SAXS study of chain-like structures formed by magnetic nanoparticles

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Abstract

Nanoparticles consisting of a magnetic core (γ-Fe$_2$O$_3$) and an organic shell were prepared by thermal decomposition of an iron carbonyl complex in the presence of oleic acid. The nanoparticles were then dispersed in cyclohexane to form a stable ferrofluid. These dispersions were investigated by means of Small Angle Scattering of X-rays (SAXS) and the data were interpreted according to a "pearl necklace" model, opportunely modified to account for the core-shell structure of the magnetic nanoparticles. The results of the fittings show that nearly monodisperse spherical particles with a radius of the magnetic core of about 3.9 nm and a shell of about 2 nm were obtained. These nanoparticles self-assemble in chain-like structures, even in the absence of an applied magnetic field.
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1. Introduction

During recent years a great effort has been devoted to the synthesis and the characterization of magnetic nanoparticles, and to their behavior when they are dispersed in a liquid carrier to form a ferrofluid, i.e. a stable colloidal suspension of magnetic nanoparticles dispersed in a liquid [1]. Since their first appearance [2], magnetic fluids have been studied especially because of their potential large number of applications in different fields such as magnetism, optics, rheology, biophysics, medicine, and thermodynamics [3].

Many synthetic methodologies have been used to prepare magnetic nanoparticles. Among them, the use of microemulsions as nanoreactors [4,5], the synthesis from supersaturated solutions [6] and the thermal decomposition of suitable precursors are probably the most prominent [7,8]. In particular, this last technique has been proven as a powerful tool to obtain nearly monodisperse particles, with a size control as small as 1 nm [9–12]. The possibility to achieve a fine size control through the systematic adjustment of the reaction parameters, such as time, temperature, and concentration of both the precursors and the stabilizing surfactants, is of fundamental importance: in fact, the peculiar properties often exhibited by the nanomaterials strongly depend on their size and polydispersity.

Magnetic nanoparticles show super-paramagnetic behavior, i.e. each single particle behaves as a single magnetic domain. In surfactant-stabilized ferrofluids, the stability of the suspension is due to the steric hindrance of the surfactant molecules that counteracts the dipolar attraction between the magnetic cores, taking to the complete dispersion of the particles with randomly oriented magnetic moments (see Fig. 1, left side). When an external magnetic field is applied, the magnetic moments align along the direction of the field, eventually forming chain-like aggregates in which the dipoles are oriented in a head-to-tail configuration [13,14]. Several experimental and theoretical studies have been performed in order to explain the formation of these aggregates; nevertheless, this process is still not completely understood [15–17]. Moreover, the self-assembly of magnetic nanoparticles into head-to-tail linear aggregates has been predicted even in the absence of an applied magnetic field. (Fig. 1, right side) [13,14,18,19].

In this paper we report a SAXS (Small Angle Scattering of X-rays) study of magnetic fluids obtained through the dispersion of γ-Fe$_2$O$_3$ nanoparticles in cyclohexane at different concentrations. The nearly monodisperse magnetic nanoparticles were obtained through the thermal decomposition of the precursor in the presence of oleic acid acting as templating and stabilizing

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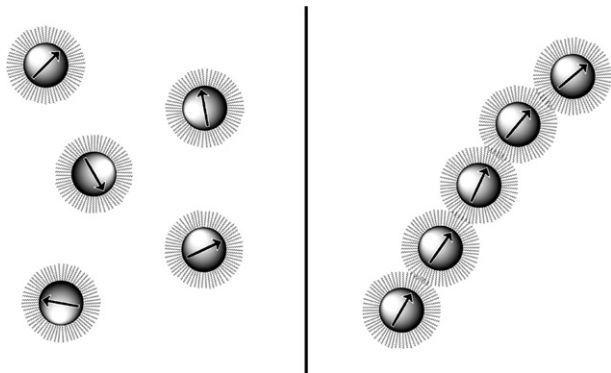*E-mail address:* baglioni@csgi.unifi.it (P. Baglioni).

Fig. 1. Sketch of the hypothetical self-assembly of magnetic nanoparticles in a ferrofluid: fully dispersed nanoparticles with randomly oriented magnetic moments (on the left) and chain-like assembly of particles through the alignment of the magnetic moments (on the right).

agent. Thanks to their size distribution, these systems are good models for the study of the fundamental processes taking place inside ferrofluids.

2. Experimental section

2.1. Reagents

Iron pentacarbonyl $Fe(CO)_5$, octyl ether (purity grade, 99%), oleic acid (99%), trimethylamine N-oxide (98%), and cyclohexane (>99.9%) were obtained from Aldrich (Milan, Italy). Ethyl alcohol (>99.8%) was obtained from Fluka (Milan, Italy). All the reagents were used as supplied, except for trimethylamine N-oxide that was dehydrated immediately before using it.

2.2. Synthesis of magnetic nanoparticles

Maghemite (γ-Fe_2O_3) nanoparticles were prepared according to the method previously described by Hyeon et al. [8] Oleic acid (13 g, 46 mmol) was added to 100 ml of octyl ether and the solution heated up to 100 °C. Iron pentacarbonyl (3 g, 15.31 mmol) was then added and the resulting mixture kept refluxing for 1 h. At the end of this step, the black dispersion of nanoparticles was cooled down to room temperature and purged with argon. Still under an argon atmosphere, the previously dehydrated trimethylamine N-oxide (3.455 g, 46 mmol) was added and the dispersion was heated to 130 °C and kept to this temperature for 2 h. The argon flux was then removed and the temperature was slowly increased up to the boiling point. After refluxing for 1 h, the dispersion was cooled to room temperature. Maghemite nanoparticles were collected by adding ethyl alcohol and centrifuging the destabilized dispersion. The dried precipitate was then dissolved in cyclohexane to obtain a magnetic fluid with a concentration of 1.375 mg/ml, as obtained by thermo-gravimetric analysis. Aliquots of this magnetic fluid were then diluted in cyclohexane in 1:40, 1:100, and 1:200 ratios. Hereinafter, these samples will be referred to simply as 1/1, 1/40, 1/100, and 1/200.

2.3. TEM

Transmission electron microscopy investigations have been carried out using a Philips EM201C apparatus operating at 80 kV. Samples were prepared by placing a 20 µl drop of the magnetic fluid onto a carbon-coated copper grid. In order to make the evaluation of the particle size easier, the most diluted fluid (1/200) was used. During the depositions the TEM grid was placed on a filter paper and dried overnight in a nitrogen atmosphere. To obtain a good statistic, the diameters of more than three hundred nanoparticles were measured.

2.4. SAXS

SAXS measurements were carried out with a HECUS SWAX-camera (Kratky) equipped with a position-sensitive detector (OED 50 M) containing 1024 channels of width 54 µm. CuK_α radiation of wavelength 1.542 Å was provided by a Seifert ID-3003 X-ray generator (sealed-tube type), operating at a maximum power of 2 kW. A 10-µm thick nickel filter was used to remove the CuK_β radiation. The sample-to-detector distance was 281 mm. The volume between the sample and the detector was kept under vacuum ($P<1$ mBar) during the measurements to minimize scattering from the air. The Kratky camera was calibrated using silver behenate, which is known to have a well-defined lamellar structure ($d=58.48$ Å) [20]. Scattering curves were monitored in a Q-range from 0.01 to 0.3 Å^{-1}. The liquid samples were filled into 1 mm quartz capillary using a syringe. Measurement was done at 25 °C. The temperature was controlled by a Peltier element, with an accuracy of ±0.1 °C. All scattering curves (slit smeared data) were corrected for the empty cell contribution (quartz capillary). The data were slit desmeared by linear method [21].

3. Results and discussion

Maghemite nanoparticles were successfully prepared by first generating monodisperse nanoparticles through the templating effect of oleic acid and then oxidizing them to iron oxide. Two representative TEM micrographs are shown in Fig. 2. The particles are spherical and are arranged in clusters: in fact, during the deposition and the drying of the magnetic fluid onto the carbon film, the evaporation of the cyclohexane lowers the stabilization effect of the oleic acid grafted on the surface of the particles, taking to the formation of clusters because of the dipole–dipole attraction between the magnetic cores. Fig. 3 shows the size distribution as obtained by measuring the diameter of more than three hundred particles. The full line represents the best fit according to a lognormal size distribution, corresponding to a mean diameter of 6.9 nm and a width of the distribution of 0.186. It is important to note that the electronic contrast is almost entirely at the level of the magnetic cores, while the hydrophobic tails result virtually not detectable. As a consequence, the diameter reported in Fig. 3 accounts only for the iron cores and not for the total size of the particles. A rough estimation of the surfactant shell thickness could be extracted from the separation of the particles that is about 2–3 nm. This