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# Convenient preparation methods for magnetic colloids

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## Abstract

We present convenient laboratory-scale preparation methods for maghemite grafted with fatty acids as well as maghemite–silica core–shell colloids. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Maghemite; Oleic acid; Silica; Colloids; Ferrofluids; Magnetic colloids

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## 1. Introduction

Ferrofluids with a wide variety of magnetic materials and solvents are currently available. Oleic acid stabilized magnetite in an organic solvent, by now a classical system, is still widely used. Basically, two methods are known to graft magnetite with oleic acid: long-term grinding of bulk magnetite in the presence of pure surfactant and grafting of surfactants onto chemically precipitated magnetite in an alkaline aqueous solution. The latter method, described by Khalafalla and Reimers [1], is still frequently used to synthesize organophilic magnetite. Here we present a new and convenient laboratory-scale preparation method for this type of fatty acid stabilized ferrofluid. Unlike Khalafalla's method, heating is not required and the grafting step takes only a few minutes to complete.

A second type of colloid we investigated are the silica spheres with iron oxide cores [2,3]. They are prepared by hydrolyzing tetraethoxysilane (TES) which subsequently polymerizes as silica on the surface of the magnetite particles. Since this reaction is carried out in an alkaline ethanol/water mixture, the point of zero charge (PZC) of magnetite must be lowered before these particles can be dispersed in the reaction mixture. Originally, the PZC was lowered by precipitating a very thin silica layer from a metastable sodium silicate solution [2]. However, the PZC can also be lowered by adsorption of citric acid. This makes the tricky precipitation step obsolete, but still allows further silica growth using TES.

## 2. Experiments

### 2.1. Preparation of maghemite

Magnetite was precipitated by dissolving 2.08 g  $\text{FeCl}_2$  anh. and 5.22 g  $\text{FeCl}_3$  anh. in 380 ml

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demineralized water and adding 20 ml of 25%  $\text{NH}_3$  to this solution while stirring vigorously [4]. After sedimenting the precipitate with a permanent magnet, the supernatant was removed by decantation. 40 ml 2 M  $\text{HNO}_3$  was then added to the black sediment and the mixture was stirred for 5 min. The oxidation to maghemite was completed by adding 60 ml 0.35 M  $\text{Fe}(\text{NO}_3)_3$  to the mixture and stirring it at its boiling temperature for 1 h [4]. After sedimentation and washing with 2 M  $\text{HNO}_3$ , the reddish yellow sediment was dispersed by adding demineralized water. The resulting black dispersion, coded FF, contained 5.6 g of solid material per liter. The X-ray diffraction pattern of FF corresponds well to reference patterns for maghemite; other crystalline products could not be detected. The lattice spacing was calculated from the position of the 400-peak using Bragg's law. This yields a  $d$ -value of 8.35 Å, which equals the value for colloidal maghemite [5]. From the line broadening of the four most intense diffraction peaks, a particle diameter of 11.5 nm was calculated using Scherrer's equation [6]. The average diameter  $\langle d \rangle$  can be calculated from this number, knowing that the X-ray diameter equals  $\langle d^3 \rangle / \langle d^2 \rangle$  [6]. Using a binomial expansion one can find  $\langle d^n \rangle \cong \langle d \rangle^n [1 + 0.5 n (n - 1) \sigma^2]$ . With this approximation a mean particle diameter of 9.0 nm was calculated ( $\sigma = 0.4$ ).

### 3. Grafting maghemite with oleic acid

A typical experiment was conducted as follows. 2 ml FF was diluted by adding 50 ml demineralized water. The sol was flocculated by adding a few drops of 25%  $\text{NH}_3$ , and sedimented using a permanent magnet. After washing with 50 ml water, 100 ml water was added to the precipitate. Under mild mechanical stirring, 2 ml oleic acid was added. Within a few minutes, all magnetic material was transferred to the oil phase. The black oil droplets were separated from the colorless water phase and washed three times with 10 ml ethanol to remove water and excess surfactant. After drying under a gentle nitrogen stream the particles redispersed easily in cyclohexane. With a small modification, this procedure can also be applied for coating mag-

netic particles with other fatty acids, such as dodecanoic acid. Since fatty acids with saturated chains are solid at room temperature, the extraction must be performed above the melting temperature of the fatty acid (usually around 50°C). Repeated experiments showed that the amount of water has no noticeable effect on the final product; it merely facilitates stirring. Excessive washing with ethanol did not decrease the stability of the final product. The amount of oleic acid does not play a role as long as it is large; at least 13 ml oleic acid per gram maghemite was needed to extract and stabilize all particles.

The diffuse reflectance IR (DRIFT) spectrum of dried product shows peaks at 1428 and 1531  $\text{cm}^{-1}$ , which correspond to the symmetric and asymmetric stretching of carboxylate groups [7]. The presence of carboxylate groups shows that a condensation reaction has occurred between the hydroxylated maghemite surface and the fatty acid. The strong C=O stretching vibration ( $\sim 1750 \text{ cm}^{-1}$ ) is absent; apparently washing the precipitate removes all free oleic acid. Thermogravimetry was performed by heating some powder in a nitrogen stream from room temperature to 1200°C at a rate of 10°C  $\text{min}^{-1}$ . The surface area per oleic acid molecule was calculated from the weight loss at 600–750°C, and amounted to 0.28  $\text{nm}^2$ , which agrees with other works [8,9].

### 4. Silica deposition from a TES solution

The PZC of FF was lowered by adding a 0.01 M citric acid solution [4] to 45 ml FF until flocculation was visible. The precipitate was redispersed by increasing the pH to 7 with tetramethylammonium hydroxide. Of the resulting dispersion 1 ml was added to a mixture of 75 ml ethanol, 20 ml water and 5 ml 25%  $\text{NH}_3$ . While stirring, 0.1 ml TES was added, and after a day an additional amount of 0.2 ml TES was added. TEM micrographs show particles similar to those in earlier work [2,3]. The average particle radius is  $39.0 \pm 8.1 \text{ nm}$ . This radius is corrected for the shrinkage of approximately 5% of these particles in the electron microscope. Most of the silica particles contain clusters of magnetic particles; these clusters were also present

in the magnetic silica spheres prepared before [2]. An estimate of the number of magnetic particles per silica sphere was made using

$$C = \frac{V_{\text{Fe}_2\text{O}_3, \text{total}} / \langle V_{\text{Fe}_2\text{O}_3, \text{grain}} \rangle}{V_{\text{m-SiO}_2, \text{total}} / \langle V_{\text{m-SiO}_2, \text{grain}} \rangle} = \frac{V_{\text{Fe}_2\text{O}_3, \text{total}}}{kV_{\text{TES}} + V_{\text{Fe}_2\text{O}_3, \text{total}}} \left( \frac{\langle d_{\text{m-SiO}_2}^3 \rangle}{\langle d_{\text{Fe}_2\text{O}_3}^3 \rangle} \right), \quad (1)$$

where  $d$  and  $V$  indicate diameter and volume, respectively, and  $k \equiv V_{\text{SiO}_2}^{\text{mol}} / V_{\text{TES}}^{\text{mol}} = 0.1422$ . The lower density of TES-hydrolyzed silica is taken into account in the calculation of  $k$ .  $V_{\text{Fe}_2\text{O}_3}$  was calculated from the total mass of  $\gamma\text{-Fe}_2\text{O}_3$  and its density. The subscript ‘m-SiO<sub>2</sub>’ denotes a magnetic silica particle. Taking  $\langle d^3 \rangle \approx \langle d \rangle^3 (1 + 3\sigma^2)$ , an average cluster size of 13 is found. This is roughly twice as large as the estimated cluster size in Ref. [2]. Clusters of this size are also thought to be present in other ferrofluids [10].

How silica is linked to the surface of magnetic particles is not resolved, but it is probably anchored on spots where no citric acid is adsorbed. Since gold particles stabilized with citric acid are ‘vitroreophobic’ [11], attachment of silica to citric acid itself seems unlikely.

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### References

- [1] S.E. Khalafalla, G.W. Reimers, IEEE Trans. Magn. MAG-16 (1980) 178.
- [2] A.P. Philipse, M.P.B. van Bruggen, C. Pathmamanoharan, Langmuir 10 (1994) 92.
- [3] L.N. Donselaar, Silica-magnetite colloids and magnetic fluids – Synthesis and particle interaction, Ph.D. Thesis, Utrecht University, 1998.
- [4] A. Bee, R. Massart, J. Magn. Magn. Mater. 122 (1990) 1.
- [5] J.P. Jolivet, E. Tronc, J. Colloid Interface Sci. 125 (1988) 688.
- [6] V. Cabuil, R. Perzynski, in: B. Berkovski (Ed.), Magnetic Fluids and Applications Handbook, Begell House, New York, 1996.
- [7] A.D. Buckland, C.H. Rochester, S.A. Topham, J. Chem. Soc. Faraday Trans. I 76 (1980) 302.
- [8] C. Rocchiccioli-Deltcheff, R. Franck, V. Cabuil, R. Massart, J. Chem. Res. (S) (1987) 126.
- [9] A. Wooding, M. Kilner, D.B. Lambrick, J. Colloid Interface Sci. 144 (1) (1991) 236.
- [10] V.M. Buzmakov, A.F. Pshenichnikov, J. Colloid Interface Sci. 182 (1996) 63.
- [11] L.M. Liz-Marzán, M. Giersig, P. Mulvaney, Langmuir 12 (1996) 4329.