Micelles

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Reverse Micelles in Carbon Dioxide with Ionic-Liquid Domains**

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Supercritical CO_2 is an attractive green solvent.[1] However, CO_2 is generally a poor solvent for high-molecular-weight or hydrophilic molecules, which rules out many potential applications. An effective way to solve this problem is to create reverse micelles or microemulsions with supercritical CO_2 as the continuous phase. Many studies have been carried out on water-in-CO_2 microemulsions and reverse micelles in supercritical CO_2 with water domains.[2] Researchers have also investigated the applications of water-in-CO_2 microemulsions, for example, for the extraction of biomolecules[2c,d] and metal ions,[3] for the preparation of nanoparticles,[4] and as media for chemical reactions.[5]

Room-temperature ionic liquids, which are organic salts with melting points below 100 °C, have attracted much attention.[6] They can dissolve many organic and inorganic substances, and their properties are tunable to satisfy the requirements of a variety of tasks. Many ionic liquids can be considered as cleaner solvents than standard solvents because they are nonvolatile and often nontoxic or low toxic. Ionic liquids have potential applications in a range of areas, such as separations,[7] chemical reactions,[8] and materials synthesis.[9] It was reported that ionic liquids could dissolve supercritical CO_2, whereas the solubility of ionic liquids in supercritical CO_2 was negligible.[10]

Very recently, reverse micelles with ionic-liquid cores have attracted much interest,[11] and a variety of reverse micelles with organic solvents[11a,b] and with water[11c] as the continuous phase have been studied. The combination of supercritical CO_2 and ionic liquids is interesting from academic, environmental, and practical points of view. The creation of reverse micelles in supercritical CO_2 with ionic-liquid domains is certainly a very interesting topic: Ionic liquids can be dispersed in supercritical CO_2, and the systems may combine some advantages of the two fluids. Herein, we report our findings that *N*-ethyl perfluorooctylsulfonamide ($C_2H_5NHSO_2C_8F_{17}$; *N*-EtFOSA) can form reverse micelles in supercritical CO_2 with 1,1,3,3-tetramethylguanidinium ($[(CH_3)_2N]_2C{=}NH_2^+$) acetate (TMGA), 1,1,3,3-tetramethylguanidinium lactate (TMGL), and 1,1,3,3-tetramethylguanidinium trifluoroacetate (TMGT) domains, and that the reverse micelles can solubilize salts, such as methyl orange, $CoCl_2$, and $HAuCl_4$.

Figure 1 shows the effect of temperature and the ionic-liquid-to-surfactant molar ratio, *w*, on cloud-point pressure for the CO_2/*N*-EtFOSA/TMGA system. The cloud-point pressure is the minimum pressure required to keep the system in the one-phase region. Therefore, a single phase is observed at pressures above the corresponding cloud-point-pressure curve, and phase separation occurs when the pressure is decreased below that indicated by the curve. The dependence of cloud-point pressure on temperature and *w* for the CO_2/*N*-EtFOSA/TMGL and CO_2/*N*-EtFOSA/TMGT systems is shown in the Supporting Information.

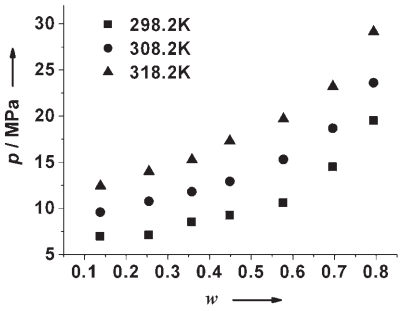

Figure 1. The effects of *w* and temperature on the cloud-point pressure *p* of CO_2/*N*-EtFOSA/TMGA; [*N*-EtFOSA] = 0.064 g mL^{-1}.

At a fixed molar ratio *w*, the cloud-point pressure increases as the temperature rises, because the density of CO_2 decreases with increasing temperature. As expected, the cloud-point pressure also increases with increasing *w*. Our experiments showed that the solubility of the ionic liquids in neat CO_2 was negligible, as reported by Blanchard et al.[10] Therefore, we can suppose that all the ionic liquid in the system was solubilized in the reverse micelles. At readily accessible pressures, the value of *w* can reach 0.8 for the CO_2/TMGA/*N*-EtFOSA system. At this *w* value, the ionic-liquid-to-surfactant weight ratio in the reverse micelles is equivalent to the water-to-surfactant weight ratio of water-in-CO_2 reverse micelles with a water-to-surfactant molar ratio of about 10, as the molecular weights of TMGA and water are 175.2 and 18.0 g mol^{-1}, respectively. A similar value can also be reached for the other two systems. The cloud-point pressure is not sensitive to the concentration of the surfactant in the range 0.041–0.077 g mL^{-1} (see the Supporting Information).

The maximum absorption wavelength, λ_{max}, of methyl orange (MO) is sensitive to the local environment around the

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compound. MO is often used as a probe to investigate the micropolarity of water-in-oil or water-in-CO_2 microemulsions.[12] The absorption band of MO is not observed for supercritical CO_2/MO and supercritical CO_2/MO/*N*-EtFOSA systems. It can be deduced that the solubility of MO in supercritical CO_2 and supercritical CO_2/*N*-EtFOSA is very low. However, the absorption band of MO is observed for CO_2/MO/*N*-EtFOSA/TMGA, CO_2/MO/*N*-EtFOSA/TMGL, and CO_2/MO/*N*-EtFOSA/TMGT systems, which indicates the formation of ionic-liquid domains in the reverse micelles. As an example, Figure 2 shows UV spectra of MO in the

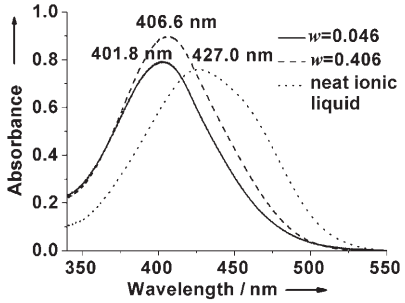

Figure 2. UV/Vis absorption spectra of MO in reverse micelles with TMGL domains at 308.2 K and 20.50 MPa; [*N*-EtFOSA] = 0.060 g mL^{-1}.

reverse micelles with TMGL domains; spectra of MO in the reverse micelles with TMGA and TMGT domains under a variety of conditions are given in the Supporting Information. The shift in the λ_{max} value for MO to longer wavelengths with increasing w indicates that the polarity of the environment of the solubilized MO increases with w. However, the polarity inside the reverse micelles is lower than that of the neat ionic liquids, in analogy with reverse micelles with water domains or water cores.[2d]

$CoCl_2$ is soluble in the ionic liquids used in these studies and has an absorption band at a wavelength of about 608 nm. We also studied the solubilization of $CoCl_2$ in the reverse micelles by UV/Vis spectroscopy. The results show that the reverse micelles can solubilize $CoCl_2$, whereas the CO_2/*N*-EtFOSA system can not (see the Supporting Information), and provide further evidence for the formation of reverse micelles with ionic-liquid domains. Similarly, our experiments indicated that the reverse micelles with ionic-liquid domains could solubilize $HAuCl_4$. To demonstrate the application of reverse micelles with ionic-liquid domains, we prepared gold particles by a process known as rapid expansion of a supercritical solution into a liquid solvent (RESOLV).[13] Thus, we expanded a CO_2/*N*-EtFOSA/TMGT reverse-micellar solution containing $HAuCl_4$ into a solution of $NaBH_4$ (0.5 g L^{-1}) in ethanol. Transmission electron microscopy (TEM) images and the electron-diffraction pattern of the Au particles are shown in Figure 3. The TEM images show that spherical Au nanoparticles were formed when the weight ratio of $HAuCl_4$ to TMGT (W_{HAuCl_4}/W_{TMGT}) in the reverse micelles was 0.01 (Figure 3a), and that Au networks were obtained at a higher concentration of $HAuCl_4$ (Figure 3b). In the electron-diffraction pattern (Figure 3c), the characteristic

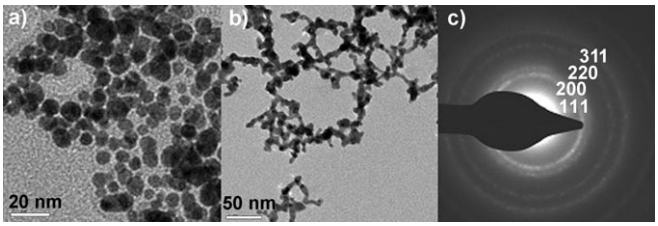

Figure 3. TEM images and electron-diffraction pattern of Au nanoparticles prepared by the RESOLV method at 308.2 K and 20.00 MPa; [*N*-EtFOSA] = 0.060 g mL^{-1}, w = 0.41. a) W_{HAuCl_4}/W_{TMGT} = 0.01; b) W_{HAuCl_4}/W_{TMGT} = 0.04; c) electron-diffraction pattern of the Au particles in (b).

rings for a polycrystalline material are observed and correspond to standard face-centered-cubic Au.

It is well known that the $=NH_2^+$ group in the cation of the ionic liquids can form a strong hydrogen bond with the S = O group in the surfactant. We believe that the formation of the reverse micelles with ionic-liquid domains is closely related to the affinity for CO_2 of the fluorinated chain of the surfactant and the strong hydrogen bond between the polar heads of the surfactant and the ionic liquid. This argument is supported partially by the finding in this study that the degree of solubilization of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and 1-butyl-3-methylimidazolium hexafluoroborate ([bmim]PF_6) under similar conditions is very small ($w < 0.05$); [bmim]BF_4 and [bmim]PF_6 can not form a strong hydrogen bond with the polar head of the surfactant. Recently, we studied the solubilization of [bmim]BF_4 in reverse micelles of Surfynol-2502 (a surfactant that contains an alkoxylated acetylenic diol group) in supercritical CO_2. It was demonstrated that the amount of the ionic liquid solubilized in the reverse micelles was extremely small, and that ionic-liquid domains could not be formed.[14] One of the reasons for the poor solubility of [bmim]BF_4 in these reverse micelles may be that the polar head of the surfactant can not form a strong hydrogen bond with [bmim]BF_4. This result supports the hypothesis that the strong hydrogen bond formed between the polar heads of *N*-EtFOSA and the guanidinium-based ionic liquids is favorable to the formation of ionic-liquid domains.

In summary, *N*-EtFOSA can form reverse micelles with TMGA, TMGL, and TMGT domains in supercritical CO_2. These reverse micelles can solubilize salts, such as methyl orange, $CoCl_2$, and $HAuCl_4$. These new CO_2–ionic-liquid systems may have certain advantages, especially when water-sensitive compounds are involved. Future research will include the creation of more micellar systems with ionic-liquid domains, in particular by using nonfluorous surfactants, the study of their structures, and the exploration of applications.

Experimental Section

N-EtFOSA (> 95 %) purchased from Guangzhou Leelchem Corporation was purified by recrystallization three times from chloroform. TMGA, TMGL, and TMGT were synthesized by direct neutralization of 1,1,3,3-tetramethylguanidine with the corresponding acid.[15]

Methyl orange, $CoCl_2$, and $HAuCl_4$ (AR grade) were produced by Beijing Chemical Reagent Factory. $HAuCl_4$ and $CoCl_2$ were dried under vacuum at 353.2 K and 423.2 K, respectively, to remove any moisture or water of crystallization before they were used. CO_2 (99.995% purity) was supplied by Beijing Analytical Instrument Factory.

The apparatus used to determine the phase behavior was similar to that described previously.[16] It consisted mainly of a stainless-steel view cell with two windows, a temperature-controlled water bath, and a pressure gauge. The volume of the view cell could be changed in the range of 20–40 cm^3. The chemicals in the view cell were stirred by a magnetic stirrer.

The experimental procedures used to determine the phase behavior were also similar to that reported previously.[16] In brief, a suitable amount of the surfactant and the ionic liquid was loaded into the view cell, and the air in the cell was removed by vacuum. The view cell was placed into the temperature-controlled water bath. After thermal equilibrium had been reached, the cell was charged slowly with CO_2, which was added by a syringe pump (DB-80), until the mixture became clear (one phase), and the pressure was recorded. The mixture became cloudy if the pressure was reduced slightly from this recorded pressure, which was defined as the cloud-point pressure.

The apparatus and procedures for the UV/Vis spectroscopic study were also similar to those described previously.[16] In a typical experiment, a suitable amount of *N*-EtFOSA and a solution of methyl orange (or $CoCl_2$) in the ionic liquid were loaded into the temperature-controlled high-pressure UV sample cell, the optical path length and the volume of which were 21 mm and 8.8 mL, respectively. The air in the sample cell was replaced by CO_2, and after thermal equilibrium had been reached more CO_2 was compressed into the sample cell to the desired pressure with a high-pressure pump (DB-80). Spectra were recorded with a UV/Vis spectrometer (TU-1201, Beijing Instrument Company) until the absorbance was independent of equilibration time.

The nanoparticles were prepared by RESOLV with $HAuCl_4$ in a CO_2/*N*-EtFOSA/TMGT reverse-micellar solution.[13] The reverse-micellar solution with the ionic liquid and $HAuCl_4$ was first prepared by using the apparatus described above for the determination of the phase behavior. The reverse-micellar solution was then expanded into a solution of $NaBH_4$ (0.5 $g\,L^{-1}$) in ethanol. The particles were collected, and the TEM images and electron-diffraction pattern were recorded on a FEI Tecnai G20 transmission electron microscope operating at 120 kV.

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