

LETTERS

Advances in the Preparation of Magnetic Nanoparticles by the Microemulsion Method

J. A. López Pérez and M. A. López Quintela

*Departamento de Química-Física, Universidade de Santiago de Compostela,
E-15706 Santiago de Compostela, Spain*

J. Mira* and J. Rivas

*Departamento de Física Aplicada, Universidade de Santiago de Compostela,
E-15706 Santiago de Compostela, Spain*

S. W. Charles

*Department of Chemistry, University College of North Wales, Bangor,
Gwynedd LL57 2UW, United Kingdom*

Received: June 23, 1997; In Final Form: August 21, 1997[®]

A method based on a microemulsion route is presented to obtain magnetic nanoparticles of different sizes, offering several advantages with respect to other similar methods. It consists basically of the development of a microemulsion route above room temperature. Magnetic iron oxide particles with sizes ranging from 2 to 8 nm are obtained. The as-obtained product presents defined X-ray diffraction patterns, without the complications of working in an inert atmosphere or with extra amounts of Fe^{2+} , thereby eliminating the need for further steps in order to achieve good crystallization of the material.

1. Introduction

The synthesis of magnetic nanoparticles has been an area of study for a long time because of the interesting practical applications of such particles in magnetic recording, magnetic fluids, permanent magnets, etc.¹

To synthesize such particles several methods are used.² Among them, the microemulsion method has appeared as a powerful tool in the past decade.³ A microemulsion is an isotropic and thermodynamically stable single phase formed by at least three components; two of them are nonmiscible, and a third, called surfactant, has an amphiphilic behavior.^{4,5} Specifically, the synthesis of magnetic iron oxides has been attempted

in this way.⁶ Nevertheless, the particles are obtained with a poor degree of crystallization, and a further process is needed in order to improve it, consisting typically of annealing the obtained particles.⁷ The drawback of the lack of crystallization can also be avoided by working in an inert atmosphere or by using large amounts of Fe^{2+} .⁸

We present here a method of synthesis based on the microemulsion route that eliminates the above-mentioned problems. For this purpose, the reaction does not take place at room temperature, as it did in the methods reported up to date, but does so at a higher temperature. In this Letter we demonstrate the efficacy of this improvement of the microemulsion method, obtaining crystallized magnetic iron oxide nanoparticles.

* Corresponding author. Fax: +34 81 520676. E-mail: fajmirap@usc.es.

[®] Abstract published in *Advance ACS Abstracts*, September 15, 1997.

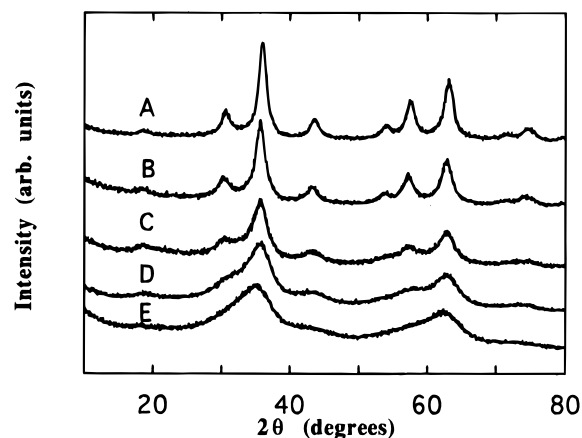


Figure 1. X-ray diffraction patterns of the as-obtained nanoparticles.

TABLE 1: Splitting Temperature between FC and ZFC dc Magnetizations (T_S), Interplanar Spacing (d), and Average Particle Size, Obtained from X-ray Diffractograms (RX) and Fits to the Langevin Law (mag.)

sample	T_S (K)	d (Å)	size (RX) (Å)	size (mag.) (Å) ^a
A	210	2.511	73	7 (0.44)
B	140	2.512	56	63 (0.47)
C	75	2.511	36	41 (0.53)
D	60	2.527	24	30 (0.42)
E	45	2.542	19	24 (0.09)

^a The standard deviation of a log-normal volume distribution is given in parentheses.

2. Synthesis Procedure

In this microemulsion route inverse micelles are used, i.e., water nanodroplets are formed in an organic compound and used as nanoreactors in order to control particle size. These nanodroplets are surrounded by a surfactant coat that limits their size and separates them from the organic compound. A nonionic surfactant (Brij-97) and cyclohexane as organic phase have been used here. The ternary system cyclohexane/Brij-97/water forms microemulsions at low water concentrations for a wide range of Brij-97 concentrations.⁹

The synthesis procedure involves the mixture of two microemulsions M(I) and M(II) at 65 °C. The microemulsion M(I) is of cyclohexane/Brij-97/aqueous solution of iron salts in the $(93 - x)/7/x$ volume ratio ($1 < x < 3$). The molarities of the salts in the aqueous solution are 1 M in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 M in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 0.1 M in HCl. Acidic medium is used in order to avoid oxidation of Fe^{2+} . The microemulsion M(II) is similar to M(I), but without salts in the aqueous solution and with a 20% greater volume of cyclohexylamine. Cyclohexylamine is used in order to produce an alkaline medium, necessary to precipitate the iron salts. All chemicals were supplied by Aldrich Chemicals and used without further purification.

M(I) (200 mL) and M(II) (25 mL) were heated separately in a water bath until 65 °C was reached. At this temperature one single transparent phase of every microemulsion was formed. The M(I) was added to the M(II) under mechanical stirring. After 15 min of aging, the mixture was cooled to room temperature. The obtained precipitate was decanted with the aid of a magnet and washed several times with large amounts of acetone and water and finally dried at room temperature in a desiccator. Five samples, labeled A, B, C, D, and E, were obtained from microemulsions with $x = 3, 2.5, 2, 1.5$, and 1. Given the high concentration of reagents employed and that the same amount of surfactant is present for each microemulsion, the smaller x , the smaller the size of the nanoreactors, and therefore smaller particles should be obtained.¹⁰

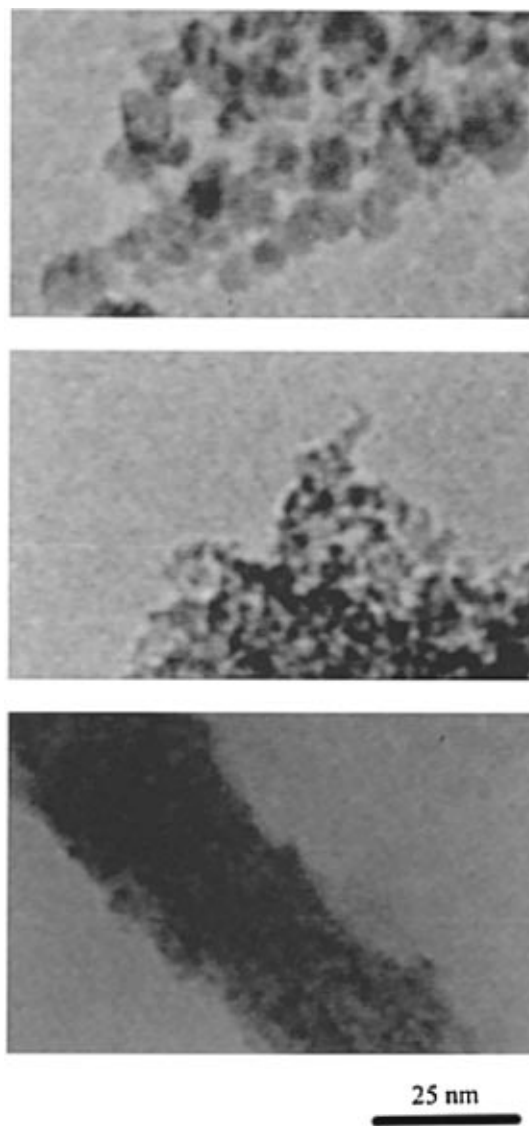


Figure 2. TEM micrographs of some samples: (a, top) sample A, (b, middle) sample C, and (c, bottom) sample E.

3. Results and Discussion

X-ray diffraction patterns of the samples were taken from 10 to 80° (2θ) using Cu K α radiation. Diffractograms are presented in Figure 1 showing a progressive broadening of the peaks when going from sample A to E, indicating a decrease in particle size. The obtained patterns can be identified with $\gamma\text{-Fe}_2\text{O}_3$. From these data we obtained the interplanar space, d , and the mean particle diameter using the Debye–Scherrer formula¹¹ for the most intense peak, corresponding to the (311) reflection in maghemite (Table 1). d values increase slightly from sample A to E and are similar to the characteristic value of maghemite ($d = 2.52$ Å).¹²

TEM micrographs were taken with a 200 KV-JEOL microscope. For this purpose the samples were dispersed in ethanol and deposited onto a copper grid. Aggregates of particles with a clear decrease in particle size from sample A to E are observed, in agreement with data from X-ray fits (Figure 2).

Zero-field-cooled (ZFC) and field-cooled (FC) data were recorded at 5 Oe between 4 and 300 K with a Quantum Design SQUID. They are presented in Figure 3, showing that moving from sample E to sample A the temperature at which FC and ZFC split, T_S , and the temperature of the maximum of the ZFC susceptibility are largely modified. Also the curves become broader and broader. These changes, which reflect an increase

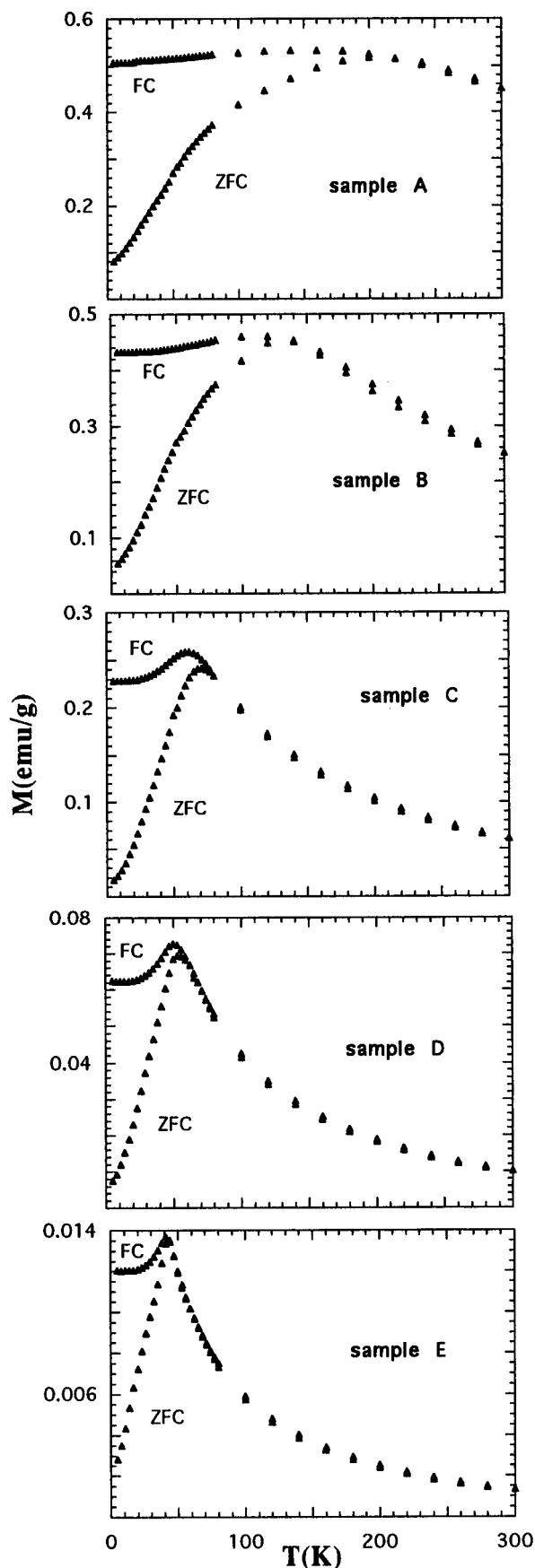


Figure 3. Magnetization versus temperature (ZFC and FC) for the samples, taken with an applied field of 5 Oe.

of the average blocking temperature $\langle T_B \rangle$ and a broadening of the size distribution with increasing the particle size,¹³ can be considered as another probe of the trend in the particle size

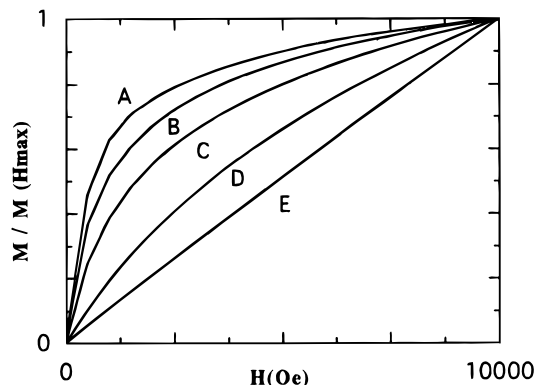


Figure 4. Magnetization versus field at room temperature for the samples.

control, due to the known dependence of the magnetic particle volume with the blocking temperature of a superparamagnetic system.¹⁴ Above the temperature of splitting between ZFC and FC curves, all the particles are in the superparamagnetic state; actually the splitting temperature corresponds to the highest T_B .

A DMS-1660 Vibrating Sample Magnetometer was used to obtain magnetization versus field curves from 77 to 300 K in fields up to 10 kOe. In Figure 4 we show the results at room temperature. The maximum magnetization values decreased from A to E, as well as the curvature of the M/H lines. Providing that these data are taken at the superparamagnetic state, a simple estimate of the average size can be deduced from a fit to the Langevin law with a log-normal size distribution,¹⁵ yielding a reduction in the magnetic particle volumes (Table 1), in agreement with data from TEM and X-ray fits.

In summary, we demonstrate that the use of stable microemulsions above room temperature represents an advance in the synthesis of iron oxide magnetic nanoparticles, compared to the classical use of microemulsions at room temperature. We show also that with easy modifications in the synthesis procedure the final particle size can be controlled.

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