# Effects of the Intermicellar Exchange Rate and Cations on the Size of Silver Chloride Nanoparticles Formed in Reverse Micelles of AOT

Rahul P. Bagwe and Kartic C. Khilar*

*Department of Chemical Engineering, Indian Institute of Technology, Mumbai-400 076, India*

Nanoparticles of silver chloride have been synthesized by the method of mixing of two microemulsions, one containing silver ions and other containing chloride ions. The effects of changing the intermicellar exchange rate by varying the continuous phase, by adding benzyl alcohol, and by varying the water to surfactant molar ratio as well as the effect of cations (metal chlorides from the first and second group of the periodic table) on the particle size and the size distribution and the number density have been studied. The particle diameters are measured from the photomicrographs obtained by transmission electron microscopy. The average particle size, the polydispersity, and the number of particles formed are shown to be dependent on the intermicellar exchange rate and/or the rigidity of the surfactant shell. This dependency can be qualitatively explained by means of nucleation and growth phenomena, as mediated by the intermicellar exchange of contents.

## 1. Introduction

Synthesis of nanoparticles is an emerging field in material science, as they exhibit novel and useful material properties which differ from bulk properties.[1] Synthesis using reverse micelles seems especially suited to tailoring particle properties at the nanolevel. In these systems, nanodrops (3−30 nm) of the aqueous phase are trapped within aggregates of surface active molecules dispersed in an external oil phase.[2−4] The surfactant-stabilized cavities (reverse micelles) provide a cagelike effect that can control nucleation, growth, and agglomeration.[2,5−7] Given, the scale of surfactant aggregates, the solubilized reactant species are effectively distributed in separate "microreactors" at the molecular level. Thus, a unique capablity to control nucleation and growth is achieved. The feasibility of the microemulsion-based synthesis method for production of various colloidal particles has been extensively demonstrated for a number of materials.[2,7] However, data on the effect of the dynamic properties of the microemulsion on particle size and polydispersity are found to be scarce. In this paper we have attempted to study the effects of intermicellar exchange rate on particle size and the size distribution of silver chloride nanoparticles. In addition, the effect of cations of reactants on the formation of particles is also investigated. The intermicellar exchange rate is varied by varying the continuous medium, by adding benzyl alcohol, and by varying the water to surfactant molar ratio (R). Silver chloride nanoparticles find application in the photographic industry.

Various research groups have synthesized silver halide nanoparticles using the reverse micellar route.[8−13] These studies have clearly documented that silver halide nanoparticles can be synthesized using the technique of mixing microemulsions of silver nitrate and chloride salt. The intermicellar exchange of solubilizate and subsequent reaction can be thought of consisting of a number of sequential elementary steps as follows:[14] (1) Brownian diffusion of reverse micelles; (2) surfactant layer opening and coalescence (fusion); (3) diffusion of solubilizate molecules; (4) reaction between solubilizate molecules; and (5) decoalescence (fission) to return as reverse micelles. The time scales of these five basic rate processes may differ substantially, and the slowest step will scale the temporal aspects of exchange between reverse micelles containing reactant solubilizates. Information on the time scale of the processes of the micellar fusion and fission steps is not available while reasonable estimates of other time scales can be obtained. Furthermore, it is likely that not all collisions can lead to fusion. Under these circumstances and considering the fact that, excluding the last step, other steps are second-order processes, it has been a practice to represent the intermicellar exchange rate in terms of a second-order rate constant, $k_{ex}$.

## 2. Experimental Section

**2.1. Materials.** AOT or Aerosol OT (dioctyl sulfosuccinate) of 99% purity was obtained from Sigma and was used as received. The salts such as silver nitrate and chloride salts of alkali and alkaline earth metals were purchased from S. D. Fine Chemicals,

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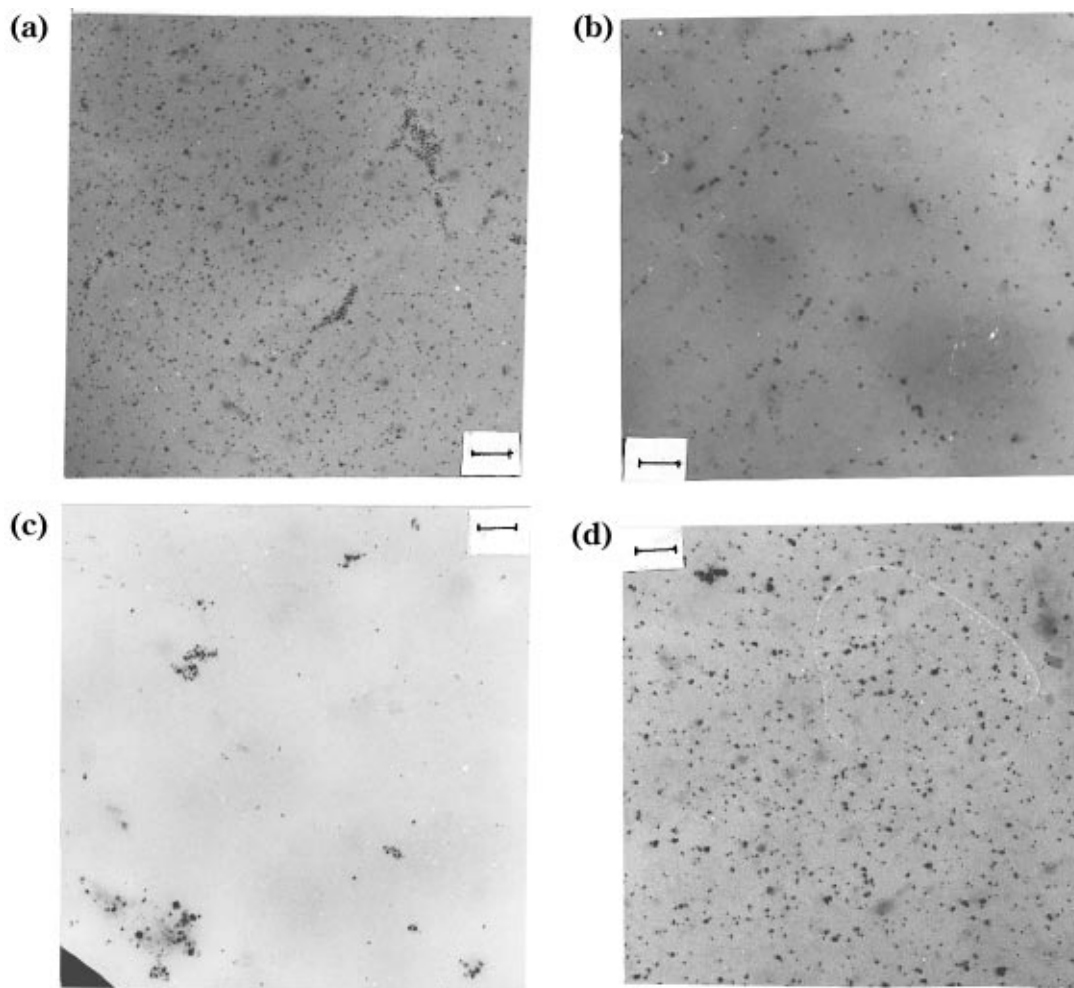(17) Hatton, T. A.; Bommarius, A. S.; Holzwarth, J. F. *Langmuir* **1993**, *9* 1241.

**Figure 1.** Transmission electron micrograph of silver chloride particles prepared in AOT microemulsion showing the effect of organic solvent and additives. The mark represents 133 nm: (a) decane; (b) heptane; (c) cyclohexane; (d) benzyl alcohol added to AOT/heptane.

India, and were of AR grade. The water used for the preparation of electrolyte solutions was doubly distilled. The organic solvents were procured from SISCO research laboratories, India and were of HPLC grade.

**2.2. Methods.** *2.2.1. Sample Preparation.* The microemulsions were prepared by adding aqueous salt solutions of silver nitrate (0.1 N) or metal chlorides (0.1 N) from group I or II of the periodic table to the AOT/alkane solution (0.1 M). To reach a finer and more stable state of the microemulsion, an ultrasonic bath was used. The method was also used by Nagy and co-workers.[12]

*2.2.2. Transmission Electron Microscopy.* The transmission electron microscopy measurements for finding the particle size were carried out at Cancer Research Institute, Mumbai, at an operating voltage of 80 kV. The electron micrographs were obtained with a transmission electron microscope (Zeiss model 109, Germany). Approximately 12 h after mixing of the microemulsions containing reactants, several drops of the mixture were diluted under vigorous shaking in 1 g of alkane solution. Several drops of this last dilution was then deposited on a TEM copper grid covered with Formvar and carbon. In order to characterize the population of synthesized particles, their diameters were measured with the aid of an Image Pro Plus image analyzer system.

### 3. Results and Discussion

**3.1. Effect of the Continuous Phase.** In this study, silver chloride nanoparticles were prepared in AOT microemulsions with cyclohexane, *n*-heptane, and *n*-decane, as the oil phase. The micellar dynamics is affected by changing the chain length of the oil phase. The longer the chain length of the oil, the more difficult it is to

penetrate into the surfactant tail and align itself parallel to the surfactant tails. As a result, the extent of interaction between surfactant tail and the solvent chain decreases with an increase in chain length of the alkyl solvent. On the other hand, interdroplet tail–tail interaction of two surfactant molecules increases, due to the weak presence of solvent molecules in the tail region of the droplet. The net effect results in an increase in the micellar exchange rate with an increase in the chain length of the alkyl solvent. In the case of cyclohexane, the molecules penetrate between surfactant tails, leading to an increase in surfactant curvature and rigidity. The micellar exchange rate constants for cyclohexane, *n*-heptane, and *n*-decane are of the order of $10^6$, $10^7$, and $10^8$ $M^{-1}$ $s^{-1}$, respectively.[19]

Figure 1a–c shows transmission electron photomicrographs of silver chloride nanoparticles using various organic solvents. The particles are spherical in *n*-heptane and *n*-decane while there are spherical and cubical particles in the AOT/cyclohexane medium. We further

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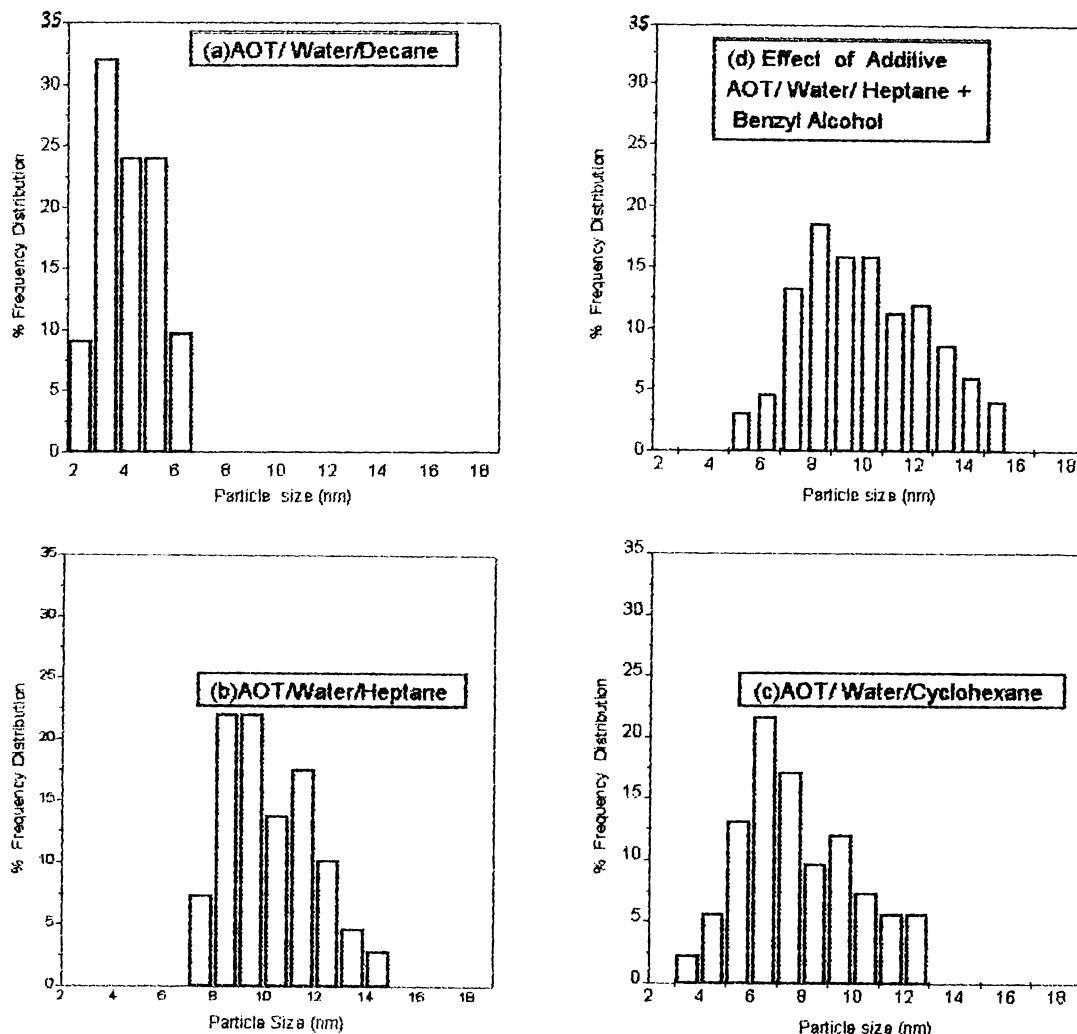
**Figure 2.** Size distribution of silver chloride nanoparticles showing the effect of solvent and additive.

**Table 1. Effect of the Intermicellar Exchange Rate Coefficient on the Average Particle Size**

| system | $k_{ex}$,[a] $M^{-1}$ $s^{-1}$ | $d_p$,[b] nm | $\sigma_d$,[c] nm | $N_{Ag^+}/N_m$[d] |
|---|---|---|---|---|
| (A) Effect of Oil Phase | | | | |
| AOT/cyclohexane | $10^6$ (19) | 7.6 | 2.44 | 2.87 |
| AOT/heptane | $10^7$ (19) | 10.1 | 1.88 | 2.87 |
| AOT/decane | $10^8$ (19) | 4.4 | 1.16 | 2.87 |
| (B) Effect of Additive | | | | |
| AOT/heptane and benzyl alcohol | $10^9$ (25) | 9.9 | 2.21 | 1.69 |

[a] The reference from which the value of $k_{ex}$ is taken is given in parentheses. $k_{ex}$ = second-order exchange rate constant. [b] $d_p$ = number average particle size. [c] $\sigma_d$ = standard deviation = $[\sum_{i=1}^{N} (d_i - d_p)^2/N - 1]^{1/2}$. [d] $N_{Ag^+}$ = number of Ag ions. $N_m$ = number of micelles = $V_{sol.AgNO_3}/(^4/_3\pi r_m^3)$ with $r_m$ = radius of micelle and $V_{sol.AgNO_3}$ = volume of aqueous silver nitrate solution.

observe that in the AOT/decane medium the particles formed are smaller in size and larger in number as compared to those in the other two systems. The size distributions obtained in various cases are shown in the form of a histogram in Figures 2a–c. From the histograms, we observe that the size and size distribution are influenced by changing the solvent. A unimodal size distribution similar to the micellar size distribution was found for all three solvents. However, in the case of cyclohexane the size distribution is relatively broader.

Table 1 presents the data on the silver ion occupancy number and the number average diameter of the silver chloride particles formed. In calculating the number of reverse micelles, it is assumed that the aggregation number does not change in the presence of silver and chloride ions. It can be seen from the table that the number average particle size decreases as one goes from heptane to decane, i.e. at high $k_{ex}$, and that again it decreases at low $k_{ex}$, i.e. in cyclohexane. There are corresponding changes in the number density of particles, and the calculations show that the ratio of the number of particles formed to the number of micelles is typically of the order of $10^{-4}$.

Recent simulation and experimental studies have shown that the final particle size is a function of the water to surfactant molar ratio ($R$), the concentration of the reactant species, the ion occupancy number, the initial distribution of the reactant, the water core size, and the intermicellar exchange coefficient.[16,17] In our experiments, we have kept the water to surfactant molar ratio and the concentration of reactant species the same in all cases. Therefore, the only parameter that can influence the particle size is the intermicellar exchange rate coefficient ($k_{ex}$).[15] For intramicellar nucleation to occur the number of ions present inside the micelle should be greater than the critical nucleation number. A value of at least 2 has been proposed for the synthesis of $Co_2B$ and $Ni_2B$ particles, as required by the stoichiometry.[24] The higher the number of micelles having a number of ions greater than the nucleation number, the higher will be the number of nuclei formed. At high $k_{ex}$, i.e. in decane, due to rapid collision

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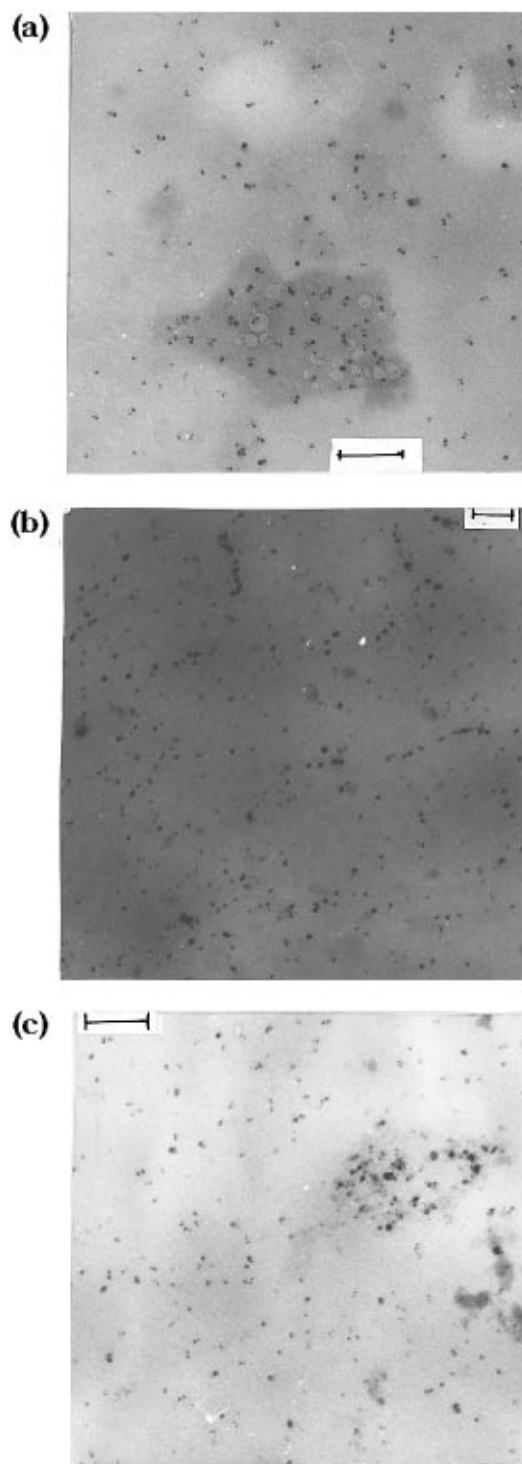(25) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103* (12), 3543.

**Figure 3.** Transmission electron micrograph of silver chloride nanoparticles prepared in AOT microemulsion showing the effect of the water to surfactant molar ratio. The mark represents 133 nm: (a) $R = 5$; (b) $R = 10$; (c) $R = 15$.



**Figure 4.** Size distribution of silver chloride nanoparticles showing the effect of the water to surfactant molar ratio.

between micelles, there will be rapid exchange of material, which results in the formation of a larger number of micelles with the number of silver chloride atoms greater than the critical nucleation number. This will result in smaller particle size, as the number of silver chloride atoms left for growth will be relatively low. In addition, a relatively larger number of particles will be formed. In the case of heptane the exchange rate coefficient decreases by an order of magnitude. Slow exchange of materials will lead to formation of a smaller number of nuclei of silver chloride. Consequently, a higher amount of silver chloride atoms as compared to that in the case of decane
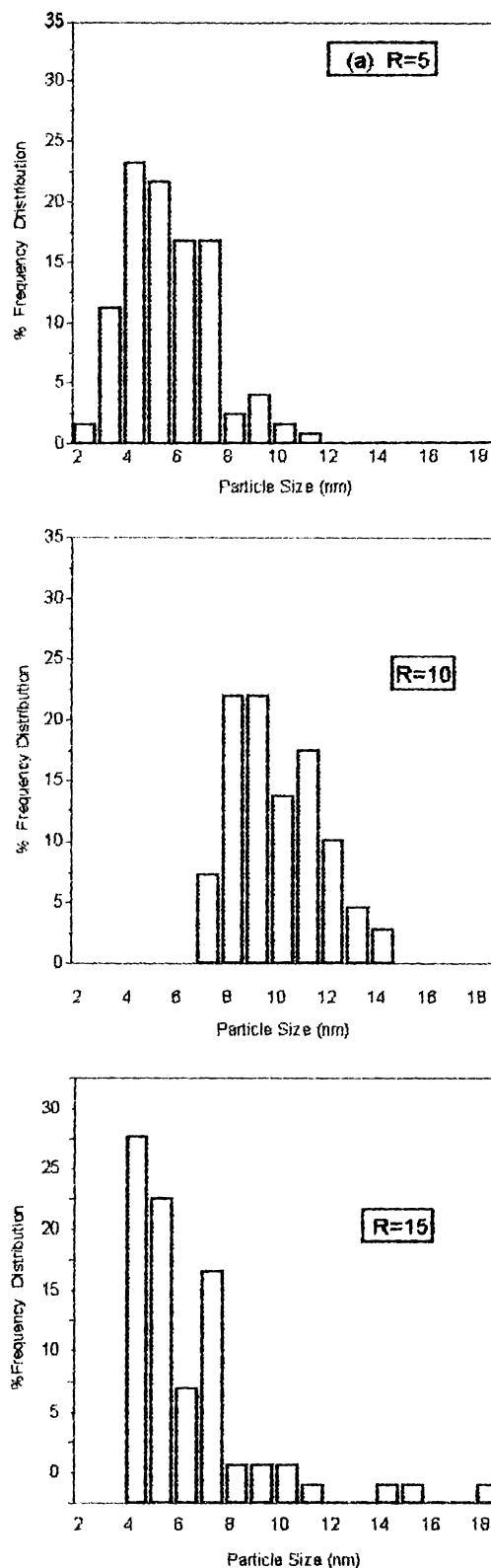
will be available for growth. Hence the terminal particle size is found to be larger than that in the case of decane. In the case of cyclohexane, the surfactant layer is believed to be rigid and hence the exchange rate is slow. The slow exchange rate adversely affects the formation of metal atoms. Therefore, the nucleation and growth processes continue in parallel, resulting in a broader range in the size of the particles, as seen in Figure 2c. In the case of heptane with benzyl alcohol as an organic phase, the
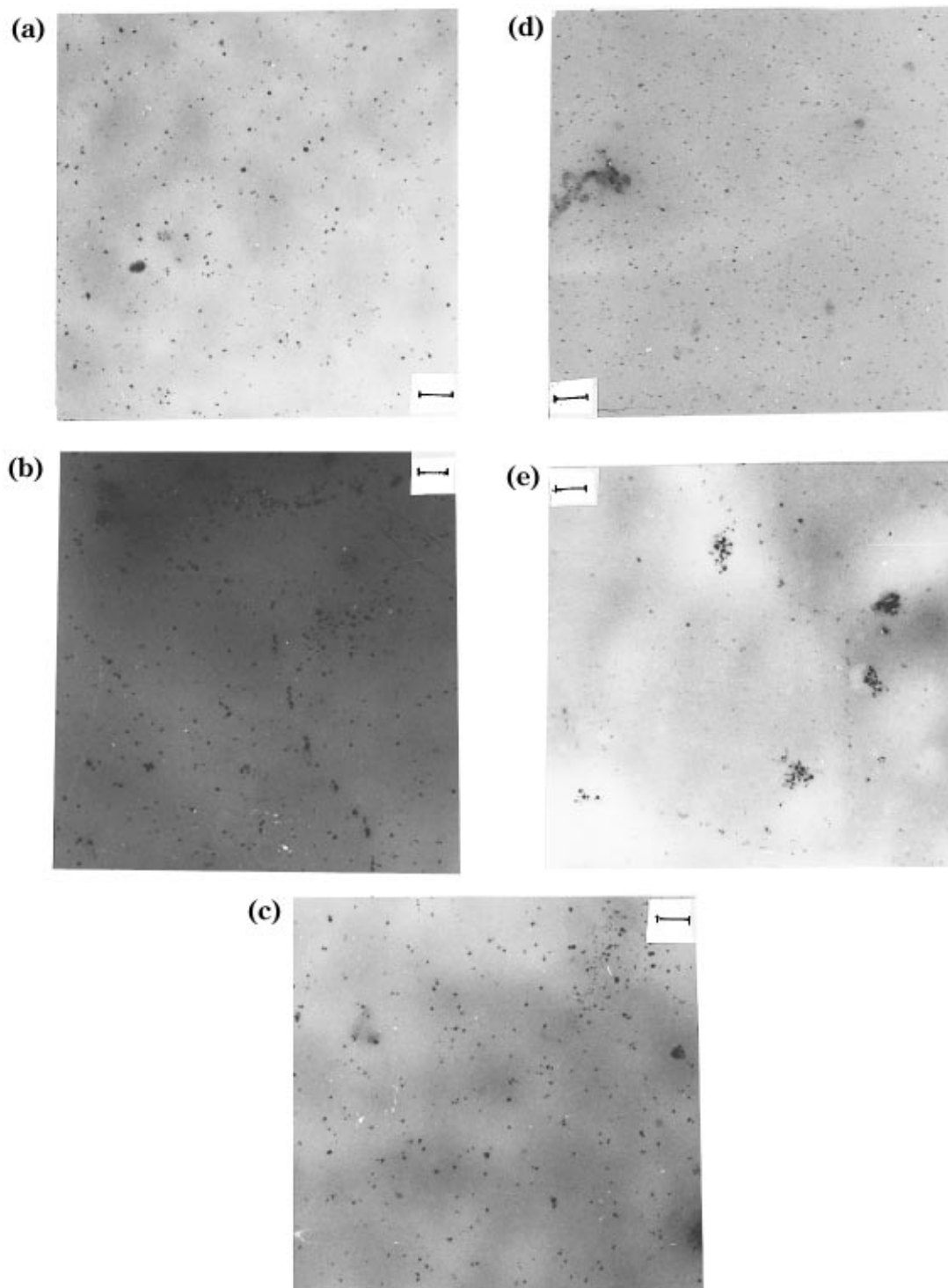
**Figure 5.** Transmission electron micrograph of silver chloride particles prepared in AOT microemulsion showing the effect of cations. The mark represents 133 nm: (a) LiCl; (b) NaCl; (c) KCl; (d) CsCl; (e) CaCl$_2$.

**Table 2. Effect of the Water to Surfactant Molar Ratio on the Occupancy Number and the Average Particle Size**

| $R^a$ | $d_p,^b$ nm | $\sigma_d,^c$ nm | $N_m^d$ | $N_{Ag^+}/N_m^c$ |
|-------|------------|------------------|---------|-------------------|
| 5 | 5.7 | 1.02 | $4.2 \times 10^{18}$ | 0.62 |
| 10 | 10.1 | 1.88 | $1.9 \times 10^{18}$ | 2.87 |
| 15 | 5.7 | 2.3 | $5.1 \times 10^{17}$ | 7.9 |

$^a$ $R$ = water to surfactant molar ratio. $^b$ $d_p$ = number average particle size. $^c$ $\sigma_d$ = standard deviation. $^d$ $N_m$ = number of micelles. $^e$ $N_{Ag^+}$ = number of Ag ions.

surfactant layer becomes fluid-like due to the penetration of the benzyl alcohol molecule into the interfacial region.[18] The increased water/oil interfacial area brought about by the presence of benzyl alcohol induces a rearrangement in the system, resulting in an increase in the number and a decrease in the size of the reverse micelles, as shown in Table 1. Therefore, there is a proportional decrease in the average number of Ag ions per micelle. The size and size distribution of the particles formed in this case can be observed from Table 1, the photomicrograph (Figure 1d), and the histogram (Figure 2d). We observe that the average particle size is larger and that there is a wide size distribution of the particles. In this case, a large number of nuclei are formed initially due to the higher exchange rate, resulting from the labile interface. Some of these nuclei then aggregate to form larger particles, hence
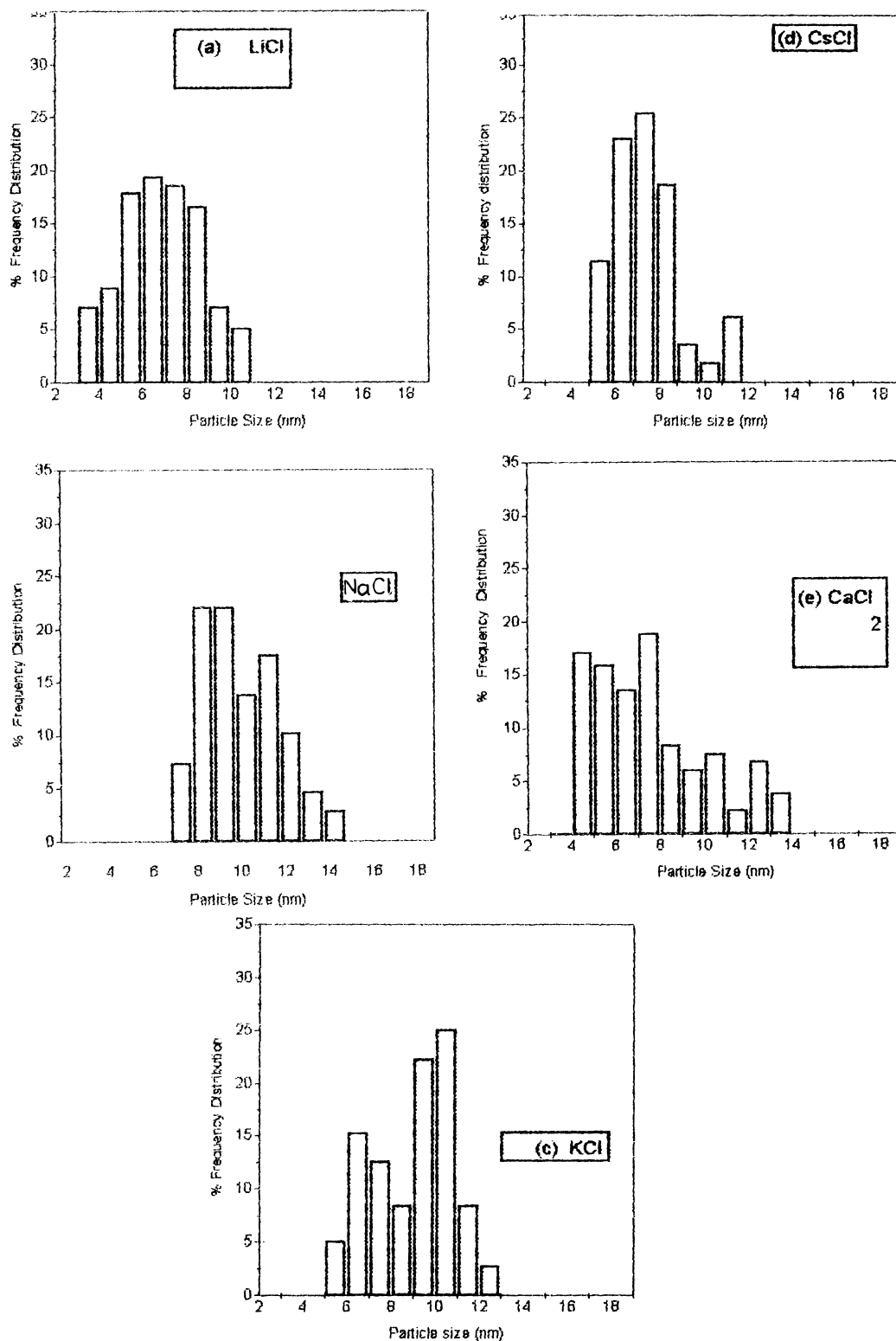
**Figure 6.** Size distribution of silver chloride nanoparticles showing the effect of cations.

resulting in a wide size distribution. A similar observation was made by Modes and Lianos[20] for CdS particles prepared in AOT/heptane and benzyl alcohol systems.

**3.2. Effect of the Water to Surfactant Molar Ratio.** In this part, the effect of the water to surfactant molar ratio (*R*) on the particle size and size distribution is studied. This is a well studied effect, and there is a consensus that, with an increase in *R*, the particle size initially increases and then decreases.[21,22] Explanations vary, and these are mostly related to the concept of bound water and the rigidity of the surfactant layer. The particle size was

measured at the *R* values 5, 10, and 15. The radius of the microemulsion at different *R* values is given by $r_m = (1.8R + 4.5)$ in angstroms.[16] As expected, the average particle size increased from $R = 5$ to $R = 10$ and then it decreased at $R = 15$. The increase in *R* affects two parameters, crucially important to the formation of particles: the average occupancy number of the ions and the micellar exchange rate coefficient. Both these parameters increase with an increase of *R*. The increase in occupancy numbers, however, is expected to be more significant than that in the exchange rate coefficent. As shown in Table 2 the

average occupancy increases from 0.62 to 7.9 as $R$ increases from 5 to 15.

At $R = 5$, the average occupancy is below 1, and hence for nucleation to occur, intermicellar exchange of silver chloride atoms must occur. As the interface is rigid due to close packing of the head groups the number of successful collisions leading to exchange of matter is less. Hence, a smaller number of nuclei will be produced and the particle size is expected to be large. The smaller size and smaller number of particles as observed by TEM photograph (Figures 3 and 4) indicate that the rate of growth of particles is slow. At $R = 15$, there are some structural changes in reverse micelles. The water is present now as free water molecules, i.e., it is no longer bound to the interface. As a result, the ions are mobile. From Table 2 one observes that the average ion occupancy is very high due to an increase in the micellar size. This condition favors intramicellar nucleation. Moreover an increase in $R$ favors a greater intermicellar exchange rate due to an increase the fluidity of the interface. All these conditions favor rapid formation of nuclei, resulting in a smaller number average particle size.

When the $R$ value is equal to 10, the average occupancy is greater than that at $R = 5$ but less than that at $R = 15$. Also the water present is in the bound form; hence, ions are not mobile to favor intramicellar nucleation. Hence a smaller number of nuclei will be formed. As a result the final particle size is found to be large.

**3.3. Effect of Cations.** The effect of cations on the formation of particles was studied as a means of changing the exchange rate of the microemulsion containing the salt molecules. This was achieved by affecting the electrostatics of the polar head layer of the AOT surfactant molecules. Salts are mainly known to reduce the size of the effective polar region of the surfactant due to the screening of the electrostatic repulsion between the head groups. Such a reduction will cause an increase in the curvature and rigidity of surfactant aggregates. On the basis of the valence and specific effects in light of the electric double-layer theory, it can be argued that the higher the valency and the smaller the size of the hydrated cation, the higher will be the screening effect on electrostatic repulsion between the surfactant head groups. Consequently, the head groups will have a shorter equilibrium distance, resulting in a tightly packed surfactant layer. Therefore, it can be thought that the charge to size ratio can be a representative parameter of the cationic effect on the rigidity of the surfactant layer. On the basis of this knowledge an attempt has been made to study the effect of cations of chloride salt series of groups I and II.

Figure 5 shows the photomicrographs of silver chloride particles obtained via the microemulsion route with chlorides of different cations. Particles were found to be spherical in all cases. Figure 6 shows the histograms of the particles obtained in these cases. Table 3 presents the number average particle size and the number of particles counted from the photomicrographs. The numbers presented in the last column can be used to

**Table 3. Effect of Cations on the Size and Number of Silver Chloride Particles**

| salt | valence/$r_h$,[a] nm$^{-1}$ | $d_p$,[b] nm | $\sigma_d$,[c] nm | $N_p$*[d] |
|---|---|---|---|---|
| LiCl (0.1 M) | 2.6 | 7.0 | 1.72 | 600 |
| NaCl (0.1 M) | 2.7 | 10.1 | 1.88 | 400 |
| KCl (0.1 M) | 3.0 | 9.0 | 1.86 | 320 |
| CsCl (0.1 M) | 3.0 | 7.9 | 1.77 | 320 |
| CaCl$_2$ (0.05 M) | 4.8 | 7.6 | 2.59 | 80 |

[a] $r_h$ = hydrodynamic radius. [b] $d_p$ = number average particle size. [c] $\sigma_d$ = standard deviation. [d] $N_p$* = number of particles observed from TEM micrograph.

quantitatively compare the number densities of the particles formed.

We observe from Table 3 that there is a weak effect on the average size of the particles formed. The size only varies from 7.0 to 10.1 nm. Excluding for the cases of sodium and potassium, the variation is virtually negligible. Interestingly, we also observe that a smaller number of particles are formed for the cases of higher ratios of charge to hydrated cation size. For example, Li$^+$ and Na$^+$, being the most hydrated cations, produce relatively larger numbers of particles due to the labile surfactant shell which results in higher exchange coefficients. While for other cations, particularly Ca$^{2+}$, the number density of particles formed is significantly low. This indicates that the rigid surfactant shell formed due to the presence of a few Ca$^{2+}$ ions near the interfacial region inhibits the material exchange and hence adversely affects the particle formation. This is a useful finding which suggests that the use of hydrolyzable monovalent cations such as Li$^+$ and Na$^+$ is preferable in the process of formation of silver halide particles using reactions in reverse micellar systems.

## 4. Conclusions

(1) The exchange rate is found to affect both the particle size and the rate of growth of particle formation. A higher exchange rate gives rise to a smaller size of the particles while at a lower exchange rate due to the slow growth rate the particle size and number density are found to be smaller.

(2) The particle size is also found to vary with water to surfactant molar ratio. At higher $R$ values particle size is found to be smaller while it is larger at $R = 10$ due to the difference in the structural makeup of the water cores. The particle size is found to be still lower at $R = 5$ due to the rigid interface, thus indicating the importance of intermicellar exchange rate.

(3) The average particle size is weakly affected by changing the cations of the salt. A smaller number of particles are found to form for cations of higher charge to hydrated size ratio.