Recovery of Silver Nanoparticles Synthesized in AOT/$C_{12}E_4$ Mixed Reverse Micelles by Antisolvent CO_2[**]

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Abstract: Silver nanoparticles were synthesized in sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) reverse micelles in isooctane with tetraethylene glycol dodecyl ether ($C_{12}E_4$) as a cosurfactant. Recovery of the Ag particles from the reverse micelles by dissolving antisolvent CO_2 in the micellar solution was investigated. All the Ag particles in the reverse micelles could be precipitated by compressed CO_2 at suitable pressures, while the surfactants remained in the isooctane continuous phase, and well-dispersed Ag nanoparticles were obtained. The effects of operating conditions on the size and size distribution of the Ag particles were investigated. The particle size decreased with decreasing molar ratio (w) of water to surfactant. A higher CO_2 pressure in the recovery process favored production of smaller particles. A decrease in the molar ratio of reductant KBH_4 to $AgNO_3$ resulted in larger Ag particles with higher polydispersity.

Keywords: carbon dioxide · micelles · nanostructures · silver · surfactants

Introduction

Many efforts have been devoted to the preparation of nanoparticles, a newly emerging field in solid-state chemistry, and to studying their properties.[1] Such crystallites exhibit many novel properties that differ from the bulk properties, because of their small size. Their surface-enhanced Raman spectroscopy and their application in the photographic process have been studied widely.[2]

Reverse micelles are thermodynamically stable aggregates of amphiphilic surfactants, resulting in a hydrophilic head group region surrounding a nanometer-sized water core with hydrophobic tails extending into an apolar continuous phase.[3] Addition of a cosurfactant can be used to further stabilize, modify, and control the reverse micellar structure.[4] The capacity of the micelle cores to host a variety of polar and ionic species in the continuous phase has attracted considerable attention. Extensive basic and applied research has been conducted into reverse micelles in organic solvents because of their inherently interesting chemistry as well as their diverse applications, for example, in chemical engineering,[5] micellar catalysis,[6] and biotechnology.[7] In particular, the use of micellar water droplets as a novel environment for nanoparticle synthesis has potential advantages over the traditional nanoparticle synthesis method.[8] Recently, elegant studies have shown that some of the surfactants can also form reverse micelles in supercritical (SC) CO_2, ethane, and propane,[9] and cosurfactants such as *n*-pentanol have been used to stabilize the reverse micelles.[10] Reverse micelles in supercritical fluids (SCFs) have also been used advantageously as nanometer-sized reactors to prepare nanoparticles because the properties of SCFs such as density, solvency, diffusivity, and viscosity can be manipulated by small variations in pressure and temperature.[11]

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is a popular surfactant in reverse micelle applications because of its ability to solubilize relatively large amounts of water in a variety of hydrophobic organic solvents and to form thermodynamically stable reverse micelles and microemulsions.[12] The size of the micelle cores is characterized by the molar ratio w of water to surfactant ($[H_2O]/[AOT]$). Some alcohols of appropriate chain length can serve as stabilizers to increase the uptake of water and solutes in the microemulsions.[13] The synthesis of organic and inorganic nanoparticles within the water cores of AOT reverse micelles in liquid organic solvents has been investigated.[14] As the reaction is confined to the water cores, the diameter of the particles produced can be controlled by the size of these cores. The mode of recovery of the product nanoparticles from the reverse micelles has a key effect on the particle size and dispersion. The traditional recovery method

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[**] AOT = sodium bis(2-ethylhexyl)sulfosuccinate; $C_{12}E_4$ = tetraethylene glycol dodecyl ether

0947-6539/02/0817-3879 $ 17.50+.50/0

is by flocculation,[15] evaporation to dryness,[16] or addition of certain chemical reagents[17] which cause phase separation and simultaneous precipitation of the surfactant. The subsequent processing is troublesome because the products contain a large amount of surfactant.

Compressed CO_2 is quite soluble in various organic solvents and causes them to expand greatly. Many solutes are soluble in organic solvents but not in CO_2. Thus the CO_2 in organic solvents can act as a gas antisolvent (GAS). Many GAS processes, such as extraction and fractionation,[18] recrystallization of chemicals,[19] and micronization,[20] have been explored. We recently used compressed CO_2 to recover ZnS nanoparticles synthesized in AOT reverse micelles in isooctane.[21] In a GAS process the liquid solvent properties can be tuned by pressure adjustment, because the solubility of the gas in the solvent is a function of pressure, and the separation of GAS and liquid solvent can be achieved easily by depressurization.

In the present work, we explored the recovery of Ag nanoparticles synthesized in AOT/$C_{12}E_4$ mixed reverse micelles using CO_2 as antisolvent. By control of the pressure, the Ag particles in the reverse micelles could be precipitated and recovered, while the surfactants remained in the solvent continuous phase. The effects of the operating conditions on the nanoparticles obtained by this method were also investigated.

Experimental Section

Materials: CO_2 (>99.995% purity) was provided by Beijing Analysis Instrument Factory. The surfactants AOT and $C_{12}E_4$ were purchased from Sigma (purity 99%). The isooctane, KBH_4, $AgNO_3$, and ethanol supplied by Beijing Chemical Plant were all A.R. grade. Double-distilled water was used.

Phase behavior of reverse micellar solution: The apparatus for determining the expansion curves and the phase behavior of the reverse micellar solutions was the same as that used previously to study polymer solutions.[22] It consisted mainly of a viewing cell (34.0 mL), a high-pressure pump, a constant-temperature water bath, and a pressure gauge. The high-pressure pump (Model DB-80) was used to charge the system with CO_2. The accuracy of the pressure gauge, which comprised a transducer (Foxboro/ICT) and an indicator, was ±0.025 MPa in the pressure range 0–20 MPa. The temperature of the water bath was controlled by a Haake D8 digital controller; the accuracy of the temperature measurement was ±0.1 °C.

The reverse micellar solutions were prepared by dissolving the desired amounts of AOT, $C_{12}E_4$, and water in isooctane. In a typical experiment, the viewing cell was charged with a suitable amount of reverse micellar solution, then with CO_2 to a suitable pressure after the thermal equilibrium had been reached. A magnetic stirrer was used to enhance the mixing of CO_2 and the reverse micellar solution. The volume of the liquid phase did not change with time after equilibrium was reached. The pressure and volume at equilibrium were recorded. More CO_2 was added and the volume of the liquid phase was determined at this higher pressure. The volume expansion coefficients were calculated on the basis of the liquid volumes before and after dissolution of CO_2. Some surfactant could be precipitated when the pressure of CO_2 equaled or exceeded the cloud point pressure, which was determined also.

Abstract in Chinese:

摘要：利用 $C_{12}E_4$ 作为助表面活性剂，首先在 AOT/$C_{12}E_4$ 反向胶束中制备了银纳米粒子，然后用 CO_2 抗溶剂法进行了回收。实验结果表明，在适当压力下，反向胶束中的银纳米粒子全部发生沉降，而表面活性剂稳定地存在于液相中。由该方法得到了粒度小，分散性好的纳米银粒子。我们还研究了实验条件对产物粒子大小和分布的影响。结果表明，随 CO_2 压力的升高，W 值的减小，以及还原剂 KBH_4 和 $AgNO_3$ 的浓度比的增大，银纳米粒子的尺寸减小。

Synthesis of Ag nanoparticles in the reverse micelles: The procedures were similar to those reported by other authors.[23] The solution of AOT in isooctane was prepared, and an appropriate amount of cosurfactant $C_{12}E_4$ was added to the solution ($[AOT]:[C_{12}E_4] = 1$). Reverse micellar solutions were prepared by adding an aqueous solution of either $AgNO_3$ or KBH_4 to the surfactant solution. Then the two micellar solutions, containing respectively $AgNO_3$ and KBH_4, were mixed, Ag nanoparticles were formed in the reverse micelles, as the water pools could then exchange their contents by a collision process.[24] The reduction of Ag^+ by BH_4^- in reverse micelles has been described in detail.[23]

UV spectral study of the precipitation of Ag: The precipitation of Ag particles from the reverse micelles at different CO_2 pressures was monitored with a Model TU-1201 spectrophotometer. The temperature-controlled high-pressure sample cell and experimental procedures were the same as those used to study the UV spectra of protein in AOT reverse micelles.[25] The cell, consisting mainly of a stainless steel body and two quartz windows, was thermostated to within ±0.1 °C of the desired temperature by an electric heater and temperature controlling system. The sample cell had an optical path length of 1.32 cm and a volume of 1.74 cm^3. A magnetic stirrer in the sample cell provided rapid mixing of the CO_2 and reverse micellar solutions. In the experiment, the appropriate amount of micellar solution with synthesized Ag particles was loaded into the sample cell by syringe. The temperature was controlled at 295.2 K. The sample cell was then charged with CO_2 by high-pressure pump until it was full. The UV spectrum of the solution was recorded every 10 min until it no longer changed, which was an indication that equilibrium had been reached. The spectra at equilibrium were used to calculate the percentage of Ag particles precipitated under the different conditions. In each experiment, the loaded solution contained AOT (0.0193 g) and $C_{12}E_4$ (0.0157 g).

Recovery of nanoparticles from reverse micelles: The known amounts of micellar solution with the synthesized Ag nanoparticles were loaded into the cylinder-shaped autoclave (32.60 mL), which was charged with CO_2 by high-pressure pump to the desired pressure. The solution was stirred (120 r.p.m.) for 0.5 h. When the stirring was stopped the precipitated Ag particles were deposited at the bottom of the autoclave. The solution and CO_2 were released slowly. Under these experimental conditions most of the surfactants remained in the removed solution; they were not precipitated because the pressure was below the cloud point pressure. The precipitated Ag particles were collected and washed with water to remove the by-products and the small amount of surfactants left in the solution absorbed on the product. The products were dried under vacuum at 303.2 K for 4 h.

Characterization of particles: The size and shape of the Ag particles obtained were determined by transmission electron microscopy (TEM) with a Hitachi H-600A electron microscope. The maximum resolution of the microscope was 0.5 nm. Particles were sonicated for 5 min in ethanol and then deposited directly on the copper grid.

Results and Discussion

Ag nanoparticles can be synthesized by reduction of Ag^+ and BH_4^- in reverse micelles.[23] However, the usual reactants such as $AgNO_3$ are poorly solubilized in the AOT reverse micelles.[26] Our experiments also showed that reverse micelles of AOT in isooctane could not solubilize the desired amounts of reactants for Ag particle synthesis. One way to solve this problem is to use functionalized surfactant Ag(AOT),[26, 27] and another is to add a suitable cosurfactant to the micellar solution.[28] Our experiments indicated that tetraethylene glycol dodecyl ether ($C_{12}E_4$) is a very effective cosurfactant to enhance the solubilization of the reactants ($AgNO_3$ and KBH_4) in AOT reverse micelles. We have therefore used AOT/$C_{12}E_4$ mixed reverse micelles in isooctane to synthesize Ag nanoparticles.

Volume expansion and cloud point pressure of the solution: The solution expands after dissolution of CO_2 in it. We determined the volume expansion coefficient ΔV [%], defined in Equation (1) where V is the volume of the solution

$$\Delta V = 100\left(\frac{V - V_0}{V_0}\right) \qquad (1)$$

saturated with CO_2 and V_0 the volume of the CO_2-free solution, of the reverse micellar solutions at 295.2 K at different pressures for $5 \leq w \leq 15$, $[AOT] = 25\,mmol\,L^{-1}$, $[AOT]/[C_{12}E_4] = 1$. ΔV is a very important parameter for the UV experiments and the Ag particle recovery process.

The effect of w on ΔV was negligible. For example, Figure 1 shows the ΔV of the solution with $w = 10$ at 295.2 K and different pressures. The solution became cloudy at the cloud point pressure, when the surfactant began to precipitate. The cloud point pressure of the AOT/$C_{12}E_4$/water/isooctane micellar solutions was determined (4.80 ± 0.03 MPa). All the experiments were conducted below the cloud point pressure for the Ag nanoparticle recovery, so precipitation of the surfactant did not occur.

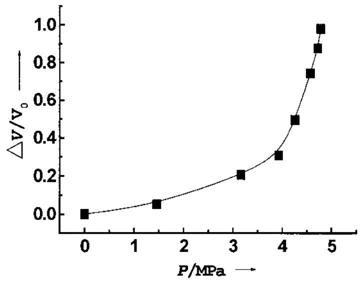

Figure 1. Dependence of volume expansion coefficient of the reverse micellar solution ($w = 10$) on CO_2 pressure at 295.2 K.

UV study of precipitation of Ag nanoparticles from the reverse micelles by CO_2: Colloidal dispersions of Ag exhibit absorption bands in the UV/Vis range due to the resonant excitation of surface plasmons. Thereby Ag nanoparticles stabilized in the reverse micelles can be analyzed in situ by their UV/Vis spectra.[11a, 11b, 26, 29] The characteristic absorption spectrum for Ag nanoparticles has a peak at about 400 nm. The nanoparticles formed in the reverse micelles are not precipitated in the absence of CO_2. However, our UV study has shown that the Ag particles can be precipitated by dissolution of antisolvent CO_2 in the micellar solution. Figure 2 illustrates the UV spectra of the reverse micellar solution ($w = 15$) containing synthesized Ag particles at some typical pressures. For all the experiments, the concentration of Ag synthesized in the reverse micellar solutions after expansion should be $0.022\,mg\,mL^{-1}$ if the Ag is not precipitated. The absorption band at about 407 nm in Figure 2 is attributed to the absorption of Ag in the reverse micelles, and that at 225 nm is assigned to the surfactant AOT.[25] The intensity of the absorption at 407 nm decreases with increased pressure, while that for AOT remains unchanged over a certain pressure range. This indicates that the Ag particles can be precipitated from the reverse micelles, and the surfactant remains in the organic continuous phase. Some AOT is precipitated when the pressure exceeds the cloud point pressure (4.80 MPa), since AOT precipitation begins at cloud point pressure.

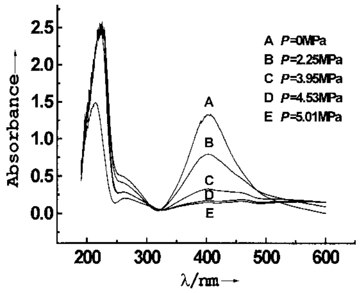

Figure 2. UV spectra of Ag in the reverse micelles ($w = 15$) at 295.2 K and various pressures.

The position and the number of peaks in the absorption spectra also indicate the shape of the particles. For spherical Ag particles there is only one band, centered at about 400 nm, and there are two peaks for ellipsoidal particles.[29] UV spectra suggest that there are only spherical Ag particles in the reverse micelles.

Our experiments showed that at a fixed w the absorbance of Ag nanoparticles is a linear function of the Ag concentration when $[Ag] < 0.030\,mg\,mL^{-1}$. Thus the percentage precipitation of Ag ($P_{Ag}\% = 100 \times$ mass of the precipitated Ag/total mass of Ag) can be calculated from the absorbance and the working curve. Figure 3 shows the dependence of $P_{Ag}\%$ on CO_2 pressure at $w = 5$, 10 and 15; more Ag particles are precipitated at the higher pressures, and it is more difficult to precipitate the Ag particles at the lower w values. This can be explained by the stronger interaction of particles with the matrices at lower w values (smaller micellar core radii). At 4.53 MPa, which is still below the cloud point pressure of the micellar solution(4.80 MPa, determined as discussed above), $P_{Ag}\%$ can reach 100 %, while the absorbance of AOT remains unchanged. Thus at suitable pressures, Ag particles in the reverse micelles can be precipitated completely, leaving the

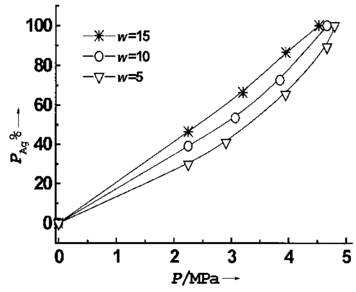

Figure 3. Percentage precipitation of Ag (P_{Ag}%; average values) from reverse micelles at 295.2 K and various pressures. For each case, the experiment was repeated three times and the reproducibility was better than ±4%.

surfactants in organic continuous phase. At 5.01 MPa (which is above the cloud point pressure) the absorption band of AOT is much smaller because some of the surfactant has been precipitated above the cloud point pressure, in agreement with the phase behavior study.

Effects of operating conditions on the particle size: To study the effects of operating conditions on the particle size and size distribution by this method, we changed the following experimental conditions for the synthesis and recovery of Ag particles: *w* of the reverse micelles; molar ratio $[KBH_4]/[AgNO_3]$; and CO_2 pressure in the antisolvent process.

The particle size and distribution data were obtained by measuring the diameter of the particles in the TEM images of Ag recovered from the reverse micelles under the different conditions (Figure 4).

From the TEM images the estimated particle size was in the range 2–5 nm at $w = 5$ (Figure 4a), and 3–8 nm at $w = 15$ (Figure 4b), so the particles are larger at the greater *w*. The main reason is that the water cores in the reverse micelles are smaller at lower *w* values, which restricts the particle growth in the reverse micelles.

The effect on the particle size of the molar ratio $[KBH_4]/[AgNO_3]$ in the reverse micelles was studied by controlling the concentrations of $AgNO_3$ and KBH_4 in the reverse micellar solutions at $w = 15$. The particle size increased with decreasing $[KBH_4]/[AgNO_3]$ (Figures 4b–4d). The particle size increased from 3–8 nm to 6–20 nm upon decreasing $[KBH_4]/[AgNO_3]$ from 1 to 0.2, and the degree of polydispersity increased with the decrease in $[KBH_4]/[AgNO_3]$. This is attributed to the acceleration of the nucleation rate that occurs when the amount of reducing agent per droplet increases,[28] so that smaller particles are formed in the reverse micelles at higher $[KBH_4]/[AgNO_3]$ values.

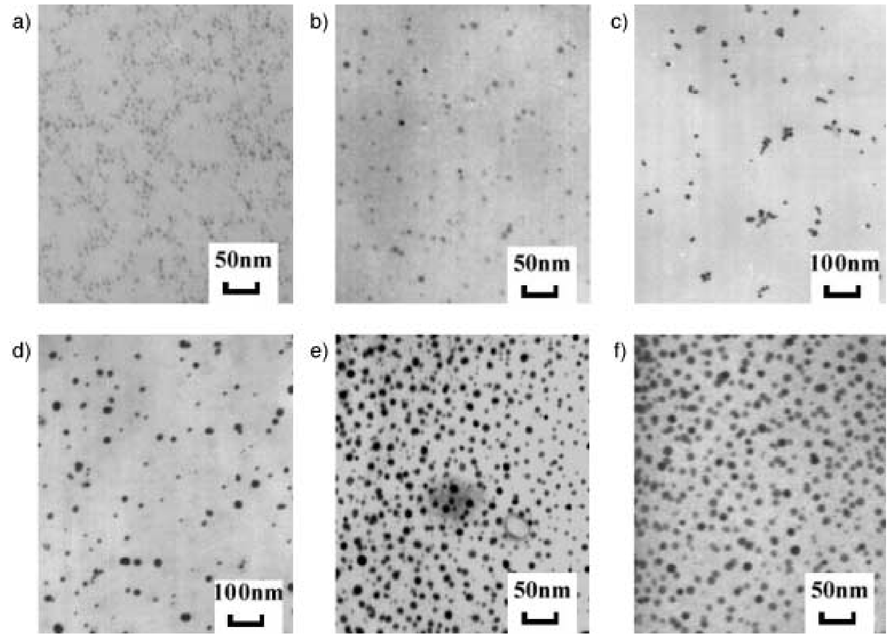

Figure 4. TEM images of Ag particles recovered from the reverse micelles: a) 4.50 MPa, $w = 5$, $[KBH_4]/[AgNO_3] = 1$; b) 4.50 MPa, $w = 15$, $[KBH_4]/[AgNO_3] = 1$; c) 4.50 MPa, $w = 15$, $[KBH_4]/[AgNO_3] = 0.5$; d) 4.50 MPa, $w = 15$, $[KBH_4]/[AgNO_3] = 0.2$; e) 3.81 MPa, $w = 15$, $[KBH_4]/[AgNO_3] = 1$; f) 2.57 MPa, $w = 15$, $[KBH_4]/[AgNO_3] = 1$.

As the CO_2 pressure in the recovery process increases from 2.57 to 4.50 MPa, Ag particles decrease in size from 6–12 to 3–8 nm (Figures 4f, 4e, 4b). The effect of pressure on the particle size is very complicated. For example, the dissolved CO_2 influences the diffusivity and the viscosity of the solution. Some of the CO_2 may dissolve in the water cores of the reverse micelles and change their pH, which affects the interaction between the Ag particles and the other components. All of these effects may influence the particle size and the size distribution. It is very difficult to give a more detailed explanation.

Conclusion

The Ag nanoparticles synthesized in the mixed reverse micelles of $AOT/C_{12}E_4$ in isooctane can be recovered by using compressed CO_2, and well-dispersed Ag nanoparticles can be obtained. In this method, the Ag particles can be precipitated from the reverse micellar solution by controlling the pressure, while the surfactant remains in the solvent continuous phase. The Ag particle size can be tailored by controlling the operating conditions, such as the CO_2 pressure, the water/surfactant molar ratio, and the reductant/$AgNO_3$ molar ratio.

Acknowledgement

The authors are grateful to the National Natural Science Foundation of China (20133030) and the Ministry of Science and Technology for financial support (G2000078103).

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Received: December 5, 2001
Revised: March 22, 2002 [F3726]