An Application of the Water/Supercritical CO_2 Microemulsion to a Novel "Microreactor"

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Water/supercritical CO_2 microemulsions were prepared by using ammonium carboxylate perfluoropolyether (PFPE) as a surfactant. The de-aggregation of the J-aggregate of cyanine dyes and the formation of fairly small silver particles in these microemulsions would indicate the realization of the chemical reactions in the small space. In this sense, the water/supercritical microemulsion is regarded as a novel "microreactor" of the nanometer size.

In recent years, supercritical fluids as a new reaction medium have been extensively investigated by taking advantage of their unique properties. Although carbon dioxide is the most widely available supercritical fluid because of gentle critical conditions (T_c = 304 K, P_c = 7.38 MPa), the poor solubility for the inorganic compounds prevents the application to an inorganic reaction medium. In order to overcome this disadvantage, Johnston et al. have recently demonstrated the water/supercritical CO_2 microemulsion by using a perfluorinated surfactant, PFPE.[1,2] The formation of water/supercritical CO_2 microemulsion makes it possible for ionic solutes to disperse in the supercritical CO_2, extending its application to an inorganic reaction medium. On the other hand, only a few research groups have reported the inorganic reaction in this system. Clarke and coworkers have reported simple aqueous inorganic reaction in the water/supercritical CO_2 microemulsion.[2] In this study, we have examined the de-aggregation of cyanine dyes and the photochemical formation of silver nanoparticles in water/supercritical CO_2 microemulsions.

PFPE (average MW = 700) was supplied from Ausimont (Italy) in the form of carboxylic acid.[3] It was then neutralized by ammonia solution and dried for 10 h by the evaporator. The stainless high-pressure cell (9.4 cm^3 in volume, 3 cm in the optical path length) equipped with three quartz windows was used to generate the supercritical conditions. The mixture of PFPE, water and the solute compounds was first placed in the cell and then CO_2 was introduced by the intelligent HPLC pump (SCF-Get, JASCO Co.) up to the prescribed pressure. The temperature was maintained at 308 ± 0.5 K by circulation of water from a thermostat. The solution was stirred for 2 h at constant pressure and temperature before each experiment. Absorption spectra were measured by using the Xe arc-lamp and MCPD-100 detection system (Otsuka Electronics).

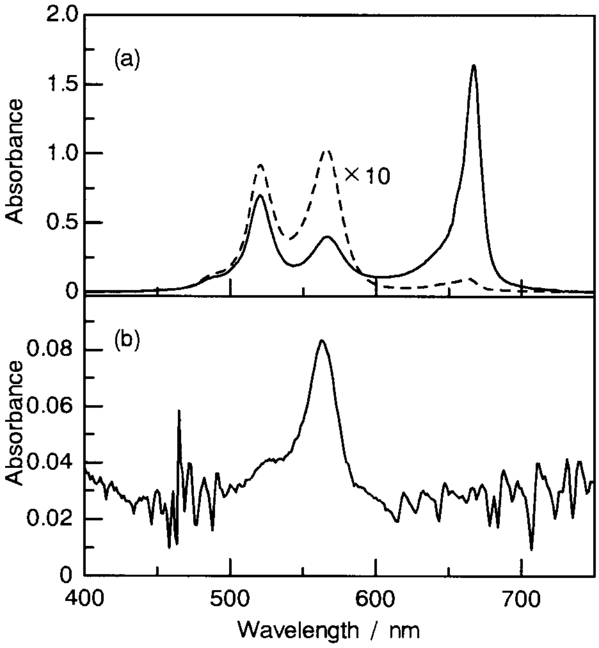

Figure 1. (a) Absorption spectra of aqueous solutions of 1×10^{-4} (solid line) and 1×10^{-5} M Thia(ph) (dashed line). The optical path length is 1 mm. (b) Absorption spectra of water/supercritical CO_2 microemulsions containing 1×10^{-4} M Thia(ph). The optical path length is 3 cm.

The PFPE solution in supercritical CO_2 looked cloudy immediately after increasing pressure and then it became transparent soon. These observations are almost the same as those reported by Johnston et al.,[1] indicating that water/super-critical CO_2 microemulsions are successfully prepared. We should note that in certain cases, some of the solute compounds are lost during the preparation of the microemulsions because not all of them are incorporated into the microemulsions except under optimum conditions. We have tried to dissolve an anionic cyanine dye, 3,3'-disulfopropyl-5,5'-dichloro-9-phenylthiacarbocyanine triethylammonium salt (Thia(ph)) in this solution. It should be noted that Thia(ph) is almost insoluble in the pure supercritical CO_2. Figure 1a shows the absorption spectra of the aqueous solutions of 1×10^{-4} M and 1×10^{-5} M Thia(ph). The monomer-, dimer-, trimer- and J-bands of Thia(ph) appear at 575, 520, 485 and 665 nm, respectively, indicating that Thia(ph) easily forms dye aggregates in the aqueous solution. Thia(ph) was dissolved in water/supercritical CO_2 microemulsions so that the concentration inside the microemulsion core is 1×10^{-4} M. Here, the nominal concentrations of Thia(ph) and PFPE in the high-pressure cell are 6×10^{-7} M and 18 mM, respectively, the molar ratio of water to PFPE, W_0=20, and the pressure is 18 MPa. The solution looked red color and was stable for more than 10 h, suggesting that Thia(ph) is homogeneously dispersed. The absorption spectrum of this solution is shown in Figure 1b. We can see only the single band at 575 nm, indicating that Thia(ph) molecules are in the monomeric form in the microemulsions. We have considered three possibilities to explain our observation; (1) the acidic environment (pH=3)[4] inside the microemulsion core affects the aggregation of Thia(ph), (2) the concentration of Thia(ph) inside the microemulsion core is lowered due to the loss during the preparation of microemulsions, (3) the small space of the microemulsion core restricts the aggregation of Thia(ph). The case (1) is excluded since no change was observed in the absorption spectra of the aqueous Thia(ph) solution even at pH = 3.

To check the case (2), the actual concentration of Thia(ph) inside the microemulsions was estimated from the absorbance and the molar extinction coefficient of the monomer band. The resulting concentration is about 3×10^{-5} M, which is within the range of 1×10^{-5}–1×10^{-4} M in Figure 1a. As shown in Figure 1a, the dimer band is evident and further, trimer- and J-bands are still detectable at 1×10^{-5} M. Therefore, the case (2) was rejected, although the concentration of Thia(ph) is somewhat lowered, because about 70% of Thia(ph) are lost due to, e.g., adsorption on the wall. However, this does not influence the considerations in this letter. According to the small angle neutron scattering measurement by Zielinski et al., the microemulsion core radius is in the range of 2.0–3.6 nm, varying with the molar ratio of water to PFPE.[5] As a result, the average number of Thia(ph) molecules per a microemulsion can be less than 1. It is thus reasonable that Thia(ph) molecules are isolated in the monomeric form in the individual microemulsions due to the small space of the microemulsion core (case (3)). These observations suggest the realization of chemical reactions in the small isolated space of the nanometer size.

To confirm our suggestion, we have tried to synthesize the small silver particles in water/supercritical CO_2 microemulsions by the photoreduction method. Water/supercritical CO_2 microemulsions containing $AgClO_4$ was prepared at 36 MPa so that the concentration of $AgClO_4$ inside the microemulsion core could be 1.0 M and then irradiated with UV light (λ=254 nm) from a 200 W low-pressure mercury lamp. The nominal concentration of $AgClO_4$ and PFPE was 4.5 mM and 25 mM, respectively, and W_0 = 10. 2-Propanol (0.1 M) was added to the water phase to promote the photoreduction of Ag^+.[6] The formation of small silver particles was monitored in situ by the measurements of absorption spectra. The solution was almost transparent before the photoreduction of Ag^+ and showed no absorption in the range of 320–600 nm. However, it became light yellow gradually with UV irradiation. Here, it should be noted that the carboxylate group of PFPE can promote the photoreduction of Ag^+.[6] Figure 2 shows the difference-spectra of water/supercritical CO_2 microemulsions containing $AgClO_4$ before and after UV irradiation. These spectra show the peak at about 360 nm, whose absorbance increases with increasing UV irradiation time. The spectra do not change significantly when W_0 are varied in the range of W_0=5–30. It is well-known that the surface plasmon band of Ag colloid appears around 390–420 nm, depending on the size and shape of the colloid as well as the kind of medium.[6] The 360-nm band is blue-shifted by 30–40 nm from the usual surface plasmon band. Henglein and coworkers have reported the absorption band around 360–380 nm assigned to small Ag particles consisting of 4–12 Ag atoms.[7] We have thus attributed this band to extremely small Ag particles. Assuming that the microemulsion core radius is 2 nm,[5] the number of Ag^+ per a microemulsion is estimated to be 10–20 considering the 0–50% loss of $AgClO_4$ during the preparation of microemulsions. If the agglomeration between Ag particles in the different microemulsions is almost hindered, it is not unreasonable that such a small Ag particle is formed in the individual microemulsions. We are now trying to collect Ag particles on the substrate by the rapid expansion technique. Ji and coworkers have synthesized small Ag particles in the similar water/supercritical CO_2 microemulsions by the chemical reduction method.[8] However, the size of Ag particles was about 10–15 nm, which is much larger than the microemulsion core radius. In case of the chemical reduction method, the water/ supercritical CO_2 microemulsion do not work as microreactor, since the structure of the microemulsion has to be destroyed to introduce the reducing agent inside the microemulsion core. In contrast, the present photoreduction method has an advantage that the reaction can be homogeneously initiated without destruction of the microemulsion. Further, we point out that UV irradiation of $AgClO_4$ in the water-in-hexane microemulsions containing Aerosol-OT yielded the Ag particles whose size is much larger than the microemulsion core radius.

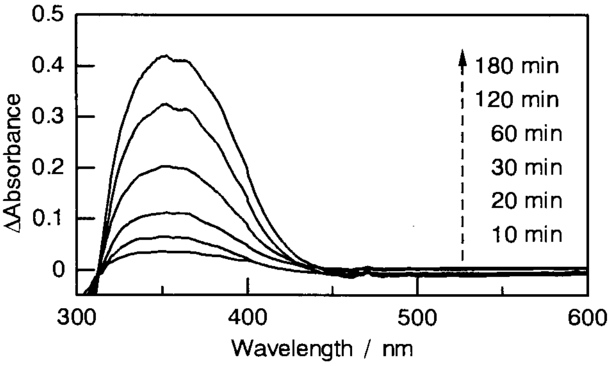

Figure 2. Difference-spectra of the absorption of water/supercritical CO_2 microemulsions containing $AgClO_4$. Irradiation times are 10, 20, 30, 60, 120, and 180 min, respectively. The optical path length is 3 cm.

In conclusion, we have successfully demonstrated the deaggregation of cyanine dyes and the photochemical formation of small Ag particles in the water/supercritical CO_2 microemulsion. These results suggest that the water/supercritical CO_2 micro-emulsion can be applied to a novel "microreactor" of the nanometer size for photochemical reactions. This would arise from the unique properties of the supercritical CO_2, e.g., the very weak affinity for the inorganic solutes. Finally, we will point out that the photochemically formed small Ag particles are relevant to the new application of metal nanoparticles to catalytic reactions in the supercritical CO_2.

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Refereces

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