J Mater Sci (2007) 42:9015–9020
DOI 10.1007/s10853-007-1834-0

A novel method to prepare magnetic nanoparticles: precipitation in bicontinuous microemulsions

**Jesús Esquivel · Isabel A. Facundo · M. Esther Treviño ·
Raúl G. López**

Received: 18 September 2006 / Accepted: 8 May 2007 / Published online: 20 July 2007

Abstract A novel method to prepare iron oxide nanoparticles by precipitation in bicontinuous microemulsions is reported. Precipitation reactions were carried out in microemulsions stabilized with a mixture of dodecyltrimethylammonium bromide/didodecyldimethylammonium bromide (3/2, w/w). Nanoparticles were characterized by X-ray diffraction, transmission electronic microscopy (TEM) and vibrating sample magnetometry (VSM), and consisted of magnetite or a mixture of magnetite and maghemite. The particles have an average diameter of 8 nm with a relatively narrow particle size distribution and show possible superparamagnetic behavior. Noticeably higher yields of precipitate are observed for this new approach in comparison with those typicall obtained using reverse microemulsions.

Introduction

Nanoscale superparamagnetic iron oxide particles, such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), offer very attractive possibilities in biomedical applications because of their magnetic properties and size specifically in chemotherapy, radiotherapy and hyperthermia for treatment of solid tumors [1–4]. For these applications the magnetic particles should be coated with such materials as natural or synthetic polymers to allow for the attachment of drugs and other molecules capable of specific recognition of, and binding to, malignant cells. Although many synthesis methods are available for preparing superparamagnetic iron oxide particles [3], many papers have demonstrated that precipitation in reverse microemulsions is the most adequate method for preparing magnetic particles with diameters smaller than 10 nm and narrow particle size distribution in a direct way [5–14]. In the other known methods the obtained particles must be subjected to a size-selection process in order to narrow the particle size distribution [15, 16]. Within the reports on precipitation in reverse microemulsions are noticeable the works of: Gobe et al. [5], Bandow et al. [6], Dresco et al. [10], Santra et al. [12] and, more recently, Lee et al. [14], who prepared magnetic particles with mean diameters of 3, 3.6, 7.3, 1 and 3 nm, respectively, and with relatively narrow particle size distribution. In spite of all this work, which deals mainly with the synthesis and characterization of the particles, little attention has been paid to the mechanistic of such systems [8–10, 12]. However, it is now recognized that the nucleation and growth of the nanoparticles in these systems occur inside of the swollen micelles (or droplets) of the reverse microemulsions, which usually have diameters smaller than 10 nm. In this way, swollen micelles function as nanoreactors for the preparation of the particles [17].

Despite the size control and distribution of the magnetic particles, the precipitation method using the reverse microemulsions has the drawback of a relatively low yield. Calculations based on the reported recipes for preparing magnetic nanoparticles using this technique, show

J. Esquivel · I. A. Facundo · M. E. Treviño ·
R. G. López (✉)
Centro de Investigación en Química Aplicada, Boul. Ing.
Enrique Reyna No. 140, Saltillo, Coahuila 25253, Mexico
e-mail: glopez@ciqa.mx

J. Esquivel
Facultad de Ciencias Químicas, Universidad Autónoma de
Coahuila, Saltillo, Coahuila 25240, Mexico

yields from 0.1 g [7] to 0.4 g [5] of product per 100 g of total mixture. Surprisingly, and as far as we know, the precipitation in bicontinuous microemulsions has not been considered as an option that could increase this yield. In contrast to reverse microemulsions, which consist of aqueous droplets dispersed in an oleic continuous phase, bicontinuous microemulsions are formed from interconnected aqueous channels with diameters usually smaller than 10 nm immersed in an oleic continuous phase [18]. This structure allows bicontinuous microemulsions to accept contents of the aqueous phase usually between 50 and 100% higher than those accepted by reverse microemulsions [18, 19]. We speculate that the reason why bicontinuous microemulsions have not been considered earlier as media for the precipitation of magnetic particles is because of their microstructure. On the first hand one would not expect to obtain spherical or equiaxial particles from the cylindrical channels of a bicontinuous microemulsion in contrast to what can be obtained or expected from the spherical droplets of reverse microemulsions. Nowadays, it is accepted that the mechanism through which particles are obtained in reverse microemulsions includes nucleation in those droplets that contain a minimum number of precipitate molecules and further growth through recruiting precursor ions from those droplets containing no particles inside either by diffusion or droplet collision [17]. Although particle growth in bicontinuous microemulsions cannot proceed by droplet collision, there is no obvious reason why nucleation inside the channels and further growth of nuclei through recruiting precursors ions from surroundings could not occur.

In this paper, we report a new method that uses the channels of bicontinuous microemulsions as media to prepare nanoscale magnetic particles. The results of the characterization of these particles by X-ray diffraction, transmission electron microscopy and vibrating sample magnetometry were compared with those of the particles prepared in a reverse microemulsion.

Experimental

Materials

All reagents were high-purity grades from Aldrich used without further purification: ferric chloride ($FeCl_3·4H_2O$, 99%), ferrous chloride ($FeCl_2·6H_2O$, 98%), methyl methacrylate (MMA, 99%), aqueous ammonia (NH_4OH, 57.6 wt.%), dodecyltrimethylammonium bromide (DTAB, 99%) and didodecyldimethylammonium bromide (DDAB, 98%). Water was triple-distilled deionized grade.

Phase diagram determinations

Microemulsion regions at 80 °C were determined by titration of solutions of the DTAB/DDAB mixture (3/2, w/w) in MMA with 0.75 M aqueous solution of a $FeCl_3·6H_2O$/$FeCl_2·4H_2O$ mixture (3/2, mol/mol). Phase boundary was detected visually at each one of the constant (DTAB/DDAB)/MMA lines studied. Then, samples with compositions slightly below and above that of the visually determined phase boundary were prepared by weighting each component and allowing to reach equilibrium in a water bath at 80 °C to determine more precisely the phase boundary.

Synthesis of magnetic particles

Precipitation reactions were carried out at 80 °C in a 100 mL jacketed glass reactor equipped with a reflux condenser and inlets for argon, mechanical agitation and feed of the microemulsion and ammonium hydroxide aqueous solution. To help stabilize the system during the reaction, the reactor was immersed in an ultrasonic bath. Two precipitation reactions in bicontinuous microemulsions were carried out along with one precipitation reaction in a reverse microemulsion with the same surfactant content (33 wt.%) for comparison. When the reaction media was the reverse microemulsion a stirrer speed of 300 rpm was used; mechanical agitation was not provided when the reactions were carried out in the bicontinuous microemulsions. Reverse microemulsion was prepared with 57 wt.% MMA and 10 wt.% aqueous solution of a mixture of ferric and ferrous chlorides in a molar ratio of 3/2 with an overall concentration of 0.75 M. The bicontinuous microemulsions were composed by 30 and 40 wt.% of the same aqueous solution of the mixture of ferric and ferrous chlorides and 37 and 27 wt.% MMA, respectively. In all cases, an excess of ammonium hydroxide (twice the stoichiometric requirements) was used. The typical procedure for the precipitation reaction started with charging the previously deoxygenated microemulsion in the reactor and then raising the temperature to 80 °C. To initiate the reaction aqueous solution of ammonium hydroxide was added to the reactor. The reacting system was continuously purged with argon during the entire process. The precipitation reaction was allowed to proceed for 30 min whereupon a mixture of acetone and water was added to cause the final precipitate recovered by magnetic separation. Noticeably the supernatant contained no visible particles in suspension. After several washes with acetone, the precipitate was dried yielding a black powder.

Characterization

Electrical conductivities were measured at 80 °C and 1 KHz with an Orion 115 conductivity meter. Magnetic measurements were determined in fields up to 12.5 kOe using Lake Shore vibrating sample magnetometer model VSM 735. X-ray determinations were done on a Siemens D-5000 X-ray diffractometer. Particle size was determined from micrographs obtained using a JEOL 1200 EXII transmission electron microscope. TEM samples were prepared by dispersing the powders in ethanol using an ultrasonicator, and depositing the dispersion on a copper grid.

Results and discussion

The partial phase diagram at 80 °C of the system composed by DTAB/DDAB (3/2, w/w) mixture, MMA and an aqueous solution of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ in 3/2 molar ratio with an overall concentration of 0.75 M is shown in Fig. 1. We note the one-phase microemulsion region initiating at the MMA-(DTAB/DDAB) side which extends to the central zone of the phase diagram. The form of this region suggests a transition from reverse to bicontinuous microemulsions when the system goes from the MMA-(DTAB/DDAB) side to the central zone of the diagram.

In order to determine where the transition occurs, the electrical conductivities of the microemulsions samples with the same surfactant concentration (33 wt.%), but different contents of aqueous solutions of the mixture of iron chlorides, were measured at 80 °C. The results are shown in Fig. 2 where it is possible to identify an interval of low conductivity (up to 15 wt.% aqueous solution). This agrees with the typical behavior of reverse microemulsions where low conductivities are observed due to the discontinuous nature of reverse microemulsions. On the other hand, there is a second interval of higher conductivity from the 20 wt.% aqueous solution in which electrical conductivity increases linearly. The higher conductivity agrees with the increased capacity of the bicontinuous microemulsions for conducting electrical current as a result of their continuous long aqueous phase. Accordingly, the transition from reverse to bicontinuous microemulsions prepared with 33 wt.% surfactant should occur at some point between 15 and 20 wt.% aqueous solution. Circles on the horizontal line crossing the diagram (33 wt.% surfactant concentration) in Fig. 1 indicate the composition of microemulsions in which precipitation reactions were carried out.

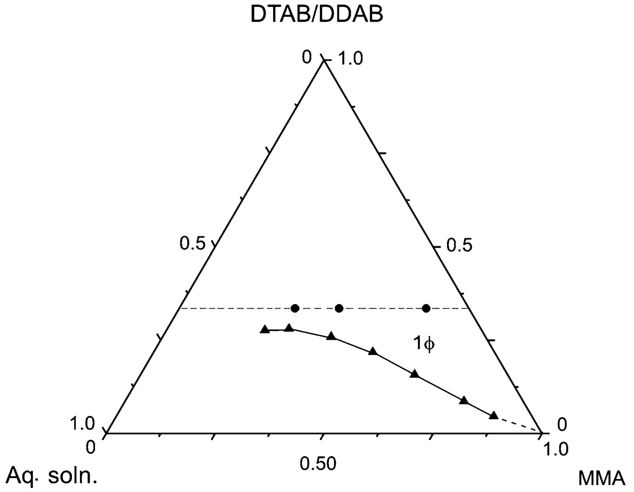

Fig. 1 Partial phase diagram at 80 °C of system DTAB/DDAB, MMA and a 0.75 M aqueous solution of the mixture of iron chlorides showing microemulsion regions (1ϕ). Circles on the horizontal line crossing the diagram (33 wt.% surfactant concentration) indicate the composition of microemulsions in which precipitation reactions were carried out

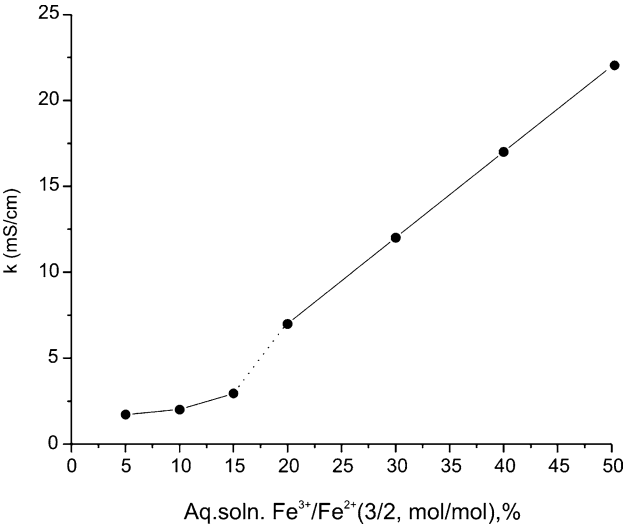

Fig. 2 Electrical conductivity at 80 °C of microemulsions containing 33 wt.% surfactant and different concentrations of 0.75 M aqueous solution of the mixture of iron chlorides

All of the precipitation reactions turned black upon the addition of aqueous ammonium hydroxide. This is typical of precipitation reactions where magnetite has been obtained [10]. Once the products of the reactions were recovered, yield calculations indicated 0.51 and 1.16 g of magnetic particles per 100 g of total mixture for bicontinuous microemulsions with 30 and 40 wt.% aqueous solution of chlorides, respectively, compared to 0.29 g of magnetic particles per 100 g of total mixture for the reverse microemulsion. Under the conditions studied, these data demonstrate the yield advantage of bicontinuous over reverse microemulsions in the synthesis of nanoscale

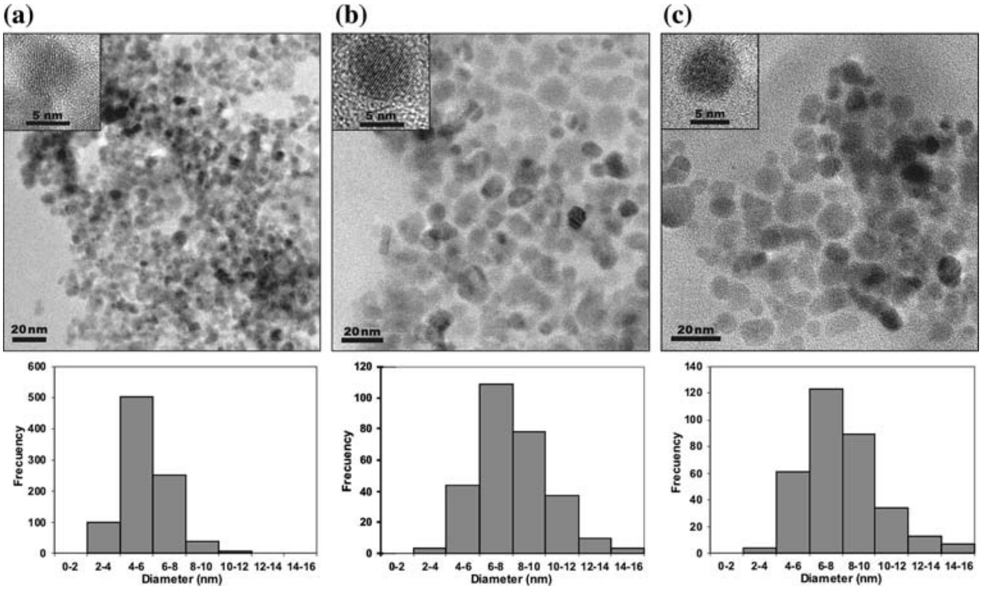

Fig. 3 TEM micrographs of particles prepared in: reverse microemulsion (**a**) and bicontinuous microemulsion with 30 (**b**) and 40 (**c**) wt.% aqueous solution of the mixture of iron chlorides. Insets show the corresponding high-resolution images. Histograms of the size distributions are also included

particles. It should be noted that we found it difficult to compare our results with those reported in other studies on precipitation of magnetic particles in reverse microemulsions. The reason is that the authors do not report the yields obtained in their studies but only a few of them provide the sufficient data for calculating the theoretical yields. Using the data reported was possible to estimate the yields in those studies carried out by Gobe et al. [5], Lee et al. [7] and Selim [20], as 0.4, 0.1 and 0.2 g of magnetic particles per 100 g of total mixture, respectively. In comparison, the yields obtained in our study resulted in similar values for the reverse microemulsion; however, those obtained from precipitation in bicontinuous microemulsion were higher.

Low and high magnification TEM images are shown in Fig. 3 along with histograms. Table 1 shows the number-average diameter (D_n) and the polydispersity index (D_w/D_n) calculated from the TEM photomicrographs. Data in Table 1 indicate that the precipitation reaction carried out in the reverse microemulsion produces small diameter particles (5.6 nm) with a relatively narrow particle size distribution. For particles prepared in the bicontinuous microemulsions, small diameters are also observed (≈8 nm) with relatively narrow particle size distributions. The results demonstrate that nucleation and growth of nanoparticles can be carried out in the channels of bicontinuous microemulsions. This observation opens the possibility that the channel diameters may play a role in determining the final particle size.

X-ray diffraction patterns of the samples are shown in Fig. 4. Peak broadening observed is consistent with the small particle size [12, 21] with patterns matching those of

Table 1 Average diameter and polydispersity index of particles prepared by precipitation in reverse and bicontinuous microemulsions as determined from TEM micrographs

Precipitation reaction media	D_n (nm)	D_w/D_n
Reverse microemulsion	5.6	1.20
Bicontinuous microemulsion (30 wt.% aq. solution)	8.1	1.22
Bicontinuous microemulsion (40 wt.% aq. solution)	7.9	1.25

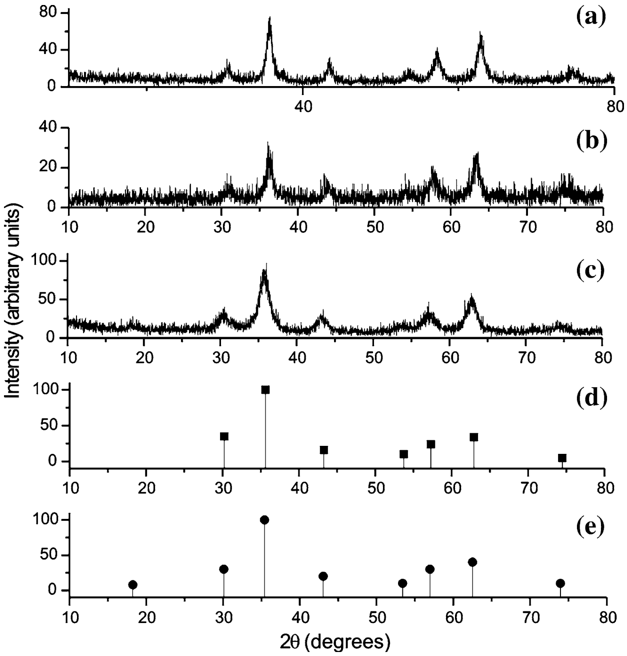

Fig. 4 X-ray diffraction patterns of particles prepared in: reverse microemulsion (**a**) and bicontinuous microemulsion with 30 (**b**) and 40 (**c**) wt.% aqueous solution of the mixture of iron chlorides. Standard patterns of magnetite (**d**) and maghemite (**e**) are included

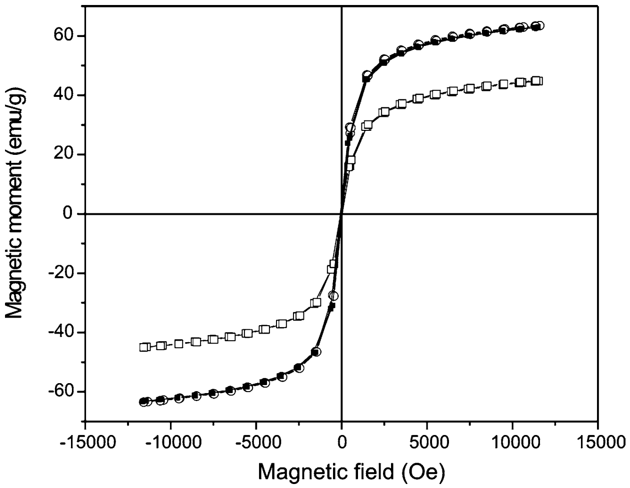

Fig. 5 Magnetization curves for particles prepared in reverse microemulsion (□) and bicontinuous microemulsion with 30 (○) and 40 (■) wt.% aqueous solution of the mixture of iron chlorides

magnetite and maguemite. Although, differentiation between the species is not possible from the present X-ray data, Fe (II) is present as indicated by the black color of the samples. Thus, the particles produced by precipitation reactions carried out in the bicontinuous microemulsions may consist of magnetite or a mixture of the two species. Differentiation is left for future studies using bicontinuous microemulsions.

Figure 5 shows the room temperature magnetization curves of the particles. None of the samples are saturated up to 12.5 kOe. This behavior, typical of magnetite particles with diameters smaller than 15 nm, has been consistently reported in the literature [8, 12–14, 22] and arises from the difficulty for aligning the magnetic moments of the surface atoms, which constitute a large fraction of the total volume of a particle, in the direction of applied magnetic field [23]. Superparamagnetic behavior of all the samples is suggested by the low remnant magnetization (1.7 emu/g) and coercitive field (45 Oe). This behavior was expected because of the very small sizes of the particles in our samples. The explanation is that superparamagnetism implies that the magnetic particles have essentially single domains, i.e., all magnetic moments in the particle are aligned in one direction [10], and as is well known, magnetic particles below 10 nm become single domains [24].

The magnetization values of the samples at 12.5 kOe obtained by precipitation in the bicontinuous microemulsions (63–65 emu/g) are higher than that prepared in the reverse microemulsion (45 emu/g). This agrees with the known fact that magnetization of small particles (diameters smaller than ca. 15 nm) decreases as particle size decreases [8, 12]. In general, the magnetization values obtained in our study are higher than those reported for magnetic particles prepared by precipitation in reverse microemulsions at relatively low temperatures (25–50 °C) [20, 25] but they are close to those values obtained from the particles prepared at higher temperatures [14, 25]. Our explanation for this behavior is that an increase in precipitation temperature enhances the crystallinity of the iron oxide nanoparticles [14] and, as is well known, magnetization of magnetic nanoparticles depends in a direct way on their crystallinity.

Conclusions

Magnetic nanoparticles were obtained by precipitation reactions in bicontinuous microemulsions. X-ray diffraction analysis demonstrated that the particles consist of magnetite or a mixture of magnetite–maghemite. TEM analyses showed that the particles have average diameters close to 8 nm and a relatively narrow particle size distribution. VSM data suggest superparamagnetic behavior. The bicontinuous microemulsion synthesis for the preparation of the present nanoparticles shows yields appreciably higher than those obtained using reverse microemulsions technique. We propose the bicontinuous microemulsion technique as a general method for the preparation of nanoscale particles.

Acknowledgment CONACyT supported this research through grant SEP 2003-CO2-45436. Two of us (IAF and JE) acknowledge scholarships from CONACyT to pursue her Doctoral and MSc works, respectively. We are grateful to Selene Guzmán for her support in TEM measurements and Janet Valdés and Patricia Siller for their assistance in acquiring various specialized documents.

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