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# Novel Nanodispersed Coal Liquefaction Catalysts: Molecular Design Via Microemulsion-Based Synthesis

Technical Progress Report
April - June 1992

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## PROJECT OBJECTIVES

The objective of this project is to pursue the development of highly dispersed and inexpensive catalysts for improved coal solubilization and upgrading of coal liquids. A novel study of the synthesis of liquefaction catalysts of nanometer size will be carried out. It is based on the molecular design of reverse micelles (microemulsions). These surfactant-stabilized, metal-bearing microdrops offer unique opportunities for synthesizing very small particles by providing a cage-like effect that limits particle nucleation, growth and agglomeration. The emphasis will be on iron- and molybdenum-based catalysts, but the techniques to be developed should also be generally applicable. The size of these very small and monodispersed particles will be accurately determined both separately and after *in situ* and *ex situ* coal impregnation. The as-prepared nanoparticles as well as the catalyst-impregnated coal or char matrix will be characterized using the following techniques: dynamic light scattering, x-ray diffraction, x-ray photoelectron spectroscopy, scanning and/or transmission electron microscopy, and selective chemisorption. Catalytic activity tests will be conducted under standardized conditions in both hydrogenation and hydrodesulfurization reactions. The effect of particle size of these unsupported catalysts on the product yield and distribution during liquefaction of a bituminous and a subbituminous coal will thus be quantitatively determined.

## INTRODUCTION

Our previous work has shown that the catalytic efficiency of molybdenum sulfide particles is inversely proportional to the particle size (1). In this quarter we report the effect of ammonium tetrathiomolybdate concentration on the synthesis of molybdenum sulfide in the 0.15 M NP-5/cyclohexane/water microemulsion system. The results of this study provide evidence that knowledge of the water-to-surfactant molar ratio and the ion occupancy number is vital in designing the optimum conditions needed to make particles of desired size.

## EXPERIMENTAL SECTION

*Materials.* The following chemicals were obtained from Aldrich: the non-ionic surfactant polyoxyethylene(5)nonylphenyl ether (NP-5), ammonium tetrathiomolybdate (99.97%), and cyclohexane (99%). Before use, cyclohexane was dried with molecular sieves.

*Phase Behavior and Microemulsion Characterization.* The phase diagram of the microemulsion system 0.15 M NP-5/cyclohexane/sulfuric acid was recorded as follows: The phase behavior of a number of samples containing a fixed surfactant-to-oil molar ratio and different water contents was observed as a function of temperature. The solubility and solubilization limits were found to be reproducible for a given R value. The density of the NP-5/cyclohexane/water microemulsion for each water-to-surfactant molar ratio (R) was measured with a digital densitometer (DMA 40, Paar Co.) at 25 °C. The partial molar volume of solubilized water at various water-to-surfactant molar ratios was calculated as in Reference 2.

*Particle Synthesis.* The reverse microemulsion NP-5/cyclohexane/aqueous sulfuric acid was prepared at room temperature by adding 12 μL of 1.1 M aqueous sulfuric acid to a 10 mL solution of 0.15 M NP-5/cyclohexane. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen gas through it for five minutes. This procedure was followed by adding 12.8 μL of $2.5 \times 10^{-3}$ M - $5 \times 10^{-3}$ M ammonium tetrathiomolybdate to the 0.15 M NP-5/cyclohexane/sulfuric acid microemulsion. Nitrogen was further bubbled while the molybdenum sulfide was being precipitated according to the reaction:

$$MoS_4^{2-} + 2H^+ = MoS_3 + H_2S \quad (1)$$

The concentrations of the reactant species with respect to the total microemulsion volume were as follows: $3.2 \times 10^{-6}$ - $6.4 \times 10^{-6}$ M ammonium tetrathiomolybdate and $1.3 \times 10^{-3}$ M sulfuric acid.

*Particle Characterization.* Samples for transmission electron microscopy were prepared by directly dropping a very small amount of molybdenum sulfide dispersion on carbon-coated copper grids and drying at room temperature. Prior to sample extraction each sample bottle was sonicated for one minute. Particle size was determined with a Philips 420 transmission electron microscope operating at 120 kV with a resolution of about 0.6 nm. The diameters of at least 300 particles were measured for each sample to obtain an average particle diameter and standard deviation.

## RESULTS AND DISCUSSION

*Phase Behavior and Microemulsion Characterization.* Figure 1 presents the solubilization diagram of the 0.15 M NP-5/cyclohexane/aqueous sulfuric acid microemulsion. The region between the solubilization and solubility curves represents the one phase microemulsion domain in which the nanosize molybdenum sulfide particles were synthesized. Figure 2 presents a plot of the partial molar volume of water (0.15 M NP-5/cyclohexane/water microemulsion) versus the water-to-surfactant molar ratio (R). The rate of change of the partial molar volume with R is initially high and slows down at $R = 2$. At $R > 2.5$-4 the partial molar volume of water in the microemulsion approaches that of bulk water (18.069 at 25 °C). This result suggests that at $R <$

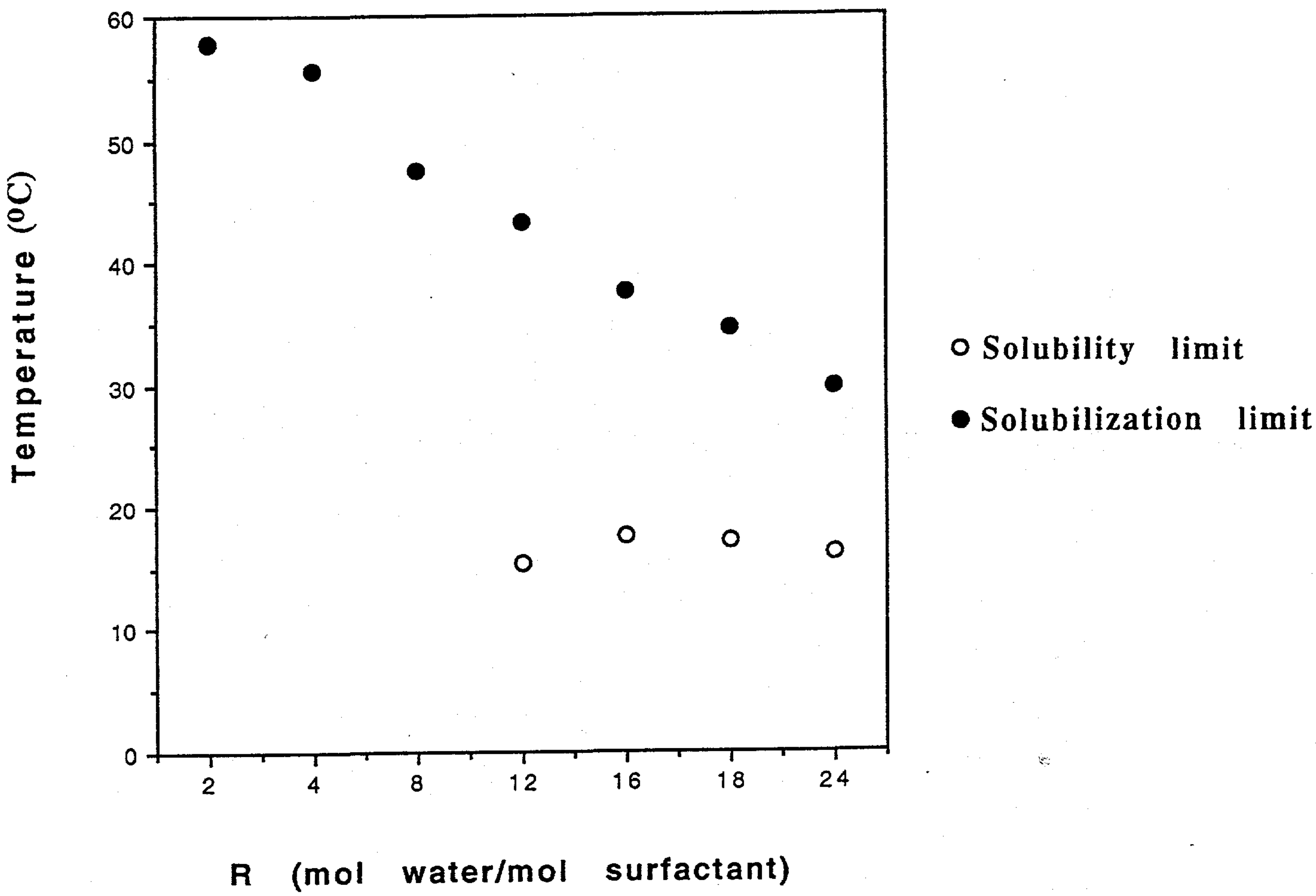


**Figure 1.** Solubilization diagram for aqueous sulfuric acid in the 0.15 M NP-5/cyclohexane system. $[H_2SO_4] = 1.3 \times 10^{-3}$ M.

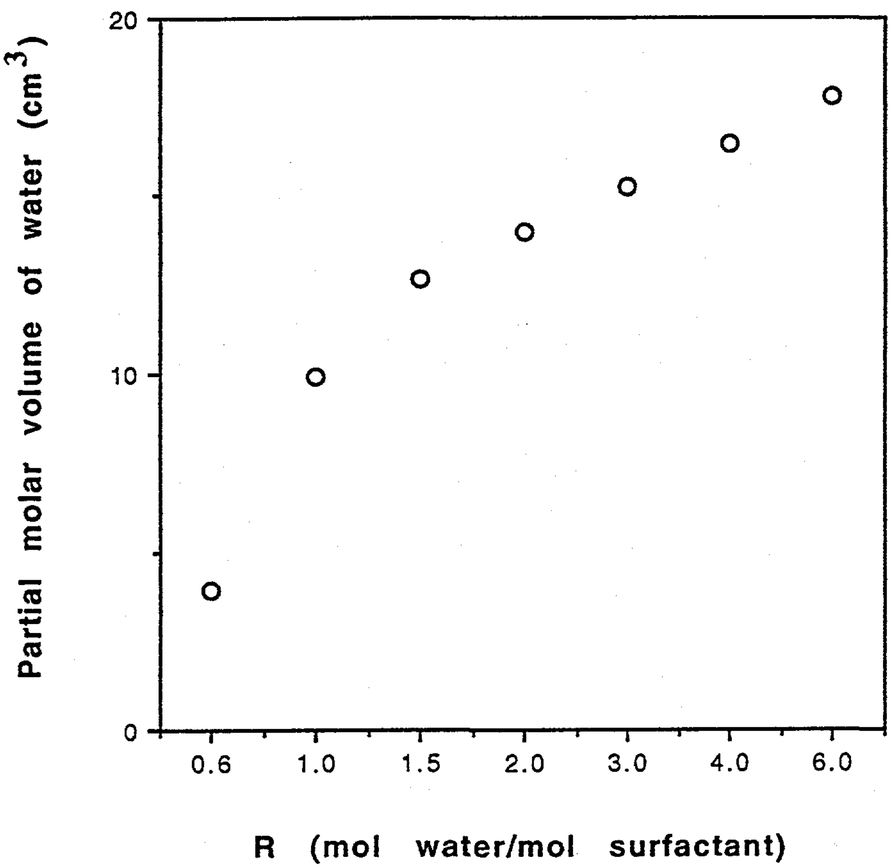


**Figure 2.** Effect of water-to-surfactant molar ratio (R) on the partial molar volume of water at 25 °C in the 0.15 M NP-5/cyclohexane/water microemulsion system.

2 the water molecules are relatively immobilized - they are bound to the hydrophilic portion of the amphiphile (NP-5) via hydrogen bonding) - and that free or unbound water molecules are found in the hydrophilic core of the reverse micelles at $R > 2$. This finding is in agreement with previously reported studies (3,4) on the state of water solubilized in reverse micellar systems formulated with polyoxyethylene nonylphenyl ether.

*Effect of Water-to-Surfactant Molar Ratio (R) on Particle Size.* Figures 3 and 4 respectively present plots of average particle diameter versus the water-to-surfactant molar ratio and the size histogram of molybdenum sulfide particles for two different catalyst precursor concentrations, $[MoS_4^{2}] = 3.2 \times 10^{-6}$ and $[MoS_4^{2}] = 6.4 \times 10^{-5}$ M. Figure 5 presents TEM micrographs of molybdenum sulfide particles in the 0.15 M NP-5/cyclohexane/water microemulsion system. For $[MoS_4^{2-}] = 3.2 \times 10^{-6}$ M, the average particle diameter decreases with R to a value of 2 and then increases with R, while for $[MoS_4^{2-}] = 6.4 \times 10^{-6}$ M the average particle diameter increases monotonically with R.

These trends may be rationalized by considering the underlying nucleation and growth phenomena (5,6). The process of particle formation from dissolved ions can be represented in the following order: Ions -> Monomer -> Nuclei -> Particles (5,6). After a stable nucleus is formed, it can grow by the following growth processes: (a) incorporation of ions and monomers in solution to already formed nuclei (5), and (b) aggregation of primary particles or nuclei to form bigger particles (6,7). In order to form a stable nucleus, a cluster containing a critical number of monomers ($N_c$) must form (5,6). A critical parameter in this connection is the ion occupancy number, i.e., the number of reactant species in a reverse micelle. A nucleus is formed if the ion occupancy number is greater than $N_c$.

As the water-to-surfactant molar ratio is increased, the surfactant aggregation number increases (4,8), and consequently the micellar concentration decreases. This corresponds to an increase in the ion occupancy number. For a given set of experiments, the concentrations of the reactant species ($MoS_4^{2-}$ and $H^+$) with respect to the total microemulsion volume are maintained

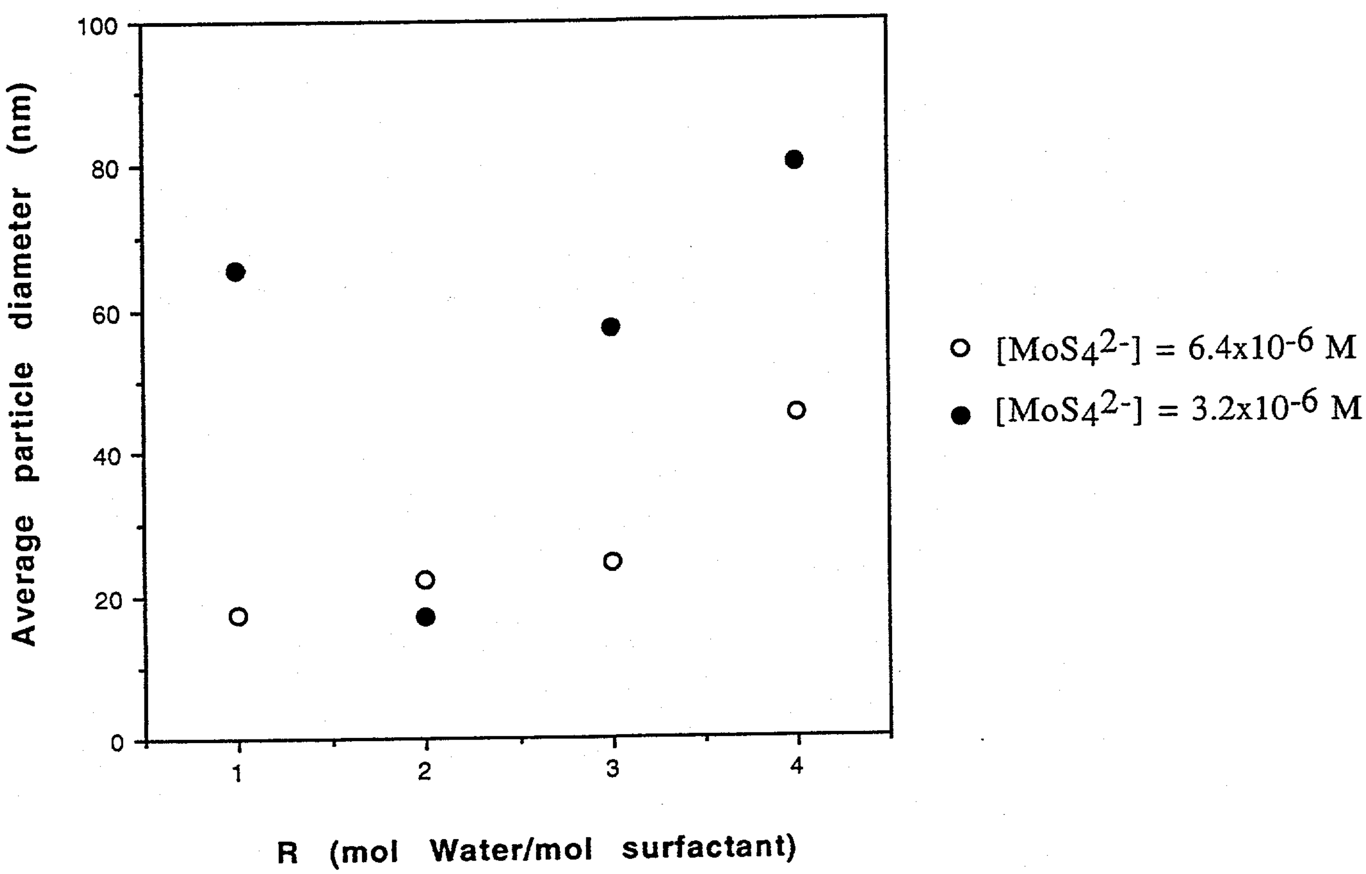


**Figure 3.** Effect of water-to-surfactant molar ratio (R) on the average molybdenum sulfide particle size for the 0.15 M NP-5/cyclohexane/water microemulsion. $[H_2SO_4] = 1.3x10^{-3}$.

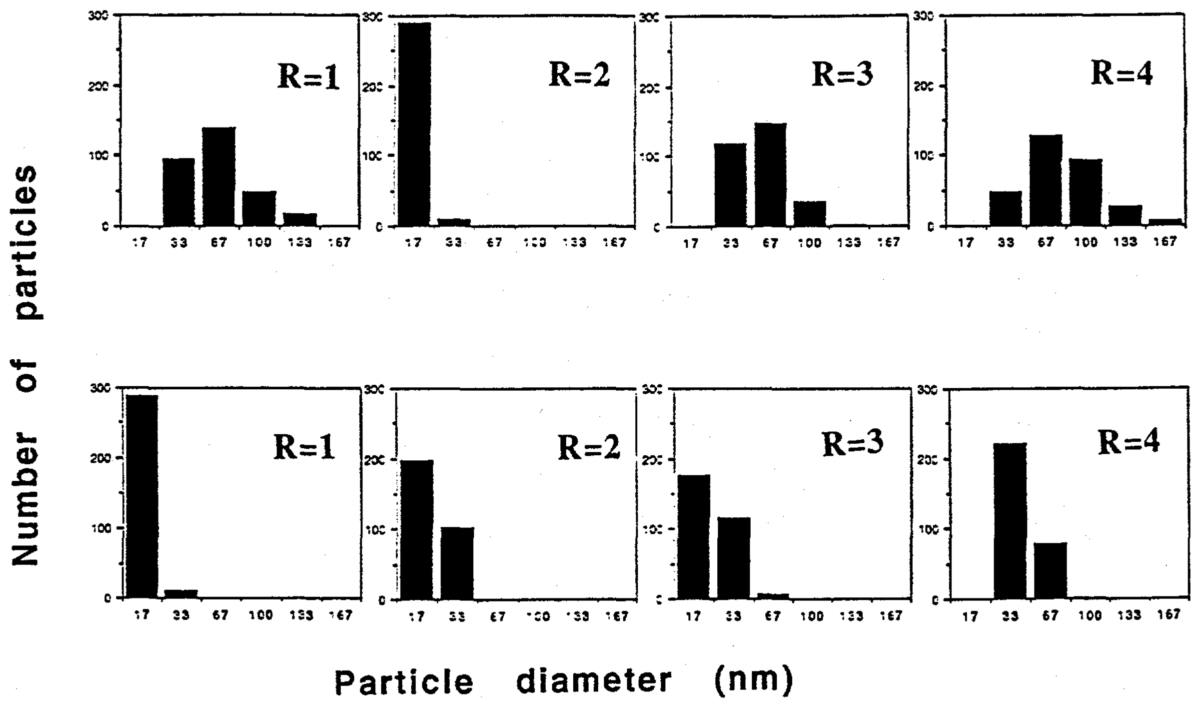


**Figure 4.** Size histogram of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsion system. Top, $[MoS_4^{2-}] = 3.2x10^{-6}$; bottom, $[MoS_4^{2-}] = 6.4x10^{-6}$ M.

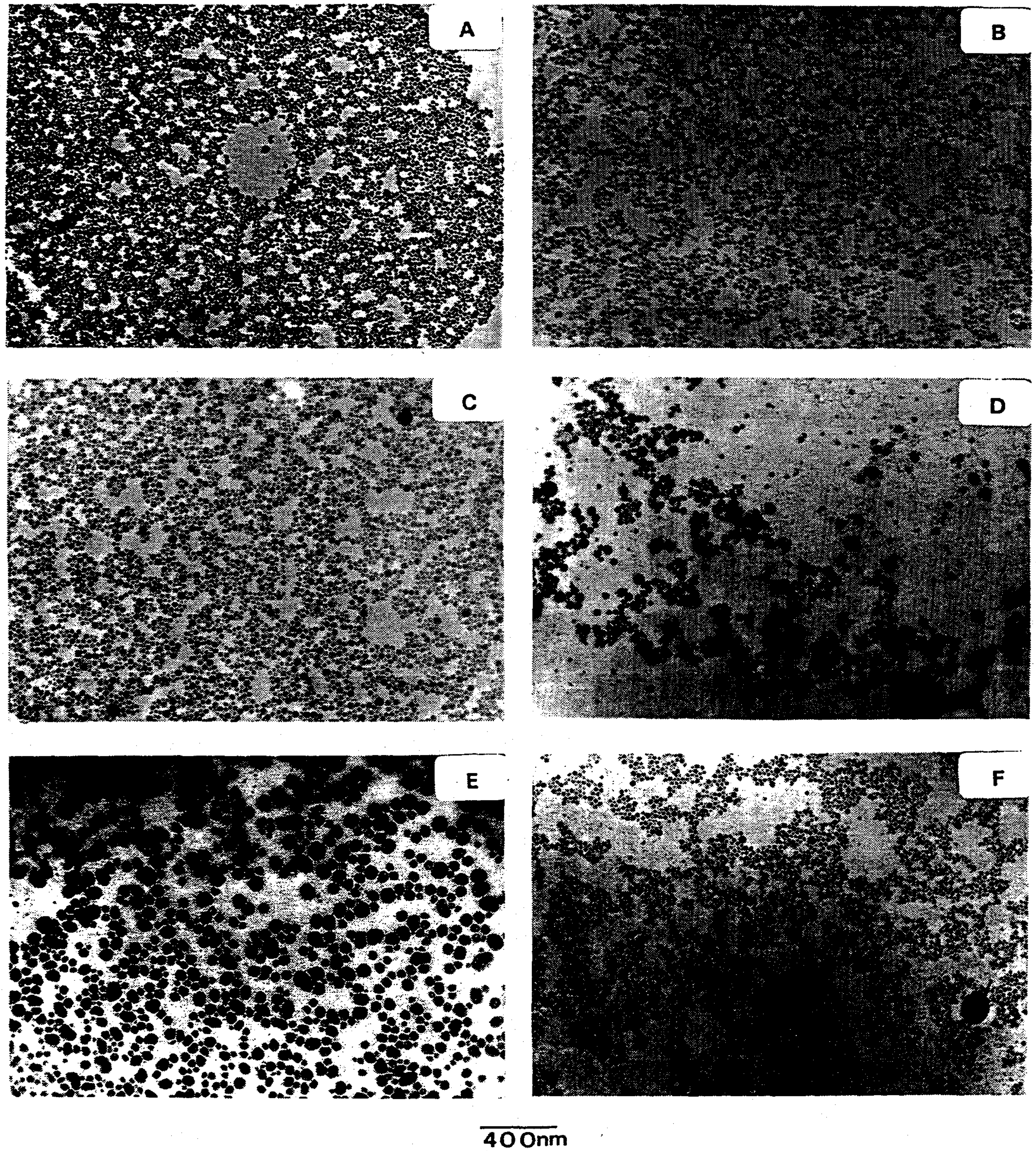


**Figure 5.** TEM micrographs of molybdenum sulfide particles prepared in the 0.15 M NP-5/cyclohexane/water microemulsions.

[$MoS_4^{2-}$] = $6.4 \times 10^{-6}$ M: (A) R=1; (B) R=2; (C) R=3; (D) R=4.

[$MoS_4^{2-}$] = $3.2 \times 10^{-6}$ M: (E) R=1; (F) R=2.

constant. Molybdenum sulfide will precipitate when the protons and tetrathiomolybdate ions find themselves in the same reverse micelle. The probability of such an encounter increases as the ion occupancy number increases, and hence, an increase in the number of nuclei in the reverse micelles is to be expected with increase in the ion occupancy number. The nucleation and initial growth of particles takes place in the reverse micelles through collision, fusion and splitting of reverse micelles.

Summarized in Table 1 are data on the number of reverse micelles ($N_m$), the average molybdate occupancy number ($N_{oc}$), i.e., the ratio of the number of tetrathiomolybdate ions to the number of reverse micelles ($N_{oc} = N_{MoS_4^{2-}}/N_m$), the number of particles in 10 mL of microemulsion ($N_p$), and the ratio $N_m/N_p$ for different water-to-surfactant molar ratios. The calculation of the average molybdate occupancy number is based on the assumption that all ions are solubilized and are confined in the cores of the reverse micelles. As demonstrated by the data in Table 1, the surfactant aggregation number decreases, and the micellar concentration increases, as the water-to-surfactant molar ratio is decreased (4,8). Thus, for a constant reactant concentration (e.g., $[MoS_4^{2-}] = 3.2x10^{-6}$ M and low R values), relatively few water cores will contain the minimum number of ions required to form a nucleus. As a result, the ions left over after the nucleation are relatively large. These ions will be incorporated into the already formed nuclei via inter-micellar communication and will contribute to growth, leading to large particles, as demonstrated for R=1 and $[MoS_4^{2-}] = 3.2x10^{-6}$ M. As the concentration of ammonium tetrathiomolybdate is increased from $3.2x10^{-6}$ to $6.4x10^{-6}$ and the water-to-surfactant molar ratio is kept constant at R=1, the ion occupancy number increases and particle size decreases, as illustrated in Figure 3. Similar observations have been reported by Lianos and Thomas (9) in the synthesis of CdS in the AOT/heptane/water microemulsion; at R=32, larger particle sizes were formed at smaller occupancy numbers.

For $[MoS_4^{2-}] = 3.2x10^{-6}$ M, the observed decrease in the particle size with an increase in R below R=2, can be attributed to the increase in ion occupancy number with R. As R increases, the aggregation number increases, the micellar concentration decreases, and therefore the ion

**Table 1**

Statistical Parameters for the Formation of Molybdenum Sulfide Particles Prepared in the 0.15 M NP-5/Cyclohexane/Water Microemulsion

| R | N (a) | $N_m$ | $N_{oc} = \frac{N_{MoS_4^{2-}}}{N_m}$ | |
|---|---|---|---|---|
| | | | $[MoS_4^{2-}]=3.2x10^{-6}$ M | $[MoS_4^{2-}]=6.4x10^{-6}$ M |
| 1 | 45 | $2.0x10^{19}$ | $1.0x10^{-3}$ | $1.9x10^{-3}$ |
| 2 | 77 | $1.2x10^{19}$ | $1.7x10^{-3}$ | $3.3x10^{-3}$ |
| 3 | 113 | $0.8x10^{19}$ | $2.4x10^{-3}$ | $4.8x10^{-3}$ |
| 4 | 148 | $0.6x10^{19}$ | $3.2x10^{-3}$ | $6.3x10^{-3}$ |

| R | $N_p$ $(x10^{-14})$ | | $N_m/N_p$ $(x10^{-5})$ | |
|---|---|---|---|---|
| | $[MoS_4^{2-}]=$ $3.2x10^{-6}$ M | $[MoS_4^{2-}] =$ $6.4x10^{-6}$ M | $[MoS_4^{2-}]=3.2x10^{-6}$ M | $[MoS_4^{2-}]=6.4x10^{-6}$ M |
| 1 | 0.08 | 9.1 | 24 | 0.2 |
| 2 | 4.6 | 4.1 | 0.2 | 0.3 |
| 3 | 1.3 | 3.2 | 6.3 | 2.5 |
| 4 | 0.05 | 0.7 | 13 | 9.1 |

(a) Aggregation numbers from Kitahara's data (8).

occupancy number increases as indicated in Table 1. From nucleation theory (5), it is expected that the greater the number of nuclei in the microemulsion, the smaller the corresponding final particle size. This is because there will be relatively few ions left over for growth after the nucleation process, i.e., almost all the ions are used up in the nucleation process.

For $[MoS_4^{2-}] = 3.2\times10^{-6}$ M and $R > 2$, the proportion of water in the microemulsion is relatively high, hence the aggregation number is large, the concentration of swollen reverse micelles is reduced, and the occupancy number is significantly increased. Thus a greater number of nuclei and therefore smaller particle sizes are expected. Contrary to expectation, however, large particle sizes are obtained. The trend observed at $R > 2$ may be rationalized by considering the ratio $N_m/N_p$. It can be seen from the $N_{oc}$ data in Table 1 that on the average one $MoS_4^{2-}$ ion is solubilized per $10^3$ reverse micelles. As a first approximation, if two molybdenum sulfide monomers form a particle, then the magnitude of $N_m/N_p$ should be on the order of $10^3$. However from Table 1, $N_m/N_p$ is on the order of $10^5$. That is, one out of every $10^5$ reverse micelles forms a particle. This suggests primary particle aggregation via fusion of reverse micelles, and this may be the mechanism of particle growth at $R > 2$.

## CONCLUSION

Small monodispersed molybdenum sulfide particles have been synthesized in 0.15 M NP-5/cyclohexane/water microemulsions. The results indicate that careful control of the water-to-surfactant molar ratio and the ion occupancy number is vital in the designing the optimum conditions needed to make particles of desired size.

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