Phase Behavior and Micropolarity of Ammonium Carboxylate Perfluoropolyether Reverse Micelles in Supercritical Carbon Dioxide

Baogen Su, Wei Chen, Huabin Xing, Yiwen Yang, and Qilong Ren*

National Laboratory of Secondary Resources Chemical Engineering, Zhejiang University,
Hangzhou 310027, People's Republic of China

The phase behavior of the ammonium carboxylate perfluoropolyether (PFPE-NH_4) + water + $SCCO_2$ system was determined at temperatures of (308.15 to 328.15) K. The effects of water content and temperature on the polarity of the microenvironment in PFPE-NH_4 reverse micelles in $SCCO_2$ were investigated by UV−vis spectroscopy of a solvatochromic probe, methyl orange. The λ_{max} of methyl orange in reverse micelles in supercritical CO_2 was found to be between (408.2 and 430.7) nm under experimental conditions which indicated the micropolarity in reverse micelles was between cyclohexane and water. The micropolarity increased with the increase of water content after excess water appeared and increased with a decrease in temperature. This could be explained by more water dispersing into the surfactant aggregates with the increase of water content and the decrease of temperature.

Introduction

Supercritical carbon dioxide ($SCCO_2$) has been proposed as an alternative to many traditional solvents since it is nontoxic, nonflammable, inexpensive, and relatively nonpolluting. However, it is a poor solvent for most polar molecules. One common solution to this problem is to add a small quantity, typically (1 to 5) % molar concentration, of an entrainer/cosolvent to the CO_2-based system. The cosolvent preferentially solvates the polar solute and leads to the increase of solute loading. Unfortunately, although cosolvents can serve as an attractive means to solubilize many polar solutes, they are not ideally suitable for solubilizing high molecular weight or hydrophilic molecules, such as proteins and metal ions.[1,2] One of the most promising approaches to enhance the solubility is to use the reverse micelles in $SCCO_2$.[3,4] Reverse micelles in $SCCO_2$ are formed as the nanodroplets of the aqueous phase surrounded by a monolayer of surfactant molecules dispersing in the continuous $SCCO_2$ phase.[5] Using reverse micelles in $SCCO_2$ may be advantageous in some chemical processes, such as extraction, cleaning, nanoparticle synthesis, and chemical reactions.

Due to the rather peculiar chemical and physical properties of the polar interior of reverse micelles, substantial efforts have been focused on investigating their microenvironmental properties, such as the micropolarity.[6] Though the micropolarity of the reverse micelles formed in organic solvents has been widely investigated in past decades, there were few studies on the micropolarity of the reverse micelles formed in supercritical fluids. The micropolarity within reverse micelles in $SCCO_2$ is generally characterized by UV−vis solvatochromic probes. 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate (ET(30) reagent), 1-ethyl-4-methoxycarbonyl pyridinium iodide (EMCPI), and Auramine O (AuO) have been used as solvatochromic probes to quantitatively measure the micropolarity of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles prepared in supercritical ethane and near-critical propane.[7−9] It was indicated that the micropolarity of the aqueous core increased with the water content increase and became independent of pressure after the system changed to a one-phase reverse micelle solution. Methyl orange (MO), 1-methyl-8-oxyquinolinium betaine (QB), and Dimidium Bromice (DB)[2,10−15] are generally used as solvatochromic probes to investigate the micropolarity of the reverse micelles in $SCCO_2$ formed by different surfactants. In the previous studies, micropolarity domains were proven to exist in the reverse micelles in $SCCO_2$.

The effects of operating conditions on the micropolarity should be important for the solubilization of polar substances in the reverse micelles in $SCCO_2$. The purpose of this article was to obtain the relationship between micropolarity of the reverse micelles in $SCCO_2$ and water content and temperature using UV−vis spectrometry. Ammonium carboxylate perfluoropolyether (PFPE-NH_4) with an average molecular weight of 2500 was used to stabilize the reverse micelles in $SCCO_2$, and methyl orange was used as a solvatochromic probe. Since surfactant concentration and water to surfactant molar ratio W_0 are known to affect the stability of the reverse micelles in $SCCO_2$, the phase behavior of the PFPE-NH_4 + water + $SCCO_2$ system was determined and employed for micropolarity studies.

Experimental Section

Materials. Carbon dioxide (≥ 99.99 %) was purchased from Shanghai Praxair-Baosteel, Inc. (China). Perfluoropolyether [$(F_3C(OCF_2CF(CF_3))_n(OCF_2)_m)OCF_2COOH$, PFPE] with an average molecular weight of 2500 from DuPont (USA) was used without further purification. PFPE-NH_4 was prepared according to the literature.[16,17] Methyl orange (MO) was obtained from Guangzhou Chemical Reagent Factory (China) and used as received. Deionized water with conductivity lower than 0.063 μS was made by Waters Nanopure system (USA). Ammonia and methanol of analytical grade were used.

High-Pressure Apparatus. Experiments were performed in a high-pressure variable-volume view cell which was similar to that reported previously.[18] The working volume of the cell

---

* To whom correspondence should be addressed. E-mail: renql@zju.edu.cn. Tel.: +86 571 8795 2773. Fax: +86 571 8795 2773.

10.1021/je900024f CCC: $40.75

could vary from (8.14 to 9.64) mL including the volume of pipes and connectors. A USB2000 Fiber Optic Spectrometer (OOIbase32, USA) was coupled with the two cell windows by optical fibers. The temperatures and pressures of the view cell were controlled with uncertainties of ± 0.1 K and ± 0.01 MPa, respectively.

Phase Behavior Study. Phase boundaries of the PFPE-NH_4 + water + $SCCO_2$ ternary system were measured by visual observation of cloud points. At a fixed composition and temperature, the cloud point indicating the single two-phase transition was defined as the pressure at which the solution became cloudy when decreasing it. In all experiments, the cell was charged with 186.0 mg of PFPE-NH_4, and the air in the cell was replaced with gaseous CO_2. The desired volume of water was then injected into the cell. The cell volume was adjusted to the minimum and placed inside the air bath. When the temperature became constant for 10 min, CO_2 was then compressed into the cell slowly to the designed pressure. When the system reached a transparent single phase after stirring about 30 min and then equilibrium for 30 min, the pressure was then reduced at a rate of about 0.5 MPa per minute until the solution became cloudy. The pressure was reduced so slowly that enough time was allowed for thermal equilibrium during the pressure reduction. To obtain consistent measurements, the experiment was repeated at least three times at each temperature. The apparatus had been calibrated through measuring the solubility of naphthalene in $SCCO_2$, and there was a difference of less than 4 % from literature values.[19] The experimental repeatability was satisfying with an uncertainty of less than 2.8 %, which was gained through repeating an experiment at the same conditions after a week.

UV−Vis Study. The polarity of the microenvironment in the PFPE-NH_4 reverse micelles in $SCCO_2$ was studied by UV−vis spectrometry. First, 50 μL of the solvatochromic probe MO in methanol was injected into the view cell. The cell was heated to about 313 K, and CO_2 gently flowed through the cell for more than 3 h to ensure the removal of methanol. Then, 186.0 mg of PFPE-NH_4 was charged into the cell, and the desired volume of water was injected into the cell by a syringe. Similar to the phase behavior study, CO_2 was charged into the cell to a desired pressure after the temperature became constant. The contents in the cell were stirred and equilibrated for 30 min in sequence. Then the USB2000 spectrometer was used to detect and record the absorption spectra of MO in the PFPE-NH_4 reverse micelles at different water contents and temperatures.

Results and Discussion

Table 1. Cloud Point Pressure (P_{cp}) and Density (ρ_{cp}) of the 2.5 % Mass Fraction of the PFPE-NH_4 + Water + $SCCO_2$ System at Different Water Contents and Temperatures[a]

T/K	W_0	P_{cp}/MPa	ρ_{cp}/g·mL^{-1}	$W_0^{CO_2}$	corrected W_0
308.15	0	12.27 ± 0.01	0.774	9.49	0
	5.00	12.49 ± 0.01	0.778	9.54	0
	10.00	12.84 ± 0.03	0.784	9.63	0.37
	15.00	13.85 ± 0.02	0.801	9.88	5.12
	20.0	14.41 ± 0.01	0.809	9.99	10.01
	25.0	15.02 ± 0.02	0.817	10.11	14.89
313.15	0	13.34 ± 0.02	0.752	11.07	0
	5.00	13.67 ± 0.01	0.758	11.16	0
	10.00	14.04 ± 0.01	0.765	11.26	0
	15.00	14.86 ± 0.03	0.779	11.46	3.54
	20.00	15.35 ± 0.01	0.787	11.58	8.42
	25.00	15.90 ± 0.02	0.795	11.69	13.31
318.15	0	14.55 ± 0.01	0.734	12.94	0
	5.00	14.85 ± 0.01	0.740	13.02	0
	10.00	15.22 ± 0.01	0.747	13.11	0
	15.00	15.80 ± 0.02	0.758	13.25	1.75
	20.00	16.39 ± 0.02	0.767	13.37	6.63
	25.00	16.85 ± 0.01	0.774	13.46	11.54
323.15	0	15.66 ± 0.02	0.716	14.69	0
	5.00	16.06 ± 0.01	0.724	14.79	0
	10.00	16.41 ± 0.02	0.731	14.88	0
	15.00	16.71 ± 0.01	0.738	14.97	0.03
	20.00	17.25 ± 0.01	0.746	15.07	4.93
	25.00	17.70 ± 0.02	0.753	15.16	9.84
328.15	0	16.81 ± 0.01	0.701	16.93	0
	5.00	17.09 ± 0.05	0.707	17.02	0
	10.00	17.27 ± 0.01	0.710	17.06	0
	15.00	17.66 ± 0.01	0.718	17.17	0
	20.00	18.18 ± 0.03	0.727	17.29	2.71
	25.00	18.64 ± 0.02	0.734	17.39	7.61

[a] $W_0^{CO_2}$ is the solubility of water in pure $SCCO_2$ expressed as the mole ratio of the water in pure $SCCO_2$ to the corresponding surfactant in the PFPE-NH_4 + water + $SCCO_2$ system; W_0^{corr} is the exact amount of water in surfactant aggregates estimated by subtraction of $W_0^{CO_2}$ from W_0.

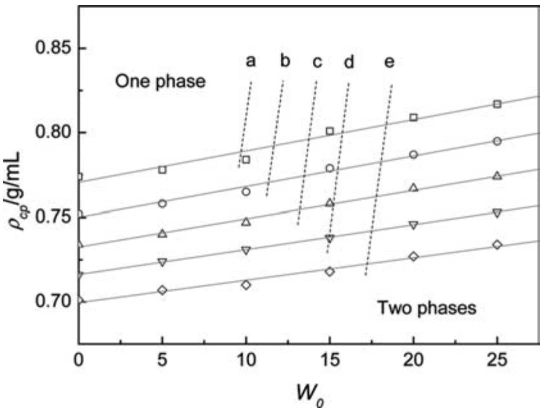

Figure 1. Phase boundary of the PFPE-NH_4 + water + $SCCO_2$ system. ρ_{cp} is the cloud point pressure; W_0 is the water to surfactant molar ratio. The mass fraction of PFPE-NH_4 in $SCCO_2$ is 2.5 %, and temperatures are: □, 308.15 K; ○, 313.15 K; △, 318.15 K; ▽, 323.15 K; and ◇, 328.15 K. Dashed lines are solubility of water in $SCCO_2$ at temperatures of: a, 308.15 K; b, 313.15 K; c, 318.15 K; d, 323.15 K; e, 328.15 K. Solid lines are a guide for the eye.

Phase Behavior of the PFPE-NH_4 + Water + $SCCO_2$ System. The cloud point pressures (P_{cp}) of the PFPE-NH_4 + water + $SCCO_2$ system for a mass fraction of 2.5 t % PFPE-NH_4 at various water contents W_0 (defined as water to surfactant mole ratio) and temperatures were determined and listed in Table 1. Since the concentrations of PFPE-NH_4 and water were relatively dilute, the cloud point densities (ρ_{cp}) of this system were assumed as the values of pure carbon dioxide at P_{cp}, which were calculated using Huang's equation of state.[20] Because the following studies were at constant density, the phase boundaries of the PFPE-NH_4 + water + $SCCO_2$ system were plotted by ρ_{cp} (see Figure 1) to keep consistency. As shown in Figure 1, the ternary system became transparent one phase at densities above each isotherm, which means the added PFPE-NH_4 and water could completely dissolve in $SCCO_2$ at appropriate conditions. It was also shown that the phase transition densities increase with the increase of W_0 and decrease with the increase of temperature. To compare the solubilized water in the ternary system and pure $SCCO_2$, the solubility of water in pure $SCCO_2$ is expressed as the mole ratio of the water in pure $SCCO_2$ to the corresponding surfactant in the PFPE-NH_4 + water + $SCCO_2$ system ($W_0^{CO_2}$). The water solubility under the conditions in this study was estimated from the data of Wiebe[21] correlated by Chrastil's empirical equation.[22] The $W_0^{CO_2}$ values are presented as dashed lines in Figure 1. At

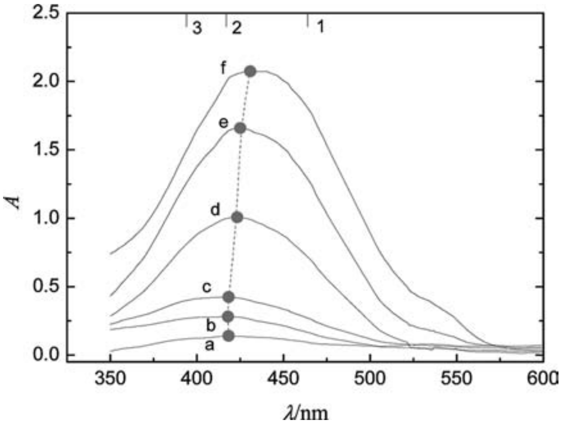

Figure 2. UV−vis absorption spectra of MO in 2.5 % mass fraction of PFPE-NH_4 reverse micelles in $SCCO_2$ with various water contents at 308.15 K and density of 0.856 g·mL^{-1}. The spectra are for the following values of W_0 = a, 0; b, 5.0; c, 10.0; d, 15.0; e, 20.0; f, 25.0. ● represents λ_{max} in each spectrum. 1, 2, and 3 represent the λ_{max} of water (462 nm), ethanol (417 nm), and cyclohexane (394 nm), respectively.

the right of each dashed line, the overall amount of solubilized water is higher than the solubility of water in pure $SCCO_2$. Since the water that can dissolve in bulk CO_2 is limited, the excess water seems to be solubilized in another portion of the system, which indirectly suggested the formation of the reverse micelles in $SCCO_2$.[2] Though the exact amount of water dispersed into surfactant aggregates was not known, it was estimated by subtraction of the solubility of water in pure $SCCO_2$ ($W_0^{CO_2}$) from total solubilized water (W_0) according to previous studies.[14] The calculated $W_0^{CO_2}$ and corrected W_0 were both listed in Table 1.

Micropolarity Study. The shift in the absorbance maximum (λ_{max}) of a solvatochromic probe is a sensitive measurement of the local environment about the probe. MO is the most commonly used probe molecular to investigate the micropolarity of the reverse micelles in $SCCO_2$. As a red-shift indicator, the λ_{max} of MO shifts to longer wavelength as the medium polarity increases. Before the micropolarity investigation, a blank experiment was performed. No detectable UV−vis absorbance of MO in $SCCO_2$ and the water + $SCCO_2$ system was observed.

The λ_{max} of MO was measured for a mass fraction of the 2.5 % PFPE-NH_4 + water + $SCCO_2$ system with various W_0 values. The nominal loading of MO in the view cell was 10^{-5} g·L^{-1}, but only a portion of it was solubilized into the surfactant aggregates based on the measured absorbance. Density in the view cell was maintained at 0.856 g·mL^{-1}. The resulted absorption spectra and λ_{max} were shown in Figures 2 and 3 and Table 2. The λ_{max} of MO in this study was compared to those in bulk water (λ_{max} = 462 nm), ethanol (λ_{max} = 417 nm), and cyclohexane (λ_{max} = 394 nm)[23,24] and shown in Figure 2. In all experiments, PFPE-NH_4 and water were fully solubilized in $SCCO_2$ based on the data of phase boundary in Figure 1 and visual observation of the view cell. The formation of stable PFPE-NH_4 reverse micelles in $SCCO_2$ with various water contents was proved by the remarkable absorption spectra of MO. Similar to the previous studies,[2,10,11,13,15] our work also indicated that MO molecules were located in an environment of polarity between cyclohexane and water. It was also noted that the λ_{max} in this study was smaller than that (λ_{max} = 460 nm) in the literature.[10,11] This may be due to the longer fluorinated chain because of its characteristic of more CO_2-philic in this study.

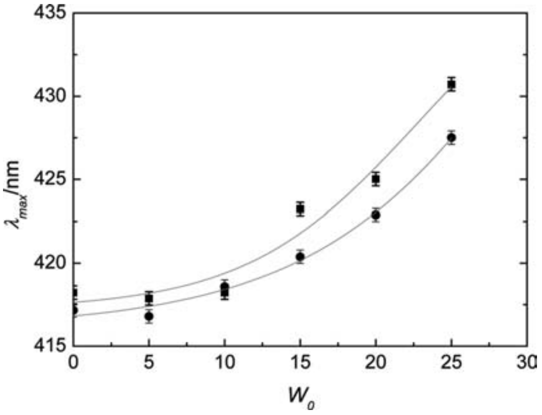

Figure 3. λ_{max} of MO in 2.5 % mass fraction of PFPE-NH_4 reverse micelles in supercritical CO_2 with various water content at ■, 308.15 K; and ●, 313.15 K. Density of the system is 0.856 g·mL^{-1}.

Table 2. Maximum Absorbance of MO in 2.5 % Mass Fraction of PFPE-NH_4 Reverse Micelles in $SCCO_2$ for Different Water Contents at (308.15 and 313.15) K

T/K	W_0	$W_0^{CO_2}$	corrected W_0	λ_{max}/nm
308.15	0	10.67	0	418.2 ± 0.4
	5.00	10.67	0	417.9 ± 0.4
	10.00	10.67	0	418.2 ± 0.4
	15.00	10.67	4.33	423.2 ± 0.4
	20.00	10.67	9.33	425.0 ± 0.4
	25.00	10.67	14.33	430.7 ± 0.4
313.15	0	12.58	0	417.2 ± 0.4
	5.0	12.58	0	416.8 ± 0.4
	10.0	12.58	0	418.6 ± 0.4
	15.0	12.58	2.42	420.4 ± 0.4
	20.0	12.58	7.42	422.9 ± 0.4
	25.0	12.58	12.42	427.5 ± 0.4

As shown in Figure 3, the λ_{max} of MO was kept almost unchanged at lower water content ($W_0 \leq 10.00$). However, it shifted obviously from the short wavelength (λ_{max} = 418.2 nm at 308.15 K and λ_{max} = 418.6 nm at 313.15 K) to the long wavelength (λ_{max} = 430.7 nm at 308.15 K and λ_{max} = 427.5 nm at 313.15 K) when the W_0 value increased from 10.00 to 25.00. This can be explained by the assumed water distribution between the $SCCO_2$ continuous phase and the surfactant aggregates using corrected W_0. When the water content was lower than 10.00 (corrected $W_0 = 0$, see Table 2), there was no excess water dispersing into the surfactant aggregates. It means that the reverse micelles were "dry" micelles and the water had no influence on the interior microenvironment of reverse micelles. So the micropolarity (λ_{max} of MO) of the reverse micelles stayed unchanged at low W_0 values. When the water content was higher than 10.00 (corrected $W_0 > 0$, see Table 2), there was some excess water dispersing into the surfactant aggregates. These waters increased the polarity (λ_{max} of MO) of the interior microenvironment of reverse micelles where MO was located, and the micropolarity increased with the increase of excess water. Furthermore, the relationship between λ_{max} and W_0 (corrected W_0) suggested that it may be the truth that the water in the PFPE-NH_4 + water + $SCCO_2$ system should first saturate the $SCCO_2$ continuous phase and then disperse into the surfactant aggregates.

The absorption spectra and λ_{max} of MO in the reverse micelles in $SCCO_2$ at various temperatures were shown in Figures 4 and 5 and Table 3. The composition and density of the system in Figures 4 and 5 were the same as those in Figure 3. When temperature increased from (308.15 to 328.15) K, the λ_{max} shifted from long wavelength (423.2 nm at W_0 = 15.00 and 425.0 nm at W_0 = 20.00) to short

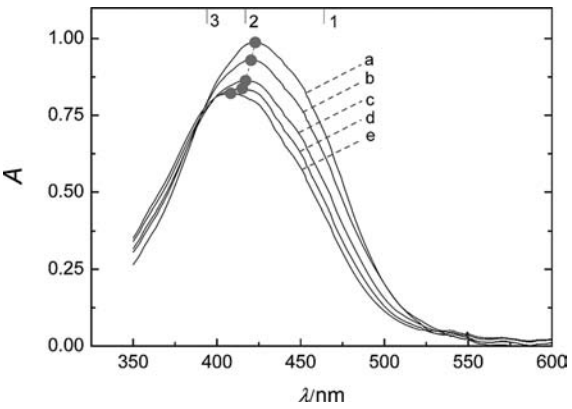

Figure 4. UV−vis absorption spectra of MO in 2.5 % mass fraction of PFPE-NH_4 reverse micelles in $SCCO_2$ with $W_0 = 15.0$ at different temperatures and density of 0.856 $g \cdot mL^{-1}$. The temperatures of these spectra are: a, 308.15 K; b, 313.15 K; c, 318.15 K; d, 323.15 K; e, 328.15 K. ● represents λ_{max} in each spectrum. 1, 2, and 3 represent the λ_{max} of water (462 nm), ethanol (417 nm), and cyclohexane (394 nm), respectively.

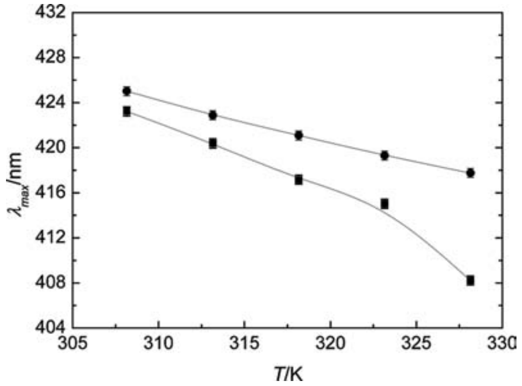

Figure 5. λ_{max} of MO in 2.5 % mass fraction of PFPE-NH_4 reverse micelles in $SCCO_2$ with W_0 = ■, 15.00; and ●, 20.00 at different temperatures. Density of the system is 0.856 $g \cdot mL^{-1}$.

Table 3. Maximum Absorbance of MO in 2.5 % Mass Fraction of PFPE-NH_4 Reverse Micelles in $SCCO_2$ for Different Temperatures at W_0 = 15.00 and 20.00

W_0	T/K	$W_0^{CO_2}$	corrected W_0	λ_{max}/nm
15.00	308.15	10.67	4.33	423.2 ± 0.4
	313.15	12.58	2.42	420.4 ± 0.4
	318.15	14.54	0.46	417.2 ± 0.4
	323.15	16.46	0	415.0 ± 0.4
	328.15	19.08	0	408.2 ± 0.4
20.00	308.15	10.67	9.33	425.0 ± 0.4
	313.15	12.58	7.42	422.9 ± 0.4
	318.15	14.54	5.46	421.1 ± 0.4
	323.15	16.46	3.54	419.3 ± 0.4
	328.15	19.08	0.92	417.8 ± 0.4

wavelength (408.2 nm at $W_0 = 15.00$ and 417.8 nm at $W_0 = 20.00$), which indicated that the micropolarity decreased with the increase of temperature. This can also be explained by the distribution of water between the $SCCO_2$ continuous phase and surfactant aggregates. When temperature increased at the fixed density, the solubility of water in the $SCCO_2$ continuous phase increased, and the excess water (expressed as corrected W_0, see Table 3) dispersed into the surfactant aggregates decreased, which resulted in the decrease of the micropolarity of the reverse micelles in $SCCO_2$.

Conclusions

The phase behavior of the PFPE-NH_4 + water + $SCCO_2$ system was determined at temperatures of (308.15 to 328.15) K and employed for micropolarity study. The phase transition densities of this system increased with the increase of W_0 and decreased with the increase of temperature. The results of micropolarity investigation showed that the solvatochromic probe MO molecules locate in a microenvironment of polarity between cyclohexane and water. The micropolarity of reverse micelles in $SCCO_2$ increased with the increase of water content after excess water appeared and increased with the decrease in temperature. The increase in micropolarity may be due to more water dispersing into the surfactant aggregates residing in the $SCCO_2$ continuous phase at higher water content and lower temperature.

Literature Cited

(1) Niemeyer, E. D.; Bright, F. V. The pH within PFPE reverse micelles formed in supercritical CO_2. *J. Phys. Chem. B* **1998**, *102*, 1474–1478.

(2) McFann, G. J.; Johnston, K. P.; Howdle, S. M. Solubilization in nonionic reverse micelles in carbon-dioxide. *AIChE J.* **1994**, *40*, 543–555.

(3) Sagisaka, M.; Yoda, S.; Takebayashi, Y.; Otake, K.; Kondo, Y.; Yoshino, N.; Sakai, H.; Abe, M. Effects of CO_2-philic tail structure on phase behavior of fluorinated Aerosol-OT analogue surfactant/water/supercritical CO_2 systems. *Langmuir* **2003**, *19*, 8161–8167.

(4) Gao, Y. N.; Wu, W. Z.; Han, B. X.; Li, G. Z.; Chen, J. W.; Hou, W. G. Water-in-CO_2 microemulsions with a simple fluorosurfactant. *Fluid Phase Equilib.* **2004**, *226*, 301–305.

(5) Park, J. Y.; Lim, J. S.; Lee, Y. W.; Yoo, K. P. Phase behavior of water-in-supercritical carbon dioxide microemulsion with sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate. *Fluid Phase Equilib.* **2006**, *240*, 101–108.

(6) Ueda, M.; Schelly, Z. A. Reverse micelles of Aerosol-OT in benzene 4. Investigation of the micropolarity using 1-methyl-8-oxyquinolinium betaine as a probe. *Langmuir* **1989**, *5*, 1005–1008.

(7) Shervani, Z.; Ikushima, Y. The investigation of water/AOT/supercritical ethane reverse micelles by UV-VIS spectroscopy. *J. Supercrit. Fluids* **1998**, *13*, 375–379.

(8) Shervani, Z.; Ikushima, Y. Micropolarity of sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles prepared in supercritical ethane and near-critical propane. *Colloid Polym. Sci.* **1999**, *277*, 595–600.

(9) Shervani, Z.; Ikushima, Y. E-T(N) values and effective dielectric constants of water/AOT/near-critical propane reverse micelles. *Colloids Surf. A* **2000**, *168*, 97–99.

(10) Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph, T. W. Water in carbon dioxide microemulsions, An environment for hydrophiles including proteins. *Science* **1996**, *271*, 624–626.

(11) Clarke, M. J.; Harrison, K. L.; Johnston, K. P.; Howdle, S. M. Water in supercritical carbon dioxide microemulsions, Spectroscopic investigation of a new environment for aqueous inorganic chemistry. *J. Am. Chem. Soc.* **1997**, *119*, 6399–6406.

(12) Hutton, B. H.; Perera, J. M.; Grieser, F.; Stevens, G. W. Investigation of AOT reverse microemulsions in supercritical carbon dioxide. *Colloids Surf. A* **1999**, *146*, 227–241.

(13) Keiper, J. S.; Simhan, R.; Desimone, J. M.; Wignall, G. D.; Melnichenko, Y. B.; Frielinghaus, H. New phosphate fluorosurfactants for carbon dioxide. *J. Am. Chem. Soc.* **2002**, *124*, 1834–1835.

(14) Li, J. C.; Zhang, J. L.; Han, B. X.; Gao, Y. N.; Shen, D.; Wu, Z. H. Effect of ionic liquid on the polarity and size of the reverse micelles in supercritical CO_2. *Colloids Surf. A* **2006**, *279*, 208–212.

(15) Liu, J. C.; Ikushima, Y.; Shervani, Z. Investigation on the solubilization of organic dyes and micro-polarity in AOT water-in-CO_2 microemulsions with fluorinated co-surfactant by using UV-Vis spectroscopy. *J. Supercrit. Fluids* **2004**, *32*, 97–103.

(16) Loeker, F.; Marr, P. C.; Howdle, S. M. FTIR analysis of water in supercritical carbon dioxide microemulsions using monofunctional perfluoropolyether surfactants. *Colloids Surf. A* **2003**, *214*, 143–150.

(17) Su, B. G.; Xing, H. B.; Ren, Q. L. Solubilization of oxymatrine in water-in-supercritical carbon dioxide microemulsions. *J. Chem. Eng. Data* **2008**, *53*, 1705–1707.

(18) Su, B. G.; Lv, X. B.; Yang, Y. W.; Ren, Q. L. Solubilities of dodecylpolyoxyethylene polyoxypropylene ether in Supercritical carbon dioxide. *J. Chem. Eng. Data* **2006**, *51*, 542–544.

(19) Gonenc, Z. S.; Akman, U.; Sunol, A. K. Solubility and partial molar volumes of naphthalene, phenanthrene, benzoic-acid, and 2-methoxynaphthalene in supercritical carbon-dioxide. *J. Chem. Eng. Data* **1995**, *40*, 799–804.

(20) Huang, F. H.; Li, M. H.; Lee, L. L.; Staring, K. E.; Chung, F. T. H. An accurate equation for carbon-dioxide. *J. Chem. Eng. Jpn.* **1985**, *18*, 490–496.

(21) Wiebe, R. The binary system carbon dioxide-water under pressure. *Chem. Rev.* **1941**, *29*, 475–481.
(22) Chrastil, J. Solubility of solids and liquids in supercritical gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.
(23) Karukstis, K. K.; D'Angelo, N. D.; Loftus, C. T. Using the optical probe methyl orange to determine the role of surfactant and alcohol chain length in the association of 1-alkanols with alkyltrimethylammonium bromide micelles. *J. Phys. Chem. B* **1997**, *101*, 1968–1973.
(24) Karukstis, K. K.; Savin, D. A.; Loftus, C. T.; D'Angelo, N. D. Spectroscopic studies of the interaction of methyl orange with cationic alkyltrimethylammonium bromide surfactants. *J. Colloid Interface Sci.* **1998**, *203*, 157–163.

Received for review January 7, 2009. Accepted March 9, 2009. The authors are grateful for the financial support from the Ministry of Science and Technology of the People's Republic of China (project Nos. 2006BAD27B03 and 2007AA100404) and the National Natural Science Foundation of China (No. 20676112).

JE900024F