

Preparation of colloidal Fe_3O_4 ultrafine particles in microemulsions

L. LIZ, M. A. LÓPEZ QUINTELA, J. MIRA*, J. RIVAS*

Departments of Chemical Physics and Applied Physics, University of Santiago de Compostela, E-15706 Santiago de Compostela, Spain

The preparation of magnetite particles is reported from the precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ with NH_4OH in several kinds of microemulsions: AOT/*n*-heptane/water microemulsions and a new non-toxic microemulsion system whose phase behaviour and structure has been recently studied. It is shown that both the droplet size and the presence of interactions in the dispersed phase greatly influence the final size of the obtained particles. In addition, the size of the particles can be increased by successive repetition of the reaction inside the droplets of the microemulsion.

1. Introduction

In our research group several kinds of magnetic particles [1, 2] have been synthesized by the method of chemical reaction in microemulsions. Traditionally, the microemulsion system AOT/*n*-heptane/water has been used for this reaction, but other systems have also been tested. In the present work, the preparation of magnetite particles was investigated from the precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ with NH_4OH in both the usual AOT/*n*-heptane/water microemulsions and a new non-toxic microemulsion system composed of labrasol (a mixture of glycerides and polyglycerides of fatty acids, acting as a non-ionic and non-toxic surfactant), isostearic plulol (polyglycerol isostearate, acting as a long-tail cosurfactant), ethyl oleate as an oil, and the aqueous phase. The phase behaviour and structure of this system has been recently studied [3]. It is shown that the bigger droplet size achieved in this system, as well as the presence of interactions in the dispersed phase, lead to the formation of bigger particles than those obtained in AOT-based microemulsions. Furthermore, the size of the particles can be increased by successive repetition of the reaction inside the droplets of the microemulsion.

2. Materials and methods

AOT, *n*-heptane, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and NH_4OH were high-purity products (Aldrich), but the ethyl oleate used (Aldrich) was commercial grade. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was Panreac high purity, and both labrasol and isostearic plulol were kindly supplied by Gattefossé. All the reactants were used without further purification. Water was always doubly distilled, deoxygenated water to avoid maximum oxidation of Fe^{2+} .

The general method for the preparation of particles in these media consists mainly in mixing two microemulsions with the same structure and composition,

except for the content of their aqueous phase: one of them contains the mixture of both metallic salts ($\text{Fe}^{2+}/\text{Fe}^{3+}$), and another the precipitating agent (NH_4OH). Several authors (e.g. [4, 5]) proposed a method based on the reaction of a mixture of a microemulsion and an aqueous solution, but in the present work this method was rejected because the mixture of these two kinds of media would lead to the destruction (or at least to big changes) in the microemulsion structure, destroying the pools where particle growth should take place for the control of the reaction.

Dynamic light scattering (DLS) measurements of droplet size in AOT microemulsions have been performed using an Ar^+ laser operating at 514.5 nm, a commercial goniometer ALV/SP81 and an ALV 5000 multiple tau digital correlator.

Small-angle neutron scattering (SANS) experiments for the investigation of the structure of labrasol/plulol/ethyl oleate/water microemulsions were carried out at the Jeep II reactor of the Institutt for energiteknikk at Kjeller (Norway). The radiation used had a wavelength of 0.55 nm, with a sample to detector distance of 1.56 m, and a cuvette optical path of 1 mm.

For analysis of dry samples the following techniques were used. X-ray diffraction analysis was performed using a powder diffractometer Philips PW1710 with CuK_α radiation. Magnetic measurements were made at room temperature using a vibrating sample magnetometer Digital Measurement Systems Inc., model VSM 1660.

Transmission electron microscopy (TEM) measurements were performed at Philips Laboratories, Eindhoven (The Netherlands) using a transmission electron microscope CM20/STEM, with punctual resolution of 0.27 nm and linear resolution of 0.14 nm. The same apparatus permits simultaneous sample analysis by means of X-ray detection by a dispersive energy analyses (EDAX 9900 Multichannel Analyser).

3. Results and discussion

The preparation of magnetite was performed by mixing two microemulsions, one containing mixture of salts of Fe(II) and Fe(III) in the stoichiometric molar ratio (1:2) in the water phase; and the other with NH_4OH in excess with respect to the iron salts.

One problem that can occur during the preparation is the oxidation of part of the Fe(II) before the addition of the precipitating agent, which would cause the loss of the stoichiometry, permitting the formation of other iron oxides. However, this problem is mostly overcome by the use of deoxygenated water for the solutions.

The identification of these oxides by X-ray diffraction analysis is also not easy, because the characteristic peaks of the different kinds of oxides occur in very close positions. Fig. 1a shows the X-ray diffraction data for a sample prepared in a microemulsion of AOT/*n*-heptane/water with $R = [\text{H}_2\text{O}]/[\text{AOT}] = 10$ and 15% aqueous phase, and using salt concentrations of Fe(II) and Fe(III) of 0.15 M and 0.3 M, respectively. As a reference, Fig. 1b shows the X-ray diffraction data for a sample of Fe_3O_4 obtained by reaction in water. It can be clearly observed that all the main peaks coincide in both cases, but the peaks for the particles obtained in the microemulsion are broader, due to their smaller size.

The preparation of samples for such measurements was performed by separation of the particles by centrifugation, followed by washing of the particles first with *n*-heptane to eliminate excess AOT, and finally with acetone to facilitate drying. Afterwards the com-

bustion of AOT that could be attached to the particles was performed, to avoid the possible interaction in the measurements to be performed. For that, the samples were introduced into a furnace at $\approx 400^\circ\text{C}$ for about 1 h.

With respect to the magnetic properties of the obtained particles, Fig. 2 shows the hysteresis loop corresponding to the described sample (after the separation process). Its superparamagnetic character ($H_c \approx 0$), can be seen which is due to the small size of the particles produced when prepared in the microdroplets of the microemulsions used (of the order of 4 nm, as measured by DLS).

Some influence of reactant concentration on the stability of the obtained suspension was also observed, which agrees with the observations of Palkar *et al.* [6] and Lee *et al.* [7]. When the reactant concentration is low enough, stable suspensions can exist for periods of weeks; on the other hand, for bigger concentrations it is observed that in a few hours, flocculation of the particles occurs, which promotes their sedimentation.

Transmission electron micrographs of two samples of magnetite with different reactant concentrations show this influence. The preparation of the samples was performed by redispersion of the flocculated sample in an ultrasonic bath for ≈ 15 min in heptane (dilution 1:100); ultrasound shaking for a further 15 min; dropping of a small droplet onto a carbon-coated grid, and finally drying under an infrared lamp.

Fig. 3a shows a micrograph obtained for a sample of Fe_3O_4 prepared under the same conditions as Fig. 1, but with defect of NH_4OH . The magnification used was 275 000 at 120 kV, which shows an average particle size of ≈ 4 nm. Fig. 3b shows X-ray dispersive analysis corresponding to the same sample; a clear peak corresponding to iron and a peak for sulphur

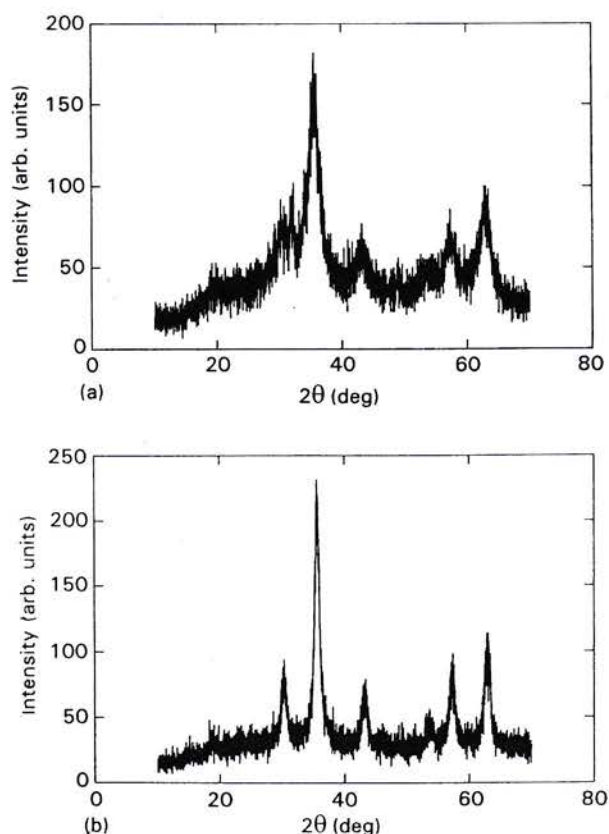


Figure 1 X-ray diffraction data for samples of Fe_3O_4 obtained by (a) reaction in a microemulsion of AOT/*n*-heptane/aqueous solution with $R = 10$; (b) reaction in aqueous solution.

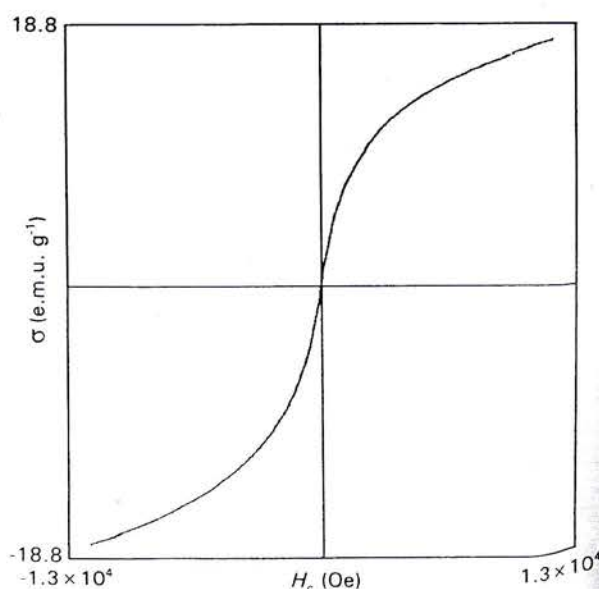


Figure 2 Hysteresis loop at room temperature for a sample of Fe_3O_4 obtained by reaction in a microemulsion of AOT/*n*-heptane/aqueous solution with $R = 10$, and further separation and combustion of the surfactant. The characteristic parameters are: $H_c \approx 1.5$ Oe; $\sigma = 19$ e.m.u. g^{-1} .

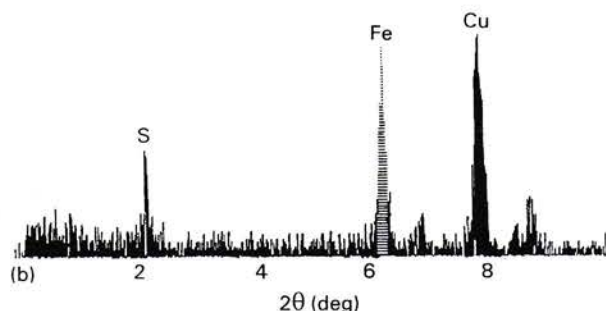
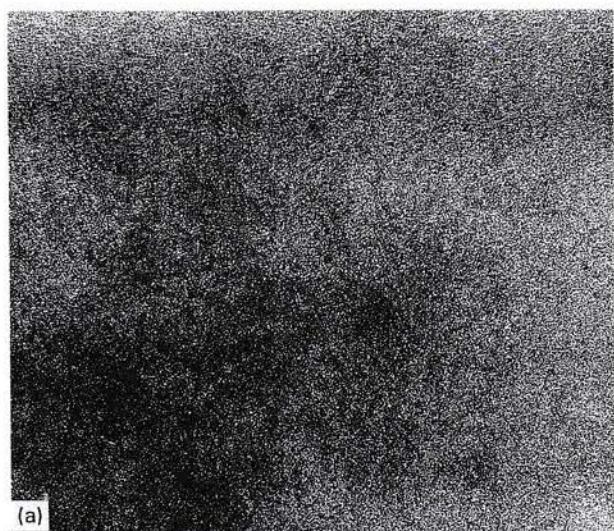


Figure 3 (a) Transmission electron micrograph for a sample of magnetite prepared in microemulsion with low reactant concentration. $\times 110\,000$. (b) X-ray dispersive analysis for the same sample as in (a).

(from the AOT molecules present) can be seen (the peak for copper is the one used as a reference). The presence of the peak for sulphur confirms the idea that AOT molecules remain attached around the particles, thus avoiding their irreversible aggregation or growth.

Fig. 4a shows an electron micrograph for a sample obtained under the same conditions as the last one, but with excess NH_4OH . The magnification used in this case was $\times 250\,000$. It can be observed that clear differences occur with respect to Fig. 3a. The presence of particle aggregates, new evidence of the flocculation process produced when increasing the size of the obtained particles, can be easily seen. The average size of the floccules is $\approx 12\text{ nm}$, indicating an aggregation of ≈ 10 particles per floccule. In this case, the X-ray dispersive analysis (Fig. 4b) shows an aspect similar to the previous one, with peaks corresponding to sulphur and sodium from the AOT salt, confirming that the particles are surrounded by a surfactant layer, which prevents their growth.

It should be noted that in this sample a slow sedimentation of the particles was observed, while the preceding one could exist as a stable suspension, showing the small effect of the concentration of reactants on the size of the particles, and its bigger effect on the reversible flocculation process, thus decreasing the colloidal stability of the suspensions of the prepared particles.

On the other hand, the variation of coercive field with the size of the particles can serve as a method for

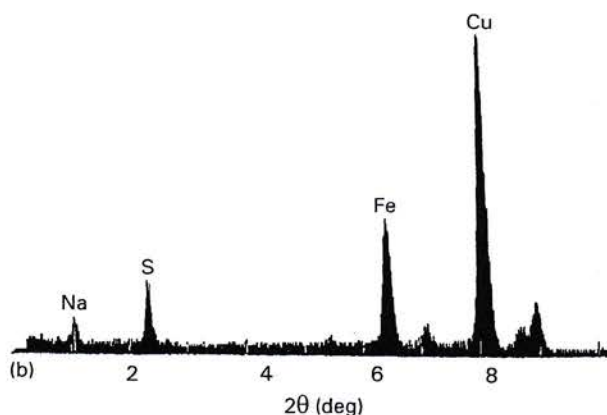
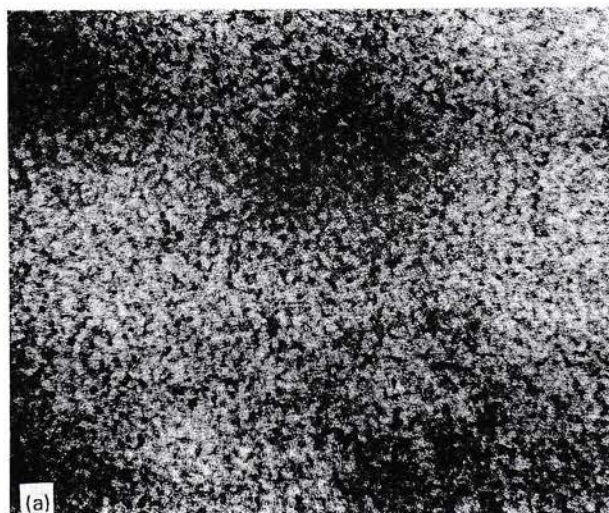


Figure 4 (a) Transmission electron micrograph for a sample of magnetite prepared in a microemulsion with high reactant concentration. $\times 100\,000$. (b) X-ray dispersive analysis for the same sample as in (a).

the confirmation of the formation mechanism of the particles in microemulsions. Fletcher and Robinson [8] have proposed a mechanism for the formation of particles in microemulsions, with the following steps: a first step of exchange of reactants between the microdroplets, followed by a nucleation step in which the formation of the particles is begun, and finally a growth step of the formed nuclei until the limiting reactant for the reaction is exhausted.

Following such a mechanism, it can be postulated that the lower the reactant concentration, as smaller are the particles obtained, as is confirmed by the results presented above. Furthermore, once a series of nuclei has been formed within the droplets of the microemulsion, the growth reaction on those nuclei will be favoured.

To check this mechanism, we performed an experiment consisting in the formation of magnetite particles via successive reactions in AOT-based microemulsions. For that, the following reactant concentrations in the respective aqueous solutions were used: $[\text{FeCl}_2] = 0.1\text{ M}$; $[\text{FeCl}_3] = 0.2\text{ M}$; $[\text{NH}_4\text{OH}] = 2\text{ M}$. After the mixture of both microemulsions and shaking to facilitate the reaction, part of the final microemulsion with particles (sample M1) was separated, with the subsequent addition to it of new micro-

emulsions with the same reactants concentration. In this way a sample of microdroplets with new particles (M2) is obtained. Finally, we performed the same procedure by the addition of new microemulsions to sample M2, obtaining a new sample (M3). According to previous results, the obtained particles should present an increasing order of sizes, because the addition of new reactants should promote the growth of the particles by reaction on the particles formed in the preceding steps. The hysteresis loops at room temperature for every sample (measured after the separation process) are shown in Figs 5–7.

It can be observed that M1 shows a superparamagnetic behaviour ($H_c \approx 0$), which is lost with successive additions of reactants, as can be seen from the increase in coercive field

$$H_c(M1) \approx 0 < H_c(M2) \approx 11 < H_c(M3) \approx 38 \text{ Oe} \quad (1)$$

This fact clearly shows the increase of particle size in the successive steps

$$r_{\text{particles}}(M1) < r_{\text{particles}}(M2) < r_{\text{particles}}(M3) \quad (2)$$

Finally, we tested the system labrasol/isostearic pluriol/ethyl oleate/aqueous solution as a reaction medium for the preparation of particles, for which we prepared Fe_3O_4 particles using this system, with a volume composition 13%W/52%O/35%S + C.

From the SANS measurements performed for the study of the structure of this system, the existence of microdomains of bigger size than those for the system AOT/*n*-heptane/aqueous solution, as well as the presence of much bigger interactions between domains, could be suggested. When comparing the hysteresis loop corresponding to a sample obtained in labrasol-based microemulsions with the preceding results, it can be observed that the magnetization is similar to

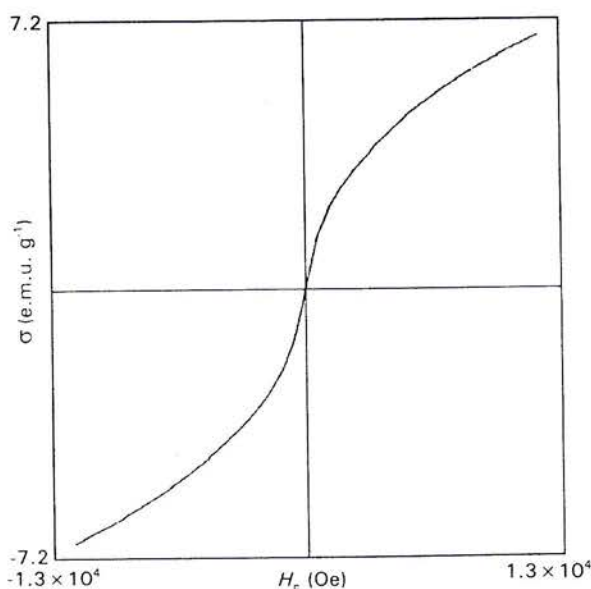


Figure 5 Hysteresis loop at room temperature for sample M1, obtained by reaction in a microemulsion of AOT/*n*-heptane/aqueous solution with $R = 10$, and further separation and combustion of the surfactant. $H_c \approx 0$; $\sigma = 7.2 \text{ e.m.u. g}^{-1}$, measured at $H = 1.3 \times 10^4 \text{ Oe}$.

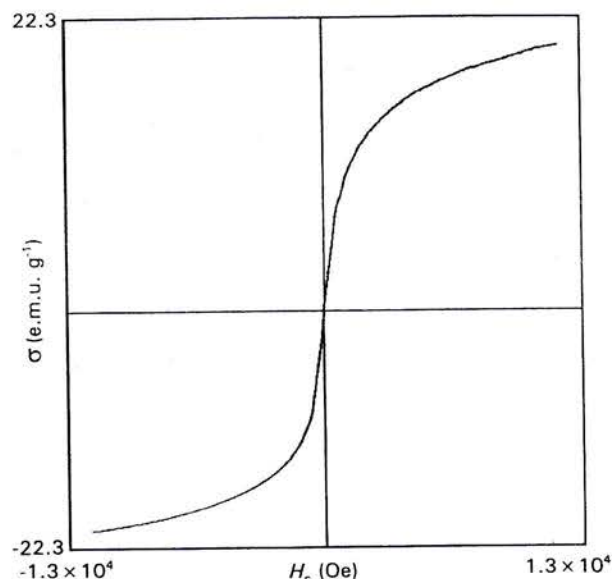


Figure 6 Hysteresis loop at room temperature for sample M2, formed from M1 by the addition of new microemulsions with reactants. $H_c = 11 \text{ Oe}$; $\sigma = 22 \text{ e.m.u. g}^{-1}$, measured at $1.3 \times 10^4 \text{ Oe}$.

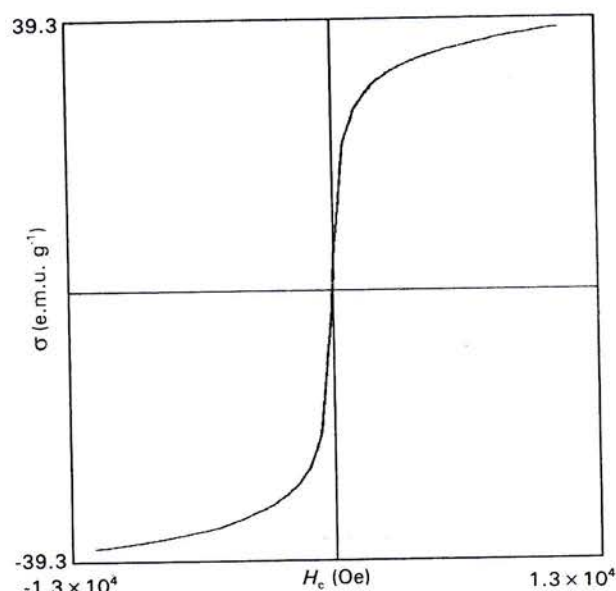


Figure 7 Hysteresis loop at room temperature for sample M3, obtained from M2 by the addition of new microemulsions with reactants. $H_c = 38 \text{ Oe}$; $\sigma = 39 \text{ e.m.u. g}^{-1}$, measured at $1.3 \times 10^4 \text{ Oe}$.

that obtained for sample M3 ($\sigma = 40 \text{ e.m.u. g}^{-1}$), though the coercive field is much smaller ($H_c = 3 \text{ Oe}$). This fact shows that the size of the particles is above the predicted maximum for a H_c versus r plot.

In order to obtain quantitative results on the dependence of the coercive field with the size of the particles, an estimation can be made of their size taking into account the results shown. The size of the particles of system M1 can be obtained from the size of the droplets composing the microemulsion, and from the TEM measurements shown

$$r_{\text{droplets}} \approx 4 \text{ nm} \approx r_{\text{particles}}(M1) \quad (3)$$

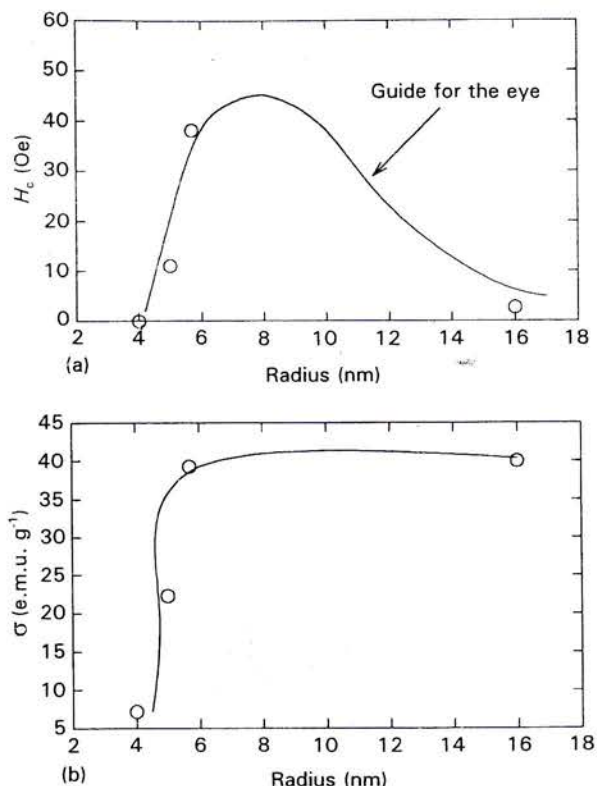


Figure 8 Plot showing the dependence of particle size on the magnetic properties of magnetite at room temperature. (a) Coercitive field, (b) magnetization measured in a magnetic field $H = 1.3 \times 10^4$ Oe.

In order to estimate the particle size for the system M2, it can be assumed that the reaction takes place exactly on the already formed particles, and because the reactant concentration is the same, the size will be given by

$$V_{\text{final particles}} = 4/3 \pi r_{M2}^3 = 2(4/3 \pi r_{M1}^3) \quad (4)$$

$$r_{M2} = 2^{1/3} r_{M1} \approx 5 \text{ nm} \quad (5)$$

In the same way we can obtain the radius of the particles of system M3

$$V_{\text{final particles}} = 4/3 \pi r_{M3}^3 = 4/3 \pi r_{M1}^3 + 4/3 \pi r_{M2}^3 \quad (6)$$

$$r_{M3} = (r_{M1}^3 + r_{M2}^3)^{1/3} \approx 5.7 \text{ nm} \quad (7)$$

Finally, the size of the particles obtained in labrasol-based microemulsions will coincide approximately with that of the microdroplets of this system [3], i.e.

$$r_{\text{labrasol}} \approx r_{\text{droplets}} \approx 15 \text{ nm} \quad (8)$$

Fig. 8 shows a plot of the variation observed for both the coercive field (Fig. 8a) and magnetization measured at 1.3×10^4 Oe (Fig. 8b) as a function of particle size. It can be observed in Fig. 8 that the data follows the general behaviour of the magnetic properties of small particles [9].

It can be seen that the maximum coercive field is found for particles with an approximate size of 10 nm, which is within the range of the typical values found to date ($5 \text{ nm} \leq R_{\text{max}} \leq 25 \text{ nm}$). One should also mention that the change of behaviour superparamagnetic $\rightleftharpoons$ ferromagnetic takes place in a very sharp way (here between 4 and 5 nm), thus confirming the results obtained by other authors for this change of behaviour [10].

4. Conclusions

It is concluded from the results that by using microemulsions it is possible not only to control the growth of the particles but also to vary the size by means of any of the following procedures:

- (i) by successive repetition of the reaction;
- (ii) by variation of the size of the microdroplets composing the microemulsion (for instance, by varying the ratio $[H_2O]/[AOT]$ in AOT-based microemulsions) – see for example [2];
- (iii) by choosing microemulsions with bigger domains (for instance, using labrasol-based microemulsions).

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