Investigation of magnetic and hyperthermic effects in ferrofluids with PEG biocompatible surfactant

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Abstract. The aim of this study was to investigate the influence of poly(ethylene glycol) surface-active coating on the magnetic and thermal properties of biocompatible magnetic liquids. The magnetization of the samples was measured using VSM method. From the magnetization data the distribution function of the size of the magnetite particles was determined. Heating ability of the PEG-stabilized magnetic fluids was determined by the calorimetric measurement of the heating rate at 750 kHz frequency and 0.52 kA/m field to evaluate the possibilities of their successful use in hyperthermia treatment. The experimental data of the heating rate were compared with theoretical expression derived by Rosensweig.

1. Introduction

Biocompatible magnetic liquids (MF) are stable colloidal suspensions of nanosized magnetic particles covered with biocompatible molecules and dispersed in a physiological carrier liquid. The biocompatibility of magnetic liquids is determined by both the core ferrite material and the coatings. A good candidate for the core ferrite material is magnetite, Fe₃O₄, which has been proved to be biocompatible [1] and can be conveniently synthesized using chemical coprecipitation reactions [2]. The coating of ferrite particles with long chain polymer molecules serves as protective layer that prevents agglomeration of the particles and minimizes the direct exposure of the ferrite surface to the biological environment. Nanoparticles have a large surface area/volume ratio and they tend to agglomerate and adsorb plasma proteins. When the nanoparticles agglomerate, or are covered with adsorbed plasma proteins, they are quickly cleared by macrophages before they can reach target cells. One possible approach to increase the circulation time of nanoparticles in the blood stream is to modify the particles with poly(ethylene glycol) (PEG) films to disperse them and minimize or eliminate protein adsorption. Surfaces covered with PEG are biocompatible, i.e. nonimmunogenic, nonantigenic and protein-resistant. This is because PEG has uncharged hydrophilic residues, and a very high surface mobility leading to high steric exclusion [3].

The heating effect of a ferrofluid is a result of absorbing energy from the alternating magnetic field and converting it into heat by means of three mechanisms: (1) eddy currents losses; (2) hysteresis losses during reversal of magnetization; and (3) relaxation losses accompanying demagnetization. The eddy currents losses are negligible since a ferrofluid has very low electrical conductivity. Thermal energy from a hysteresis loss depends on the type of the remagnetization process. Over ceratin portions the magnetization curve is irreversible and energy of the magnetic
field is dissipated into the medium with each flux-reversal cycle in the form of heat. It is known that hysteresis losses strongly depend on the size of magnetic particles [4]. The third mechanism of the heating effect is associated with a lag between the field and magnetization due to the relaxation nature of the magnetization process in ferrofluid.

The purpose of this study was to assess the thermal characteristics of aqueous-based magnetic liquid with additional PEG coating and to compare them with theoretical predictions.

2. Materials and Methods
The synthesis of our aqueous magnetic fluid was based on coprecipitation of Fe$^{2+}$ and Fe$^{3+}$ salts by NH$_4$OH at 60 °C. Sodium oleate (C$_{17}$H$_{33}$COONa) as a first surfactant (10 wt % with respect to Fe$_3$O$_4$) was used for the modification of prepared magnetic particles to prevent their agglomeration. To improve stability and increase the circulation half time of the particles, the polyethylene glycol (PEG) as a second surfactant was added to the system magnetite-oleate and stirred over 3 hrs. The sample denoted as MF Oleate+PEG was prepared using PEG from Sigma (1000 g/mol) with the ratio of magnetite to PEG equal to 40 mg/1 mg. The magnetic liquid labeled as MF-Oleate contained only oleate surfactant layer and was also studied for comparison.

The purpose of this study was to assess the thermal characteristics of PEG-based ferrofluids and to compare them with theoretical predictions.

Magnetic measurements of the samples were carried out with the aid of a vibrating sample magnetometer (VSM) at the temperature of 300K, within the range of variation of external magnetic field induction, $B = 1$ T.

The heating system consisted of sine wave power oscillator, an induction coil (length 78 mm) and an oscilloscope (Philips). A glass tube containing the sample was thermally isolated by a layer of material from the solenoid winding supported on a plastic sleeve. The temperature of the sample was monitored using a thermocouple (LT Lutron TM-917). The measuring setup permitted a continuous recording of the temperature inside the sample upon its heating by the external alternate magnetic field in the range of 500–2000 A/m and frequency of 750 kHz.

![Figure 1](image.png)

Figure 1. The curves of original magnetization (left graph), and particle size distribution function (right graph) obtained from VSM data for MF Oleate and MF Oleate+PEG magnetic fluids.

3. Results and discussions
The magnetization curves obtained for MF Oleate and MF Oleate+PEG ferrofluids by means of VSM are shown in Figure 1 (left graph). The original magnetization can be expressed as a superposition of the Langevin functions [5]

$$M_L = M_s \int_0^\infty L(\xi)f(x)dx,$$

(1)
Table 1. Magnetic parameters of MF-Oleate/PEG samples obtained by means of VSM method from the processing of magnetization curves.

| Sample            | $M_s$ (A/m) | $\chi_i$ | $\phi_V$ (%) | $D_0$ (nm) | $S$    | $D_m$ (nm) | $\sigma$ (nm) |
|-------------------|-------------|----------|--------------|------------|--------|------------|--------------|
| MF Oleate+PEG     | 1213        | 0.0598   | 0.273        | 8.72       | 0.499  | 9.88       | 5.3          |
| MF Oleate         | 2331        | 0.0754   | 0.522        | 8.92       | 0.374  | 9.57       | 3.7          |

where $M_s$ is the saturation magnetization, $L(\xi) = \coth(\xi) - 1/\xi$ is the Langevin function with $\xi = \mu_0 m H/ k_B T$, $m$ is the magnetic moment of the particle, $\mu_0$ is the magnetic permeability of vacuum, $H$ is the magnetic field strength, $k_B$ is Boltzmann constant, and $T$ is the absolute temperature.

For the description of the dispersion of magnetite particles the lognormal distribution is usually used [5]

$$f(x) = \frac{1}{x S \sqrt{2\pi}} \exp\left(-\frac{\ln^2(x/D_0)}{2S^2}\right),$$

where $x$ is the magnetic particle diameter, and $D_0$ and $S$ are the parameters of the distribution function which can be extracted from the magnetization curve. On the basis of these parameters, the mean diameter, $D_m$, and the standard deviation, $\sigma$, of particle size can be determined as well as the saturation magnetization, $M_s$, and initial susceptibility, $\chi_i$ [5]. From the saturation magnetization the volume fraction of magnetite phase can be determined from the expression $\phi_V = M_s / M_d$, where $M_d = 466$ kA m$^{-1}$ is the spontaneous magnetization of magnetite grains.

The particle size functions of the MF Oleate and MF Oleate+PG magnetic liquids extracted from VSM measurements are shown in Figure 1 (right graph). The other magnetic parameters of the studied magnetic fluids studied obtained form the analysis of magnetization curve are presented in Table 1.

Figure 2. Temperature vs time for the sample MF Oleate (left graph) and MF Oleate+PEG (right graph) for different values of an alternating magnetic field and frequency $f = 750$ kHz.

Figure 2 shows the plot of temperature of the ferrofluids studied as a function of time for different values of the amplitude of the alternate magnetic field and the frequency $f = 750$ kHz. As it is seen from the figure, for small heating times the temperature increase $\Delta T$ is roughly linear. From the initial slope the heating rate $(\Delta T/\Delta t)_{t=0}$ can be calculated [6]. Fig. 3 presents the heating rate for the ferrofluids studied as a function of the magnetic field intensity.
According to Rosensweig [7] for magnetic fluids with superparamagnetic particles, the temperature rise $\Delta T$ of the magnetic fluid during the period of the heating $\Delta t$ is given by:

$$\frac{\Delta T}{\Delta t} = \frac{1}{C_p \rho} \int_0^\infty \pi \mu_0 \chi_0 H_0^2 \frac{2\pi f \tau}{1 + (2\pi f \tau)^2} f(x) dx,$$

where $C_p$ is the sample specific heat capacity, $\rho$ is the mass density of the sample, and $\chi_0 = 3\chi_i L(\xi)/\xi$. There are two distinct mechanisms by which the magnetization of a ferrofluid may relax after removing the applied magnetic field: the Brown and the Néel one, characterized by appropriate relaxation times:

$$\tau_B = \frac{3\eta V_h}{k_B T}, \quad \tau_N = \tau_0 \exp \frac{K_a V_M}{k_B T}, \quad \tau = \frac{\tau_B \tau_N}{\tau_B + \tau_N},$$

where $\eta$ is the viscosity of the carrier liquid, $V_h$ is the hydrodynamic volume larger than particle volume $V_M$ by the size of the surfactant shell, and $K_a$ is the anisotropy constant of the magnetic material. When both mechanisms act simultaneously the mechanism with the shortest relaxation time is dominant.

Solid lines on Fig 3 show predictions of expression (3). The calculations were done assuming the heat capacity of both samples to be similar to that of water, i.e. $4180 \text{ J kg}^{-1} \text{ K}^{-1}$. The measured values of mass density and shear viscosity were equal to $1096 \text{ kg m}^{-3}$ and $1.91 \times 10^{-3} \text{ Pa s}$ and $1015 \text{ kg m}^{-3}$ and $2.68 \times 10^{-3} \text{ Pa s}$ for MF Oleate and MF Oleate+PEG, respectively. Surfactant layer was set at 2 nm and $\tau_0$ at $10^{-9} \text{ s}$. As it is seen from the figure the theoretical curves, obtained without any adjustable parameters, show excellent agreement with experimental data.

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