 8.** Schematic diagram of the arrangement of the experimental apparatus used for the addition of reactant gas to microemulsions. The gas 'bomb' (B) was filled with a known pressure (P) from gas source (G). This was then swept into the reaction cell (R) containing the microemulsion, through valves (V) using a high pressure (ca. 200 bar) of CO<sub>2</sub> from a high-pressure pump (PP). The subsequent reaction was monitored spectroscopically (IR)



**Figure 9.** Trace (i) UV-vis absorption spectrum of aqueous acidified potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in scCO<sub>2</sub> microemulsions, (143 bar, 32 °C). Measured concentration ca. 8 × 10<sup>-4</sup> M. When SO<sub>2</sub> is added, the broad distinctive feature at 380 nm decreases, and two much weaker product bands appear at 430 and 600 nm (trace ii). These product bands may be assigned to the presence of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(aq) dissolved within the microemulsions. These product bands are d'-d transitions and are formally forbidden, hence their low intensity. Inset: expansion of product bands for clarity.

the appearance of weak features assigned to chromium(III) ions in aqueous solution. The assignment is confirmed by comparison to a UV-vis spectrum of an authentic aqueous chromium(III) sulfate [Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] solution. Over a period of several hours, precipitation of green crystals was observed on the spectroscopic windows, but FTIR spectroscopy confirmed the continued presence of microemulsions in the scCO<sub>2</sub> solution. The presence

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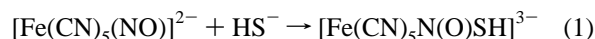
**Figure 10.** FTIR difference spectrum showing the effect of adding H<sub>2</sub>S to aqueous sodium nitroprusside in scCO<sub>2</sub> microemulsions. The bands of nitroprusside ( $\nu(\text{C}-\text{N})$  2143 cm<sup>-1</sup> and  $\nu(\text{N}-\text{O})$  1939 cm<sup>-1</sup>) decrease with concomitant generation of two product bands at 2086, and 2051 cm<sup>-1</sup>. At the same time, the solution was observed to change in color from red to pale yellow/green, indicating that the H<sub>2</sub>S had readily reacted with the nitroprusside in the micelle core. A weak band was also observed at ca. 2610 cm<sup>-1</sup>, corresponding to the  $\nu(\text{S}-\text{H})$  vibration of H<sub>2</sub>S in the scCO<sub>2</sub> solution. Infrared bands associated with scCO<sub>2</sub> have been removed by computer subtraction.

of the microemulsions was also confirmed on lowering of the pressure below the cloud point, leading to a cloudiness and precipitation of water and PFPE.

Sodium nitroprusside (Na<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)]·2H<sub>2</sub>O) is an air-stable, water-soluble, red, crystalline material which is insoluble in scCO<sub>2</sub>. On exposure of scCO<sub>2</sub> to a concentrated aqueous solution of nitroprusside, only free water from the aqueous solution was observed to dissolve in scCO<sub>2</sub> as characterized by the sharp  $\delta(\text{O}-\text{H})$  vibration in the infrared spectrum at 1609 cm<sup>-1</sup>. No such water solubility was encountered in the scCO<sub>2</sub> solution exposed to solid nitroprusside.

Microemulsions were prepared, as before, of an aqueous solution of nitroprusside in the presence of PFPE, leading to a clear scCO<sub>2</sub> solution with a distinct pale red coloration. The FTIR spectrum of this solution shows two sharp vibrations which are almost identical to the  $\nu(\text{C}-\text{N})$  and  $\nu(\text{N}-\text{O})$  bands observed in conventional aqueous solution, thus indicating formation of microemulsions containing sodium nitroprusside dissolved in water.

The reaction of Na<sub>2</sub>Fe(CN)<sub>5</sub>(NO) with sulfide, including HS<sup>-</sup>, has been known for many years.<sup>37</sup> It is used for the assay of low levels of aqueous sulfide in mineral waters and, in particular, for detection of H<sub>2</sub>S in "sour" water by the petroleum and paper industries.<sup>38</sup> In aqueous alkaline solution, the reaction of Na<sub>2</sub>Fe(CN)<sub>5</sub>(NO) with H<sub>2</sub>S is described in eq 1.<sup>39</sup>



H<sub>2</sub>S gas was added to the solution as shown in Figure 8. When H<sub>2</sub>S was added, an immediate color change was observed from red to pale yellow-green. The FTIR spectrum of the resultant solution (Figure 10) was recorded as the H<sub>2</sub>S was flushed into the reaction cell and showed instantaneous and complete decay of the starting complex, with concomitant appearance of two new FTIR bands. These product bands were found to be stable in the microemulsion solution for ca. 30 min but, after several hours, had disappeared from the spectrum. There was no regeneration of the original [Fe(CN)<sub>5</sub>(NO)]<sup>2-</sup>

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parent bands, but rather the formation of a second stable (ca. 36 h) species, as yet unidentified, with strong infrared vibrations at (1798 and 1766 cm<sup>-1</sup>). To the best of our knowledge, these data provide the first direct observation by infrared spectroscopy of the intermediates in the reaction of nitroprusside with sulfide in aqueous solution.

The nature of the reaction of nitroprusside with H<sub>2</sub>S and other thiols has been the subject of debate for over three decades. It is now clear that under aqueous alkaline conditions, there is nucleophilic attack at the nitrosyl group leading to red-colored products<sup>37,39,40</sup> that are unstable and may subsequently decay via redox reactions to various iron aquo-containing species which may well be polymeric in nature and are generally yellow. Our work with the methyl orange probe,<sup>36a</sup> and that of others<sup>36b</sup> has highlighted that *acidic* conditions are found in the presence of CO<sub>2</sub> and water. These conditions are known to accelerate the decomposition of nitroprusside adducts<sup>41</sup> and may well explain our observation of immediate formation of an as yet unidentified yellow/green species in the water in scCO<sub>2</sub> microemulsions.

## Conclusion

We have demonstrated that FTIR spectroscopy may be used to determine the presence of thermodynamically stable water-in-scCO<sub>2</sub> microemulsions. Specifically, FTIR spectroscopy allows identification of "bulk" and "interfacial" water within the microemulsions and "free" water dissolved in scCO<sub>2</sub>.

Our studies have revealed that in the PFPE water-in-scCO<sub>2</sub> microemulsions, the "bulk" water is sufficiently well formed to support solubility of ionic species, and spectroscopic data indicate that the species are in aqueous solution. We have demonstrated the first ionic inorganic reactions within water-in-scCO<sub>2</sub> microemulsions, an organic reaction that was briefly described earlier.<sup>18</sup> Specifically, we have exploited the miscibility of added gases with scCO<sub>2</sub> to study reactions of aqueous ionic species with SO<sub>2</sub> and H<sub>2</sub>S.

The UV-vis absorption spectra for methyl orange indicate three microenvironments within PFPE microemulsion droplets: (1) a polar microenvironment found in dry PFPE reverse micelles, (2) a bulk-water-like environment, and (3) an acidic microenvironment due to carbonic acid. The observation of "bulk-like" water is consistent with the FTIR spectra and the solubilization of aqueous ionic species. The acidic microenvironment in the microemulsion droplets is less prevalent than for carbon dioxide in bulk water at the same pressure and temperature.

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