

## Solvent Effects on Copper Nanoparticle Growth Behavior in AOT Reverse Micelle Systems

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In this paper, we present the results of variations in the bulk solvent type and the addition of cosolvents on the growth rate of metallic copper nanoparticles produced through a reduction reaction within AOT reverse micelles. The metallic copper particles were characterized using both UV–vis spectroscopy and TEM microscopy. Growth rates are discussed in terms of an absorbance ratio, which provides a correlation between UV–vis absorption spectra and particle size. Time-resolved measurements showed that the intermicellar exchange rate and subsequent particle growth rate is a function of water content, bulk solvent, and the addition of cosolvents and cosurfactants. The copper particle growth rate was found to increase with increasing water content, but essentially the same particle size was eventually approached at all water contents. Copper particle growth was faster in isooctane than in cyclohexane because of the structure of the bulk solvent and the resulting degree of solvation into the micellar tail region. The cosolvent 1-octanol was found to decrease the copper particle growth rate when added in small amounts (up to 3 mol %) at two different water contents, but larger amounts of the cosolvent destabilized the micelle, increasing the growth rate and decreasing the terminal particle size. The cosolvent benzyl alcohol had the opposite effect, increasing the copper particle growth rate and decreasing the terminal particle size at all of the concentrations studied.

## Introduction

There is significant interest and ongoing research in the preparation and applications of nanometer-sized materials.<sup>1</sup> A technique that has been developed over the past decade involves the use of reverse micelles of surfactants in solution as “nano-reactors” within which controlled reactions leading to the formation of nanosized metallic and metal halide particles are carried out. The nanometer-sized water cores of the reverse micelles and the narrow aggregate size distributions provide an appropriate stabilized environment for the production of nanoparticles of fairly uniform size through chemical reactions within the cores.<sup>2–4</sup>

A popular surfactant used in these reverse micelle applications is the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (commonly known as AOT). AOT, when dissolved in organic solvents, is described as forming thermodynamically stable reverse micelle aggregates consisting of a hydrophilic core that is compartmentalized by the hydrophilic headgroup of the AOT with the hydrophobic alkyl tails extending into the nonpolar continuous-phase solvent. The size of the micelle core is described by the molar ratio of water to surfactant molecules in solution,  $W$  ( $= [\text{H}_2\text{O}]/[\text{AOT}]$ ). For AOT reverse micelles, the size of the core in nanometers is approximately  $1.8W$ .<sup>2</sup>

Some examples of this micellar synthesis route for the production of silver, copper, and semiconductor nanoparticles, to name a few, have been described in several review articles.<sup>2–4</sup> One reaction that has been examined in some detail is the formation of metallic copper nanoparticles through reactions within the cores of AOT reverse micelles in normal liquid

hydrocarbon solvents.<sup>5–7</sup> Specifically, this reaction was executed by the reduction of copper ions from either the functionalized surfactant  $\text{Cu}(\text{AOT})_2$  or the copper salt  $\text{CuSO}_4$  incorporated within the cores of the AOT reverse micelles with various reducing agents such as  $\text{NaBH}_4$  or  $\text{N}_2\text{H}_4$ . These reactions were examined using both isooctane and cyclohexane as the bulk solvents. The authors stated that the size of the metallic copper particles collected after allowing the reaction to proceed for a fixed reaction period of 5 h was influenced primarily by the water content of the micelle,  $W$ ; the average number of copper ions and reducing agent molecules per micelle; and the intermicellar potential as affected by the bulk solvent type and  $W$ . Interestingly, these researchers found that changing the solvent from isooctane to cyclohexane resulted in an effective decrease in the copper particle size after the 5-h reaction. These results suggest a solvent effect on this particle growth process. Lisiecki and Pileni<sup>7</sup> and Bagwe and Khilar<sup>8,13</sup> found that the solvent properties can play an important role in the dynamics of nanoparticle formation because of the different interactions between the solvent and the surfactant tails, and hence, they can influence the attractive interactions between micelles.

Whereas there have been numerous reports on the production of nanoparticles through the reverse micellar synthesis route that focus on the final product obtained, few have systematically examined the controlling variables of the particle “growth” process and the factors affecting the rate of particle formation (e.g., effect of fluid properties on particle growth rates).<sup>8–14</sup> Reverse micelles in solution will exchange the contents of their cores via both fusion and redispersion processes.<sup>10</sup> As a result, the reduction of a metal salt within the cores of reverse micelles can result in the growth of nanometer-sized metal particles within the core of the micelle. This particle growth within the cores of reverse micelles depends strongly on the exchange of the reactants between micelles. This exchange process occurs

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when micelles collide because of Brownian motion and the attractive forces between the micelles. These collisions result in fusion of the reverse micelles, an exchange of the contents within the cores, and a redispersion of the micelles.<sup>8,10</sup> Hence, depending on the rate of the inherent chemical reaction, particle production can be controlled by the rate of this intermicellar exchange process.<sup>8,11,12</sup>

This micellar exchange process is governed by the attractive interactions between droplets,<sup>15</sup> which can be modified by changing the amount of water within the micelle core (*W*), the properties of the bulk (or continuous-phase) solvent, and the degree of interaction between the bulk solvent and the surfactant tails.<sup>7,8</sup> The amount of water within the core of the reverse micelles affects the fluidity of the interface and, therefore, the probability that a collision will lead to coalescence. Changing the solvent from isooctane to cyclohexane results in a decrease in the micellar exchange rate constant by a factor of 10, as measured by Towey et al.<sup>11</sup> This solvent effect is of particular interest in this paper. We are also interested in the influence of added cosolvents to the bulk solvent that will modify the solvation of the surfactant tails of the reverse micelles and thereby impact the exchange rate. The way in which the bulk solvent or added cosolvent interacts with the micelle tails also affects the fluidity of the micelle interface. By varying these factors, the rate of particle growth within the reverse micelles can be tightly controlled.

This paper presents the results of an investigation of the formation of metallic copper particles within AOT reverse micelles. These studies investigate the particle growth process through time-dependent measurements rather than after fixed reaction times. We show that particle size is dependent on the growth rate, which is a function of the intermicellar exchange process. Specifically, we demonstrate the effect of water content, bulk solvent, and the addition of cosolvents on the growth rate of copper nanoparticles in AOT reverse micelles.

## Experimental Section

**Materials.** The surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was purchased from Fisher Scientific, and hydrazine (98%, anhydrous) was purchased from Aldrich. Isooctane (HPLC grade) and cyclohexane (>99%) were purchased from Acros Organics. The cosolvent benzyl alcohol (>99%) was purchased from Acros Organics, and 1-octanol was purchased from Fisher Scientific. All were used without further purification.

Cu(AOT)<sub>2</sub>, the functionalized form of the surfactant NaAOT, was used as the source of copper ions in the reduction reaction and was synthesized in a method similar to that previously described in the literature.<sup>5</sup> The synthesis occurred through a two-step ion-exchange process, which was performed in a batch process. In the first step of the synthesis, a 1.00 M CuSO<sub>4</sub> solution was put into contact with sodium resin (Bio-Rex 70 Resin, purchased from Bio-Rad Laboratories). Once the solution had been stirred with the resin, the CuSO<sub>4</sub> solution was poured off, and the resin was washed with a mixture of ethanol and H<sub>2</sub>O. The pH was equilibrated using 10 N NaOH (purchased from Fisher Scientific). In the second ion-exchange step, NaAOT was dissolved in an ethanol/H<sub>2</sub>O mixture and then put into contact with a strong cation-exchange resin (AG 50W-X8 Resin, purchased from Bio-Rad Laboratories). The exchanged H-AOT was then put into contact with the exchanged and equilibrated resin prepared in first step, and the two were allowed to mix. Finally, the solution was separated from the resin through filtration or pipetting and placed in a vacuum oven. Unfortu-

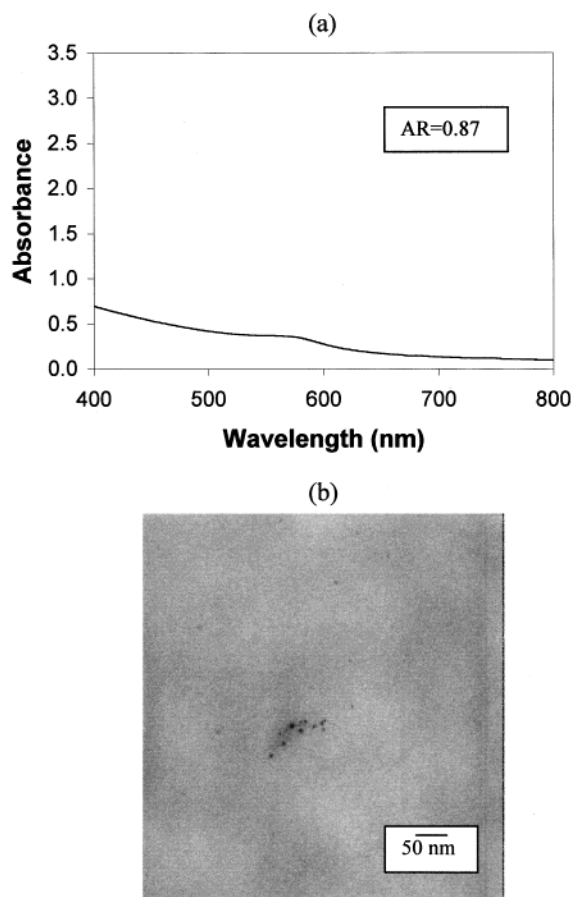
nately, this batch process does not allow for complete exchange of the AOT. Therefore, each batch of Cu(AOT)<sub>2</sub> had to be calibrated to ensure that the correct concentration (number of copper ions) was present in each experiment.

**Particle Formation.** The reverse micelle solutions were prepared by dissolving AOT at a concentration of 0.1 M and adding Cu(AOT)<sub>2</sub> as a source of copper ions at a concentration of 0.01 M (i.e., the ratio of Na to Cu in solution is roughly 10 to 1) in an organic solvent. Appropriate amounts of water were added to obtain a desired water content,  $3 < W < 15$ , and the solutions were allowed to mix for at least 2 h. The flask was deaerated by purging the solution with nitrogen gas to inhibit the formation of copper oxide. Once the surfactants were in solution, the reaction was initiated by adding hydrazine as the reducing agent at a concentration of three times that of the Cu(AOT)<sub>2</sub>. The initial reduction reaction is essentially instantaneous,<sup>12</sup> followed by the subsequent growth of the metallic copper clusters. The 1-cm path length suprasil quartz cuvette was placed in a UV-vis spectrophotometer and left unstirred. UV-vis absorption spectra were obtained on a Varian 3E UV-vis spectrophotometer periodically throughout each experiment. A small droplet of the solution was transferred to a TEM grid (carbon type-A, 400 mesh nickel grid), enabling direct measurement of the particle size on a Zeiss EM-10 transmission electron microscope (TEM).

## Results and Discussion

Colloidal dispersions of metals exhibit absorption bands or broad regions of absorption in the UV-vis region, thereby allowing in situ analysis of the copper nanoparticle size. These bands are due to the excitation of plasmon resonance or interband transitions and are characteristic properties of the metallic nature of the particles.<sup>16</sup> The absorption spectrum of colloidal copper particles has been described, including the effect of varying particle size.<sup>7</sup> In short, a progressive appearance of the 566-nm plasmon peak occurs as the size of the copper cluster increases. The absorption spectrum can be correlated to particle size on the basis of the ratio of the absorbance of the peak at 566 nm to an absorbance off the peak, in this case at the 500-nm wavelength ( $AR = \epsilon_{566}/\epsilon_{500}$ ). As an example, Figures 1a and 2a show the absorption spectra of copper particles synthesized in Cu(AOT)<sub>2</sub>/AOT reverse micelles, along with the AR value for the spectra. TEM grids were prepared from these samples, and examples of these micrographs are shown in Figures 1b and 2b. From these micrographs, a mean particle size can be calculated. The value of AR increases with increasing mean particle size, where  $AR = 0.87$  corresponds to a particle size of  $6 \pm 2$  nm and  $AR = 1.06$  corresponds to a mean particle size of  $12 \pm 4$  nm. Figure 3 presents a comparison of the correlation of AR to mean particle size from this study with that of Lisiecki and Pileni.<sup>7</sup> Good agreement between the two studies is obtained, with differences in the AR values at a given mean particle size differing by less than 5%.

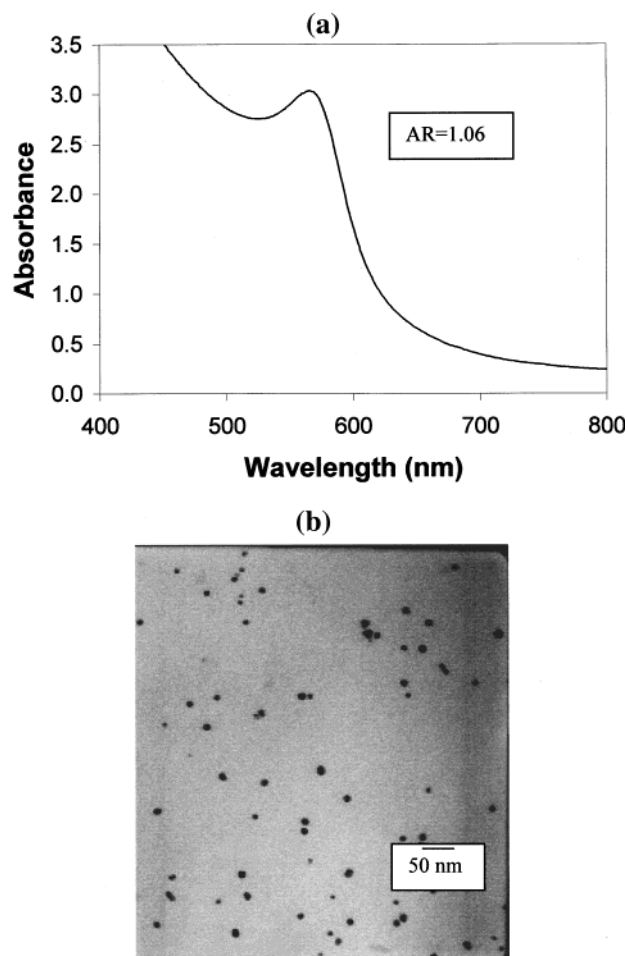
Copper particle growth in AOT/Cu(AOT)<sub>2</sub> reverse micelles in isooctane solvent was initially studied as a function of water content (*W*). Figure 4 presents the values of AR as a function of time for copper particles synthesized in isooctane at various water contents. This figure clearly demonstrates that the time required to reach a terminal particle size is strongly dependent on the water content. At larger values of *W*, the maximum particle size is reached within 4–6 h, as evidenced by the steady, unchanging AR value. In contrast, the lower values of *W* require as many as 15 h to reach a maximum particle size. In all cases, the AR values in this study are within 2% of those reported by



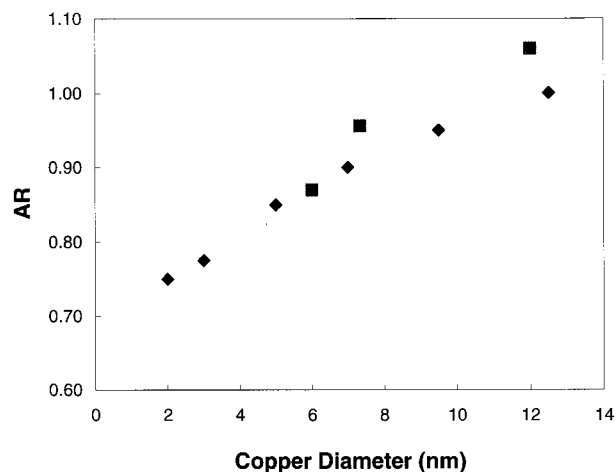
**Figure 1.** (a) Examples of UV-vis absorption spectra for copper nanoparticles and (b) TEM micrographs from the solutions from which the spectra were obtained. Average size for AR = 0.87 is approximately  $6 \pm 2$  nm.

Lisiecki and Pileni<sup>7</sup> at their reported reaction time of 5 h. At this 5-h mark, the AR value, and therefore the particle size, does increase with increasing values of  $W$ . However, it can be seen in Figure 4 that, if the reaction is allowed to proceed past 5 h, each curve approaches approximately the same AR value and, thus, essentially the same particle size, regardless of water content. From an examination of the entire growth curve, it is clear that, whereas the water content has a tremendous effect on the growth rate of the metallic particles, it might not be the sole controlling influence on the terminal particle size. In fact, given enough time, metallic particles with roughly the same size can be produced regardless of the water content. The results of copper particle growth in cyclohexane solvent at various water contents are shown in Figure 5. As was the case in isooctane, particle growth rates increase with increasing water content. Once again, the AR values at the 5-h sampling time as previously reported by Lisiecki and Pileni<sup>7</sup> are again very consistent, with errors of  $\leq 4\%$ .

Figures 4 and 5 clearly demonstrate the strong influence that water content has on the copper particle growth rate. Particle growth occurs much more rapidly at high values of  $W$  ( $W > 5$ ) than at low values of  $W$ , regardless of the bulk solvent. This is consistent with the results of Hirai and co-workers,<sup>10</sup> in their study of the coagulation rates of CdS and ZnS. The authors reported that the coagulation rate constant increases with increasing water content. Both Bagwe and Khilar<sup>8</sup> and Natarajan and co-workers<sup>12</sup> have explained this phenomenon in terms of metal occupancy number. As the water content increases, the average metal occupancy number increases. The larger the

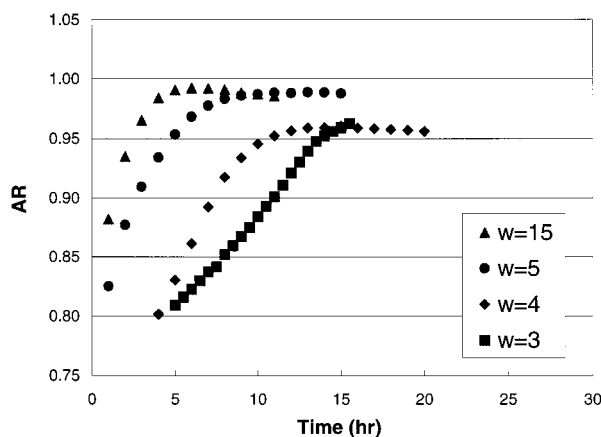


**Figure 2.** (a) Examples of UV-vis absorption spectra for copper nanoparticles and (b) TEM micrographs from the solutions from which the spectra were obtained. Average size for AR = 1.06 is approximately  $12 \pm 4$  nm.

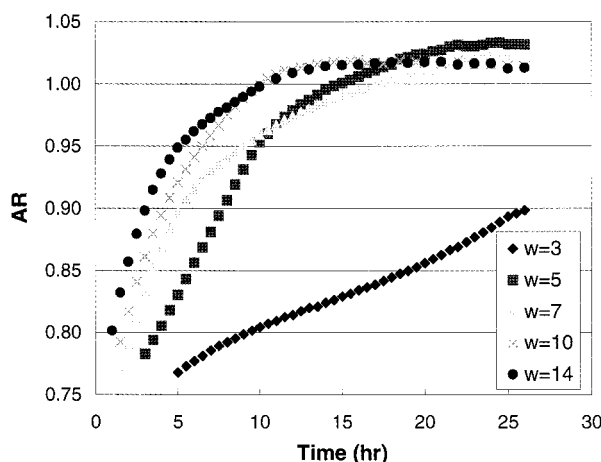


**Figure 3.** Correlation of AR value with copper particle size. (■) represent this study, (◆) data of Lisiecki and Pileni.<sup>7</sup>

occupancy number per micelle, the fewer the successful collisions required to reach a certain particle size. Another factor involved in the decreased growth rate at smaller  $W$  values involves the number of successful collisions being decreased at lower water contents because of the structure of the micelle. At low water contents, the water is "bound" to the surfactant headgroup, creating a tight interface.<sup>17</sup> As the water content increases, the water becomes free within the micelle core,



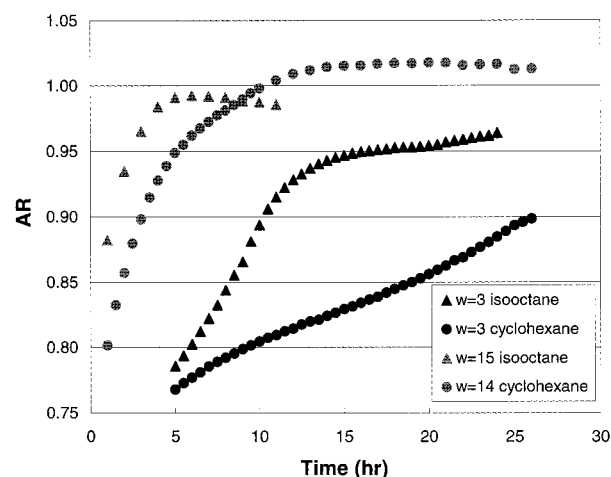
**Figure 4.** Comparison of growth curves for copper particles in AOT reverse micelles in isooctane solvent at various water contents. [AOT] =  $1 \times 10^{-1}$  M,  $[\text{Cu}(\text{AOT})_2] = 1.5 \times 10^{-2}$  M.  $W = 3$  (■);  $W = 4$  (◆);  $W = 5$  (▲);  $W = 15$  (●).



**Figure 5.** Comparison of copper particle growth curves in AOT reverse micelles in cyclohexane solvent at various water contents. [AOT] =  $1 \times 10^{-1}$  M,  $[\text{Cu}(\text{AOT})_2] = 1.5 \times 10^{-2}$  M.  $W = 3$  (■);  $W = 4$  (◆);  $W = 5$  (▲);  $W = 15$  (●).

increasing the size of the micelle and spreading out the surfactant headgroups. This creates a more fluid interface, increasing the number of successful collisions and resulting in coalescence of particles.

Another influence on the intermicellar exchange, and hence on the particle growth process, is the bulk solvent. Figure 6 illustrates the changes seen in the particle growth rates for copper in isooctane and cyclohexane solvents at two different water contents. These growth curves demonstrate a generally lower growth rate in cyclohexane as compared to that found in isooctane at both values of  $W$  presented. Although a limiting value for AR is not reached for a  $W$  of 3 because of the termination of the experiment, the slope of the cyclohexane curve at  $W = 3$  is certainly less than that of isooctane at  $W = 3$ , indicating a slower growth rate. At a  $W$  of 14, a limiting value for AR is reached in approximately 5 h in isooctane. However, the reaction in cyclohexane requires almost three times longer, reaching a limiting value after 15 h. This is consistent with the results of Fletcher et al.,<sup>9</sup> who calculated the exchange rate constant in AOT reverse micelles to be  $6.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for isooctane solvent and only  $0.80 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for cyclohexane solvent. These markedly different particle growth kinetics are a result of the changed micellar dynamics with the changed solvent properties. Bagwe and Khilar<sup>8</sup> explained similar behavior on the basis of the structures of the

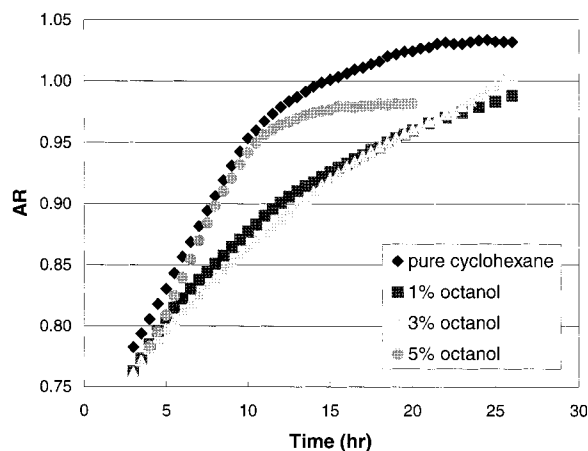


**Figure 6.** Comparison of copper particle growth curves in AOT reverse micelles at various water contents in isooctane (▲) and cyclohexane (●) solvents. [AOT] =  $1 \times 10^{-1}$  M,  $[\text{Cu}(\text{AOT})_2] = 1.5 \times 10^{-2}$  M.

different solvents. In the case of cyclohexane, the molecules can penetrate between the surfactant tails efficiently, leading to an increase in surfactant curvature and rigidity.<sup>8</sup> The more bulky isooctane solvent has more difficulty penetrating and solvating the surfactant tails. This creates a more fluid interface and, consequently, decreases interactions between the AOT tails and the isooctane compared to those with cyclohexane. Because of the decreased presence of isooctane solvent molecules in the tail region of the micelle compared to cyclohexane, the interdroplet tail–tail interactions are increased, resulting in an increase in the collision frequency and intermicellar exchange rate, which leads to an increase in the particle growth rate. Binks et al.<sup>18</sup> measured the bending elasticity constant (or rigidity) of AOT monolayers in various chain-length  $n$ -alkanes from  $\text{C}_7$  to  $\text{C}_{14}$ . Their results suggest that the rigidity of AOT microemulsions for  $\text{C}_7$ – $\text{C}_{10}$   $n$ -alkanes ( $\sim 1.0 \text{ kT}$ ) decreases only very slightly for an increase in  $n$ -alkane chain length up to  $\text{C}_{10}$  and then falls abruptly, reaching a value of  $0.06kT$  in tetradecane. The authors state that the decrease in rigidity with increasing chain length might be related to the differing degrees of oil penetration into the surfactant chain region. Moreover, Eastoe and Sharpe<sup>19</sup> studied the film rigidities of microemulsions of dichain phosphocholines in  $\text{C}_6$ – $\text{C}_{16}$   $n$ -alkanes. From  $\text{C}_6$  to  $\text{C}_{10}$   $n$ -alkanes, the rigidity decreased slightly, and it then decreased more smoothly above the  $n$ -decane chain length. This rigidity decrease has been linked to alkane penetration. Unfortunately, the AOT film rigidities presented by Binks et al.<sup>18</sup> were in various  $n$ -alkanes, and those in cyclohexane and isooctane were not compared. However, given cyclohexane's small size and ability to effectively pack into the surfactant tail region compared to the more bulky isooctane, one might anticipate that the film rigidity would decrease in going from cyclohexane to isooctane solvent. This might further contribute to the difference in the copper particle growth rates presented here. However, the modest change in rigidity for the microemulsions in  $n$ -alkanes between  $\text{C}_6$  and  $\text{C}_{10}$  might further suggest that the micelle exchange kinetics are more important than film rigidity in this case. Figure 6 also shows that, at  $W = 15$ , the terminal AR value in cyclohexane is larger than that in isooctane, indicating that the potentially more rigid micellar interface created by the cyclohexane molecule might support a larger particle.

Given that the properties of the bulk solvent have a strong influence on the particle growth kinetics, other means of

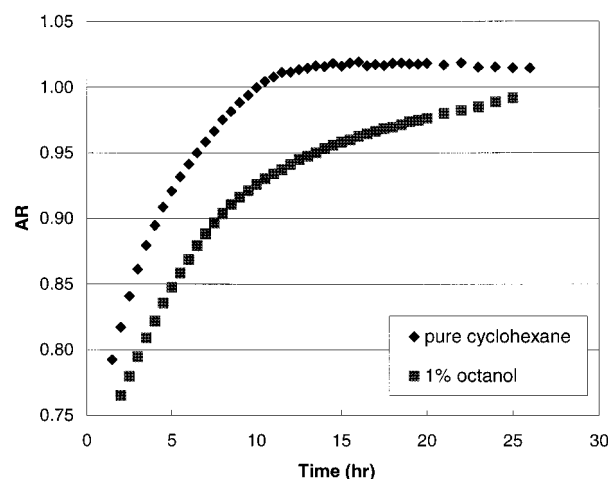




**Figure 7.** Comparison of copper particle growth curves in AOT reverse micelles in cyclohexane solvent at various concentrations of 1-octanol cosolvent.  $[AOT] = 1 \times 10^{-1}$  M,  $[Cu(AOT)_2] = 1.5 \times 10^{-2}$  M,  $W = 5$ . Pure cyclohexane (◆); 1 mol % 1-octanol (■); 3 mol % 1-octanol (▲); 5 mol % 1-octanol (○).

modifying the continuous phase should have additional influences. These modifications can be made through the addition of cosolvents or cosurfactants to a micellar solution. Traditional cosurfactants that have been used to promote the formation of reverse micelles are medium-chain-length alcohols (5–8 carbons) that have intermediate polarity similar to that found at the surfactant interface. These medium-chain alcohols are attracted to the micellar interfacial region, and the alkyl tails of the alcohols interact with the surfactant tails of the reverse micelles. Several studies have been performed to explore the effects of added cosolvent or cosurfactant on the structure of reverse micelles.<sup>8,9,20–22</sup> Intermicellar exchange can also be affected by the addition of cosurfactants and cosolvents. For example, Atik and Thomas<sup>23</sup> demonstrated in laser photolysis studies that ion transport between reverse micelles occurs on collision of the water pools and that various additives can affect the efficiency of mixing. In their study, for example, benzyl alcohol and hexanol were shown to have marked and opposing effects. The addition of benzyl alcohol resulted in an increase in the bimolecular rate constant for the exchange process by a factor of 25. The authors explained that the benzyl alcohol locates at the surfactant interface, causing disruption of the headgroup layer, which in turn facilitates solute penetration. On the other hand, the addition of hexanol at the interface resulted in a decrease in the rate constant for exchange by a factor of 0.58. An examination of these authors' work suggests that there is potential to further control copper particle growth kinetics with appropriate cosurfactants. In this paper, we have examined the effects of the addition of 1-octanol and benzyl alcohol on the growth rate of copper nanoparticles in AOT reverse micelles with cyclohexane as the bulk solvent.

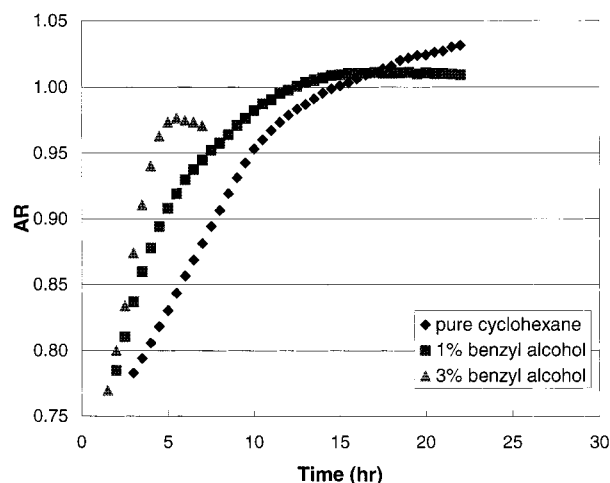
Figures 7 and 8 demonstrate the effects of the addition of 1-octanol to a reverse micelle solution in cyclohexane solvent at two different water contents. Figure 7 shows the addition of 1, 3, and 5 mol % of octanol at a  $W$  of 5. Samples with the smaller amounts of added octanol (1 and 3%) exhibit a relatively dramatic decrease in copper particle growth rate but ultimately appear to approach the final AR value of the pure solvent. These effects are most probably due to the effective interaction of the octanol at the micellar interface with the alcohol's linear alkyl tail interacting with the tails of the micelles, thus producing a more rigid interface and reducing the coalescence rate. The addition of 5% octanol to the cyclohexane follows the trend of



**Figure 8.** Comparison of copper particle growth curves in AOT reverse micelles in cyclohexane solvent at various concentrations of 1-octanol cosolvent.  $[AOT] = 1 \times 10^{-1}$  M,  $[Cu(AOT)_2] = 1.5 \times 10^{-2}$  M,  $W = 10$ . Pure cyclohexane (◆); 1 mol % 1-octanol (■).

the pure solvent very closely until a reaction time of 10 h, at which point the octanol system quickly levels off at an AR value considerably lower than that of the pure solvent. Figure 8 presents the effect of 1% octanol addition at a  $W$  of 10 in cyclohexane. As in the case of the lower  $W$  value, the small addition of octanol seems to decrease the particle growth rate considerably; however, the system seems to reach the same terminal particle size as particles produced in pure cyclohexane. Higher concentrations of octanol could not be studied with the larger  $W$  value because of phase separation. As described previously, higher  $W$  values create a more fluid interface. The addition of more than 1% octanol to an already fluid interface seems to create a more unstable system, breaking up the micelles. The reduced growth rate at the low cosurfactant concentrations seems to indicate that the octanol is able to penetrate to the interface and stabilize the micelle, causing fewer collisions that lead to an exchange of the contents. These results with 1-octanol are consistent with those for the addition of hexanol in the laser photolysis study of exchange rate constants in reverse micelles by Atik and Thomas.<sup>23</sup> The highest concentration in Figure 7, however, might actually weaken the interface, causing the micelles to coalesce more readily. This weakened interface created by 5% 1-octanol in Figure 7 is also indicated by the lower terminal particle size upon addition of the cosolvent.

Figure 9 displays the effect of the addition of 1 mol % benzyl alcohol to cyclohexane solvent at a  $W$  of 5. In this case, the growth rate actually increases with the addition of the cosolvent when compared to the pure solvent, whereas the terminal particle size decreases. This is consistent with work by Fletcher and co-workers<sup>9</sup> and Bagwe and Khilar,<sup>8</sup> who explain that the polar headgroup of the benzyl alcohol molecule favors the micelle headgroup region, whereas the benzene ring tends to open the interface. This increases the fluidity of the micelle and therefore increases the chance that the micelles will share the contents of the core when they collide. This is also consistent with the findings of Atik and Thomas<sup>23</sup> upon addition of benzyl alcohol in their laser photolysis studies. Once again, larger concentrations and water contents could not be studied here, as these conditions produce an unstable interface and hence phase separation. The smaller terminal particle size is likely to be due to an inability of the fluidlike interface to support a large particle.



**Figure 9.** Effect of benzyl alcohol addition on copper particle growth rate in AOT reverse micelles in cyclohexane solvent.  $[AOT] = 1 \times 10^{-1}$  M,  $[Cu(AOT)_2] = 1.5 \times 10^{-2}$  M,  $W = 5$ . Pure cyclohexane ( $\diamond$ ); 1 mol % benzyl alcohol ( $\blacksquare$ ); 3 mol % benzyl alcohol ( $\blacktriangle$ ).

## Conclusions

Various factors that affect the collision of reverse micelles in solution, thereby affecting the growth rate of copper nanoparticles, have been examined. One of the main factors that influence the rate of particle formation is the water content,  $W$ , within the cores of the reverse micelles. In two different solvents, the particle growth rate was shown to increase as  $W$  increased. This effect was due to the increased fluidity of the micelle interface as the water environment transitioned from bound water to free water within the micelle core. Whereas the particle growth rate was found to be strongly dependent on water content, the terminal particle size was independent of micelle size for the copper system.

Another factor that strongly influences the copper particle growth rate was the bulk solvent for the microemulsion. The copper particle growth was found to be significantly faster in isooctane solvent than in cyclohexane solvent. Cyclohexane was also able to support a slightly larger terminal particle size than isooctane. This dependence is due to the fact that cyclohexane is able to pack into the micelle tails and effectively solvate the surfactant tails, whereas the bulky nature of isooctane does not allow it to solvate the tails as readily.

The addition of liquid cosolvents and cosurfactants was also found to affect the growth of the copper nanoparticles. The long-chain alcohol 1-octanol was found to decrease the copper particle growth rate in concentrations up to 3 mol % for  $W = 5$  and at 1 mol % for  $W = 10$ . This is due to the ability of the octanol headgroup to bind to the micelle interface and the tails to effectively pack within the surfactant tails. This leads to a

decrease in micelle coalescence and therefore particle growth rate. At 5 mol % at  $W = 5$ , the particle growth rate was the same as in the pure solvent; however, the terminal particle size was lower because of the penetration of the alcohol into the water core and the consequent disruption of the micelle core. The addition of benzyl alcohol as a cosolvent led to an increase in the copper particle growth rate, as well as a decrease in the terminal particle size. This is due to the packing of the polar headgroup into the micellar interface, while the benzene ring tends to separate the surfactant tails, causing increased collision and coalescence and decreased stability.

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