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COMPARISON AMONG THE PHYSICAL PROPERTIES OF VARIOUS SUSPENSIONS OF MAGNETITE NANOPARTICLES STABILIZED IN WATER USING DIFFERENT ORGANIC SHELLS

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The stability of magnetic nanoparticle suspensions, designed for biomedical purposes can be ensured by coating magnetic cores with various organic shells. In this work, the magnetite powder was successfully dispersed in water by using steric stabilization and electrostatic interactions - with volume fraction ranging between 2.42 and 3.14 %. The mean physical diameter of colloidal nanoparticles was of 9.2 ÷ 11.98 nm with non-magnetic shell of 2.7 ÷ 3.42 nm ensuring good magnetic properties, i.e. mass density of saturation magnetization of 24 ÷ 58 A·m^2/kg. Sodium oleate, tetramethylammonium hydroxide and rifampicin were found to ensure better microstructural and magnetic properties compared to citric acid.

Keywords: magnetic core; non-magnetic shell; biocompatible suspension

1. Introduction

Nanotechnology is defined by the understanding and control of matter at the nanoscale, where unique phenomena enable novel applications [1]. An improved definition and more general descriptions of nanotechnology application (Wilson et al., 2002) refer to the capacity to design a whole new range of machines from nanoscale objects, but not necessarily by breaking up matter into individual atoms [2].

Nanomaterials is nowadays a widely used term that refers to nanosized matter ranging between 1 and 100 nanometers in 1, 2, or 3-dimensions, mainly incidental nanoparticles that resulted from natural phenomena or as waste products of anthropic processes and engineered nanoparticles, that are purposefully manufactured with nanoscale dimensions. By dispersing the nanoparticles in fluids, like water or organic solvents, the nanofluids will result - a type of colloidal fluids having as ferrophase particles of metals, metal oxides or carbon [3-5]. Unlike the micrometric suspensions, these fluids can potentially have a good stability in normal environmental conditions over a long time, since nanoparticle aggregation and settling can be avoided. In particular, nanoparticles often aggregate, i.e. they generate clusters, because of forces of different nature, leading to the settling down of aggregates. These dispersions can be used as-is, or diluted with suitable (compatible) solvents. Since nanoparticles can sometimes

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settle during dispersions storage, they can be mixed before use. Magnetizable nanofluids or magnetic fluids contain nanoparticles with magnetic properties, mainly mixed iron oxides having unique properties that make them specifically useful in conjunction with magnetic fields [6-8]. Magnetite (Fe_3O_4) nanoparticles have attracted much interest in the field of magnetic recording media, data storage, magneto-optics devices, magnetic sensing, magnetic fluids, drug delivery systems, medical imagistic and therapy.

In the next, several suspensions of magnetite nanoparticles are presented, their microstructural and magnetic properties being discussed comparatively aiming putative applications in medical imagistic and therapy.

2. Experimental

The ferrophase was prepared from pure $FeSO_4 \times 7H_2O$ and $FeCl_3 \times 6H_2O$ salts by autocatalysis reactions between ferric and ferrous salts in alkali reaction medium [9]. The precursor salt solutions in their respective stoichiometry were prepared and warmed at 80 °C. NH_4OH (25%) was poured into the mixed solution under constant non-magnetic stirring. Magnetite nanoparticles were generated by conversion of metal salts into hydroxides and further transformation of hydroxides into ferrite particles.

$$FeSO_4 + 2H_2O \rightarrow SO_4^{2-} + 2H^+ + Fe(OH)_2$$

$$2FeCl_3 + 6H_2O \rightarrow 6Cl^- + 6H^+ + 2Fe(OH)_3$$

$$2FeCl_3 + FeSO_4 + 8NH_4OH \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 4H_2O$$

The solution mixing was continued at 75 °C for one hour, this duration being sufficient for the transformation of hydroxides into spinel ferrite nanoparticles [10]. The magnetic particles were separated from the reaction medium in magnetic field gradient, being washed several times with distilled water at room temperature. Fine precipitated particles were collected in magnetic field gradient, several washings being also carried out with distilled water. After filtration, for every 4 g of magnetite mould, we added the next organic molecule solutions to get the four ferrofluid samples (magnetite/citric acid, magnetite/tetramethyl ammonium hydroxide, magnetite/rifampicin and magnetite/sodium oleate) under continuous stirring for more 2 h at about 80 °C:

(a) SO-FF: 1 g sodium oleate (SO) in 15 ml distilled water;
(b) RIF-FF: 3 ml rifampicin (RIF) aqueous solution (154 mg rifampicin in 12 ml water);
(c) TMA-FF: 7 ml of 25% tetramethyl ammonium hydroxide (TMA-OH);
(d) CA-FF: 4 g citric acid (CA) in 8 ml distilled water.

Sodium oleate was chosen to coat the magnetite powder as being the best water-soluble substitute of oleic acid (known for its suitability for stabilizing oily magnetite suspensions) - the biocompatibility of water-soluble sodium oleate being evidenced in the literature [11-13]. Rifampicin was included within this study following the mathematical modeling of its structural and energetic parameters that revealed several molecular sites of putative interactions with iron cations [14-15]. Tetramethyl ammonium hydroxide is known as representative for electrostatic stabilization of magnetic nanoparticles in water [16-17]. Citric acid was chosen as able to provide also steric interactions with iron ions from the ferrophase [18-19].

The volume fraction of ferrophase within the magnetic fluid samples was assessed based on picnometric density measurements, and calculated with the following relation:

$$\Phi_M = \frac{\rho_F - \rho_L}{\rho_S - \rho_L} \tag{1}$$

where ρ_F – ferrofluid density, ρ_L - carrier liquid density, ρ_S – solid phase density.

Transmission Electron Microscopy (TEM) device from TESLA, having a resolution of 1.0 nm, was used to evidence and measure the physical diameter of colloidal nanoparticles, after ferrofluid sample 10^4 dilution in toluene and deposition on collodion sheet [9].

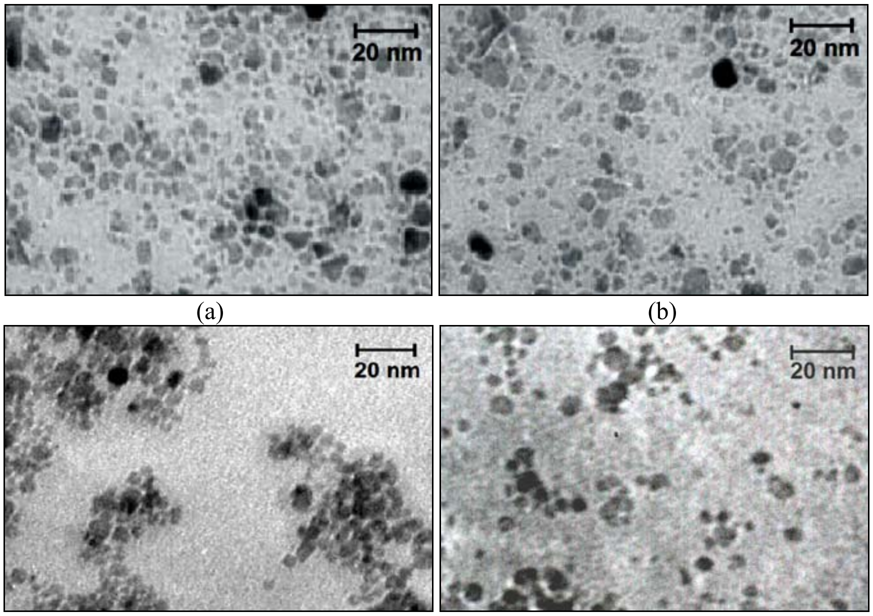
To characterize the crystalline structure of the magnetic nanoparticles, X-ray diffraction (XRD) method was applied on colloidal particles, using a DRON 2.0 X-ray diffractometer and Cu Kα radiation at 1.5418 Å [20].

Magnetization measurements were carried out by Gouy method using a Walker Scientific MG 50D Gaussmeter with a Hall probe and an electronic balance ACULAB-200 with 10^{-4} g accuracy. The measurements were performed at constant temperature (22.0±0.1 °C), using in all cases the same airtight nonmagnetic cylindrical sample holder with 3 mm diameter and 25 cm length, placed perpendicular to the magnetic field. Magnetic core diameter was estimated from Langevin's theory [21].

3. Results and discussion

The images recorded from TEM investigation of each sample are presented in Figure 1 a-d.

Mostly cvasi-spherical nanoparticles were visualized with rare particle aggregates of up to 35 nm sizes – that could actually exist into the ferrofluid or might result during diluted sample evaporation and deposition on the collodion sheet support. The average values of over 1,000 particles measurement were found of about 10 nm as can be seen in Table 1.



(a) (b) (c) (d)

Fig. 1. TEM recording images of the four ferrofluid samples: (a) SO-FF; (b) RIF-FF; (c) TMA-FF and (d) CA-FF

In the case of SO-FF and also for RIF-FF the physical diameter (d_{TEM}) was found to be higher than in the other two samples; however ferrophase volume fraction was higher in the mentioned samples (Table 1) with positive consequences on the sample magnetization.

Magnetometry investigation has led to the magnetization curves presented in Fig. 2. Similar values of mass density of saturation magnetization were recorded for SO-FF, TMA-FF, while lower mass density of saturation magnetization was evidenced for CA-FF one. For RIF-FF samples the saturation seems not to be reached up to the magnetization field of 800 kA/m – where the magnetometric recording was limited by the used device features. Sodium oleate is known as efficient surfactant for the steric stabilization in aqueous media almost like oleic acid for the stabilization in hydrocarbons so that it was actually expected to get a good ratio of ferrophase incorporation within the carrier fluid. TMA-OH is also known as an efficient stabilizer by electrostatic forces. RIF molecule was shown to present specific interaction sites with cations so we presume that good steric stabilization was also obtained for RIF-FF in spite of RIF large molecular size. CA molecule seems to develop lower strength interaction with magnetite particles resulting in lower level of ferrophase incorporation i.e. higher magnetization.

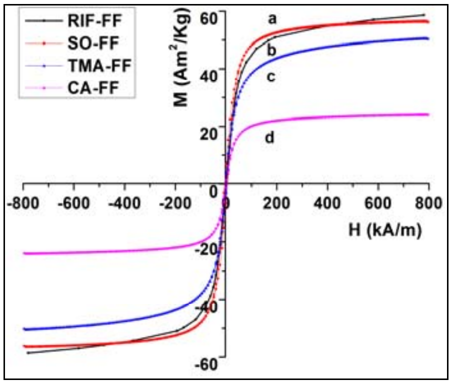


Fig. 2. Magnetization curves recorded for the prepared samples: (a) SO-FF; (b) RIF-FF; (c) TMA-FF and (d) CA-FF

From the magnetization curves the slope in the graph origin was assessed $((dM/dH))_{H\rightarrow 0}$ and the largest magnetic diameter d_M was calculated following Langevin's equation:

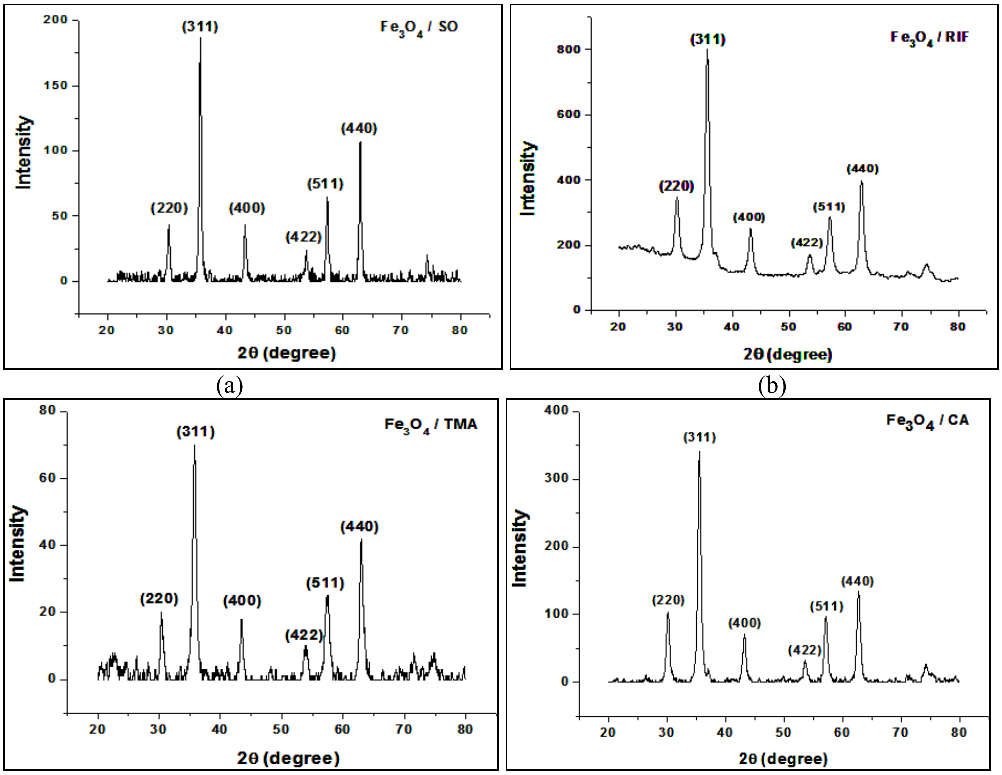
$$d_M^3 = \frac{18 \cdot k_B T}{\pi\mu_0 \cdot M_S \cdot m_S}\left(\frac{dM}{dH}\right)_{H\rightarrow 0} \qquad (2)$$

where d_M - magnetic particle diameter, k_B - Boltzmann's constant, T - absolute temperature, μ_0 - vacuum magnetic permeability, M_s - saturation magnetization of sample, m_s – saturation magnetization of the bulk magnetite [9]. The differences evidenced between d_{TEM} values and d_M values can be assigned to the surfactant shell of the magnetite core d_{shell} (Table 1) that resulted to be of about several nanometers in accord with fundamental theoretical studies [9]. The largest size of the non-magnetic coating shell might be the cause of lowest saturation magnetization noticed for CA-FF sample.

Table 1

Microstructural and magnetic parameters of the magnetite colloidal suspensions

Sample	Φ (%)	d_{TEM} (nm)	d_M (nm)	d_{shell} (nm)	M_S (A·m^2/kg)
SO-FF	3.14	11.98	9.28	2.70	56.00
RIF-FF	3.01	10.20	7.26	2.94	58.60
TMA-FF	2.42	9.20	6.23	2.97	50.00
CA-FF	3.11	9.70	6.28	3.42	24.00



(a) (b)

(c) (d)

Fig. 3. X-ray diffraction patterns corresponding to the prepared ferrofluids: (a) SO-FF; (b) RIF-FF; (c) TMA-FF and (d) CA-FF

All XRD recordings revealed the typical peaks of spinel structure – specific to magnetite with minor additional peaks provided by non-significant amounts of secondary crystalline structures like maghemite or hematite (Fig. 3).

The interpretation of the XRD diagram intensities (that depends on the experimental arrangement and the recording device, being proportional with the crystalline phase weight in the sample) has evidenced lower relative intensities (related to the highest peak) for the CA-FF sample (data not shown). This is consistent with lower crystallinity degree in the magnetite coated with citric acid although the preparation conditions were designed to be the same, but it is possible that some uncontrollable changes in certain reaction parameter have led to higher amorphous phase. The co-precipitation method – applied in this work – appears as one of most convenient and available laboratory technique to provide fine granulated submicron particles. However there are some practical issues related to the width of the size distribution curve of the fabricated nanoparticles with consequences not only on the particle suspension stability but also on the method reproducibility. Indeed it is difficult to ensure quite uniform temperature within the continuously stirred volume of the reaction medium and to control the stirring efficacy, which is crucial for the ferrophase coating and dispersion within the carrier fluid.

Some adjustments on the experimental details could be considered depending on the actual observations of each research group that has acquired some experience in the field – such as the replacing of distilled or deionized water with hydrochloric acid weak solutions for the dissolving of the metal salt precursors, the variation of the two phase time durations, the shortening of contact time with the air of the reaction vessel content, of the wet ferrophase during washings and filtration steps etc. This is why although the same background protocol is applied, different researchers may obtain different results and consequently the experimental details of the co-precipitation method remain an open problem.

4. Conclusions

The ferrophase nano-cores were obtained by applying the chemical co-precipitation method from precursor iron salts in alkali medium. Organic shells that we used to yield the stable magnetic nanoparticle suspensions were sodium oleate, citric acid, tetramethyl ammonium hydroxide and rifampicin. Comparative discussion on the four types of ferrofluids revealed similar microstructural and magnetic properties for magnetite coated with sodium oleate, rifampicin and tetramethyl ammonium hydroxide, while citric acid appeared as having lower efficiency in the interaction with magnetite cores. New investigations are planned to develop drug-targeting methods based on magnetite/rifampicin nanosystems magnetically controllable in order to improve their overall structural features like grain size, stability and especially magnetic properties that are going to be better emphasized - by magnetometric measurements at higher magnetic fields.

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