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Compressed CO_2-Assisted Formation of Reverse Micelles of PEO−PPO−PEO Copolymer

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Introduction. Reverse micelles are surfactant aggregates surrounding a polar core dispersed in an apolar solvent.[1] They can solubilize a significant amount of water, and water domains exist in the micelles; the solutions are clear and thermodynamically stable. The reverse micelles in different solvents have been studied.[2−7] To date, reverse micelles have been successfully used in many fields, such as separation and extraction of proteins[4] and as nanoreactors for enzymatic or catalytic reactions.[5] Undoubtedly, investigation of new method to create reverse micelles is of great importance to both pure and applied sciences. It is ideal that forming and breaking the reverse micelles can be easily controlled.

Micelle formation of a number of copolymers in organic solvents has been reported.[8−10] However, many polymeric surfactants cannot form reverse micelles at some desired conditions. How to control the formation of the reverse micelles is an interesting and important topic.

Compressed gaseous CO_2 is quite soluble in a number of organic solvents and expand them largely, which can reduce the solvent strength. This process is often referred to as gas antisolvent process (GAS).[11,12] GAS techniques have been used in different fields, such as fractionation,[13] recrystallization,[14] and particle generation.[15,16] Recently, we used compressed CO_2 to break the sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles.[17]

Some copolymers can form reverse micelles in organic solvents, and different methods to induce micellization, such as changing temperature and adding salts, have been studied.[18] In this work, we report the novel finding. Compressed CO_2 can facilitate the formation of reverse micelles of the copolymer $(EO)_{27}(PO)_{61}(EO)_{27}$ (P104) in *p*-xylene. The reverse micelles can solubilize a significant amount of water, methyl orange (MO), and $CoCl_2$, while the polymer solution cannot solubilize these substances in the absence of CO_2. We expect that this method can make more polymeric surfactants form reverse micelles and open up some new applications.

Experimental Section. a. Materials. P104 was provided by BASF Corporation with a composition of $(EO)_{27}(PO)_{61}(EO)_{27}$. Methyl orange (MO), anhydrous $CoCl_2$, and *p*-xylene were produced by Beijing Chemical Reagent Factory (A.R. Grade). CO_2 (99.995% purity) was supplied by Beijing Analytical Instrument Factory. Double distilled water was used.

b. Apparatus and Procedures To Determine Water Solubilization. The experiment is based on the fact that the solution is clear and transparent if the water is all solubilized; otherwise, the solution is hazy or milky.[18,19] The apparatus to study water solubilization of *p*-xylene/P104/H_2O/CO_2 quaternary system is shown schematically in Figure 1. It consisted mainly of a high-pressure view cell with a volume of 40 cm^3, a constant temperature water bath, a high-pressure syringe pump (DB-80), a pressure gauge, a magnetic stirrer, and a gas cylinder. The temperature of the water bath was controlled to 40.0 ± 0.1 °C by a HAAKE D8 temperature controller. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, model 93) and an indicator, which was accurate to ±0.025 MPa in the pressure range 0−20 MPa.

In a typical experiment, the air in the view cell was replaced by CO_2; 5 g of solution of P104 in *p*-xylene and the desired amount of double distilled water were loaded into the high-pressure view cell. The cell was placed into the constant temperature water bath. After thermal equilibrium had been reached, the stirrer was started, and the solution was hazy and milky. CO_2 was charged into the cell slowly until the hazy and milky liquid solution became transparent and completely clear, which was an indication of the solubilization of all the water.[18,19]

c. UV−vis Experiment. The solubilization of MO and $CoCl_2$ in the reverse micelles was studied by UV spectroscopy. The apparatus and procedures were similar to those reported previously.[20] It consisted of a gas cylinder, a high-pressure pump, a pressure gauge, an UV−vis spectrometer, a temperature-controlled high-pressure UV sample cell, and valves and fittings. The UV/vis spectrophotometer was produced by Beijing General Instrument Co. (model TU-1201, resolution 0.1 nm). The sample cell was composed mainly of a stainless steel body, two quartz windows, a stirrer, and a temperature controlling system. The optical path length and the inner volume of the cell were 1.32 cm and 1.74 cm^3, respectively. In the experiment, the sample cell was flushed with CO_2 to remove the air. Desired amounts of MO (or $CoCl_2$) aqueous solution of suitable concentration and polymer solution in *p*-xylene were charged into the sample cell. After thermal equilibrium had been reached, CO_2 was compressed into the UV cell to the desired pressure. The UV spectrum at equilibrium condition was recorded, which was confirmed by the fact that the UV spectra recorded were independent of equilibration time. Generally, about 10 min was required for the system to reach equilibrium after suitable pressure was reached.

Results and Discussion. a. Solublization of Water. P104 can form reverse micelles in *p*-xylene at 25 °C.[19] The cmc is 9 wt %, which was determined by the abrupt increase in the water solubilization capability.[19] The cmc at this temperature determined in present work by water solubilization is 10 wt %, which agrees reasonably with the literature value.[19] However, our experiments indicate that P104 solution in *p*-xylene cannot form reverse micelles at 40 °C, which was known from the fact that the amount of the solubilized water was negligible even the concentration of P104 was as high as 30 wt %. This is consistent with the results of

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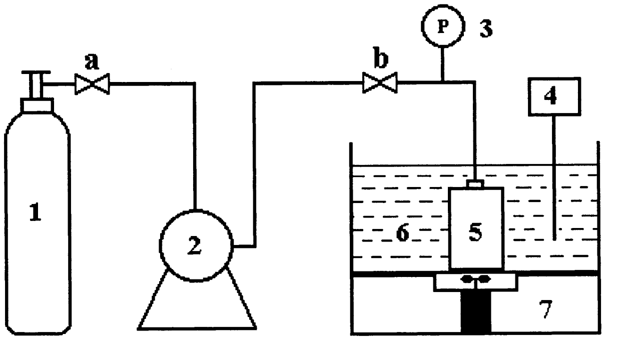

Figure 1. Schematic diagram of the apparatus for studying the solubilization of water: 1, gas cylinder; 2, high-pressure syringe pump; 3, pressure gauge; 4, temperature controller; 5, high-pressure view cell; 6, water bath; 7, magnetic stirrer; a, b, valves.

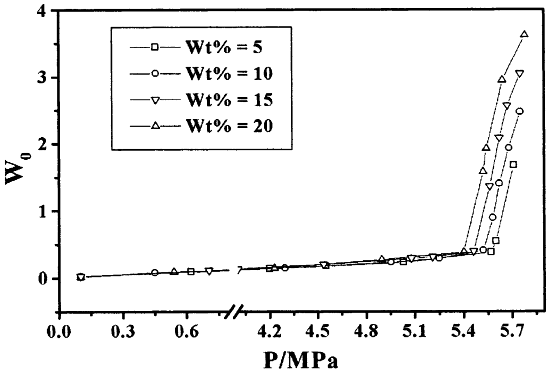

Figure 2. Dependence of maximum W_0 on pressure of CO_2 and initial concentration (*p*-xylene-basis) of P104 in *p*-xylene.

Alexandridis et al.[18] It was reported that the cmc of PEO/PPO and PEO/PBO copolymers in *p*-xylene increases with temperature.[18] The authors explained this results with the solvent quality change of both water and *p*-xylene. On one hand, the solubility of PEO homopolymer in water decreases, and its solubility in *p*-xylene increases with increasing temperature, which disfavors the association of the copolymer. On the other hand, PPO is soluble in *p*-xylene at room temperature, and it is expected that *p*-xylene becomes an even better solvent for PPO at higher temperatures. Thus, an increase in temperature of a PEO/PPO copolymer solution in *p*-xylene is expected to render *p*-xylene a better solvent overall, and the copolymer is less prone to association.[18]

Considering the fact that dissolution of compressed CO_2 can tune the solvent quality,[11,12] we expect that the addition of CO_2 may induce the aggregation of P104 copolymer in *p*-xylene. Figure 2 shows a maximum W_0 (the molar ratio of water to EO segments) as a function of CO_2 pressure at 40.0 °C for the solutions of different P104 concentrations. The trace amount of water dissolved in the solvent (*p*-xylene/CO_2) has been corrected; i.e., the W_0 is calculated from the following equation.

$$W_0 = \frac{(m_{\mathrm{w}} - m_{\mathrm{w},0})/M_{\mathrm{w}}}{54 m_{\mathrm{p}}/M_{\mathrm{p}}} \qquad (1)$$

where m_{w} is the total mass of water, $m_{\mathrm{w},0}$ stands for the mass of water dissolved in the solvent at the experimental temperature and pressure, M_{w} is the molar mass of water, m_{p} denotes the mass of the surfactant, and M_{p} is the molecular weight of P104.

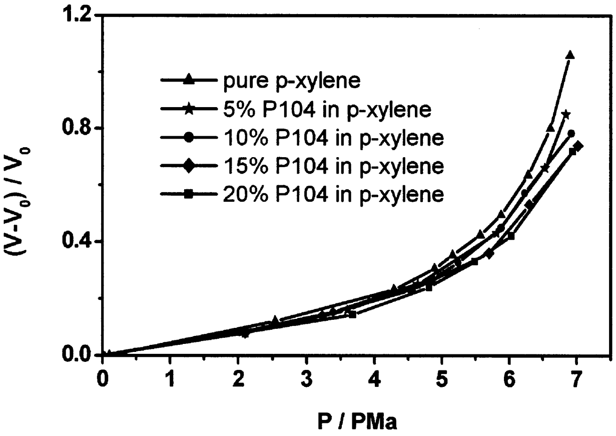

Figure 3. Dependence of volume expansion coefficient ($(V - V_0)/V_0$) on CO_2 pressure for some typical solutions. V_0 and V are the volumes of the solution before and after dissolving CO_2, respectively.

It can be seen from Figure 2 that W_0 is very small and increase very slowly with the pressure of CO_2 when the pressure is low. It is interesting that in each curve there is a pressure where W_0 increases sharply with increasing pressure, indicating the reverse micelle begin to form. We define the pressure at which reverse micelle begin to form as critical micelle pressure (cmp). As expected, the cmp decreases with the concentration of the copolymer. The cmp for the solutions of 5, 10, and 15, and 20 wt % are 5.60, 5.53, 5.47, 5.41 MPa, repectively. Figure 2 also indicates that the maximum W_0 can be as high as 3.6 at suitable condition; i.e., one polymer molecule can solubilize about 200 water molecules, while the amount of water in the solvent is only 2% of the total water amount. This indicates that water domains exist, which is further proved by the solubilization of MO and $CoCl_2$.

The concentration of CO_2 in the solution is an important factor. In this work, the volume expansion coefficient at different pressures, which is directly related to the volume fraction of CO_2 in the solution, is determined, and the results are shown Figure 3. As expected, the volume expansion coefficient or the concentration of CO_2 in the solutions increases with increasing pressure of CO_2. The volume fraction of CO_2 in the solution at different conditions in Figure 2 can be estimated from the data in Figure 3. The solubility of PEO–PPO–PEO copolymer in CO_2 at our experimental conditions should be extremely low, which can be known from the results in the literature.[21]

b. Solvatochromic Probe Studies. The shift of the absorbance maximum ($\lambda_{\max}$) of a solvatochromic probe is a sensitive measure of the local environment about the probe.[22] To confirm that water domains exist and to characterize their properties, the solvatochromic probe study is carried out in this work by UV–vis spectroscopy. We choose the ionic probe MO to test the environment polarity.

The absorbance profiles of MO in the CO_2-expanded P104 solution with different W_0 are illustrated in Figure 4. The solubility of MO in *p*-xylene is extremely low, and the absorption band of MO cannot be observed in the absence of any of the three additives: H_2O, P104, and CO_2 of suitable pressure (Figure 4, curve a). However, the absorption band of MO in the MO/P104/H_2O/CO_2/*p*-xylene system can be observed as shown in curves b–d, indicating the solubilization of MO. As

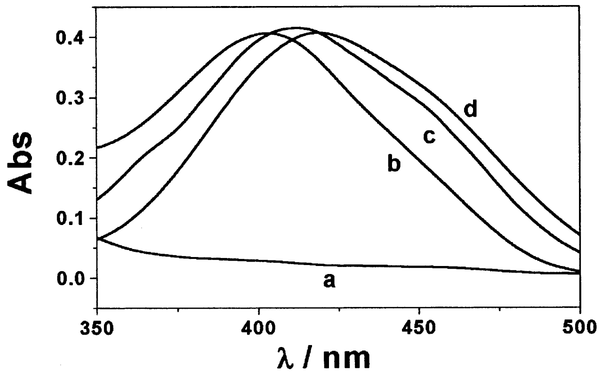

Figure 4. UV−vis spectra of MO in different solutions. (a) MO/P104/CO_2/*p*-xylene, MO/H_2O/CO_2/*p*-xylene, and MO/P104/H_2O/*p*-xylene. (b−d) MO/P104/H_2O/CO_2/*p*-xylene. The concentration of MO is 3.1×10^{-5} mol L^{-1} (based on the bulk volume), and the concentration of P104 is 15 wt %. (b) $P = 5.01$ MPa, $W_0 = 0.17$, $\lambda_{max} = 403$ nm. (c) $P = 5.51$ MPa, $W_0 = 0.81$, $\lambda_{max} = 412$ nm. (d) $P = 5.64$ MPa, $W_0 = 2.32$, $\lambda_{max} = 420$ nm.

expected, λ_{max} increases with W_0 because the polarity of the environment of the solubilized MO increases with W_0 (curves b, c, d). The λ_{max} at $W_0 = 0.17$, 0.81, and 2.32 are 403, 412, and 420 nm, respectively. The λ_{max} of MO in pure water determined is 464 nm, suggesting that the polarity of the water domains is lower than that of the bulk water, which was also discussed for other reverse micelles.[23,24]

Besides the UV absorbance of MO at the concentration of 3.1×10^{-5} mol L^{-1} shown in Figure 4, we also have determined MO spectra in the reverse micelle solutions (15 wt % P104, $P = 5.64$ MPa, $W_0 = 2.32$) with MO concentrations of 5.4×10^{-5} and 1.2×10^{-4} mol L^{-1} (based on the bulk volume). The results illustrate that the absorbance increases with the increase of MO concentration, suggesting that the water domains has not been saturated by MO at these conditions. Our UV−vis experiments have also showed that the reverse micelles can solubilize $CoCl_2$. The results are not discussed in detail in this communication. We would like to mention that the solubilization of MO and $CoCl_2$ can also be observed directly (by color change) from the windows of the sample cell.

Figure 2 shows clearly that the maximum W_0 is a function of pressure of CO_2, and the pressure can be easily controlled because CO_2 is a gas at experimental conditions. Our experiments showed that, as expected, the solubilized water, MO, and $CoCl_2$ could be precipitated in about 20 h after depressurization, and solubilization occurs again as compressed by CO_2. In other words, formation and breaking of the reverse micelles can be repeated easily by controlling pressure, which provides special advantage for the applications of the reverse micelles formed by this method.

Water becomes acidic in the presence of CO_2, which might affect the solubilization of water. This can be ruled out because the maximum W_0 of hydrochloric acids in the pH range of 2−6 is the same as that of distilled water in the absence of CO_2.

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References and Notes

(1) Hamid, R. R.; Martin, E. W.; Juan, H. V. *J. Colloid Interface Sci.* **1995**, *174*, 1.
(2) Schwuger, M. J.; Shinoda, K.; Schomacker, R. *Chem. Rev.* **1995**, *95*, 849.
(3) Solans, C.; Kunieda, H. *Industrial Applications of Microemulsions;* Surfactant Science Series Vol. 66; Dekker: New York, 1997.
(4) 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.
(5) Beckman, E. J. *Science* **1996**, *271*, 613.
(6) Liu, J. C.; Han, B. X.; Zhang, J. L.; Li, G. Z.; Zhang, X. G.; Wang, J.; Dong, B. Z. *Chem. Eur. J.* **2002**, *8*, 1356.
(7) Cooper, A. I.; Londono, J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L. C.; Frechet, J. M. J.; Desimone, J. M. *Nature (London)* **1997**, *389*, 368.
(8) Quintana, J. R.; Janez, M. D.; Villacampa, M.; Katime, I. *Macromolecules* **1995**, *28*, 4139.
(9) Alexandridis, P.; Hatton, T. A. In *The Polymric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996.
(10) Chu, B. *Langmuir* **1995**, *11*, 414.
(11) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluids Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Stoneham, MA, 1994.
(12) Eckert, C. A.; Barbara, L. K.; Debenedetti, P. G. *Nature (London)* **1996**, *383*, 313.
(13) Catchpole, O. J.; Hochmann, S.; Anderson, S. R. J. In *High-Pressure Chemical Engineering*; von Rohr, P. R., Trepp, C., Eds.; Elsevier: Amsterdam, 1996; p 309.
(14) Gallagher, P. M.; Coffey, M. P.; Krukonis, V. J. *J. Supercrit. Fluids* **1992**, *5*, 130.
(15) Mawson, S.; Johnston, K. P.; Betts, D. E.; McClain, J. B.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 71.
(16) Bungert, B.; Sadlowski, G.; Arlt, W. *Ind. Eng. Chem. Res.* **1998**, *37*, 3208.
(17) Zhang, H. F.; Lu, J.; Han, B. X. *J. Supercrit. Fluids* **2001**, *20*, 65.
(18) Alexandridis, P.; Andersson, K. *J. Colloid Interface Sci.* **1997**, *194*, 166.
(19) Alexandridis, P.; Andersson, K. *J. Phys. Chem. B* **1997**, *101*, 8103.
(20) Lu, J.; Han, B. X.; Yan, H. K. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3269.
(21) O'Neill, M. L.; Cao, Q.; Fang, M.; Jonhston, K. P.; Wilkinson, S. P.; Smith, C. D.; Kerschner, S. P.; Jureller, S. H. *Ind. Eng. Chem. Res.* **1998**, *37*, 3067.
(22) McFann, G. J.; Johnston, K. P.; Howdle, S. M. *AIChE J.* **1994**, *40*, 543.
(23) Hutton, B. H.; Stevens, G. W. *Colloids Surf. A* **1999**, *146*, 227.
(24) Lay, M. B.; Drummond, C. J.; Grieser, F. *J. Colloid Interface Sci.* **1989**, *128*, 602.

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