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# FORMATION AND CHARACTERIZATION OF ULTRAFINE SILVER HALIDE PARTICLES

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## SUMMARY

Ultrafine silver chloride particles were precipitated by the reaction of silver nitrate and sodium chloride in microemulsion medium. The formation mechanism, aggregation state and colloidal stability of these ultrafine particles were studied by stopped-flow photometry, quasi-elastic light scattering, spectrophotometry, and electron microscopy. The ultrafine particles were found to be 50 to 100 A in diameter with very uniform size distribution. The dispersions of these particles were very stable as a result of the steric stabilization provided by the surfactant layer. The colloidal stability of such dispersions was found to increase as one decreased the chain length of alkane, decreased the concentration of alcohol, increased the chain length of alcohol, or added the nonionic surfactant Arlacel-20. The observation was explained from both equilibrium and dynamic points of view.

## INTRODUCTION

Preparation of monodispersed, ultrafine metallic particles has been one of the most pursued goals in many industries. It is, however, difficult to obtain small and nearly monodispersed particles by classical methods, particularly for particle sizes smaller than 10 nm. This difficulty stems from the fact that a lot of metallic particles sinter easily during the reactions of their precursor species (1). In practice, the precipitation of metallic particles has been done sometimes in the presence of protective colloids such as gelatins and surfactants to control the particle size. In this respect, water-in-oil (W/O) microemulsions have been shown to be ideal media for the precipitation of metallic particles (2-8).

Microemulsions are thermodynamically stable, isotropic dispersions consisting of microdomains of oil and/or water stabilized by an interfacial film of surface active molecules (9). The microstructure of microemulsions has been described as spherical droplets of 10-60 nm dispersed in the continuous medium (10-19), although it has also been reported that microemulsions may also exist as other structures such as bicontinuous (18,20-21) or cubic structure (22). Several experimental studies (23-25) have shown that the reacting species solubilized in the water pools of microemulsion droplets can exchange rapidly among different droplets so that reaction took place in the "cages" constituted by

the microemulsion droplets. This is made possible due to the energetic collisions among microemulsion droplets, which lead to the temporary fusion and split of droplets. Utilizing the dynamic nature, small dimension and uniform size distribution of microemulsions, several researchers (2-8) have successfully prepared, by precipitation in microemulsions, small and nearly monodispersed particles of various materials. However, there is little discussion on the mechanism of the growth of these ultrafine particles and the colloidal stability of such ultrafine particle dispersions. The importance of this knowledge cannot be over emphasized in the preparation of ultrafine particles in microemulsions. Furthermore, it is less known with regard to the effects of the microemulsion components on the precipitation in microemulsions, which would be extremely vital in designing the optimal formulation to precipitate ultrafine particles. This paper reports the results of our study on the precipitation of silver chlorides in microemulsions consisting of AOT (sodium di-2-ethylhexyl sulphosuccinate), alkane and aqueous solutions of metal salts. Particular attention has been focused on the discussion of the sequence of particle growth, the effects of microemulsion components on precipitation and the colloidal stability of dispersions.

## EXPERIMENTAL

### Materials

Silver nitrate of analytical reagent grade was purchased from J.T. Baker Chemical Co.. Sodium chloride and potassium chromate of certified reagent grade were purchased from Fisher. AOT of 99% sodium purity was from Sigma. Alkanes of 99 mole % purity, including n-hexane, n-heptane, n-octane, n-nonane, n-decane and n-dodecane, were purchased from Fisher. Alcohols of 99 mole % purity, including n-propanol, n-butanol and n-pentanol, were purchased from Sigma. Arlacel-20 was obtained from ICI Americas. All reagents were used without further purification.

### Methods

Sample preparation. Microemulsions containing different metal salts were prepared by solubilizing the salt aqueous solutions into AOT/alkane solutions under vigorous stirring. The precipitation of silver chlorides was done by mixing a microemulsion containing silver nitrate with the one containing sodium chloride.

Stopped-flow photometry. A stopped-flow apparatus can provide rapid and homogeneous mixing in 1 to 2 ms. In this study, the microemulsion containing silver nitrate was mixed, by stopped-flow method, with the one containing sodium chloride and the indicator, potassium chromate. Meanwhile, an attached

photometer was used to monitor the transmittance of the mixture at 420 nm (the characteristic absorption of silver chromate). The stopped-flow photometer used was purchased from Durrum Instrument Co. (Durrum Rapid Kinetics Systems Series D-100).

Quasi-elastic Light Scattering. Quasi-elastic light scattering (QELS) was used to monitor the variation of the hydrodynamic radius of the dispersions after mixing of microemulsions containing different metal salts. The optical source of the light scattering apparatus was a Spectra Physics Argon ion laser (model 2000) operating at 514.5 nm. The scattered light was collected at an angle of 90 degree by a laser light scattering goniometer (model 200SM) and was focused on a photomultiplier cathode (EMI-9865), both from Brookhaven Instrument. The time dependent correlation function of the scattered intensity was recorded by using a fast clipped real time correlator (model BI 2030) with 72 channels and a time resolution of 100 ns. During the measurement, the data were rejected to avoid any error caused by dust contamination if the difference between the calculated and measured baselines was greater than 1%. The normalized correlation function of the scattered electric field, $g^{(1)}(t)$, was analyzed by using the method of cumulant (26-27), in which the logarithm of the normalized $g^{(1)}(t)$ was fitted to a polynomial equation using a nonlinear least-square fitting routine. The fitting equation is described as follows:

$$\ln[(c_1 b)^{1/2} g^{(1)}(t)] = \ln(c_1 b)^{1/2} - \Gamma t + \mu_2(t^2/2!) \qquad [1]$$

where $c_1$ and b are baseline and instrument constant. The first cumulant, $\Gamma$, of linewidth distribution is equal to $Dq^2$, where D is the z-averaged diffusion coefficient. The magnitude of scattering vector, q, is defined as $q = (4\pi n/\lambda_o) \sin(\theta/2)$, where n is the refractive index of continuous medium, $\lambda_o$ the wavelength of light in vacuum and $\theta$ the scattering angle. The second cumulant $\mu_2$ provides the polydispersity of the linewidth distribution. The polydispersity, Q, is defined as $Q = \mu_2/\Gamma^2 = (\overline{D^2}-\bar{D}^2)/\bar{D}^2$. The hydrodynamic radius, $R_H$, was calculated by Stokes-Einstein equation $D = kT/(6\pi\eta R_H)$, where k is the Boltzmann constant, T the absolute temperature and $\eta$ the viscosity of the continuous medium.

Transmittance measurements. The transmittance of mixture was measured as the function of time at 550 nm after mixing the microemulsion containing silver nitrate with the one containing sodium chloride. The spectrophotometer used was from Perkin-Elmer (Model 575 UV-VIS Spectrophotometer).

Electron Microscopy. Electron microscopy study was done at The Major Analytical Instrumentation Center (MAIC) at The University of Florida. All electron micrographs were taken by a JEOL 200CX transmission electron

microscope. The samples were prepared by directly dropping a very small amount of silver chloride dispersion on the polyvinyl fomal film stretched on a copper mesh. Electron diffraction patterns of AgCl microcrystals were also taken by the same instrument. In the latter case, the voltage used is 200 kV and the camera length is 82 cm.

## RESULTS

### Completion of Reaction between Silver Nitrate and Sodium Chloride

Dvolaitzky et al. (5) have shown that the rapid exchange of reagents between water pools can be inferred from the instantaneous formation of a red silver chromate precipitate after mixing the microemulsion containing silver nitrate with the one containing sodium chloride and an indicator, potassium chromate. In this procedure, known as Mohr method (28), the chlorides were titrated by silver nitrate solution, and the indicator formed a red precipitate with an excess of silver nitrate solution after all chlorides have been precipitated as silver chlorides. Thus, the precipitation rate of silver chromate is negligibly small in the presence of $Cl^-$, and one would expect this rate to increase after the concentration of $Cl^-$ has decreased to a negligible level. We have used a stopped-flow photometer to monitor the precipitation rate of silver chromate through the decrease of the transmittance of the mixture at 420 nm, the characteristic absorption wavelength of silver chromate.

Figure 1.a shows a typical decay of the transmittance at 420 nm after mixing the microemulsion containing potassium chromate with the one containing silver nitrate. Note that the initial rise of the curve is due to the replacement of old sample (previous determination) with the fresh mixture. Immediately after that, the curve showed a quick and exponential decay. Figure 1.b shows the variation of transmittance at 420 nm after mixing the microemulsion containing silver nitrate with the one containing both sodium chloride and potassium chromate. We observed that the decay of transmittance was very slow initially due to the presence of chlorides. After approximately 60 ms, we found that the transmittance of the mixture suddenly dropped, and the transmittance decayed exponentially, indicating that the chloride concentration have been decreased to a negligible level.

### QELS Study During the Growth of AgCl Particles

We have used QELS to monitor the variation of the time dependent correlation function of the scattered light intensity after mixing the microemulsions containing different reactants. The system studied is AOT/n-heptane/metal salts aqueous solution, with [AOT] = 0.14 M (in heptane), $n_w/n_{AOT} = 8$, and $[AgNO_3] = [NaCl] = 0.4$ M (in water). Note that $n_w$ and $n_{AOT}$ are the number of water and AOT molecules. This sample did not show any variation in transmittance during

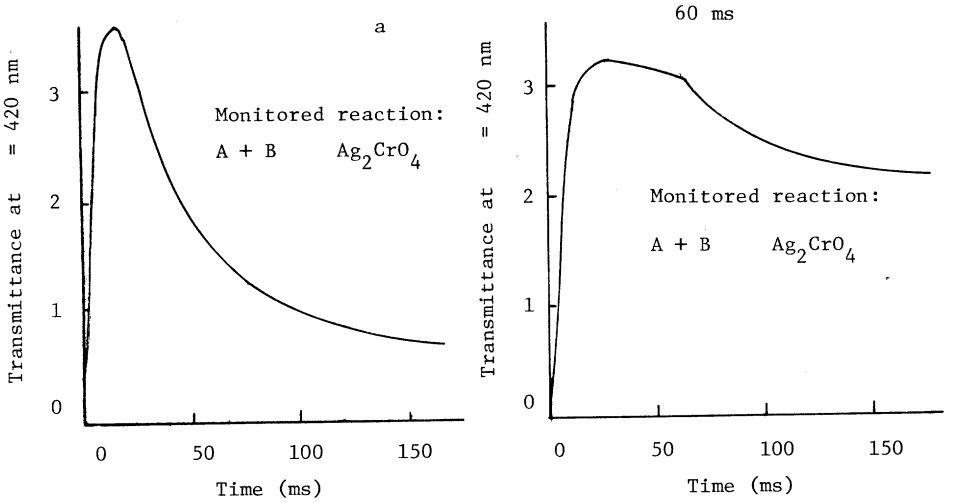



Figure 1. Decrease of transmittance at = 420 nm due to the formation of red silver chromate precipitate. (a) Controlled observation in the absence of NaCl, A: 15 mL AOT/n-heptane(o.15M) + 0.4 mL $AgNO_3$(0.4M), B: 15 mL AOT/n-heptane(0.15 M) + o.1 mL $K_2CrO_4$(0.077M) + 0.3 mL distilled water. (b) Inhibited precipitation in the presence of NaCl, A: same as in (a), B: same as in (a) except replacing distilled water with 0.4 M NaCl aqueous solution.

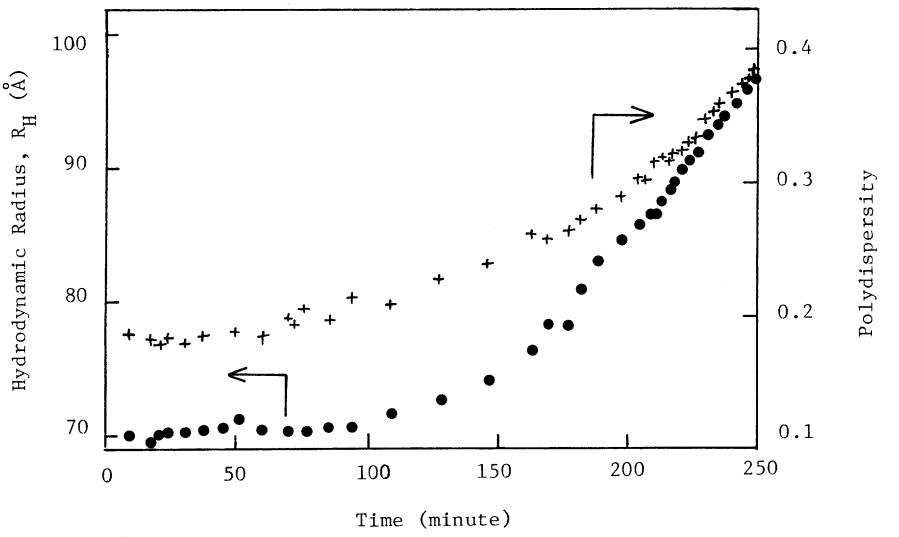



Figure 2. Effective hydrodynamic radius and polydispersity of particle dispersion as a function of time after mixing.

the QELS study and remained visually clear for weeks after mixing. By fitting the time dependent correlation function with equation [1], we obtained two important parameters, the first cumulant of linewidth, $\Gamma$, and the second cumulant, $\mu_2$. The z-averaged hydrodynamic diameter calculated from $\Gamma$ and the polydispersity were shown in Figure 2. It was found that both hydrodynamic diameter and polydispersity remained almonst constant initially and started to increase after approximately 100 minutes. We also noted that the microemulsions containing metal salts also showed strong time dependent correlation function in the scattered intensity before their mixing. Thus, the contributions of both AgCl microcrystals and microemulsion droplets have to be considered in the interpretation of Figure 2, although AgCl microcrystal are generally better scatters. The constancy of the hydrodynamic diameter and the low polydispersity suggested that we only observed a single mode of translational diffusion in the initial period of observation. This is consistent with the picture that in the initial stage the AgCl microcrystals are very small and restricted inside the microemulsion droplets. Thus, in this stage, AgCl microcrystals have to grow through the constant collision, fusion and split of microemulsion droplets. The increase in both polydispersity and mean hydrodynamic diameter inferred a more significant contribution of AgCl microcrystals to the observed correlation function of intensity, as a result of the growth or aggregation of microcrystals. The sudden increase in the polydispersity also suggested that the correlation time of the translational diffusion of microcrystals started to deviate from that of microemulsion droplets. Thus, the motion of microcrystal at this stage probably is not restricted in the "cages" of microemulsion droplets.

Effects of the Variation in Microemulsion Components

It is well known that the turbidity of the aqueous solution increases rapidly upon mixing silver nitrate and alkali halide in the absence of protective colloids. Matijevic and Ottewill (29-30) have attributed such turbidity increase to the fast coagulation and precipitation of silver halide sols. When precipitation occured in microemulsions, the increase of turbidity was drastically reduced or even negligible. Such slow increase in turbidity has been shown to be the slow flocculation of primary particles in dispersions by X-ray diffraction study (5). In this study, the variation of transmittance of the mixture has been monitored after mixing the microemulsion containing $AgNO_3$ with the one containing NaCl. The effects of microemulsion components on the variation of transmittance was studied by systematically changing various components of microemulsions. Basically, transmittance T is related to turbidity $\tau$ by (ref. 29):

$$T = I_t/I_o = \exp(-\tau l) \qquad [2]$$

for a scattering but non-absorbing sample, where $I_t$ and $I_o$ are respectively the intensities of transmitted and incident beams and l the length of optical path. For small particles ($r < \lambda/20$), $\tau$ is further related to the number of particles per unit volume, $N_p$, and their individual volume, $v_p$, by Rayleigh equation

$$\tau = AN_p v_p^2 = A \phi_p v_p \qquad [3]$$

where $\phi_p$ is the volume fraction of particles and A is an optical constant defined by

$$A = \frac{24 \pi^3 n_o^4}{\lambda^4} \frac{n^2 - n_o^2}{n^2 + 2n_o} \qquad [4]$$

In the above expression, n and $n_o$ are the refractive index of particles and solvent, while $\lambda$ is the wavelength of light used (in vacuo). Therefore, one expects the transmittance to decrease as the mean aggregated volume increases.

Figure 3.a shows the effect of alkane on the growth of AgCl microcrystal aggregates. In general, the growth rate increased as the chain length of alkane used was increased. It is noted that the microcrystal dispersions were relatively stable for the systems with n-hexane, n-heptane or n-octane, while only moderate stability (but still better than in aqueous medium) was observed in systems with n-nonane or n-decane. The effect of the addition of alcohols is shown in Figure 3.b. When n-pentanol was added to relatively stable n-octane system, the growth rate of microcrystal aggregates was greatly enhanced, and this enhancement increased with the amount of n-pentanol added. Figure 3.c shows the effect of the chain length of the alcohols used. The enhancement of the growth rate of aggregates was found to increase with the decrease of the chain length of the alcohol used. Thus, the addition of shorter-chain alcohol further destabilized the microcrystal dispersions. Figure 3.d shows the effect of the addition of long chain nonionic surfactant, Arlacel-20. For relatively unstable n-decane system, we found that the addition of Arlacel-20 improved the colloidal stability of microcrystal dispersions so that the growth rate of aggregates was greatly slowed down.

Electron Microscopy Study

We have used transmission electron microscopy to study the morphology and the aggregation state of AgCl microcrystals prepared from various microemulsions. In this study, the following variables were kept constant for all samples, i.e., [AOT] = 0.14 M (in alkane), [NaCl] = [$AgNO_3$] = 0.4 M (in aqueous solution), and $n_w/n_{AOT}$ = 8. Figures 4.a-b show the electron micrographs of

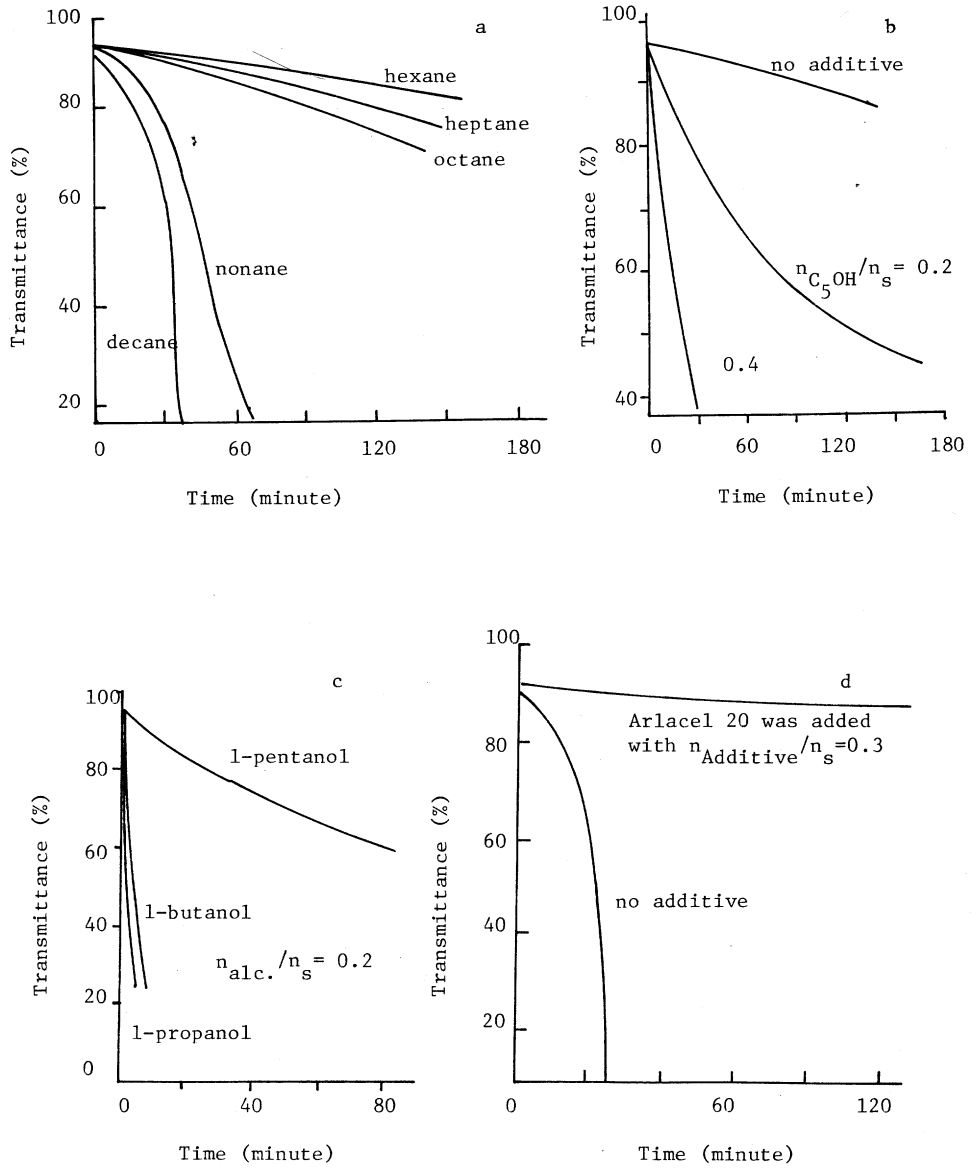


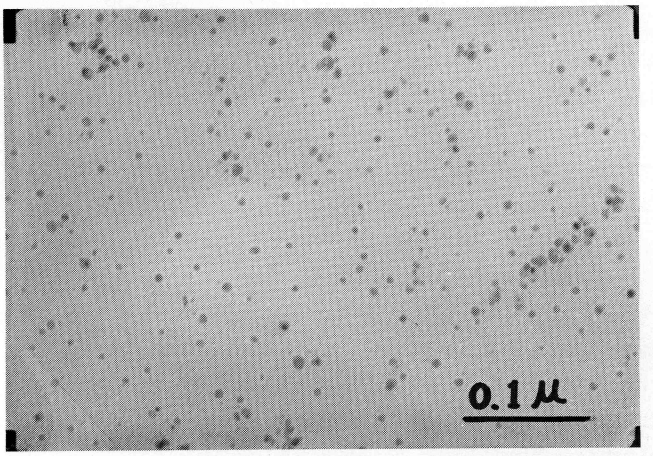

Figure 3. Variation of transmittance as a function of time. (a) Effect of chain length of alkane. (b) Effect of the addition of 1-pentanol. (c) Effect of the chain length of alcohol (d) Effect of nonionic surfactant, Arlacel 20.

AgCl microcrystals precipitated in n-heptane system at different time corresponding to 1 day and 1 week after mixing. As shown in these micrographs, no significant aggregation of AgCl microcrystals was observed even after 1 week, indicating this system is a very stable dispersion. We also noticed that this dispersion remained visually clear and did not show any sign of sedimentation. From these electron micrographs, the shape of AgCl microcrystals appeared to be very close to sphere and the size of AgCl particles was estimated to be 50 to 100 A. Figures 4.c-e show the electron micrographs of AgCl microcrystals precipitated in n-dodecane system. For this system at the above specified concentration, no significant aggregation was observed 4 hours after mixing. Note that the concentrations of surfactant used in TEM study are much smaller than in turbidity measurement. This may explain the observation of relative dispersed particles. Significant aggregation of AgCl particles was observed after 5 days. However, such aggregation of microcrystals seemed easy to be dispersed by sonication, as shown in Figure 4.e. The shape and the size of AgCl particles observed in this system are similar to that found in n-heptane system. The diffraction pattern of these microcrystals was also obtained by focusing electron beam on the selected area shown in Figures 4.d and 4.e. Four d-planes of AgCl crystal have been identified from these diffraction patterns, namely, (1,1,1), (2,0,0), (2,2,0) and (4,2,0). From the electron micrographs, it is easy to see that the big aggregates in Figure 4.d are consisted of many small microcrystals. We also noticed that the size of microcrystals did not show significant difference when precipitated in different systems.

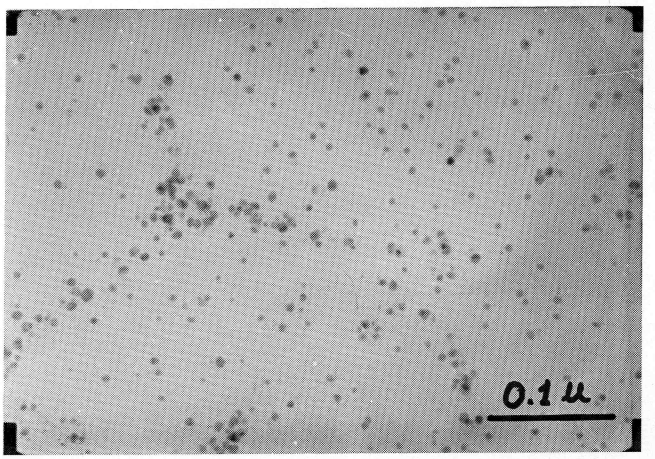
## DISCUSSIONS

### A Possible Sequence of the Events during Precipitation

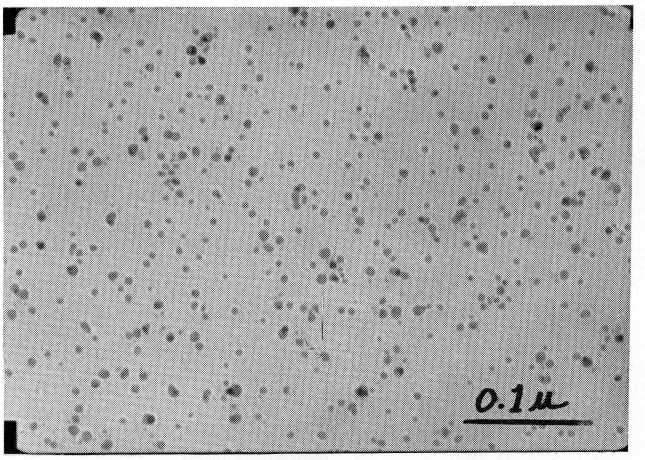
From the results presented in the preceeding sections, we can roughtly sketch a sequence of the events occurred during the precipitation of of silver chloride in microemulsions. First of all, we found that the reaction between $Ag^+$ and $Cl^-$ completed in a very short period of time (approximately 60 ms for the case studied). This observation is not surprising at all considering the time scale of the dynamic processes occurred in microemulsions. The time scale of the exchange of reagents in water pools has been reported to be less than 1 microsecond (31-35), although the presence of high ionic strength in the systems studied may slow down this exchange process (5, 24) due to the



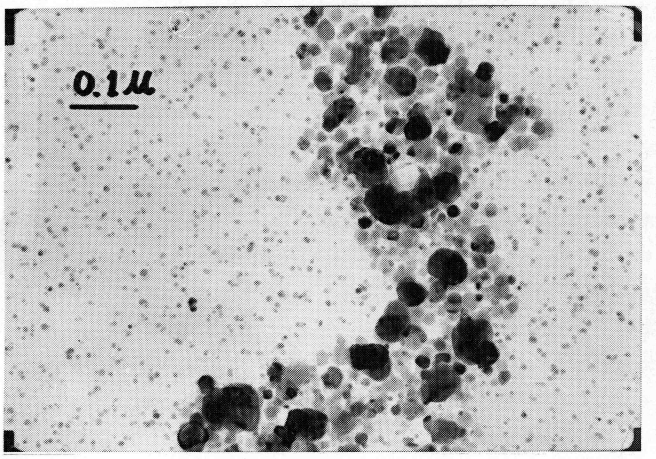

(a)



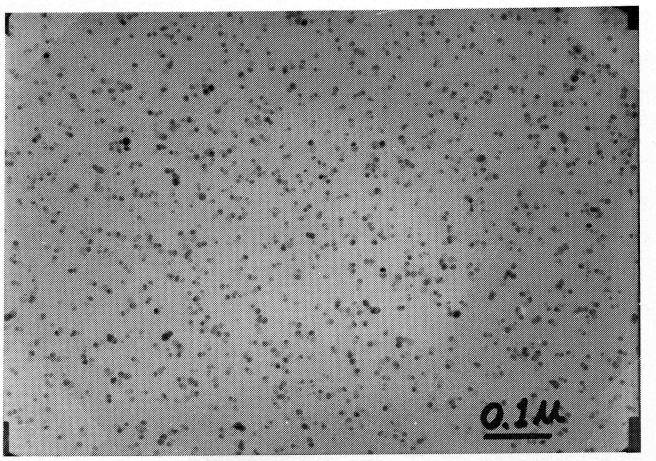

(b)




(c)




(d)




(e)

Figure 4. Transmission electron micrographs of AgCl particles precipitated in microemulsions; the composition is as follows: [AOT] = 0.14 M in alkane, [NaCl] = [$AgNO_3$] = 0.4 M in aqueous solution, $n_w/n_s$ = 8. (a) Picture taken 1 day after reaction with n-heptane as solvent. (b) Picture taken 1 week after reaction with n-heptane as solvent. (c)Picture taken 4 hours after reaction with n-dodecane as solvent. (d) Picture taken 5 days after reaction with n-dodecane as solvent. (e) Picture taken 5 days after reaction with n-dodecane as solvent; the sample was sonicated before being examined by TEM.

condensation of interfacial film. After the reaction was completed, the nucleation and the initial growth of microcrystals were expected to take place inside the microemulsion droplets through the collision, fusion and split of droplets. Such a realization is very important in explaining the ability of microemulsions to precipitate ultrafine particles by providing the steric barrier (interfacial film) to prevent these nucleus or microcrystals from rapid sintering. Considering the salt concentration we used (0.4 M in aqueous solution), the mass of AgCl in each droplet is only 1/200 of the amount needed to grow to a 50 Å AgCl particle, thus numerous of fusions have to occur during the growth of microcrystals either by the deposition of ions on growing nucleus and microcrystals or by the coagulation of these microcrystals. One would expect the former process to be the dominant one before the depletion of ions. The latter process, however, is the only way, if it is possible at all, for microcrystals to grow further after all ions have been depleted. One also expects more difficulty for larger microcrystals to diffuse through the channel opened during the lifetime of the transient dimer of droplets. On the other hand, there is not much difficulty for water to redistribute among the droplets. Once all these processes are over, the AgCl microcrystals probably are left with a layer of surfactants adsorbed on particle surface. At this stage, we can consider the following possibilities. On one hand, AgCl microcrystals can grow bigger through the coagulation of existing microcrystals. In this case, these AgCl particles have to overcome the energy barrier provided by the surfactanr film and stick long enough to sinter. The experimental results showed that most of the AgCl particles obtained were about 50 to 100 Å in diameter. Thus, this process must stop, if it exists at all, when microcrystals grow to this size. On the other hand, these microcrystals can present as a fairly stable dispersion or undergo slow flocculation (aggregation of microcrystals). This picture seemed to be consistent with the experimental results of this study and Dvolaitzky et al. (5).

Stability of the Ultrafine AgCl Particles Formed in Microemulsions

For dispersions of fine particles in liquid media, encounters between particles frequently occur due to Brownian motion and gravitation. Whether such encounters result in permanent contact or the particles rebound and remain free is determined by the inter-particle forces between them. In the dilute dispersions such as the case we considered, it is sufficient to consider only interaction between pairs of particles. Thus, the work, $V_t$, required to bring the particle surface from infinity to an inter-particle distance, h, is given by $V_t(h) = F(h) - F(\infty)$, where $F(\infty)$ represented the total free energy contributed from all interparticle forces at infinite separation of two particles. Therefore, we can write

$$V_t = V_A + V_S + V_E \qquad [5]$$

where $V_A$, $V_S$ and $V_E$ are the potential energies due to van der Waals attraction, steric interaction and electrostatic repulsion.

Our theoretical calculation (36) revealed that $V_S$ and $V_A$ are relatively large and comparable in magnitude, while the magnitude of $V_E$ is negligibly small, indicating that the electrostatic repulsion is not significant compared to either van der Waals attraction or steric repulsion. Furthermore, the results showed that the magnitude of the primary maximum decreased when the chain length of alkane used increased o that the solvancy became poor. This may partly explain the observation of the increase in the growth rate of microcrystal aggregates with alkane chain length. Nevertheless, it is disputable whether the increase of alkane chain length from $C_6$ to $C_{12}$ could induce so drastic change in the solvency that the instability of the dispersion was induced. Thus, other factors may also need to be considered to fully explain the observed enhancement of the flocculation of AgCl particles. The effect of surfactant adsorption was also analyzed by the same calculation. For a marginally good solvent, the decrease of volume fraction from 0.3 to 0.1 eventually eliminated the primary maximum and totally destabilized the particle dispersions. This result may partly explain the profound effects of the addition of short chain alcohols or long chain nonionic surfactant Arlacel-20.

Dynamic Point of View

It is important to notice that the precipitation of AgCl is *in statu nascendi* when using microemulsion as reaction media. One would expect the dynamic processes of microemulsions have significant influences on reaction, nucleation and crystal growth. Thus, it is pertinent to discuss, from the dynamic point of view, the effects of the variation in microemulsion components on the observed transmittance variation. If we assumed the commonly used second order flocculation kinetics (37-38), i.e.,

$$\frac{dN_p}{dt} = -\frac{k_o}{W} N_p^2 \qquad [6]$$

where $k_o = 4kT/(3\eta)$ and

$$W = 2a \int_{2a}^{\infty} \frac{\exp[V(R)/(kT)]}{R^2} dR \qquad [7]$$

Thus, the flocculation rate is also dependent on the concentration of particles. One would expect that the number of the particles precipitated in the initial stage depends on the effectiveness of the collision and fusion of the

microemulsion droplets. This effectiveness of mass exchange has been shown (33-34) to strongly depend on the fluidity of the interface of microemulsion droplets. A more fluid interface not only facilitates the exchange of the content of water pools during the collisions, but also drastically increases the attractive interaction between microemulsion droplets, which may further increases the frequency of sticky collisions. From many studies on the dynamics and the inter-droplet interaction of microemulsions, it has been shown that (39-41) the droplet interface became more fluid and the inter-droplet interaction became more attractive as one increased the chain length of alkane, or increased the concentration of alcohols, or decreased the chain length of alcohols. or decreased the concentration of the nonionic surfactant Arlacel-20 (42). Therefore, one would expect the increase in the number of particles due to more effective collisions when the microemulsion components were changed as described above. Our observation of the effects of the microemulsion components on the variation of transmittance thus can also be accounted for by the above explanations from the dynamic point of view.

## CONCLUSIONS

We have studied the precipitation of AgCl in Microemulsions by uing stopped-flow photometry, quasi-elastic light scattering, spectrophotometry and transmission electron microscopy. We also analyzed the colloidal stability of the dispersions of ultrafine AgCl particles formed in microemulsions. The following conclusions were made based on the experimental results and foregoing discussions.

1. The reaction between $AgNO_3$ and NaCl in microemulsion media was completed in a very short period of time (approximately 60 ms for the studied case), as would be expected from the dynamic nature of microemulsions.

2. Ultrafine AgCl particles were obtained by precipitation in microemulsions. From the electron micrographs, the particle size was found to be 50 to 100 Å and the distribution of particle size appeared to be very uniform. From the analysis of electron diffraction patterns, the face-centered cubic lattice structrue of AgCl was identified.

3. The dispersions of these AgCl microcrystals were found to be very stable. Some dispersions (such as n-heptane system) can stay visually clear for weeks. From the TEM study, such system did not show any significant aggregation of particles even after 1 week.

4. From the transmittance and TEM studies, some dispersions were found to undergo very slow but reversible flocculation. The aggregates observed appeared to be consisted of many small AgCl particles with the same size as the dispersed particles. No significant difference in the size of primary particles was found from system to system.

5. The colloidal stability of the dispersions of AgCl ultrafine particles was found to increase as one decreased the chain length of alkanes, decreased the concentration of short chain alcohols, increased the chain length of the alcohols, or added the nonionic surfactant Arlacel-20.

6. The analysis of the colloidal stability of the dispersions revealed that the most important stabilization factor is the steric barrier provided by the surfactant film adsorbed on the particle surface. On the other hand, the electrostatic repulsion is negligibly small.

ACKNOWLEDGEMENT

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