Preparation of Magnetic Fluids with Particles Obtained in Microemulsions

J. A. López-Pérez, M. A. López-Quintela, J. Mira, and J. Rivas, Senior Member, IEEE

Abstract—Ternary mixtures of organic solvent, surfactant, and aqueous solution forming a single phase are used for the synthesis of magnetic particles of magnetite. These particles, washed and covered with oleic acid, were stabilized in a carrier liquid, producing a magnetic fluid. X-ray diffraction, transmission electron microscopy, and magnetic measurements of the particles, and the prepared liquid are reported.

Index Terms—Ferrofluids, magnetic nanoparticles, microemulsion.

I. INTRODUCTION

MICROEMULSION is an isotropic and thermodynamically stable single phase formed by at least three components: two of them are inmiscible and a third, called surfactant, is amphiphilic [1], [2]. The presence of nanostructures in these systems has opened the possibility of the use of microemulsions for the synthesis of nanoparticles of different kinds of materials, since the nanostructures can be used as nanoreactors to achieve size control of the formed particles.

The basic procedure consists of the preparation of waterin-oil microemulsions composed of nanodroplets of a water solution of salts dispersed in an organic liquid. Then, a reaction of formation of the particles will follow. This can be achieved, for example, by introducing into the microemulsion a reducing or precipitating agent by external means or by mixing this microemulsion with another water-in-oil microemulsion containing this agent [3]–[7].

The most common magnetic fluids are formed from particles of magnetite or maghemite dispersed and stabilized in a liquid carrier. Coprecipitation methods are a typical procedure to obtain these ferrite particles. They consist of the mixture of two aqueous solutions, one of them containing metallic salts and the other containing an alkali hydroxide. The influence of different experimental parameters in the preparation procedure has already been reported [8]–[13].

In our case, the formation of magnetite particles was carried out by precipitation of iron salts passing ammonia gas through the microemulsion, producing an alkaline medium necessary for the synthesis of the magnetic particles.

J. A. López-Pérez and M. A. López-Quintela are with the Departamento de Química-Física, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain (e-mail: uscqfjlp@ds.cesga.es).

J. Mira and J. Rivas are with the Departamento de Física Aplicada, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain.

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The stabilization of ferrite particles in a carrier liquid to prepare a stable magnetic fluid is, basically, carried out in two ways. The first involves the use of surfactants covering the particles, producing a steric stabilization [14], [15]. The second, based on the electrostatic repulsion of the particles, involves the introduction of charged surfaces in the particles [16]. In this work, we employed a steric stabilization of the particles in an organic solvent. The size of the particles is another very important factor involved in the stability of magnetic fluids. Normally, particles of magnetite must have an upper limit of approximately 10 nm in diameter (in order to avoid precipitation due to gravitational forces) to get stable magnetic fluids [17].

The preparation of magnetite particles using microemulsions, reported by some authors [18]–[20], offers the advantage of producing smaller and more uniform particles than is found in other standard methods. Therefore, we have used this method to produce magnetic nanoparticles of magnetite with the appropriate sizes (lower than 10 nm) required for the preparation of magnetic fluids.

II. EXPERIMENTAL PROCEDURE

All chemicals used in this work were reagent grade and were used without further purification. $FeCl_3 \cdot 6H_2O$ and oleic acid were provided by Merck; $FeCl_2 \cdot 4H_2O$, Igepal CA-520 (pentaethyleneglycol monoisononylphenylether), and n-heptane 99% were provided by Aldrich; and kerosene was provided by Fluka.

Microemulsions containing a volume ratio 10/80/10 of aqueous solution/Igepal/n-heptane were prepared dissolving 40 ml of surfactant in 5 ml of n-heptane, and adding 5 ml of aqueous solution 2 M in Fe(III) and 1 M in Fe(II), and stirring until a transparent single phase is achieved, indicating that a stable microemulsion has been formed. The use of a big amount of Igepal is necessary for obtaining a single phase due to the high concentration of salts used in the aqueous solution.

 N_2 was bubbling through this microemulsion for 1 h to avoid the possible oxidation of the particles. Then, a solution of 30% NH₃ was placed in the way in which the N₂ gas flowed. The NH₃ carried into the microemulsion produces the alkaline medium needed for the precipitation of the particles. N₂ was bubbled until the appearance of a black precipitate indicated the end of the reaction. Then, 100 ml of acetone was added to the solution, and the precipitate was isolated by magnetic separation. Several washes of the precipitate with acetone, ethanol, and water were performed.

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The obtained particles were redispersed in a water alkaline solution of NH_3 , and 1.5 ml of oleic acid was added. After 1 h, the solution was acidified by addition of dilute HCl. Mechanical stirring was performed during all these processes. The precipitate obtained was washed with copious amounts of water, followed with acetone to remove the salts and the rest of the surfactant. The particles were dispersed again in the carrier liquid kerosene. The excess of acetone was eliminated under vacuum at room temperature. Finally, the magnetic liquid was centrifuged to eliminate large aggregates present in the fluid.

III. RESULTS

A. X-Ray Powder Diffraction Studies

Diffraction patterns of the particles obtained were recorded on a Philips diffractometer PW 1710 with Cu anode and a graphite monochromator, using two radiation CuK α with an intensity ratio ($\alpha 2/\alpha 1$) = 0.5 and wavelengths of 1.54060 and 1.54439 Å, respectively.

For these studies, a few milliliters of magnetic fluid were flocculated with acetone and centrifuged. The solid obtained was washed several times with acetone and dried in a desiccator. A diffraction pattern of the powder (Fig. 1) shows the presence of a magnetic phase (either Fe₃O₄ or γ -Fe₂O₃) and another nonmagnetic phase which may be associated to α -FeOOH. The presence of this nonmagnetic component is probably due to surface effects, because of the high surface/volume ratio of the nanoparticles.

To solve the overlapping peaks in the 2θ range, $28 < 2\theta < 46$, we used the profile fitting procedure of the PC-APD Software (version 3.5b) [21] based on a Marquardt nonlinear least squares algorithm. Fig. 2 shows the fitted function indicating the presence of five peaks, three of which clearly correspond to the fcc inverse spinel phase. The other two are unclear, but they could be attributed to an amorphous or poorly crystalline phase of α -FeOOH.

The average diameter particle size D_{hkl} was determined by the Debye–Scherrer formula (1) using the half maximum width β of X-ray diffraction lines

$$D_{hkl} = \frac{0.9\lambda}{\beta \sin \theta}.$$
 (1)

For the powder obtained from the magnetic fluid, we found $D_{311} = 64$ Å.

The lattice parameter for the sample obtained from the main diffraction line (311) is a = 8.368 Å. This value lies between the lattice parameter corresponding to magnetite a = 8.396 Å and that corresponding to maghemite a = 8.33 Å. The lattice parameter value obtained seems to indicate that partial oxidation of magnetite to maghemite can take place.

B. Magnetic Measurements

Room temperature magnetization measurements were carried out using a DMS 1660 vibrating sample magnetometer (VSM). Demagnetizing effects have been taken into account. Fig. 3 shows the typical superparamagnetic behavior observed in magnetic fluids, owing to the free rotations of the magnetic



Fig. 1. Diffraction patterns of powders obtained in microemulsions and of standard materials.



Fig. 2. Portion of the experimental diffraction pattern fitted to five peaks. (*) peaks corresponding to the fcc inverse spinel structure.

particles [17]. From the magnetization curve and using (2) and (3) proposed by Chantrell *et al.* [22], it is possible to estimate the mean particle diameter (D_v) and its standard deviation (σ) for a log-normal particle distribution size within the magnetic



Fig. 3. Magnetization curve versus magnetic field for the magnetic fluid. Inset: the initial magnetization.

fluid

$$D_{v} = \left[\frac{18 \text{ kT}}{\pi I'_{s}} \sqrt{\frac{\chi_{i}}{3\varepsilon I'_{s}} \frac{1}{H_{0}}}\right]^{1/3}$$
(2)
$$\sigma = \frac{1}{3} \left[\ln \left(\frac{3\chi_{i}}{\varepsilon I'_{s} \frac{1}{H_{0}}}\right) \right]^{1/2}.$$
(3)

Here, ε is the volume particle packing fraction, I'_s is the intensity of saturation magnetization of the bulk material, χ_i the initial susceptibility, and $1/H_0$ is the value of 1/H for I = 0. Applying these formula to our system, $D_v = 70$ Å and $\sigma = 0.37$ were obtained. This mean size agrees with the size obtained by XRD.

C. Electron Microscopy

Electron micrographs of the ferrofluid were made in a 200kV ultrahigh-resolution analytical electron microscope JEOL JEM-2010. For this purpose, an aliquot of magnetic fluid was dissolved in n-heptane followed by a deposition in a copper grid.

Fig. 4 shows an electron micrograph of the particles in the magnetic fluid. In Fig. 5 we can observe a good agreement of the log-normal particle size distribution assumed in (2) and (3), i.e., magnetic size, with that obtained from micrographs, i.e., physical size.

IV. CONCLUSIONS

In this work, we have explored the possibility of the use of particles synthesized by the microemulsion method for the preparation of magnetic fluids. The presence of nondesired, nonmagnetic phases could be explained by taking into account: 1) that inside the nanodroplets of the water solution in the microemulsion, there is a nonhomogeneous distribution of pH and dielectric constant (this aspect can have a great influence on the formation of the particles leading to amorphous phases) and 2) the high surface/volume ratio of the nanoparticles



Fig. 4. Electron micrograph of the particles in the magnetic fluids.



Fig. 5. Particle size distribution of particles in the magnetic fluid obtained from Transmission Electron Microscopy compared to the log-normal size distribution (solid line) calculated from fits to (2) and (3). Dashed line: fit of the physical size to a log-normal distribution (D = 6.9 nm and $\sigma = 0.31$).

obtained due to their small size favors the presence of quantitatively important amounts of non-well-crystallized phase at their surfaces.

It can be concluded that the microemulsion method allows a good control of the particles preventing their growth and providing particles small enough to get stable magnetic fluids.

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REFERENCES

- [1] Physics of Amphiphilic Micelles, Vesicles and Microemulsions, V. Degiorgio and M. Corti, Eds. Amsterdam: North Holland, 1985.
- [2] Micelles Solutions and Microemulsions: Structure, Dynamics and Statistical Thermodynamics, S. H. Chen and R. Rjagopal, Eds. New York: Springer, 1990.
- [3] J. B. Nagy and Claerbont, *Surfactants in Solution*, K. L. Mittal and D. O. Shah, Eds. New York: Plenum, 1991.
- [4] V. Pillai, P. Kumar, and D. O. Shah, "Magnetic properties of barium ferrite synthesized using a microemulsion mediated process," J. Magn. Magn. Mater., vol. 116, p. L299, 1992.
- [5] M. P. Pileni, J. Lisiecki, L. Motte, C. Petit, J. Cizeron, N. Moumen, and P. Lixon, "Synthesis 'in situ' of nanoparticles in reverse micelles," *Prog. Colloid Polym. Sci.*, vol. 93, pp. 1–9, 1993.

- [6] M. A. Lopez-Quintela and J. Rivas, "Chemical reactions in microemulsions: A powerful method to obtain ultrafine particles," J. Colloid Interface Sci., vol. 158, pp. 446–451, 1993.
- [7] P. Lianos and J. K. Thomas, "Cadmiun sulfide of small dimensions produced in inverted micelles," *Chem. Phys. Lett.*, vol. 125, p. 299, 1986.
- [8] T. Sato, T. Iijima, M. Seki, and N. Inagaki, "Magnetic properties of ultrafine ferrite particles," J. Magn. Magn. Mater., vol. 65, pp. 252–256, 1987.
- [9] R. Massart and V. Cabuil, "Synthese en milieu alcalin de magnetite colloidale: Controle du rendement et de la taille des particules," J. Chim. Phy., vol. 84, no. 7/8, pp. 967–973, 1987.
- [10] F. Tourinho, R. Franck, R. Massart, and R. Perzynski, "Synthesis and magnetic properties of manganese and cobalt ferrite ferrofluids," *Progr. Colloid Polym. Sci.*, vol. 79, pp. 128–134, 1989.
- [11] R. V. Upahyay, K. J. Davies, S. Wells, and S. W. Charles, "Preparation and characterization of ultrafine MnFe₂O₄ and Mn_XFe_{1-X}Fe₂O₄ spinel systems: I. Particles," *J. Magn. Magn. Mater.*, vol. 132, pp. 249–257, 1994.
- [12] A. E. Regazzoni and E. Matijevic, "Formation of uniform colloidal mixed cobalt-nickel ferrite particles," *Colloids Surfaces*, vol. 6, pp. 189-201, 1983.
- [13] T. Atarashi, T. Imai, and J. Shimoiizaka, "On the preparation of the colored water-based magnetic fluids (red, yellow, blue and black)," J. Magn. Magn. Mater., vol. 85, pp. 3-6, 1990.
- [14] S. E. Khalafalla and G. W. Reimers, "Preparation of dilution-stable aqueous magnetic fluids," *IEEE Trans. Magn.*, vol. 16, pp. 178–183, 1980.
- [15] A. Wooding, M. Kilner, and D. B. Lambrick, "Proteins and carbohydrates as alternative surfactants for the preparation of stable magnetic fluids," *IEEE Trans. Magn.*, vol. 24, pp. 1650–1652, 1988.
- [16] R. Massart, "Preparation of aqueous magnetic liquids in alkaline and acidic media," *IEEE Trans. Magn.*, vol. 17, pp. 1247–1248, 1981.
 [17] S. W. Charles and J. Popplewell, "Ferromagnetic liquids," in *Ferro-*
- [17] S. W. Charles and J. Popplewell, "Ferromagnetic liquids," in *Ferro-magnetic Materials*, Vol. 2, E. P. Wohlfarth, Ed. Amsterdam: North-Holland, 1980.
- [18] M. Gobe, K. Kon-no, K. Kyori, and A. Kitahara, "Preparation and characterization of monodisperse magnetite sols in W/O microemulsions," *J. Colloid Interface Sci.*, vol. 93, p. 293, 1983.
- [19] K. M. Lee, C. M. Sorensen, K. J. Klabunde, and G. C. Hadjipanayis, "Synthesis and characterization of stable colloidal Fe₃O₄ particles in water-in-oil microemulsions," *IEEE Trans. Magn.*, vol. 28, pp. 3180–3182, 1992.
- [20] L. Liz, M. A. López-Quintela, J. Mira, and J. Rivas, "Preparation of colloidal Fe₃O₄ ultrafine particles in microemulsions," *J. Mater. Sci.*, vol. 29, pp. 3797–3801, 1994.
- [21] PC-APD Software by Nederlandse Philips Bedrijven, IE Systems Division, The Netherlands.
- [22] R. W. Chantrell, J. Popplewell, and S. W. Charles, "Measurements of particle size distribution parameters in ferrofluids," *IEEE Trans. Magn.*, vol. 14. pp. 975–977, 1978.

J. A. López-Pérez was born in Pontevedra, Spain, in 1968. He received the B.S. and M.S. degrees in physical chemistry from the University of Santiago de Compostela in 1991 and 1992, respectively. He is currently working toward the Ph.D. degree.

M. A. López-Quintela was born in Ourense, Spain, in 1953. He received the B.S. and Ph.D. degrees in physical chemistry from the University of Santiago de Compostela in 1976 and 1980, respectively.

He was an Assistant Professor at the same university (1976–1980), a Fellow at DAAD Gottinga, Germany (1981), and a research worker at the University of Bielefeld, Germany (1981–1983). Since 1983, he has been a Professor of Chemistry at the University of Santiago de Compostela. He was an A. von Humboldt Fellow, Stuttgart, Germany (1990). His topics of research involve fields as colloids, ultrafine particles technology, and polymer science. He has more than 100 scientific publications.

J. Mira was born in Baio, Spain, in 1968. He received the B.S. and M.S. degrees in physics from the University of Santiago de Compostela in 1991 and 1992, respectively, and the Ph.D. and European Ph.D. degrees in physics from the same university in 1995. He received the most outstanding Ph.D. award of that university in 1996.

He is currently a Postdoctoral Fellow at the University of Santiago de Compostela. His topic of research involves the study of magnetic materials. He has published more than 30 scientific papers.

J. Rivas (SM'93) was born in Lugo, Spain, in 1947. He received the Ph.D. degree in physics from the University of Valladolid, Spain, in 1973.

He has been a research worker at the Max-Planck-Institüt, Stuttgart, Germany (1974–1975), and an Assistant Professor at the Universities of Valladolid and Murcia, Spain (1975–1981). Since 1981, he has been a Professor of Physics at the University of Santiago de Compostela, Spain. His topic of research involves the study of magnetic materials. He has more than 100 scientific publications.