Some Physical Parameters of PEG-modified Magnetite Nanofluids

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Abstract: The development of the synthesis of stable aqueous suspensions of superparamagnetic iron oxide nanoparticles stabilized with unmodified polyethylene glycol (PEG) at two molecular weights (4000 and 6000 Da) and several PEG/iron ratios has been reported. The obtained biocompatible polymer (PEG) coated nanoparticle dispersive solution with pH ≈ 6.5 and solid phase content ranging from 0.02-0.75 % w/v has been investigated for optical and magnetic properties. Biomedical application requires the biocompatible superparamagnetic iron oxide nanoparticles (SPION), which are stable and well dispersed in water at physiological pH or in physiological salinity. Biocompatible 10-20 nm sized SPIONs have been synthesized via co-precipitation method in the vacuum environment. These SPIONs have been modified with PEG in one-pot synthesis. Vibrating Sample Magnetometer (VSM) studies show the effect of phase transformations on the magnetic properties of the nanoparticles and surfactant influence on the characteristic of the magnetization at room temperatures into high and low magnetic fields.

Keywords: Magnetic nanofluid, SPION, Biocompatible nanoparticles, Core/shell magnetic nanoparticles

1 Introduction

Magnetic nanoparticles are of great interest for researchers from a wide range of disciplines. In the past decade, the synthesis of superparamagnetic nanoparticles has intensively developed not only for its fundamental scientific interest but also for many technological applications [1-8].

Magnetic nanofluids (MNF) refer to the stable colloidal suspensions of magnetic nanoparticles (MNPs) in a nonmagnetic carrier fluid. Dispersion medium could be water, hydrocarbons, mineral and vacuum oils, silicon-organic liquids, physiological solutions and liquid metals [1-5] and dispersed phase of nanofluids - particles of iron, magnetite, cobalt, and other magnetic materials [3-4].

In most applications, to the nanoparticles demand to have specific sizes to prevent sedimentation. These sizes vary about 10-20 nm depending on the material [2-8]. If magnetic particles have a mean diameter of ~10 nm, thermal energy efficiently prevents sedimentation in a gravitational field or agglomeration produced by the dipole interaction resulting from the existence of a single magnetic domain in the particles. However, thermal energy does not prevent coagulation produced by the Van der Waals forces that induce a strong short range isotropic interaction [4,9]. To overcome this problem, the inorganic nanoparticle core must be coated with surfactants, polymers, polyelectrolytes, block copolymers or inorganic materials [3-5].

Another property that arises from finite size and surface effects is the existence of superparamagnetism at room temperatures. Each nanoparticle becomes a single magnetic domain. Such individual nanoparticles have a large constant magnetic moment and behave like a giant paramagnetic atom. Magnetizing strongly depends on the applied field, but retains no permanent magnetism once the field is removed. In other words, magnetic moments of superparamagnetic nanoparticles experience rapid relaxation, and in consequence, they show neither remanence nor coercivity [2-5,10].

In the last decade magnetic fluids based on iron oxide have

been successfully used in medicine among which magnetite (Fe_3O_4) and maghemite (γ–Fe_2O_3) are the very promising reagents since their biocompatibility has already been proven [13,14, 24].

The control of the monodisperse size is very important because the properties of the nanocrystals strongly depend upon the dimension of the nanoparticles. Besides, in order to understand ferrofluid behavior, improve applications or develop new ones, careful studies related to fluid stability, control of surfactants, particle sizes, materials, and physico-chemical properties are essential [13-16].

In the bio systems, surface modification of magnetic nanoparticles plays important role as uncovered nanoparticles with natural hydrophobicity of the surface experience agglomeration and are discoverable from body's system, mainly from the Kupffer cells in the liver. Usually, it should to Fe_3O_4 particles coated with an amphiphilic polymeric surfactant such as PEG to keep them from agglomerating, and in a such way minimize unwanted protein adsorption [17, 25].

PEG by its hydrophilicity, nontoxicity, absence of antigenicity and immunogenicity can be selected as a successful surfactant for magnetic iron oxide nanoparticles. The hydrophilic PEG molecules reduce phagocytic capture of nanoparticles by cellular components of the immune system leading to the extended circulation and subsequent accumulation in tumor cell as a consequence of the enhanced permeability and retention effect due to leaky vasculature and poor lymphatic drainage in tumors [13,19].

Because of nanoparticles are small enough to enter almost all areas of the body, including the circulatory system and cells, they have been and continue to be exploited for basic biomedical research as well as clinical diagnostic, magnetic bioseparation, detection of biological entities (cell, protein, nucleic acids, enzyme, bacteria, virus, etc.) [2,7,11], magnetic fluid hyperthermia (MFH), targeted drug delivery and biological labels [12,14].

In general, it is crucial to choose the materials for the construction of nanostructure materials and devises with adjustable biomedical, physical and chemical properties. On this basis, iron oxide MNPs are the strong candidates for such devices, and the application of iron oxide MNPs in in vitro diagnostics has been in practice for nearly half a century [13, 24].

In this work we are studying the magnetic and optical properties of PEG (4000 and 6000 Da) modified iron oxide nanoparticles which was synthesized via chemical co-precipitation in the vacuum (-0.1 Mpa). The influence of ultrasound processing on the stability and monodispersity of magnetic fluid has been investigated.

2 Experimental

The chemical co-precipitation method was used for obtaining Fe_3O_4 nanoparticles. 3g PEG-4000 (provided by Carl Roth Gmbh+ co. Kg - Germany) was diluted into 5 ml distilled water by magnetic stirring in vacuum environment separately at 40^0C. Once the polymer was dissolved, 0.16 g of $FeCl_2 \cdot 4H_2O$ and 0.435 g of $FeCl_3 \cdot 6H_2O$ (1:2 molar ratio of $FeCl_2/FeCl_3$) were added [9]. When the PEG and iron salts were well dissolved, 10 mL of a 0.75 M NH_4OH solution was added under vigorous stirring at a speed of 0.6 mL/min in vacuum(- 0.1 Mpa). After the addition of NH_4OH, the suspension was stirred further 30 min at 40^0C.

After synthesis, the ferrofluid poured into a beaker and placed on the permanent magnet. The ferrofluid washed several times with water by decanting the supernatant in order to remove excess of chemical reaction residues and polymer, since reversible flocculation and rapid sedimentation observed before washing. This caused by the depletion attraction created by unabsorbed polyelectrolytes in solution [9]. Finally, we got pH = 6.5 Sample labeled as "sample 1-1". After we processed this sample by ultrasound wave, (Sample labeled as "sample 1-2").

3g PEG-6000 covered magnetic nanoparticles has been prepared in the same way described above. Sample labeled as "sample 2-1". This sample processed by ultrasound wave also and labeled as "sample 2-2".

The TOPT-500 ultrasonic homogenizer with operating frequency 22 kHz and ultrasonic power 10-500W used for ultrasound processing. Horn diameter 10mm. 20ml Nanofluid processing time 7 minute in 20% of the ultrasound energy. One pulse Processing time 3 sec, pulse delay - 2 seconds. All samples (1-2, 2-2) processed with above-mentioned parameters.

For the magnetic measurements we selected 0.18 ml ferofluid samples with solid phase concentration range 0.6-0.75 g/100ml. Optical measurements was carried out with the samples of solid phase concentration range 0.02-0.03 g/100ml.

3 Results and Discussion

3.1 Magnetic Properties

Magnetization curves of all the above samples measured on the Vibrating Sample Magnetometer (VSM) at room temperature. Fig. 1 and Fig. 2 illustrates the magnetization curves M(H) of the samples 1-1, 1-2 , 2-1, 2-2 separately measured in the high magnetic field (up to 3 T) and low filed (0.2 T) regime (see insets). M (H) curves shows that the curves of all the samples have the similar character.

Any residual magnetization on the magnetization curve didn't observed. as seen from the graphs, In the low field, the magnetization increases rapidly with increasing magnetic field, becoming saturated at $H_a \approx 0.5$ T,This M(H) curve may be satisfactorily described by a Langevin profile:

$$\frac{M}{\varphi_t M_{sat}} = \left[\operatorname{cth}(\xi) - \frac{1}{\xi} \right] \qquad (1)$$

Where φ_t the volume concentration of magnetic material, and $\xi = \frac{\pi}{6} \frac{\mu_0 M_S \, H \, d^3}{k_b T}$ is Langevin argument for spherical particles, where H is the magnetic field strength, $k_b = 1,38 \cdot 10^{-23} \, J/K$, $\mu_0 = 4\pi \cdot 10^{-1}$ H / m is the magnetic constant, $M_{sat} -$ saturation magnetization [18].

The magnetization curves (Fig 1, Fig 2) indicates the presence of superparamagnetic nanoparticles in a magnetic ferrofluid. But it should be stressed that in the high field regime for the samples 1-1 (Fig. 1) in the range of |0.5|-|3| T the decrease of magnetization was observed (inset Figure 1's bottom left corner).

So, two magnetic components are observed: a paramagnetic component that may be described using the Langevin profile, plus a diamagnetic one that responds linearly to magnetic field.
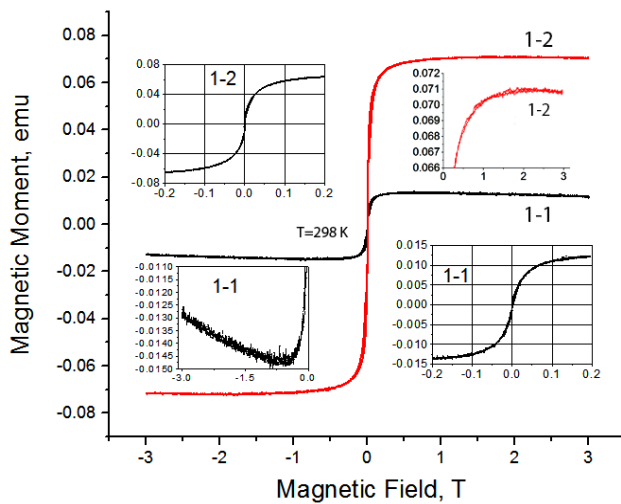

Figure 1. Magnetization curve of PEG- 4000 modifeid magnetite nanoparticles. 1-1 sample is unprocessed and 1-2 sample is processed by ultrasound wave.

As seen in the sample 1-1 (Fig.1) phenomenon of saturation magnetization in the direction of high external magnetic fields were not observed. Linear decrease of saturation magnetization on the magnetization curve of the sample 1-1, it seems caused due to the small diamagnetism of dispersion medium and surfactant molecules (in our case the PEG and distilled water). It should be noted that in the same sample this phenomenon after ultrasonic processing is not observed (2-2 Inset in the upper right corner of Fig. 1). This occurs when Lenz diamagnetic share is comparable to the saturation magnetization of the nanoparticles in magnitude (when the concentration of magnetic nanoparticles is small).

The difference in magnitude of saturation magnetization between the samples 1-1 and 1-2 (Fig 1) between the 2-1 and 2-2 (Fig 2) indicates an unequal distribution of PEG modified magnetic nanoparticles and surfactant molecules in unit volume for untreated samples. Apparently, ultrasonic processing stimulates uniform distribution of magnetic

nanoparticles and surfactant molecules in to the nanofluid providing further modifying of partially covered deaglomerated particles. Thus improves the degree of stabilization of the magnetic nanofluid.
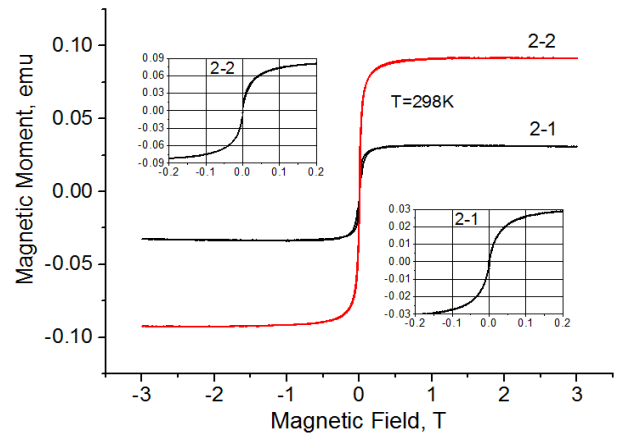

Figure 2. Magnetization curve of PEG- 6000 modified magnetite nanoparticles. 2-1 sample is unprocessed and 2-2 sample is processed by ultrasound wave.

With regard to the difference in magnitude of saturation magnetization between the PEG-4000 stabilized and PEG-6000 pegylated samples, this indicates the dependence of saturation magnetization on the type of the surfactant and thus full size of the nanoparticles.

3.2 Optical properties

The absorption of light, reflection, scattering and radiation of any material are highly dependent on the electrons of material, electrons' energy spectrum, and collective motion of the electrons into material. The last, the light induced collective vibration of electrons in the electrical field of lattice positive ions, described by quasiparticles called as Plasmon - a quantum of plasma oscillation that arises from the quantization of plasma oscillations. In the optical properties of materials, especially for metals plasmon plays an important role. The Incident light with lower frequencies than Plasmon frequency will not pass the material as the incident electromagnetic wave the faster moving electrons shielded. In addition, opposite, if the plasma frequency is lower than incident light, the electrons can no longer respond to the wave of change in the field and light passes through the material.

Figure 3 shows the optical absorption (A) of PEG-modified magnetic nanolfuid of Fe_3O_4 which measured in a scanning range of wavelength from 200 to 1000 nm, with scan interval of 0.2 nm. All sample concentration (0.6-0.75 wt/vol %) for the visibility of spectrophotometer reduced to about 0.03 wt/vol % by adding distilled water to the samples. Optical properties of nanoparticles investigated by measuring optical absorption spectra in the UV–visible region with AvaSpec-2048 Fiber Optic Spectrometer. By the optical absorption measurements, it is possible to monitoring the stability of nanoparticle solutions. The optical properties

of magnetite nanoparticles change when particles aggregate and the conduction electrons near each particle surface become delocalized and shared amongst neighboring particles. When this occurs, the surface Plasmon resonance shifts to lower energies, causing the absorption and scattering peaks to red-shift to longer wavelengths [28,29].
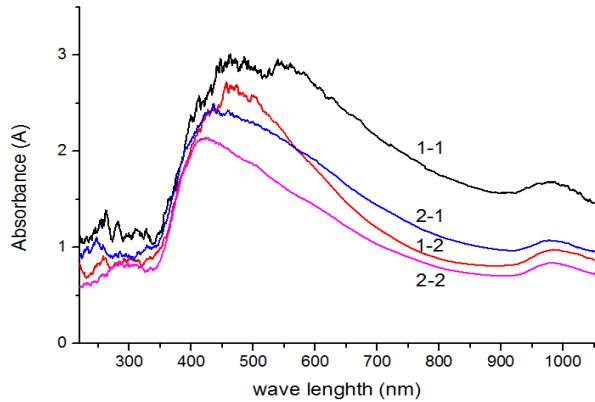

Figure 3.Optical absorbance spectra of PEG-4000 (1-1, 1-2) and PEG-6000 (2-1, 2-2) functionalized magnetite nanoparticles. Curve 1-1, 2-1 – Unprocessed ferrofluid; 1-2, 2-2 - ultrasound wave processed ferrofluid.

We compared unprocessed and ultrasound processed PEG modified fluids. Sample 1-1 on the Fig 3. Is primary fluid without processing, curve is wide than curve 1-2. The agglomerates in this case represented in a large scale. Larger spheres scatter more light both because they have larger optical cross sections. Ultrasound processing dispergates large particle by ultrasound wave and we get defined peak at 420 nm wavelength (curve 1-2).
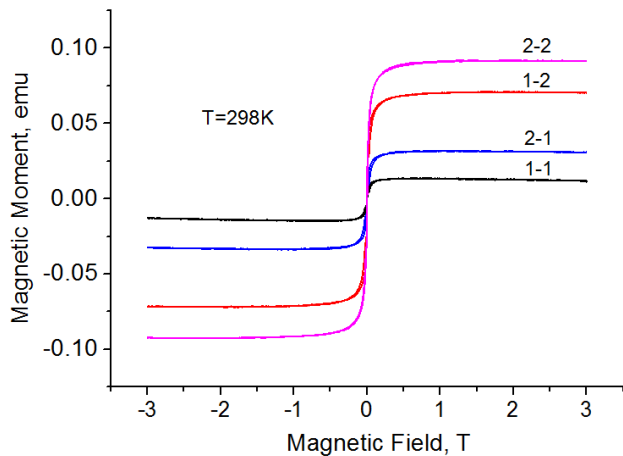

Figure 4. Magnetization curve of PEG- 4000 and PEG-6000 modifeid magnetite nanoparticles. Curve 1-1, 2-1 – Unprocessed ferrofluid; 1-2, 2-2 - ultrasound wave processed ferrofluid.

We get the same results for PEG-6000 samples (pic 2-1,2-2). The ultrasound processing makes the adsorption peak

narrower that indicates a high degree of dispersion (curve 2-2). UV–visible spectrometry can be used as a characterization technique that provides information on whether the nanoparticle solution has destabilized over time. Optical graphs are in good agreement with magnetic curves. The curves of narrower peak corresponds the magnetic curves of better magnetic and dispersive properties (Fig.4).

4 Conclusion

Thus, from the present work can be concluded that PEG-4000 and PEG-6000 stabilized magnetite nanofluid's magnetic properties depends not only the volume concentration of magnetic part, but on the size of the particles, types of the surfactant and processing after synthesis. Optical and magnetic measurement showed the priority of ultrasound processing of prepared samples.

Acknowledgments

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