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Controlled preparation of nanosize cobalt ferrite magnetic particles

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Abstract

Cobalt and iron (II) dodecylsulphate [Co(DS)₂ and Fe(DS)₂] form micelles. They have been used to make nanosize magnetic particles. The size of the particles is controlled by the surfactant concentration. The average size of the particles, determined by Transmission Electron Microscopy and by Small Angle X-Ray Scattering, varies from 2 to 5 nm, with less than 30% in polydispersity. The magnetic properties have been studied for various sizes of magnetic particles.

1. Introduction

Cluster science has focused on the size dependent evolution of solid state properties in systems where chemical bonding and electron delocalization are fairly strong. The physical properties of very small clusters generally differ from those of the free atoms or molecules themselves as well as from the properties of the bulk solids. Techniques have recently been developed which enable the synthesis of novel metal and semiconductor clusters and their physical characterization with an unprecedented precision. A challenge now exists to explore a wide array of new cluster-based materials.

Several groups have made these nanosize particles using organized assemblies [1]. The use of dispersed media to solubilize or synthesize microparticles in situ has made considerable progress in the last few years: reverse micelles, Langmuir–Blodgett films, vesicles, polymerized vesicles, double layers, on inert polymeric matrix have been used as the incorporation media for nanoparticles.

Magnetic fluids (ferrofluids) are defined as very stable colloidal suspensions of ultrafine particles (≤ 10 nm) of ferro- and ferri-magnetic materials in carrier liquids [2]. The particles are sufficiently small that thermal energy maintains them in a stable dispersion. Many phenomena in magnetic fluids have been interpreted under the assumption

that the colloidal particles are well dispersed, i.e. that aggregates are absent [3].

The present paper reports, for the first time, the control of the magnetic particle sizes of cobalt ferrite, CoFe₂O₄, from 2 to 5 nm, using colloidal solutions. The size of the magnetic particles changes with the reactant concentration. The cobalt ferrite particles were characterized by transmission and diffraction electron microscopy (TEM and DEM). A good agreement between the size determined by TEM and SAXS measurements were obtained. The relation between average particle size and magnetic properties is explored.

2. Experimental section

Sodium dodecyl sulphate (SDS) was bought from BDH while iron chloride, Fe(Cl₂), and cobalt acetate, Co(CH₃CO₂)₂, were procured from Fluka. All the compounds have been sold as 99.99% purity.

A Phillips electron microscope (model CM 20, 200 kV) was used to obtain electron micrographs of cobalt ferrite particles.

The Small Angle X-Ray Scattering (SAXS) experiment is performed at the Laboratoire d'Utilisation des Rayonnements Electromagnétiques (LURE), CNRS–CEA – Paris XI, Orsay, France, on the D22 diffractometer.

Magnetic studies were performed by using two different devices: The magnetic susceptibility of CoFe₂O₄ powder, at room temperature, has been determined by using a commercial alternative gradient magnetometer (Princeton

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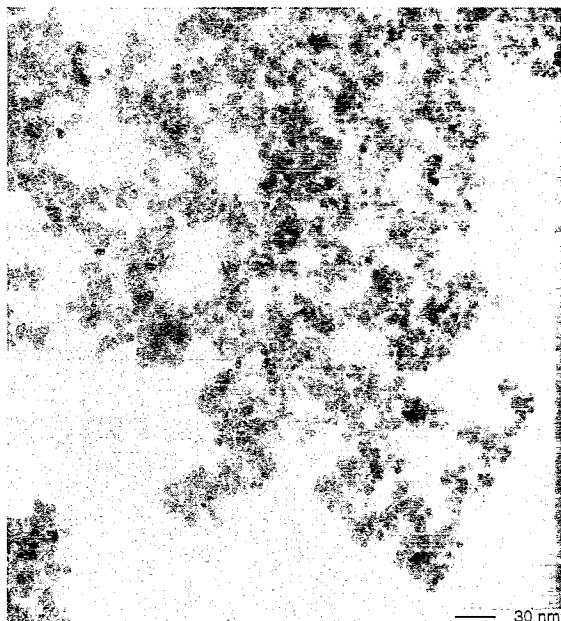


Fig. 1. Electron micrograph of magnetic fluid made from 8.4×10^{-3} M of $[\text{Co}(\text{DS})_2]$ and 2.6×10^{-2} M of $[\text{Fe}(\text{DS})_2]$ in aqueous solution and 2 M of $\text{CH}_3\text{NH}_3\text{OH}$.

measurements Corporation Micomag model 2900) operating at room temperature in a field up to 2 T. In order to compare the behavior of magnetic fluid at room temperature and at 20 K, a SQUID magnetometer has been used.

3. Treatment of the SAXS experiments

The scattered intensity $I(q)$ is given by

$$I(q) = P(q)S(q),$$

where q , $P(q)$ and $S(q)$ are the wave vector $4\pi(\sin q)/\lambda$ ($2q$ is the diffusion angle), the form factor and the structure factor respectively.

From the form factor, the shape of the aggregates is deduced whereas the structure factor takes into account interactions between the particles.

In dilute solutions, the intermicellar interactions can be neglected and $S(q)$ is assumed to be equal to 1.

The form factor is described by the homogeneous sphere model:

$$P(q) = [(\rho_s - \rho_{\text{CoFe}_2\text{O}_4})V_{\text{CoFe}_2\text{O}_4}B(qr_{\text{CoFe}_2\text{O}_4})]^2,$$

$$B(qr_i) = 3 \left\{ \frac{\sin qr_i - qr_i \cos qr_i}{(qr_i)^3} \right\},$$

where $V_{\text{CoFe}_2\text{O}_4}$ and $r_{\text{CoFe}_2\text{O}_4}$ are the volume and the radius of the particle. The electronic densities of CoFe_2O_4 , $\rho_{\text{CoFe}_2\text{O}_4}$, and the solvent, ρ_s , are $1.5 \text{ e}^- \text{ \AA}^{-3}$ and $0.33 \text{ e}^- \text{ \AA}^{-3}$ respectively.

From the Porod plot ($I(q)q^4$ vs. q) the characteristic diameter of homogeneous sphere [4], $D_c(\text{nm})$, is related to the first maximum and minimum of this representation as

$$D_c = 0.54/q_{\text{max}} = 0.90/q_{\text{min}}.$$

4. Synthesis of CoFe_2O_4 nanosize particles

The procedure used is similar to that described in literature [6]: Methylamine, $\text{CH}_3\text{NH}_3\text{OH}$, is added to a micellar solution made by using cobalt, $[\text{Co}(\text{DS})_2]$, and iron, $[\text{Fe}(\text{DS})_2]$, dodecyl sulphate surfactants. The solution is stirred during two hours with appearance of a magnetic precipitate. The supernatant is removed and replaced by pure bulk solvent. A brown magnetic solution is obtained, usually called magnetic fluid. The percentage of surfactant remaining in solution is less than 0.1 wt%.

Several syntheses have been performed by changing the cobalt and iron dodecyl sulphate concentration, keeping the $[\text{Co}(\text{DS})_2]/[\text{Fe}(\text{DS})_2]$ and $[\text{Fe}(\text{DS})_2]/[\text{CH}_3\text{NH}_3\text{OH}]$ ratios constant and equal to 0.325 and 1.3×10^{-2} respectively.

5. Characterization of CoFe_2O_4 nanosize particles

A synthesis is performed by mixing 8.5×10^{-3} M of $\text{Co}(\text{DS})_2$, 2.6×10^{-2} M of $\text{Fe}(\text{DS})_2$ in aqueous solution and 2 M of $\text{CH}_3\text{NH}_3\text{OH}$. A drop of the magnetic fluid is placed on a carbon film supported by copper grid. Fig. 1 is an electron micrograph showing particles about 5 nm in diameter. The histogram given on Fig. 2 shows a relatively low size distribution (close to 30%). No particles larger than 6 nm have been observed. The electron diffractogram pattern (Fig. 3) is in good agreement with the most intense peaks listed for cobalt ferrite in standard reference tables. This indicates that the particles formed using a micellar solution have the spinel crystalline structure as in the bulk phase. Electron microanalysis confirms the relative ratio of

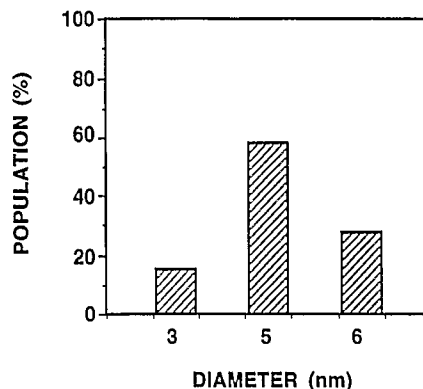


Fig. 2. Histogram of magnetic fluid described in Fig. 1.

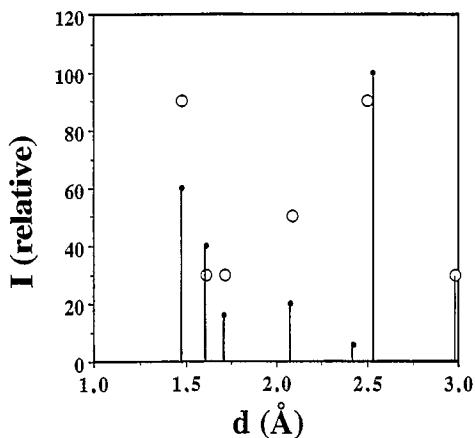


Fig. 3. The electron diffractogram of magnetic fluid described in Fig. 1. The lines are given by standard reference tables and the points are the experimental data obtained for particles having 5 nm diameter.

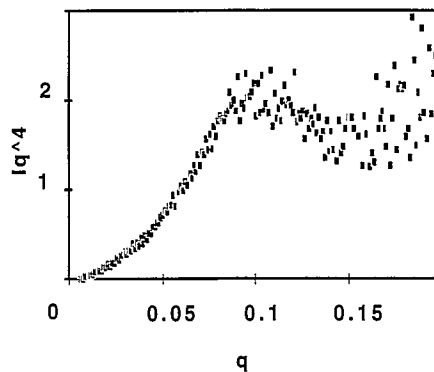


Fig. 4. Porod plot, $I(q)q^4$ versus q , obtained from SAXS for sample given in Fig. 1.

cobalt and iron elements in the cobalt ferrite particles (the percentages of the iron and cobalt elements are found equal to 65.63% and 34.37% respectively).

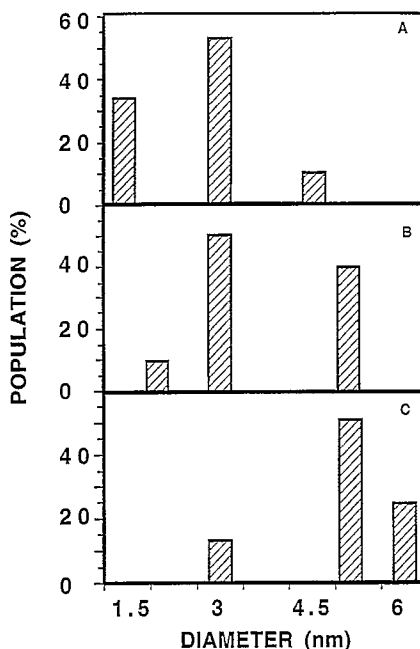
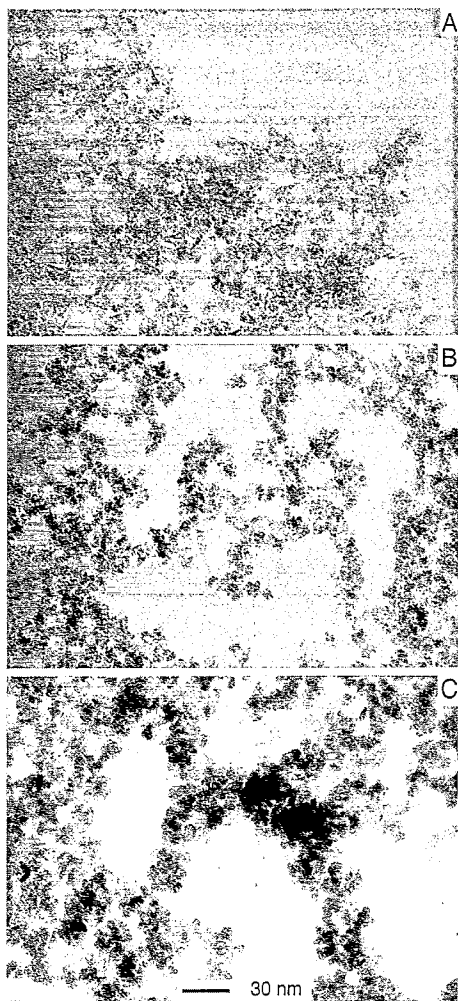


Fig. 5. Electron micrographs (a) and histograms (b) of magnetic fluid made at various surfactant concentrations keeping $[Co(DS)_2]/[Fe(DS)_2] = 0.325$, $[Co(DS)_2]/[NH_2CH_3] = 1.3 \times 10^{-2}$, $[Fe(DS)_2] = 6.5 \times 10^{-3}$ M (A), $[Fe(DS)_2] = 1.3 \times 10^{-2}$ M (B), $[Fe(DS)_2] = 2.6 \times 10^{-2}$ M (C).

The average radius of the particles has been determined by SAXS. By using a Porod representation, Iq^4 versus q , from the value of q at the maximum and the minimum, the average radius can be determined. Fig. 4 shows a well defined maximum and the minimum indicating a rather narrow distribution. The average diameter of the particles is found equal to 5.4 nm with 27% in size distribution. Both SAXS and TEM data yield an average diameter of the particles equal to 5 nm. Similar data, as presented above, have been obtained by Small Angle Neutron Scattering (SANS) [5].

Similar syntheses have been performed keeping the ratios $\text{Co}(\text{DS})_2/[\text{Fe}(\text{DS})_2]$ and $[\text{Fe}(\text{DS})_2]/[\text{CH}_3\text{NH}_3\text{OH}]$ constant and equal to 0.325 and 1.3×10^{-3} respectively. Fig. 5 compares the electron microscopy patterns and histograms of CoFe_2O_4 particles obtained from syntheses performed at various $\text{Fe}(\text{DS})_2$ concentration ($6.5 \times 10^{-3} \text{ M} < \text{Fe}(\text{DS})_2 < 2.6 \times 10^{-2} \text{ M}$). It is shown that the average particle size increases with the concentration of $\text{Fe}(\text{DS})_2$. The increase of $\text{Fe}(\text{DS})_2$ concentration by a factor of four induces an increase in the average particle size by a factor 2.5 (from 2 to 5 nm). It has to be noticed that the distribution in particle size remains close to 30%.

6. Magnetic properties

Magnetic particles are dispersed in 50% of ethylene glycol in water. For particles having 5 nm as an average diameter, the variation of magnetization M with applied

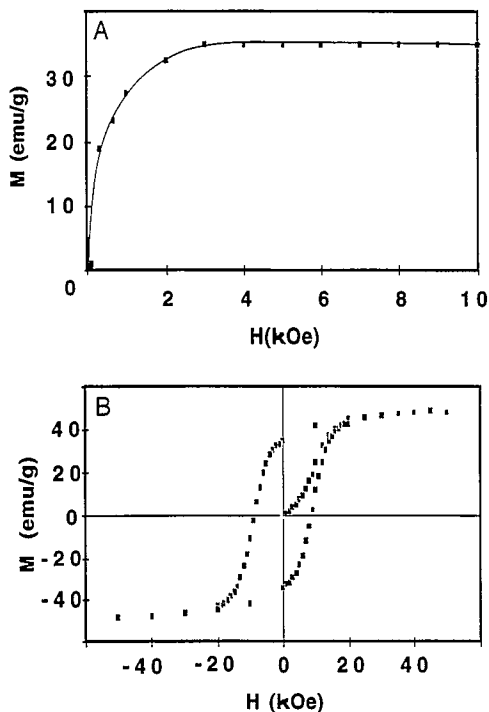


Fig. 6. Magnetization as function of applied field at room temperature and at 20 K for particles having 5 nm average diameter.

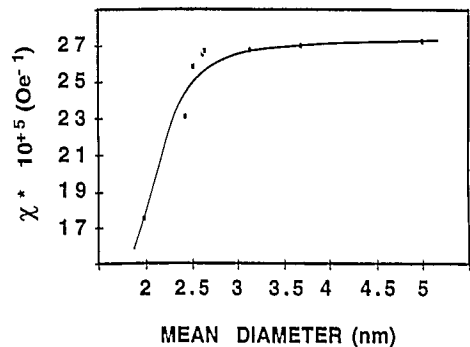


Fig. 7. Variation of the magnetic susceptibility with the particle sizes.

field H is given, at room temperature, in Fig. 6A. As expected, no hysteresis is observed indicating that the particles are in a superparamagnetic regime. By decreasing the diameter of the particles to 2 nm, the saturation magnetization cannot be reached for an applied field equal to 30 kOe. This decrease in saturation magnetization with the particle size can be attributed to a surface effect with formation of inert layer(s).

The magnetic particles having an average diameter equal to 5 nm are frozen in zero field at 20 K. Fig. 6B shows the presence of an hysteresis. For random distribution of easy axes of particles with cubic magnetocrystalline anisotropy, the ratio of the remanence to saturation magnetizations is expected to be equal to 0.83 at 0 K. At 20 K it is found equal to 0.74. If the anisotropy had been primarily due to shape, then the ratio would have been 0.5 at 0 K. The coercivity at 20 K is found to be 8.8 kOe for particles having a diameter of 5 nm. By decreasing the diameter of the particles from 5 to 2 nm, the coercivity decreases from 8.8 to 4.8 kOe. The large remanence and coercivity values and the remanence to saturation magnetization of 0.83 indicate that the system consists of randomly oriented equiaxial particles with cubic magnetocrystalline anisotropy [6].

Fig. 6 shows an increase in the saturation magnetization with decreasing temperature from 300 K (Fig. 6A) to 20 K (Fig. 6B). This is similar to the data obtained in bulk phase. As a matter of fact, the ratio of the saturation magnetizations at 300 and 20 K is found equal to 0.83 and 0.88 for particles having 5 nm diameter and for the bulk phase respectively.

7. Variation of the magnetic susceptibility with particle sizes

The magnetization curves have been obtained by using a commercial alternating gradient magnetometer. Such equipment does not allow the study of liquid, so the experiments have been performed, at room temperature, using dry particles obtained after removing the surfactant and solvent. The reduced magnetic susceptibility is ob-

tained by dividing the value of the initial slope of the magnetization by the saturation magnetization.

Below 3 nm diameter, Fig. 7 shows an increase in the magnetic susceptibility with the average size of the particles. Above 3 nm, a plateau is observed. According to Chantrell et al. [7], for non-interacting particles, the susceptibility depends on the average magnetic diameter. The behavior of magnetic susceptibility given in Fig. 7 could be explained as follows: Below 3 nm the particles are small enough to permit interaction between particles. By increasing the particle size, the interactions between the particles increases leading to a reduction in the change of reduced susceptibility with increasing particle size.

8. Conclusion

For the first time, the preparation of cobalt ferrite having a size varying from 2 to 5 nm is described. This has been achieved by using functionalized surfactants. The size of the cobalt ferrite particles decreases when the total reactant concentration is decreased and when the sodium dodecyl sulphate concentration is increased. It is now possible to make various size of cobalt ferrite particles with 30% in size distribution.

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