

Synthesis and Characterization of Stable Colloidal Fe_3O_4 Particles in Water-In-Oil Microemulsions

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Abstract--We have prepared nanometer-size magnetite particles in Aerosol OT (AOT)/water/iso-octane water-in-oil (w/o) microemulsions. The sizes of the particles in the colloids were inferred from dynamic light scattering (DLS) and were on the order of one nanometer. Those in dried samples were measured using transmission electron microscopy (TEM) and were 5-20 nm. This implies that aggregation occurs during drying. X-ray diffraction showed that the particles' phase was consistent with magnetite. Magnetic properties were studied using a SQUID magnetometer. The colloids showed a superparamagnetic behavior and the dried samples showed a ferromagnetic behavior supporting the size measurements using DLS and TEM, respectively.

I. INTRODUCTION

Recently, inverted micelles have been used to synthesize very small quasi-monodisperse particles. Using this technique, small particles of Pt [1], Au [2], Fe boride [3], Co boride [4], Ni boride [5], Fe_3O_4 [6], and CdS [7,8] were prepared. In particular, Lianos and Thomas made very small, ~ 0.5 nm radius CdS particles [8]. It is our desire to make similarly small magnetite particles. In this work we prepared nano-scaled magnetite particles using the micellar reaction technique and characterized the particles using DLS, TEM, x-ray diffractometry (XRD), and SQUID magnetometry. The micellar system used was the Aerosol OT (AOT)/water/iso-octane water-in-oil (w/o) microemulsion. In this technique water droplets in the microemulsion interact and exchange their contents, and a reaction can occur in these confining micropools. Magnetite particles can be easily prepared by a precipitation reaction of aqueous Fe(III)/Fe(II) and NaOH solutions.

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II. EXPERIMENTAL METHODS

All the materials used in this work were of the purest quality commercially available and were used without further purification: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH (Fisher Sci.), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Aldrich), bis (2-ethylhexyl) sulfosuccinate sodium salt (Aerosol OT, AOT) (Sigma).

0.15 M FeCl_3 /0.1 M FeCl_2 and 1 M NaOH aqueous solutions were prepared by dissolving in distilled, deionized water. The stoichiometric molar ratio of Fe(III) to Fe(II) in Fe_3O_4 is 2:1, but we used an initial ratio of 3:2 because some oxidation of the Fe(II) can occur during the reaction [9]. 111.3 ml of 0.27 M AOT in iso-octane, which consists of 100 ml of iso-octane (69.2 g) and 11.3 ml of AOT (13.3 g), was mixed with either 2 ml, 4.5 ml, 6 ml, or 8 ml of 0.15 M FeCl_3 /0.1 M FeCl_2 or 1 M NaOH aqueous solutions which were previously prepared. Here we kept the concentration of solute in the water core of the micelle constant. The molar ratios of water to AOT ($w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$) were 3.7, 8.4, 11.1, and 14.9, respectively. Figure 1 shows a phase diagram for the AOT/water/iso-octane system (taken from [10]) and the positions for above w_0 values are marked. The preparation of the colloidal Fe_3O_4 particles was achieved by mixing the two w/o microemulsion solutions; one containing Fe(III)/Fe(II) and the other NaOH. Upon mixing a color change from bright yellow to brown was immediately observed for all the solutions. All the colloidal solutions prepared have been stable for more than one month. Dried samples were prepared by evaporating the iso-octane at room temperature. Powder samples were obtained by coagulating the colloids with acetone, filtering, and washing the particles with acetone several times to remove the AOT.

Absorption spectra were performed using a Bausch and Lomb Spectronic 2000 spectrometer before and after reaction to ascertain that a reaction had occurred. Dynamic light scattering (DLS) was performed at $\theta = 90^\circ$ using a 35 mW He-

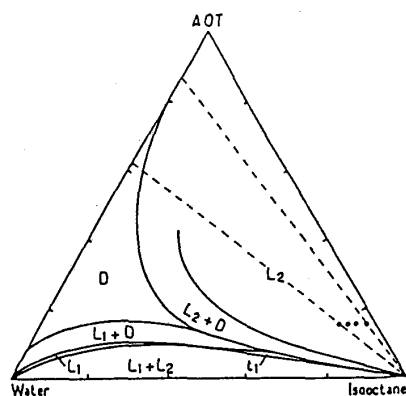


Fig. 1 The phase diagram (in wt. %, ref. [10]) of the ternary system AOT/water/iso-octane at 25°C, showing the points included in this work (the molar ratio $w_0=3.7, 8.4, 11.1, 14.9$ from right to left). L_2 is a w/o microemulsion phase and D is a lamellar phase. Dashed lines through the experimental w_0 points represent the path taken by the solution as the iso-octane dries.

Ne laser and a Langley-Ford correlator. Two cumulant fits to the measured correlation functions were performed to determine the diffusion coefficient, which was corrected for finite concentration effects. The size of the micelles was calculated from the diffusion coefficient using the known viscosity of iso-octane. A Philips 201 TEM was used to size the particles in the dried samples. X-ray diffraction (XRD) was used to study the structure of the powder samples.

III. RESULTS AND DISCUSSION

Figure 2 shows absorption spectra for solutions before and after reaction with $w_0=14.9$. Essentially identical spectra were obtained for all w_0 . After reaction, the threshold was shifted to the red indicating that a reaction had occurred. We could see the small shoulders at 490 nm for all the reacted solutions except $w_0=3.7$.

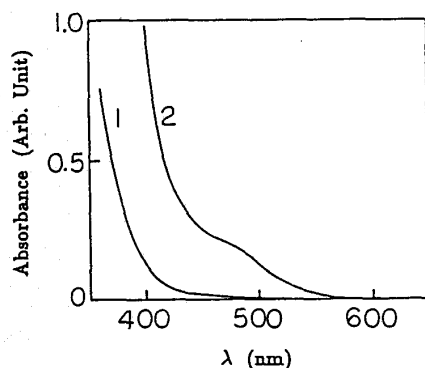


Fig. 2 Absorption spectra of the w/o microemulsions with $w_0=14.9$ before (1) and after (2) reaction.

DLS was used to infer the size of the particles in the w/o microemulsion. The sizes of particles can not be directly decided using DLS, but the sizes of the micelles and hence of the water droplets containing particles can be measured. Figure 3 shows the sizes of water droplets before and after reaction. There was no significant change upon reaction. The size of the particle should be smaller than that of water droplets of the reacted solution, and we can conclude that the particle size in the droplets might be very small, a nanometer or less. The size of the microemulsion without any solute in the water droplet agreed well with the work of others [11].

TEM was used to size the particles of the dried samples and larger sizes than those from DLS were obtained for all the w_0 values except for $w_0=3.7$. We could not observe any particles in the dried sample with $w_0=3.7$ from TEM measurement indicating that they are very small. The results of the TEM measurement are shown in Fig. 4. The size of particles depended on the w_0 value.

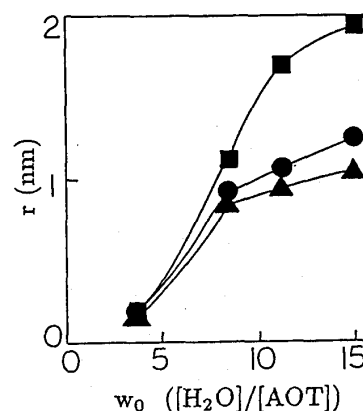


Fig. 3 Dependence of the radius of the water droplets (r) containing NaOH (■), Fe(III)/Fe(II) (▲), and Fe_3O_4 particles (●) on w_0 .

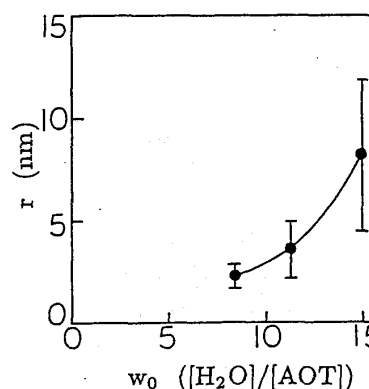


Fig. 4 Dependence of the radius of the Fe_3O_4 particles in the dried samples on w_0 . The bars denote the ranges of the particle size.

The sizes of the particles in the dried samples were larger than those in the colloidal solutions. We propose that this occurs because the particles aggregate during drying. The aggregation can occur when the drying solution crosses over from the inverse micellar to the lamellar liquid crystal region as shown in Fig. 1. In this lamellar phase the particles lose their surfactant coatings and hence can aggregate. Note that this transition does not occur when $w_0=3.7$, which is consistent with our TEM observation for this w_0 .

Figure 5 shows X-ray diffraction data for powders obtained from aqueous reactions both with and without micelles. The latter show all the peaks corresponding to magnetite and the former show an amorphous structure, but the broad peaks overlap those of magnetite consistent with the interpretation that small magnetite particles were prepared.

Magnetic properties were measured using a SQUID magnetometer for the reacted solution and dried sample for $w_0=11.1$. The reacted solution showed superparamagnetic behavior. The dried sample showed a ferromagnetic behavior as shown in Fig. 6 indicating that the size of the particles is larger than that in the colloidal solution. This is consistent with our size measurements for both systems using DLS and TEM.

IV. CONCLUSIONS

We prepared very tiny magnetite particles using the micellar reaction technique and the size of particles depended on the w_0 value. The particles in the colloidal solution were very small, but they aggregated when they were dried or flocculated by the addition of acetone. Superparamagnetic behavior was seen for the unaggregated particles. Magnetic behavior of very small particles of systematically controlled size should be achievable with this technique.

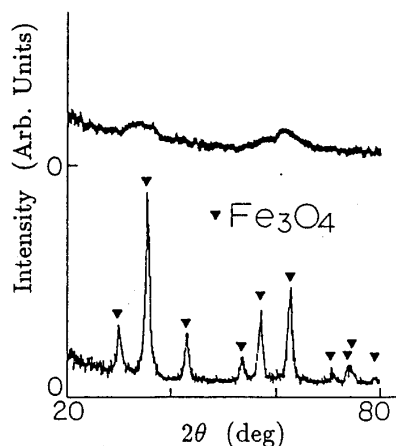


Fig. 5 X-ray diffraction data for the powders obtained from aqueous reactions both with (above diagram) and without (below diagram) micelles.

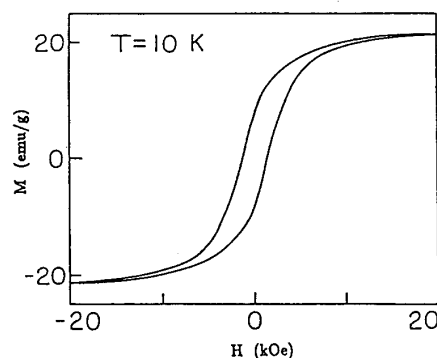


Fig. 6 Hysteresis loop for the dried sample with $w_0 = 11.1$ at $T = 10$ K. Only the mass of the Fe_3O_4 particles was considered in calculating M .

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