

Room temperature synthesis of magnetic nanoparticles

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In this study, we report a rapid solvent-free synthesis method, using inorganic ferrous and ferric solids together with surfactant molecules to produce mono-dispersed magnetite - the reaction being induced at room temperature this way avoiding any heating. Such a solvent free experimental approach provides environmental advantages since the toxic chemicals generation does not occur. Dimensional analysis of magnetic nanoparticles was accomplished by means of transmission electron microscopy (TEM) and by magnetic measurements revealing mean values of 9.17 nm and respectively 3.8 nm. Infrared absorption spectra (FT-IR), recorded aiming to get some information on the functionalized magnetic nanoparticles composition revealed the presence of iron oleate onto the magnetic core. The colloidal suspensions density, viscosity and surface tension were measured using standard methods their values indicating convenient rheological properties for technical applications.

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1. Introduction

Magnetic nanoparticles are useful for a wide variety of scientific, technological and biomedical applications. In such applications iron oxides, such as Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$, represents one of most utilized classes of magnetic materials. In nano-sized form, both Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ exhibit superparamagnetic behavior at room temperature.

Many researches were focused on magnetite nanoparticles preparation, since their synthesis is fairly convenient and rather facile. Stable concentrated suspensions of magnetic nanoparticles in either organic or inorganic solvents are known as magnetic fluids or ferrofluids [1]. The most common preparation method of magnetic nanoparticles, nowadays, is the chemical precipitation, developed by Massart, since it remains the most simple, efficacious and cheap comparatively to any other preparation methods [2, 3] including variants for both high and low temperature. So, Montagne *et al.*, 2002 used iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, and ammonium hydroxide to synthesize Fe_3O_4 nanoparticles at room temperature [4].

Recently, a special attention has been paid to the size selective synthesis of magnetite nanoparticles in high temperature, Sun *et al.* developing a very successful method to achieve in this way monodisperse magnetite nanoparticles [5].

The ensuring of a narrow distribution of physical diameter of magnetic nanoparticles continues to represent an important research goal. In the scientific literature there are various reports regarding the avoiding of the aggregation of the magnetite nanoparticles either by creating an electrostatic double layer [6], or by using

surfactant steric stabilization [7], or by shifting the isoelectric point with citric acid [8].

In this study we report the application of a rapid solvent-free synthesis method of magnetite, from ferrous and ferric hydrated salts mixed carefully in the presence of oleic acid to obtain the magnetic particles in the colloidal form at room temperature. Oleic acid was chosen to stabilize magnetite in kerosene as carrier liquid, which represents an already classical system to ensure a narrow dimensional distribution, still widely used. Among the method advantages we mention: (i) it does not requires sophisticated devices or maneuvers; (ii) it enables the synthesis of rather large amounts of colloidal suspensions with almost uniform size suspended nanoparticles; (iii) it does not require high or peered controlled temperature; (iv) liquids are the least involved their vaporization impact on the environment and people being minimalized; (v) the total preparation time is short – of the order of minutes.

2. Experimental

Samples synthesis. The following amounts or reagents (Merck products) were used: 0.50g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 1.35 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.8 ml oleic acid - these being thoroughly mixed for 5-10 minutes into a grinding mortar provided with pestle.

During the grinding process the mixture transformed gradually in a dense liquid, the color changing from light brown to dark brown. In the next step 0.89 g of powdered NaOH was added to the reaction medium the whole mixture being mixed continuously for 5 more minutes. After that, 20 ml of kerosene was added over the mixture and

vigorously mixed for 2 minutes in the grinding mortar. The resulted fluid was transferred to a centrifuge tube being processed for 5 minutes at 4000 rpm. All necessary reactive substances were reactive grade. Thus, the magnetic nanoparticles were extracted into kerosene phase while the residual products, mostly sodium chloride, remained precipitated on the bottom of the centrifuge tube. All reaction processes were carried out at room temperature. A detailed model proposed for the mechanism of Fe_3O_4 crystallization can be developed based on the formation of molecular complexes between each iron salt and the oleic acid molecules in the first step - that further interact, in the second step, in the presence of NaOH, leading to the magnetite (and occasionally maghemite) and sodium chloride.

Dimensional analysis. To obtain the profile of the nanoparticles dimensions the transmission electron microscopy and magnetization measurements and were chosen as main investigation methods. Using a TESLA device with a resolution of 1.0 nm the transmission electron microscopy (TEM) physical diameter distribution was obtained from magnetic fluid samples 10^4 diluted in kerosene and deposited on collodion sheet. TEM image analysis was accomplished on about 1,000 nanoparticles diameter (d_{TEM}) of kerosene magnetic fluid.

Magnetic measurements. Magnetization measurements were performed using a Vibrating Sample Magnetometer, type LakeShore 7400. Using magnetization data, the average sizes of magnetic diameter (d_M) can be calculated according to Langevin's equation. The mean magnetic diameter can be calculated as follows:

$$d_M^3 = \frac{18k_B T}{\pi\mu_0 M_b \cdot M_s} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \quad (1)$$

where d_M is the average 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.

Structural investigations. Infrared absorption spectra have been recorded aiming to get some information on the composition of colloidal nanoparticles as well as on the interaction between the magnetic core and the non-magnetic shell. The FT-IR investigation was carried out using a Bruker Vertex 70 infrared spectrometer, the magnetic fluid specimens being prepared as thin films.

Physical properties measurements. The suspension density (picnometric method), viscosity (capillary method using an Ubbelohde viscosimeter) and surface tension (stalagmometric method) were measured by applying standard methods.

3. Results and discussion

The magnetic fluid samples synthesized in our laboratory were dark brown and kept their colloidal characteristics for about 2 months. One of TEM images of the kerosene based magnetic fluid coated with oleic acid is shown in Fig.1.

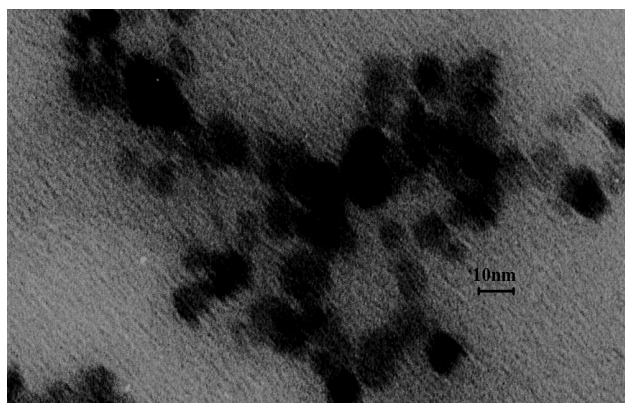


Fig. 1. TEM images of the kerosene based magnetic fluid sample.

The TEM micrographs show that the physical diameter of magnetic nanoparticles ranges between 4 and 24 nm, exhibiting mostly spherical shape, with minimal agglomeration.

The analysis of all TEM pictures measurements (about 1,000 particles from kerosene based magnetic fluid sample) resulted in physical diameter distribution histogram (Fig. 2) having maximum frequency at about 9.178 nm – Gaussian function fitting the measured data

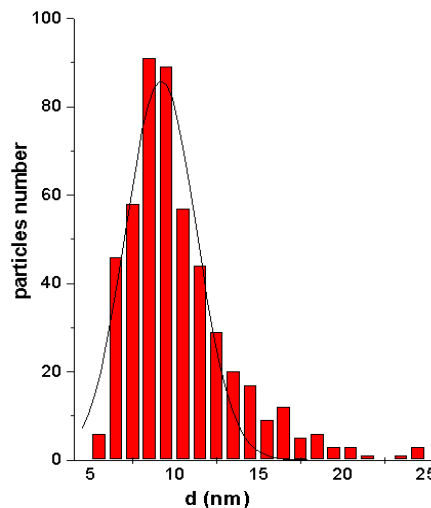


Fig.2. Distribution histogram of magnetic fluid based on kerosene.

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. Magnetization curve obtained for the magnetic fluid sample is presented in Fig.3. The saturation magnetization was obtained from magnetization (M) versus $1/H$ curves, by extrapolating to $1/H = 0$. For the magnetic fluid discussed inhere, the saturation

magnetization value is low, about 5.6 A/m.

Using magnetization measurements data and assuming a spherical particle shape, the magnetic diameters (d_M) were calculated according to Langevin's equation. The magnetic measurement results are presented in Table 1.

Table I. The magnetic measurements results data..

Nr. crt.	d_{TEM} (nm)	d_M (nm)	d_{layer} (nm)	M_S (A/m)
1	9.178	3.8	5.378	5.6

Differences evidenced between d_{TEM} values and d_M values, can be assigned to the surfactant shell of the magnetite core (d_{layer}). The surfactant layer is often considered in the scientific literature, as a magnetically dead coating, which can affect the uniformity or magnitude of magnetization due to quenching of surface moments [9].

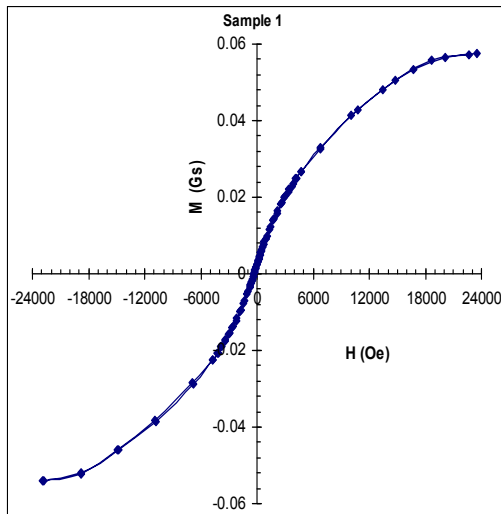


Fig. 3. Magnetization curves of the kerosene based magnetic fluid.

Physical tests have been performed in order to reveal their microstructural and rheological features. The results of the physical properties investigations as well as the volume fraction, Φ , of the solid nanoparticles in the magnetic fluid sample are presented in Table II. The average values calculated following ten repetitions of every measurement are given.

Table II. The physical properties and volume fraction data.

Nr. crt.	Φ (%)	Density (kg/m ³)	Surface tension (*10 ⁻³ N/m)	Viscosity (*10 ⁻³ kg/ms)
1	1.0	764.77±1.21	22.33±0.7	1.273±0.03

Further analysis was carried out by means of FT-IR spectra (3,500 cm⁻¹ – 500 cm⁻¹), which are presented in Fig.4.

The FT-IR recordings revealed four groups of vibration bands. The large band of low intensity ranging at about 3.468 cm⁻¹ may be assigned to the symmetrical and asymmetrical stretching of the OH group generated from the hydroxyl groups attached by hydrogen bonds to the iron oxide surface.

The intense band that was recorded in the range 2.800–3.000 cm⁻¹ is generated by the vibrations of the CH groups (symmetrical and asymmetrical stretchings), i.e. the CH₂ and CH₃ stretching bands, belonging to the free hydrocarbons within the carrier fluid.

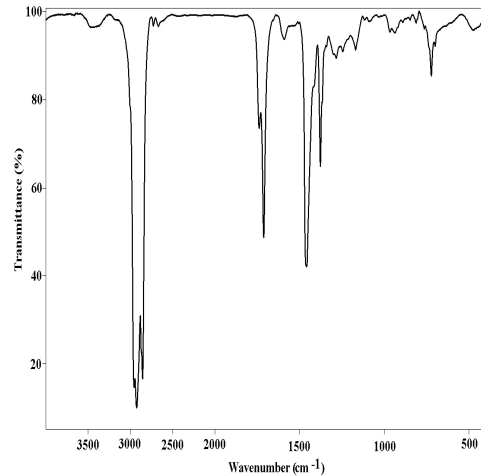


Fig.4. FT-IR spectrum of kerosene based magnetic fluid.

In the range 1.400–1.600 cm⁻¹ there is a group of two bands that provided some information about the ferrophase surface structure. The two bands of relatively low intensity ranging between 1.591 and 1.458 cm⁻¹ could be assigned to the small amount of oleate ions, chemically bounded to the iron atoms from the ferrophase particle surface at the level of the oxygen atoms, according to [10].

The print region, recorded at wave numbers less than 800 cm⁻¹ revealed the vibrations of the iron oxide skeleton from the ferrophase particle volume. The two bands, situated between 400 and 800 cm⁻¹ can be assigned to the iron oxides and, respectively, to the iron oxide coupled with the oleate ions - at the level of the ferrophase superficial sheet. Such patterns suggest the coexistence of the magnetite with the maghemite nanoparticles, in accord to scientific literature reports [11].

Other authors succeeded in applying similar solvent free preparation method to obtain magnetic nanoparticles without the addition of surfactants – with better mono-dispersity but having higher mean size of the particles (about 8 nm according to their TEM data) and significant agglomeration tendency [12].

4. Conclusions

The soft magnetic materials synthesized by us following solvent free reaction are characterized by relatively small ferrophase particles and narrow distribution

of physical diameter. The future project will be focused on the improving of the saturation magnetization as well as on the increasing of mono-dispersity. Nevertheless, aqueous magnetic fluids are planned to be obtained also by this method considering the potential biomedical applications.

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