Reverse micelle synthesis of oxide nanopowders: Mechanisms of precipitate formation and agglomeration effects

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ABSTRACT

We present an analysis of reverse micelle stability in four model systems. The first two systems, composed of unstable microemulsions of isooctane, water, and Na-AOT with additions of either iron sulfate or yttrium nitrate, were used for the synthesis of iron oxide or yttrium oxide powders. These oxide powders were of nanocrystalline character, but with some level of agglomeration that was dependent on calcination temperature and cleaning procedures. Results show that even though the reverse micellar solutions were unstable, nanocrystalline powders with very low levels of agglomeration could be obtained. This effect can be attributed to the protective action of the surfactant on the surfaces of the powders that prevents neck formation until after all the surfactant has volatilized. A striking feature of the IR spectra collected on the iron oxide powders is the absence of peaks in the $\sim$1715 cm^{-1} to 1750 cm^{-1} region, where absorption due to the symmetric C=O (carbonyl) stretching occurs. The lack of such peaks strongly suggests the carbonyl group is no longer free, but is actively participating in the surfactant-precipitate interaction. The final two microemulsion systems, containing CTAB as the surfactant, showed that loss of control of the reverse micelle synthesis process can easily occur when the amount of salt in the water domains exceeds a critical concentration. Both model systems eventually resulted in agglomerated powders of broad size distributions or particles that were large compared to the sizes of the reverse micelles, consistent with the notion that the microemulsions were not stable and the powders were precipitated in an uncontrolled fashion. This has implications for the synthesis of nanopowders by reverse micelle synthesis and provides a benchmark for process control if powders of the highest quality are desired.

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1. Introduction

Microemulsions are systems that consist of a mixture of two immiscible fluids, typically oil and water, that form a thermodynamically stable and isotropic dispersion *via* the use of surfactants to stabilize the system. For a system in which the greater volume of the two liquids is constituted by oil, then water droplets surrounded by the surfactant are formed and can serve as reactors for the preparation of a variety of nanoparticles. These structures are known as reverse micelles and their stability is of the highest importance for the formation of homogeneous fine particles. Extensive literature on reverse micelle systems is available describing fundamental behavior of these systems as well as the preparation of a variety of nanopowders [1–17].

The preparation of nanopowders usually involves mixing two microemulsions, one containing metal cations and the other containing a precipitating/reducing agent, such as NH$_4$OH for the preparation of hydroxide nanoparticles and NaBH$_4$ for the preparation of metallic nanoparticles. After mixing of the two microemulsions, a fast reaction takes place resulting in a nucleation and growth process. In most cases, once the nanoparticles attain the final size, the surfactant molecules attach to the surface of particles, thus stabilizing and protecting them against further growth and agglomeration. In some cases the size of the final nanoparticles is defined by the size of the reverse micelles, but there are many

cases where this is not the case. For example, Kandori et al. [18] found that the resultant $CaCO_3$ particle size of their powders was an order of magnitude larger than the size of the reverse micelles. In fact, it is now generally accepted that there is exchange of material among the reverse micelles and that the synthesis of the nanoparticles is not necessarily limited to the water droplets, but that it is a collective phenomenon [19].

In a previous contribution [13], we presented a detailed analysis of isooctane/AOT/water reverse micelle behavior with the addition of $Al(NO_3)_3$, $ZrOCl_2$, and NH_4OH. We found that as salt concentration was increased, the reverse micelles became progressively smaller, eventually resulting in a two-phase mixture of reverse micelles and free water. For example, in the $Al(NO_3)_3$ system, the average reverse micelle size decreased from $\sim$10.3 nm for the isooctane/AOT/water system with no salt to $\sim$6.1 nm at a salt concentration of 0.4 M (the maximum concentration for which the microemulsions were stable and there was no free water). In the $ZrOCl_2$ system, reverse micelle size decreased from $\sim$10.3 nm to 7.0 nm at a concentration of 0.3 M; in the NH_4OH system average reverse micelle size decreased from $\sim$10.3 nm to 7.8 nm at a concentration of 0.6 M. In general, salt concentration and cation valence were found to be critical parameters for system stability. Based on our analysis, an isooctane/AOT/water reverse micellar solution containing Fe^{2+} ions should lose stability at a concentration of 0.6 M. Indeed, as will be described later in this contribution, this is the case for systems with $FeSO_4$ salt additions. Thus, careful consideration must be given to salt concentration in reverse micellar solutions if they are to remain stable.

As useful counterexamples, there are studies in which higher salt concentrations were used and which likely consisted of unstable microemulsions or bicontinuous systems [19]. As a first example, Carpenter et al. [20] used the isooctane/AOT/water system at a water to surfactant ratio (ω_o) of 10 to prepare $MnFe_2O_4$ powders using microemulsions of 1 M $FeSO_4$ and 1 M $MnSO_4$ at a ratio of $[Fe^{2+}]/[Mn^{2+}]$ of 2:1. Reverse micellar solutions of isooctane/AOT/water containing 1.5 M NH_4OH, 3.0 M NH_4OH, and a large excess of NH_4OH were also prepared. The Fe^{2+}/Mn^{2+} microemulsion was subsequently mixed with NH_4OH microemulsions to precipitate $Fe_xMn_y(OH)_z$ of varying Fe/Mn ratios, which were subsequently calcined to obtain the desired $MnFe_2O_4$ composition. Similarly, Li et al. [21] prepared γ-Fe_2O_3 by mixing a reverse micellar solution containing 1 M $FeSO_4$ (ω_o = 10) and an NH_4OH reverse micellar solution with a volume ratio of 1:8 (30% NH_4OH to 0.5 M AOT with respect to the total isooctane and water volume). As a final example, Calero-DdelC and Rinaldi [22] used the isooctane/AOT/water system at a ω_o = 10 to prepare $CoFe_2O_4$ powders using microemulsions of 1 M $FeSO_4$/$CoCl_4$. The ammonia reverse micelle solution was prepared by adding 10% ammonia solution to an AOT/isooctane solution in a volume ratio of 1:8. The reaction was allowed to proceed over a 2 h period. Afterwards, the isooctane and water were removed by drying in a vacuum oven at 40 °C for 12 h, leaving a dry dark residue. To remove the surfactant and excess ions, the residue was washed several times using methanol, ethanol, and DI water successively, with each wash step followed by centrifugation. The final powder was obtained by drying the washed precipitate in a vacuum oven at 100 °C for 14 h.

In this study, we present results on system stability of four separate reverse micellar systems. The first two systems consisted of microemulsions that were utilized for the synthesis of iron oxide and yttrium oxide powders. These powders were of nanocrystalline character, but with some level of agglomeration that was dependent on calcination temperature and cleaning procedures. Since the powders were purposefully produced in destabilized microemulsions, the precipitation processes did not occur only in droplet-phase microemulsions, instead forming a two-phase system of reverse micelles and free water or possibly bicontinuous microemulsions that can be useful for obtaining higher powder yields [19], although the latter is not likely considering the ratios of water, surfactant, and oil used in this work. Even under these circumstances, the presence of the surfactant was useful because it resulted in protection of the precipitates during calcination. Thus, many studies have made use of this technique and have resulted in powders of good quality, even though full advantage of the reverse micelle synthesis process did not take place during precipitation. The final two systems in our study showed that loss of control of the reverse micelle synthesis process can easily occur when the amount of salt in the water domains exceeds a critical concentration. Both systems eventually resulted in agglomerated powders of broad size distributions or particles that were large compared to the sizes of the reverse micelles, consistent with the notion that the microemulsions were not stable and the powders were precipitated in an uncontrolled fashion.

2. 2.Experimental procedure

2.1. System I

A reverse micellar solution consisting of 100 mL of 2,2,4-trimethylpentane/isooctane/C_8H_{18} (99.8%, Sigma–Aldrich, Inc., St. Louis, MO), 8.8912 g of the anionic surfactant sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate/Na-AOT/$C_{20}H_{37}NaO_7S$ (99.0–100.5%, Sigma–Aldrich, Inc., St. Louis, MO), and iron (II) sulfate heptahydrate/$FeSO_4 \cdot 7H_2O$ ($\geqslant$99%, Sigma–Aldrich, Inc., St. Louis, MO), was prepared. The $FeSO_4 \cdot 7H_2O$ was incorporated into the isooctane and Na-AOT by first mixing the salt into 3.6 mL of water at varied concentrations of 0.1–0.9 M based on the water volume and then adding to the well-dispersed Na-AOT/isooctane solution. The water-to-surfactant ratio (ω_o) was fixed at 10 and the concentration of Na-AOT with respect to isooctane was 0.2 M ([Na-AOT]/[isooctane] = 0.026). These reverse micellar solutions were allowed to stir at room temperature for 2 h before analysis was performed. Separately, reverse micellar solutions of isooctane, Na-AOT, and sodium borohydride / $NaBH_4$ (98%, Sigma–Aldrich, Inc., St. Louis, MO) were prepared in concentrations of 0.1–2.7 M of $NaBH_4$ with respect to the water volume of 3.6 mL. All other characteristics of these solutions were the same as described for the $FeSO_4$ solutions. The 0.9 M $FeSO_4$ was then mixed for two hours with the 2.7 M $NaBH_4$ in a nitrogen atmosphere at room temperature in order to precipitate nearly amorphous iron nanoparticles via reduction of the Fe^{2+} ions with the $(BH_4)^-$ reducing agent. To recover the powders, the precipitates were centrifuged at 6000 rpm for 15 min and cleaned with isopropyl alcohol. The washed precipitates were then dried overnight at room temperature. After drying, the products were lightly ground in an alumina mortar and pestle and subsequently calcined at 500 and 800 °C for a period of one hour in an air atmosphere.

2.2. System II

A reverse micellar solution consisting of 41.09 g of yttrium nitrate hydrate/$Y(NO_3)_3 \cdot xH_2O$ (99.99%, Alfa Aesar, Ward Hill, MA 01835) in 16 mL of de-ionized water, 35.56 g of bis(2-ethylhexyl) sulfosuccinate sodium salt/Na-AOT/$C_{20}H_{37}NaO_7S$ (99.0–100.5%, Sigma–Aldrich, St. Louis, MO 63103), and 400 mL of 2,2,4-trimethylpentane/isooctane/C_8H_{18} (99.8%, Sigma–Aldrich, St. Louis, MO 63103) was prepared. This solution was stirred until all components were thoroughly mixed, after which dry ammonia gas/NH_3 (99.99%, Linde AG, Weisbaden, Germany) was passed for 15 min to form yttrium hydroxide precipitates. The precipitate gel was allowed to sit at room temperature for 12 h and was then centrifuged three times at 5000 rpm with a decanting step after each