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Acoustic properties of PEG biocompatible magnetic fluid under perpendicular magnetic field

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Abstract

Biocompatible magnetic fluids of nanoparticles coated with polyethylene glycol show stable acoustic properties up to a field intensity of $H = 70$ kA/m. In higher fields, the ultrasonic wave absorption coefficient significantly increases and is strongly dependent on temperature, magnetic field intensity, magnetic field sweep rate and time of exposure to magnetic field. Adjustment of these parameters leads to control of the acoustic properties of the magnetic ferrofluids. © 2005 Elsevier B.V. All rights reserved.

Keywords: Magnetic fluid; Ultrasonic absorption; Polyethylene glycol; Acoustic properties

1. Introduction

Water-based magnetic fluids have been used for diagnostics and therapy in medical applications, in pharmacy and in biosensors. In order to be used for biomedical purposes, magnetic particles must be pre-coated with substances that ensure their stability, biodegradability and non-toxicity in a physiological medium. After pre-coating, biological effectors can be absorbed at the particle surface to produce biocompatible materials with specific biomedical applications [1].

The use of biocompatible magnetic fluids in living organisms needs a thorough recognition of

their properties under the influence of magnetic field. The changes in the magnetic fluid structure affect the acoustic properties of the fluid such as the propagation velocity and absorption coefficient of ultrasonic wave, so the acoustic spectroscopy can be used to investigate magnetic fluid. One of the methods of studying changes in ferrofluid structure, under the influence of the external magnetic field, is the method based on the measurement of changes in ultrasonic wave absorption $\Delta\alpha$. The paper presents acoustic properties of a biocompatible magnetic fluid whose particles are coated with polyethylene glycol (PEG) layer. The experimental data are expected to bring information on the effect of the second layer of the biocompatible surfactant on the stability of the magnetic fluid.

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2. Experimental details

The magnetic fluids used in this work were obtained by chemical precipitation. The subjects of the study were two water-based biocompatible fluids MF, whose magnetite particles (Fe_3O_4) were coated with oleate sodium and magnetic fluid MF-PEG, which was coated with oleate sodium and PEG (bilayer of surfactants). Table 1 presents the properties of the samples of the biocompatible magnetic fluids.

The ferrofluids studied were placed in a thermostated ($\pm 0.1^\circ\text{C}$) closed measuring cell kept at a constant distance of 1.49 cm between two piezoelectric transducers. The changes in the ultrasonic wave attenuation were measured by the pulse method based on measurement of intensity of the ultrasonic pulse passed through or reflected by the medium studied [2]. The frequency of the ultrasonic wave was 3.6 MHz and the direction of the magnetic field was perpendicular to the direction of ultrasound wave propagation ($H \perp k$).

3. Results and discussion

Figs. 1 and 2 present changes in the ultrasound wave absorption coefficient $\Delta\alpha$ as a function of the magnetic field intensity at different temperatures for magnetic fluid MF and MF-PEG, respectively. For slowly increasing magnetic field up to 70 kA/m, small changes in the ultrasonic wave absorption were observed. The fluids MF and MF-PEG have highly stable acoustic properties in this range. With increasing intensity of the field, then is a significant increase in the ultrasound absorption coefficient, which is a result of aggregation of magnetic particles. The aggregation of particles into chain-like clusters, induced by an external

magnetic field, leads to an increase in the ferrofluid viscosity [3] and thus also in the acoustic absorption coefficient. According to the Stokes–Kirchhoff

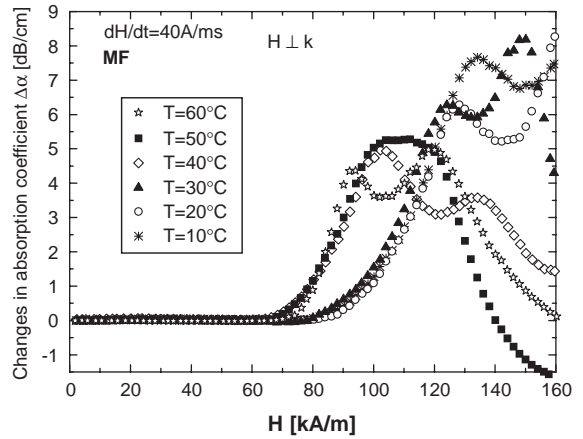


Fig. 1. Changes in ultrasonic wave absorption coefficient for magnetic fluid MF with single layer of surfactant as a function of the magnetic field for different temperatures.

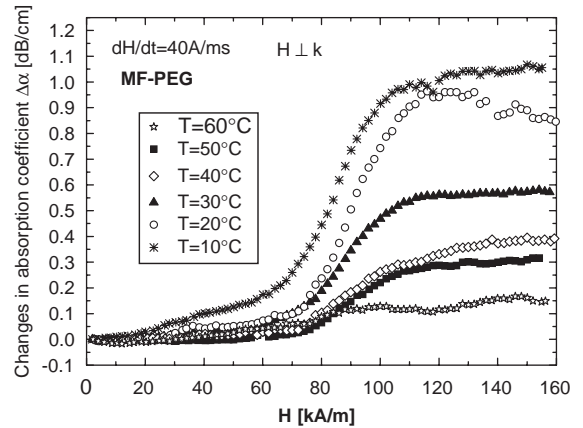


Fig. 2. Changes in ultrasonic wave absorption coefficient for magnetic fluid MF-PEG with two layers of surfactant as a function of the magnetic field for different temperatures.

Table 1
Characteristic properties of the tested magnetic fluids

Name	Particles	Carrier liquid	Surfactant	Saturation magnetization (Gauss)	Average diameter of particles (nm)	Density (g/cm^3)
MF	Fe_3O_4	Water	Oleate sodium	95	9.35	1.084
MF-PEG	Fe_3O_4	Water	Oleate sodium + polyethylene glycol (PEG)	65.2	9.04	1.065

equation, increasing the viscosity should increase the absorption coefficient of the ultrasonic wave. The maxima of $\Delta\alpha$ in Fig. 1 appear as a result of the additional resonance absorption of the ultrasonic wave by the spherical clusters (the energy of the wave is transferred to the translational and rotational degree of freedom of the clusters) [4]. Application of a second surfactant layer (PEG) causes better stability of magnetic fluid structures. The changes in ultrasonic wave attenuation for MF-PEG (Fig. 2) were a few times smaller than for MF. An addition of the second layer of surfactant modifies the particles surface properties, and the attractive van der Waal's forces are reduced, which prevents aggregation of particles even in a strong magnetic field.

The changes in absorption strongly depend on temperature. With increasing temperature of the MF-PEG ferrofluid the changes in the ultrasound absorption by the ferrofluid decrease, as illustrated in Fig. 3 showing $\Delta\alpha$ as a function of temperature for different intensities of the magnetic field. Smaller changes in the acoustic absorption are interpreted as due to a smaller increase in viscosity, caused by less aggregation of the particles. An increase in temperature causes an increase in the thermal energy of the particles, which hinders the aggregation of particles. At high

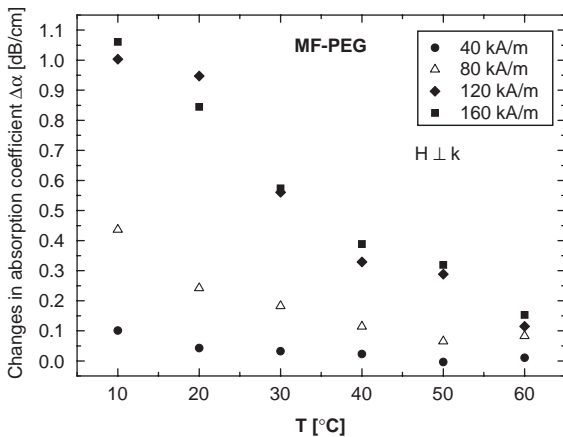


Fig. 3. Changes in ultrasonic wave absorption coefficient as a function of temperature for different magnetic fields. The magnetic field and wave propagation are in perpendicular direction.

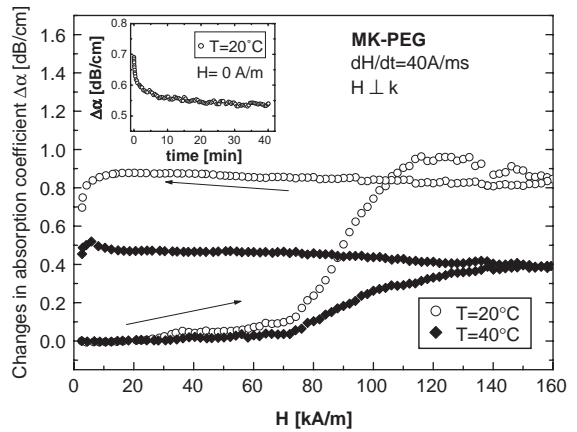


Fig. 4. Changes in ultrasonic wave absorption coefficient as a function of the magnetic field intensity for different temperatures. The increase and decrease of magnetic field was performed at a constant rate dH/dt of 40 A/ms. The inset shows the changes in ultrasonic wave absorption coefficient as a function of time when the magnetic field returned to a value H of 0 A/m.

temperatures, the ferromagnetic fluid MF-PEG shows a greater structural stability.

Fig. 4 presents the changes in ultrasonic wave absorption coefficient as a function of the magnetic field intensity when the magnetic field increases and decreases at the same rate $dH/dt = 40$ A/ms. When the magnetic field intensity decreases, the character of the absorption coefficient changes is significantly different. The ultrasound wave absorption coefficient remains at a constant level up to a field of about $H = 10$ kA/m, and with slightly decreases a further, field intensity decrease. These results imply that the process of restructuring of the ferrofluid has ended at the maximum value of the magnetic field reached at a low sweep rate (40 A/ms). The new state of equilibrium is stable and the clusters break up only when the field decreases to $H = 10$ kA/m. After removal of the magnetic field, the ultrasound wave absorption coefficient decreases, but not to the initial value during 40 min, as shown in the inset of Fig. 4. Probably the magnetic fluid needs a very long time relaxation to reach the initial equilibrium state. The absorption coefficient shows a hysteresis in the ferrofluid with an additional biocompatible layer similarly as has been reported earlier for a

ferromagnetic fluid whose particles are coated with only one layer of surfactant [2].

Figs. 5 and 6 present the ultrasonic wave absorption coefficient changes in the MF and MF-PEG ferrofluids subjected to a magnetic field for 30 min and after the removal of the magnetic field. The ultrasonic wave absorption coefficient was measured as a function of time in the following conditions: when the magnetic field increased in 1 min to a certain value at different

sweep rates (80 kA/m at a sweep rate $dH/dt = 1.3 \text{ kA/ms}$, 160 kA/m at a sweep rate $dH/dt = 2.7 \text{ kA/ms}$), when a constant value of the field was maintained for 30 min and then when the field decreased in 1 min, at the same sweep rate as that of the increase and after the field disappearance (60 min), see the scheme in inset of Fig. 5. The area between the broken lines corresponds to the range of time in which the fluid was subjected to a maximum value of the magnetic field.

For the ferrofluid MF (Fig. 5) with a single surfactant layer, the changes in $\Delta\alpha$ were significant. In the first minute during the magnetic field increase, the $\Delta\alpha$ changes were small, but later the ultrasonic wave absorption coefficient significantly increased. This phenomenon was explained by progressing aggregation of magnetic particles in clusters [5]—it is known that the fluid structure needs some time to reach a new state of equilibrium [6]. With increasing magnetic field intensity, $\Delta\alpha$ increase because of the viscosity of the ferrofluid increases. The maxima in $\Delta\alpha$ are a result of an additional resonance absorption of the ultrasonic wave by the spherical clusters formed in the fluid [4]. After the magnetic field removal, the wave absorption coefficient drastically decreases but not to the initial value.

For MF-PEG ferrofluid (Fig. 6), at a very high magnetic field sweep rate, also the structural changes in the ferrofluid are not complete immediately after the magnetic field has reached a final value, but the equilibrium state is approached in a certain time [7], therefore, the absorption coefficient reaches a maximum value after about 12 min. At the sweep rate of $dH/dt = 40 \text{ A/ms}$ (Fig. 4) a new equilibrium state has been reached immediately after the last change of the field, which confirms that the process of reaching a new equilibrium state by a ferrofluid subject to an external magnetic field depends on the sweep rate of this field [6]. On decreasing the external magnetic field intensity, the wave absorption coefficient rapidly increases and then drastically decreases but not to the initial value. Further changes in the absorption coefficient in time are small and the value of $\Delta\alpha$ stabilises at about 0.3 dB/cm. A comparison of Figs. 4 and 6 shows

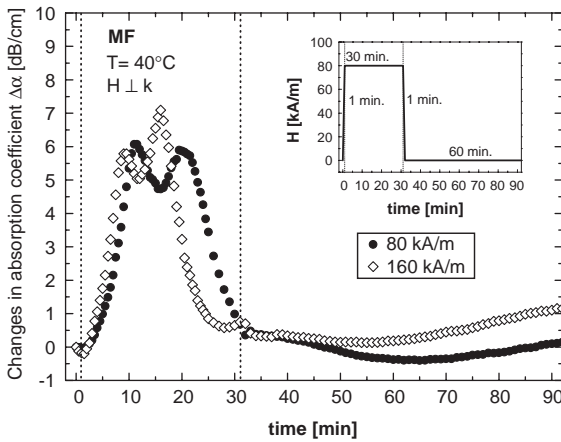


Fig. 5. Changes in ultrasonic wave absorption coefficient as a function of time in ferrofluid MF. The magnetic field changes are as shown in insets.

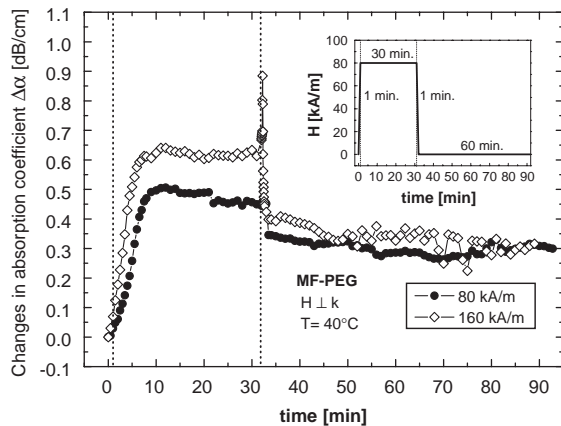


Fig. 6. The changes in ultrasonic wave absorption coefficient as a function of time in ferrofluid MF-PEG when the magnetic field changes as shown in the inset.

that an increase in the absorption coefficient produced by a very fast increase (Fig. 6— $dH/dt = 2.7 \text{ kA/ms}$) reaches about 0.6 dB/cm and is higher than at a low sweep rate of 0.45 dB/cm (Fig. 4— $dH/dt = 40 \text{ A/ms}$). The changes in the ultrasonic wave absorption coefficient are greater, as a result of a deeper structural changes in the ferrofluid [8], which proves that the sweep rate of the magnetic field has a great effect on the acoustic properties of a biocompatible magnetic fluid, not only with a single [9] but also with a double layer of surfactants.

The application of the second biological coating brings about further changes in the ferromagnetic fluid properties. Fig. 6 clearly shows that time dependence of the changes in the absorption coefficient produced by the same magnetic field in MF-PEG are a few times smaller than those in MF, and in MF-PEG no spherical clusters were detected (no maxima of $\Delta\alpha$). Biocompatible ferrofluid containing nanoparticles coated with oleate sodium and polyethylene glycol is characterised by a better stability of its acoustic parameters in time than ferrofluid containing nanoparticles coated with oleate sodium only, which proves a structural stability of this fluid and is much promising for potential applications in medicine.

4. Conclusions

Biocompatible magnetic fluid with nanoparticles coated with additional biocompatible layer of polyethylene glycol, subjected to a slow growing magnetic field shows a high stability of acoustic

properties up to the field intensity of $H = 70 \text{ kA/m}$. In higher fields the ultrasonic wave absorption coefficient significantly increases and this increase strongly depends on the ferrofluid temperature (an increase in temperature causes a smaller increase in α), magnetic field intensity, magnetic field sweep rate and the time of the ferrofluid exposure to magnetic field. Thus, by adjustment of these parameters it is possible to control the acoustics properties of the magnetic ferrofluids.

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