

## THE EFFECT OF INTERFACIAL VISCOSITY ON THE KINETICS OF FORMATION OF SILVER NANOPARTICLES USING WATER-IN-OIL MICROEMULSIONS AS NANOREACTORS

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### ABSTRACT:

Silver nanoparticles were prepared by the method of mixing of two microemulsions having similar chemical composition but different reactants in their respective aqueous core. One microemulsion contains silver nitrate in the aqueous core and other contains sodium borohydride. The silver nanoparticles formed were characterized using UV-Visible absorption spectra and TEM micrographs. Effect of chain length of solvent and addition of Arlacel-20 to the AOT/Heptane, AOT/Decane and AOT/Dodecane microemulsion on particle size and absorption spectra of silver nanoparticles was studied. TEM photographs showed agglomerated and bigger particles in case of pure AOT/dodecane whereas addition of Arlacel-20 showed dispersed and smaller particles. Reaction kinetics was observed for silver nanoparticles using UV-visible spectrophotometer. Silver nanoparticles prepared using pure AOT surfactant showed plasmon band (416 nm) immediately after preparation whereas no absorption band of silver nanoparticles was observed for mixed surfactant microemulsion of AOT and Arlacel 20 for few hours indicating the reaction kinetics is slowed down upon addition of Arlacel-20. Growth rate of silver nanoparticles was plotted by monitoring absorption coefficient ratio ( $\epsilon_{416}/\epsilon_{475}$ ) as a function of time. AOT/heptane system showed slower growth rate as compared to AOT/decane and AOT/dodecane and also larger particle size. Presence of Arlacel-20 significantly decreases the growth rate in all three alkanes and this observation can be explained using the concept of rigidity of surfactant film at the oil/water interface. It is proposed that higher the interfacial viscosity, slower is the coalescence rate of nanodroplets in the microemulsion system, and hence slower the growth rate of particles and smaller is the final particle size.

### INTRODUCTION:

The study of synthesis and physico-chemical characterization of metal and semiconductor nanoparticles has been active field of research for more than a decade. These nanoparticles are known to show novel and hybrid properties between the molecular and

bulk solid state limits which finds application in various chemical processes (1), biology (2) and in the area of optical and opto-electronic devices (3). Among various methods of preparation of nanoparticles water-in-oil microemulsion method is popular because of its simplicity (i.e it does not require extreme conditions of temperature and pressure). In this technique, water droplets stabilized by surfactant and dispersed in organic media can be used as nanoreactors, favoring the formation of small crystallites with a sufficiently narrow size distribution.

Whereas there have been numerous report on the production of nanoparticles through water-in-oil microemulsion synthesis route that focus on the final product, few have systematically examined the controlling variables of the particle "growth" process and the factors affecting the rate of particle formation (eg. effect of fluid properties on the particle growth rates). The method consist of mixing two microemulsions having same chemical composition but differing in the aqueous content for example metal salt in one and reducing agent in the other. The water droplets in the microemulsion will exchange the contents of the cores via both fusion and fission processes. As a result, the reduction of metal salt within the cores of reverse micelles leads to nucleation and growth of nanometer-sized metal particles. The particle growth inside reverse micelle depends strongly on the exchange of reactant between micelles. The exchange process occurs when micelles collide because of brownian motion and the attractive forces between the micelles. These collision result in the fusion of reverse micelles, an exchange of content between the cores and a redispersion of the micelles. Hence, depending on the rate of inherent chemical reaction, particle production can be controlled by the rate of this intermicellar exchange process.

This manuscript describes the effect of interfacial viscosity of microemulsion on growth rate of silver nanoparticles prepared within the cores of microemulsion. The interfacial viscosity is varied by changing the chain length of organic solvent and addition of non-ionic surfactant Arlacel-20 (sorbitan monolaurate) to the microemulsion of anionic surfactant, AOT.

## **EXPERIMENTAL DETAILS:**

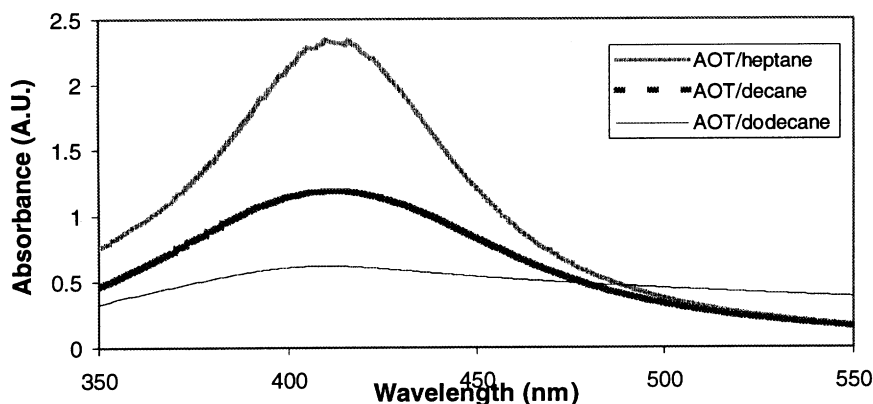
The water-in-oil microemulsions were prepared by mixing either the aqueous solution of silver nitrate (0.1 M) (Sigma, St. Louis, MO) or reducing agent, sodium borohydride (0.05 M) (Sigma, St. Louis, MO) to sodium bis (2-ethyl hexyl) sulfosuccinate (AOT) (Sigma, St.Louis, MO) or a mixture of AOT and Arlacel-20 (ICI, Wilmington, DE) in an organic solvent (heptane, decane or dodecane purchased from Sigma). The total surfactant concentration was kept around 0.1 M. The water-to-surfactant molar ratio was kept at 5 while studying the effect of chain length of solvent and was kept to 10 while studying the effect of addition of Arlacel-20.

The absorption spectra were recorded on HP 8453 UV-Visible spectrophotometer at regular intervals. A microemulsion containing only the organic solvent, surfactant and water was used as reference. Transmission Electron Microscopy (TEM) studies of silver nanoparticles were subsequently performed on JEOL 200 CX electron microscope at an operating voltage of 200 kV after depositing few drops of the solution on carbon coated copper grid.

## RESULTS AND DISCUSSION:

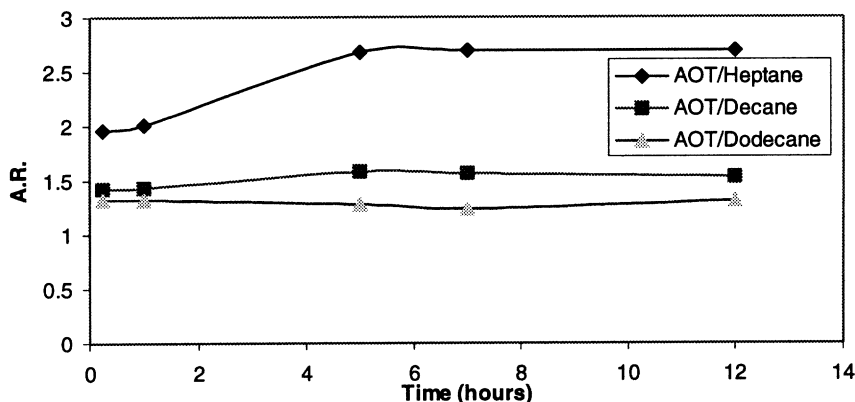
Colloidal dispersion of metals exhibits absorption bands or broad regions of absorption in UV-visible region thereby allowing in situ analysis of the silver nanoparticle size. These bands are due to excitation of plasmon resonance or inter-band transitions and are characteristic properties of metallic nature of the particles. The correlation of absorption spectrum with particle size of copper nanoparticles have been described by Pileni et al. (4) and Cason et al.(5). These authors observed that ratio of intensity of plasmon absorption band of copper nanoparticles to the absorption intensity off the peak with particle size (as determined by TEM measurements). The authors observed linear relationship between particle size and absorption intensity ratio. Similar, correlation can be assumed for silver nanoparticles measuring the ratio of absorption coefficient of plasmon band at 416 nm to the absorption coefficient off the peak (475 nm). Fig. 1 shows the effect of various solvents on the absorption spectra of silver nanoparticles in AOT microemulsion after 15 minutes.

**Fig. 1 Absorption Spectra of Silver Nanoparticles showing the effect of chain length of solvent after 15 minutes of mixing**



It can be seen that AOT/heptane show intense plasmon absorption band at 416 nm and the intensity decreases from AOT/heptane to AOT/decane to AOT/dodecane. The concentration of silver nitrate and sodium borohydride was kept at 0.05 M and 0.025 M and water to surfactant molar ratio kept to 5 while studying the effect of solvent. The growth rate of the silver nanoparticles was plotted by taking Absorption coefficient ratio (A.R.) as a function of time as shown in Fig. 2. It can be seen from the figure that growth rate is slow comparatively in case of AOT/heptane and also

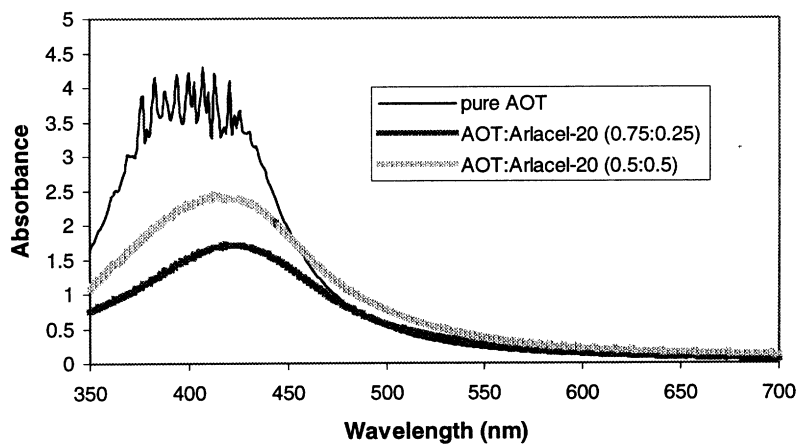
**Fig. 2 Comparison of silver nanoparticles growth curves in AOT reverse micelles showing effect of chain length of solvent (A.R.=Absorption Coefficient ratio at 416 and 475 nm)**



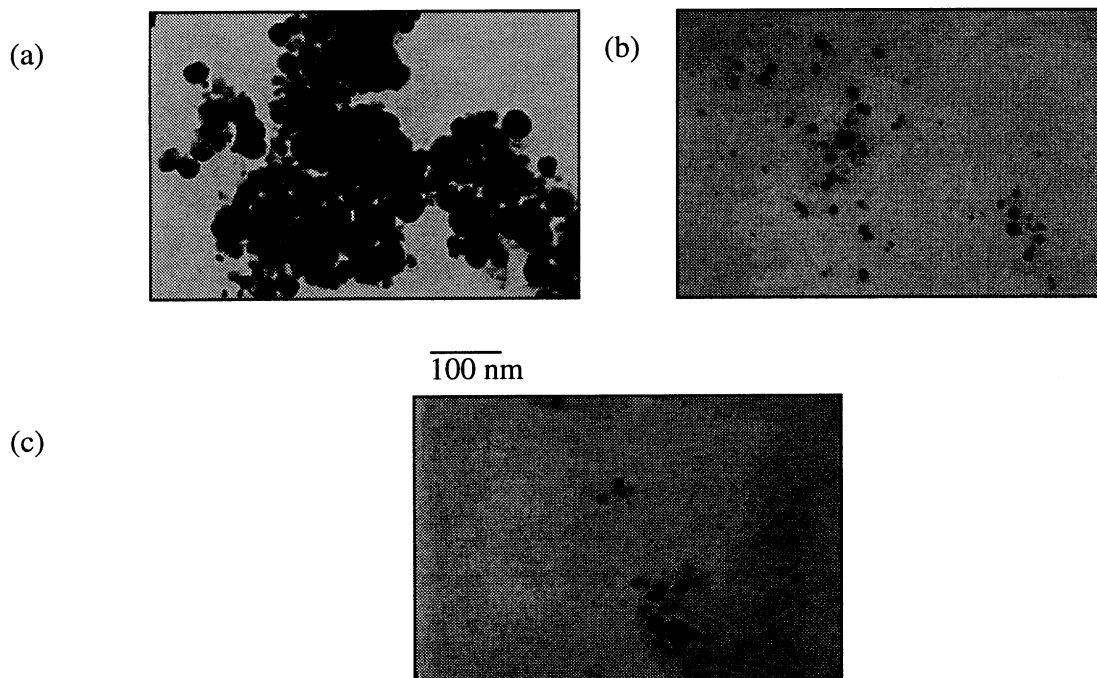
terminal particle size is higher in case of heptane solvent as compared to decane and dodecane which reached terminal particle size immediately after mixing. The particle size respectively were 9.2, 10.1 and 18 nm for AOT/heptane, AOT/decane and AOT/Dodecane system. The size distribution was measured as given by Bagwe and Khilar (7) which takes into account mono and polydispersity. The standard deviation for the above mentioned particles were 8.2 nm, 6.2 nm and 12.1 nm for AOT/dodecane, AOT/decane and AOT/heptane respectively. The above results can be explained by diffusion studies done using Quasi Elastic Light Scattering done by Hou et al. (6) wherein they observed that virial coefficient of diffusion decreases dramatically with increase in chain length. This was explained due to relatively smaller chain heptane molecules can penetrate between the surfactant tails efficiently and increase the surfactant curvature and rigidity whereas more bulky decane and dodecane have difficulty penetrating and solvating the surfactant tails. This creates a more fluid interface which promotes coalescence between reverse micelles. Because of decreased presence of decane molecules in the tail region of the micelle compared to heptane, the inter-droplet tail-tail interaction are increased, resulting in an increase in collision frequency and intermicellar exchange rate, which leads to an increase in particle growth rate. Similar, results were obtained by Cason et al. (5) and Bagwe and Khilar (7).

Given that the properties of the bulk solvent have a strong influence on the particle growth kinetics, we further studied the effect of addition of Arlachel-20 to the micellar solution. Hou et al.,(6) had shown using Quasi Elastic Light Scattering (QELS) that the addition of Arlachel-20 increases the diffusion coefficient indicating increased packing of the surfactant molecules. This can be explained due to the fact that non-ionic surfactant sitting between two anionic surfactant not only reduces the repulsion between headgroups but also increases interaction between non-polar ends or tail of surfactant molecules thereby increases packing and rigidity at the interface. The effect of addition of Arlachel-20 on the absorption spectra of silver nanoparticles can be seen in Fig.3.

**Fig.3 Effect of Arlachel-20 on Absorption Spectra of Silver nanoparticles in AOT/Heptane Microemulsion after 24 hrs**



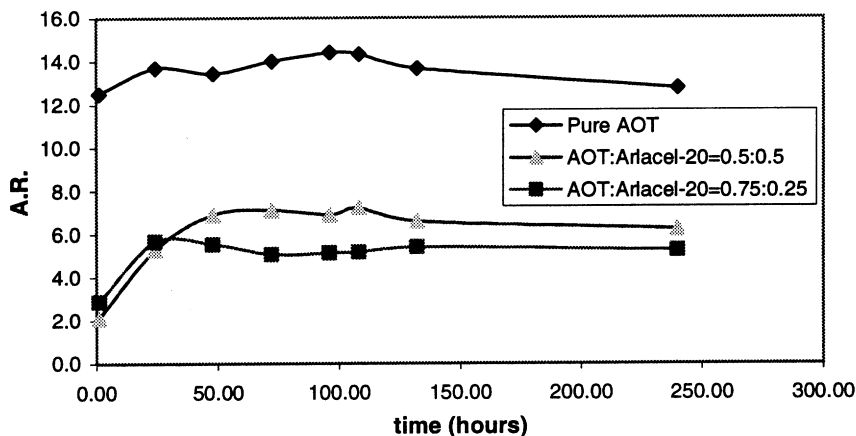
The absorption intensity was found to decrease after addition of Arlachel-20. Fig.4 shows



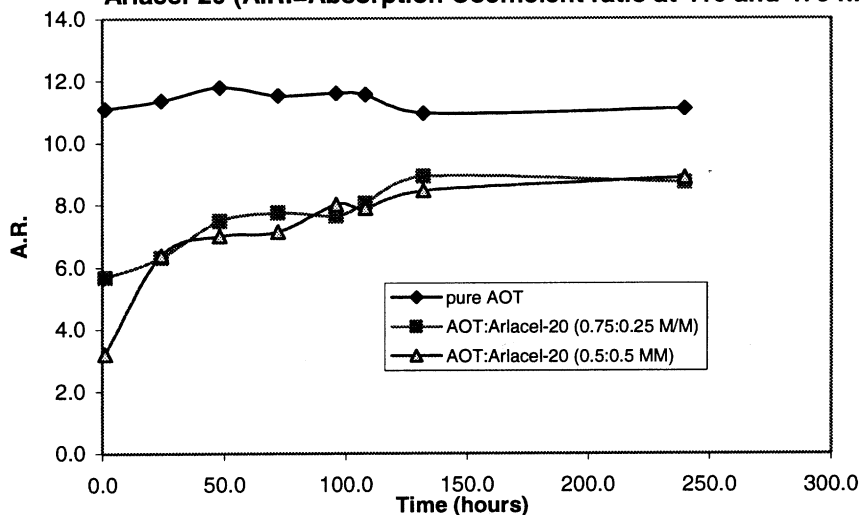
**Fig. 4 Transmission Electron Micrograph of silver nanoparticles showing the effect of Addition of Arlachel-20 (a) pure AOT (b) AOT: Arlachel-20 (1:3 mole/mole) (c) AOT:Arlachel-20 (1:1 mole/mole) (The scale represent 100 nm) in dodecane**

the TEM micrograph of silver nanoparticles showing effect of addition of Arlachel-20 to the AOT/dodecane microemulsion. It can be seen that addition of Arlachel-20 decreases agglomeration and number and size of particles. The AOT/dodecane microemulsion produces 40-60 nm aggregates whereas particle size and standard deviations were 14.8 nm and 5.2 nm respectively for 1:1 mole/mole ratio of AOT and Arlachel-20 and 12.6 nm and 9.1 nm respectively for 2:1 mole/mole ratio of AOT and Arlachel-20. However, increase in concentration of Arlachel-20 was found to produce not much change in size. Fig. 5-7 demonstrate the strong effect, Arlachel-20 produces on absorption coefficient ratio of silver nanoparticles on addition to pure AOT microemulsion. Silver nanoparticles prepared using AOT/dodecane microemulsion lead to immediate aggregation leading to black color and hence no absorption spectra could be recorded. However, in presence of Arlachel-20 the growth rate and agglomeration was reduced and the plasmon band started evolving in few hours. The particle size and size for pure AOT, AOT:Arlachel (2:1 mole/mole) and AOT/Arlachel (1:1) in heptane solvent were 22 nm, 16.2 nm and 17.0 nm and size distribution were 8.3 nm, 9.1 and 10.2 nm respectively and particle size with decane continuous phase were 20 nm, 16.2 nm and 16.8 nm and size distribution were 6.2 nm, 8.9 nm and 9.6 nm respectively.

**Fig. 5 Comparison of Silver nanoparticle growth curve in AOT reverse micelles in heptane solvent at various concentration of Arlachel-20 (A.R.=Absorption Coefficient ratio at 416 and 475 nm)**

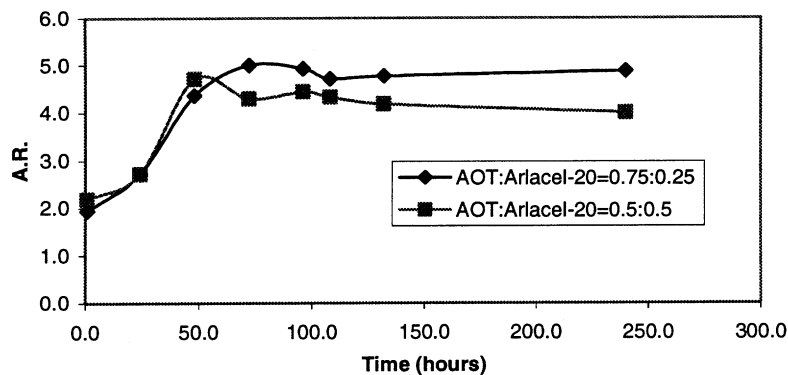


**Fig. 6 Comparison of silver nanoparticle growth curves in AOT reverse micelles in decane solvent at various concentration of Arlachel-20 (A.R.=Absorption Coefficient ratio at 416 and 475 nm)**



It can be seen the growth rate decreases in all cases and also the terminal particle size.

**Fig. 7 Comparison of silver nanoparticles growth curves in reverse micelles of AOT in dodecane at various concentrations of Arlachel-20 (A.R.=Absorption Coefficient ratio at 416 and 475 nm)**



The increase in rigidity of the micelles introduced by addition of Arlachel-20 will reduce the successful collision leading to fusion between microemulsions and hence the exchange of reactants between microemulsions. Thus leading to decrease in growth rate. The smaller terminal particle size of the particle thus observed on addition of Arlachel-20 indicates the inability of the microemulsion to expand and support the growth of particle further.

## Conclusions:

The growth rate of silver nanoparticles was studied by changing intermicellar exchange (by varying the chain length of organic solvent) and interfacial rigidity (by addition of Arlacel-20).

It was found that silver nanoparticle growth rate was slower in heptane than decane and dodecane. AOT/Heptane microemulsion was also able to support larger terminal particle size than AOT/Decane and AOT/Dodecane. This dependence is due to the fact that heptane molecules are able to pack into microemulsion tails and effectively solvate the surfactant tails, whereas the bulky nature of decane and dodecane does not solvate the tails as readily.

Addition of Arlacel-20 was found to decrease the growth rate of silver nanoparticles and also terminal particle size reached in presence of Arlacel-20 was smaller. However, increase in concentration of Arlacel-20 from 0.25 M to 0.5 M had no significant effect on particle growth rate and terminal particle size.

## Acknowledgement:

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## Reference:

1. Y.M. Tricot and J.H. Fendler, *J.Am.Chem.Soc.*, **106**, 7359 (1984)
2. V.I. Colvin, M.C. Schlamps, A.P. Alivisatos, *Nature*, **370**, 354 (1994)
3. C.J. Loveth, W.B. Caldwell, X.G. Peng and A.P. Alivisatos, *Angew Chem.-Int. Ed. Engl.*, **38**, 1808 (1999)
4. I. Lisiecki and M.P. Pileni, *J. Phys. Chem.*, **99**, 5077 (1995)
5. J.P. Cason, M.E. Miller, J.B. Thompson and C.B. Roberts, *J. Phys. Chem. B*, **105**, 2297 (2001)
6. M.J. Hou, M. Kim and D.O. Shah, *J. Colloid and Interface Sci.*, **123** (2), 398 (1988)
7. R.P. Bagwe and K.C. Khilar, *Langmuir*, **16**, 905 (2000).