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Magnetic hyperthermia of laponite based ferrofluid

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ABSTRACT

Magnetic Hyperthermia experiments have been performed on different concentrations of magnetic iron oxide nanoparticles immobilized on nano-clay disks. The specific absorption rate (SAR) was measured in AC field amplitudes H_0 from 7 to 30 kA/m. At low field amplitudes, SAR followed the usual H_0^2 law whereas for higher field amplitudes a linear dependence was found for the higher concentrations. Measurements at three different field amplitudes were also performed for a wide range of iron oxide concentrations in order to determine the effect of the Brownian relaxation time to SAR. A field dependent maximum was observed and for fields up to 20 kA/m the power dissipation losses were well explained according to theoretical predictions.

1. Introduction

Magnetic fluids are stable colloidal suspensions of magnetic nanoparticles dispersed in solvents. The long term colloidal stability of these magnetic fluids is usually insured by coating the nanoparticles with appropriate non magnetic materials in order to prevent agglomeration. A promising application of magnetic fluids in the field of nanomedicine [1] is hyperthermia. Hyperthermia is induced by irradiation of the magnetic fluids with an alternating electromagnetic field (AC) and absorption of the energy of the AC field. The energy is dissipated to heat by several physical mechanisms [2,18]. The power dissipation depends on several parameters like the size of the particles, the frequency of the AC field, the field amplitude, the coating, the nature and shape of the particles and so on. A measure of the power dissipation is the specific power absorption rate (SAR), measured in watts per gram of magnetic material [3,18,25].

Induction heating can be used in hyperthermia treatment of cancer since malignant cells are more sensitive to heat than normal tissue [2]. Magnetic fluids are introduced to the tumor tissue and then irradiated with an AC field until the temperature rises to 42–46 °C. The irradiation time of a treatment must not exceed half an hour and the concentration of the iron oxide in the magnetic fluid must not be toxic. So it is necessary to increase the values of SAR with as low concentration of magnetic material as possible. The SAR value of the magnetic fluid cannot be raised simply by raising the frequency and amplitude of the AC field since the inductive heating of the healthy tissue will be too high [14]. Secondly the blood flow of the tissue will disperse the magnetic fluid and/or change its concentration. Finally the solvent and the coatings must be bio-compatible and the magnetic material must have low toxicity. The most suitable magnetic fluid for hyperthermia consists of aqueous dispersions of coated iron oxide nanoparticles due to the low toxicity of iron oxide. Even so, SAR values depend strongly on the core size and on the core size distribution of the nanoparticles.

In this paper we investigate the dependence of SAR versus the applied field amplitude in three different concentrations of aqueous magnetic fluids of γ-Fe_2O_3 nanoparticles on laponite disks produced by our group [4], up to field amplitude of 30 kA/m. Laponite disks consist a very suitable base to investigate the influence of viscosity on SAR since laponite solutions vary in viscosity for more than three orders of magnitude, depending on their concentration. We performed an extensive study of the SAR influence versus the viscosity of laponite – γ-Fe_2O_3 solutions that range from ferrofluids to ferrogels in three selected AC field amplitudes namely 28, 24, 20 kA/m in order to study the influence of the Brown relaxation time as power dissipation mechanism.

2. Experimental

Different concentrations of γ-Fe_2O_3 nanoparticles on laponite nanodisks were synthesized according to previously published work [4]. For the first experiment three concentrations were used, S1, S2 and S3 with 9.09 mg iron oxide/ml ferrofluid, 15.16 mg/ml

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and 17.58 mg/ml respectively. For the second experiment the concentrations of the samples was ranging from 6 to 20.5 mg/ml. Briefly, the synthesis is based on the alkaline precipitation of Fe^{2+} cations in the presence of exfoliated laponite nanodisks under air atmosphere. Firstly, by the addition of concentrated NH_3, $Fe(OH)_2$ species were formed which slowly oxidized by atmospheric oxygen according to the following reactions:

$$Fe^{2+} + 2OH^- + xH_2O \rightarrow Fe(OH)_2 \cdot xH_2O$$

$$2Fe(OH)_2 \cdot xH_2O + O_2 \xrightarrow{\text{dehydration,condensation}} \gamma{-}Fe_2O_3 + (x+1)H_2O + 2OH^-$$

The composite iron oxide/laponite nanostructured material have 50% wt. magnetic loading based on Fe_2O_3 phase. The magnetic particles reveal near spherical shape and around 12 nm mean diameter according to the TEM images and deposit on the surface of laponite nanodisks (Laponite RD) which have 25–35 diameter and 1 nm thickness. [4]

Magnetic measurements were performed on liquid samples S1, S2, S3 at room temperature and with varing external magnetic field 0–6 T.

Magnetic hyperthermia experiments were performed using a water cooled induction coil of four loops. The power generator was operating at a fixed frequency of 150 kHz and delivered a maximum output power of 10 kW. The samples were measured in various AC fields H_0 ranging from 7 to 30 kA/m. All the samples were sonicated and placed to a heat sink (22 °C) before measurements. The samples were measured in a thermal isolated glass tube and the temperature was recorded with a Vitek probe (thermistor).

The specific absorption power (SAR), i.e. the power absorption in watts per gram of Fe, is given by the following formula [6]:

$$SAR = \frac{W}{m_{Fe}} = \frac{\Delta Q}{\Delta t m_{Fe}} = c\frac{m_f}{m_{Fe}}\frac{\Delta T}{\Delta t}, \quad \text{in} W/g_{Fe}. \tag{1}$$

where c is the specific heat capacity of the ferrofluids, calculated as the mass weighted mean value of magnetite and water, m_f is the mass of the ferrofluids, and m_{Fe} is the mass of the iron in the ferrofluids. Measurements of the heating rate ($\Delta T/\Delta t$) were performed for the various ferrofluids. The SAR values are calculated by Eq. (1), using the initial slopes ($\Delta T/\Delta t$) of the temperature–time curves.

Viscosities measurements were carried out with a Viscolite 700 viscometer.

3. Results and discussion

In Fig. 1 we present the SAR values for the three samples (S1, S2, S3) versus the AC field amplitude. The hyperthermia measurements were performed for AC field amplitudes ranging from 7 to 30 kA/m with 1 kA/m step. Each sample was measured three times and the values of Fig. 1 are the mean values of the results.

The dependence of SAR to the AC field amplitude follows the [5]:

$$SAR = \mu_0 \pi \chi_0 f {H_0}^2 \frac{2\pi f \tau}{1+(2\pi f \tau)^2}. \tag{2}$$

according to the Linear Response Theory (LRT), where μ_0 is the permeability of free space, χ_0 is the susceptibility, f the frequency and τ the effective relaxation time.

The effective relaxation time τ, depends on the Brownian (τ_B) and Neel processes (τ_N) according to [5]:

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_N}$$

$$\tau_B = \frac{3\eta V_H}{kT}$$

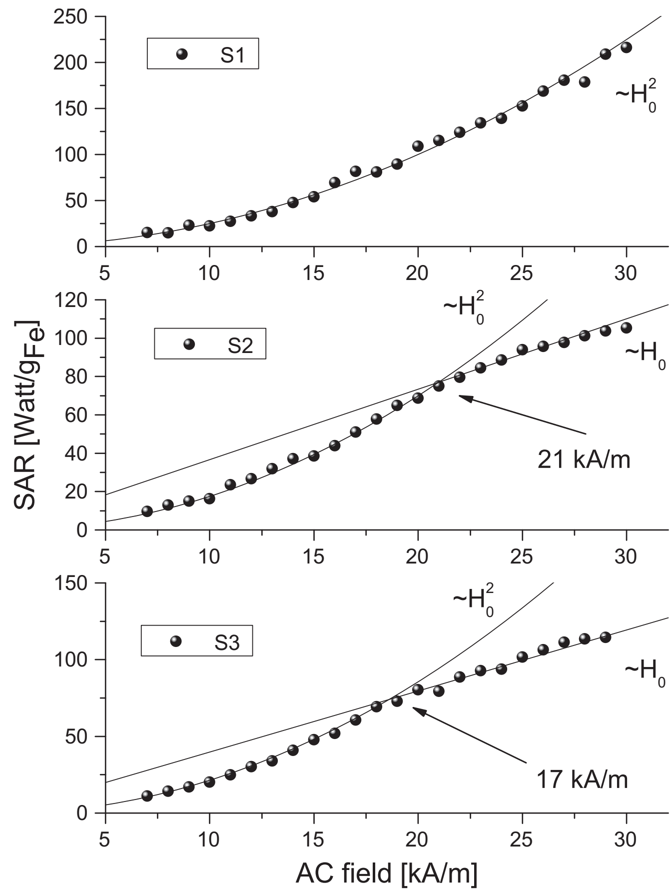

Fig. 1. SAR values versus AC field amplitude for the samples S1, S2, S3. The frequency of the AC field is fixed at 150 kHz. The lines are the best fit to the data.

$$\tau_N \sim \frac{\exp(KV/kT)}{\tau_0}. \tag{3}$$

where, $\tau_0 \sim 10^{-9}$ s [9,12,13], η the viscosity, $V = 4\pi R^3/3$ the magnetic volume of the particle with radius R, $V_H = (1+\delta/R)^3 V$ the hydrodynamic volume of the particle with δ the thickness of a sorbed surfactant layer [11,17], T the temperature, k the Boltzman constant.

For sample S1 we observe a field dependency according to Eq. (2) for the whole range of AC fields. On the other hand, for the samples S2 and S3 the dependence of SAR with the amplitude of the AC is more complicated. At low fields the dependence is proportional to ${H_0}^2$ as expected from the theory (Eq. (2) [2,5,20,23]) however, at high field amplitudes, i.e. greater than 17 kA/m, for the sample S3, and greater than 21 kA/m, for the sample S2, the relation between SAR and ${H_0}^2$ diverges from linearity and we observe a transition point. The fact that above a given magnetic field, the SAR deviates from the square law has been observed experimentally in several works and is expected theoretically [2,5,20,24]. In Ref. [24], a linear relation between SAR and the AC field amplitude is also observed for high fields. In order to validate the above field values, at which Eq. (2) is not valid, we conducted magnetization measurements versus field for S1, S2, S3 concentrations in liquid samples up to 6 T field (Fig. 2). All the samples show very small remnant magnetization and neglectable coercivity (insert of Fig. 2). Eq. (2) is expected to be valid only when $\mu_0 H M_s V/k_b T < 1$ [9,19,20]. We calculated this condition for all the samples and derived $\mu_0 H < 57$ mT for sample S1, $\mu_0 H < 25$ mT for sample S2 and $\mu_0 H < 15$ mT for sample S3. The field value for