Effects of Intermicellar Exchange Rate on the Formation of Silver Nanoparticles in Reverse Microemulsions of AOT

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We report the effects of intermicellar exchange rate on absorption spectra and particle size of silver nanoparticles synthesized in reverse micelles of AOT. The silver nanoparticles are prepared by the method of mixing of two microemulsions, one containing the silver nitrate and the other containing sodium borohydride. The intermicellar exchange rate is varied by changing the organic solvent, surfactant (SDS, NP-5, and DTAB), and organic (benzyl alcohol and toluene) additives. The higher intermicellar exchange rate is found to give smaller particle size and blue shift in the absorption spectra. An interesting and potentially useful effect has been observed in that addition of a small amount of a nonionic surfactant significantly reduces the particle size.

1. Introduction

Colloidal assemblies such as reverse micelles/water in oil microemulsions seem to be good candidates for growing nanoparticles.[1] These microemulsions are transparent, isotropic liquid media with a continuous oil phase and discrete aqueous droplets that are thermodynamically compartmentalized by surfactants into nanometer-sized liquid entities. These surfactant-stabilized aqueous nanoentities called microemulsions offer a unique environment for inorganic precipitation reactions; that is, they act not only as microreactors for hosting the reaction but also as steric stabilizers to inhibit aggregation. Various nanoparticles have been prepared using this route, the account of which can be obtained from a recent review by Eastoe et al. (1996).[2] The advantage of this method is that (1) it is a soft technique, i.e., it does not require extreme conditions of temperature and pressure, and (2) the particle size and shape can be controlled by simply varying the microemulsion composition and dynamics.[3,4]

Although a significant amount of work has been done on the synthesis of a variety of nanoparticles, the information on the effect of intermicellar dynamics of the microemulsion on the particle size appears to be scarce. It has recently been shown both theoretically and experimentally that intermicellar exchange processes significantly affect the size of particles formed.[5,6]

In our previous work we have made an attempt to study the effect of intermicellar exchange rate by varying the organic solvent, the water-to-surfactant molar ratio, and the charge-to-size ratio of the cations on the particle size of silver chloride nanoparticles.[6]

In this study we have investigated the effect of intermicellar exchange rate on the particle size and absorption spectra of silver nanoparticles. The effect of intermicellar exchange rate has been studied by varying the organic

solvent, additives benzyl alcohol and toluene, and addition of cationic (dodecyl trimethyl ammonium bromide), anionic (sodium dodecyl sulfate), and nonionic (NP-5) surfactants to the AOT/heptane solution.

Various research groups have synthesized silver nanoparticles using the microemulsion route.[7–11] These silver nanoparticles thus synthesized have potential uses as substrates in studies in surface enhanced Raman spectroscopy,[11] in nonlinear optical technology,[12] and in catalysis.[13] The silver nanoparticles show a narrow intense plasmon absorption band at 400 nm, that is susceptible to size and surface/interface effects.[10]

The intermicellar exchange of solubilizate (for example, silver nitrate or sodium borohydride) and subsequent reaction can be thought of as consisting of a number of sequential elementary steps. The important among them are as follows.[14,15]

(1) Brownian diffusion of reverse micelles leading to collisions.

(2) Surfactant layer opening and coalescence (energetic collisions).

(3) Diffusion of solubilizate molecules (exchange of materials).

(4) Reaction between solubilizate.

(5) Decoalescence (fission) to return as reverse micelles.

The time scales of these five basic rate processes differ substantially, and the slowest step will scale the temporal aspects of exchange between reverse micelles containing reactant solubilizates. The information on the time scale of the process of the micellar fission and the fusion steps is not available, while the estimates of the other time scales relating to reaction and Brownian diffusion can be obtained. Furthermore, it is not likely that all collisions

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(1) Ozin. G. A. *Adv. Mater.* **1992,** *4,* 612.

(2) Eastoe, J.; Warne, B. *Curr. Opin. Colloid Interface Sci.* **1996,** *1,* 800.

(3) Tanori, J.; Pileni, M. P. *Langmuir* **1997,** *13,* 639.

(4) Limin, Qi; Jiming, Ma; Humin, Chang; Zhenguo, Zhao. *Colloids Surf.: Physico-chemical Engineering Aspects* **1996,** *108,* 117.

(5) Natarajan, U.; Handique, K.; Mehra, A. M.; Bellare, J.; Khilar K. C. *Langmuir* **1996,** *12,* 2670.

(6) Bagwe, R. P.; Khilar K. C. *Langmuir* **1997,** *13* (24), 6432.

(7) Bagwe, R. P.; Mishra, B. K.; Khilar K. C. *J. Disp. Sci. Technol.* **1999,** *20* (6), 1569.

(8) Petit, C.; Lixon P.; Pileni, M. P. *J. Phys. Chem.* **1993,** *97,* 12974.

(9) Meldrum, F. C.; Kotov. N. A.; Fendler J. H. *J. Chem. Soc., Faraday Trans.* **1994,** *90* (4), 673.

(10) Barnickel, P.; Wokaun, A.; Sager, W.; Eicke, H. F. *J. Colloid Interface Sci.* **1992,** *148,* 80.

(11) Taleb, A.; Petit, C.; Pileni, M. P. *Chem. Mater.* **1997,** *9,* 950.

(12) Pileth, W. J. *J. Phys. Chem.* **1982,** *86,* 3461.

(13) Hache, F.; Richard, D.; Flytzanis, C. *J. Opt. Soc. Am.* **1986,** *B3,* 1647.

(14) Henglein, A.; Lillie, J. *J. Phys. Chem.* **1981,** *85,* 1246.

(15) Bommarius, A. S.; Holzwarth, J. F.; Wang, D. I. C.; Hatton, T. A. *J. Phys. Chem.* **1990,** *94,* 7232.

are sufficiently energetic and can lead to fusion and hence to intermicellar exchange. The first two processes are important and are second-order processes. It has been a practice to represent the intermicellar exchange rate in terms of a lumped second-order rate coefficient, k_{ex}.

2. Experimental Procedures

2.1. Materials Used. The surfactants, dioctyl sulfosuccinate sodium salt (AOT), and sodium dodecyl sulfate (SDS), were obtained from Sigma with 99% purity. The other chemicals were obtained as follows: dodecyl trimethyl ammonium bromide (DTAB) was from Fluka, and NP-5 was a gift from ICI, India, ltd. The silver nitrate was from S. D. Fine Chem, India, AR grade, while sodium borohydride was from S. D. Fine Chem, India, LR grade. The water used for preparing the electrolyte solutions was doubly distilled. The organic solvents were procured from SISCO research laboratories, India, and were of AR grade. All the solvents were refluxed over sodium for 3−4 h followed by distillation in order to remove moisture.

2.2. Microemulsion Preparation and Particle Characterization. The microemulsions were prepared by mixing the aqueous solution of silver nitrate (0.1 M) or reducing agent sodium borohydride (0.05 M) to the 0.1 M AOT/alkane solution with or without additives (surfactant or organic). The molar concentration of silver nitrate and sodium borohydride was 1.8×10^{-3} and 9×10^{-4}, respectively, in the microemulsion. The molar ratio of reductant and silver ions was held constant for all experiments at a value of 2.

The water-to-AOT molar ratio, R, was kept the same in all cases and was equal to 10. For facilitating the preparation of microemulsions, an ultrasound bath was used as in our previous studies.[6] The microemulsion containing sodium borohydride was added all at once to the microemulsion containing silver nitrate. Half an hour after the addition the absorption spectra were recorded on Shimadzu UV−visible spectrophotometer (UV-165). The transmission electron microscopy (TEM) measurements for measuring the particle size were carried out at Saha Institute of Nuclear Physics, Calcutta, at an operating voltage of 75 kV. A few drops of the microemulsion were added to the Formvar-covered carbon-coated copper grids, and they were dried on filter paper at room temperature. Size distribution and number average particle diameters were obtained using the Image Pro Plus Image Analysis System as in our previous studies.[6] The photomicrographs were obtained with a transmission electron microscope (Hitachi model, H-600).

3. Results and Discussions

3.1. Effect of Continuous Phase. In these experiments, we have studied the influence of intermicellar exchange by varying the solvent, viz., cyclohexane, heptane, and decane, on the particle size and the absorption spectra of silver nanoparticles. An increase in the chain length of the oil results in an increase in the value of intermicellar exchange rate coefficient, k_{ex}. This is because as the chain length of the oil increases it becomes increasingly coiled and therefore its penetration in the surfactant layer becomes more difficult. As a result the mutual interaction between surfactant tails is stronger than that between the surfactant tail and oil molecules. On the other hand, interdroplet tail−tail interactions of two surfactant molecules increase, owing to the weak presence of solvent molecules in the tail region of the droplets. The net effect results in an increase in micellar exchange rate with the increase in chain length of solvent. Shorter oil and cyclohexane molecules penetrate more easily, resulting in additional interfacial area and interfacial rigidity. The micellar exchange rates of cyclohexane, heptane, and decane are approximately 10^6, 10^7, and 10^8 M^{-1}·s^{-1}, respectively.[16]
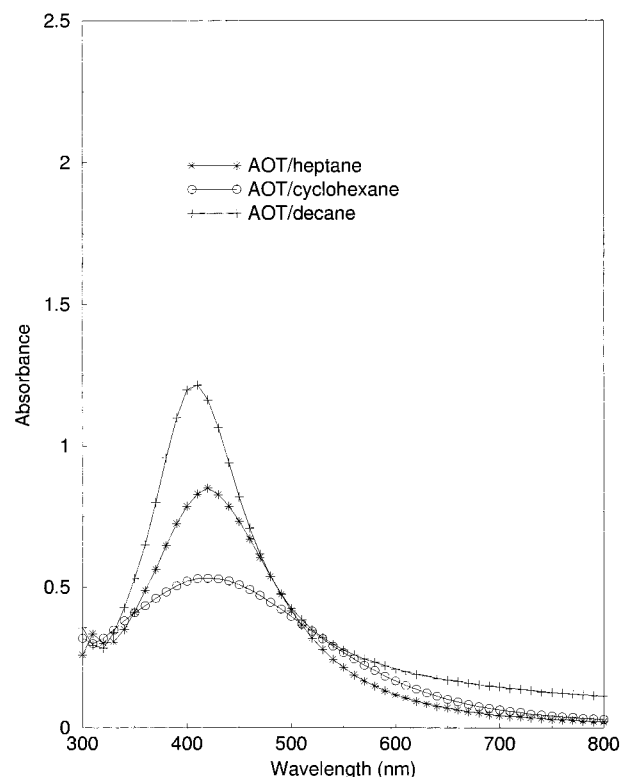

Figure 1. Absorption spectra of silver nanoparticles showing the effect of continuous medium: (a) AOT/decane; (b) AOT/heptane; (c) AOT/cyclohexane.

Table 1. Effect of Solvent on the Particle Size and Absorption Spectra of Silver Nanoparticles Synthesized in Reverse Micelles of AOT[a]

system	k_{ex} (M^{-1}·s^{-1})	λc_{max} (nm)	d_p (nm)	σ_d	N_p
AOT/decane	10^8	406	6.0	6.41	188
AOT/heptane	10^7	414	22.0	9.97	
AOT/cyclohexane	10^6	422	5.4	4.70	72

[a] k_{ex} = second-order exchange rate coefficient, the values of which are taken from ref 16. λ_{max} = wavelength of maximum aborbance. d_p = number average particle size. σ_d = standard deviation. N_p = number of particles as seen on TEM micrograph for approximately the same amount of sample.

UV−visible absorption spectra have proved to be quite sensitive to the formation of silver colloids. The plasmon absorption peak at 400 nm is the characteristic plasmon absorption peak of silver nanoparticles. The position of the plasmon absorption peak depends on the particle size and shape and the adsorption of nucleophile or electrophile to the particle surface. Usually, a red shift is associated with an increase in particle size or with the withdrawal of electron density from the surface. It is well-known that adsorption of the nucleophile to the particle surface increases the Fermi level of the silver particle owing to its donation of electron density to the particles.[20]

Figure 1 compares the absorption spectra of silver nanoparticles formed in three different organic solvents. The plasmon absorption peak shifts toward longer wavelengths (red shift) as we move from decane to heptane to cyclohexane. Further, from Table 1, one observes that the particle size increases as one moves from decane to heptane

(16) Fletcher, P. D. I.; Howe, A. M.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1,* **1987**, *83*, 985.

(17) Howe, A. M.; McDonald, J. A.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1,* **1987**, *83*, 1007.

(18) Lisecki, I.; Bjorling, M.; Motte, L.; Ninham, B.; Pileni, M. P. *Langmuir* **1995**, *11*, 2385.

(19) Dirk, S.; Ilgenfritz, G. *Langmuir* **1997**, *13*, 4246.

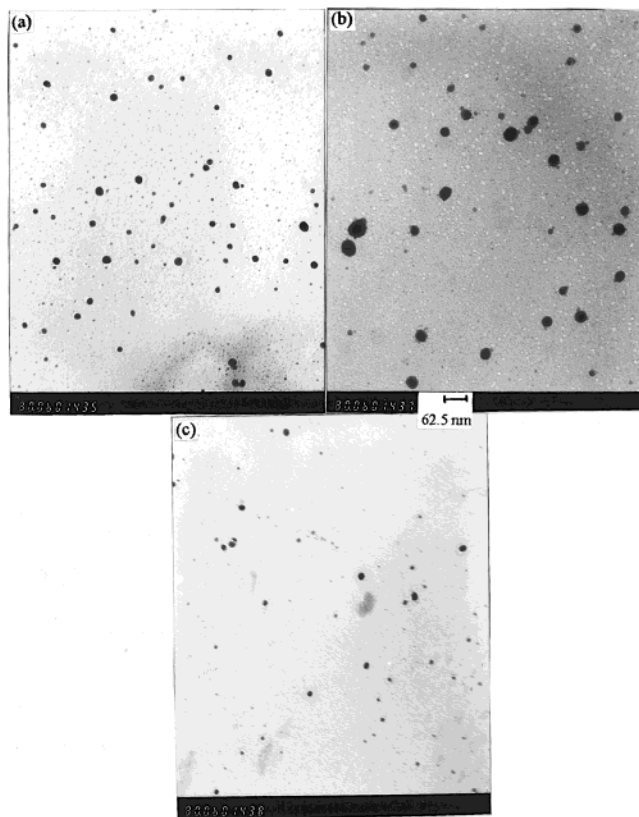(20) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457.

Figure 2. Transmission electron micrograph of silver nanoparticles showing the effect of continuous medium: (a) AOT/decane; (b) AOT/heptane; (c) AOT/cyclohexane.

Figure 3. Absorption spectra of silver nanoparticles showing the effect of concentration of reducing agent: (a) $NaBH_4 = 0.05$ M; (b) $NaBH_4 = 0.07$ M.

but decreases for cyclohexane. The number average particle sizes are 6.0, 22.0, and 5.4 nm corresponding to the absorption spectra of 406, 414, and 422 nm for decane, heptane, and cyclohexane, respectively.

We shall first discuss the effects when cyclohexane was used as the organic phase. From the transmission electron micrographs in Figure 2 one observes that the number density of particles formed in the AOT/cyclohexane medium seems to be less, which indicates that since the rate of formation of particles is slow owing to slower exchange rate the particle formation process may be incomplete. To further investigate this hypothesis, an experiment was conducted where the concentration of sodium borohydride was increased from 0.05 to 0.07 M. We observe from Figure 3 that an increase in intensity and blue shift from 434 to 423 nm occur, resulting from the formation of higher number density and smaller size particles. The increase in number density and particle size can be attributed to an increase in ion-occupancy number leading to an increase in the formation of nuclei. It may be noted here that the kinetics of the reaction is controlled by intermicellar exchange and therefore the reaction is incomplete in a short duration. Therefore, the observed small particle size can be attributed to the possiblity that the reaction might not have been completed. Similar observations were made by Petit et al. (1993)[8] when comparing the particle size and absorption spectra of silver nanoparticles in AOT/cyclohexane and AOT/isooctane medium. With regard to red shift in the case of cyclohexane, Henglein (1998)[21] has shown that the plasmon absorption band red shifts upon addition of Ag^+ ions to the Ag colloid. This change was explained as being due to a change in electron density owing to chemisorption of
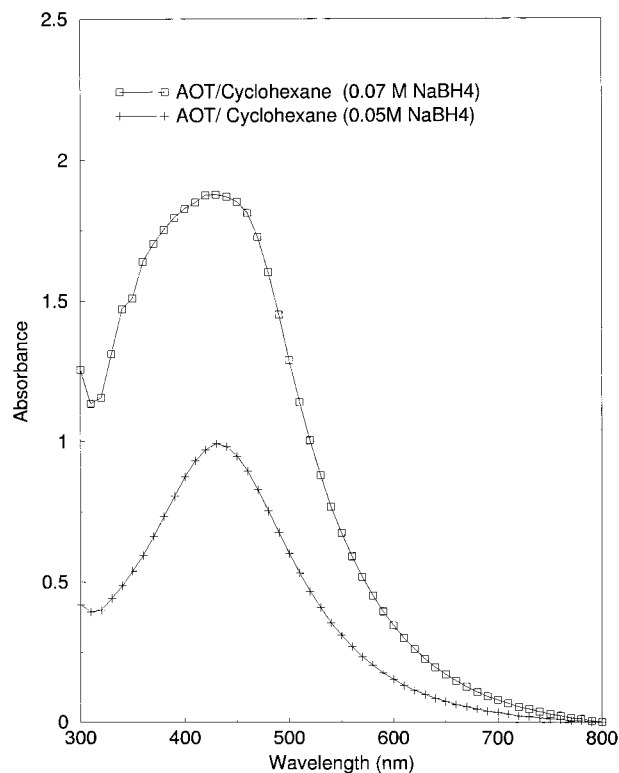
silver ions on the particle surface as well as a shift in Fermi level to a more positive potential. Thus the red shift in the absorption spectra and smaller number density of particle size in the case of AOT/cyclohexane medium indicate that there will be unreacted ions in the form of Ag_2O and $AgNO_3$ which form an ionic layer around the particle. Owing to the presence of this ionic layer, there is comparatively less density of electron gas than the AOT/decane and AOT/heptane medium, resulting in an increase of bandwidth and change in absorption maximum toward higher wavelength. Similar explanations were given by Barnickel et al. (1992)[10] and Henglein et al. (1998, 1991)[21,22] to account for the red shift in absorption spectra of silver nanoparticles.

At high k_{ex} (in decane) there will be rapid exchange of material, which will result in the formation of a larger number of micelles containing silver atoms greater than the critical nucleation number. This will result in smaller particle size as the silver atoms left for growth will be relatively low. In addition large numbers of particles will be formed.

In the case of heptane the exchange rate decreases by an order of magnitude. Slow exchange of materials will lead to formation of a lower number of nuclei of silver. Consequently, a higher amount of silver atoms as compared to decane will then be available for the growth of a relatively lower number of nucleated particles. Hence the terminal particle size is found to be larger than in the case of decane, and the number of particles formed is found to be lower.

3.2. Effect of Additives. *3.2.1. Effect of Surfactant as Additives.* In this part we have studied the effect of the addition of a small amount of different surfactants, viz., cationic, anionic, and nonionic (10^{-3} M), to the AOT/

(21) Henglein, A. *Chem. Mater.* **1998**, *10*, 444.

(22) Henglein, A.; Mulvaney, P.; Linnert, T. *Faraday Discuss.* **1991**, *92*, 31.
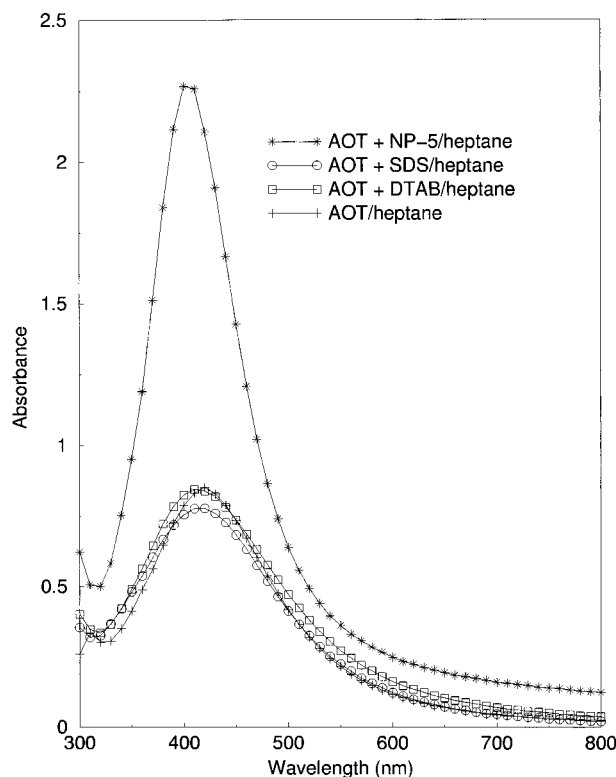
Figure 4. Absorption spectra of silver nanoparticles showing the effect of surfactant additives: (a) AOT/heptane + NP-5; (b) AOT/heptane + SDS; (c) AOT/heptane + DTAB; (d) AOT/heptane.

Figure 5. Transmission electron micrograph of silver nanoparticles showing the effect of continuous medium: (a) AOT/heptane + NP-5; (b) AOT/heptane + SDS; (c) AOT/heptane + DTAB; (d) AOT/heptane.

Table 2. Effect of Surfactant Additives on the Particle Size and Absorption Spectra of Silver Nanoparticles Synthesized in Reverse Micelles of AOT[a]

system	λ_{max} (nm)	d_p (nm)	σ_d	N_p	A_c (cm^2)
AOT/heptane + SDS	416	24.5	9.50	12	32
AOT/heptane + DTAB	411	18.4	5.40	17	32
AOT/heptane + NP-5	404	7.14	4.18	180	59
AOT/heptane	414	22.0	9.97		32

[a] λ_{max} = wavelength of maximum aborbance. d_p = number average particle size. σ_d = standard deviation. N_p = number of particles as seen on TEM micrograph for approximately same amount of sample. A_c = area under the absorption curve.

heptane solution. The surfactants selected were sodium dodecyl sulfate (SDS) as anionic, dodecyl trimethyl ammonium bromide (DTAB) as cationic, and (poly(oxyethylene)) × 5 nonyl phenyl ether (NP-5) as nonionic. Studies conducted by Pileni et al.[18] using QELS have shown that the addition of a very small amount of cetyl trimethyl ammonium chloride (CTAC) does not alter the micellar size of the AOT/heptane system but the intermicellar exchange rate gets significantly affected. Therefore, we assume that the addition of such a small amount of surfactant additives to the 0.1 M AOT/heptane system does not alter the micellar radius but can vary the intermicellar exchange rate significantly

Figure 4 shows the absorption spectra of silver nanoparticles showing the effect of different surfactant additives. It can be seen that the position of the plasmon band and intensity seem to be hardly affected by addition of DTAB and SDS while there is a strong blue shift and increase in absorption intensity and sharpness of peak height on the addition of NP-5, which indicate that the particle size decreases, the number of particles increases, and the distribution becomes narrow. It may be noted here that since the bases of the triangle are virtually of the same length the peak can represent the area for comparison purposes. This is further supported by the TEM results in Figure 5, which indicate that the particle size decreases and number density increases on addition of NP-5. Table 2 also shows the data on the number average particle size, standard deviation, and number density of silver nanoparticles. It can be seen that SDS and DTAB have negligible effects on the particle size. Addition of NP-5, however, seems to have a strong effect on the particle size reducing the average particle size from 25 to 7 nm and increasing the number density of particles.

Both DTAB and SDS have a hydrocarbon chain length of 12 carbon atoms, while the longest part of AOT has a
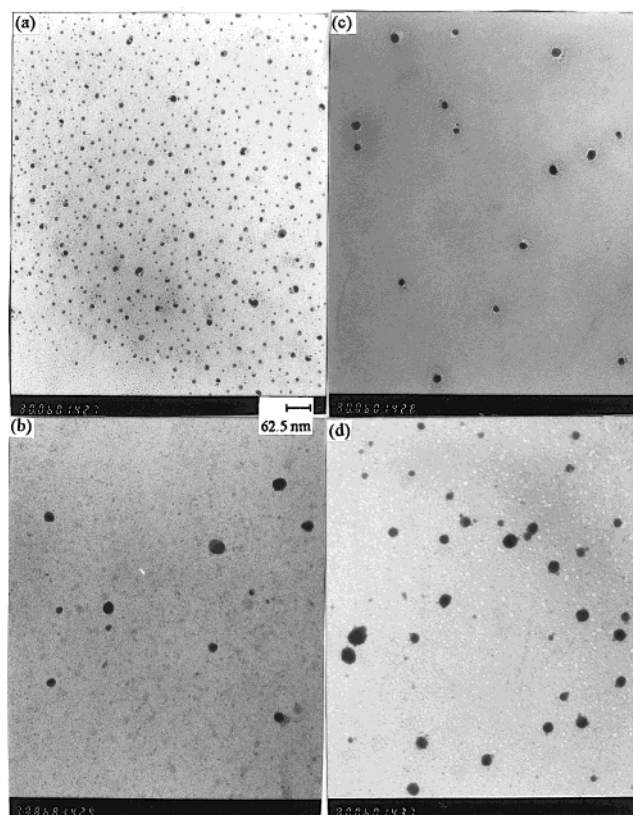
chain length of six carbon atoms.[18] Therefore for AOT molecules with tails of six carbon atoms, DTAB/SDS molecules may remain outside the steric range of AOT tails. This causes local steric repulsions and perturbs the formation of dimers and multimers caused by attraction between micelles. As a result, the intermicellar exchange process is inhibited with a net reduced value of k_{ex}. Therefore, the number of nuclei formed will be less, resulting in formation of larger particles. Correspondingly, the particle density is also found to decrease. In the case of DTAB as additive, initially there maybe formation of AgBr nanoparticles in the microemulsion containing silver nitrate. But after addition of sodium borohydride containing microemulsion, the solution turns yellow in color with a 400 nm characteristic absorption band indicating formation of silver nanoparticles.

In the case of NP-5 as additive, the NP-5 molecule has five oxyethylene units. These oxyethylene units are believed to act as a cosurfactant bringing about fluidity of the interface.[19] As a result the number of collisions leading to exchange of ions/atoms will increase resulting
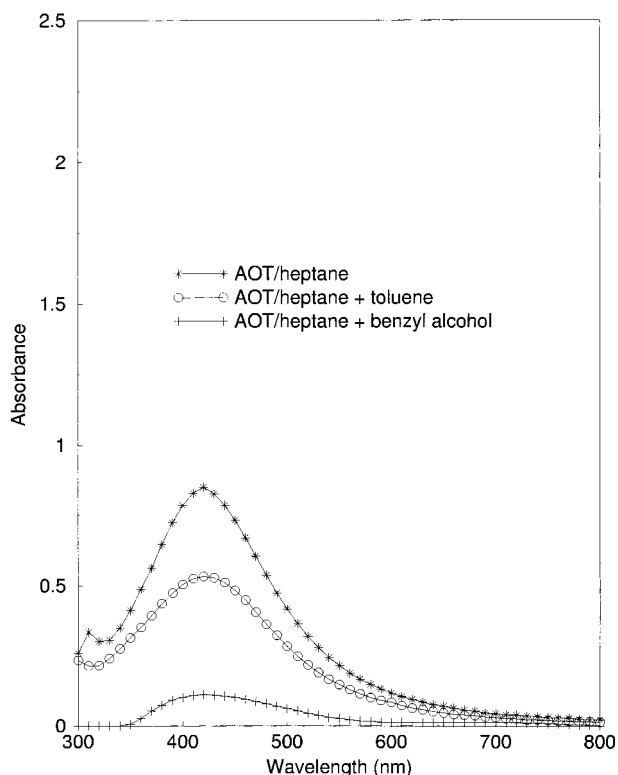
Figure 6. Absorption spectra of silver nanoparticles showing the effect of continuous medium: (a) AOT/heptane + benzyl alcohol; (b) AOT/heptane; (c) AOT/heptane + toluene.

Table 3. Effect of Additives on the Particle Size and Absorption Spectra of Silver Nanoparticles Synthesized in Reverse Micelles of AOT[a]

system	k_{ex} (M^{-1}·s^{-1})	λ_{max} (nm)	d_p (nm)	σ_d	n_i
AOT/heptane + benzyl alcohol	10^8	406	8.8	5.90	1.5
AOT/heptane	10^7	414	22.0	9.97	2.9
AOT/heptane + toluene	10^6	424	7.6	4.90	2.0

[a] k_{ex} = second-order exchange rate coefficient, the values of which are taken from ref 16. λ_{max} = wavelength of maximum absorbance. d_p = number average particle size. σ_d = standard deviation. n_i = ion-occupancy number.

in the formation of a large number of nuclei and corresponding decrease in the particle size.

3.2.2. Effect of Benzyl Alcohol and Toluene as Additives. Addition of 3.8 M toluene and 0.2 M benzyl alcohol to the AOT/heptane system decreases and increases, respectively, the intermicellar exchange rate by an order of magnitude.[16] The benzyl alcohol molecule acts as a cosurfactant, and its addition to the AOT/heptane system makes the interface more fluidlike as it is increasingly partitioned into the interfacial region. The toluene molecules, however, penetrate into the surfactant shell and make it rigid. While their effects on shell rigidity are of contrasting nature, these additives alter the micellar size in a similar manner. Both benzyl alcohol and toluene decrease the micellar size and increase the number density of micelles.[16] As a result, the ion-occupancy number decreases.

Figure 6 shows the absorption spectra of silver nanoparticles showing the influence of additives. From Table 3 and Figure 7 the particles size are found to be 8.8, 22.0, and 7.6 nm corresponding to the absorption spectra of 416, 414, and 424 nm for AOT/heptane + benzyl alcohol, AOT/heptane, and AOT/heptane + toluene, respectively.
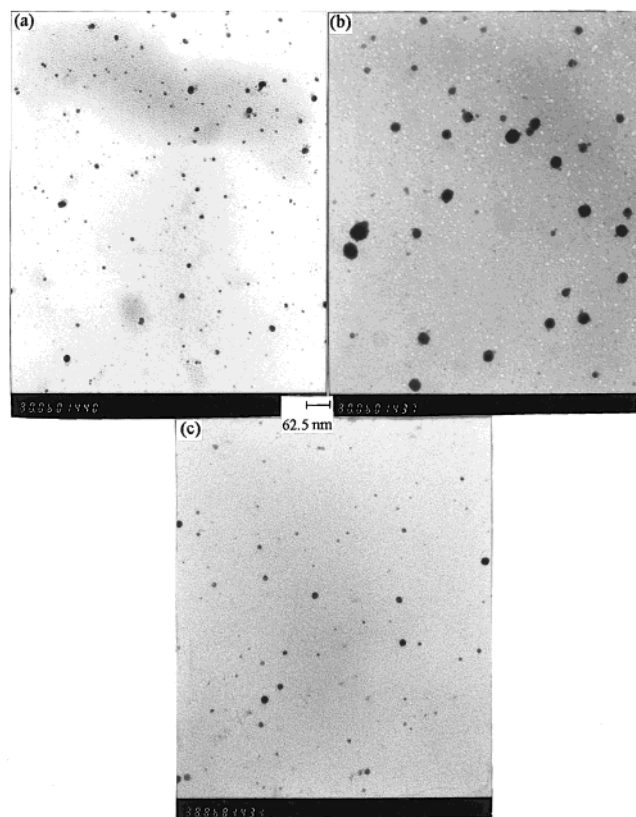

Figure 7. Transmission electron micrograph of silver nanoparticles showing the effect of organic additives: (a) AOT/heptane + benzyl alcohol; (b) AOT/heptane; (c) AOT/heptane + toluene.
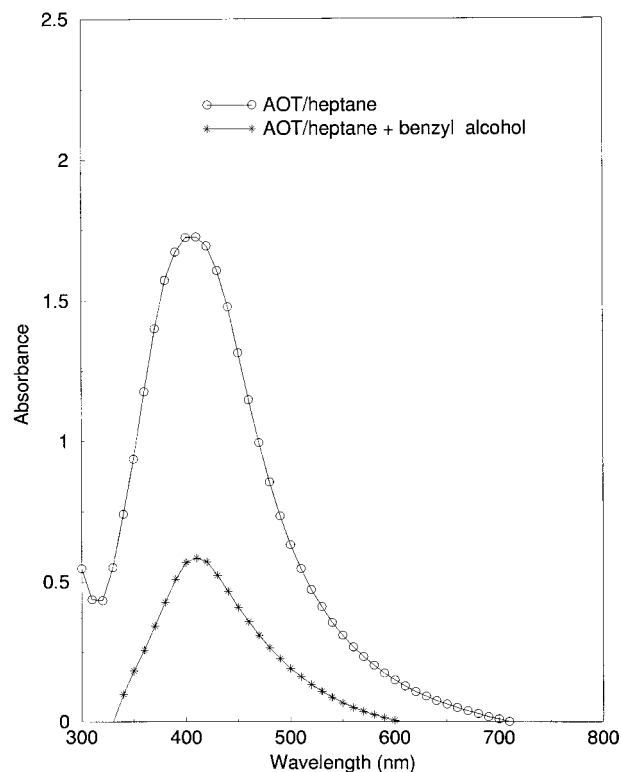

Figure 8. Absorption spectra of silver nanoparticles showing the effect of addition of 0.2 M benzyl alcohol to the silver nanoparticles in AOT/heptane: (a) AOT/heptane + benzyl alcohol; (b) AOT/heptane.

Also from Table 3 one observes that although there is a large difference in particle size between the case with

benzyl alcohol additive and the one without any additive the plasmon band remains at the same position. There is, however, a decrease in absorption intensity and broadening of the peak. This can be attributed to benzyl alcohol acting as a nucleophile on the particle surface resulting in red shift and decrease in intensity and broadening of the plasmon peak. The red shift on addition of various nucleophiles on the plasmon band has already been explained by Henglein et al.[22] as being due to a decrease in the mean free path of electrons in silver colloids, leading to a decrease in conductivity and an increase in bandwidth. This hypothesis was further checked by addition of benzyl alcohol to silver nanoparticles already prepared in AOT/heptane microemulsion. Figure 8 shows a red shift from 407 to 411 nm and a decrease in intensity of the plasmon band upon addition of benzyl alcohol to Ag nanoparticles containing AOT/heptane microemulsion.

In the case of addition of toluene to the AOT/heptane system, the situtation seems similar to that of cyclohexane wherein owing to very slow exchange rate the unreacted ions act as nucleophiles resulting in a red shift and smaller average particle size. In other words, the smaller particle size and red shift in absorption spectra indicate slow growth rate of particles owing to addition of toluene to the AOT/heptane system.

Table 3 shows the data on the number average particle size and ion occupancy in reverse micelles. It can be seen that the ion occupancy decreases upon addition of additives (from 2.9 to 2.0 in the case of addition of 40% v/v toluene and from 2.9 to 1.5 upon addition of 0.2 M benzyl alcohol).

In the case of benzyl alcohol as additive, the compounded effects of smaller ion occupancy and the larger exchange rate arising from the fluidity of surfactant shell result in a large number of nuclei. As a result the final particle size becomes smaller.

In the case of toluene as additive, the slow exchange rate and low ion occupancy lead to a slow rate of formation of particles. The effect is similar to the cyclohexane case.

4. Conclusions

The following conclusions have emerged from this study:

(1) When the intermicellar exchange rate has been changed by varying the organic solvent, the particle size and plasmon absorption band have been found to be affected. The particle size decreases at higher intermicellar exchange rate, while both particle size and number density become lower at very low intermicellar exchange rate, indicating partial reduction of silver salt.

(2) Addition of benzyl alcohol molecule results in a decrease in particle size. Addition of toluene also decreases the particle size by decreasing the growth rate.

(3) Addition of DTAB and SDS does not bring about any significant change in particle size. Addition of NP-5 decreases the particle size significantly with corresponding increase in the number of particles formed.

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