Control of the synthesis of magnetic fluids by relaxometry and magnetometry

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Abstract

The aim of this work is the development of a new and quick method for the quality control of magnetic fluids. The method is based on the analysis of proton nuclear magnetic relaxation dispersion curves which give the evolution of the relaxation rate of the solvent protons as a function of the magnetic field. These profiles provide physical information about the magnetic nanocrystals namely the average radius $r$ and the specific magnetization $M_s$. This technique has been used to establish the conditions for reproducible and size controlled synthesis of dextran coated superparamagnetic nanomagnets.

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1. Introduction

Superparamagnetic colloids are used in medicine as contrast agents for magnetic resonance imaging (MRI). They could also be used as therapeutic agents in the context of hyperthermia [1]. Evaluating and understanding the performances of these magnetic nanomaterials as contrast agent for MRI was made possible by establishing a theory of the magnetic interactions of superparamagnetic compounds with water protons [2]. Thanks to this theory, the main characteristics of the nuclear magnetic relaxation dispersion (NMRD) profiles (i.e. the field dependence of the proton relaxation rate) are well understood and information about the superparamagnetic crystals are provided, namely, their average radius $r$, their specific magnetization $M_s$, their Néel relaxation time $\tau_N$ and the magnitude of the anisotropy energy $E_a$. The aim of this work is the development of a new and fast method for the quality control of these materials based on proton relaxometry.

2. Material and methods

Colloidal dextran-coated nanomagnets are synthesized by coprecipitation of a solution of ferric and ferrous ions with an alkali in the presence of dextran. The reaction is carried out in a mini mixing chamber which ensures an accurate control of the mixing conditions as for example the temperature ($70^\circ$C) and the flow rate of the reactants. Mössbauer investigations (results not shown) show that the magnetic core is a crystal of maghemite. The NMRD profiles were recorded on a fast field cycling relaxometer (Stelar, Mede, Italy) measuring the longitudinal relaxation rate over a field range extending from 0.24 mT to 0.47 T. Additional measurements of the solvent relaxation rates were performed on Minispec PC 20 (0.47 T), MQ-60 (1.4 T) and spectrometer AMX 300 (7 T) (Bruker, Karlsruhe, Germany). Iron concentration was measured.
3. Results and discussion

Performed in identical conditions, the syntheses are perfectly reproducible. For example, Fig. 1 shows the NMRD curves of different syntheses carried out in the same experimental conditions: \([\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 0.67\), \([\text{Fe}] = 6 \text{ mM}\), \([\text{Dextran}] = 0.11 \text{ mM}\). The mean size and the mean specific magnetization measured by relaxometry are, respectively, \(r_{\text{relaxo}} = (4.15 \pm 0.05) \text{ nm}\) and \(M_s \text{ relaxo} = (2.7 \pm 0.3) \times 10^5 \text{ A m}^{-1}\).

The corresponding values obtained by magnetometry are \(r_{\text{magneto}} = (3.1 \pm 0.1) \text{ nm}\) for the crystal radius and \(M_s \text{ magneto} = (3.7 \pm 0.1) \times 10^5 \text{ A m}^{-1}\) for the magnetization. The magnetometric mean radius is about 30% lower than the relaxometric one. This difference can be explained by a distribution of the crystal sizes which influences the mean size obtained by various methods.

<table>
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<th>([\text{Fe}^{2+}]/[\text{Fe}^{3+}])</th>
<th>(r_{\text{relaxo}}) (nm)</th>
<th>(M_s \text{ relaxo} \times 10^5 \text{ A m}^{-1})</th>
<th>(r_{\text{magneto}}) (nm)</th>
<th>(M_s \text{ magneto} \times 10^5 \text{ A m}^{-1})</th>
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Fig. 2. Evolution of the NMRD curves with the \([\text{Fe}^{2+}]/[\text{Fe}^{3+}]\) ratio.

This size dispersion is also responsible of the lower relaxometric specific magnetization as compared to the magnetometric one.

As for the synthesis of noncoated magnetite [4], the size of the nanomagnets can be controlled by the ratio \([\text{Fe}^{2+}]/[\text{Fe}^{3+}]\) (Table 1 and Fig. 2). Indeed nanomagnet radius and specific magnetization both increase with this ratio. Dynamic light scattering measurements of the hydrodynamic sizes confirm this evolution. A widening of the size dispersion can be at the origin of the increasing discrepancy between the mean sizes and the specific magnetization obtained by relaxometry and magnetometry when the \([\text{Fe}^{2+}]/[\text{Fe}^{3+}]\) ratio is enhanced.

In conclusion, NMRD profiles and magnetometry curves are very well suited to control the reproducibility of the nanomagnets syntheses. Additionally, this work points out that the \([\text{Fe}^{2+}]/[\text{Fe}^{3+}]\) ratio influences the crystal size.

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References


