

Dimensional comparative study of magnetic nanoparticles dispersed in water or kerosene

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The present study is focused on a comparison of the physical properties and dimensional characterization of magnetic nanoparticles suspensions in water or kerosene (aqueous versus oily magnetic fluids) prepared in our laboratories for biomedical or technical applications. The magnetic nanoparticles were prepared by chemical co-precipitation from ferric and ferrous salts in alkali medium. In the kerosene based magnetic fluids magnetic particles were coated with oleic acid at relatively high temperature in hexane medium. In the aqueous magnetic fluid the magnetic nanoparticles obtained by similar chemical co-precipitation method were dispersed following functionalizing with citric acid also at high temperature. Both types of nanoparticles colloidal suspensions were investigated by transmission electron microscopy (TEM), atomic force microscopy (AFM) and differential thermal analysis (DTA).

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1. Introduction

Nanoparticles have received considerable attention in the past two decades due to the interesting properties related to their size. Functionalized magnetic nanoparticles stably dispersed in polar or non polar fluids represent colloidal suspensions with superparamagnetic bulk properties (named magnetic fluids or ferrofluids) [1], were more and more used in science, technique, biology and medicine. Magnetic fluids have unique physical properties, thus they are useful in many areas, such as medicine, industry and education, having different applications.

Within the magnetic fluid systems the colloidal particles suspended in polar or non-polar solvents are near-spherical magnetic grains. Depending on the type of solvent, the nanoparticles are coated either with single or double layers of surfactant to prevent coalescing at room temperature. Some researchers was reported that hydrocarbon based magnetic fluids have a long stability in time than water based magnetic fluid [2]. The inherent particle clusters observed in water based magnetic fluid under zero applied fields were found by Jeyadevan *et al* [3]. But, ionic magnetic fluid that also uses water or kerosene as solvent didn't show inherent aggregates [4]. The complex structure of the magnetic colloids involves the assurance of their stability as required by both technical and biomedical applications. In order to prevent ferrophase particles agglomerations, good quality coating of small size particles need to be carried out.

2. Experimental

The basic procedure for ferrophase preparation was that proposed by Massart [5] consisting in the co-precipitation of ferric and ferrous oxides in alkali medium (NaOH 25%). Magnetite and possibly maghemite were precipitated from auto-catalysis reactions between ferric and ferrous salts namely $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Magnetic stirring was applied to favor chemical processes. After the solid phase separation by filtration and repeated washings with distilled water, the water traces were removed by repeated washings with acetone. Ferrophase particles yielded were coated with oleic acid respectively citric acid, at high temperature (over 80°C) under continuous (forty minutes), vigorous mechanical stirring and further kerosene respectively water was added as carrier liquid.

TEM investigation was performed using a TESLA device the particles being deposited on collodion sheet after convenient dilution (10^4) in toluene and evaporation of the initial suspension.

The AFM device used for this investigation works in the tapping mode with commercial standard silicon nitride cantilever (NSC21) having a force constant of 17.5 Nm^{-1} , 210 kHz resonance frequency and tips with radii between 10 and 20nm, the magnetic fluid dispersion (of adequately diluted samples) being deposited on mica substrate.

DTA investigations were carried out using a Mettler device and aluminum oxide as reference substance, the starting temperature being 20 °C and running at a heating rate of 10 °C per minute.

Comparative discussion was carried out on the average values of particles diameter distribution as resulted from TEM data while the particle aggregates were discussed mainly on the basis of AFM data – the 3D visualization allowing the measurement of aggregate height.

The box-plot technique, proposed by Koopmans [6], was applied to get comparative picture of magnetic fluid size distributions in the cases analyzed inhere.

The DTA data revealed the relatively high thermal stability of the magnetic fluids intended for technical applications.

3. Results and discussions

The TEM micrographs show that the size of nanoparticles ranges between 5 and 21 nm for water based magnetic fluid sample and respectively between 4 and 39 nm for kerosene based magnetic fluid, exhibiting mostly spherical shape. TEM image analysis was realized on about 1000 particles of magnetic fluid samples analyzed in this study. Fig. 1 shows a TEM image of the water based magnetic fluid stabilized with citric acid. Mostly round particles for both magnetic fluids were noticed but also some large aggregates and particle chains, especially for kerosene based magnetic fluid sample, have been also observed.

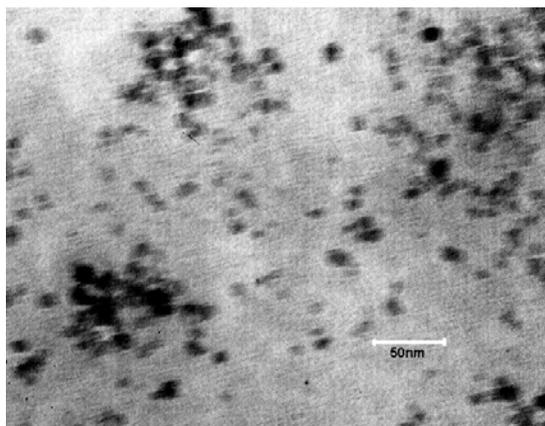


Fig.1. TEM image of water based magnetic fluid.

The analysis of all TEM pictures measurements resulted in physical diameter distribution histograms, built to evidence size distribution of the coated magnetic nanoparticles (Fig. 2), having maximum frequency at about 10.74 nm for water based magnetic fluid sample, respectively 11.65 nm for kerosene based magnetic fluid sample – lognormal function fitting the measured data. The narrowest distribution curve was obtained for water based magnetic fluid sample analyzed in this study.

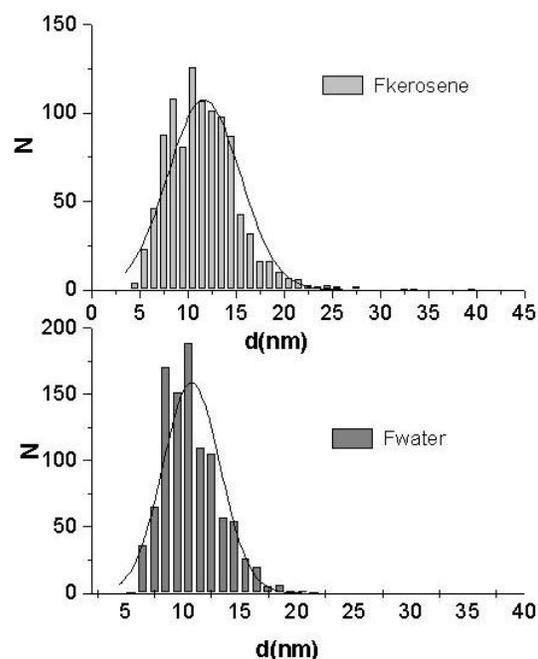


Fig. 2. Distribution histogram of magnetic fluids analyzed; F_{water} –represent the water based magnetic fluid sample while $F_{kerosene}$ represent the kerosene based magnetic fluid sample.

AFM investigation (with 5-10 times lower accuracy than TEM analysis method as limited by the radius of the available cantilever) gave the 2-D phase recordings as shown in Fig. 3 in the water based magnetic fluid sample case. In the Fig.4 the phase recording for kerosene based magnetic fluid sample is presented.

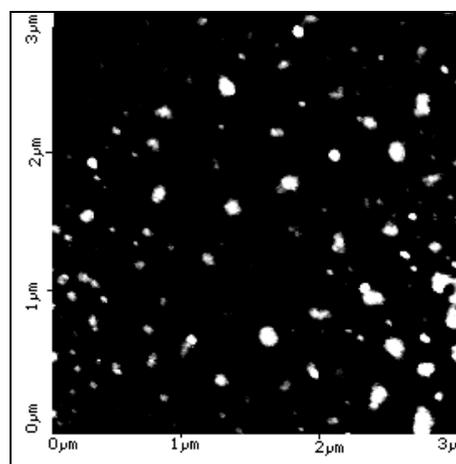


Fig. 3. 2-D image recorded using the AFM device for water based magnetic fluid.

Aggregates having quasi-spherical shape or short particle chains were revealed. Repeated scanning was performed on numerous areas in the frame of the mica deposition preparation so that the final number of the analyzed particles was equal to about 1,000.

Further investigations based on 3-D visualization by using AFM scanning to measure the height of the aggregates, was carried out (Fig. 5). The aggregate height was found to reach up to 38 nm in the cases of kerosene based magnetic fluid sample. It was shown that short chains of quasi-spherical particles were predominant among the particle aggregates.

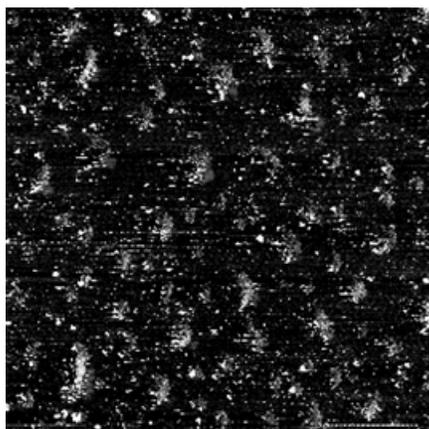


Fig. 4. Phase recording of ferrophase within kerosene magnetic fluid sample ($3 \times 3 \mu\text{m}$).

The presence of aggregates and short chains as evidenced on ferrophase deposition on solid support need to be considered also in the context of possible particle agglomeration even during solvent evaporation – the agglomerate presence in the magnetic fluid body being detectable by other methods such as neutron diffraction.

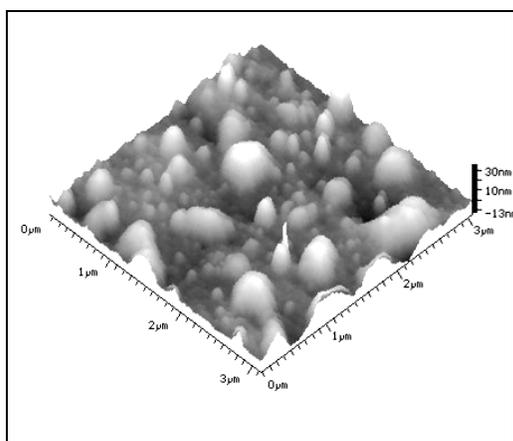


Fig. 5. AFM 3-D image recorded for kerosene based magnetic fluid sample.

Details on the structure of nanoparticles agglomerations from the carefully examination of the 3-D images obtained by means of AFM scanning can be extracted. Indeed, unlikely the TEM images, the AFM pictures can provide qualitative and quantitative information on the height of the scanned particles. In the

present cases of magnetic fluids analyzed in this study, the particles height was smaller than its diameter in most of the cases. However when we are dealing with nanoparticles agglomeration, the superposition of several nanoparticles may result in particle aggregates with relatively big height. In the 3-D recording the variable height of the mica substrate might contribute to the increase of the apparent height of the particle aggregates visualized on the respective mica sample.

The box-plot technique, proposed by Koopmans [3], was applied to get comparative picture between of these magnetic fluid samples size distribution. The box-plot representation is able to represent a distribution curve by means of a draw box, since practically all the values are shown.

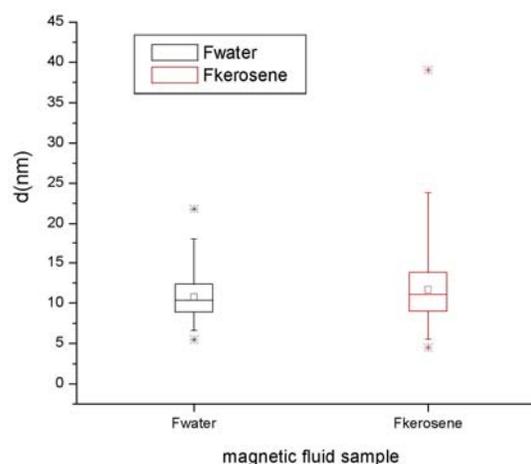


Fig. 6. Comparative box-plot diagram for dimensional distribution of magnetic fluids samples analyzed in this study. “o” represent average dimension of magnetic nanoparticles and “*” exceptionally small or large values of magnetic particles diameter.

From the box-plot data comparison (Fig. 6) one might see that the smallest size of colloidal nanoparticles and the most symmetrical and smaller box was obtained for magnetic fluid sample with water as carrier liquid.

The magnetic fluid sample with kerosene as carrier liquid, prepared by us, is characterized by greater values of the box parameters in comparison to the water based magnetic fluid sample analyzed in here. For kerosene based magnetic fluid the exceptionally large size particles was around 39 nm.

The box-plot representation method seems to be a convenient analytical method for the comparative study of ferrophase particles sizing regarding the special importance of magnetic fluid sample feature in the assurance of stability and biocompatibility.

Complementary data were obtained from DTA measurement (such information regarding the magnetic fluid composition and its behavior under thermal constraint are important when considering its technical applications). Significant temperatures were noticed at 95 °C, 150 °C, 200 °C and 250 °C - corresponding to the

magnetic fluid modifications that could be assigned to: (i) the loss of hydrocarbons and water traces from the carrier liquid; (ii) the free oleic acid or citric acid loss; (iii) the elimination of both ammonium ions (remaining from the synthesis alkali medium) and hydroxyl groups, respectively, attached to the ferrophase nanoparticles by hydrogen bonds.

4. Conclusions

The soft magnetic materials prepared by us are characterized by relatively small ferrophase particles and narrow distribution of physical diameter especially in the water based magnetic fluid sample. The revealing of exceptionally large diameter particles or agglomerations is useful in the microstructure analysis imposing the further improvement of preparation procedure.

The rather small diameter values and relative rare aggregates sustain the conclusion of the relative high stability of the prepared water based magnetic fluid and, consequently, their suitability for further applications in the specific fields.

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