Formation of Water-in-CO_2 Microemulsions with Non-fluorous Surfactant Ls-54 and Solubilization of Biomacromolecules

Juncheng Liu,[a, b] Buxing Han,*[a] Jianling Zhang,[a] Ganzuo Li,[b] Xiaogang Zhang,[a] Jun Wang,[c] and Baozhong Dong[c]

Abstract: The solubility of Ls-54 surfactant in supercritical CO_2 was determined. It was found that the surfactant was highly soluble in SC CO_2 and the water-in-CO_2 microemulsions could be formed, despite it being a non-fluorous and non-siloxane nonionic surfactant. The main reasons for the high solubility and formation of the microemulsions may be that the surfactant has four CO_2-philic groups (propylene oxide) and five hydrophilic groups (ethylene oxide) and its molecular weight are relatively low. The results of this work provide useful information for designing CO_2-soluble non-fluorous and non-siloxane surfactants. The phase behavior of the CO_2/Ls-54/H_2O system, solvatochromic probe study, and the UV spectrum of lysozyme proved the existence of water domains in the SC CO_2 microemulsions. The method of synchrotron radiation small-angle X-ray scattering was used to obtain the structural information on the Ls-54 based water-in-CO_2 reverse micelles. By using the Guinier plot ($\ln I(q)$ versus q^2) on the data sets in a defined small q range (0.022 – 0.040 Å^{-1}), the radii of the reverse micelles were obtained at different pressures and molar ratio of water to surfactant, W_0, which were in the range of 20.4 – 25.2 Å.

Keywords: carbon dioxide · microemulsion · supercritical fluids · surfactants · X-ray diffraction

Introduction

In recent years, the use of supercritical fluids (SCFs) has offered the opportunity to replace conventional organic solvents in a variety of applications. Supercritical (SC) CO_2 is generally viewed as environmentally benign alternative for organic solvents because it is inexpensive, nontoxic, nonflammable, readily available in large quantities, and has moderate critical temperature and pressure (31.1 °C and 7.38 MPa); moreover, it can be easily recaptured and recycled after use. Such advantages combined with unique properties of SCFs such as adjustable solvent power, enhanced mass transfer characteristics and low surface tension have promoted extensive research efforts on development of SC CO_2-based processes. However, CO_2 has no dipole moment, very low dielectric constant and polarizability per volume. Even when highly compressed, CO_2 has far weaker van der Waals forces than those of hydrocarbon solvents. Consequently, high molecular weight or hydrophilic solutes such as proteins, metal ions and most polymers are only sparingly soluble in carbon dioxide. One effective way to make CO_2 accessible for dissolving proteins and other nonvolatile hydrophilic substances is using suitable surfactants to produce water-in-CO_2 microemulsions, which consist of thermodynamically stable and optically transparent polar micro-aqueous domains.

Water-in-CO_2 microemulsions offer new opportunities for protein and polymer chemistry, separation science, reaction engineering science such as providing a "nanoreactor" for the synthesis of nanoparticles, environmental science for waste minimization and treatment, materials science, and dry-cleaning technology. Unfortunately, early attempts to disperse water into SC-CO_2 phase were unsuccessful despite the testing of over 150 surfactants.[1] Later, Hoefling et al.[2] synthesized CO_2-soluble fluorous surfactants. The solutions of several surfactants in CO_2 were able to extract thymol blue, a hydrophilic dye, from aqueous solutions. Recently, a fluorocarbon – hydrocarbon hybrid surfactant [$C_7F_{15}CH(OSO_3^-Na^+)C_7H_{15}$,(H-F)] has been shown to dissolve in CO_2.[3] However, this fluorocarbon – hydrocarbon surfactant hydrolyzes over time.[3, 4] Johnston et al.[4] found that the surfactant

---

[a] Prof. B. Han, Dr. J. Liu, Dr. J. Zhang, Dr. X. Zhang
Center for Molecular Science
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (China)
Fax: (+86) 10-62559373
E-mail: hanbx@pplas.icas.ac.cn

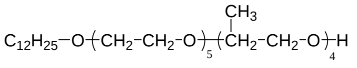
[b] Dr. J. Liu, Prof. G. Li
Key Laboratory of Colloid and Interface Chemistry
of State Education Ministry
Shandong University
Jinan 250100 (China)

[c] Prof. J. Wang, Prof. B. Dong
Institute of High Energy Physics
Chinese Academy of Sciences
Beijing 100039 (China)

0947-6539/02/0806-1356 $ 17.50+.50/0

with perfluoroalkylpolyether tail [$CF_3(CF_2CF(CF_3)O)_3$-$(CF_2O)_3COO^-NH_4^+$ (PFPE)] could form CO_2-based microemulsions, and other researches of PFPE-based water-in-CO_2 microemulsions were subsequently reported.[5] Nonetheless, there are concerns about toxicity of this class of surfactants.[6] In addition, fluorous and non-fluorous analogues of AOT[7] have been synthesized to form water-in-CO_2 mcroemulsions. Some of the water-in-CO_2 microemulsions have been applied to produce nanoparticles.[8] extract metal ions[9] and macromolecules,[10] conduct chemical reactions,[11] and voltammetric analysis[12] in SC CO_2. The non-ionic surfactants, $C_{12}EO_3$ and $C_{12}EO_8$, formed small aggregates in CO_2 that contained approximately 3–5 surfactant molecules per aggregate.[13] McFann et al. found that certain non-ionic surfactants solubilized excess water into CO_2 when a cosurfactant was added.[14] So far, the formation of SC CO_2 microemulsions by non-fluorous and non-siloxane nonionic surfactant has been seldom reported in the literature.[14]

In this work, we tested the solubility of some surfactants in SC CO_2 and found that the Ls-54 surfactant was soluble in SC CO_2 and the water-in-CO_2 microemulsions could be formed at accessible conditions although it is a non-fluorous and non-siloxane nonionic surfactant. And this surfactant has advantages of low toxicity and low price compared with fluorous surfactants. The microemulsions can solubilize biomacromolecule lysozyme and methyl orange (MO), which have been demonstrated by UV/Vis spectra. SAXS technique was used to obtain the radii of Ls-54 based reverse micelles formed in SC CO_2. The results indicate that the radii of the reverse micelles is about 20.4–25.2 Å at different pressures and loading water (W_0), and the linear relation of $\ln I(q)$ versus q^2 curves in small angle region (0.022–0.040 $Å^{-1}$) is consistent with spherical micelles, which further prove the formation the Ls-54 surfactant based SC CO_2 microemulsions.



$C_{12}H_{25}{-}O{-}(CH_2{-}CH_2{-}O)_5{-}(\overset{\displaystyle CH_3}{\overset{|}{C}}H_2{-}CH_2{-}O)_4{-}H$

Ls-54

Results and Discussion

Solubility of Ls-54 surfactant in SC CO_2: The solubility of Ls-54 in SC CO_2 was studied at 308.15 and 318.15 K and at pressures up to 22.00 MPa. The results are shown in Figure 1. The results in the Figure indicate that the solubility of the surfactant in SC CO_2 can be as high as 0.05 M (about 4 wt.%) at easily accessible temperatures and pressures. The solubility increases with increasing pressure, and decreases with increasing temperature. The reason for the high solubility may be that the surfactant has four propylene oxide groups, which have been proved to be "CO_2-philic".[15] Moreover, it has low molecular weight.

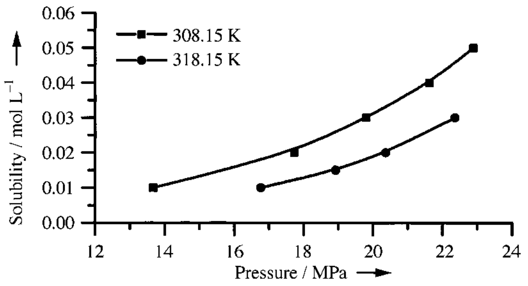


Figure 1. Solubility of Ls-54 surfactant in SC CO_2 at different conditions.

Loadings of water in CO_2/Ls-54 system: Usually, the molar ratio of water to surfactant (W_0) is used to characterize the content of loading water for water-in-CO_2 microemulsions. CO_2 itself has a noticeable affinity for water.[16] The corrected amount of water, W_0^{corr}, solubilized in the micelles can be obtained by subtracting the amount of water dissolved in the bulk CO_2 from the total amount of the loading water, W_0^{total}, and the amount of water in the bulk CO_2 can be considered as the same as that dissolved in pure CO_2 at the same temperature and pressure. Table 1 lists W_0^{total} and W_0^{corr} for the Ls-54 based SC CO_2 microemulsions at different pressures and temperatures. As expected, the W_0 increases with increasing dissolution pressure of the Ls-54/H_2O/CO_2 system, and the W_0 at the lower temperature is larger. The results of W_0^{corr} suggest that some type of aggregated water domains are present in reverse micelles, which has been further proved by the solubilization of MO and lysozyme and will be discussed in the following sections.

Table 1. Dissolution pressure for 0.02 M Ls-54 based water-in-CO_2 microemulsions with variety of loading water at 308.15 and 318.15 K.

[Ls-54] [M]	T [K]	P [MPa]	CO_2 density [g cm^{-3}]	W_0^{corr}	W_0^{total}
0.02	308.15	19.00	0.858	2.0	6.1
0.02	308.15	19.40	0.862	4.2	8.3
0.02	308.15	20.28	0.869	5.8	10.0
0.02	308.15	21.79	0.880	8.0	12.3
0.02	318.15	21.56	0.829	2.0	7.2

Solvatochromic probe studies: The shift in the absorption maximum of a solvatochromic probe is a sensitive measure of the local environment about the probe. For MO, the absorption maximum λ_{max} shifted to larger wavelengths (red shift) as the solvent polarity increases.[14] The absorption band of MO can not be observed for SC CO_2/MO, SC CO_2/MO/water and SC CO_2/MO/Ls-54 systems. It can be deduced that the solubility of MO in SC CO_2, SC CO_2/Ls-54, and SC CO_2/

Abstract in Chinese:

摘要：本文测定了表面活性剂 Ls-54 在超临界二氧化碳中的溶解度。结果表明，虽然它是不含氟、不含硅的表面活性剂，但在超临界二氧化碳中的溶解度很高，并且可以形成二氧化碳包水的微乳液。其主要可能是因为 Ls-54 含有四个亲二氧化碳基团（氧丙烯基团）和五个亲水基团（氧乙烯基团）并且具有相对低的分子量。本工作的结果为设计不含氟、不含硅、溶于二氧化碳的表面活性剂提供了重要的信息。CO_2/Ls-54/H_2O 体系的相态、溶剂化显色探针研究以及体系中溶菌酶的紫外光谱都证明了超临界二氧化碳微乳液中微水区域的存在。本文利用同步辐射小角 X 射线散射方法获得 Ls-54 形成的二氧化碳包水反相胶束的结构信息。利用 Guinier 近似方法计算了反相胶束的半径，在不同压力和水与表面活性剂的摩尔比（W_0）条件下，其值在 20.4～25.2Å 的范围内变化。

water mixtures is extremely low. However, the absorption band can be observed for SC CO_2/MO/Ls-54/water system as shown in Figure 2 and Table 2 and indicate that the existence of polar environment where MO can reside in. The results in Table 2 and Figure 2 show that λ_{max} increases with W_0^{corr}. The λ_{max} at $W_0 = 4.2$ and 8.0 are 423 and 438 nm, respectively, while the λ_{max} of MO in ordinary water is 464 nm. These results suggest that the polarity of the environment of the solubilized MO is lower than that of the bulk water, which was also discussed for other reverse micelles.[17] As expected, the polarity of the environment of the solubilized MO increases with W_0^{corr}. The Ls-54 has five hydrophilic ethylene oxide groups, which can form hydrogen bonds with water. So there was multiple hydrogen bonding sites on the chains of ethylene oxide. Thus, the water may act as a "glue" to bond the surfactant head groups together, which acts as driving force for the aggregation of the surfactants. Moreover, the CO_2-phobic effect may also be one main reason for aggregation of surfactants. As discussed above, the surfactant has four "CO_2-philic" propylene oxide groups, which is also a very beneficial factor for the formation of water-in-CO_2 microemulsions. As for the structure of the reverse micelles, the CO_2-philic groups (PO groups) should be on the outside of the micelles, and the CO_2-phobic groups (EO groups) on the inside of the micelles because of the hydrogen bonding force between water and EO groups.

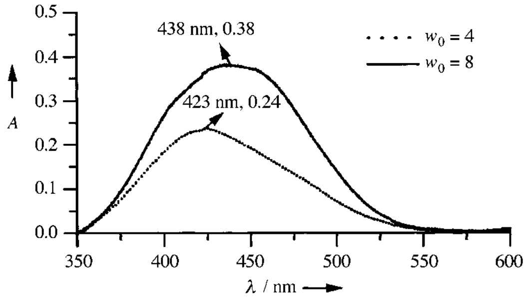


Figure 2. Absorption spectra of MO in 0.02 M Ls-54 based water-in-CO_2 microemulsions with different loading water at 22.00 MPa and 308.15 K.

Table 2. The maximum absorption wavelengths of MO (λ_{max}) in SC CO_2 at 308.15 K and 22.00 MPa and various compositions.

Number	[Ls-54] [M]	W_0^{corr}	MO [10^{-5} M]	λ_{max} [nm]	Absorbance
1	0	0	5.6	–	–
2	0	0	5.6	–	–
3	0.02	0	5.6	–	–
4	0.02	4.2	5.6	423	0.24
5	0.02	8.0	5.6	438	0.38

Solubilization of lysozyme in the microemulsions: Lysozyme has an absorption at about 275 nm.[18] Similarly, experiments showed that SC CO_2, SC CO_2/water, and SC CO_2/Ls-54 mixtures can not dissolve the biomacromolecule lysozyme. Figure 3 shows the absorption spectrum of lysozyme in 0.02 M Ls-54 based water-in-CO_2 microemulsions with $W_0^{corr} = 8.0$ at 308.15 K and 22.00 MPa, which was obtained by subtracting SC CO_2/Ls-54/water spectrum from that of SC CO_2/Ls-54/water/lysozyme. Obviously, an absorption peak of lysozyme is present at 276 nm with absorption value of 0.41, which indicates the Ls-54 based SC CO_2 microemulsions can solubilize lysozyme in the polar micro-aqueous domains. Thus, the water-in-CO_2 microemulsions have potential importance for separation and extraction of biomacromolecules.

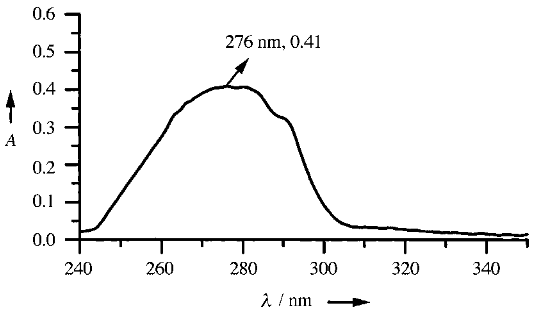


Figure 3. Absorption spectrum of lysozyme solubilized in 0.02 M Ls-54 based water-in-CO_2 microemulsions with $W_0 = 8.0$ at 308.15 K and 22.00 MPa.

Effect of pressure on Rg and *r* of the reverse micelles: In the lower q region, contributions to the total excess X-ray scattering, $I(q)$, due to microemulsions can rise from two sources: the droplet contribution, which solely depends upon the radius of the droplet, and an appropriate structure factor, which accounts for attractive or repulsive interactions between the droplets. When the system is sufficiently dilute, inter-droplet interactions are negligible. The magnitude of the scattering vector, q, is given in terms of the scattering angle θ by $q = (4\pi/\lambda)\sin\theta$. For dilute aggregated systems the micelle radii r can be obtained by using the Guinier approximation law, which is valid at low q region ($rq < 1$)[7b, 19] and can be expressed by Equations (1) and (2).

$$\ln I(q) = \ln I(0) - \frac{(qR_g)^2}{3} \tag{1}$$

$$r = (5/3)^{1/2} R_g \tag{2}$$

where $I(0)$ denotes the scattering intensity extrapolated to zero angle, and R_g the radius of gyration. The Guinier approximation is derived from the assumption that the system can be characterized as a monodispersed system of spheres. The Guinier plots give a precise value of the gyration radius only if the representation is linear at small values of q where rq is less than 1. In this work, by using Guinier plot ($\ln I(q)$ versus q^2) on the data sets in a defined small q range (0.022 – 0.040 Å^{-1}),[20] linear regression analyses of the data in this small angle region of the intensity curves were used to obtain R_g values.

Figures 4 and 5 show the SAXS curves of 0.02 M Ls-54 based water-in-CO_2 microemulsions with $W_0 = 4$ at 20.00 and 22.00 MPa and corresponding Guinier plots, respectively. As shown in Figure 5, the size of the reverse micelle increases as the pressure is reduced. For the Ls-54 based reverse micelles of $W_0 = 4$ at 20.00 and 22.00 MPa, the gyration radii (R_g) of the reverse micelles are 18.9 and 15.8 Å, respectively, and the micelle radii (r) are 24.4 and 20.4 Å, respectively. These are

0947-6539/02/0806-1358 $ 17.50+.50/0

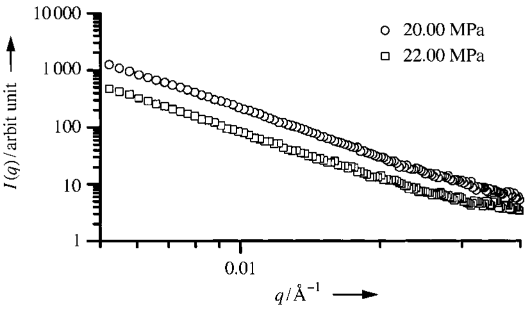


Figure 4. SAXS plots of the 0.02 M Ls-54 based water-in-CO$_2$ microemulsions with $W_0 = 4$ at 308.15 K and different pressures.

comparable to the size of reverse micelles determined by small angle neutron scattering (SANS) in the D$_2$O/CO$_2$/PFPE[21] and D$_2$O/CO$_2$/H-F[22] systems, which is known as a typical reverse micellar system in SC CO$_2$. In the small angle region the scattering intensity increases with the decrease of pressure, as can be seen from Figure 4. These results from decrease in the density of the SC CO$_2$ solvent and increase in the micelle radii as pressure is reduced, which leads to the increase of overall scattering intensity of the micelles. On the data sets, the defined small q range is 0.022–0.040 Å^{-1}, where the rq is less than 1, which in turn proves the validity of using Guinier approximation law at this small angle region. And the linear relation at the small angle region is consistent with the sphere shape of the reverse micelles.

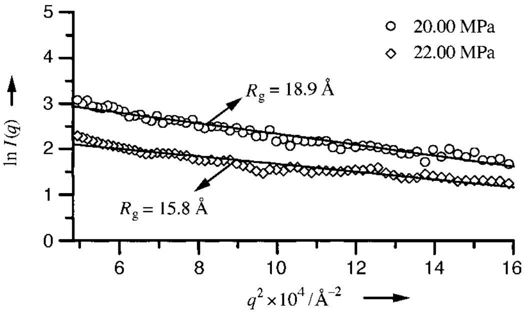


Figure 5. Guinier plots for the 0.02 M Ls-54 based water-in-CO$_2$ microemulsions with $W_0 = 4$ at 308.15 K and different pressures.

Effect of W_0 on the scattering intensity and Rg: The SAXS plots of 0.02 M Ls-54 based water-in-CO$_2$ microemulsions for $W_0 = 4$ and $W_0 = 8$ at 22.00 MPa and corresponding Guinier plots were shown in Figures 6 and 7, respectively. The size of the reverse micelles is increased as W_0 becomes larger, as can be known from Figure 7. It is estimated from Figure 7 and Equations (1) and (2) that the values of R_g of the reverse micelles for $W_0 = 8$ and $W_0 = 4$ are 19.5 and 15.8 Å, respectively, and the micelle radii (r) are 25.2 and 20.4 Å, respectively. The use of Guinier approximation law in the small angle region (0.022–0.040 Å^{-1}) is also valid because rq is less than 1. Figure 6 indicates that the scattering intensity for the system at $W_0 = 8$ is higher than that at $W_0 = 4$. This indicates that the size of reverse micelles increases with the increasing of loading water. Moreover, linear relation in small angle region was also consistent with the spherical shape of the reverse micelles.

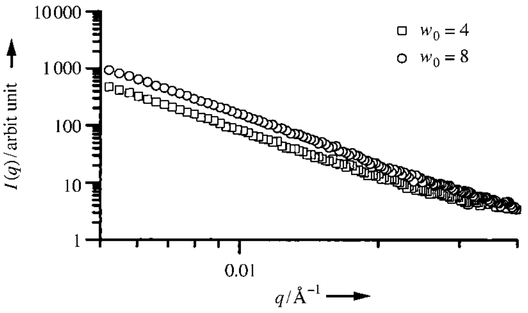


Figure 6. SAXS plots of the 0.02M Ls-54 based water-in-CO$_2$ microemulsions with $W_0 = 4$ and $W_0 = 8$ at 308.15 K and 22.00 MPa.

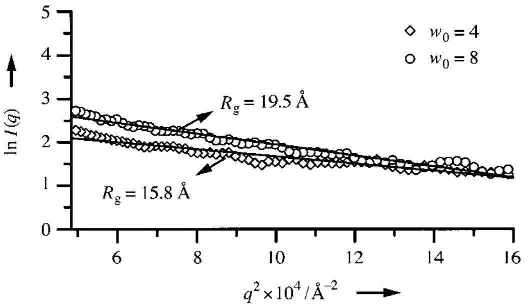


Figure 7. Guinier plots for the 0.02 M Ls-54 based water-in-CO$_2$ microemulsions with $W_0 = 4$ and $W_0 = 8$ at 308.15 K and 22.00 MPa.

Conclusion

Recently, water-in-CO$_2$ microemulsions have received much attention because they offer new opportunities for clean industrial processes. Exploration of the surfactants is a key for these processes. Unfortunately, the solubility of most commercially available surfactants in CO$_2$ is very low, and most researchers used expensive and toxic fluorous surfactant in their study. So far, the formation of water-in-CO$_2$ microemulsions by non-fluorous and non-siloxane non-ionic surfactants has been seldom reported in the literature. In this work, we determined the solubility of some surfactants in SC CO$_2$ and found that the Ls-54 surfactant was soluble in SC CO$_2$ and the water-in-CO$_2$ microemulsions could be formed, although it is a non-fluorous and non-siloxane, non-ionic surfactant. The reasons may be that the surfactant has four CO$_2$-philic groups (propylene oxide) and five hydrophilic groups (ethylene oxide) and its molecular weight is relatively low. The results of this work are useful for designing CO$_2$-soluble non-fluorous and non-siloxane surfactants. The Ls-54 based water-in-CO$_2$ microemulsions can solubilize biomacromolecule lysozyme and methyl orange, and it also has advantages of low toxicity and low price compared with fluorous surfactants. The direct structural evidence from small-angle X-ray scattering indicates that the radii of the reverse micelles is in the range of 20.4–25.2 Å at different pressures and W_0, which further proved the formation of Ls-54 based water-in-CO$_2$ microemulsions. The Ls-54 based water-in-CO$_2$ microemulsions have potential applications in some industrial processes, such as separation and extraction of biomacromolecules and metal ions, thus providing nanoreactors for chemical reactions, and dry-cleaning technology by using SC CO$_2$.

Experimental Section

Materials: Ls-54 surfactant was obtained from Henkel (Germany). CO_2 (99.995% purity) was supplied by the Beijing Analytical Instrument factory. Methyl orange (MO) and methanol were obtained from Beijing Chemical Agent Factory (A. R. Grade). Double distilled water was used throughout the experiments. The lysozyme ($M_W = 14300$) was supplied by Sino-American Biological Chemical Corporation with a purity of $>98\%$.

Solubility and phase behavior: To determine the solubility of the surfactant in SC CO_2 and the phase behavior of the SC CO_2/Ls-54/water mixture, a high-pressure stainless steel view cell of 40 cm^3 volume was used. The view cell was immersed in a water bath, which was controlled by a Haake-D8 controller, and the temperature was measured by accurate mercury thermometers with an accuracy of better than ± 0.05 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, Model 93) and an indicator, which was accurate to ± 0.04 MPa in the pressure range of 0–34 MPa. The chemicals in the cell were stirred by a magnetic stirrer. The procedures for studying phase behavior of the SC CO_2/Ls-54/H_2O ternary system is given because that for CO_2/Ls-54 is simpler. In a typical experiment, a suitable amount of the Ls-54 was charged into the high-pressure view cell, and the air in the cell was replaced by CO_2. The desired amount of double distilled water was then injected into the cell by a syringe. The cell was then placed into the constant temperature water bath. CO_2 was compressed into the cell slowly by the pump after thermal equilibrium had been reached. The fluid was stirred at fixed pressure, and stirring was stopped when observing the phase behavior. The pressure was increased gradually until the Ls-54 rich phase disappeared completely and the system became homogeneous transparent single phase. This pressure is defined as dissolution pressure. This procedure was repeated three times at each condition and the uncertainty for the dissolution pressure was ± 0.05 MPa. To determine the density of the mixed fluid, a stainless steel sample cell with 40 cm^3 volume without windows was used to replace the view cell. The density of the fluid can be easily obtained from the mass of the fluid and the volume of the sample cell.

UV/Vis experiments: The solubilization of MO and lysozyme in the water-in-CO_2 microemulsions was studied by UV method, which was similar to that reported previously.[23] The apparatus consisted mainly of a gas cylinder, a high pressure pump, a pressure gauge, a temperature controller, a high pressure UV cell, valves and fittings. The UV/Vis spectrometer was produced by Beijing Instrument Company (TU-1201). The high-pressure UV cell with two quartz windows has the internal volume and the path length of 1.5 cm^3 and 1.2 cm, respectively. The procedure for studying the solubilization of MO is described because that for lysozyme is similar. The desired amount of solution of MO in methanol was injected into the sample cell using a 0.1 mL syringe. Gaseous CO_2 was then flushed slowly through the UV cell to remove the methanol and the air. A suitable amount of Ls-54 was added into the UV cell. The desired amount of double distilled water was then injected into the sample cell with a 0.01 mL syringe. After thermal equilibrium had been reached, CO_2 was compressed into the sample cell slowly by a syringe pump until the desired pressure was reached. The solution was stirred for at least 30 minutes. Experiments showed that about 20 minutes were required for reaching equilibrium. However, the spectrum was recorded after an equilibration time of one hour. All the measurements were carried out at 308.15 K.

SAXS experiment: The set-up for the SAXS study was similar to that described previously.[24] Briefly, the apparatus consisted mainly of a gas cylinder, a high-pressure pump, a digital pressure gauge, a high-pressure SAXS cell, a thermometer and temperature controller, and valves and fittings of different kinds. The pressure gauge consisted of a transducer and an indicator as described above. The temperature-controlled SAXS cell was made of stainless steel body with two diamond windows of 8 mm in diameter and 0.4 mm in thickness. The cell body was wrapped in an electric heater and heat insulating tape outside. The X-ray path length of the cell was 1.5 mm and the internal volume of the cell was 2.7 cm^3. There was a small magnetic stirrer in the cell to stir the fluids before the SAXS measurements. The insulated cell was electrically heated to ± 0.1 K of the desired temperature using a temperature controller with a platinum resistance temperature probe (Model XMT, produced by Beijing Chaoyang Automatic Instrument Factory). SAXS experiments were carried out at Beamline 4B9A at the Beijing Synchrotron Radiation Facility, using a SAXS apparatus constructed at the station. The data accumulation time was 3 min. The angular range was chosen to provide data from $q = 0.005$ Å^{-1} to $q = 0.15$ Å^{-1}, where the magnitude of scattering vector $q = 4\pi \sin\theta/\lambda$, and θ and λ being the scattering angle and incident X-ray wavelength of 1.54 Å. The distance between the sample chamber and the detector was 1.485 m. The SAXS experimental procedure was similar to that for UV/Vis measurement described above. The SAXS cell was flushed with CO_2 and then a suitable amount of Ls-54 and double distilled water were added to the cell. CO_2 was charged into the cell with stirring after thermal equilibrium had been reached. The cell was connected to the apparatus after 20 minutes of equilibration time, and the X-ray scattering was recorded.

Acknowledgement

The authors are grateful to the National Natural Science Foundation of China (20133030), Ministry of Science and Technology of China (G20000781), UK-China R&D Project, Chinese Academy of Sciences for the financial support.

---

[1] K. A. Consani, R. D. Smith, *J. Supercrit. Fluids* **1990**, *3*, 51.

[2] T. A. Hoefling, R. M. Enick, E. J. Beckman, *J. Phys. Chem.* **1991**, *95*, 7127.

[3] K. Harrison, J. Goveas, K. P. Johnston, *Langmuir* **1994**, *10*, 3536.

[4] K. P. Johnston, K. L. Harrison, M. J. Clarke, S. M. Howdle, M. P. Heitz, F. V. Bright, C. Carlier, T. W. Randolph, *Science* **1996**, *271*, 624.

[5] a) M. J. Clarke, K. L. Harrison, K. P. Johnston, S. M. Howdle, *J. Am. Chem. Soc.* **1997**, *119*, 6399; b) M. P. Heitz, C. Carlier, J. deGrazia, K. L. Harrison, K. P. Johnston, T. W. Randolph, F. V. Bright, *J. Phys. Chem. B* **1997**, *101*, 6707; c) D. E. Fremgen, E. S. Smotkin, R. E. Gerald, R. J. Klingler, J. W. Rathke, *J. Supercrit. Fluids* **2001**, *19*, 287.

[6] K. P. Johnston, T. W. Randolph, F. V. Bright, S. M. Howdle, *Science* **1996**, *272*, 1726.

[7] a) Z. T. Liu, C. Erkey, *Langmuir* **2001**, *17*, 274; b) J. Eastoe, A. Paul, S. Nave, D. C. Steytler, B. H. Robinson, E. Rumsey, M. Thorpe, R. K. Heenan, *J. Am. Chem. Soc.* **2001**, *123*, 988.

[8] a) M. Ji, X. Y. Chen, C. M. Wai, J. L. Fulton, *J. Am. Chem. Soc.* **1999**, *121*, 2631; b) J. D. Holmes, P. A. Bhargava, B. A. Korgel, K. P. Johnston, *Langmuir* **1999**, *15*, 6613; c) H. Ohde, J. M. Rodriguez, X. R. Ye, C. M. Wai, *Chem. Commun.* **2000**, 2353.

[9] M. Z. Yates, D. L. Apodaca, M. L. Campbell, E. R. Birnbaum, T. M. McCleskey, *Chem. Commun.* **2001**, 25.

[10] a) E. J. Beckman, *Science* **1996**, *271*, 613; b) A. I. Cooper, J. D. Londono, G. Wignall, J. B. McClain, E. T. Samulski, J. S. Lin, A. Dobrynin, M. Rubinstein, A. L. C. Burke, J. M. J. Frechet, J. M. Desimone, *Nature* **1997**, *389*, 368.

[11] a) G. B. Jacobson, C. T. Lee, K. P. Johnston, *J. Org. Chem.* **1999**, *64*, 1201; b) M. A. Kane, G. A. Baker, S. Pandey, F. V. Bright, *Langmuir* **2000**, *16*, 4901.

[12] H. Ohde, F. Hunt, S. Kihara, C. M. Wai, *Anal. Chem.* **2000**, *72*, 4738.

[13] G. G. Yee, J. L. Fulton, R. D. Smith, *Langmuir* **1992**, *8*, 377.

[14] G. J. McFann, K. P. Johnston, S. M. Howdle, *AIChE Journal* **1994**, *40*, 543.

[15] S. Mawson, R. H. Bott, K. P. Jonhston, M. L. O'Neill, L. M. Robeson, R. D. Smith, S. P. Wilkinson, **1997**, *Eur. Patent Appl.* EP 0814112 A3.

[16] R. Wiebe, *Chem. Rev.* **1941**, *29*, 475.

[17] a) B. H. Hutton, J. M. Perera, F. Grieser, G. W. Stevens, *Colloids Surf. A* **1999**, *146*, 227; b) M. B. Lay, C. J. Drummond, F. Grieser, *J. Colloid Interface Sci.* **1989**, *128*, 602.

[18] H. F. Zhang, J. Lu, B. X. Han, *J. Supercrit. Fluids* **2001**, *20*, 65.

[19] J. L. Fulton, D. M. Pfund, J. M. Desimone, M. Capel, *Langmuir* **1995**, *11*, 4241.

[20] a) M. Hirai, R. Kawai-Hirai, S. Yabuki, T. Takizawa, T. Hirai, K. Kobayashi, Y. Amemiya, M. Oya, *J. Phys. Chem.* **1995**, *99*, 6652; b) M. Hirai, R. Kawai-Hirai, M. Sanada, H. Iwase, S. Mitsuya, *J. Phys. Chem. B* **1999**, *103*, 9658.

[21] R. G. Zielinski, S. R. Kline, E. W. Kaler, N. Rosov, *Langmuir* **1997**, *13*, 3934.

[22] J. Eastoe, Z. Bayazit, S. Martel, D. C. Steytler, R. K. Heenan, *Langmuir* **1996**, *12*, 1423.

[23] J. Lu, B. X. Han, H. K. Yan, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3269.

[24] D. Li, B. X. Han, Z. M. Liu, J. Liu, X. G. Zhang, S. G. Wang, X. F. Zhang, J. Wang, B. Z. Dong, *Macromolecules* **2001**, *34*, 2195.

Received: September 11, 2001 [F3547]