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 τ_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°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

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by inductively coupled plasma (JOBIN YVON JY 70+, Longjumeau, France). The fitting of the NMRD profiles by the appropriate theory [2] allows for the determination of the following parameters:

The average radius (*r*): the inflection point appearing at high magnetic field corresponds to the condition $\omega_1\tau_D \sim 1$ with $\tau_D = r^2/D$ and, where r, D and ω_1 are, respectively, the average radius of the superparamagnetic crystals, the relative diffusion coefficient and the proton Larmor pulsation.

The specific magnetization (M_s): M_s can be obtained from the equation $M_s \sim C(R_{max}/\tau_D)^{1/2}$, where C is a constant and R_{max} the maximal relaxation rate.

The values of the average radius and of the specific magnetization were also obtained from the fitting of the magnetometric curves with the Langevin equation (magnetometer VSM-NUVO. MOLSPIN, Newcastle Upon Tyne, UK).

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: $[Fe^{2+}]/[Fe^{3+}] = 0.67$, $[Fe] = 6$ mM, $[Dextran] = 0.11$ mM. The mean size and the mean specific magnetization measured by relaxometry are, respectively, $r_{relaxo} = (4.15\pm0.05)$ nm and $M_{s\ relaxo} = (2.7\pm0.3)10^5$ A m^{-1}.

The corresponding values obtained by magnetometry are $r_{magneto} = (3.1\pm0.1)$ nm for the crystal radius and $M_{s\ magneto} = (3.7\pm0.1)10^5$ 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
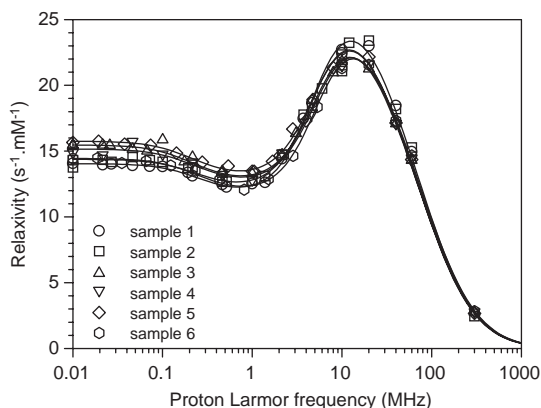

Fig. 1. Reproducibility of the NMRD profile of different samples (relaxivity is the water proton relaxation rate increase induced by a concentration of 1 mM of iron in the solution).

Table 1
Evolution of the crystal radius and of the magnetization obtained by relaxometry and magnetometry with the $[Fe^{2+}]/[Fe^{3+}]$ ratio

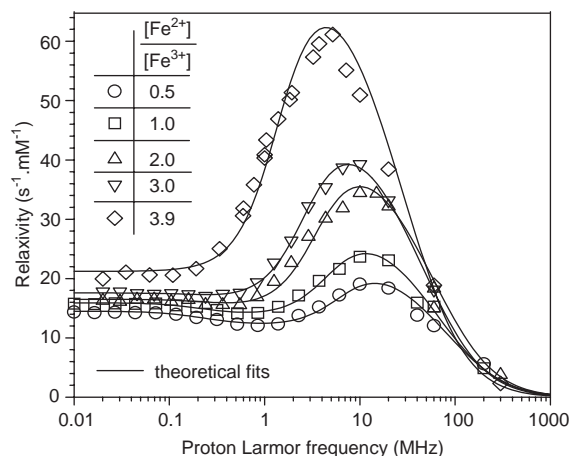| $[Fe^{2+}]/[Fe^{3+}]$	r_{relaxo} (nm)	$M_{s\ relaxo}$ ($\times 10^5$ A m^{-1})	$r_{magneto}$ (nm)	$M_{s\ magneto}$ ($\times 10^5$ A m^{-1})
0.5	3.8	2.7	3.1	3.7
1.0	4.2	2.7	2.9	3.9
2.0	4.5	3.1	3.5	4.4
3.0	5.1	2.9	3.6	4.5
3.9	6.4	2.8	4.3	4.7

Fig. 2. Evolution of the NMRD curves with the $[Fe^{2+}]/[Fe^{3+}]$ ratio.

[3]. 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 $[Fe^{2+}]/[Fe^{3+}]$ (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 $[Fe^{2+}]/[Fe^{3+}]$ 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 $[Fe^{2+}]/[Fe^{3+}]$ ratio influences the crystal size.

Acknowledgements

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