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

Technical Progress Report
January - March 1993

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DISCLAIMER

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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 is being 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 is on molybdenum- and iron-based catalysts, but the techniques being 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 are characterized using a battery of techniques, including dynamic light scattering, x-ray diffraction and transmission electron microscopy. Catalytic activity tests are conducted under standardized coal liquefaction conditions. The effect of particle size of these unsupported catalysts on the product yield and distribution during conversion of a bituminous and a subbituminous coal are being determined.

INTRODUCTION

In this quarter we report the results of the solubilization of aqueous ammonium tetrathiomolybdate and the synthesis of molybdenum sulfide particles in the following microemulsion systems: 0.4 M NP-5/tetralin/methanol, 0.4 M NP-5/tetralin/propanol and 0.4 M NP-5/tetralin/hexanol. The solubilization data are discussed in terms of the spontaneous curvature of the interface and inter-micellar interaction. Although the reverse micelles provide a protective environment that inhibits particle growth, the particle size was found to depend on the concentration of ammonium tetrathiomolybdate in the aqueous domain and the chain length of the co-surfactant.

EXPERIMENTAL

Materials. The following chemicals were obtained from Aldrich and used as received: the non-ionic surfactant polyoxyethylene(5)nonylphenyl ether (NP-5), ammonium tetrathiomolybdate (99.97%), methanol (99.9%), propanol (99%) and hexanol (98%).

Solubilization. The solubilization capacity was measured by titrating directly into each microemulsion sample under vigorous stirring. A Hamilton microsyringe was used. The quantity of aqueous species added is determined by weight difference. The onset of permanent turbidity was taken to be the limit of solubilization of the aqueous phase in the microemulsion.

Particle synthesis. The synthesis experiments were conducted at 50 °C. Solutions of 0.4 M NP-5/tetralin/methanol, 0.4 M NP-5/tetralin/propanol and 0.4 M NP-5/tetralin/hexanol were first made at room temperature. The alcohol-to-surfactant mass ratio was fixed at 2.5 for each microemulsion. The microemulsion-plus-a-second-reactant method was used. Here 36.2 µL of 1.1 M aqueous sulfuric acid was added to a 10 mL solution of tetralin-alcohol solution. The acid-solubilized microemulsion samples were deoxygenated by bubbling high purity nitrogen gas. This procedure was followed by adding 36.2 µL of $1.25\text{x}10^{-2}$ - $7.50\text{x}10^{-2}$ M ammonium tetrathiomolybdate to each microemulsion. Nitrogen gas was further bubbled while molybdenum sulfide precipitated according to the reaction:

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

The concentration of ammonium tetrathiomolybdate was varied from $4.53\text{x}10^{-5}$ to $3.62\text{x}10^{-4}$ M, depending on the type of microemulsion, while that of sulfuric acid was kept constant at $4\text{x}10^{-3}$ M.

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. Before sampling each 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 200 particles were measured for each sample to obtain an average particle diameter.

Catalyst Testing. Catalyst screening tests were performed with two coals - a Wyodak subbituminous coal (PSOC 1401) and a Blind Canyon bituminous coal (DECS-6) - both obtained from the Penn State Coal Sample Bank. The coal was ground to -200 mesh and dried under vacuum at 110 °C for 2 h prior to reaction. Molybdenum sulfide particles synthesized in two different micellar systems were tested. The first system employed benzyl alcohol as a co-surfactant, while the second (more recently developed) uses methanol to strengthen the oil-water interface. In our earlier reports, it has been pointed out that the evaluation of the effectiveness of catalyst particles synthesized in microemulsions requires careful consideration of the catalyst/solvent system. This is because the microemulsion is a mixture of several distinct components, each of which might be expected to play a different role during the liquefaction process. Therefore, over the last six months a protocol has been developed that enables a distinction to be made between those effects that are the result of employing a highly dispersed catalyst and those that arise from other *influences (e.g., coal/solvent ratio or solvent composition). Briefly, this involves* performing tests with two types of microemulsion. The first is the micellar system alone - designated as "blank microemulsion" to indicate the absence of any catalyst particles - and the second is the "metal-loaded" microemulsion, so called because it carries catalyst particles in suspension. The test with the blank microemulsion corresponds to the conventional "thermal" (uncatalyzed) experiment. Subtracting this result from that obtained in the second ("catalyzed") test would thus provide an indication of catalyst effectiveness.

All tests - unless otherwise indicated - were performed at 350 °C, 1000 psi H_2 (cold) for 30 min (including heat-up time) in 25 cc stainless-steel microautoclave reactors. The reactors were subsequently quenched in water. After depressurizing, the contents of the reactor were washed using THF into tared ceramic thimbles. Overnight extraction with THF was performed in a soxhlet apparatus under N_2 flow. The THF-insoluble residue in the thimble was then washed with acetone and pentane to remove THF, dried in a vacuum oven for over 6 h at 110 °C, and weighed. The THF-soluble portion was further separated into oils and asphaltenes by adding approximately 50 volumes of hexane after removing the THF in a rotary evaporator. Following agitation, the asphaltenes were allowed to settle overnight and separated from the hexane-solubles by filtration. The asphaltenes were dried in a similar fashion as the residue and weighed. The total conversion was based on the THF-insoluble residue. The yield of oils was calculated by difference. All conversions are reported on a dry, ash-free basis.

RESULTS AND DISCUSSION

Task 1: Catalyst Characterization

Solubilization: Theoretical Background. Recently, Shah and coworkers (1,2) presented a model that qualitatively explains the differences in water solubility for water-in-oil (w/o) microemulsions formulated with alcohols of different chain lengths as co-surfactants. The solubility capacity also depends on the ionic strength of the aqueous domain and the oil phase. The model outlines the induction of phase separation as a consequence of (i) the curvature of the interface and (ii) the attractive interactions of the swollen reverse micelles.

The curvature effect, which applies only to relatively rigid interfaces, is said to arise from the differences in interaction between adjacent polar head groups of the reverse micelles and those of the adjacent hydrocarbon moiety (2). It represents the tendency of the surfactant interface to bend towards the aqueous phase or the oil. The total free energy of the interface of a w/o microemulsion is represented as:

$$F = n[4pR^2g + 16pK(1 - R/R^o)^2] \qquad (2)$$

where R^o is the radius of spontaneous curvature (natural radius), R is the equilibrium radius of the swollen reverse micelles, g is the surface tension of the interface, n is the number of swollen reverse micelles and K is the curvature elasticity constant (with units of energy). The interfacial tension term is the first term in Equation 2 and the interfacial curvature term is the second term. High and low values of K correspond to rigid and fluid interfaces, respectively. The value of K is of the order of 10^{-14} erg for microemulsions (3,4). This implies that, for the curvature effect to be important, the surface tension of the interface should approach zero.

For a stable w/o microemulsion with a relatively rigid interface and low water content, the equilibrium radius is less than the natural radius ($R<R^o$). The equilibrium radius R increases as water molecules are added. In the limit when $R>R^o$ the excess water is expelled from the microemulsion droplet. At this stage there is phase separation. The composition of the system is w/o microemulsion in equilibrium with excess water. This type of phase separation is referred to as type 1 separation (1).

As the rigidity of the microemulsion interface is decreased, e.g., by adding short-chain-length alcohols, the inter-micellar interaction increases, leading to inelastic collisions and the formation of transient dimers and relatively large reverse micelles. As the fluidity is further increased, the micellar radius approaches a critical value R^c which represents the solubility of the water in the microemulsion. At $R>R^c$ there is phase separation. Here relatively few large reverse micelles exist in equilibrium with the continuous oil phase. This type of phase separation, which is driven by inter-micellar interactions, is referred to as type 2 separation (1).

Solubilization: Results and Discussion. Figure 1 presents the results of solubilization of water and ammonium tetrathiomolybdate in the 0.4 M NP-5/tetralin/n-alcohol/microemulsion. The solubility is expressed as the water-to-surfactant molar ratio above which phase separation occurs. As the alcohol chain

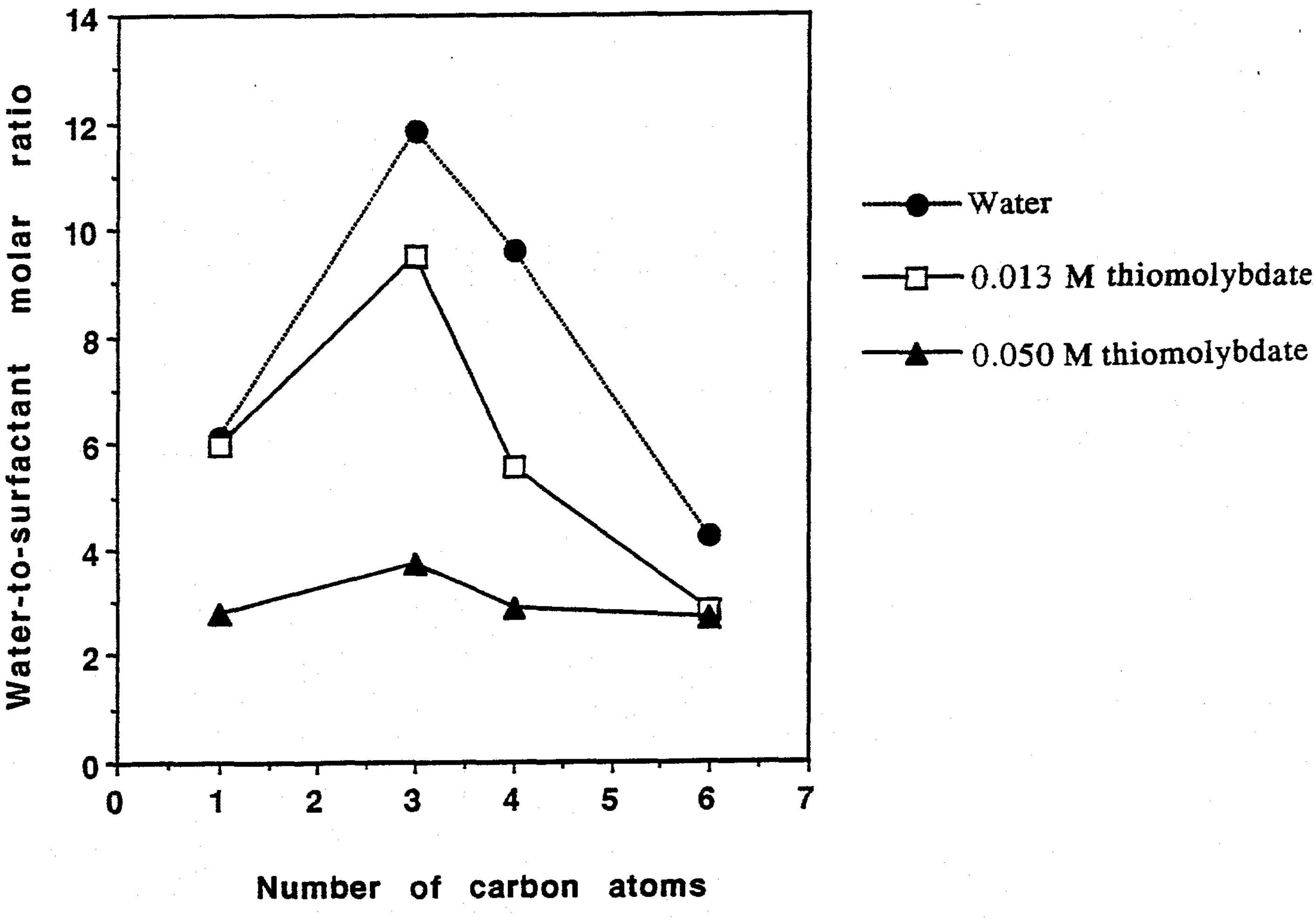

Figure 1. Effect of alcohol chain length on the solubility; (a) water (b) 0.013 M ammonium tetrathiomolybdate (c) 0.05 M ammonium tetrathiomolybdate.

length is increased, the solubility first increases with the number of carbon atoms in the alcohol and then decreases. Similar results have been found for microemulsion systems formulated with cationic and anionic surfactants (2,5).

The results presented in Figure 1 can be rationalized by invoking the model presented by Shah and coworkers (1,2). As the co-surfactant chain length is increased, the rigidity of the interface increases (1,2,5). Here the induction of phase separation is dominated by the curvature effect (i.e., it is limited by the natural radius R^o). However, when the fluidity of the interface is increased by using short-chain-length alcohols as co-surfactants, the natural radius of the reverse micelles increases. As a result, more water molecules will be added before the condition $R>R^o$ is reached and hence the solubility increases. As the fluidity of the interface is further increased, by using shorter-chain-length alcohols as co-surfactants, the interdroplet interaction concomitantly increases to an extent that transient dimers and relatively fewer large reverse micelles will be in equilibrium with the continuous oil phase, which corresponds to phase separation of type 2. At this stage $R>R^c$.

From the above discussion, it is reasonable that a maximum exist for the solubilization of the aqueous phase in the microemulsion. The maximum solubilization capacity therefore corresponds to a combination of the interfacial curvature and the inter-micellar interaction effects.

For a microemulsion system with a fixed cosurfactant-to-surfactant molar ratio, one would expect the effective size of the polar head group to decrease (i.e., double layer contraction) as the ionic strength of the aqueous domain of the microemulsion is increased. Consequently the natural radius of the reverse micelles decreases as well. This corresponds to decreasing solubilization as the condition $R>R^o$ is reached at a relatively low water content of the microemulsion compared to the case where R^o is large (i.e., no electrolyte present). In general, an increase in the ionic strength of the aqueous phase makes the interface more rigid, reduces the inter-micellar interactions, decreases the aggregation number (6,7) and reduces the solubility, as shown in Figure 1.

Synthesis of NP-5/tetralin/methanol. Figures 2 and 3, respectively, present the TEM micrographs and a plot of average particle diameter versus the molybdate concentration of molybdenum sulfide particles synthesized in the 0.4 M NP-5/tetralin/methanol microemulsion system. The average particle diameter decreases monotonically as the thiomolybdate concentration is increased. Robinson et al. (8) have reported similar observations. This trend may be rationalized by considering the following particle formation and growth scheme (9-13): (i) When ammonium tetrathiomolybdate and sulfuric acid meet in a swollen reverse micelle, they react to form molybdenum trisulfide monomer; (ii) before a stable nucleus is formed a critical number of molybdenum trisulfide monomers must combine in a specific micelle (13); (iii) after a stable nucleus is formed, it can grow by incorporating molybdate ions and monomers in the aqueous domain via intra- and inter-micellar interactions; (iv) primary particles or nuclei may aggregate through inter-micelar interactions to form bigger particles (11,14).

In order to generate small and monodispersed particles, the nucleation and growth steps should occur on different time scales. To satisfy this condition, it will be necessary to produce a large number of nuclei in specific reverse micelles and then transform them into particles. Further, the particles should be prevented from aggregating. This condition is met if the reverse micelles act as perfect cages. This implies that the inter-micellar exchange of the particles in the micelles is controlled to a minimum extent.

As discussed in our previous reports, an important parameter that controls the nucleation rate in the inverse micelles is the average molybdate occupancy

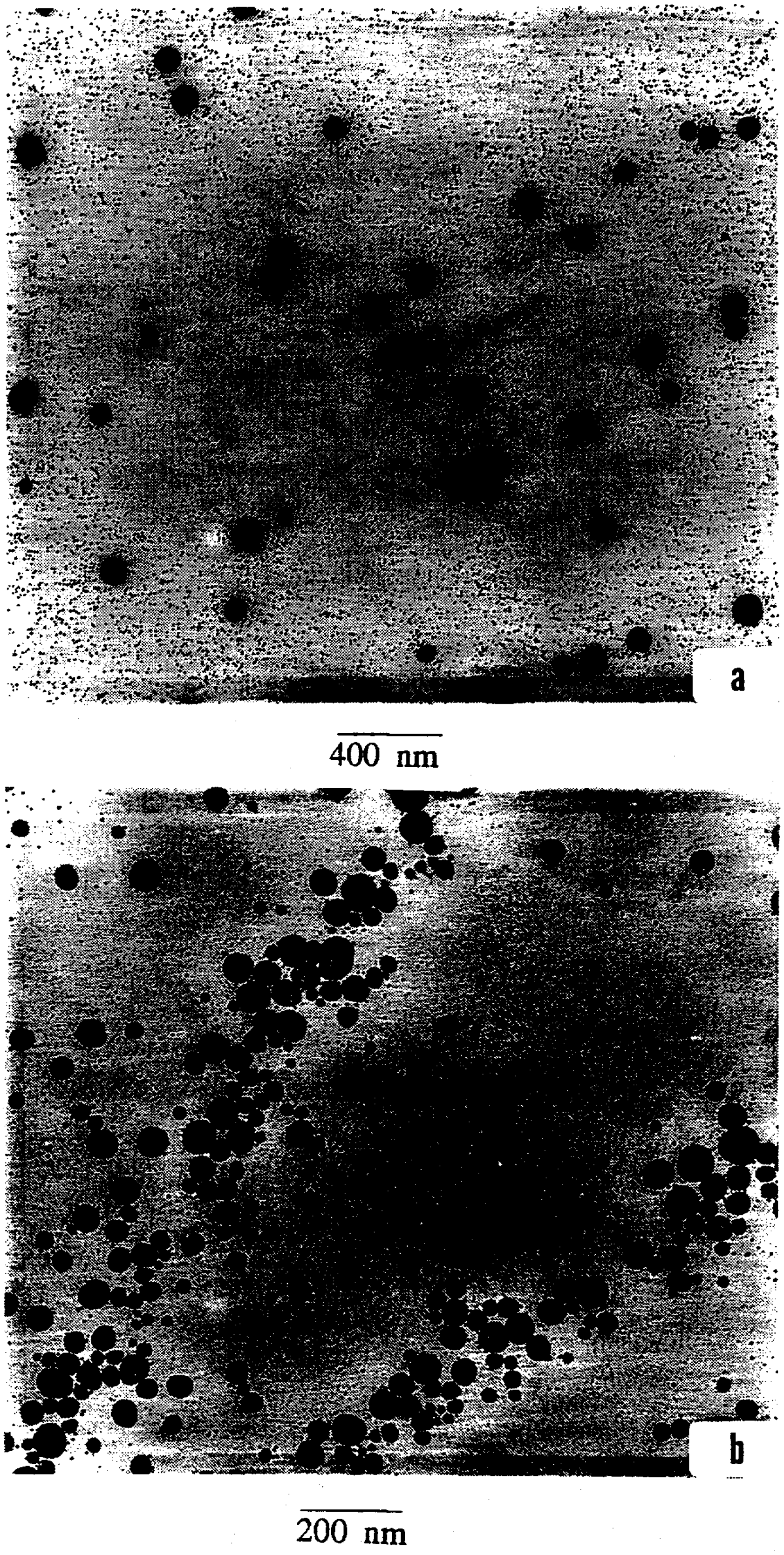

Figure 2. TEM micrographs of molybdenum sulfide particles prepared in the 0.4 M NP-5/tetralin/methanol/water microemulsion. (a) $[\mathrm{MoS4}^{2-}]$ = $4.5\mathrm{x}10^{-5}$ M : (b) $1.8\mathrm{x}10^{-4}$ M.

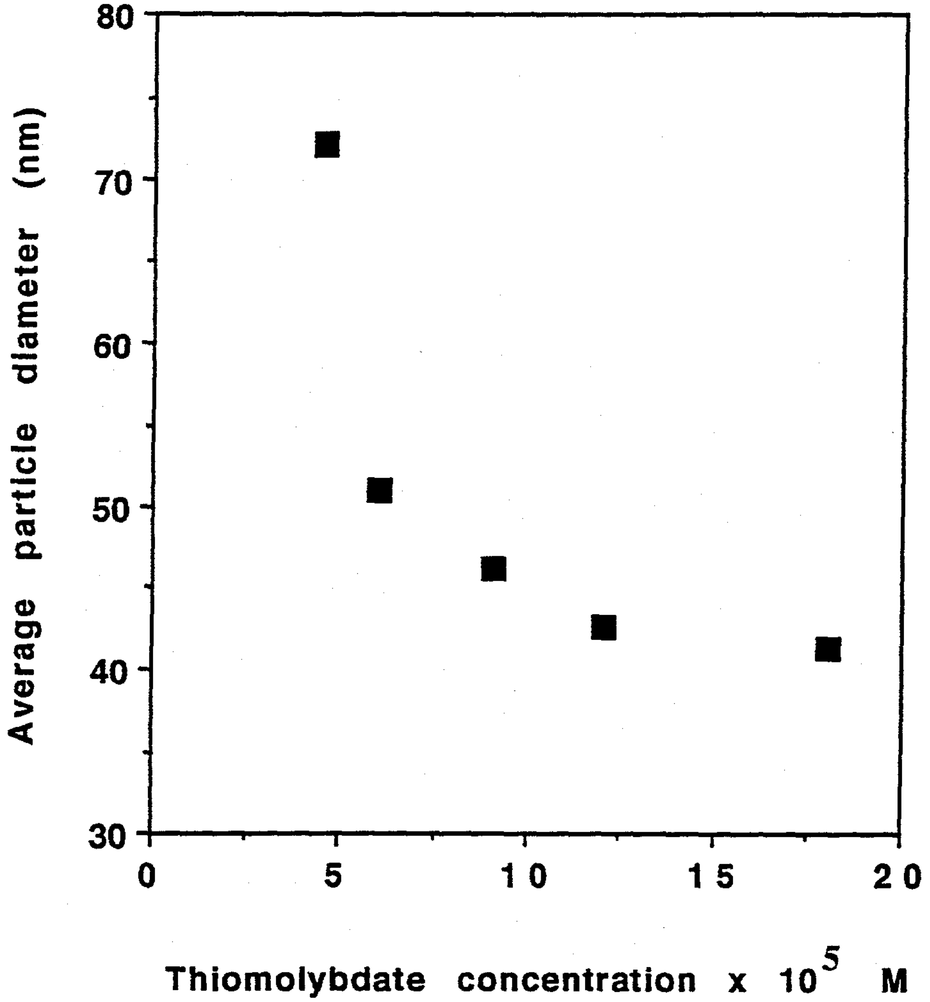

Figure 3. Effect of ammonium tetrathiomolybdate concentration on the average molybdenum sulfide particle size for the 0.4 M NP-5/tetralin/methanol/water microemulsion. $[H_2SO_4] = 4.0 \times 10^{-3}$ M.

number (i.e., the number of tetrathiomolybdate ions per micelle). For a constant water-to-surfactant molar ratio, the molybdate occupancy number increases as the concentration of ammonium tetrathiomolybdate is increased. As a result the nucleation rate will increase and more nuclei and smaller particles will be made. This is because relatively few ions will remain after the nucleation process.

From the TEM micrographs a bimodal distribution is seen to have been obtained for all concentrations of ammonium tetrathiomolybdate investigated. This may be the result of particle aggregation occurring simultaneously with ion and monomer additions. Primary particles of 2-7 nm may have aggregated to form particles in the size range of 40-80 nm.

Among the important observations in these solubilization studies was that, for the phase separation induced by the inter-micellar interaction, (e.g., microemulsions with relatively short side chain alcohols as co-surfactants), the oil/water interface becomes relatively rigid when the ionic strength of the aqueous phase of the microemulsion is increased. This causes a decrease in intermicellar interaction which reduces particle aggregation. Thus the decrease in particle size with increasing concentration of ammonium tetrathiomolybdate may be due to either an increase in the nucleation rate or a decrease in inter-micellar interaction. Both mechanisms cause a decrease in particle size with increasing thiomolybdate concentration.

Synthesis of NP-5/tetralin/propanol. Presented in Figures 4 and 5 are the TEM micrographs and a plot of particle size versus the thiomolybdate concentration of molybdenum sulfide particles synthesized in the microemulsion system 0.4 M NP-5/tetralin/propanol. The particle size first decreases with increasing thiomolybdate concentration to $MoS_4^{2-} = 1.81 \times 10^{-4}$ M) and then increases.

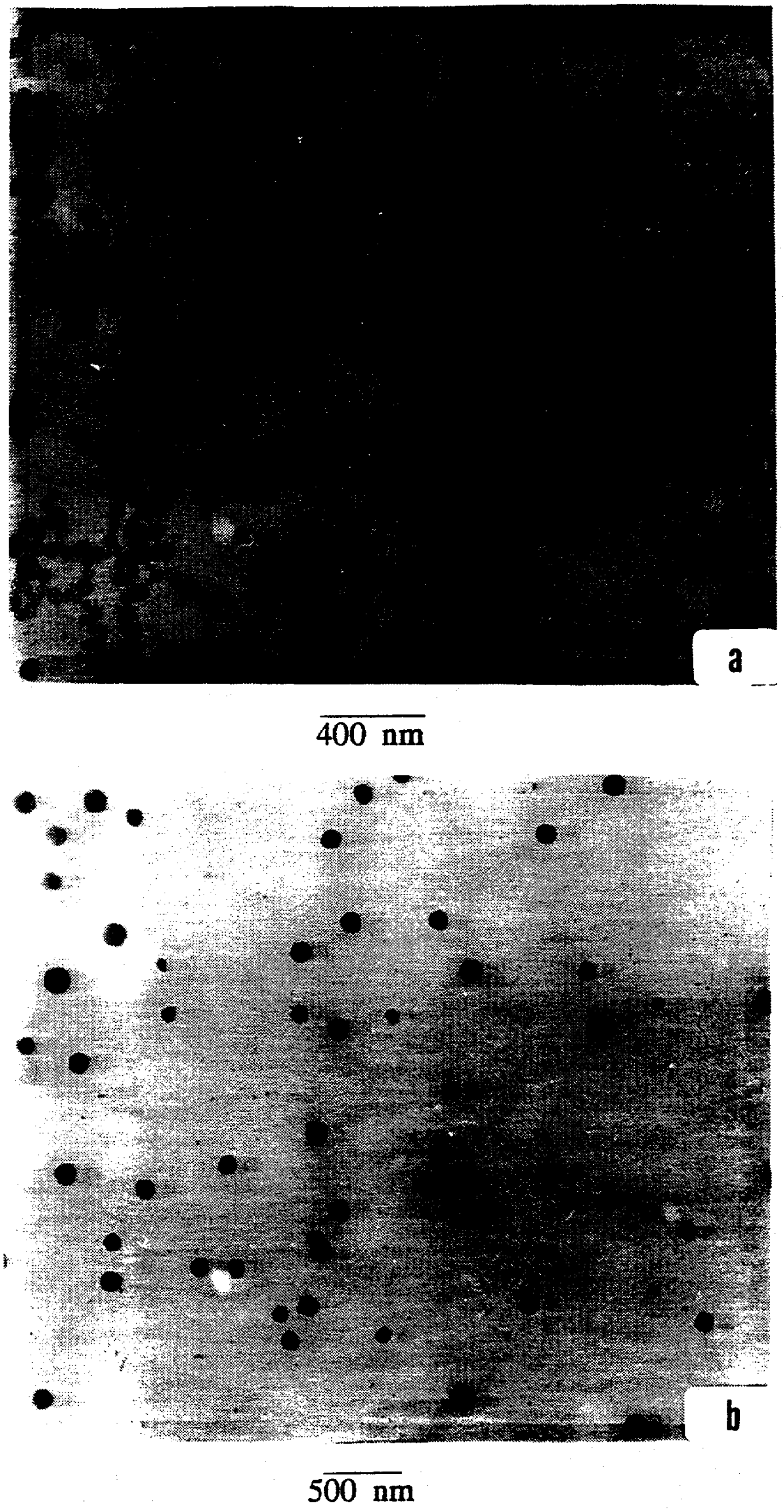

Figure 4. TEM micrographs of molybdenum sulfide particles prepared in the 0.4 M NP-5/tetralin/propanol/water microemulsion. (a) [MoS_4^{2-}] = 1.8×10^{-4} M : (b) 2.7×10^{-4} M.

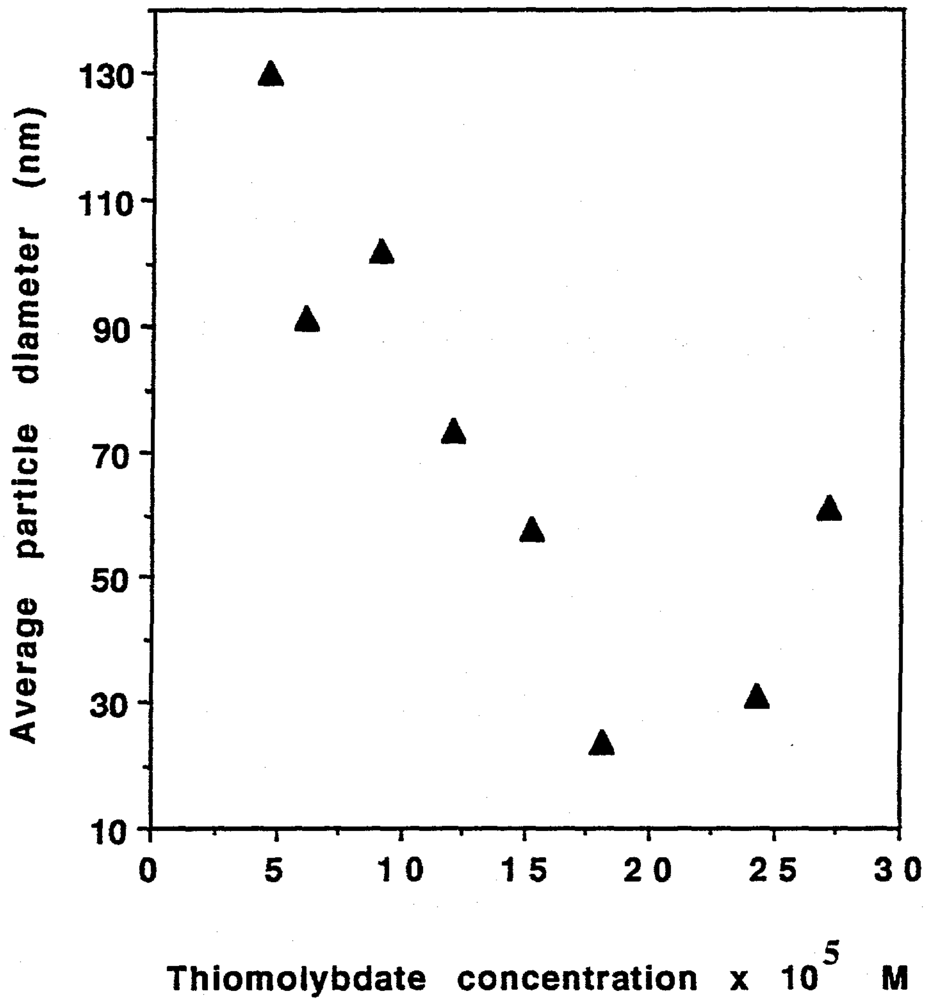

Figure 5. Effect of ammonium tetrathiomolybdate concentration on the average molybdenum sulfide particle size for the 0.4 M NP-5/tetralin/propanol/water microemulsion. [H_2SO_4] = 4.0×10^{-3} M.

This trend is also interpreted by considering the particle formation scheme presented above. For a fixed water-to-surfactant molar ratio, the thiomolybdate occupancy number increases as the ammonium tetrathiomolybdate concentration is increased. The rate of nucleation increases as the thiomolybdate concentration is increased. As a result, few ions and monomers not utilized in the nucleation process contribute to the growth process. Also, as suggested in the discussion for particles made in the NP-5/tetralin/methanol microemulsion system, the water/oil interface is made relatively rigid as the ionic strength of the aqueous domain is increased (i.e., increasing thiomolybdate concentration). This reduces the importance of aggregation phenomena and hence small particles are made. This is confirmed by the few 2-7 nm particles seen on the TEM micrographs. Thus, for thiomolybdate concentrations less than 1.81×10^{-4} M the decreasing particle size may be due to an increase in the nucleation rate or a decrease in the extent of aggregation.

For thiomolybdate concentrations greater than 1.81×10^{-4} M, the average molybdate occupancy number is relatively high and hence smaller particles were expected to be made. Contrary to expectation, the particle size was found to increase as the thiomolybdate occupancy number was increased. This trend can be rationalized by considering particle aggregation.

Synthesis of NP-5/tetralin/hexanol. Figures 6 and 7 present the TEM micrographs and a plot of the average particle diameter versus the thiomolybdate concentration of molybdenum sulfide particles made in the microemulsion. The average particle diameter decreases with increasing thiomolybdate concentration (to a concentration of 6.045×10^{-5} M) and then increases. The explanation of this trend is similar to that given for the 0.4 M NP-5/tetralin/propanol microemulsion system.

For thiomolybdate concentrations $<6.045 \times 10^{-5}$ M, the molybdate occupancy number increases as the concentration of ammonium tetrathiomolybdate is

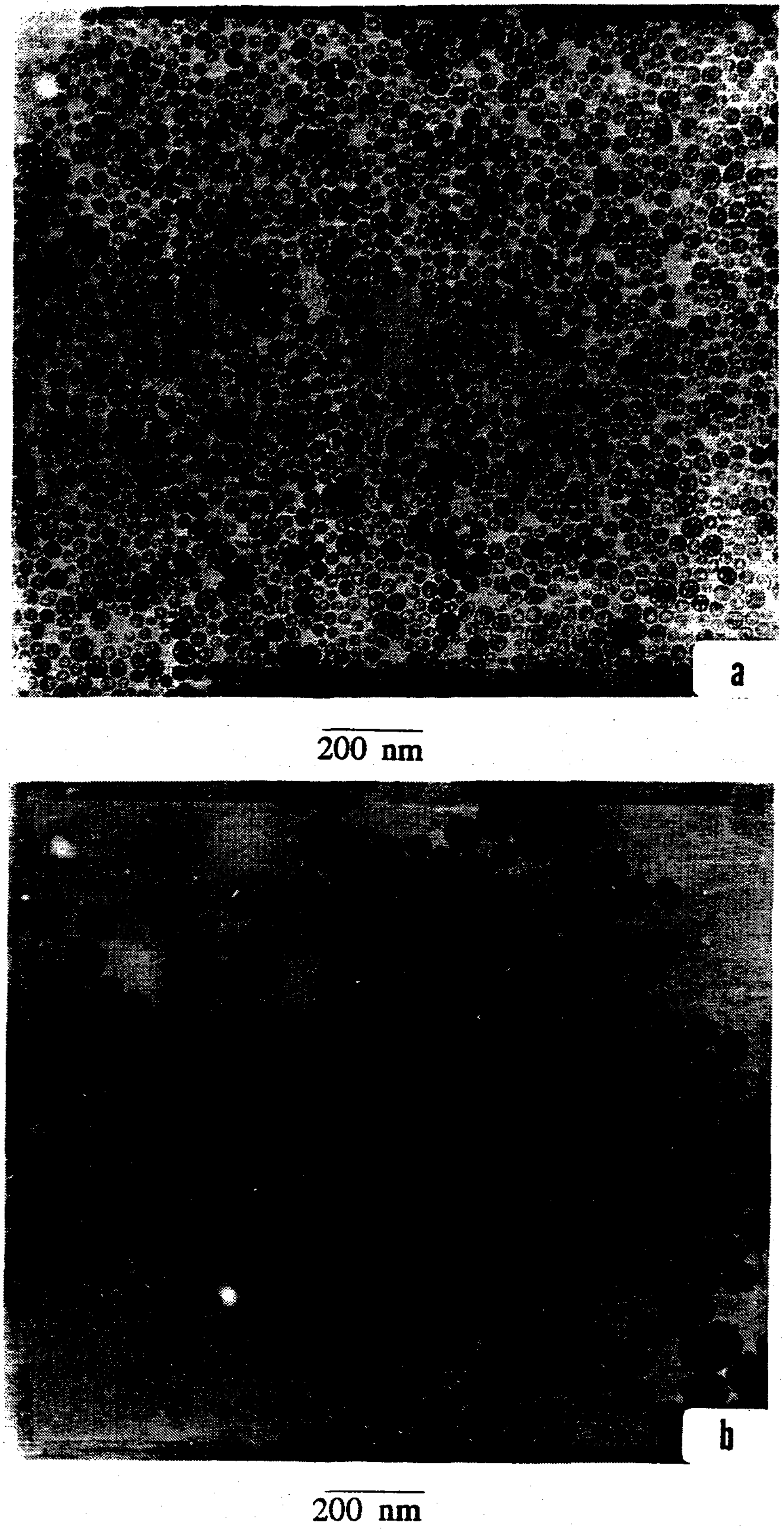

Figure 6. TEM micrographs of molybdenum sulfide particles prepared in the 0.4 M NP-5/tetralin/hexanol/water microemulsion. (a) $[MoS_4{}^{2-}]$ = $6.0x10^{-5}$ M : (b) $1.8x10^{-4}$ M.

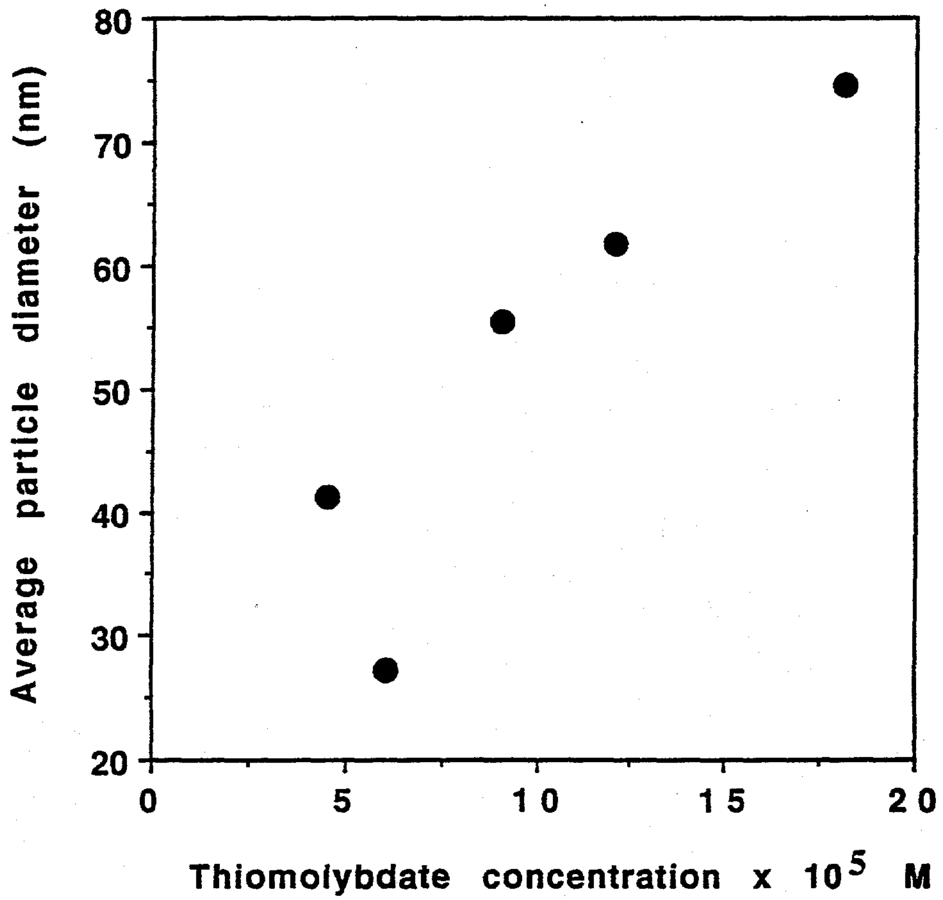

Figure 7. Effect of ammonium tetrathiomolybdate concentration on the average molybdenum sulfide particle size for the 0.4 M NP-5/tetralin/hexanol/water microemulsion. $[H_2SO_4] = 4.0 \times 10^{-3}$ M.

increased. As a result the nucleation rate increases and small particles are made. For thiomolybdate concentrations $>6.045 \times 10^{-5}$ M, particle aggregation is expected to be the principal mechanism of growth.

An interesting observation worthy of special comment is that the onset of particle aggregation (i.e., the right-hand side of the minima of the plots of average particle diameter versus thiomolybdate concentration) occurs at a lower thiomolybdate concentration for the microemulsion system formulated with hexanol as a co-surfactant compared with that of propanol. This may be explained by considering the interfacial curvature effect in conjunction with the concept of temporary destabilization of the microemulsion system as a result of phase separation (15,16).

For a microemulsion system formulated with a long-chain alcohol as a co-surfactant, the oil/water interface is relatively rigid. The solubilization capacity of the aqueous phase is determined by the size of the natural radius, which decreases as the ionic strength of the polar phase is increased. As discussed in the previous section, the solubilization capacity decreases with increasing ionic strength of the polar domain. Furthermore, since the condition $R>R^o$ corresponds to the onset of phase separation, the extent of temporary destabilization of the microemulsion increases as the ionic strength of the polar domain is increased, hence facilitating aggregation of particles and increasing polydispersity. Also the natural radius of the microemulsion formulated with hexanol is expected to be smaller than that of propanol, due to the rigidity of the interface of the former microemulsion. Therefore the induction of temporary phase separation is expected to occur at a lower thiomolybdate concentration for the microemulsion system NP-5/tetralin/hexanol compared with NP-5/tetralin/propanol. As a consequence, particle aggregation occurs at a lower thiomolybdate concentration for the former microemulsion system.

Task 3: Catalyst Testing

The results for the subbituminous coal were reported previously. A 16.5% increase in total conversion (with respect to the thermal experiment) was achieved with just 25 ppm Mo. This is quite remarkable, considering the low severity of the operation and the relatively minute amount of catalyst used. When catalyst loading was increased to 50 ppm, the improvement decreased to 8.8%. As the catalyst (and thus solvent) loading was further increased, there appeared to be no catalytic effect at all.

Analogous results for the bituminous coal are reported in Table 1. Total conversion is not affected significantly by the amount of catalyst (and thus, solvent) present. However, the yield of oils (plus gas) is adversely affected when catalyst loading is increased.

The trend shown by these two coals is consistent with the coal structure/reactivity relationships reported by Burgess et al. (17). They found that molybdenum catalyst primarily aids in the depolymerization of subbituminous coal, while for bituminous coals, conversions without catalyst tend to be relatively high. The anomalous behavior observed when catalyst loading is increased may be due to a detrimental solvent effect. As mentioned earlier, the solvent employed in these tests is (necessarily) a complex one. In the presence of certain solvents, catalyst activity may be masked or suppressed. Therefore, an explanation for this observation was sought in terms of the behavior of individual solvent components under liquefaction conditions. Saini et al. (18) have recently reported that, under coal liquefaction conditions, benzyl alcohol can induce extensive crosslinking reactions involving itself and coal, leading to extremely low and even negative conversions. Its presence in the microemulsion may thus mask the catalytic effect of molybdenum sulfide particles.

Table 1

Results of Liquefaction Tests for PSOC-1401 Coal with 0.4 M NP-5/Tetralin/Benzyl Alcohol Microemulsion Molybdenum Sulfide Catalyst

Experiment number	Amount of solvent (g)	Catalyst loading (ppm Mo)	Yield of oils (plus gas) (%)	Yield of asphaltenes (%)	Total conversion (%)
27 (t)	3.4303	0	n/a	n/a	60.0
31 (c)	3.3374	25	4.8	56.3	61.1
28 (t)	6.7962	0	0	61.3	61.3
32 (c)	7.3835	50	-5.0	67.0	62.0
29 (t)	13.4341	0	n/a	n/a	60.4
33 (c)	13.6444	100	-17.5	84.8	67.3
30 (t)	26.5506	0	-6.9	66.2	59.4
34 (c)	27.3218	200	-12.2	80.8	68.6

n/a = data not available

Table 2

Results of Liquefaction Tests for PSOC-1401 Coal with 0.4 M NP-5/Tetralin/Methanol Microemulsion Molybdenum Sulfide Catalyst

Experiment number	Amount of solvent (g)	Catalyst loading (ppm)	Yield of oils (plus gas) (%)	Yield of asphaltenes (%)	Total conversion (%)
48 (t)	2.544	0	-4.1	35.5	30.4
50 (c)	2.561	~100	1.6	44.0	45.6

The methanol-based microemulsion was also tested in a similar fashion. Table 2 summarizes the results for the bituminous coal. In addition to being a hydrogen-donor, methanol is known to swell coals and can thereby aid in improving catalyst dispersion (19). However, the suggested application of methanol as a swelling agent also envisages its removal and recovery once dispersion has been achieved. Also, there appears to exist some evidence in the literature (20) that alcohols can participate in retrogressive reactions and lower the process efficiency. This may explain the rather low conversion to oils that was observed.

SUMMARY AND CONCLUSIONS

The solubilization of water and ammonium tetrathiomolybdate has been studied. The results show that the solubilization capacity first increases as the carbon chain length is increased and then decreases. Particle sizes can be controlled by varying the average thiomolybdate occupancy number, the degree of exchange of the contents of the reverse micelles and the induction of temporary phase separation of a relatively rigid interface, which depends in turn on the value of the natural radius of the reverse micelles.

The demands made by microemulsion-based catalyst particle synthesis and the coal liquefaction process can often be conflicting. Our future work will attempt to reconcile these differences and formulate micellar systems that can be used to produce highly dispersed catalyst particles, and, in addition, have a benevolent effect on the hydroliquefaction of coal.

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