

Synthesis of magnetic nanoparticles in bicontinuous microemulsions. Effect of surfactant concentration

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Abstract Precipitation was accomplished at 80 °C for magnetic nanoparticles in bicontinuous microemulsions that were stabilized with different concentrations of a surfactants mixture of dodecyltrimethylammonium bromide/didodecyltrimethylammonium bromide (3/2, w/w). These nanoparticles were characterized by X-ray Diffraction, Scanning Transmission Electronic Microscopy (STEM), and Vibrating Sample Magnetometry (VSM), which demonstrated that they were composed of magnetite or a mixture of magnetite-maghemite. The particles were found to have average diameters between 6.9 and 7.9 nm with relatively narrow particle size distribution and showed possible superparamagnetic behavior. In addition, we observed an inverse dependence of particle size on surfactant concentration. Yields obtained in these precipitation reactions were found to be up to three times higher than those typically reported in specialized literature about precipitation of magnetic nanoparticles in reverse microemulsions.

Introduction

Magnetic nanoparticles, such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), show very interesting properties due

to their finite size and surface effects that dominate the magnetic behavior of individual particles [1]. Superparamagnetism shown by magnetic particles with diameters <15 nm [2], are increasingly important to a variety of industrial and biomedical applications [3]; for example, current biomedical applications are magnetic separation, drug delivery, hyperthermia treatment, and magnetic resonance imaging contrast enhancement [3–6].

Precipitation in reverse microemulsions is a well-established technique for preparation of magnetic particles with diameters smaller than 10 nm and narrow particle size distribution [7–18]. The basis of this technique is the use of aqueous phase nanodroplets, with diameters usually smaller than 10 nm, that contain precursor ions of magnetic nanoparticles, to carry out precipitation reactions. In this way the droplets function as nanoreactors in which nucleation in a very small fraction of those occurs. The further growth of particles occurs by recruiting precursor ions and precipitate molecules from droplets void of particles [19].

In spite of the desirable characteristics of magnetic nanoparticles, precipitation in reverse microemulsions has the drawback of relatively low yield. Calculations based on the reported recipes for preparing magnetic nanoparticles by this technique, showed yields from 0.1 g [9] to 0.4 g [7] of product per 100 g of total mixture; however, by precipitation in bicontinuous microemulsions stabilized with a mixture of the cationic surfactants dodecyltrimethylammonium bromide (DTAB) and didodecyltrimethylammonium bromide (DDAB) in 3/2 (w/w) ratio, we were able to obtain particles with diameters near 8 nm with relatively narrow particle size distribution and yields of up to 1.16 g of product per 100 g of total mixture [20]. The increase in yield resulted from the differing capacities of aqueous phase dissolution between reverse and bicontinuous microemulsions. This is because reverse microemulsions

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usually accept up to 15 wt% while bicontinuous microemulsions are able to accept contents near 45 wt% [19]. Use of bicontinuous microemulsions provides an option to overcome the drawback of low yield while preserving the characteristics of magnetic nanoparticles.

Bicontinuous microemulsions are formed of interconnected aqueous channels, with diameters usually smaller than 10 nm, immersed in an oleic continuous phase [21], whereas reverse microemulsions are constituted of nanodroplets of aqueous phase dispersed in an oleic continuous phase. Due to the difference in microstructures between both types of microemulsions, the mechanism of the particles precipitation should be different. In bicontinuous microemulsions it would be expected that nucleation inside the channels and further growth of nuclei through recruiting precursor ions and molecules of precipitate would occur.

Our previous report on preparation of magnetic nanoparticles by precipitation in bicontinuous microemulsions was the first on this topic in the specialized literature [20]. To begin to elucidate the mechanism of particle precipitation in bicontinuous microemulsions, we report our findings on the effect of the concentration of the mixture of surfactants DTAB/DDAB (3/2, w/w) on the synthesis of magnetic nanoparticles in bicontinuous microemulsions.

Experimental

Materials

All reagents were high-purity grades from Aldrich used without further purification: ferric chloride ($\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, 99%), ferrous chloride ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, 98%), methyl methacrylate (MMA, 99%), aqueous ammonia (NH_4OH , 57.6 wt%), dodecyltrimethylammonium bromide (DTAB, 99%), and didodecyltrimethylammonium bromide (DDAB, 98%). Water was triple-distilled deionized grade.

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, 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. Three precipitation reactions in bicontinuous microemulsions were carried out with 30, 33, and 36 wt% surfactant, the same content (30 wt%) of an 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, and the corresponding MMA contents to complete the total mixture. To preserve the microstructure in bicontinuous microemulsions, agitation

was not provided when the reactions were carried out. In all cases, an excess of ammonium hydroxide (twice the stoichiometric requirements) as precipitating agent was used. Precipitation reactions were carried out following the same procedure reported in our previous work [20].

Characterization

Electrical conductivities were measured at 80 °C and 1 KHz with an Orion 115 conductivity meter. Magnetic measurements were determined at room temperature 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 Field Emission Scanning Electronic Microscope (FESEM) with a STEM module. Samples for electronic microscopy were prepared by dispersing the powders in acetone using an ultrasonicator and depositing the dispersion on a copper grid.

Results and discussion

In agreement with our previous report [20], the system composed of DTAB/DDAB (3/2, w/w) mixture, MMA as oleic phase, and an aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 3/2 molar ratio with an overall concentration of 0.75 M, was able to form at 80 °C a microemulsion region (see Fig. 1). The form of this region suggests a transition from reverse microemulsions to bicontinuous microemulsions when the system goes from

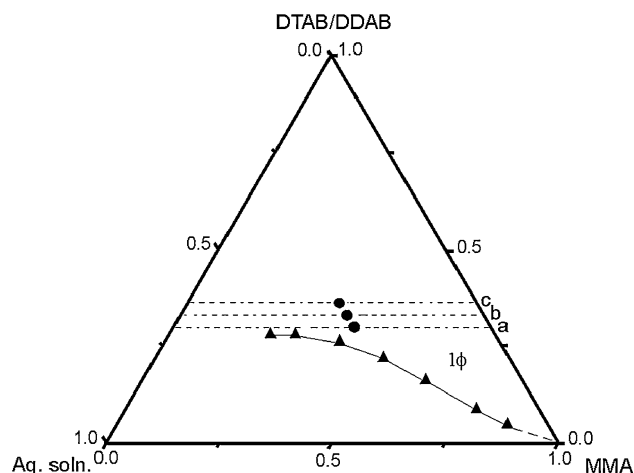


Fig. 1 Partial phase diagram at 80 °C of system DTAB/DDAB, MMA, and a 0.75 M aqueous solution of the mixture of iron chlorides showing microemulsion regions (1 ϕ) [20]. Circles on the horizontal lines crossing the diagram at (a) 30, (b) 33, and (c) 36 wt% surfactant concentration indicate the composition of microemulsions in which precipitation reactions were carried out

the MMA-(DTAB/DDAB) side to the central zone of the diagram. To identify the zone where the transition occurs, we carried out measurements of electrical conductivity.

Reverse microemulsions are poor electrical current conductors [20–22] in contrast with the higher conductivities characteristics of the bicontinuous ones [23–26]. In this study, three surfactant concentrations (30, 33, and 36 wt%) were selected to determine the effect of surfactant concentration on the synthesis of magnetic particles in bicontinuous microemulsions. The electrical conductivities were measured at 80 °C for microemulsion samples with selected surfactant concentration and different contents of aqueous solutions of the mixture of iron chlorides. The results of these measurements are shown in Fig. 2. Here it is possible to identify an interval of low conductivity (up to $\approx 15\%$ aqueous solution), that would correspond to reverse microemulsions, and another of higher conductivities, from approximately 20 wt% aqueous solution, that could be ascribed to bicontinuous ones. In accordance with these results, the transition region from reverse microemulsions to bicontinuous microemulsions, should be located between 15 and 20 wt% aqueous solutions. This agrees with conclusions reported in our previous report [20] as well as, with those reported in the literature indicating that formation of bicontinuous microemulsions typically occurs when the content of aqueous phase is higher than 20 vol% [22, 27]. Based on this information, preferable compositions could be selected to carry out precipitation reactions in bicontinuous microemulsions. Circles on the horizontal lines crossing the diagram (at 30, 33, and 36 wt% surfactant concentrations) in Fig. 1 indicate the composition of microemulsions in which precipitation reactions were carried out.

All the mixtures of reaction became immediately black after the aggregate of aqueous ammonium hydroxide, typical of precipitation reactions where magnetite has been obtained [13]. With the appearance of black powder, the

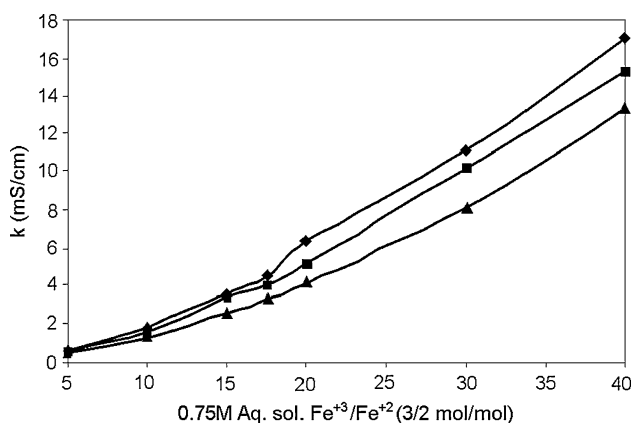


Fig. 2 Electrical conductivity at 80 °C of microemulsions containing (▲) 30, (■) 33, and (◆) 36 wt% surfactant and different concentrations of 0.75 M aqueous solution of the mixture of iron chlorides

products of the reactions were recovered and, yield calculations indicated values between 1.4 and 1.6 g of dried solids per 100 g of total mixture. These values are significantly higher than the maximum value of theoretical yield calculated from reported recipes in the specialized literature for preparing magnetic nanoparticles in reverse microemulsions [7]. The maximum value of theoretical yield being 0.4 g of magnetic particles per 100 g of total mixture. These data corroborated the yield advantage of bicontinuous over reverse microemulsions in the synthesis of magnetic nanoparticles [20].

Figure 3 shows STEM micrographs of the samples obtained in this study along with their histograms. The number-average diameter (D_n), the weight-average diameter (D_w), and the polydispersity index (D_w/D_n) calculated from the STEM micrographs are shown in Table 1. D_n and D_w were calculated using the following equations [28]:

$$D_n = \frac{\sum n_i D_i}{\sum n_i} \quad (1)$$

$$D_w = \frac{\sum (n_i D_i)^4}{\sum (n_i D_i)^3} \quad (2)$$

where n_i is the number of particles of diameter d_i .

Data in this table indicate that the precipitation reactions carried out in bicontinuous microemulsions produce small diameter particles (6.9–7.9 nm) with a relatively narrow particle size distribution. It is noticeably that the diameters of these particles were similar to those characteristic of the channels in bicontinuous microemulsions (<10 nm). This was expected, since it is known that the microstructures of the microemulsions serve like nanoreactors, thus limiting the growth of particles [19].

Considering that the estimation of response error in our measurements of particle size was ≈ 0.03 nm, data in Table 1 show a diminution in D_n when increasing surfactant concentration. This agrees with the decrease in the frequency of higher particle sizes as surfactant concentration increases as shown in the histograms in Fig. 3. When the content of the dispersed phase is maintained, it is well known that, the characteristic size of the microstructures in a microemulsion, the diameter of the droplets in normal and reverse microemulsions, as well as the channels in the bicontinuous ones, diminish with the increase in surfactant concentration. Thus, in this study, the increase in surfactant concentration caused a diminution in the diameter of the channels (nanoreactors) where the precipitation reactions would have been carried out and therefore would have restricted the particles growth.

X-ray diffraction patterns of the samples matching those of magnetite and maghemite are shown in Fig. 4. Although, differentiation between both species is not possible from the present X-ray data, Fe (II) is present as indicated by the black

Fig. 3 STEM micrographs and their histograms of particles prepared in bicontinuous microemulsion at 80 °C with 30 wt% 0.75 M aqueous solution of the mixture of iron chlorides, containing (a) 30, (b) 33, and (c) 36 wt% surfactant

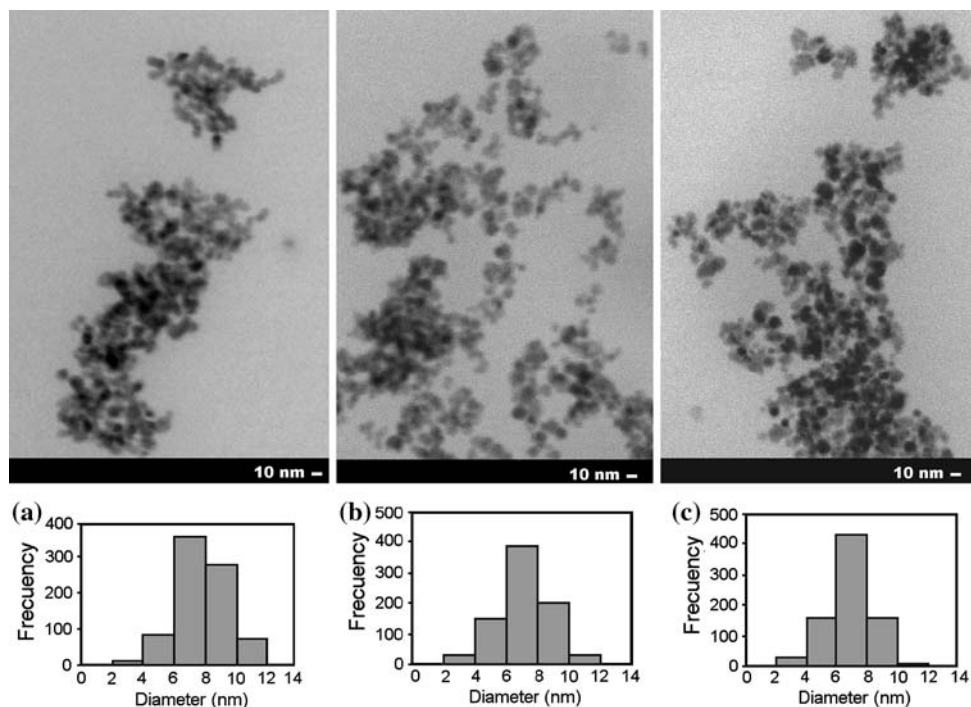


Table 1 Number-average diameter (D_n) and polydispersity index (D_w/D_n) as determined from STEM micrographs of particles prepared by precipitation in bicontinuous microemulsions with various surfactant concentrations and 30 wt% 0.75 M aqueous solution of the mixture of iron chlorides at 80 °C

Surfactant concentration (wt%)	D_n (nm)	D_w/D_n
30	7.9	1.12
33	7.2	1.15
36	6.9	1.13

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 magnetite-maghemite.

Figure 5 shows the room temperature magnetization curves of the particles. The difficulty for saturation that these samples showed under the applied magnetic field, also reported in our previous work [20], is typical of magnetite particles with diameters smaller than 15 nm [10, 12, 15–17] and arises from the difficulty for aligning the magnetic moments of the surface atoms in the direction of applied magnetic field [29]. Superparamagnetic behavior of all samples, suggested by the low remnant magnetization (1.4–2.8 emu/g) and coercitive field (27.5–49.9 Oe), was expected due to the very small sizes of the particles. The explanation for this behavior is that superparamagnetism implies that the magnetic particles have essentially single domains [13]; this is a well-known characteristic of magnetic particles with diameters below 10 nm [30].

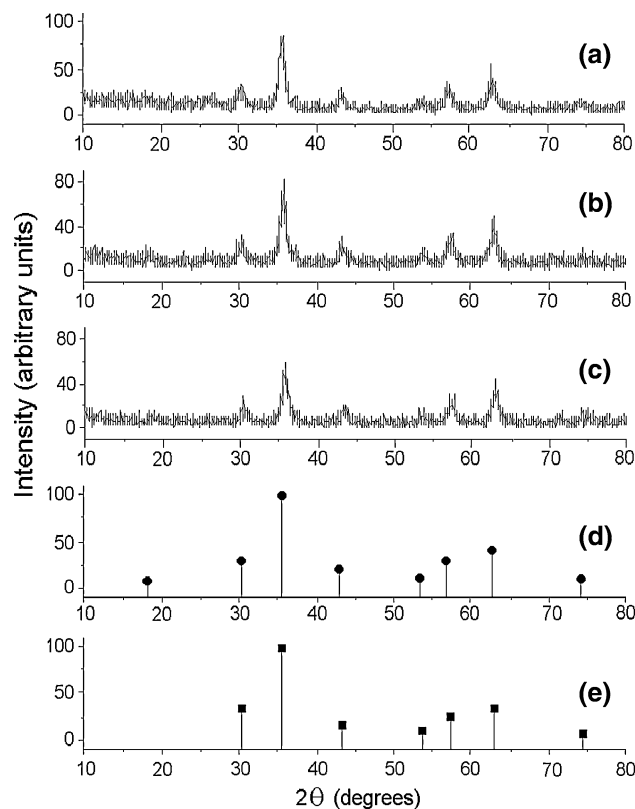


Fig. 4 X-ray diffraction patterns of samples prepared in bicontinuous microemulsions at 80 °C with 30 wt% 0.75 M aqueous solution of the mixture of iron chlorides containing (a) 30, (b) 33, and (c) 36 wt% surfactant. Standard patterns of maghemite (d) and magnetite (e) are included

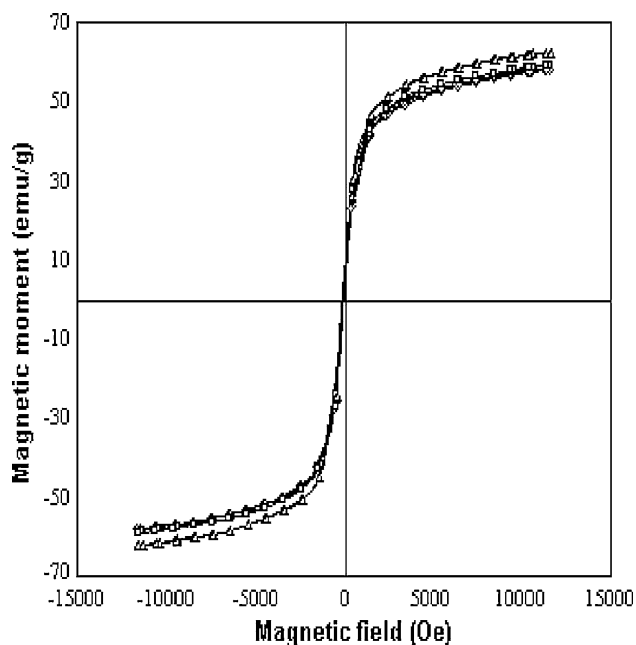


Fig. 5 Magnetization curves at room temperature for particles prepared in bicontinuous microemulsion at 80 °C with 30 wt% 0.75 M aqueous solution of the mixture of iron chlorides containing (Δ) 30, (\square) 33, and (\diamond) 36 wt% surfactant

In addition, Fig. 5 also shows that the magnetization values of the samples at 12.5 kOe decrease slightly with decreasing surfactant concentration. Because of the previously identified inverse dependency of particle size on surfactant concentration, it is easy to conclude that there is also a direct relationship between magnetization and particle size. This agrees with those reports indicating a decrease in magnetization of small particles (diameters smaller than *ca.* 15 nm) as particle size decreases [10, 15]. The magnetization values obtained in this study were similar to those previously reported by our group for nanoparticles precipitated in bicontinuous microemulsions [20] and also for those characteristics of magnetic particles precipitated in reverse microemulsions at relatively high temperatures (90 °C) [17, 32]. In contrast, they were higher than those reported for nanoparticles obtained by precipitation in reverse microemulsions at low temperatures (25–50 °C) [31, 32]. It is a known fact that magnetization of magnetic nanoparticles depends directly on their crystallinity and that an increase in precipitation temperature enhances the crystallinity of the iron oxide nanoparticles [17]. This could be the explanation for this behavior.

Conclusions

Precipitation reactions carried out in bicontinuous microemulsions at different surfactant concentrations allowed to obtain magnetic nanoparticles. X-ray diffraction analysis

demonstrated that the particles consisted of magnetite or a mixture of magnetite-maghemite. STEM measurements showed that the particles had average diameters between 6.9 and 7.9 nm and, a relatively narrow particle size distribution. VSM data suggested superparamagnetic behavior. Yields obtained in the precipitation reactions demonstrated the yield advantage of bicontinuous over reverse microemulsions in the synthesis of nanoscale particles. In addition, we found an inverse dependence of particle size on surfactant concentration, that probably was caused by a decrease in the channels diameter of the microemulsions as a response to the change in this variable.

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