

Growth Mechanism of AgCl Nanoparticles in a Reverse Micelle System

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After the initial precipitation of ultrafine AgCl particles caused by instantaneous mixing of silver nitrate and potassium chloride in a reverse micelle system of polyoxyethylene (6) nonylphenyl ether/water/cyclohexane, the AgCl nanoparticles were found to grow through Ostwald ripening, and not by the coagulation process, from their growth rate independent of the initial particle density within our experimental range.

Introduction

The reverse micelle (RM) system is one of the most useful systems for the preparation of uniform nanoparticles. For the formation mechanism of nanoparticles in RM systems, it seems to be widely believed that particles are grown by the deposition of solute or coagulation among particles through the association and dissociation of the water pools of the reverse micelles.^{1–6} In this image, each water pool is likely to be regarded as a nanoreactor, containing a limited number of solute species, as well as a nanotemplate to more or less limit the final size of the product particles.^{3–6} However, recently, it has been shown with an RM system for the preparation of AgCl nanoparticles that the size of the product particles is basically independent of the dimensions of the water pools and that each reverse micelle with solute may be regarded as a bulky solute species, since such a reverse micelle contains virtually only one solute complex or ion in its own water pool.⁷ Thus, the RM system can be dealt with in the same way as an aqueous system for particle formation. The dramatic reduction of the final particle size in RM systems is mainly due to the drastic reduction of the overall solubility of the solid and the small diffusivity of each reverse micelle as a bulky solute complex. This conclusion was suggested to be applicable to many other RM systems as well. In this study, RM solutions of AgNO₃ and KCl were continuously introduced into an RM solution at the same time, using a so-called double jet technique, as a new approach to clarify the underlying mechanism of the particle formation in RM systems. As a result, the growth of the AgCl particles in this RM system proceeded by a kind of Ostwald ripening, in the same way as in an aqueous gelatin solution system.

On the other hand, Sato et al.² speculated the growth mechanism of silver halide particles, such as AgBr and AgI, after instantaneous mixing of RM solutions of AgNO₃ and NaBr or NaI, in terms of coagulation after the initial precipitation. However, the data analysis does not seem fully clear to support the conclusion.

The objective of the present study is to examine our former conclusions on the formation mechanism of AgCl particles on the basis of the double jet technique,⁷ from a different viewpoint with a closed RM system after instantaneous mixing of RM solutions of AgNO₃ and KCl.

Backgrounds for the Analysis of the Growth Mechanism

If particles are grown by a coagulation process, the change of particle density, $-dn/dt$, may generally be written as

$$-\frac{dn}{dt} = f(v) n^2 \quad (1)$$

where $f(v)$ is a function of the mean particle volume, v , but independent of n . The particle density, n , is given by

$$n = \frac{V_m C_0}{v} \quad (2)$$

where C_0 is the concentration of AgCl in molarity and V_m is the molar volume of the solid of AgCl. Hence, eq 1 may be transformed as

$$\frac{dv}{dt} = f(v) V_m C_0 \quad (3)$$

On the other hand, if the particles are grown by Ostwald ripening with a sufficiently low particle density, the particle growth rate must be independent of the particle density, and thus may be given by

$$\frac{dv}{dt} = g(v) \quad (4)$$

where $g(v)$ is a function of v and independent of n .

Thus, if we plot dv/dt as a function of v at different C_0 values, dv/dt must be changed in proportion to C_0 at a given v in the case of coagulation, while the relationship between v and dv/dt must be unaffected by the change of C_0 as is the case of Ostwald ripening. This criterion may be used for judging the growth mechanism of the AgCl particles after their initial precipitation.

Experimental Section

Chemicals. Polyoxyethylene (6) nonylphenyl ether (NP-6) was kindly provided by Lion Co. Ltd. The NP-6 as a liquid was mixed with butanol and washed with deionized pure water repeatedly.⁸ Then, the solution of NP-6 in butanol was filtered through a membrane filter of a pore size 0.2 μm (Toyo Roshi Kaisha, Ltd.). The solvent was evaporated and finally dried at 65 °C in a vacuum. Cyclohexane (Wako Pure Chemical Industries, Ltd.) was dehydrated with a type 3A molecular sieve

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and filtered through a membrane filter of a pore size 0.2 μm . AgNO_3 and KCl were used as received (Wako Pure Chemical Industries, Ltd.). Water used was distilled and deionized (Advantec, model GSR-200) and filtered through a hollow fiber filter with a pore size 0.04 μm .

Preparation of AgCl Particles in a Reverse Micelle System.

The standard procedure is as follows. Aqueous solutions of $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ AgNO_3 , $1.20 \times 10^{-2} \text{ mol dm}^{-3}$ KCl , and $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ KCl were prepared beforehand. The ion strength of these solutions was adjusted to 0.10 mol dm^{-3} by KNO_3 . Each of these salt solutions was admixed with 0.10 mol dm^{-3} NP-6 in cyclohexane to prepare three kinds of reverse micelle solutions. Here, R_w ($\equiv [\text{H}_2\text{O}]/[\text{NP-6}]$ in molar ratio) was fixed at 3. In the standard procedure, 30 cm^3 of the AgNO_3 reverse micelle solution and the same volume of the KCl ($1.20 \times 10^{-2} \text{ mol dm}^{-3}$ in water) reverse micelle solution at 30°C were added instantaneously to 100 cm^3 of the other KCl ($1.00 \times 10^{-3} \text{ mol dm}^{-3}$ in water) reverse micelle solution at 30°C at the same time under agitation by a magnetic stirrer. Then, the RM system was continued to be aged under constant agitation. The excess concentration of chloride ion in the water phase was kept at $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ during the aging process. The concentration of AgCl in the whole final system was $1.01 \times 10^{-5} \text{ mol dm}^{-3}$. At regular intervals, a part of the RM solution (15 cm^3) was sampled, and 0.06 cm^3 of a $10^{-2} \text{ mol dm}^{-3}$ 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) aqueous solution was added to halt any further process. Then, 6 cm^3 of methanol containing $10^{-3} \text{ mol dm}^{-3}$ of TAI was added to cause phase separation between the cyclohexane and the mixed solvent of methanol and water. The AgCl particles were collected by centrifugation (6000 rpm for 45 min) and dispersed in deionized water to be used as a TEM sample. All operations were conducted in photochemically inactive red light.

The experiments for the effect of the particle density on the growth rate were performed by changing the concentrations of AgNO_3 and KCl in their original aqueous solutions without changing the excess concentration of Cl^- ion ($1.00 \times 10^{-3} \text{ mol dm}^{-3}$ in water) and the ionic strength ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$ in water). For the effect of $p\text{Cl}$ on the growth rate, the excess concentration of Cl^- ion was changed with a constant molar concentration of AgCl (C_0) at $1.01 \times 10^{-5} \text{ mol dm}^{-3}$ and an ionic strength at 0.10 mol dm^{-3} . For the effect of ionic strength, the KNO_3 concentration in the aqueous phase of each RM solution of reactants was changed under otherwise standard compositions.

The mean diameter and mean volume of the particles were obtained from their TEM images.

Results and Discussion

Figure 1 shows TEM images of AgCl particles prepared in the RM solution under the standard conditions (see Experimental section). These images demonstrate the growing process of AgCl nanoparticles after the start of aging.

Since the reaction between silver and chloride ions is known to finish within 60 ms when RM solutions of salts of these ions mixed together in a stopped flow apparatus,^{9,10} the reaction between AgNO_3 and KCl in our RM system must have been completed, at longest, within a few seconds. Thus, the following particle growth must be due to coagulation among the particles initially precipitated or Ostwald ripening for the growth of relatively large particle by dissolution of the smaller ones.

Figure 2 shows relationships between aging time and the mean diameter of particles (\bar{l}) prepared with different concentrations of silver chloride. The concentration of AgCl was varied

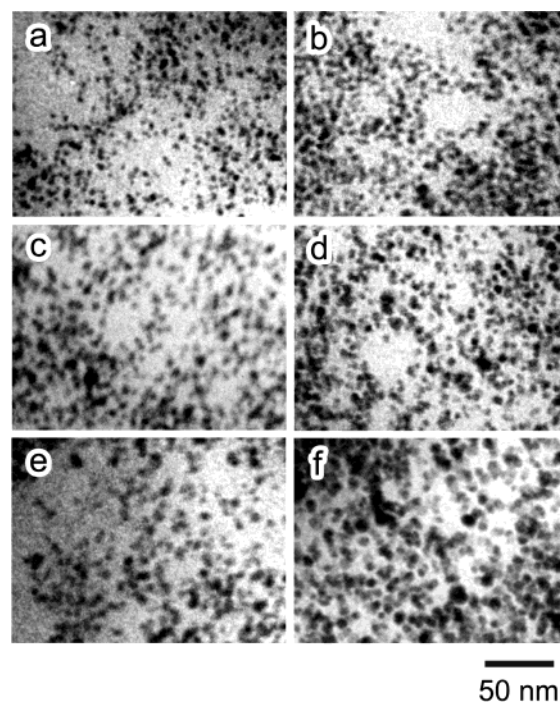


Figure 1. TEM photographs of AgCl particles at different growth stages under the standard conditions: (a) 2 min (b) 15 min, (c) 30 min, (d) 60 min, (e) 180 min, and (f) 360 min after the start of aging.

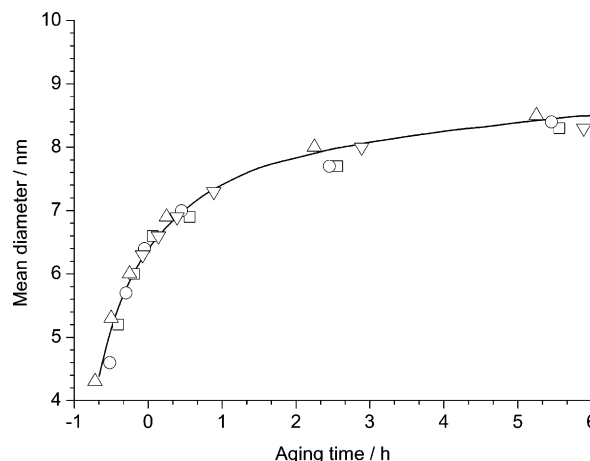


Figure 2. The relationship between the aging time and the mean particle diameter for different concentrations of AgCl (C_0): $C_0 = 5.06 \times 10^{-6} \text{ mol dm}^{-3}$ (\square), $1.01 \times 10^{-5} \text{ mol dm}^{-3}$ (\circ), $2.03 \times 10^{-5} \text{ mol dm}^{-3}$ (\triangle), and $5.06 \times 10^{-5} \text{ mol dm}^{-3}$ (∇). The zero point of the aging time was taken at the mean particle diameter 6.4 nm for all cases.

by changing the concentrations of AgNO_3 and KCl in the respective RM solutions while the excess concentration of Cl^- ion was kept at 10^{-3} ($\equiv p\text{Cl } 3$), where $p\text{Cl} \equiv -\log[\text{Cl}^-]$. In this figure, we provisionally chose a mean particle diameter 6.4 nm as the zero point of aging time ($t = 0$) for all systems with different AgCl contents to correct some time lags in the curves of mean particle diameter against real aging time among experimental runs. The negative aging time in Figure 2 thus represents a relative time before $t = 0$, when the mean particle diameter is less than 6.4 nm. In addition, Figure 2 demonstrates that the mean particle size reached a level as large as 8 nm or more, much greater than the mean size of the water pools of the reverse micelles (1.51 nm).⁷ Also, the solid line in Figure 3 exhibits \bar{v} as a function of \bar{v} , obtained from \bar{v} against t for $C_0 = 5.06 \times 10^{-6}$, 1.01×10^{-5} , 2.03×10^{-5} , and $5.06 \times 10^{-5} \text{ mol dm}^{-3}$, where \bar{v} is the mean particle volume and \bar{v} is the

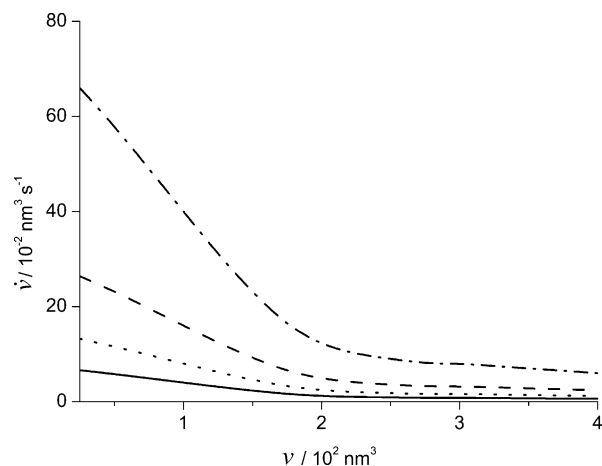


Figure 3. Volume growth rate (\dot{v}) as a function of the mean particle volume (v). The solid line (—) represents \dot{v} against v obtained from a single curve of v against t for $C_0 = 5.06 \times 10^{-6}$, 1.01×10^{-5} , 2.03×10^{-5} , and 5.06×10^{-5} mol dm $^{-3}$. The dotted line (···), dashed line (---), and chain line (— · — ·) stand for the curves of \dot{v} against v with $C_0 = 1.01 \times 10^{-5}$, 2.03×10^{-5} , and 5.06×10^{-5} mol dm $^{-3}$, respectively, as calculated using eq 3, on the basis of the coagulation model in which the solid line is assumed to correspond to the curve for $C_0 = 5.06 \times 10^{-6}$ mol dm $^{-3}$.

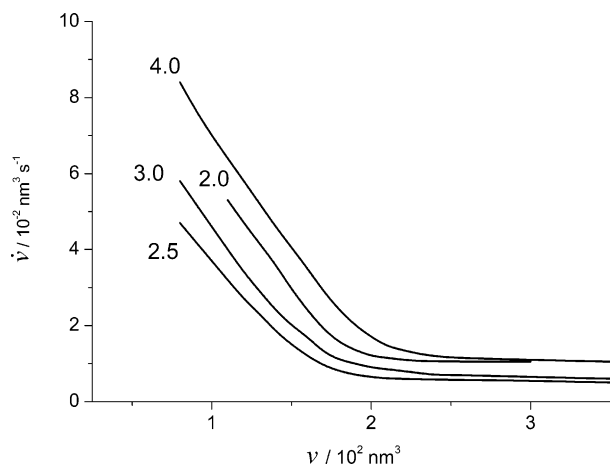


Figure 4. Volume growth rate (\dot{v}) plotted as a function of v with $C_0 = 1.01 \times 10^{-5}$ mol dm $^{-3}$ at different pCl values such as 2.0, 2.5, 3.0, and 4.0 (pCl $\equiv -\log[\text{Cl}^-]$).

growth rate in mean particle volume ($=dv/dt$), obtained from $v = \pi l^3/6$ with the continuous curve of l versus t in Figure 2. Since the relationship between v and \dot{v} is identical for the four different C_0 values, as represented by the solid line, the growth rate is completely independent of the number concentration of the AgCl particles in agreement with eq 4. On the other hand, if we postulate the coagulation model in which the solid line is assumed to correspond to the curve for $C_0 = 5.06 \times 10^{-6}$ mol dm $^{-3}$, the dotted line, dashed line, and chain line represent the expected curves of \dot{v} against v for $C_0 = 1.01 \times 10^{-6}$, 2.03×10^{-5} , and 5.06×10^{-5} mol dm $^{-3}$, respectively, as calculated from eq 3. Obviously, the experimental result supports eq 4 and not eq 3, and thus the growth of the AgCl particles is undoubtedly governed by the Ostwald ripening process, at least, within the range of the AgCl concentration of our study.

Figure 4 shows \dot{v} as a function of v with $C_0 = 1.01 \times 10^{-5}$ mol dm $^{-3}$ at different pCl values. The effect of the excess concentration of Cl^- ion on the growth rate may be ascribed to the effect of the solubility of AgCl, as supported by the parallelism between \dot{v} at mean diameter 6.4 nm and the solubility of AgCl as a function of pCl in the water phase of

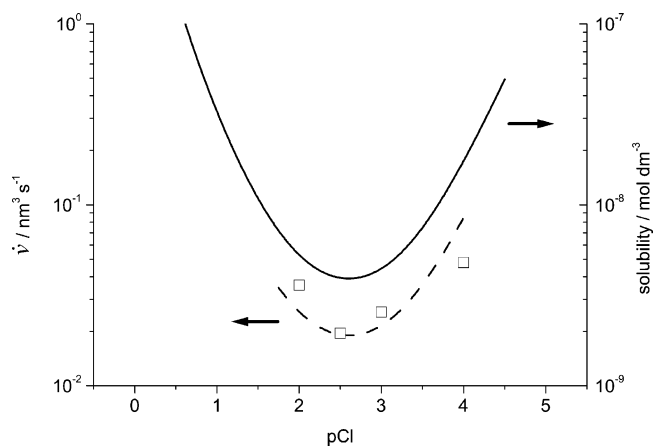


Figure 5. Volume growth rate (\dot{v}) at a mean diameter 6.4 nm in the standard RM system and the overall solubility of AgCl bulk solid estimated for the same RM system, as a function of pCl.

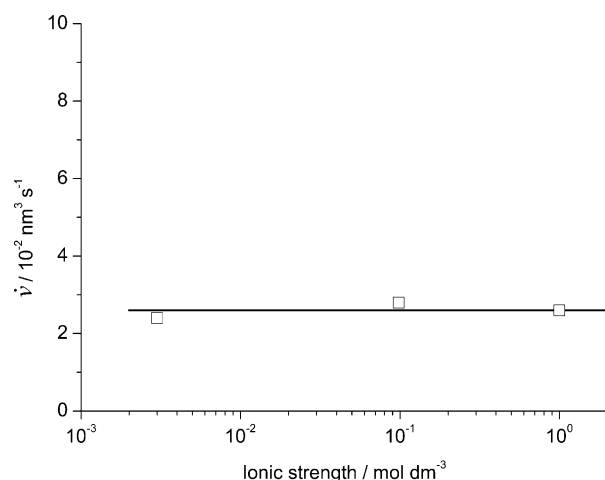


Figure 6. Dependence of the volume growth rate (\dot{v}) on the ionic strength in the water phase of the RM system with $C_0 = 1.01 \times 10^{-5}$ mol dm $^{-3}$.

the RM solution of the same composition at 30 °C⁷ in Figure 5.

According to Wagner's theory,¹¹ \dot{v} in diffusion-controlled Ostwald ripening in a closed system is proportional to the solubility of the solid C_∞ as

$$\dot{v} = \frac{32\pi\sigma DV_m^2}{27RT} C_\infty \quad (5)$$

where σ is the specific surface energy of AgCl solid, D is the diffusivity of the solute, R is the gas constant, and T is the absolute temperature. Although \dot{v} appears to depend on the mean particle volume in real systems, as found in Figure 4, Figure 5 shows that \dot{v} may approximately be proportional to C_∞ at a fixed particle size. Although the ionic strength in the water phase was kept constant at 1.0×10^{-1} mol dm $^{-3}$ in the experiments for the effect of pCl on the growth rate, there might be a possibility of some contribution of coagulation through the change of the surface electric charge of the AgCl particles by the alteration of pCl. If the contribution of coagulation is involved in this experiment, the growth rate may significantly increase with increasing ionic strength over a range including the standard ionic strength 1.0×10^{-1} mol dm $^{-3}$. However, the growth rate was kept constant in the range of ionic strength from 3.0×10^{-3} to 1.0 mol dm $^{-3}$, as shown in Figure 6, and thus one may conclude that the contribution of coagulation to

the growth of AgCl particles is not involved in the experimental range of the present study.

In the preceding paper, we concluded that the growth of AgCl particles in the RM system proceeded through Ostwald ripening and that the particle size was determined by the overall solubility of the solid in the RM system and the diffusivity of the reverse micelles and not by the size of the water pools of the reverse micelles, from the data analysis based on the double jet technique.⁷ The present study on the growth of AgCl nanoparticles in a closed RM system has clearly confirmed the conclusion of the preceding study from a different viewpoint.

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Note Added after ASAP Posting. This article was released ASAP on 3/2/2004. ν has been changed to $\dot{\nu}$ in figure captions

2, 3, 4, 5, and in paragraphs 4 and 5 of the Results and Discussion section. The correct version was posted on 3/5/2004.

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