

# EFFECT OF COMPRESSED CO<sub>2</sub> ON THE PROPERTIES OF AOT IN ISOOCTANE REVERSE MICELLAR SOLUTION AND ITS APPLICATION TO RECOVER NANOPARTICLES

Dongxia Liu, Jianling Zhang, Tiancheng Mu, Jing Chen, Weize Wu, Jun He,  
Guangying Yang, Buxing Han\*

The Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, P. R. China; Email: [Hanbx@infoc3.icas.ac.cn](mailto:Hanbx@infoc3.icas.ac.cn); Fax: 86-10-62559373

**Abstract** Effect of compressed CO<sub>2</sub> on properties of the sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane/water reverse micellar solution has been studied by phase behavior measurement. UV-vis study indicates that TiO<sub>2</sub> in the reverse micelles can be precipitated by compressed CO<sub>2</sub> at suitable pressures, while the surfactant AOT remains in the solution. Using this concept, TiO<sub>2</sub> nanoparticles synthesized in the reverse micellar solution has been recovered using compressed CO<sub>2</sub>. The transmission electron microscopy (TEM) results show that TiO<sub>2</sub> nanoparticles with small size can be obtained by controlling operating conditions.

## Introduction

It is known that compressed CO<sub>2</sub> can dissolve in many organic solvents and expand the solution, which results in considerable change in the solvent power of the solvents. Thus, the property of the liquid solvent can be tuned by pressure because the solubility of CO<sub>2</sub> in the solvent is a function of pressure, and the separation of the gas and the liquid solvent can be achieved easily by depression. In recent years, utilization of this principle has been widely explored in various areas, such as extraction and fractionation, recrystallization of chemicals.

Recently, we proposed a new method to recover ZnS nanoparticles synthesized in AOT (surfactant) reverse micelles by dissolving compressed CO<sub>2</sub> into reverse micellar solution [1]. The results show that the ZnS nanoparticles can be recovered from the reverse micelles, while the surfactant is still kept in the solution. The combination of reverse micellar solutions and compressed CO<sub>2</sub> may find various applications with some unique advantages because the properties of the reverse micelles can be tuned continuously by the pressure of CO<sub>2</sub>. It is no doubt that the related fundamental research is of great importance to both pure and applied sciences. The present work consists of two related parts. First, we study the effects of added CO<sub>2</sub> on the properties of the reverse micelles by phase behaviour measurement, which is the basis for the UV-vis measurement. Second, we probe the possibility of recovering TiO<sub>2</sub> nanoparticles synthesized in the reverse micellar solution of AOT/isooctane/water using compressed CO<sub>2</sub>, which in turn gives some information about the properties of the reverse micelles in the presence of CO<sub>2</sub>.

## Experimental

**Materials** The purity of titanium (IV) isopropoxide (TIP) (Acros) was 98+%. The surfactant AOT was purchased from Sigma with purity of 99%. The isooctane, isopropoxide and ethanol supplied by Beijing Chemical Plant were all A. R. grade. Double distilled water was used. CO<sub>2</sub> (>99.995% purity) was provided by Beijing Analysis Instrument Factory.

**Phase behavior of reverse micellar solution** The apparatus used to study the expansion curves and the cloud point pressure of the solution was the same as that used previously [1]. It consisted mainly of a view cell of 50.0 ml, a high-pressure pump, a constant temperature water bath, and a pressure gauge. The high-pressure pump was Model DB-80, which was used to charge CO<sub>2</sub> into the system. The accuracy of the pressure gauge, which was composed of a transducer (FOXBORO/ICT) and an indicator, was  $\pm 0.025$  MPa in the pressure range of 0-20 MPa. The temperature of the water bath was controlled by a HAAKE D3 digital controller, and the accuracy of the temperature measurement was  $\pm 0.1$ °C.

The reverse micellar solution was prepared by dissolving AOT into isooctane in a flask. The required amount of water was added. The flask was shaken until the solution became clear. In a typical experiment, suitable amount of reverse micellar solution was loaded into the view cell. CO<sub>2</sub> was then charged into the cell to a suitable pressure after the thermal equilibrium had been reached. A magnetic stirrer was used to enhance the mixing of CO<sub>2</sub> and reverse micellar solution. The volume of the liquid phase did not change with time after equilibrium was reached. The pressure and the volume at equilibrium condition were recorded. More CO<sub>2</sub> was added and the volume of the liquid phase at another pressure was determined. The volume expansion coefficients were calculated on the basis of the liquid volumes before and after dissolution of CO<sub>2</sub>. Water was precipitated from the reverse micelles as sufficient amount of CO<sub>2</sub> was dissolved in the solution, which could be observed at the bottom of the optical cell. With more CO<sub>2</sub> being added, the micellar solution became cloudy, indicating the precipitation of the surfactants from the reverse micelles.

**Preparation of TiO<sub>2</sub> nanoparticles in the reverse micelles** The method to synthesize TiO<sub>2</sub> nanoparticles in the reverse micelles was similar to that reported by other authors [2]. Typically, the desired amount of pre-diluted (13wt%) TIP/isopropanol solution was added to the AOT/water/isooctane reverse micelles under mild stirring.

**Precipitation of TiO<sub>2</sub> by UV spectra** The UV spectrophotometer (Model TU-1201) was used to examine the precipitation of TiO<sub>2</sub> particles from the reverse micelles at different CO<sub>2</sub> pressures. The high-pressure UV sample cell and the experimental procedures were similar to those used previously [1].

**Recovery of TiO<sub>2</sub> nanoparticles** The known amount of reverse micellar solution with the synthesized TiO<sub>2</sub> nanoparticles was added into the cylinder-shaped autoclave of 130.0 ml. The temperature was controlled at 303.2 K. CO<sub>2</sub> was injected into the autoclave by a high-pressure pump until the desired pressure was reached. A magnetic stirrer was used. After 30 minutes, the stirrer was stopped to allow the precipitation of the TiO<sub>2</sub> particles. CO<sub>2</sub> was then released slowly. After the removal of the liquid solution, the deposits at the bottom of the autoclave were collected and washed several times using water and ethanol.

**Characterization of the particles** The size and shape of the obtained TiO<sub>2</sub> particles were determined by transmission electron microscope (TEM) with a HITACHI H-600A electron microscope. The maximum resolution was 0.5 nm. Particles were ultrasonicated for 5 minutes in ethanol and then directly dropped on the copper grid.

## Results and Discussion

**Phase behavior investigation of the reverse micelles in CO<sub>2</sub>.** In this work, volume expansion ratio ( $\Delta V\%$ ) of the solution is defined by the following equation.

$$\Delta V\% = 100 \frac{V - V_0}{V_0} \quad (1)$$

where  $V$  is the volume of the solution expanded by CO<sub>2</sub>, and  $V_0$  is the volume of the CO<sub>2</sub>-free solution. Figure 1 shows the volume expansion ratio of the micellar solution ([AOT]=100 mmol/L,  $w_0=8$ ) versus the pressure at different temperatures obtained in this work. As expected, the volume expansion ratio increases with increasing pressure and decreases as temperature rises. We have also studied the effects of AOT concentration (50 mmol/L and 100 mmol/L) and  $w_0$  (2, 5 and 8) on the volume expansion in this work, which reveals that the effects are not considerable. The determined volume expansion ratio allows us to determine how much CO<sub>2</sub>-free reverse micellar solution should be loaded into sample cell for the IR and UV investigations.

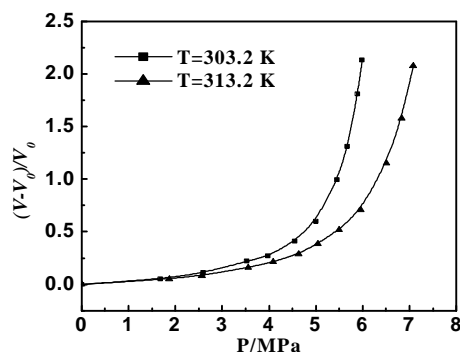


Figure 1. Effect of temperature and pressure on volume expansion coefficient of the reverse micellar solution ([AOT]=100 mmol/L,  $w_0=8$ )

The water in the reverse micelles begins to precipitate as the sufficient amount of CO<sub>2</sub> is added to the micellar solution. In this work, the pressure at which the water begins to precipitate is denoted as  $P_w$ . For the reverse micellar solutions with  $w_0 = 2, 5, \text{ and } 8$  ([AOT]=100 mmol/L), the  $P_w$  values are respectively 5.76 MPa, 5.58 MPa, and 5.41 MPa at 303.2 K. It is evident that  $P_w$  decreases with the increasing  $w_0$ . This behaviour results mainly from the fact that most water molecules in the reverse micelles are strongly hydrogen-bonded with the polar head of the surfactant at lower  $w_0$ .

A micellar solution becomes cloudy as the surfactant begins to precipitate. We determined the cloud point pressures ( $P_c$ ) of the reverse micellar solution at 303.2 K and 313.2 K in the  $w_0$  range from 2 to 8. The concentrations of the AOT are 50 mmol/L and 100 mmol/L, respectively. The obtained  $P_c$  values of different solutions are shown in Figure 3. As can be seen,  $P_c$  increases with the increasing temperature, indicating that it is more difficult to precipitate the surfactant at higher temperature. The main reason is that the solubility of  $\text{CO}_2$  in the solution decreases with increasing temperature. As expected, the  $P_c$  is increased as the concentration of AOT and  $w_0$  are reduced.

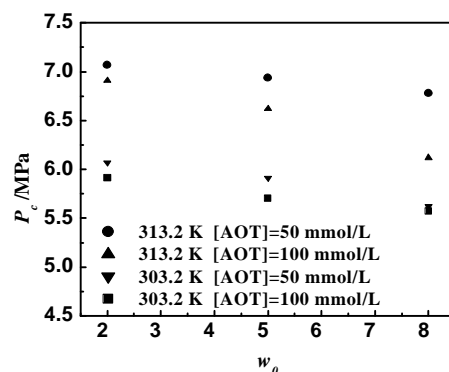


Figure 2. Cloud point pressures ( $P_c$ ) of the reverse micellar solution at different conditions

**Precipitation of  $\text{TiO}_2$  and AOT by UV spectra** In the experiment, the UV cell was full of solution after expansion with  $\text{CO}_2$ . The concentrations of  $\text{TiO}_2$  and AOT in the solution are 0.022 mg/mL and 100 mmol/L if precipitation does not occur. As an example, Figure 3 shows the UV spectra of the reverse micellar solution ( $w_0=8$ ) containing  $\text{TiO}_2$  particles at some pressures. As seen from the UV spectra, the characteristic absorbances around 220 nm and 272 nm belong to AOT and  $\text{TiO}_2$  nanoparticles [1]. The nanoparticles in the reverse micellar solution do not precipitate in the absence of  $\text{CO}_2$  (curve a). However, the absorbance of the  $\text{TiO}_2$  decreases progressively with the increasing  $\text{CO}_2$  pressure, indicating the precipitation of  $\text{TiO}_2$  from the reverse micelles, while the absorbance of AOT remains unchanged in a certain pressure range, suggesting no precipitation of AOT from the solution in this pressure range. More  $\text{TiO}_2$  nanoparticles are precipitated at higher pressures (curves b-f). When the pressure reached an enough high value i.e. 5.91 MPa, the absorbance of AOT begin to decrease (curves g and h), indicating the precipitation of AOT from the reverse micelles, which agrees well with the phase behaviour study discussed above. The UV results show that through the control of  $\text{CO}_2$  pressure, the synthesized  $\text{TiO}_2$  particles can be recovered from the reverse micelles, while AOT remains in the solution.

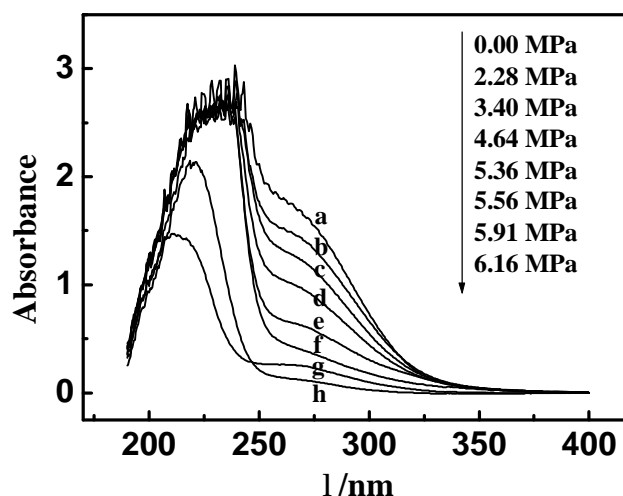


Figure 3. UV spectra of  $\text{TiO}_2$  in reverse micelles ( $[\text{AOT}]=100 \text{ mmol/L}$ ,  $w_0=8$ ) at 303.2 K and different pressures

**TEM of the recovered  $\text{TiO}_2$  nanoparticles** On the basis of the investigations above, we can select suitable experimental conditions to prepare and recover  $\text{TiO}_2$  nanoparticles from the reverse micelles using compressed  $\text{CO}_2$ . We recover the nanoparticles from the reverse micelles ( $[\text{AOT}]=100 \text{ mmol/L}$ ,  $w_0=8$ ) at 5.41 MPa, which is lower than the cloud point pressure, as can be known from Figure 3. So the surfactant is kept in the solution and only the  $\text{TiO}_2$  nanoparticles are precipitated. The TEM photographs of  $\text{TiO}_2$  recovered from the reverse micelles at different TIP concentrations are given in Figure 4 (a)-(c). The particle size is

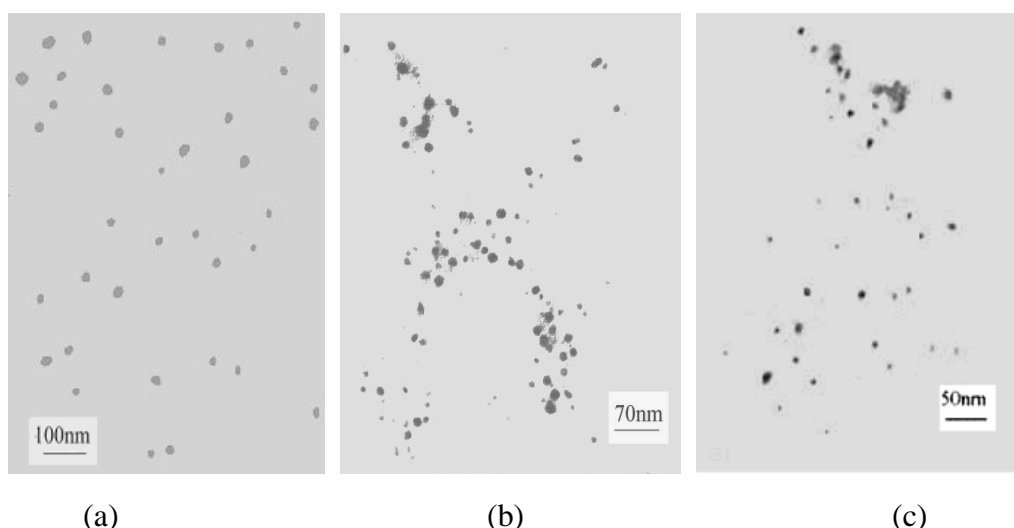


Figure 4. TEM photographs of  $\text{TiO}_2$  particles recovered from AOT reverse micelles ( $[\text{AOT}]=100 \text{ mmol/L}$ ,  $w_0=8$ ) by compressed  $\text{CO}_2$  at 303.2 K and 5.41 MPa (a)  $[\text{TIP}]=1.30 \text{ mg/mL}$ ; (b)  $[\text{TIP}]=0.86 \text{ mg/mL}$ ; (c)  $[\text{TIP}]=0.43 \text{ mg/mL}$ .

obtained by measuring the diameter of particles in the micrographs. As shown in Figure 4, the particle sizes are respectively 20-30 nm, 10-20 nm, and 2-5 nm as TIP concentrations are 1.30

mg/mL, 0.86 mg/mL to 0.43 mg/mL, i.e., the particle size decreases with the decreasing TIP concentration. The main reason is that the amount of TiO<sub>2</sub> in each micelle is smaller at the lower concentration, which is favorable to produce small particles.

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## References

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