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EXPERIMENTAL INVESTIGATION OF $CoFe_2O_4$ PARTICLE SIZE AND ACOUSTIC PROPERTIES OF MAGNETIC FLUID

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In this paper magnetic particle size and acoustic properties of the ferrofluid with $CoFe_2O_4$ particles are presented. The results acquired from atomic force microscope measurements will let us set average value for the hydrodynamic diameter of magnetic particles appearing in $CoFe_2O_4$ ferrofluids. The knowledge of these sizes is extremely useful because on the further stage of examinations it allows us to determine the size of surfactant coating particles. It is possible by making additional magnetic measurements enabling the size of average magnetic core contained in the ferrofluid. Also, it allows us to determine in a simple way the thickness of the surfactant layer. Such information on magnetic particles in a given ferrofluid is very valuable in the context of the application of the liquids either in technology or in medicine. Moreover, ultrasonic measurements carried out are providing the valuable information for us on the subject of the ferrofluid stability exposed to the action of the external magnetic field. The experimental estimation of the ultrasonic wave absorption coefficient in the function of a field for a few temperatures allows us to forecast how magnetic particles in a given magnetic liquid are capable of joining together and creating clusters, and how big aggregates can be created in this way.

Key words: ferrofluid, AFM, absorption coefficient.

1. Introduction

Magnetic fluids are still attractive research objects because of their interesting properties but also for their various applications. Either in medicine or in technology the application of ferrofluids requires their high quality and specific expertise of them. The knowledge of ferrofluid components, their magnetic and acoustic properties, as well as determination of structure are very helpful for further improvement of ferrofluids in the context of their application [1, 2].

The aims of this work are to determine the magnetic particle size in $CoFe_2O_4$ ferrofluid using atomic force microscopy (AFM) and also to measure magnetic ferrofluid susceptibility in a constant magnetic field. The mean sizes of magnetic grains (the mean magnetic diameter of a magnetite grain and its hydrodynamic diameter) were measured and the size distribution of magnetic grains was imaged.

Moreover, absorption coefficient of the ultrasonic wave in function of temperature was examined.

2. Description of experimental methods

Magnetic fluid $CoFe_2O_4$ used in this work was obtained by chemical precipitation [3]. This ferrofluid consist of three components: magnetic particles ($CoFe_2O_4$), natrium salts of oleic acid as a surfactant and water as a currier liquid.

First of all $CoFe_2O_4$ was examined using the atomic force microscopy (AFM), which enables one to specify the hydrodynamic size of magnetic grains and to image the size distribution of nanoparticles [4]. The sample should be properly prepared before AFM measurement. Preparation of the sample for the AFM measurements followed several stages. First, preparation of suitable size of silicon surfaces on which the liquid examined was placed. Second, sterilization of silicon surfaces in piranhic acid for 60 minutes in order to dissolve any impurities that might be present on the silicon plate surface. Third, washing the surfaces with MilliQ© water that removes the possible piranhic acid traces left on the plates. Fourth, removing the remains of water from the plates by washing them with pure and clean methanol and then placing them in an oven to evaporate the residual methanol. Finally, "bathing" the surface in ferrefliud for 5–10 minutes and then taking out and putting it in an oven in order to evaporate the residual solvent (temperature during the evaporation process was $40°$C).

Afterwards, magnetic susceptibility χ was determined using an *RLC* bridge in which the inductance of a cylindrical solenoid was measured. The comparison of the solenoid inductance L_1, when the cell was filled with the magnetic fluid, with the inductance L_0, when the cell was empty, enabled a determination of the real component of the magnetic susceptibility [5].

Furthermore, the changes of ultrasonic wave's absorption coefficient α were determined with the reflected impulse method, which consists in measuring the range of damping based on the relation of impulse amplitudes reflected several times in between the parallel transducers of the medium under investigation [6]. The construction of the 0.024 m long brass measurement cell used in this experiment ensured a parallel setting of converters.

The temperature of the magnetic fluid during the ultrasonic experiment was changed on each step at 5°C in the range of 10–50°C, and the ultrasound wave frequency in one case was $f = 2.8$ MHz and in the second one it was $f = 13.9$ MHz.

The measurements of the changes of ultrasonic wave absorption coefficient $\Delta\alpha$ in the magnetic fluid were performed for the two selected magnetic field intensity values (0 kA/m and 150 kA/m).

3. Results and discussion

Figure 1 presents changes in the ultrasonic wave absorption coefficient as a function of temperature for two frequency values of ultrasonic wave influencing $CoFe_2O_4$ ferrofluid both with and without external magnetic field. The temperature increased from 10 to 50°C. Without external magnetic field, in the range of temperatures studied small changes in the ultrasonic attenuation were observed only for one ultrasonic wave frequency $f = 2.8$ MHz. However, for the fequency $f = 13.9$ MHz significant decrease in the absorption coefficient value in the function of temperature was observed. On the other hand, the activation of magnetic field at the frequency $f = 2.8$ MHz caused small changes in the absorption coefficient value. Also, significant decrease in the absorption coefficient value in the function of temperature was observed. Both cases are consistent with the TAKETOMI theory [7] and result from the reconstruction of ferrofluid structure under the influence of external magnetic field. The absorption coefficient decrease in the function of temperature with the activated magnetic field results from the drop of ferrofluid viscosity while the temperature rises. However, bigger absorption coefficient changes obtained for several frequency values probably result from the influence of relaxation phenomena. The value of measurement error is about 1%.

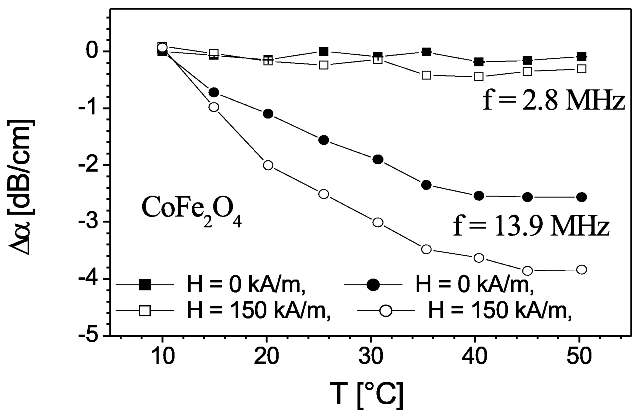

Fig. 1. The changes of ultrasonic wave absorption coefficient as a function of the temperature in the $CoFe_2O_4$ ferrofluid for two ultrasonic wave frequency values and two intensity values.

For ferrofluids with low magnetic grain concentration the susceptibility of a ferrofluid can be expressed as a superposition of Langevin functions related to the different fractions of colloidal particles [8, 9]

$$M_L(H) = n \int_0^\infty m(x)\, L(\xi)\, f(x)\, \mathrm{d}x, \qquad L(\xi) = \coth(\xi) - \frac{1}{\xi},$$
$$\xi = \frac{\mu_o m(x) H}{kT}, \qquad m(x) = \frac{\pi x^3}{6} M_g, \tag{1}$$

where $\mu_o = 4\pi \cdot 10^{-7}$ H/m, m and n are the magnetic moment and number density of particles, respectively, $f(x)$ is the particle size distribution function, x is the diameter of particle magnetic core, $L(\xi)$ is the Langevin function, ξ is the Langevin parameter, H is the strength of magnetic field, $k = 1.38 \cdot 10^{-23}$ J/K is Boltzmann's constant, and T is the absolute temperature.

Figure 2a shows the differential magnetic susceptibility of the sample measured depending on the value of external magnetic field H with the fitted function $\chi =$

dM_L/dH. On the other hand, Fig. 2b shows lognormal distribution finction which allowed us to obtain the mean magnetic diameter $<d_m> = 9$ nm and the standard deviation of particles $\sigma = 2.4$ nm.

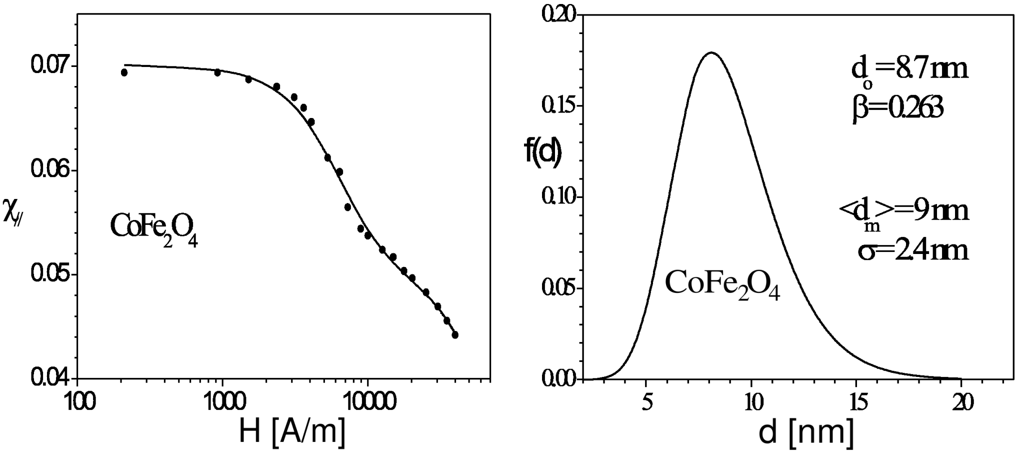

Fig. 2. Experimental values of magnetic susceptibility a) measured in parallel to the direction of the constant external magnetic field as a function of the field intensity, and b) lognormal distribution function.

Figure 3 presents spatial distribution magnetite nanoparticales appearance in cobalt ferrofluid on the surface 10×10 µm.

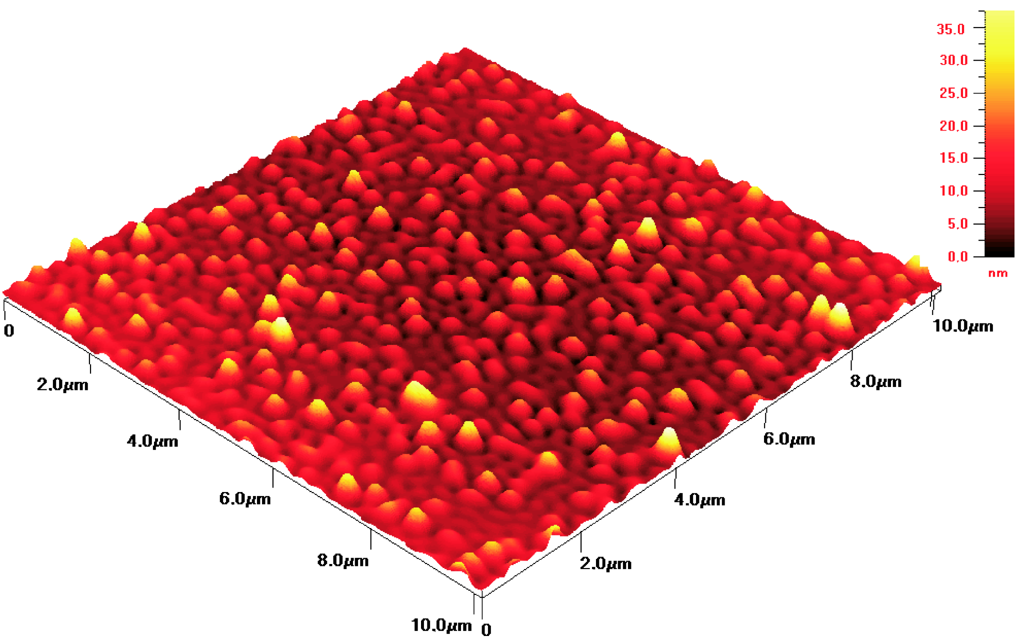

Fig. 3. AFM image obtained from the magnetite nanoparticales appearance in cobalt ferrofluid.

Figure 4 shows the best fit of the lognormal function for distribution of hydrodynamic diameters of magnetic particles scanned [8, 10]:

$$f(d) = \frac{1}{\sqrt{2\pi}\beta d} \cdot \exp\left[-\frac{\ln^2\left(\frac{d}{d_o}\right)}{2\beta^2}\right], \tag{2}$$

with the following parameters lognormal function: $d_o = 12.1 \pm 0.07$ nm, and $\beta = 0.265 \pm 0.006$. From these values we obtained a mean particle diameter of $< d_H >= 12.5$ nm, and a standard deviation of $\sigma = 2.4$ nm.

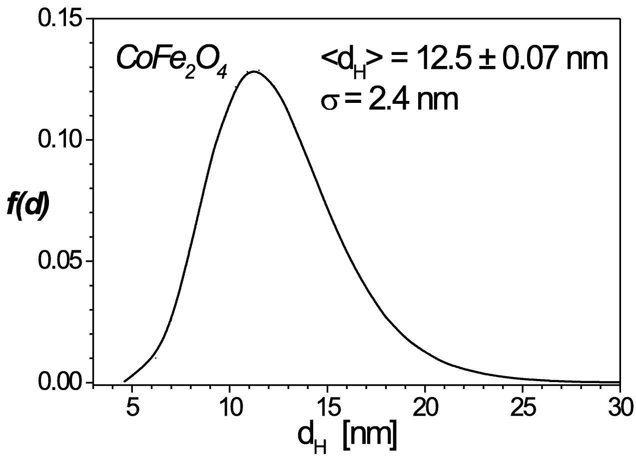

Fig. 4. Particle size distribution function obtained from AFM data.

4. Conclusions

The results acquired from atomic force microscopy measurements will let us set average value for the hydrodynamic diameter of magnetic particles in $CoFe_2O_4$ ferrofluid, which is 12.5 nm. The mean diameter of magnetic grain obtained from the magnetic susceptibility measurements is 9 nm. Thus, the thickness of the surfactant layer in the $CoFe_2O_4$ magnetic fluid is approximately 1.9 nm, which is in agreement with the sizes of surfactant molecules.

The results of the determination of the ultrasonic waves absorption coefficient in $CoFe_2O_4$ ferrofluid have shown that the activation of magnetic field leads to the decrease absorption coefficient. Moreover, the temperature increase results in the decrease of viscosity (and indirectly on α). In this experiment only α change was determined and not its absolute value. Thus, the results shown in Fig. 1 do not mean that α absolute value decreases with the frequency increase at all. Absorption coefficient allows us better understand ferrofluid behavior which is exposed to the external magnetic field as a function of temperature which is very important for their medical applications.

Such information on magnetic particles in a given ferrofluid is very valuable in the context of the application of the liquids either in technology or in medicine, where the size of the nanoparticles is involved.

Acknowledgment

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