Size Control of Metastable ZnS Particles in W/O Microemulsion

Toshiaki Hanaoka,* Teruoki Tago,† Masahiro Kishida,† and Katsuhiko Wakabayashi†

Biomass Division, National Institute for Resource and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305-8569

†Department of Chemical Engineering Group, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581

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The effect of various factors on the metastable size of ZnS particles was investigated in order to widely and precisely control the size of ultrafine particles synthesized in a microemulsion. The metastable size of the ZnS particles could be more widely changed by changing the microemulsion system, the specific permittivity of the organic solvent, the pH, and the synthesis temperature than the previously reported factors. We proposed a stabilization model of the ZnS ultrafine particles by surfactants and a new method for controlling the size of ultrafine particles synthesized in the microemulsion.

The synthesis of nanometer-sized ultrafine particles in a microemulsion is the subject of intense research because of their wide applications. Especially, some researchers have applied ultrafine particles to supported metal catalysts by immobilization of their particles on or in solid supports.[1–3] We have proposed a new method for the preparation of supported metal catalysts by immobilizing size-controlled ultrafine particles synthesized in a microemulsion in solid supports.[4]

The size of the supported metal particles is an important factor affecting most catalytic behaviors.[5] Therefore, it is necessary to control, both widely and precisely, the size of ultrafine particles synthesized in a microemulsion in order to enhance the catalytic performance. The size of these particles in a microemulsion is traditionally controlled by the molar ratio of water to surfactant (w_0), the reactant concentration, and the ratio of the potential determining ion.[6–12] Some researchers have reported the metastable size of CdS particles of which the growth rate had significantly decreased, and proposed a kinetic model for the reduced rate of the CdS particle coagulation process.[13,14] Accordingly, it is important to reveal the relationship between the metastable size and various factors in order to control, both widely and precisely, the size of ultrafine particles synthesized in a microemulsion. In this work, we studied the effect of various factors on the metastable size of the ZnS particles of which the size was easy to estimate, and proposed a new method for controlling the size of ultrafine particles synthesized in a microemulsion.

Materials and Methods

Poly(oxyethylene) ($n = 23$) dodecyl ether (Brij35), bis(2-ethylhexyl) sulfosuccinate (AOT), and hexadecyl trimethyl ammonium chloride (CTAC) were used as a surfactant. *N*-alcohols with a carbon number of 2 to 10, *n*-hydrocarbons with a carbon number of 7 to 12, cyclohexane, and isooctane were employed as the organic solvent. $Zn(NO_3)_2{\cdot}6H_2O$ and Na_2S were used as the source of ZnS particles. The concentration of the surfactant in an organic solvent was 0.1 mol dm^{-3}. The molar ratio of water to surfactant was mainly 6, and the concentrations of zinc nitrate, $[Zn(NO_3)_2]_{aq}$, and sodium sulfide, $[Na_2S]_{aq}$, were 5.0×10^{-2} mol dm^{-3} and 2.5×10^{-2} mol dm^{-3}, respectively. ZnS particles were synthesized by mixing two microemulsions, one containing $Zn(NO_3)_2$ and the other containing Na_2S.

UV-visible absorption spectra were recorded using a UV-2400 spectrophotometer (Shimadzu Co., Ltd.). The size of the ZnS particles synthesized in the microemulsion was estimated by the band gap using Brus' equation.[15]

$$E_g = E_{g,bulk} + \frac{h^2}{2d_p^2 e}\left(\frac{1}{m_e{}^*} + \frac{1}{m_h{}^*}\right) - \frac{3.6e}{4\pi\varepsilon d_p} \qquad (1)$$

The band gap for the bulk ZnS ($E_{g,\,bulk}$) is 3.7 eV. d_p is the particle diameter, $m_e{}^*$ and $m_h{}^*$ are the effective masses of the electron and hole, respectively, and e is the charge of an electron (1.602×10^{-19} C). ε is the dielectric constant. The value of $m_e{}^* = 0.25m_e$, $m_h{}^* = 0.58m_e$ and $\varepsilon = 0.52\varepsilon_0$ for ZnS.[12] Here, m_e is the electron rest mass (9.109×10^{-31} kg) and ε_0 is the dielectric constant in a vacuum (8.854×10^{-12} c^2 J^{-1} m^{-1}). In this study, the particle size, which remained unchanged for 2 hours, was defined as a metastable size.

Results

1. Effect of w_0, the Reactant Concentration and the Ratio of the Potential Determining Ion ($[Zn^{2+}]_{aq}/[S^{2-}]_{aq}$). The effect of w_0 and the reactant concentration on the metastable size of the ZnS particles was investigated. AOT/*n*-heptane was employed as the microemulsion system. Figure 1 shows the dependence of w_0 on the metastable size, together with the relationship between w_0 and the waterpool size estimated by Adachi et al.[16] In the range $w_0 < 3$, the metastable size increased from 3.0 to 3.3 nm with increasing w_0. When w_0 was more than 3, this size took a constant value, i.e., 3.3 nm. This dependence of the particle size on w_0 was similar to that in a previous study.[14] However, the metastable size was apparently independent of the waterpool size. Figure 2 shows the rela-

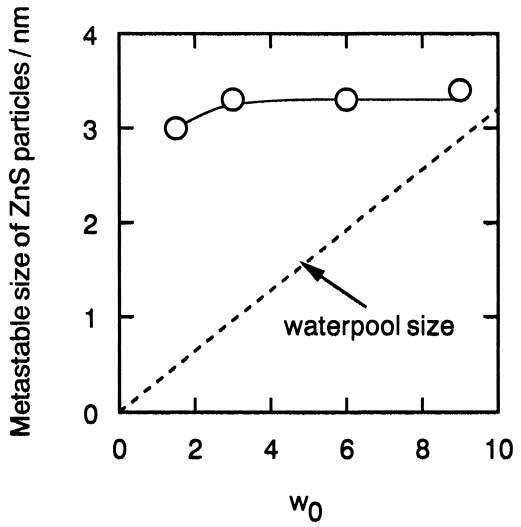

Fig. 1. Change in the metastable size of ZnS particles with w_0.
AOT/*n*-heptane, $[AOT]_{org} = 0.1$ mol dm^{-3}, $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$. Dashied line: waterpool size, $Dw = 0.32w_0$[16].

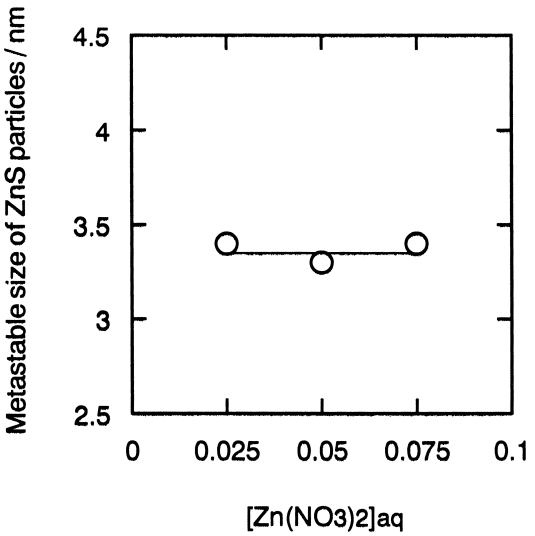

Fig. 2. Change in the metastable size of the ZnS particles with the reactant concentration inside the micelle.
$w_0 = 6$, $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$.

tionship between the metastable size with the reactant concentration ($[Zn(NO_3)_2]_{aq}$). $[Na_2S]_{aq}$ was adjusted with the molar ratio of $[Zn^{2+}]_{aq}/[S^{2-}]_{aq}$ equal to 2. The metastable size was independent of the reactant concentration, and was about 3.3 nm in all cases.

Next, the effect of the ratio of the potential determining ion on the metastable size was studied. 1-Hexanol was employed as the organic solvent. Figure 3 shows the change in the metastable size with the ratio of the potential determining ion. In each case, the metastable size did not significantly change. As a result, it was difficult to widely control the metastable size of the ZnS particles in a microemulsion by the previously reported conventional factors.

2. Effect of Microemulsion System. Next, the metastable

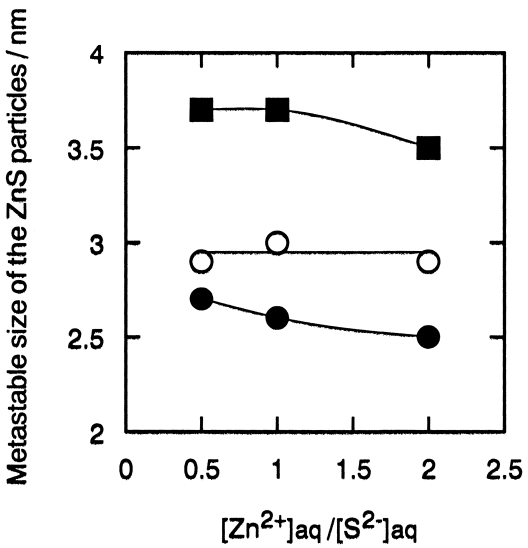

Fig. 3. Change in the metastable size of the ZnS particles with the ratio of the potential determining ion.
●; AOT/1-hexanol, ○; Brij35/1-hexanol, ■; CTAC/1-hexanol.

size of the ZnS particles synthesized using various types of microemulsion systems was studied. Figure 4 shows the relationship between the metastable size and the microemulsion systems. The ratio of the potential determining ion, $[Zn^{2+}]_{aq}/[S^{2-}]_{aq}$, was 2, and the pH was about 6. The metastable size increased in the order CTAC/1-hexanol > AOT/cyclohexane = AOT/isooctane > Brij35/1-hexanol > AOT/1-hexanol system. Moreover, this size varied in the range of 2.5 to 3.5 nm and more widely than that mentioned in section 3.1. Accordingly, altering the microemulsion system was effective to widely change the metastable size.

3. Effect of an Organic Solvent. In section 2, it is difficult to understand the reason why the metastable size widely changed, because the structure, or property, of the surfactants and organic solvents employed were not systematically changed. The effect of the types of organic solvents on the metastable size was systematically investigated. The *n*-hydro-

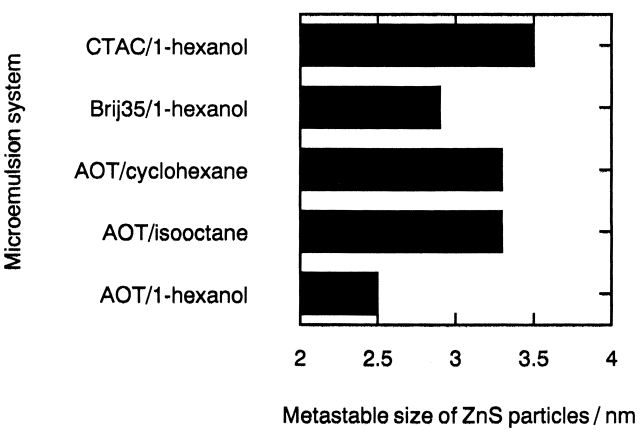

Fig. 4. Change in the metastable size of the ZnS particles with the various types of microemulsion system.
$w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$.

carbon with a carbon number of 7 to 12 and *n*-alcohol with a carbon number of 2 to 10 were employed as the organic solvent. Figure 5 shows the metastable size when the *n*-hydrocarbon was employed. AOT was employed as a surfactant because it only dissolved in the *n*-hydrocarbon. The metastable sizes were independent of the type of *n*-hydrocarbon. Next, the effect of the types of *n*-alcohol on the metastable size was studied. Figures 6, 7, 8, and 9 show the change in the UV-visible spectra with time in Brij35. In each case, while the absorption threshold slightly changed with time, the ZnS particle sizes estimated by the band gap using Brus' equation were almost constant for 2 hours. Figure 10 shows the change in the metastable size with the specific permittivity of the organic solvent employed. The specific permittivity increases with decreasing carbon number of the *n*-alcohol, and those for the *n*-hydrocarbon are almost the same, i.e., 1.9. The metastable size widely changed in the range of 2.8 to 3.8 nm and decreased with increasing specific permittivity in all cases. Accordingly, the specific permittivity of an organic solvent is an important factor for widely changing the metastable size of the ZnS particles synthesized in a microemulsion.

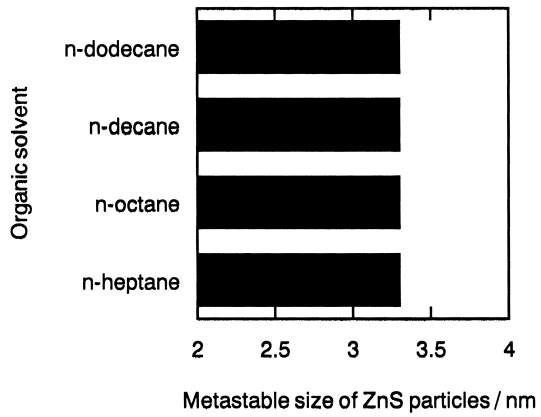

Fig. 5. Effect of the types of *n*-hydrocarbon on the metastable size.
AOT/*n*-hydrocarbon, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$.

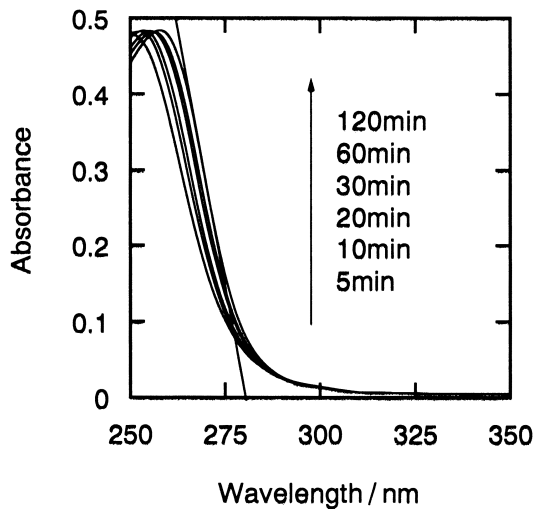

Fig. 6. Change in UV-visible spectra with time.
Brij35/ethanol, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$, absorption threshold after 120 min: 281 nm, ZnS particle size: 2.8 nm.

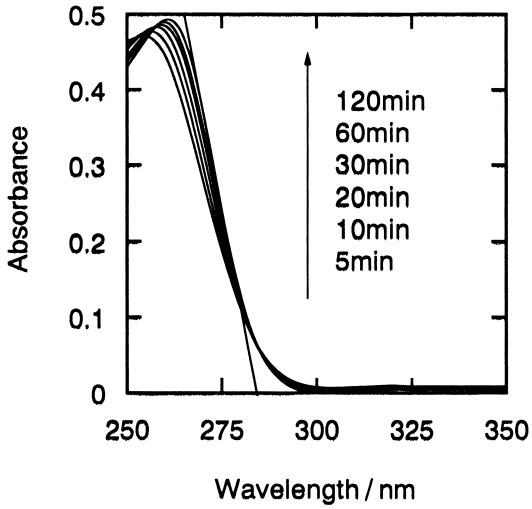

Fig. 7. Change in UV-visible spectra with time.
Brij35/1-butanol, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$, absorption threshold after 120 min: 285 nm, ZnS particle size: 2.9 nm.

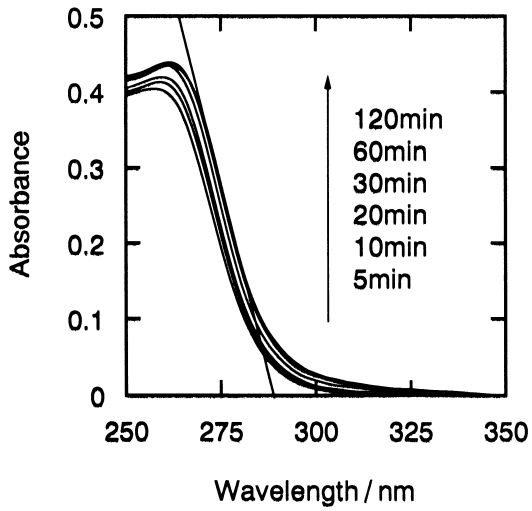

Fig. 8. Change in UV-visible spectra with time.
Brij35/1-hexanol, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$, absorption threshold after 120 min: 289 nm, ZnS particle size: 3.1 nm.

In ethanol as an organic solvent, the metastable size in Brij35 only existed, and was the smallest of all solvents. The ZnS particle size in CTAC/ethanol increased with time after mixing the two surfactant solutions and had no plateau value. In AOT/ethanol, no absorption threshold could be observed in the wide range at wavelength. The surfactant molecules are dissolved in ethanol, and no microemulsion forms. It is interesting, therefore, that in ethanol as an organic solvent, the metastable size of the ZnS particles in Brij35 only existed, and could be controlled by selecting of the *n*-alcohol, regardless of the formation of a microemulsion.

4. Effect of the pH. Next, the effect of the pH on the metastable size was investigated. The pH was adjusted by the amount of aqueous ammonia added to the microemulsion before the formation of the ZnS particles. Figure 11 shows the

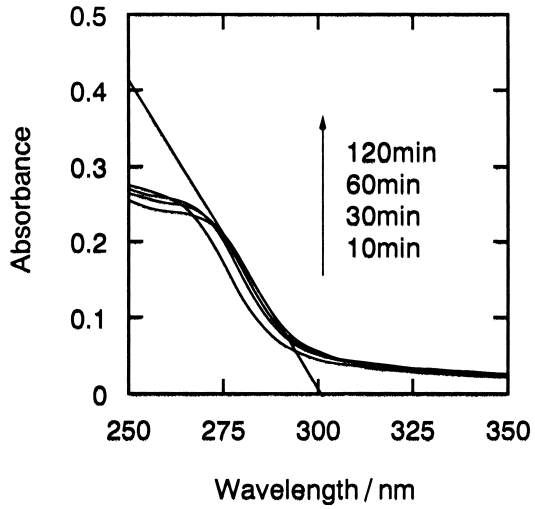

Fig. 9. Change in UV-visible spectra with time.
Brij35/1-decanol, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$, absorption threshold after 120 min: 301 nm, ZnS particle size: 3.5 nm.

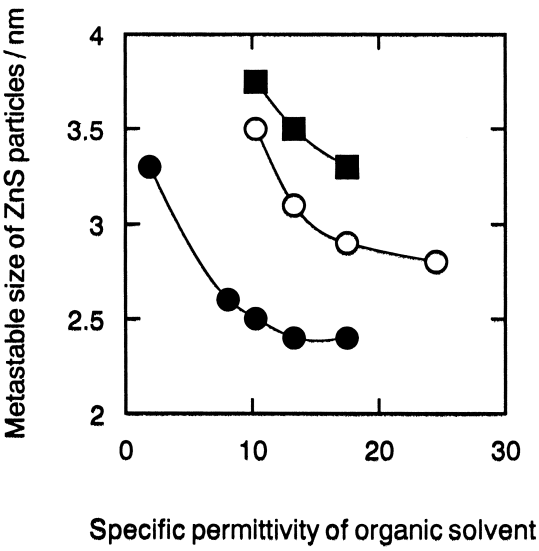

Fig. 10. Effect of the specific permittivity of organic solvent on the metastable size of the ZnS particles.
●; AOT, ○; Brij35, ■; CTAC, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$.

change in the metastable size with the pH. 1-Hexanol was employed as an organic solvent. The metastable size in AOT increased with the pH and varied in the range of 2.5 to 3.5 nm. The size in CTAC, however, decreased with increasing the pH, and changed in the range of 3.0 to 4.2 nm. When aqueous ammonia was added to the microemulsion containing Brij35, no metastable size existed. As a result, changing the pH was effective for widely varying the metastable size in AOT and CTAC.

5. Effect of the Synthesis Temperature. The effect of the synthesis temperature on the metastable size was investigated. Figure 12 shows the change in the metastable size with the synthesis temperature. In all cases, the metastable size increased with the synthesis temperature. Especially, the particle size in CTAC changed in the range of 3.5 to 4.1 nm. The particle size in AOT and Brij35, however, did not widely change.

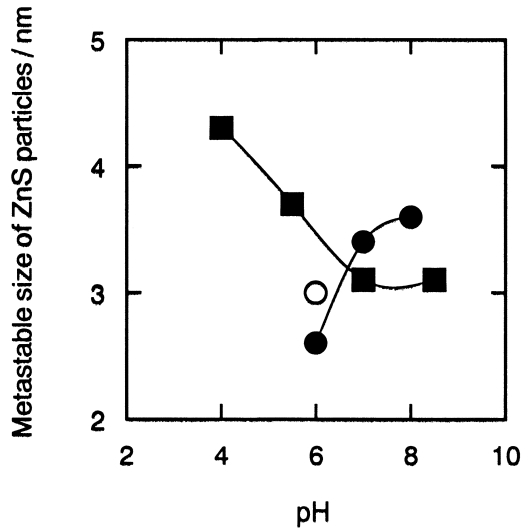

Fig. 11. Effect of pH on the metastable size of the ZnS particles.
●; AOT, ○; Brij35, ■; CTAC, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$.

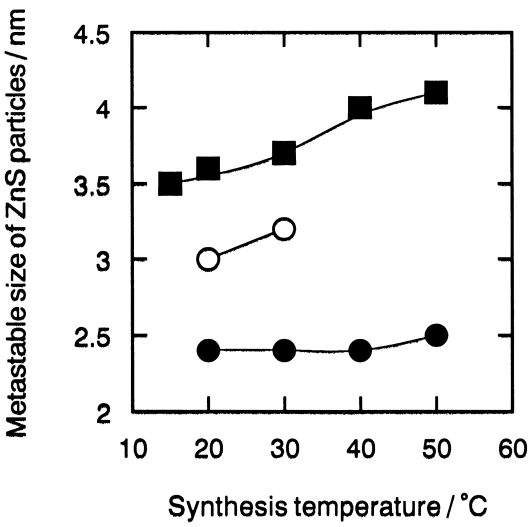

Fig. 12. Change in the metastable size with the synthesis temperature.
●; AOT, ○; Brij35, ■; CTAC, $w_0 = 6$ $[Zn^{2+}]_{aq}/[S^{2-}]_{aq} = 2$.

Thus, the synthesis temperature was an effective factor for changing the metastable size in CTAC.

Discussion

1. Stabilization Model by Surfactants. w_0 and the reactant concentration did not significantly affect the metastable size. These are the factors that are related to the number of metal ions inside a micelle. It was reported that the nucleation rate was different according to the number of metal ions inside a micelle and, as a result, the final particle size was different.[8] In this study, the metastable size of the ZnS particles, however, was almost independent of these preciously reported factors. Suzuki et al. suggested that the metastability of the ultrafine particle composed of a certain number of molecules resulted in

a drastic decrease in the particle coagulation rate.[14] Boutonnet et al. suggested that surfactant molecules would adsorb on the metal particle surface, and restricted the coagulation.[17] Therefore, it is possible that the surfactant molecules were adsorbed on the surface of the ZnS particles during the growth process, and restricted the coagulation of the particles and, as a result, the metastable size of the ZnS particles composed of a certain number of molecules would exist for several hours.

The metastable size was almost independent of the ratio of the potential determining ion. Moreover, when the ratio was not unit, since the excess ions adsorbed on the surface of the ultrafine particles and these particles positively or negatively charged,[18] it was presumed that no metastable size existed because of the repulsion between the charged ultrafine particles and surfactant molecules. The metastable size, however, the existed regardless of the ratio. From the point of view that the coagulation of the ZnS particles was restricted by the adsorption of surfactant molecules, this result suggests that the surface of the ZnS particles have two types of absorption sites, which would be positively and negatively charged.

The metastable size widely changed by altering the microemulsion system. When 1-hexanol was used as the organic solvent, the metastable size increased in the order cationic surfactant > nonionic surfactant > anionic surfactant. These results suggest that the surfactant molecules have a stronger affinity for the ultrafine particles in the order anionic surfactant > nonionic surfactant > cationic surfactant, and could restrict the coagulation of particles by the adsorption of these molecules in the early stage of the formation of ZnS particles. However, as mentioned above, this result was not due to the adsorption of the excess Zn ion. This will be mentioned later.

The metastable size was quite dependent on the specific permittivity of the organic solvent employed. Because the molecules of the organic solvent have more affinity for ultrafine particles, small particles could form. T. Hirai et al. mentioned that water molecules exist on the surface of CdS particles synthesized in the AOT/*n*-heptane microemulsion system.[14] H. Goto et al. showed that there were bounded water molecules near the hydrophilic groups of the surfactant consisting of micelle by NMR.[19] If the bounded water molecules exist near the hydrophilic groups adsorbed on the surface of the ZnS particles, it is possible to decrease the high energy on the surface of the ZnS ultrafine particles.

As a result, Fig. 13 shows the stabilization model of the ZnS particles by anionic surfactant, AOT. When surfactant molecules adsorbed on the surface of ZnS particles and restrict the coagulation of the ultrafine particles, the metastable size could exist. If the ionic surfactants stabilize the ZnS particles, the water or counter ion would be needed to restrict the repulsion between the hydrophilic groups of the surfactant molecules. As mentioned above, it is reasonable that the water molecules, which could decrease the high surface energy of ultrafine particles, would exist on the surface of the ZnS particles. Except for ethanol, organic solvents are almost immiscible with water, and the interface forms. Therefore, the water molecules and counter ion, which restrict the repulsion between the hydrophilic groups of surfactants, could remain on the surface of the particles. On the contrary, since ethanol is miscible with water and the water molecules and counter ion disperse in ethanol, ZnS particles could not be stabilized by ionic surfactants because of the repulsion between the hydrophilic groups and, thus no metastable size existed.

The effect of the specific permittivity of the organic solvent on the surface of the ZnS particles could be explained in this model. The organic solvent molecules would be in contact with the water phase on the surface of ultrafine particles. If the specific permittivity is high, the organic solvent has an affinity for the water molecules. The surface of the particles, therefore, becomes stable and small metastable particles formed. On the contrary, if it is low, the surface of the ultrafine particles becomes unstable. As a result, the particles grew, and large metastable particles formed.

The change in the metastable size with the pH was dependent on the ionicity of the surfactants. As the pH is decreased, the number of proton would increase in the water phase on the surface of ZnS particles. Sulfur ions, thus, dissolve in the wa-

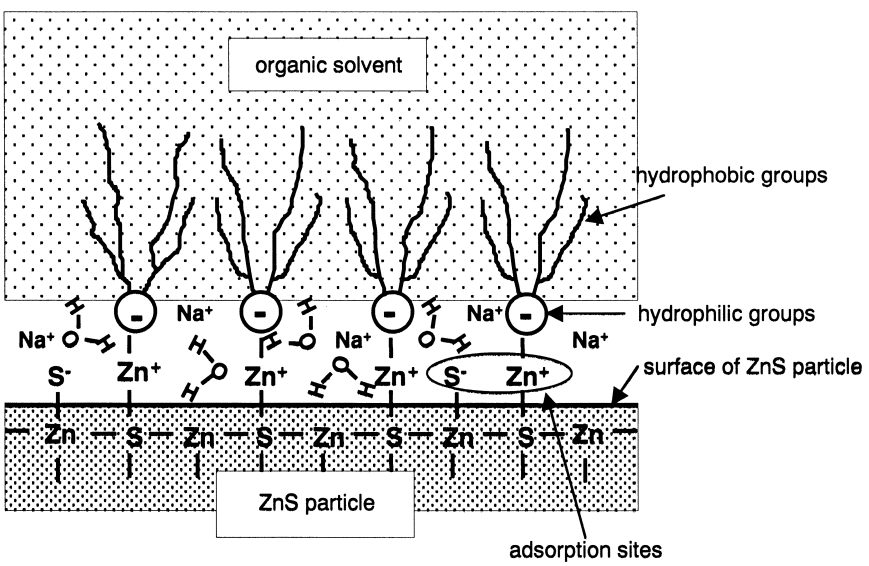

Fig. 13. Stabilization model of ZnS particles by AOT.

ter phase to neutralize the surface, and Zn sites with a positive charge increase on the surface. Accordingly, in the anionic surfactant, AOT, the number of adsorption sites would increase with decreasing the pH, and small metastable particles formed. On the contrary, in the cationic surfactant, CTAC, when the pH is decreased, the metastable particles existed. As was shown in the stabilization model, this result supports that the two types of adsorption sites with a positive and a negative charge would exist on the surface of the ZnS particles regardless of the pH. However, when the pH is low, the number of adsorption sites with a negative charge would be smaller than those with a positive charge. As a result, the ZnS particles grew and large metastable particles formed. In Brij35, if aqueous ammonia was used to adjust the pH, no metastable size existed. The hydrophilic groups of Brij35 are long oxyethylene groups. When the number of adsorption sites with a negative charge would increase with the pH, the repulsion between the hydrophilic groups and the surface of the particles might be governed because of the steric hindrance. Therefore, Brij35 could not restrict the coagulation of particles, and no metastable particles would exist when aqueous ammonia was added. In Fig. 4, the pH was about 6, and the number of adsorption sites with a positive charge would be larger than that with a negative charge. This result was consistent with that in Fig. 11.

The metastable size increased with increasing the synthesis temperature in all surfactants. This result would be due to the decrease in the amount of surfactant adsorption with the synthesis temperature.

2. Control Method of the Ultrafine Particle Size in a Microemulsion. The metastable size of the ZnS particles could be widely varied by changing the ionicity of the surfactants, the specific permittivity of the organic solvent, the pH, and the synthesis temperature. However, the effect of the pH and the synthesis temperature on the metastable size was dependent on the ionicity of the surfactant. Moreover, the addition of ammonia water to adjust the pH might affect the crystal structure of ultrafine particles synthesized in the microemulsion. Accordingly, the ionicity of the surfactant and the specific permittivity of an organic solvent could be the important factors for size control of the ultrafine particles. As a result, we proposed a new method for controlling the size of ultrafine particles synthesized in a microemulsion: 1) One can study the relationship between the ionicity of the surfactant and the metastable size of the ultrafine particles, and select the ionicity of the surfactant. 2) Using the surfactant selected in 1), one can control the size of the ultrafine particles by changing the specific permittivity of the organic solvent. 3) Using the surfactant and organic solvent employed in 2), one can precisely control the size of ultrafine particles by changing w_0.

Conclusion

In this paper, we reported the effect of various factors on the metastable size of ZnS particles. We concluded that the metastable size of the ZnS particles could be changed more widely by changing the microemulsion system, the specific permittivity of an organic solvent, the pH, and the synthesis temperature than the previously reported controlling factor. We proposed a stabilization model of the ZnS ultrafine particles by surfactants and a new method for controlling the size of ultrafine particles synthesized in the microemulsion.

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