Magnetic properties of microemulsion synthesized cobalt fine particles

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Two microemulsion systems, the ternary system H₂O/AOT/isooctane and the binary system DDAB/ toluene, were used to prepare metallic cobalt particles by borohydride reduction of a cobalt salt. The particles prepared in the AOT system were extremely small and superparamagnetic with magnetic moment per particle of 11.5 μ_B , a blocking temperature of 2 K, and $\sigma_s = 146$ emu/g at 1.7 K. The magnetic moment and σ_s combined imply a particle size of about 5.4 Å. However, the particles made in the DDAB system were relatively large, ~10 nm. They were ferromagnetic at room temperature but with no coercivity.

I. INTRODUCTION

Inversed micelles can be formed by dissolving surfactants in organic solvents either in the presence or in the absence of water. These micelles can solubilize inorganic reagents, and mixing of such solutions can be used to create very small particles. The particle size can be controlled by adjusting the water to surfactant molar ratio or reagent concentrations. Recently, the microemulsion synthesis technique has seen considerable use in preparing metallic particles,^{1,2} semiconductor particles,³ and metal boride particles.⁴ Our goal is to study the magnetic properties of very small particles, and we are exploring the microemulsion synthesis technique as a possibly viable method of synthesis. In this work we describe two different microemulsion systems to prepare cobalt particles. One of the systems is the ternary system H₂O/AOT/isooctane with the precursors of the reaction confined in the micelles in the presence of water. The other is the binary system DDAB/toluene. The precursors are trapped in the empty cavity without water. Sodium borohydride is used as the reducing reagent. The synthetic methods and concomitant small size have considerable effect on the magnetic properties.

II. EXPERIMENTAL METHODS

All organic solvents and the distilled, deionized water were degassed with Ar. All the reactions were carried out under Ar to prevent the oxidation of the final products.

The first system we used to produce Co particles was the anionic surfactant system H₂O/AOT/isooctane. 11.2 ml of 0.27 M AOT (sodium di-2-ethyl hexylsulfosuccinate) in isooctane was mixed with either 0.6 ml of 0.3 M CoCl₂ or 0.6 M NaBH₄ aqueous solutions. They were stirred and sonicated until transparent. The molar ratio w of water to AOT in the water-in-oil microemulsion was 11. The ratio of Co²⁺ to BH₄⁻ was 1:2. When the two microemulsions of CoCl₂ and NaBH₄ were mixed together, the solution turned from light pink to black in a few seconds. This black colloid was stable for about ten days. Exposed to the air, the colloid turned from black to light brown in about an hour. The isooctane could be evaporated at room temperature to yield a *paste*

sample of Co particles in AOT. *Powder* samples were obtained by flocculating the colloids with acetone and water, then filtering, and washing with water to remove the AOT. Some powder samples were heat treated at 550 °C for 2 h under Ar protection in order to make the particles grow and/or crystallize.⁵

The second system was the cationic surfactant/solvent system with didodecyldimethylammonium bromide (DDAB) at 10 wt % dissolved in toluene. CoCl₂·H₂O was dissolved in the DDAB solution at concentrations of either 0.005 or 0.01 M. A 5 M NaBH₄ aqueous solution was added in excess and stirred vigorously. The solution turned from blue to black and formed a stable colloid. The colloids were stable for more than one month, which is more stable than those made with AOT. This is most likely due to the fact that the surfactant DDAB adheres irreversibly to the metal colloid particles,² Since DDAB is insoluble in hexadecane it was added to the colloid to force the DDAB out of the solution. This procedure leaves the surfactant coated particles unprecipitated. The remaining colloid particles were slightly flocculated and could be removed from the supernatant above the precipitated DDAB by gentle filtration.

III. RESULTS AND DISCUSSIONS

A. Co particles made from the H₂O/AOT/isooctane system

The as-prepared particles in both the paste and the powder showed no structure in the x-ray diffraction (XRD) spectra, suggesting the particles were either smaller than the resolution limit of the XRD (\sim 3 nm) or amorphous. However, the XRD spectra of the powder samples heat treated at 550 °C for 2 h showed solely the presence of Co.

Transmission electron microscope (TEM) was used to size the particles in the paste and powder samples. The particle sizes in the powder were estimated at about 4 nm in diameter. In the paste sample the largest particles were ~ 3 nm or perhaps smaller, but our ability to measure this size became limited by our TEM resolution.

Magnetization is plotted in Fig. 1 as a function of the applied field for the as-prepared paste sample. We see the

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FIG. 1. Magnetization as a function of applied field for an AOT paste sample at different temperatures.

sample cannot be saturated even at 1.7 K and 55 kOe. This implies that the particles are very small. The saturation magnetization σ_s was found from a linear extrapolation of a σ vs 1/H graph. High-temperature curves of σ vs H show a kink at low field. When considered with the nonsaturability, this suggests that the sample consists of particles of two different sizes, a superparamagnetic and a ferromagnetic fraction. If we subtract the ferromagnetic fraction of magnetization and replot the data with H/T, the three curves for temperatures 20, 60, and 100 K superimpose as shown in Fig. 2, to imply superparamagnetism.

The low-field susceptibility χ was measured as a function of temperature and found to obey the Curie Law

$$\chi = \frac{\sigma_s \mu}{3kT},\tag{1}$$

where μ is the magnetic moment per particle and k is Boltzmann's constant. From the slope of χ^{-1} vs T and the σ_s value, μ was obtained. The mass saturation magnetization and magnetic moment per particle are listed in Table I. The saturation magnetization of the Co particles is ~10% smaller than that of bulk Co ($\sigma_{\rm Co}$ =162.5 emu/g). From σ_s , μ , and the density of bulk Co ($\sigma_{\rm Eo}$ =8.9 g/cm³, we calculated the particle diameter to be 5.4 Å. We also cooled the sample in zero field, then measured the magnetization at 50 Oe while warming, to find a blocking temperature of T_B =2±2 K. If we make the assumption that these particles have the bulk anisotropy K=4.5×10⁶ erg/cm³, then the particle volume



FIG. 2. Dependence of magnetization with the ferromagnetic fraction removed on H/T for the AOT paste sample at different temperatures.

TABLE I. Summary of σ_s and μ for samples made in the AOT system with w=11.

	σ_s (paste) (emu/g)	Co in 1 g paste (mg)	σ_s (Co) (emu/g)	μ (μ_B)
Sample 1	0.492	3.3	149	11.7
Sample 2	0.439	3.1	142	11.7
Sample 3	0.507	3.5	146	11.0

found from $V = 25kT_B/K$ (Ref. 6) yields a diameter of 15 Å. Often small particles have order of magnitude larger anisotropy than the bulk.⁷ If this were the case, the diameter would be 7 Å. These values are qualitatively consistent with the moment derived size.

The size calculated from the magnetic data is much smaller than that measured by TEM. One possible explanation is that each particle in the TEM pictures may consist of several 5 Å particles which are closely packed and could not be resolved by our TEM. High-resolution TEM study is necessary to determine if the substructure exists. Otherwise some unexplained and perhaps novel magnetic effect may have occurred.

B. Co particles prepared from the DDAB/toluene system

XRD of the as-prepared particles from the DDAB/ toluene system showed the particles were metallic cobalt. Note that the products prepared from both systems were cobalt instead of Co_2B . Previous work⁵ in nonmicelle aqueous solutions showed the product of the reaction to be Co_2B under anaerobic conditions, Co if in air. The difference might be related to the water structure in the water pool of the micelle. At low water content, water molecules bind at the micelle interface so that no free water can take part in the reaction. Pileni *et al.*⁸ found the oxidation states of copper metallic cluster changed with the change of water content in the micelles.



FIG. 3. TEM photograph of the cobalt particles made in the DDAB system with $[Co^{2+}]=0.01$ M.

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FIG. 4. Magnetization as a function of applied field at temperatures T=10 and 300 K for the cobalt particles made in the DDAB system with $[Co^{2+}]=0.01$ M.

TEM showed that as we changed the concentration of Co^{2+} ions from 0.005 to 0.01 M, the average particle size increased from 7.5 to 13 nm. An example TEM micrograph is given in Fig. 3. Many of the particles appear not to touch their neighbors, an indication of their thin surfactant coating.

Magnetic studies were carried with the superconducting quantum interference device (SQUID) magnetometer. After the samples were cooled in zero field, the magnetization was measured during warming. No obvious phase transition was observed from 10 to 350 K, implying the blocking temperature was >350 K. Hysteresis curves are given in Fig. 4. At T=10 K, both samples had a coercivity of several hundred oersted. At room temperature there was no coercivity, but the samples were saturated with an applied field of 5000 Oe. The reason why these ferromagnetic particles were so soft is not clear yet. Saturation magnetization per gram Co could not be measured because the Co concentration of these samples could not be determined. All the data are given in Table II.

The particle sizes were quite different with the two sur-

TABLE II. Summary of magnetic data for the cobalt particles made in the DDAB system.

(Co ²⁺ =)	0.005 M	0.01 M
TEM size	7.5±1 nm	13±2 nm
H _c (300 K)	0 Oc	0 Oe
H_c (10 K)	820 Oe	550 Oe
T_{B}	>350 K	>350 K

factant systems. Particles made from the AOT system were extremely small, 3 nm or smaller. Whereas the particles made from the DDAB system were relatively large, around 10 nm. This caused the particles to show quite different magnetic behavior: superparamagnetic as opposed to ferromagnetic.

IV. CONCLUSIONS

We have made Co particles in both the $H_2O/AOT/$ isooctane and DDAB/toluene microemulsion systems. We found the sizes of the particles to be quite different, which caused the different magnetic behavior. At room temperature the larger, ferromagnetic particles were very soft. The magnetic moment of the smaller superparamagnetic particles did not match well with the saturation magnetization and TEM determined particle size for undetermined reasons.

ACKNOWLEDGMENT

This work was supported by NSF Grant No. 9013930.

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