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Synthesis method influence on water based magnetic fluid properties

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Water based magnetic fluids containing magnetite have been prepared by a chemical precipitation method. Two samples of tetramethylammonium hydroxide coated magnetic nanoparticles (ultra-fine particles of Fe_3O_4) immersed in water have been obtained following two different preparation protocols. Physical tests have been performed on these samples of the water based magnetic fluids prepared by us, in order to reveal their microstructural and rheological features. Transmission electron microscopy (TEM) was the investigation method for the assessing of the physical magnetic nanoparticles size. Magnetic susceptibility and magnetization measurements were carried out by *Gouy* method. Fourier transform infrared absorption spectra have been recorded aiming to get some information on the solid phase structure. The dimensional distribution of the ferrophase physical diameter was comparatively presented using the box-plot statistical method. To assess the optical properties of isolated magnetic nanoparticles, UV-VIS absorbance spectra were recorded.

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1. Introduction

The union of both fluid and magnetic properties leads already to numerous industrial applications and researches in the area of physics and seems also to be full of promise in the biomedical field.

The first magnetic fluids were obtained by milling magnetic materials in presence of solvent and a surfactant [1]. The chemical process proposed by Massart in 1979 [2], leads to the synthesis, in aqueous media, of the nano-sized magnetic particles, which have a very reactive surface allowing the stabilization of the particles in a large spectrum of media including both polar and non polar solvents. Chemical precipitation is the most used method to prepare magnetic nanoparticles nowadays, because is a simple, efficacious and cheap preparation method [3]. Different procedures have been developed to achieve this intention. In general, these procedures start with a mixture of $FeCl_2$ and $FeCl_3$ and water. Co-precipitation occurs with the addition of ammonium hydroxide, and then the system is subjected to different procedures to peptization, magnetic separation, filtration and finally dilution. Chemical precipitation [4] consists of two processes: nucleation (formation of centers of crystallization) and a subsequent growth of particles.

Iron oxide (usually magnetite and maghemite) nanoparticles are mostly used as magnetic particles in magnetic fluids due to their high saturation magnetization and high magnetic susceptibility, the small magnetite nanoparticles being preferred because of their greater saturation magnetization [5].

The properties of magnetic fluids have been intensively studied due to their multiple applications, in both technical and biomedical sciences.

In the present work, we describe the differences on properties of two samples of tetramethylammonium hydroxide ($N(CH_3)_4OH$) coated magnetic fluid containing magnetic nanoparticles obtained by chemical precipitation method following two different protocols.

2. Experimental

The common way of magnetite synthesis is the alkaline hydrolysis of iron (II) and iron (III) salts. The size of formed particles depends on the relative over saturation of solution; formation of nanoparticles is expected at very low and very high concentration according to the Weimarn rule [6]. It is shown that the smallest single magnetic domain particles can be produced at the limits of the stability domain determined by three optional process parameters: the initial solution concentration, the equilibrium solubility and the operational time.

Magnetite nanoparticles were prepared by alkaline hydrolysis (in the aqueous ammonia solution presence) of the most concentrated mixed solution of $FeCl_2$ and $FeCl_3$ following different precipitation protocols [7, 8]. Two samples of magnetic fluid containing magnetic nanoparticles (mostly Fe_3O_4) coated with tetramethylammonium hydroxide ($N(CH_3)_4OH$) have been obtained. For the first magnetic fluid sample (**FF1**) the ferrophase particles was prepared utilizing an aqueous solution of 4.3g $FeCl_2 \times 4H_2O$ and 11.75g $FeCl_3 \times 6H_2O$ in

200 ml deionized water, heated to 80ºC was mixed under vigorous and continuous stirring with 25ml of 25% NH_4OH as precipitant agent [7]. For the second sample (**FF2**) the ferrophase was synthesized by means via a controlled chemical precipitation approach, at room temperature described in [8]. Acidic solution of ferric and ferrous salts was prepared in presence of 2M HCl solution since the acidic conditions prevent formation of iron hydroxides. We have combined 7.0 ml of 2M stock $FeCl_2$ solution and 28.0ml of 1M stock $FeCl_3$ solution mixed under vigorous and continuous magnetic stirring with 350ml of 1M aqueous NH_3 solution.

The magnetite amount obtained by both precipitation protocols was vigorously mechanically mixed with 7ml aqueous tetramethylammonium hydroxide ($(CH_3)_4NOH$) 25% solution each. This surfactant can surround the magnetite particles with hydroxide anions and tetramethylammonium cations to create electrostatic interparticle repulsion in an aqueous environment (Fig. 1).

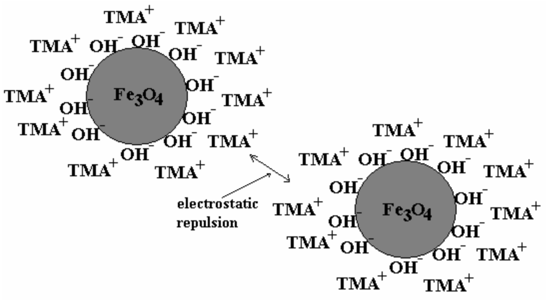

Fig.1. Illustration of a water based magnetic fluid stabilized by a tetramethylammonium hydroxide surfactant. TAM$^+$ is the tetramethylammonium cation and OH$^-$is the hydroxide anion.

Physical tests have been performed on these samples of the magnetic fluid prepared by us in order to reveal their microstructural and rheological features. The magnetic fluid density, dynamic viscosity and surface tension have been measured using standard methods. Transmission electron microscopy (TEM) was the main investigation method for the assessing of the physical magnetic nanoparticles size. TEM photographs were provided by a TESLA device with a resolution of 1.0nm (sample deposition of collodion sheet after 10^4 dilution). Infrared absorption spectra have been recorded aiming to get some information on the magnetic fluid composition. The FT-IR investigation was carried out using a Bruker Vertex 70 infrared spectrometer the magnetic nanoparticles being dispersed in KBr after previous thermal treatment at 100^{O}C up to constant weight.

Measurements of magnetization and magnetic susceptibility were performed revealing the suitability of the water based magnetic fluid for magnetic carrier utilization, following the Gouy method at constant normal ambient temperature. Magnetic field intensity was measured by means Walker Scientific MG 50D Gaussmeter with Hall probe. For sample weighting measurement an electronic balance ACULAB-200 with 10^{-4}g accuracy was used.

To assess the optical properties of isolated magnetic nanoparticles, UV-VIS absorbance spectra were recorded on CINTRA 5 spectrophotometer in double beam mode, using a 1cm quartz cuvette filled with only the solvent (deionized water) as reference.

3. Results and discussion

The water based magnetic fluid batches synthesized in our laboratory was dark (FF1) and respectively dark brown (FF2) and kept their colloidal characteristics for up to 6 months. Low level of magnetic fluid nanoparticles sedimentation in time was observed.

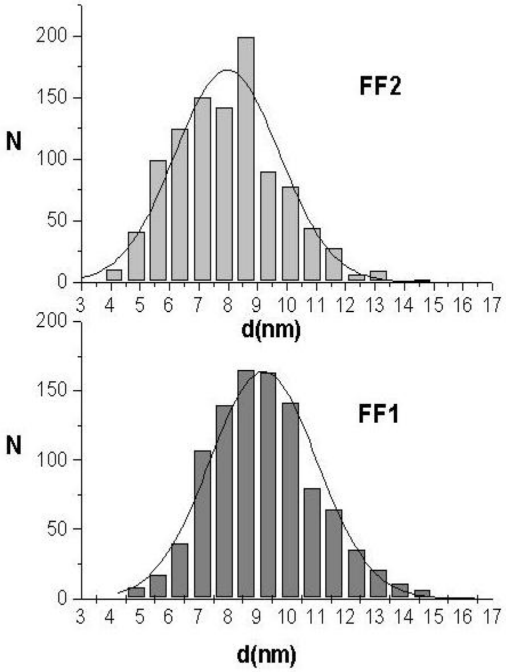

Fig. 1. Distribution histogram of nanoparticles in the magnetic fluid.

The analysis of all TEM pictures measurements resulted in physical diameter distribution histograms (Fig. 1), average of particle diameter is given in Table I. The TEM micrographs (Fig. 2) show that the size of nanoparticles ranges between 3 and 17 nm, in both magnetic fluid sample cases, exhibiting mostly spherical shape.

Magnetization curves obtained for the water based magnetic fluid samples are presented in Fig. 4. Magnetization curves can be used for the study of both particle interactions and agglomerate formation, processes which strongly influence the rheological behavior of magnetic fluids.

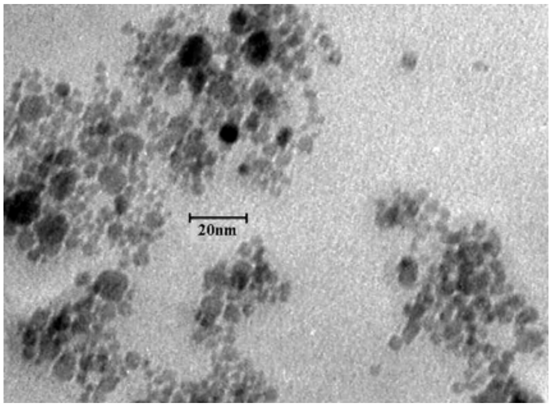

Fig.2.TEM image of FF1magnetic fluid sample.

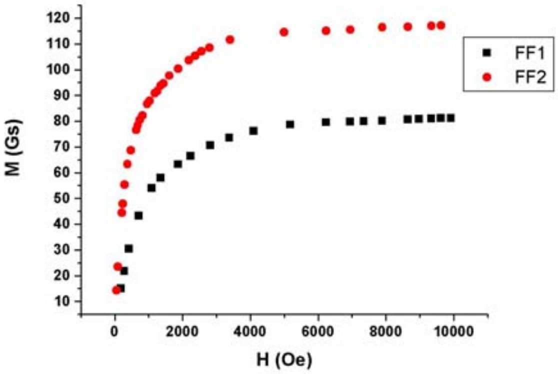

Fig. 4. Magnetization curves of the water based magnetic fluid analyzed.

Considering the Langevin equation at high field, the saturation magnetization was obtained from magnetization (M) versus $1/H$ curves, by extrapolating to $1/H = 0$. The initial susceptibility χ_0 was determined from inclination of the magnetization (M) versus magnetic filed (H) curves at low field. The results are presented in Table I. The magnetic susceptibility versus magnetic field dependences for magnetic fluid analyzed in this study are presented in Fig. 5.

Using magnetization data, the average size of the magnetic diameter (d_M) can be calculated according to Langevin's equation. The size of large particles, which are influenced by low magnetic field, can be calculated as follows:

$$d_M^3 = \frac{18k_BT}{\pi\mu_0 M_b \cdot M_s}\left(\frac{dM}{dH}\right)_{H\to 0} \qquad (1)$$

where d_M is the magnetic particle diameter, k_B is Boltzmann's constant, T is the absolute temperature, M_s is the saturation magnetization of the sample and μ_0 is the vacuum magnetic permeability.

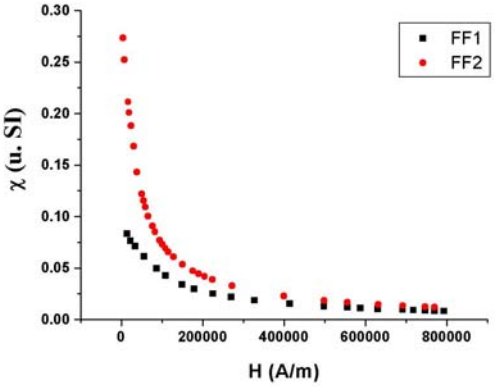

Fig. 5. Magnetic susceptibility curves of the water based magnetic fluid analyzed.

Assuming a spherical particle shape, accordingly to equation (1) and M_b value of bulk magnetite ($0.48 \cdot 10^6$A/m) [9] we obtained for average magnetic diameter of nanoparticles for magnetic fluid samples analyzed in this study, the values presented in Table 1.

Table 1. The dimensional analysis and magnetic properties data.

Magnetic fluid sample	Φ_M (%)	a_{TEM} (nm)	a_M (nm)	M_S (Gs)	χ_0
FF1	1.42	9.2025	8.70	85	0.0532
FF2	2.03	7.9728	6.70	122	0.1706

We can see that the smallest physical diameter value and high magnetization value was revealed for the magnetic fluid sample synthesized at room temperature. Differences evidenced between d_{TEM} values and d_M values, can be assigned to the surfactant shell of the magnetite core. The surfactant layer is often considered as a magnetically dead coating, which can affect the uniformity or magnitude of magnetization due to quenching of surface moments [10].

The results of the physical properties investigations as well as the volume fraction, Φ, of nanoparticles in the magnetic fluid samples are presented in Table 2.

Table 2. The physical properties and volume fraction data.

Magnetic fluid sample	Φ (%)	Density (kg/m^3)	Surface tension ($*10^{-3}$ N/m)	Viscosity ($*10^{-3}$ kg/ms)
FF1	2	1021.4	63.91	1.32
FF2	2.6	1060.4	75.72	1.45

The highest values of physical properties analyzed in this study, were revealed for **FF2** sample, synthesized at room temperature.

To assess the optical properties of isolated nanoparticles, UV-VIS absorbance spectra were recorded on spectrophotometer in double beam mode, with only the solvent (deionized water) as reference. The prepared water based magnetic fluid was diluted to 10^{-3} volume fraction and was recorded the UV-VIS absorbance spectra presented in Fig. 6.

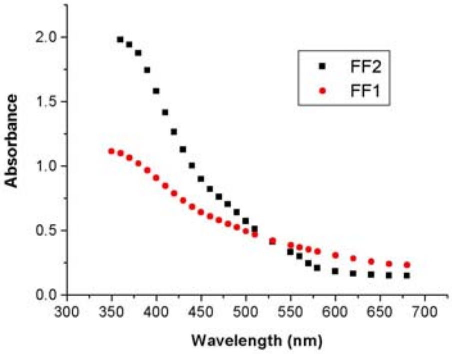

Fig. 6. UV-VIS absorbance spectra for magnetic fluid samples stabilized with tetramethylammonium hydroxide analyzed in this study.

The magnetic fluid sample synthesized at room temperature (FF2 sample) exhibits an increased absorbance toward shorter wavelengths than FF1 sample.

Further analysis was carried out by means of FT-IR spectra (3500 cm^{-1} – 500cm^{-1}), which are presented in Fig.7.

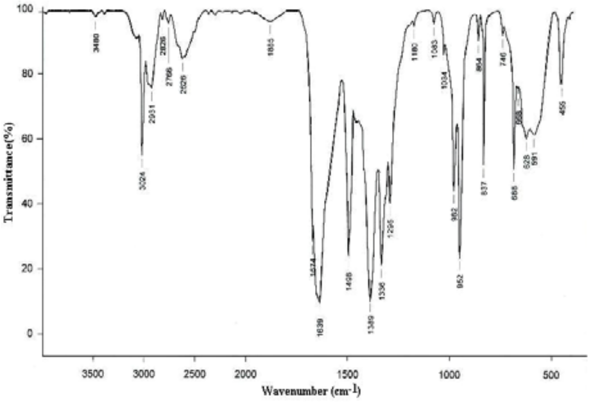

Fig.7. FT-IR spectra for magnetite coated with tetramethylammonium hydroxide.

The IR analysis of ferrophase coated with tetramethylammonium hydroxide (Fig. 7) revealed: (i) the OH group symmetrical and asymmetrical stretchings that generate the large band at about 3480 cm^{-1} - the origin of this IR band may be due to the adsorbed H_2O molecules on Fe_3O_4 surfaces; (ii) the CH_3 group from TMA molecules symmetrical and asymmetrical stretchings that gave the intense and bifurcated band around 2900 cm^{-1}; (iii) the ferrophase complex vibrations that led to the 1300-1700 cm^{-1} bands and "skeleton" vibrations appeared within 400-900 cm^{-1}. Ishii *et al* [11] recorded for Fe_3O_4 two characteristic IR bands at 565 and 360cm^{-1}.

4. Conclusions

In this study, the physical characterization of two samples of water based magnetic fluids, stabilized with tetramethylammonium hydroxide, synthesized by different methods were discussed. The highest density, viscosity, surface tension and volume fraction were evidenced for the magnetic fluid sample synthesized at room temperature. The smallest physical diameter value and high magnetization value was revealed for the magnetic fluid sample synthesized at room temperature, also. The suitability for biological purposes is ensured by the fine magnetic-particle diameter, while strong magnetic properties are indicated.

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