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Catalysts:
Molecular Design Via Microemulsion-
Based Synthesis

Technical Progress Report
October - December 1993

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E. Boakye, L. R. Radovic and K. Osseo-Asare

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SYNTHESIS OF NANOSIZE MOLYBDENUM SULFIDE IN MICROEMULSIONS : EFFECT OF THE SYNTHESIS PROTOCOL ON PARTICLE SIZE

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ABSTRACT

Three different synthesis protocols were used to synthesize nanosize molybdenum sulfide particles in the microemulsion system polyoxyethylene(5)nonylphenyl ether (NP-5)/cyclohexane/water: (a) acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT), (b) tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA) and (c) microemulsion plus microemulsion (MPM), i.e., acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion. The particle size was found to depend on the synthesis method, especially at water-to-surfactant molar ratios (R) greater than 2.5. At $R=3.5-4.5$, the average particle size increased according to the synthesis method in the order: ASMPT < MPM < TSMPTA. Furthermore, for each synthesis protocol, the average particle diameter increased with the water-to-surfactant molar ratio (R). These trends are rationalized by considering: (a) the increase in the rate of exchange of materials between the inverse micelles as R is increased, and (b) the different effects of the electrolytes (i.e., sulfuric acid and ammonium tetrathiomolybdate plus sodium hydroxide) on microemulsion stability.

INTRODUCTION

The synthesis of particles in water-in-oil (w/o) microemulsions is a technique that has prospects in a wide variety of fields, such as ceramics, photographic emulsion technology and catalysis (1-8). A w/o microemulsion is a solution that, in its simplest composition, consists of oil, surfactant and water. It is a thermodynamically stable, transparent dispersion of microdrops of water in an organic phase. The surfactant molecules stabilize the water droplets by adsorbing at the water/oil interface.

The dispersed surfactant-stabilized water pools are capable of solubilizing metal salts, enzymes and other solubilizates (e.g., polymers) that are soluble in the aqueous domain (6,9-11). In addition, the w/o microemulsions exchange their droplet contents on the millisecond time scale via collision, fusion and fission (12). These properties of the inverse micelles offer the opportunity of making monodispersed materials in their water cores. Here the microemulsion droplets act as micro-cages and hence limit particle growth and aggregation (7,11,13-18). The synthesis protocols that have been used can be classified broadly as follows: (a) microemulsion plus a second reactant, (b) two microemulsions, and (c) microemulsion plus trigger (7).

For particles made in inverse micelles, the water-to-surfactant molar ratio (R), the reactant concentrations, and the dynamic behavior of the microemulsion droplets are among the key factors that determine particle size and size distribution. Recent

publications (18-21) show that the synthesis method may predetermine the particle size, although some ambiguities exist. For example, Lianos and Thomas (18) reported that CdS particles synthesized in the AOT/heptane/water microemulsion system produced particles of different sizes when the microemulsion plus a second reactant and the two microemulsions synthesis methods were used. The differences in particle size were attributed to the unequal solubilization rates of the ions in the microemulsion system, depending on the synthesis method. However, no investigation and demonstration of the differences in the solubilization rates were presented. On the other hand, Ward et al. (19) obtained particles of similar size and size distribution when the microemulsion plus a second reactant and the two microemulsions synthesis protocols were used to synthesize PbS particles in a nonionic microemulsion.

In our recent publication (15), we reported on the effects of the water content of the microemulsion and the tetrathiomolybdate ion concentration on the molybdenum sulfide particle size. In the present paper we present a study of the effect of the synthesis protocol on the molybdenum sulfide particle size and size distribution. In order to relate the particle size to the microemulsion properties, additional experiments were conducted involving measurements of the solubilization and solubility limits of aqueous acid and of ammonium tetrathiomolybdate solutions. The effects of the electrolytes on the microemulsion droplet size were also investigated. As in the earlier work (15), the microemulsion system polyoxyethylene(5)nonylphenyl ether (NP-5)/cyclohexane/water was used. This fluid phase was also exploited previously to

synthesize silica nanoparticles in this laboratory (7,22-24). The overall chemistry of molybdenum sulfide formation from ammonium molybdate is summarized in Equations 1 and 2:

From equation 2 it follows that molybdenum sulfide will form when the thiomolybdate species combine with protons in an inverse micelle.

EXPERIMENTAL

Materials. The following chemicals were obtained from Aldrich and were used as received: the non-ionic surfactant polyoxyethylene(5)nonylphenyl ether (NP-5; molecular weight, 440.63), ammonium tetrathiomolybdate (99.97%), and cyclohexane (99%).

Phase behavior. The methodology used to characterize the phase behavior of the microemulsion system 0.15 M NP-5/cyclohexane/aqueous phase was as reported previously (15). To check for the effect of the reactant species on the solubilization and solubility limits, the phase behavior of a number of samples containing 1.3×10^{-3} M sulfuric acid or 6.4×10^{-6} M ammonium tetrathiomolybdate and different water contents was observed as a function of temperature. (The concentrations are with respect to the

total microemulsion volume.) The phase behavior of the microemulsion samples containing only water as the solubilize was also recorded to analyze the effects of the electrolytes on the solubilization and solubility limits. The measurements of solubility and solubilization limits were reproducible to within ± 0.5 °C for a given R value. In preparing the ammonium tetrathiomolybdate impregnating solution, sodium hydroxide was added to enhance the dissolution of the molybdenum salt in water. Thus in making the 6.4×10^{-6} M ammonium tetrathiomolybdate microemulsion solution, aqueous sodium hydroxide was co-solubilized. In all cases, the concentration of sodium hydroxide with respect to the total microemulsion volume was 1.4×10^{-5} M. This procedure was followed in the preparation of all the tetrathiomolybdate-containing microemulsions used in the present investigation.

Micellar size measurement. Photon correlation spectroscopy (PCS) was used to measure the microemulsion droplet size (25-28). The light source was a coherent Innova 70-2 argon ion laser operating at 488 nm. The scattered light was collected at an angle of 90° by a goniometer and focused on a photomultiplier tube (Malvern Instruments Inc.) The correlation function was recorded with a Malvern 7032-8 correlator with 256 channels. The hydrodynamic size was calculated using a particle size distribution software provided by Malvern. Before carrying out the micellar size measurements, the sample was centrifuged to remove particles that may exist in the microemulsion. The refractive index of cyclohexane was measured with an Abbe-3L refractometer (Milton Roy

Company). The viscosity was determined with an ubbelohde viscometer immersed in a thermostated bath.

In the PCS technique, the fluctuations in scattered intensity of the inverse micelles due to their Brownian motion are measured over small time intervals. The magnitudes of the intensity and its delayed version are compared. The result is represented by the intensity autocorrelation function $G(\tau)$. The measured intensity autocorrelation function is related to the autocorrelation function $g(\tau)$ by Equation 3.

$$G(\tau) = A(1 + B|g(\tau)|^2) \quad (3)$$

In Equation 3, A and B are instrumental constants. For monodispersed colloidal particles, the autocorrelation function $g(\tau)$ is represented by the equation,

$$g(\tau) = \exp(-\Gamma\tau) \quad (4)$$

where Γ (the decay constant) is related to the diffusion coefficient of the particle (D) as in Equation 5.

$$\Gamma = Dq^2 \quad (5)$$

The scattering vector q is given by

$$q = [4\pi n/\lambda] \sin(\Theta/2) \quad (6)$$

where n is the refractive index of the solvent, λ is the wavelength of the incident light and Θ is the scattering angle.

A least squares fit permits the determination of B and Γ , from which the diffusion coefficient is obtained. Finally, the diffusion coefficient is related to the micellar radius (R) via the Stokes-Einstein relation (Equation 7), which assumes that the inverse micelles are spherical in shape:

$$D = kT/6R\pi\eta \quad (7)$$

In Equation 7, η is the viscosity of the solvent, T is the absolute temperature and k is the Boltzmann constant. For polydispersed systems $g(\tau)$ deviates from a single exponential (i.e., one particle size representation). Hence the method of moments (or cumulants) (29) was used to analyze the data.

Particle synthesis. Three synthesis protocols were used in this study. Considering the reaction in Equation 2, we describe the synthesis methods as: (a) acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT), (b) tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA), and (c) microemulsion plus microemulsion (MPM), i.e., acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion. Figure 1 is a schematic illustration of how each of the methods was implemented. In the ASMPT method (a), 12 μ L of 1.1 M aqueous sulfuric acid was first solubilized in 10 mL of NP-5/cyclohexane solution while bubbling high purity nitrogen gas. This was followed by adding 12.8

μL of 5×10^{-3} M ammonium tetrathiomolybdate. Nitrogen was further bubbled while molybdenum sulfide formed. On the other hand, for the TSMIPA method (b), $12.8 \mu\text{L}$ of ammonium tetrathiomolybdate was first solubilized, followed by the addition of $12 \mu\text{L}$ of 1.1 M dilute sulfuric acid. The final concentrations of sulfuric acid and ammonium tetrathiomolybdate were, respectively, 1.3×10^{-3} and 6.4×10^{-6} M with respect to the total microemulsion volume (10 mL). The synthesis was done at a temperature of 50°C . For the microemulsion plus microemulsion synthesis method (Figure 1c), 5 mL each of two microemulsion solutions, containing 2.6×10^{-3} M sulfuric acid and 1.28×10^{-5} M ammonium tetrathiomolybdate, were mixed at 50°C while bubbling nitrogen gas. Before mixing the microemulsion solutions, they were brought to a temperature of 50°C while bubbling high purity nitrogen gas. As noted above, all the tetrathiomolybdate-containing microemulsions also contained NaOH (1.4×10^{-5} M).

RESULTS AND DISCUSSION

Phase behavior. Figure 2a shows the effect of temperature on the solubilization of water and dilute sulfuric acid in the solvent system NP-5/cyclohexane. The region between the solubilization and solubility limits represents the one-phase microemulsion domain where the surfactant-stabilized microdroplets of water are dispersed in oil (cyclohexane). The water-in-oil microemulsion exists with excess water above the solubilization limit, whereas the surfactant phase containing dissolved water is separated from the oil below the

solubility limit. The trend in Figure 2a is consistent with the previously reported solubilization studies performed with nonionic surfactants as amphiphilic agents (15,22-24,30-34). The solubilization diagrams for water and acid are superimposed for comparison. No distinct differences are observed.

Figure 2b summarizes the combined solubility and solubilization diagrams for the solvent system 0.15 M NP-5/cyclohexane with water or a mixture of sodium hydroxide and ammonium tetrathiomolybdate solution as the aqueous domain. It is obvious that for the microemulsion system 0.15 M NP-5/cyclohexane/water/ammonium tetrathiomolybdate/sodium hydroxide, the one-phase microemulsion region is shifted to lower temperatures when compared to that of water as the solubilize.

The small differences in the solubility curves obtained with ammonium tetrathiomolybdate/sodium hydroxide and dilute sulfuric acid as solubilizates may be due to the following factors: (a) the ether oxygen atom may be regarded as a weak Lewis base (this is due to its possession of two lone pairs of electrons) and the water solubilized by the amphiphile as a weak Lewis acid; (b) the surfactant molecules may be salted out in the presence of electrolytes.

To separate the effects of aqueous ammonium tetrathiomolybdate and sodium hydroxide on the solubilization limits, the following experiments were conducted. The phase behavior of a number of microemulsion samples containing 1.4×10^{-5} M NaOH and different water contents were observed as a function of temperature. The results showed that, for all water-to-surfactant

molar ratios, the solubilization limit is reduced by about the same extent for the following combinations of solubilizates: (a) ammonium tetrathiomolybdate plus sodium hydroxide and (b) sodium hydroxide. From the above observations, it is concluded that the lowering of the solubilization diagram in the ammonium tetrathiomolybdate plus sodium hydroxide system may be attributed to the presence of aqueous sodium hydroxide.

A base such as OH^- (with three lone pairs of electrons) will compete for water molecules with the oxygen atoms of the surfactant oxyethylene groups. As a result, the extent of hydrogen bonding between the ether oxygen and water, which is the driving force for the solubilization of water molecules in the microemulsion (35,36), will decrease. Consequently the solubility of the electrolyte in the microemulsion will decrease.

Other investigators have offered a complementary explanation (32,33,37,38) for this behavior in terms of the 'salting-out' effect. This mechanism refers to the effective removal of water molecules from the ether oxygen group as a result of the preferential hydration of the solubilizates (39). In support of this view, Kon-no and Kitahara (32) found that the solubilization and solubility limits of the microemulsion system NP-8/tetrachloroethylene/water depended on the nature of the anion solubilized. The order of decrease in the solubilization diagram was reported as $\text{F}^- > \text{Cl}^- > \text{NO}_3^- > \text{I}^- > \text{SCN}^-$. These results were rationalized by the argument that the more basic anion dehydrates the ether oxygen group to a greater extent, thus lowering the solubilization diagram to a greater degree. Kahlweit et al (37) have summarized the salting-out mechanism using the

principle of hard and soft acids and bases (HSAB) which states that hard acids prefer hard bases while soft acids prefer soft bases (40). In this view, bases such as F^- and OH^- , which are regarded as hard, will interact preferentially with H_2O (Lewis acid) and are therefore selectively hydrated. In other words, the ether oxygen group is dehydrated and this results in a decrease in the solubility of water in the nonionic surfactant.

Effect of salinity on micellar size. Presented in Figure 3 are the results of the micellar size measurements for the solvent system 0.15 M NP-5/cyclohexane with water, ammonium tetrathiomolybdate and aqueous sulfuric acid as solubilizates. For each solubilizate, the micellar diameter increases with the water-to-surfactant molar ratio (R). Furthermore, for each R value, the microemulsion droplet size decreases on solubilizing ammonium tetrathiomolybdate or aqueous sulfuric acid.

Particle synthesis

Effects of R and synthesis protocol on particle size. Figure 4 summarizes the effects of the synthesis method on the average particle diameter for various R values. Figures 5, 6 and 7 present the corresponding TEM micrographs of the molybdenum sulfide particles. Generally, for all the synthesis schemes, the average particle diameter increases with R. Also within the limits of the standard deviation of the average particle size, the diameter is relatively insensitive to the method of preparation for R values of 1-2.5.

However at $R > 2.5$, the particle size and the size distribution depend on the synthesis method. At $R = 3$, the dependence of the particle size on the synthesis protocol is as follows: acid-solubilized microemulsion plus aqueous tetrathiomolybdate (ASMPT) < microemulsion plus microemulsion (MPM) ~ tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA). At $R = 3.5-4.5$ the particle size strongly depends on the synthesis protocol and is in the order ASMPT < MPM < TSMPTA.

Particle morphology. For R values in the range of 1-4, sphere-like particles were obtained for all the synthesis methods. On the other hand for $R = 4.5-5$, depending on the synthesis method, particles with sphere-like or irregular morphology were produced. Figures 8 and 9 present the TEM micrographs of the molybdenum sulfide particles synthesized in the NP-5/cyclohexane/water microemulsion system at $R = 4.5$ and 5 respectively, using the various synthesis schemes. For the ASMPT protocol, the particles are spherical in shape (Figures 8a and 9a). However, as demonstrated in Figures 8b, 8c, 9c and 9d, particles with irregular morphology are obtained for the MPM and the TSMPTA synthesis methods at $R = 4.5-5$.

Particle formation scheme. To rationalize the results presented in Figure 5, the following particle formation scheme in the w/o microemulsions is considered: (a) Tetrathiomolybdate ions and protons react in the water cores of the inverse micelles to form molybdenum sulfide monomers, (b) a critical number of molybdenum sulfide monomers combine in an inverse micelle to

form a nucleus; the nuclei grow either by adding on monomers or by aggregating (2,14,17,41).

Monomer addition growth. Particle growth and polydispersity due to monomer addition can be controlled by increasing the rate of nucleation of the particles in the microemulsion system. The nucleation rate in the microemulsion fluid phase is controlled by the 'ion occupancy number', N_{oc} (15,23,24,41), which represents the number of reactant species in an inverse micelle. As N_{oc} is increased, the supersaturation ratio ($S=C/C_{eq}$, where C_{eq} and C are the solute concentrations in the equilibrium and supersaturated solutions, respectively) increases and consequently the nucleation rate increases (41,42).

Summarized in Table 1 are data on the surfactant aggregation number (N), the number of inverse micelles (N_m), and the average molybdate occupancy number (N_{oc}). From the moles of the surfactant (NP-5) in the microemulsion (N_s), the average micellar diameter (D_m), and the volume of the dispersed (aqueous plus surfactant) phase (V_a), the number of inverse micelles (N_m) and the aggregation number (N) were calculated according to Equations 8 and 9:

$$N_m = V_a / (4/3)\pi(D_m/2)^3 \quad (8)$$

$$N = 6.022 \times 10^{23} \times N_s / N_m \quad (9)$$

Here it is assumed that the solubility of water in the oil (cyclohexane) is negligible. The volume of surfactant associated with the dispersed phase in the microemulsion was found from the mass and density of NP-5 (0.997 g cm^{-3}). The average molybdate occupancy number (N_{oc}), i.e., the number of ammonium tetrathiomolybdate molecules per inverse micelle, is given by Equation 10:

$$N_{oc} = N_{mo} \times 6.022 \times 10^{23} / N_m \quad (10)$$

where N_{mo} represents the moles of MoS_4^{2-} in the microemulsion. The calculation of the average occupancy number is based on the assumption that the reactant species are confined to the cores of the inverse micelles. This assumption is reasonable in that the reactant species are ionic and therefore incompatible with the nonpolar oil phase. Since the micellar aggregation numbers were affected by the presence of the reactant species, the number of inverse micelles in Table 1 was calculated using the measured diameter of the inverse micelle for the particular solubilized electrolyte.

As shown in Table 1, for a fixed volume of microemulsion containing a constant number of reactant species, the micellar size (as reflected by the aggregation number N) increases as R is increased. Consequently, the number of inverse micelles decreases and the average occupancy number (N_{oc}) increases. The increase in N_{oc} is expected to cause a corresponding increase in the nucleation rate. As a result of the relatively high nucleation rate achieved at high R , more nuclei are produced and relatively few monomers

(which can partake in the subsequent growth process) remain after the nucleation event and thus smaller particle sizes are to be expected (41). The above qualitative analysis, based on the occupancy number and the monomer addition growth process, indicates that smaller particles should be made at high R values (i.e., high occupancy numbers), while larger particles are to be expected at low R values (low occupancy numbers). However, in contrast to expectation, the reverse result was obtained, as seen from the particle diameter data in Table 1.

Figure 10 presents a plot of the occupancy number versus R for the various synthesis methods. An interesting observation in Figure 10 is that, for $R=1-3$, the occupancy numbers are about the same for all the synthesis protocols. It therefore follows that, based on the principles of particle growth outlined above, the particle diameter should be the same for all the synthesis methods, provided that R is in the range 1-3. Experimentally this was found to be true. For a given R value in the range 1-3, the average diameter is relatively insensitive to the synthesis method, as shown in Figure 4. For $R=3.5-5$ (Figure 10), N_{oc} decreases according to the synthesis protocol in the order $ASMPT > MPM > TSMPTA$. Thus, the number of nuclei formed is expected to increase in the order $ASMPT > MPM > TSMPTA$. The number of excess monomers (which are unutilized in nuclei formation) should then decrease in the order $TSMPTA > MPM > ASMPT$. Therefore, for $R=3.5-4.5$, the particle size should increase in the order $ASMPT < MPM < TSMPTA$. This is indeed found to be true for R values of 3.5-4.5 (see Figure 4).

From the analysis of the results presented so far, it can be concluded that the monomer addition model of growth consistently explains why the particle size increases in the order ASMPT < MPM < TSMPTA. However, as already noted above, it fails to rationalize why, for all the synthesis protocols, the particle size increases with R. This suggests that there may be another growth mechanism in operation, e.g., molybdenum sulfide particle aggregation.

Reactant distribution and particle formation. To elucidate the growth mechanism in the microemulsion fluid phase, it is useful to determine the number of nuclei expected to be produced by each synthesis method for various R values. As a first approximation, the distribution of ammonium tetrathiomolybdate ions in the micellar aggregates is considered to follow the Poisson statistical distribution law (24,41,43). This distribution gives the probability (P_k) of having k ammonium tetrathiomolybdate ions per inverse micelle as:

$$P_k = N_{oc}^k (e^{-N_{oc}} / k!) \quad (11)$$

In Equation 11, N_{oc} is the molybdate occupancy number. If at least two ammonium tetrathiomolybdate ions are needed to form a critical nucleus, and if it is assumed that only one nucleus can be produced in a given water pool, then the number of molybdenum sulfide nuclei produced in the w/o microemulsion should be equivalent to the number of micellar aggregates that contain two or more tetrathiomolybdate ions. That is, the number of nuclei (N_n) formed in the microemulsion can be written as follows:

$$N_n = N_m \sum_{k=i_c}^{\infty} P_k \quad (12)$$

where $\sum P_k$ is the probability that an inverse micellar water pool contains i_c or more MoS_3 monomers.

Figure 11 presents plots of the number of nuclei (determined using Equation 12, with $i_c=2$) versus R for all the synthesis methods. From Figure 11, the following observations can be made: (a) For each synthesis protocol, the number of nuclei increases with R , (b) for $R=1-3$, the number of nuclei is independent of the synthesis protocol; however, for $R=3.5-4.5$, the number of nuclei depends on the synthesis protocol in the order $\text{ASMPT} > \text{MPM} > \text{TSMPTA}$.

Monomer addition versus particle aggregation growth. The number of particles (N_p) in the microemulsion fluid phase may be determined as in Equation 13:

$$N_p = M_{\text{MoS}_3(t)} / M_p \quad (13)$$

where $M_{\text{MoS}_3(t)}$ corresponds to the total mass of MoS_3 in the microemulsion, and M_p is the mass of one MoS_3 particle (obtained from the product of the volume and the density of one MoS_3 particle). In the post-nucleation period, if growth occurred only by monomer addition, then the (experimentally determined) number of particles calculated with Equation 13 should be equal to the expected

(theoretical) number of nuclei produced initially (i.e., N_n , given by Equation 12). This implies that, as with the number of nuclei (Figure 11), the number of particles determined from Equation 13, should increase with R . However, in contrast to expectation, and as shown in Figure 12, the experimentally determined number of particles (N_p , Equation 13) decreases with increasing R . This indicates that initially many nuclei were produced in the microemulsion fluid phase and that these nuclei subsequently aggregated.

The ratio of the theoretical number of nuclei (N_n , Equation 12) to the number of particles (N_p , Equation 13) was determined. The results are summarized in Table 2. It can be seen that, for each synthesis protocol, $N_n > N_p$, i.e., $N_n/N_p > 1$ for any given R . This trend suggests that post-nucleation events, such as aggregation of nuclei and/or primary particles occur. From Table 2, the following additional observations can be made: (a) for all three synthesis protocols, the ratio N_n/N_p increases with R ; (b) comparing the different synthesis protocols, there is no major difference in the N_n/N_p values for $R=1-2.5$; and (c) for $R=3.5-4.5$, the ratio N_n/N_p increases dramatically in the order $ASMPT < MPM < TSMPTA$. If the ratio N_n/N_p is used as a measure of aggregation, then the following conclusions, corresponding to observations (a) to (c), can be reached: (a) particle aggregation should increase with R ; (b) the degree of aggregation should be independent of R for $R=1-2.5$; (c) for $R=3.5-4.5$, the degree of particle aggregation should decrease in the order $TSMPTA > MPM > ASMPT$. It is well known that as R increases, the rate of exchange (K_{ex}) of material between the microemulsion droplets increases (44-46); this should enhance the aggregation of

particles and/or nuclei. The work of Shah and coworkers (14,17) on silver halides in w/o microemulsions demonstrates that both the size and the polydispersity of AgCl and AgBr particles increase when the chain length of oil increases, the amount of cosurfactant increases and the chain length of the cosurfactant decreases. These trends correlate very well with the increase in K_{ex} as the microemulsion components are varied (14,17).

From the N_{oc} data in Table 1, it is seen that for every 10^3 inverse micelles there is approximately one thiomolybdate ion. If two molybdenum sulfide monomers are needed to form a critical nucleus (as previously assumed) and if aggregation of nuclei and/or primary particles does not occur (so that $N_n=N_p$), then the magnitude of the ratio N_m/N_p should be on the order of 10^3 . Based on the N_p values determined from Equation 13, the ratios N_m/N_p were determined. The results are included in Table 2. It is seen that out of every 10^8 inverse micelles only one particle forms. This is in contrast to the expected $10^3:1$ ratio noted above. This supports the conclusion that particle aggregation occurs in the w/o microemulsion via micellar fusion. In addition, due to the aggregation phenomena, the number of particles (N_p) in the microemulsion fluid phase decreases as R is increased while the ratio N_m/N_p increases. This is a result of the increase in the rate of exchange of material between inverse micelles as the water-to-surfactant molar ratio (R) increases (44-46). Furthermore, for R values of 1-4.5, the particle diameter (17-127 nm) is far larger than the micellar diameter (4-10 nm), which demonstrates that particles grow when inverse micelles coalesce and that the dynamic nature of the inverted micelles is a

factor that should be considered in predicting particle growth in w/o microemulsions.

Microemulsion destabilization and particle aggregation.

It is interesting to note that for $R=3.5-4.5$, the extent of particle aggregation (as determined by the ratios N_n/N_p and N_m/N_p) strongly depends on the synthesis method. These ratios decrease in the order TSMPTA > MPM > ASMPT (Table 2). This trend may be explained by referring to Figures 2a and 2b. As discussed in the section on phase behavior, the phase stability diagram is lowered by about 4 °C, especially at relatively low R values ($R < 10$), when aqueous tetrathiomolybdate (containing NaOH) is used as the solubilize, compared to the case where dilute sulfuric acid is used. At $R=4$ the solubilization limit is 50 ± 0.5 °C, while it is below 50 ± 0.5 °C at $R > 4$. Thus, solubilization of aqueous ammonium thiomolybdate in the microemulsion at 50 °C (before the addition of acid) induced phase separation. Observations made during the experiments showed some cloudiness.

Therefore, when the TSMPTA protocol is used (i.e., solubilizing aqueous ammonium tetrathiomolybdate-containing sodium hydroxide before the addition of aqueous sulfuric acid), the solvent system 0.15 M NP-5/cyclohexane/water/thiomolybdate will be composed of excess aqueous ammonium thiomolybdate solution and dispersed droplets of aqueous thiomolybdate solution stabilized by surfactant films in cyclohexane. The phase separation will induce polydispersity in the synthesis product since some particles will form in the one phase microemulsion system whereas others will not (but

are formed in the conjugate bulk aqueous phase). In addition, the particles made outside the one-phase microemulsion domain have a greater tendency to aggregate since they are produced outside the microemulsion cages and are not protected by surfactant films. A typical example of aggregation is presented in Figure 7c: the TEM micrograph shows particles of 70 nm (average size) clustering around a central particle of ~1200 nm.

For the MPM synthesis protocol, ammonium tetrathiomolybdate and the acid are solubilized in separate microemulsions at 50 °C before mixing. Although the microemulsion containing the thiomolybdate ions will phase-separate at 50 °C (Figure 2b), that of the acid will not (Figure 2a). The degree of phase separation when the tetrathiomolybdate-solubilized microemulsion is added to the acid-solubilized microemulsion may be relatively less compared to the TSMPTA method. Thus, it is reasonable to expect that at $R=4$, particle aggregation occurs to a lesser extent when the MPM method is used compared to that of TSMPTA.

On solubilizing aqueous sulfuric acid before the addition of aqueous ammonium tetrathiomolybdate at 50 °C, there is no phase separation at $R=1-4.5$. Thus the degree of phase-separation-related particle aggregation is expected to be relatively small. Consequently, the particle size is expected to be small when the ASMPT synthesis protocol is used compared to the MPM and TSMPTA methods.

Aggregation, induced by the destabilization of the microemulsion water cores, becomes less prominent as R is decreased, and more pronounced as R increases. As R decreases the solubilization limit (the temperature limit above which the two-

phase microemulsion region is reached) increases. Thus at high R values (3.5-5) the instability of the microemulsion droplets may be the reason why the extent of particle aggregation strongly depends on the synthesis protocol. However, at $R=1-2.5$, the thiomolybdate microemulsion is stable at the synthesis conditions and hence, there is no significant dependence of the particle size on the synthesis protocol. Similar observations have been reported recently by Wilcoxon et al. (47) and Barnikel et al. (48), respectively, in the synthesis of gold and silver particles in microemulsions. Polydispersed aggregates of gold and silver particles were formed outside the one-phase microemulsion region.

At R values of 4.5 and 5 (Figures 8 and 9) particles of irregular morphology are made when the TSMIPA and the MPM synthesis methods are used. On the other hand, sphere-like particles are obtained when the ASMPT protocol is used (Figures 8a and 9a). Examples of particles of irregular morphology are presented in Figures 8b, 8c, 9c and 9d. These particles were made outside the one-phase microemulsion region (outside the micellar cages). That is, they were synthesized in the absence of protective surfactant cages. In this case extensive aggregation of the primary particle may lead to larger particles with non-spherical shape. This effect appears to be more significant for the TSMIPA method (Figure 9d), where the destabilization of the microemulsion droplets is expected to be greatest (Figure 2b). For the MPM method (Figure 9b), some sections of the TEM grid also contained spherical particles with rough surfaces, indicating particle aggregation.

Kitahara and coworkers (49,50) have shown that the particle size and the size distribution of calcium and barium carbonate particles made in the NP-6/cyclohexane/water microemulsion system depend on the microemulsion phase region where the particles are made. Monodispersed spherical calcium carbonate particles were made in the colorless one-phase microemulsion region whereas in the blue translucent region, polydispersed particles were obtained (49). In the case of the barium carbonate system (50), depending on the microemulsion region, particles of different morphology were produced. Rod-like and ellipsoidal particles were made in the colorless and blue translucent regions respectively. The above observations and the results of this study show that, depending on the microemulsion region, particles of different morphology could be made in the microemulsion system.

CONCLUSIONS

This work on the effect of the synthesis protocol on the particle size shows that at water-to-surfactant molar ratios (R) of 1-2.5 the particle size is insensitive to the synthesis protocol. On the other hand, at $R=3.5-4.5$ the average particle size increases according to the synthesis method in the following order: acid-solubilized microemulsion plus aqueous tetrathiomolybdate (ASMPT) < acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion (MPM) < tetrathiomolybdate-solubilized microemulsion plus aqueous sulfuric acid (TSMPTA). At $R=3.5-4.5$ the dependence of particle size on the synthesis method is due to the

destabilization of the microemulsion droplets, which is caused by first solubilizing the ammonium tetrathiomolybdate precursor solution containing aqueous sodium hydroxide at 50 °C. For the MPM and TSMPA synthesis protocols, particles of irregular morphology were obtained at $R=4.5$ and 5, which is also due to extensive aggregation of primary particles outside the one-phase microemulsion domain. By considering the distribution of ammonium tetrathiomolybdate ions in the microemulsion fluid phase, a quantitative growth model shows that particle growth is by aggregation. For each synthesis protocol, the extent of aggregation increases with R , which is attributed to the increasing rate of fusion and fission of water pools as R is increased.

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Figure 1 Particle synthesis methods in water-in-oil (w/o) microemulsions: (a) Acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT), (b) tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA), (c) acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion (microemulsion plus microemulsion, MPM).

Figure 2a. Solubilization diagrams of water and of dilute sulfuric acid in the 0.15 M NP-5/cyclohexane/water microemulsion; $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3}$ M.
●, solubility limit, H_2O ; ○, solubilization limit, H_2O ;
■, solubility limit, H_2SO_4 ; □, solubilization limit, H_2SO_4 .

Figure 2b. Solubilization diagrams of water and of aqueous ammonium tetrathiomolybdate/sodium hydroxide in the 0.15 M NP-5/cyclohexane/water microemulsion; $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6}$ M, $[\text{NaOH}] = 1.4 \times 10^{-5}$ M.
●, solubility limit, H_2O ; ○, solubilization limit, H_2O ;
▲, solubility limit, $(\text{NH}_4)_2\text{MoS}_4$; Δ, solubilization limit, $(\text{NH}_4)_2\text{MoS}_4$.

Figure 3. Effect of the water-to-surfactant molar ratio (R) on the hydrodynamic diameter of the inverse micelles in the microemulsion system 0.15 M NP-5/cyclohexane/water at 30 °C. $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3}$ M, $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6}$ M, $[\text{NaOH}] = 1.4 \times 10^{-5}$ M.

Figure 4. Effect of the water-to-surfactant molar ratio (R) on the average molybdenum sulfide particle size for the 0.15 M NP-5/cyclohexane/water microemulsion system using different synthesis protocols: Acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT), tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA), acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion (MPM). $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3}$ M, $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6}$ M, $[\text{NaOH}] = 1.4 \times 10^{-5}$ M.

Figure 5. TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion system, using the acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT) protocol: $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3} \text{ M}$; $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6} \text{ M}$; $[\text{NaOH}] = 1.4 \times 10^{-5} \text{ M}$; (a) $R=1$; (b) $R=2$; (c) $R=3$; (d) $R=4$.

Figure 6. TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion system, using the acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion (MPM) protocol: $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3} \text{ M}$; $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6} \text{ M}$; $[\text{NaOH}] = 1.4 \times 10^{-5} \text{ M}$; (a) $R=2$; (b) $R=2.5$; (c) $R=3$; (d) $R=4$.

Figure 7. TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion system, using the tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA) protocol: $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3} \text{ M}$; $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6} \text{ M}$; $[\text{NaOH}] = 1.4 \times 10^{-5} \text{ M}$; (a) $R=2$; (b) $R=3$; (c) $R=3$; (d) $R=4$.

Figure 8. TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion system at $R=4.5$ using different protocols: (a) acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT); (b) acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion (MPM), and (c) tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA); $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3} \text{ M}$; $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6} \text{ M}$; $[\text{NaOH}] = 1.4 \times 10^{-5} \text{ M}$.

Figure 9. TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion system at $R=5$ using different protocols: (a) acid-solubilized microemulsion plus tetrathiomolybdate (ASMPT); (b,c) acid-solubilized microemulsion plus tetrathiomolybdate-solubilized microemulsion (MPM), and (d) tetrathiomolybdate-solubilized microemulsion plus acid (TSMPTA); $[\text{H}_2\text{SO}_4] = 1.3 \times 10^{-3} \text{ M}$; $[\text{MoS}_4^{2-}] = 6.4 \times 10^{-6} \text{ M}$; $[\text{NaOH}] = 1.4 \times 10^{-5} \text{ M}$.

Figure 10. Effect of the water-to-surfactant molar ratio (R) on the average molybdate occupancy number N_{oc} ; $[MoS_4^{2-}] = 6.4 \times 10^{-6}$ M; $[NaOH] = 1.4 \times 10^{-5}$ M.

Figure 11. Effect of the water-to-surfactant molar ratio (R) on the number of nuclei (N_n , Equation 12) formed in the NP-5/cyclohexane/water microemulsion; $[H_2SO_4] = 1.3 \times 10^{-3}$ M; $[MoS_4^{2-}] = 6.4 \times 10^{-6}$ M; $[NaOH] = 1.4 \times 10^{-5}$ M.

Figure 12. Effect of the water-to-surfactant molar ratio (R) on the number of molybdenum sulfide particles (N_p , Equation 13) formed in the NP-5/cyclohexane/water microemulsion; $[H_2SO_4] = 1.3 \times 10^{-3}$ M; $[MoS_4^{2-}] = 6.4 \times 10^{-6}$ M; $[NaOH] = 1.4 \times 10^{-5}$ M.

Table 1

Statistical parameters for the formation of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion.

R	Particle diameter (nm) ^a			N ^b			N _m × 10 ⁻¹⁹ ^c			N _{oc} × 10 ³ ^d		
	ASMPT	MPM	TSMPT	ASMPT	MPM	TSMPT	ASMPT	MPM	TSMPT	ASMPT	MPM	TSMPT
1.0	17.3	16.3	21.5	44	43	42	4.1	4.3	4.5	0.94	0.90	0.87
1.5	19.5	24.9	21.8	54	50	45	3.6	3.8	4.0	1.07	1.01	0.95
2.0	22.4	26.6	29.0	65	57	50	3.1	3.4	3.6	1.24	1.15	1.07
2.5	26.1	30.2	34.0	69	65	61	2.8	2.9	3.1	1.39	1.32	1.26
3.0	26.7	40.0	37.2	73	73	73	2.5	2.5	2.5	1.57	1.56	1.55
3.5	31.8	54.8	64.1	100	89	78	2.0	2.2	2.3	1.90	1.77	1.65
4.0	48.7	60.3	85.0	127	105	82	1.6	1.9	2.2	2.42	2.04	1.76
4.5	72.9	118	127	149	120	92	1.3	1.7	2.0	2.90	2.33	1.95
5.0	-	-	-	170	155	139	1.1	1.4	1.8	3.62	2.73	2.18

^a Average molybdenum sulfide particle diameter obtained via TEM measurements.

^b N is the surfactant aggregation number (Equation 9).

^c N_m is the number of inverse micelles in 10 ml of microemulsion (Equation 8).

^d N_{oc} is the average molybdate occupancy number (Equation 10).

Table 2

Statistical parameters for the formation of molybdenum sulfide particles in the NP-5/cyclohexane/water microemulsion.

R	N_n/N_p			$(N_m/N_p) \times 10^{-8}$		
	ASMPT	MPM	TSMPTA	ASMPT	MPM	TSMPTA
1.0	13	10	23	0.29	0.25	0.59
1.5	21	41	25	0.37	0.81	0.54
2.0	37	58	69	0.49	0.86	1.2
2.5	65	95	130	0.68	1.1	1.6
3.0	80	260	240	0.65	2.1	2.0
3.5	150	760	1100	0.89	4.9	8.4
4.0	430	1100	2700	1.5	5.5	18
4.5	2900	10000	11200	7.0	38	56

Fig 1

Fig 2a

Fig 2b

Fig 3

Fig 4 Continued.

300nm

Fig 5

300nm

fig 6

300nm

Fig 7

300nm

Fig 8

300nm

Fig 9

Fig 10

Fig 11

Fig 12