The pH within PFPE Reverse Micelles Formed in Supercritical CO_2

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We report quantitative pH determinations within the water pool of reverse micelles derived from the surfactant ammonium carboxylate perfluoropolyether (PFPE) formed in supercritical CO_2. Toward this end, we use a fluorescent probe, Cl−NERF, that exhibits a pH-sensitive excitation spectrum and locates preferentially within the aqueous core region of the reverse micelle. Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (commonly know as aerosol-OT or AOT) reverse micelles were formed in liquid *n*-heptane and used to calibrate the PFPE/CO_2 system. We report the effect of CO_2 continuous phase pressure and micelle water loading on the pH within the PFPE water pool. We compare the measured water core pH to the value computed assuming CO_2 saturation within the PFPE water pool and determine that the PFPE micelle provides a 0.5 pH unit barrier to CO_2 partitioning into the micelle water pool.

Introduction

Supercritical fluids, in particular supercritical CO_2 ($scCO_2$), have been used in areas ranging from the decaffeination of green coffee beans[1−4] to the removal of natural products from barks and berries.[1,2] Much of the interest in $scCO_2$ has been driven by its relative low cost, environmentally benign potential, and its attraction as a replacement for many hazardous/environmentally unfriendly liquid solvents. When CO_2 is raised above its critical point ($T_c = 31.1$ °C; $P_c = 1073$ psia; $\rho_c = 0.472$ g/mL), its physicochemical properties (i.e., density, dielectric constant, refractive index) can be tuned continuously between gas- and liquidlike limits by simply adjusting the system pressure and/or temperature. Thus, $scCO_2$ offers the experimentalist an attractive means to conveniently access a wide range of solvent properties without the need to physically change the solvent.

Although $scCO_2$ has been proposed as an alternative to many traditional solvents, it is a poor solvent for polar molecules. One common solution to this problem is to add small quantities (typically 1−5 mol %) of an entrainer/cosolvent to the CO_2-based system.[5,6] The cosolvent preferentially solvates the polar solute and can lead to increased solute loading. Unfortunately, although the use of small volumes of cosolvents with $scCO_2$ is clearly superior than using a neat liquid solvent alone, this approach is not ideal because one does not fully eliminate the waste disposal/cleanup problem associated with the liquid solvent. Moreover, although cosolvents can serve as an attractive means to solubilize many polar solutes, they are not ideally suited for solubilizing large hydrophiles such as proteins.

It has long been known that reverse micelles offer a convenient means to solubilize hydrophiles and proteins within nonpolar liquid solvents.[7−10] A reverse micelle consists of a polar headgroup region that solubilizes polar solvents (i.e., water), surrounded by a nonpolar tail region that faces toward a nonpolar continuous phase. Reverse micelles and water-in-oil microemulsions have been used in areas ranging from the extraction of metal ores and chemically contaminated soils to reactions and syntheses within the pharmaceutical and cosmetics industry.[11−13] In addition, it has been well documented that reaction rates within reverse micelle water pools can be easily controlled and tuned by adjusting the water loading and/or pH within the water pool.[7−10,14,15]

Although the use of reverse micelles has become relatively commonplace in nonpolar liquid solvents, it has only been recently that stable reverse micelles have been formed in $scCO_2$. Johnston et al.[16] have used an ammonium carboxylate perfluoropolyether (PFPE) surfactant which incorporates a "CO_2-philic" fluorocarbon chain with a hydrophilic polar carboxylate headgroup to form reverse micelles in CO_2. These PFPE-based reverse micelles can take up significant levels of water ($R = 20$; R = [water]/[PFPE]) and have been shown to host hydrophiles as large as proteins within their water pool. To date, there have been a few studies that have aimed to characterize these novel PFPE reverse micelles. For example, Heitz et al.[17] used a variety of experimental techniques, including X-band electron paramagnetic resonance (EPR) and time-resolved fluorescence depolarization, to probe the core of the PFPE micelle formed in $scCO_2$. EPR results confirmed the presence of bulklike water within the PFPE reverse micelle core that solublized and ionized manganese ion. In addition, EPR results on Mn^{2+} showed no line broadening indicative of spin exchange. Time-resolved fluorescence rotational reorientation data showed that the rotational reorientation dynamics were described by two discrete rotational motions. Together these results suggested that PFPE surfactants formed anisotropic/nonspherical reverse micelles in $scCO_2$. Clarke et al.[18] used FTIR measurements in concert with electronic absorbance spectroscopy to estimate the water pool acidity and follow simple inorganic reactions within the PFPE/CO_2 system. These authors showed that reactions that do not proceed in neat $scCO_2$ like the reaction of $K_2Cr_2O_7$ with SO_2(g) and $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ with H_2S(g) readily occur in the presence of water-filled PFPE reverse micelles formed in $scCO_2$. The absorbance for a pH-sensitive probe, methyl orange, suggested that an acidic environment existed within the PFPE micelle water core.

The ability to perform reactions within an environmentally friendly, continuously tunable solvent environment such as $scCO_2$/PFPE/H_2O is clearly an intriguing concept. However,

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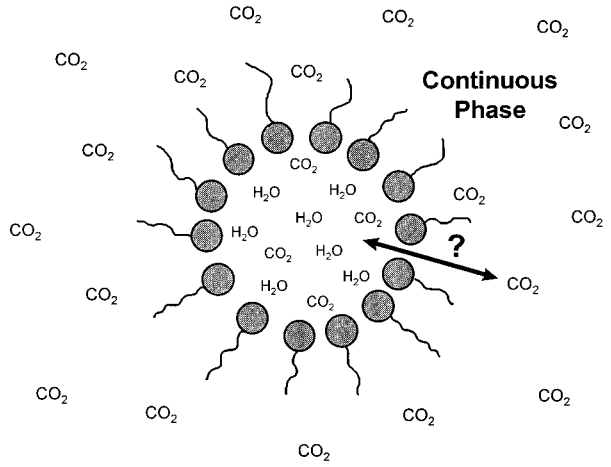

Figure 1. Depiction of CO_2 partitioning between the continuous phase and the water pool of the PFPE reverse micelle. No micelle shape is implied. The diagram is not to scale.

while the ability to do so has been recently demonstrated,[18] there is still much to be learned about the PFPE water core before one can exploit fully these systems for more complex reactions (i.e., biological or enzymatic). For example, one of the most important factors that govern reaction rates and reaction outcomes is the pH of the reaction medium. Clearly, Clarke et al.[18] showed that CO_2 can partition into the PFPE reverse micelle (Figure 1); however, there have not been any quantitative determinations of the actual pH within the PFPE water pools. In addition, it is well-known that one can tune the CO_2 continuous phase properties by adjusting the system temperature and/or pressure, but it is unclear whether one can control the micelle core pH by adjusting the CO_2 pressure over a region where the system remains a single phase.

pH is normally determined within reverse micelle water pools by using an optical probe that undergoes changes in its absorbance/emission that depend on the local pH surrounding the probe.[19−23] For example, the water pool pH has been studied extensively for the sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (commonly know as aerosol-OT or AOT) reverse micelle system formed in liquid *n*-heptane and isooctane using such common spectroscopic indicators as *p*-nitrophenol,[20] malachite green,[21] and methyl red[22] among others.[19,23] However, this work has led to modest debate about whether the pH that one measures by using an optical probe located within a reverse micelle water pool (pH_{wp}) differs from the pH of the starting buffer (pH_{st}) measured using a glass electrode before it is injected into the reverse micelle. Much of this debate stems from the close proximity of the highly charged surfactant headgroups relative to the water pool within the reverse micelle which may influence the measured acidity. In addition, depending on the nature of the optical probe, it is often difficult to determine whether the probe resides deep within the micelle water core in a more bulklike water environment or whether the probe reports from a dipolar environment more closely associated with the polar headgroups. In an attempt to alleviate this debate, ^{31}P NMR has been used to measure the chemical shifts of phosphate buffers before and after injection into the AOT reverse micelle.[24,25] These results showed that the "pH jump" ($pH_{st} - pH_{wp}$) may be as large as 0.4 pH units. However, this work also demonstrated that this pH jump or pH bias is reduced when stronger buffers are used and that any bias is generally insignificant at pH values less than 5.[25]

On the basis of these earlier studies, we have chosen the optical probe Cl−NERF (Figure 2A, inset) for the determination

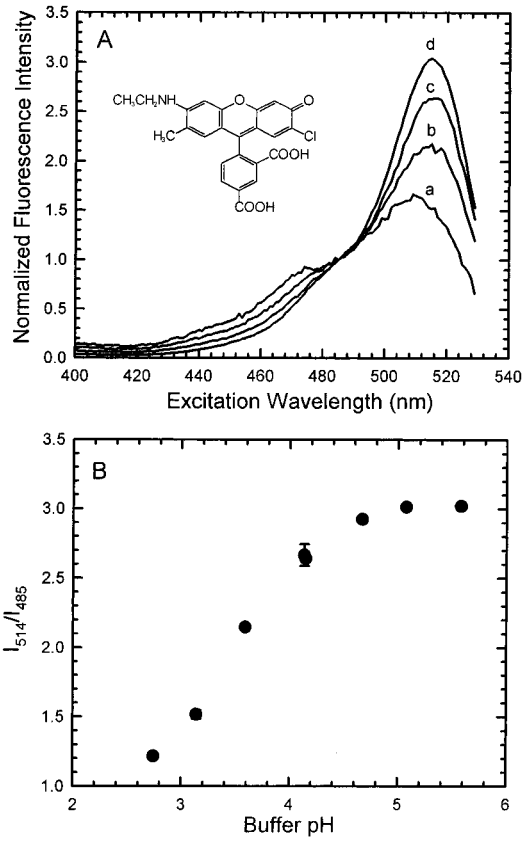

Figure 2. Fluorescence of Cl−NERF in aqueous buffer. (Panel A) Normalized (at 485 nm) Cl−NERF excitation spectra at pH = 3.14 (spectrum a), 3.59 (spectrum b), 4.15 (spectrum c), and 6.00 (spectrum d); $\lambda_{em} = 540$ nm. The inset shows the Cl−NERF molecular structure. (Panel B) Cl−NERF excitation ratio (I_{514}/I_{485}) as a function of aqueous buffer pH. The error bars denote ±1 standard deviation of at least triplicate measurements.

of pH within the PFPE reverse micelle system. Cl−NERF has several advantages as a pH-sensitive probe.[26] Cl−NERF is a rhodol derivative with an average pK_a of 3.8, which is ideal for measuring pH in acidic environments. Cl−NERF has a high molar extinction coefficient (39 000 cm^{-1} M^{-1} in acidic media) and a high fluorescence quantum yield (∼0.9). Thus, one can easily work under conditions where only one probe, at most, is sequestered within each micelle. The Cl−NERF excitation spectrum is pH-dependent, and the ratio of the intensity at 514 nm to the intensity at 485 nm is readily correlated with pH. It has been previously shown in the AOT reverse micelle system that Coulombic repulsion occurs when an anionic probe (i.e., Cl−NERF) is hosted within a reverse micelle core region surrounded by anionic headgroups (i.e., carbonyl residues).[27] Therefore, Cl−NERF is likely to reside preferentially within the polar water core of the PFPE reverse micelle.

The experiments presented in this paper are divided into three parts. In the first section, we measure the Cl−NERF excitation spectra in aqueous buffer solutions in the pH range from 2.50 to 6.00 to determine the effect of pH on the Cl−NERF excitation intensity ratio (I_{514}/I_{485}) in aqueous solution. We next determine the effect of water loading (R) on the Cl−NERF excitation ratio using AOT reverse micelles in liquid *n*-heptane, and we use this as our calibration system. Finally, we determine the Cl−NERF excitation ratio within the $scCO_2$/PFPE/H_2O system at several water loadings as a function CO_2 continuous phase pressure. We then compare the measured water core pH to the pH calculated assuming complete CO_2 saturation of the water pool.

Experimental Section

Materials and Reagents. AOT was purchased from Sigma, purified by the method of Kotlarchyk,[28] and stored in a desiccator over $CaCl_2$. *n*-Heptane (Aldrich, 99% spectrophotometric grade), Cl−NERF (Molecular Probes, Eugene, OR), citric acid, sodium citrate dihydrate, acetic acid, and sodium acetate trihydrate (J.T. Baker) were used without further purification. Ammonium carboxylate perfluoropolyether (PFPE, molecular weight = 740) was graciously provided by K. P. Johnston at the University of Texas−Austin. Supercritical fluid chromatography grade CO_2 was obtained from Scott Specialty Gases (Plumsteadville, PA), and it was further purified by passage through an O_2 trap (Matheson Gas Products, Montgomery, PA). Doubly distilled deionized water was used throughout the experiments.

Cl−NERF in Aqueous Buffer. Citrate and acetate buffers (0.01 M) were prepared in the pH range from 2.50 to 6.00 (at 0.50 pH increments). The Cl−NERF stock solution was prepared by dissolving the probe in pH = 8.00 phosphate buffer to give a final Cl−NERF concentration of 0.72 mM. Cl−NERF solutions at each respective pH were then prepared by pipetting a known quantity of the Cl−NERF stock solution into a vial and adding the appropriate amount of buffer solution to generate a final probe concentration of 1 μM. The Cl−NERF/buffer solution pH was then measured using a calibrated pH meter (Orion Model 720A, ±0.01 pH units).

Preparation of AOT Reverse Micelles. AOT reverse micelles were prepared by the following protocol. An aliquot of Cl−NERF in buffer is pipetted into a 1 cm quartz cuvette. The appropriate volume of 0.3 M AOT/*n*-heptane stock solution is then added to the cuvette. The cuvette is capped with a Teflon stopper and sealed with Parafilm. The cuvette is shaken for approximately 1 min to ensure micelle formation. If needed, the appropriate buffer volume is added to adjust the water loading. This procedure is repeated for Cl−NERF/buffer solutions in the pH range from 2.50 to 6.00. A range of micelle water/buffer loadings (R from 20 to 1; where R = [water]/[AOT]) is prepared at each pH value. All AOT samples are prepared the day of the experiment and used immediately. The final probe concentration was 1 μM.

Preparation of PFPE Reverse Micelles in $scCO_2$. The stainless steel high-pressure optical cell that was used in this work has been described previously.[29]

To prepare a sample for study, the appropriate quantity of PFPE is added to the optical cell to generate a 1.4 wt % solution at 35 °C. An aliquot of Cl−NERF in water (pH = 6.67) is then pipetted into the high-pressure optical cell such that the final probe concentration is 1 μM. Additional water is added to the system as needed to adjust the water loading. The reported water loadings (R values) are based on the total amount of water added to the system. A Teflon-coated stir bar is subsequently placed in the optical cell, and a valve assembly is used to connect the cell to a microprocessor-controlled high-pressure syringe pump (Isco, Model 260D, Lincoln, NE) which delivers CO_2 to the optical cell containing the PFPE/H_2O/Cl−NERF. Prior to beginning an experiment, the optical cell is gently flushed several times with low-pressure CO_2 to remove any residual oxygen occupying the lines and the cell. After removing residual oxygen, the cell is charged to the initial pressure (∼1500 psia), and the cell contents are vigorously stirred at the experimental temperature (35 ± 0.1 °C) for at least 2 h before any measurements are made. This mixing step ensures that the reverse micelles form and that the system is at equilibrium. Throughout an experiment, the high-pressure pump is operated in the constant pressure mode, and the system pressure is monitored (±1 psi) using a calibrated Heise gauge. A Haake A80 temperature bath is used to maintain a constant cell temperature (±0.1 °C), and the temperature is monitored using a solid-state thermocouple.

Because water is somewhat soluble in CO_2,[30] excitation spectra were obtained using the same experimental conditions (vide supra) in the absence of PFPE (Cl−NERF and water only) and with Cl−NERF only without water to determine the maximum possible contribution from free Cl−NERF not sequestered within the PFPE reverse micelles. From these experiments we determined that the maximum fluorescence contribution from Cl−NERF molecules that were not sequestered within the micelle water core was less than 15% for CO_2 + water and less than 8% for neat $scCO_2$.

Instrumentation. A SLM-AMINCO 48000 MHF spectrofluorometer was used for all steady-state fluorescence measurements. A 450 W Xe arc lamp/monochromator served as the excitation system (spectral band-pass = 2 nm). The resulting fluorescence is passed through an emission monochromator (spectral band-pass = 2 nm) and detected with a photomultiplier tube. The spectrofluorometer is configured in the standard ratiometric mode. Measurements at 514 and 485 nm are performed by using software provided with the fluorometer. These particular wavelengths were based on literature precedent.[26]

Results and Discussion

Effect of pH on Cl−NERF Excitation Spectrum. It was first necessary to quantify the effect of pH on the Cl−NERF excitation spectrum in aqueous buffer solutions. Figure 2 summarizes the results of these experiments. Figure 2A presents Cl−NERF excitation spectra (λ_{em} = 540 nm; normalized at 485 nm) in several pH buffers. Inspection of these results shows that there is a concomitant increase in the Cl−NERF intensity at 514 nm relative to that at 485 nm as the pH increases. Figure 2B presents the excitation intensity ratio (I_{514}/I_{485}) as a function of buffer pH. These data clearly shows that the Cl−NERF excitation spectrum is highly dependent on the system pH between 2.5 and 4.5. This is the pH region that is expected within the water pool of the PFPE reverse micelle formed in $scCO_2$ (vide infra).

Effect of Water Loading on Cl−NERF Sequestered in AOT Reverse Micelles. After quantifying the effect of pH on the Cl−NERF excitation spectrum in aqueous buffer, the effect of water loading (R) on the Cl−NERF excitation spectrum was determined. AOT reverse micelles in liquid *n*-heptane were chosen as a model system because of the similar chemistry (i.e., structure, pK_a) of the polar AOT (sulfonyl) and PFPE (carbonyl) headgroups.[31] Figure 3 presents the Cl−NERF excitation intensity ratio (I_{514}/I_{485}) as a function of water loading at pH values ranging from 2.89 to 4.65. Because the buffer pH that we are studying within the reverse micelle is less than 5, we have assumed, based on arguments given by Smith and Luisi,[25] that $pH = pH_{st} = pH_{wp}$.

Given this, several aspects of the data shown in Figure 3 merit special mention. First, as seen in the neat aqueous buffers (Figure 2), the I_{514}/I_{485} for Cl−NERF within the AOT reverse micelle increases consistently for all water loadings with increasing pH and levels off at higher pH (all available data not shown for clarity). Second, as we change R within the AOT reverse micelle at any given pH value, the change in Cl−NERF I_{514}/I_{485} is affected similarly regardless of pH. Specifically, between R = 0 and 5 we see an increase in I_{514}/I_{485}, between R = 5 and 10 I_{514}/I_{485} remains essentially constant, and between R = 10 and 20 we see a decrease in I_{514}/I_{485}. At the lower

water loadings ($R < 5$), this likely results from the primary hydration of the AOT surfactant headgroups, leading to water (and Cl−NERF) which is highly associated with the polar headgroups. At intermediate water loadings ($5 < R < 10$), the Cl−NERF is likely to begin to move away from the headgroups but still reside within a more associated water environment.[19] At higher water loadings ($R > 10$), Cl−NERF moves away from the headgroups and likely resides in a more "bulklike" water environment.[19] Interestingly, the same basic I_{514}/I_{485} vs R profile (save for the magnitude of I_{514}/I_{485}) is observed for all pH values investigated.

PFPE Reverse Micelles Formed in Supercritical CO_2. The effect of CO_2 on the acidity of water is well-established.[32,33] The general expression describing the behavior of a gas in contact with water is given by Henry's law:[32,33]

$$\chi = K_H P_g \tag{1}$$

where χ is the mole fraction of gas dissolved in the liquid, K_H is the Henry's law constant for a particular gas at a given temperature, and P_g is the gas partial pressure. Because the concentration of water is known (55.56 mol/L) and we are concerned with CO_2 dissolved in water ($[CO_2(aq)]$), we can rewrite Henry's law:[32,33]

$$[CO_2(aq)] = 55.56 K_H P_g \tag{2}$$

When CO_2 is dissolved in water, carbonic acid (H_2CO_3) is formed. Carbonic acid then dissociates in two steps, first to bicarbonate (HCO_3^-) and subsequently to carbonate (CO_3^{2-}):[32,33]

$$H_2CO_3(aq) \rightarrow H^+(aq) + HCO_3^-(aq) \tag{3}$$

$$HCO_3^-(aq) \rightarrow H^+(aq) + CO_3^{2-}(aq) \tag{4}$$

The system $H^+(aq)$ concentration is thus given by[32,33]

$$[H^+(aq)] = [HCO_3^-(aq)] + 2[CO_3^{2-}(aq)] + [OH^-(aq)] \tag{5}$$

For an acidic solution $[CO_3^{2-}(aq)] \ll [HCO_3^-(aq)]$, and knowing that $K_w = [H^+(aq)][OH^-(aq)] = 2.07 \times 10^{-14}$ at our experimental temperature (35 °C),[32] we can write[32,33]

$$[H^+(aq)]^2 = K_1[CO_2(aq)] + 2.07 \times 10^{-14} \tag{6}$$

where K_1 is the equilibrium constant for eq 3 which is available in the literature.[32] Table 1 presents the calculated $[CO_2(aq)]$, $[H^+(aq)]$, and pH values for water at 35 °C as a function of CO_2 pressure based on Henry's law and the carbonate equilibrium. From these simple calculations, we expect that the lower pH limit within the PFPE reverse micelle water pool between 1500 and 3000 psia of CO_2 to range from 2.8 to 3.0 if the PFPE micelle itself posed no barrier to the CO_2 partitioning. In contrast, if the PFPE surfactant/micelle offers a barrier to the CO_2 partitioning, the pH within the core would deviate from the expected pH based on Henry's law calculations.

Figure 4 presents results for Cl−NERF dissolved in PFPE reverse micelles formed in $scCO_2$ at 35 °C as a function of water loading and CO_2 pressure. Figure 4A presents representative Cl−NERF excitation spectra (normalized at 485 nm) within the PFPE reverse micelle system in $scCO_2$ at two pressures and $R = 14$. This figure shows that the spectra exhibit the characteristic Cl−NERF excitation profile seen in neat aqueous buffers. In Figure 4B, the Cl−NERF I_{514}/I_{485} is shown as a function of

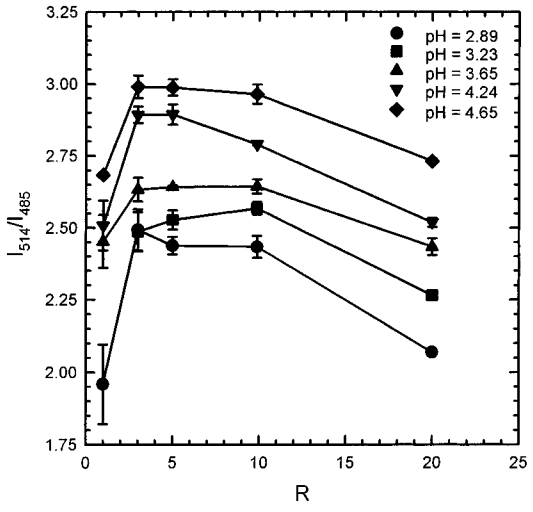

Figure 3. Cl−NERF I_{514}/I_{485} values in AOT/*n*-heptane at various water loadings, R (where R = [water]/[AOT]), at pH = 2.89 (●), 3.23 (■), 3.65 (▲), 4.24 (▼), and 4.65 (◆). The error bars denote ±1 standard deviation of at least triplicate measurements.

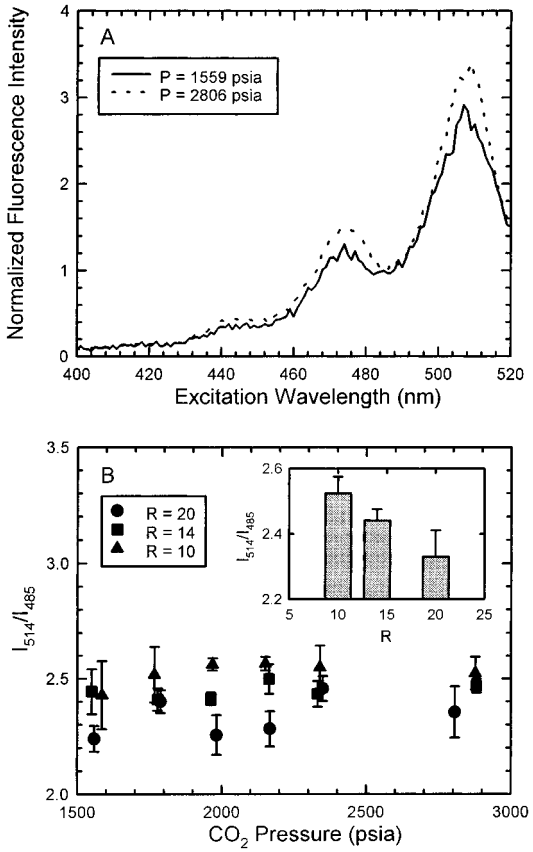

Figure 4. Fluorescence of Cl−NERF in PFPE/CO_2. (Panel A) Normalized (at 485 nm) Cl−NERF excitation spectra in the PFPE reverse micelle ($R = 14$) at a CO_2 pressure of 1559 and 2806 psia. (Panel B) Cl−NERF I_{514}/I_{485} in PFPE/CO_2 at various water loadings ($R = 20$ (●), 14 (■), 10 (▲)) as a function of CO_2 pressure. The inset shows the average Cl−NERF I_{514}/I_{485} as a function of water loading in the PFPE/CO_2 system. The error bars denote ±1 standard deviation of at least triplicate measurements.

CO_2 pressure at several PFPE water loadings ($R = 10$, 14, and 20). Interestingly, at each PFPE water loading, the Cl−NERF excitation ratio remains statistically the same (at the 95% confidence limit) even as the CO_2 continuous phase pressure is adjusted between 1500 and 3000 psia. In addition, while I_{514}/I_{485} is statistically equivalent regardless of CO_2 pressure at a

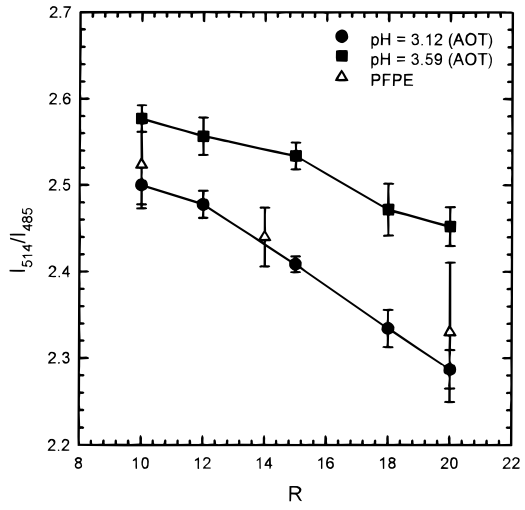

Figure 5. Cl−NERF I_{514}/I_{485} as a function of water loading (R) in the AOT/*n*-heptane system at pH = 3.12 (●) and 3.59 (■) and in the PFPE/CO_2 system (△). The error bars denote ±1 standard deviation of at least triplicate measurements.

TABLE 1: Calculated [CO_2(aq)], [H^+(aq)], and pH of the PFPE Water Core Using Henry's Law and the Carbonate Equilibrium (Eqs 2−6) Assuming CO_2 Saturation of the Water Pool

pressure (psia)	[CO_2(aq)] (mol/L)	[H^+(aq)] (mol/L)	pH
1500	2.34	1.09×10^{-3}	2.96
2000	3.12	1.26×10^{-3}	2.90
2500	3.90	1.41×10^{-3}	2.85
3000	4.68	1.54×10^{-3}	2.81

given R, the average I_{514}/I_{485} at each R are (at the 99% confidence level) statistically different from one another (see inset histogram in Figure 4B).

To estimate the pH within the PFPE micelle core encountered by the Cl−NERF molecule, we compare our average Cl−NERF I_{514}/I_{485} values for the PFPE/CO_2 system at various R values to the excitation ratios determined from the AOT/*n*-heptane calibration system. Figure 5 presents the average Cl−NERF I_{514}/I_{485} values for the PFPE/CO_2 system (△) along with the I_{514}/I_{485} for Cl−NERF in AOT/*n*-heptane at pH values of 3.12 (●) and 3.59 (■). Although we cannot precisely determine the pH within the PFPE reverse micelle, several items are apparent from the data presented in Figure 5. First, we can clearly say, according to the Cl−NERF probe emission, that the pH within the PFPE reverse micelle is between 3.1 and 3.5 over the R and CO_2 range investigated. Second, the pH within the PFPE water pool remains essentially constant as a function of continuous phase CO_2 pressure *and* water loading. Last, upon comparison of our experimentally measured pH values to the values calculated using Henry's law and the carbonate equilibrium (which assumes complete CO_2 saturation of the water pool), it appears that the PFPE reverse micelle offers a slight barrier to CO_2 partitioning which translates to approximately 0.5 pH units.

Conclusions

We have shown that the pH within the PFPE reverse micelle system formed in $scCO_2$ can be measured by using a pH-sensitive probe (Cl−NERF). Results show that the pH within the reverse micelle water pool is between 3.1 and 3.5, and the pH remains essentially constant as a function of CO_2 continuous phase pressure and micelle water loading. Comparison of the experimentally determined pH values to calculations assuming complete CO_2 saturation of the PFPE reverse micelle water pool shows that the PFPE micelle offers a 0.5 pH barrier to CO_2 partitioning into the micelle water pool. There is ample literature precedent for a reverse micelle limiting/restricting access to species sequestered within the reverse micelle water pool.[34]

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References and Notes

(1) Brennecke, J. F. *Chem. Ind. (London)* **1996**, *21*, 831.
(2) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. L. *Nature* **1996**, *383*, 313.
(3) Katz, S. N. *Sci. Am.* **1997**, *276*, 40.
(4) Bradley, D. *New Sci.* **1994**, *143*, 32.
(5) Eckert, C. A.; Knutson, B. L. *Fluid Phase Equilib.* **1993**, *83*, 93.
(6) For a recent discussion on cosolvents, see: Hutchenson, K. W.; Foster, N. R. In *Innovations in Supercritical Fluid Science and Technology*; Hutchenson, K. W., Foster, N. R., Eds.; ACS Symposium Series 608; American Chemical Society: Washington, DC, 1995; Chapter 1.
(7) Schwuger, M.-J.; Stickdorn, K.; Schomacker, R. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 849.
(8) Wolf, R.; Luisi, P. L. *Biochem. Biophys. Res. Commun.* **1979**, *89*, 209.
(9) Menger, F. M.; Yamada, K. *J. Am. Chem. Soc.* **1979**, *101*, 6731.
(10) Levashov, A. Y.; Khmelnitsky, Y. L.; Klyachko, N. L.; Chernyak, V. Y.; Martinek, K. *J. Colloid Interface Sci.* **1982**, *88*, 444.
(11) Langevin, D. In *Reverse Micelles, Biological and Technical Relevance of Amphiphilic Structure in Apolar Media*; Luisi, P. L., Straub, B. E., Eds.; Plenum Press: New York, 1984; p 267.
(12) De la Peña, A. M.; Ndou, T. T.; Warner, I. M. In *Advances in Multidimensional Luminescence*; Warner, I. M., McGown, L. B., Eds.; JAI Press: Greenwich, CT, 1993; Vol. 2, p 1.
(13) Pantini, G.; Brunetta, F.; Guidolin, V. *Cosmet. Toiletries* **1991**, *106*, 71.
(14) Mackay, R. A. *Adv. Colloid Interface Sci.* **1981**, *15*, 131.
(15) Shield, J. W.; Ferguson, H. D.; Bommarius, A. S.; Hatton, T. A. *Ind. Eng. Chem. Fundam.* **1986**, *25*, 603.
(16) 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.
(17) Heitz, M. P.; Carlier, C.; deGrazia, J.; Harrison, K. L.; Johnston, K. P.; Randolph, T. W.; Bright, F. V. *J. Phys. Chem. B*, in press.
(18) Clarke, M. J.; Harrison, K. L.; Johnston, K. P.; Howdle, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 6399.
(19) De, T. K.; Maitra, A. *Adv. Colloid Interface Sci.* **1995**, *59*, 95.
(20) Menger, F. M.; Saito, G. *J. Am. Chem. Soc.* **1978**, *100*, 4376.
(21) El Seoud, O. A.; Chinelatto, A. M.; Shimizu, M. R. *J. Colloid Interface Sci.* **1982**, *88*, 420.
(22) Terpko, A. T.; Serafin, R. J.; Bucholtz, M. L. *J. Colloid Interface Sci.* **1981**, *84*, 202.
(23) Correa, N. M.; Biasutti, M. A.; Silber, J. J. *J. Colloid Interface Sci.* **1995**, *172*, 71.
(24) Fujii, H.; Kawai, T.; Nishikawa, H. Bull. *Chem. Soc. Jpn.* **1979**, *52*, 2051.
(25) Smith, R. E.; Luisi, P. L. *Helv. Chim. Acta* **1980**, *63*, 2302.
(26) Whitaker, J. E.; Haugland, R. P.; Ryan, D.; Hewitt, P. C.; Haugland, R. P.; Prendergrast, F. G. *Anal. Biochem.* **1992**, *207*, 267.
(27) Heitz, M. P.; Bright, F. V. *Appl. Spectrosc.* **1995**, *49*, 20.
(28) Kotlarchyk, M.; Chen, S. H.; Huang, J. S. *Phys. Rev. A* **1984**, *29*, 2054.
(29) Betts, T. A.; Bright, F. V. *Appl. Spectrosc.* **1990,** *44*, 1190.
(30) Weibe, R. *Chem. Rev.* **1941**, *29*, 475.
(31) Ege, S. In *Organic Chemistry*, 2nd ed.; D.C. Heath & Co.: Lexington, MA, 1989; p 809.
(32) Tchobanoglous, G.; Schroeder, E. D. *Water Quality*; Addison-Wesley Publishing Company: Reading, MA, 1987; Chapter 2.
(33) Masters, G. M. *Introduction to Environmental Engineering Science*; Prentice Hall: Englewood Cliffs, NJ, 1991; Chapter 2.
(34) (a) Saez, M.; Abuin, E. A.; Lissi, E. A. *Langmuir* **1989**, *5*, 942. (b) Alvarez, J.; Lissi, E. A.; Encinas, M. V. *Langmuir* **1996**, *12*, 1738. (c) Buchviser, S. F.; Gehlen, M. H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1133.