JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 6, June 2007, p. 1633 - 1636

# Dimensional study about water based ferrofluids

M. RĂCUCIU*, D.E. CREANGĂ[a], N. APETROAIE[a], V. BĂDESCU[b]
*University Lucian Blaga, Faculty of Science, 10 Blvd.Victoriei, 550012, Sibiu, Romania*
[a]*University Al. I. Cuza, Faculty of Physics, 11A Blvd. Copou, Iasi, Romania*
[b]*National Institute of R. & D. for Technical Physics, 47 Blvd. D. Mangeron, Iasi, Romania*

Comparative study on the nanoparticles size of water based ferrofluids, prepared in our laboratories, as well as on other similar products presented in the literature reports was carried out by applying the transmission electron microscopy (TEM), atomic force microscopy (AFM) and magnetization measurements. The ferrophase magnetite core was prepared by chemical co-precipitation from ferric ($FeCl_3$) and ferrous salts ($FeCl_2$) in alkali medium (ammonia hydroxide) and functionalized with citric acid and respectively tetramethylammonium hydroxide. In both cases, the physical diameter of the ferrophase particles was measured using electron microscopy data. The diameter histograms revealed the main peak around 10 nm, which is concordant with a high degree of stability of the ferrofluid. The dimensional distribution of the ferrophase physical diameter was comparatively presented using graphical statistical method. The percentage of relatively small particles (under 5nm) was discussed comparatively with the percentage of relatively large particles (over 10nm). The presence of exceptionally large aggregates was also discussed in order to assess the quality of the magnetic colloids prepared by us in comparison with the similar products from several other countries. In order to extract complementary data on the ferrophase magnetic and physical diameter, measurements of magnetization and magnetic susceptibility were performed.

(Received November 14, 2006; accepted April 26, 2007)

***Keywords:*** Magnetic colloids, Acidic solutions, Box-plot analysis, Magnetic diameter

## 1. Introduction

Ferrofluids are known as a special category of smart nanomaterials, in particular magnetically controllable nanofluids. NASA was the first to develop and characterize ferrofluids in 1960's by Stephen Papell [1]. The complex structure of such magnetic colloids involves the assurance of their stability as required by both technical and biomedical applications. Nanoparticles with superparamagnetic properties have great potential to achieve such desirable properties for biomedical applications. In order to prevent ferrophase particles agglomerations, good quality coating of small size particles need to be carried out. Small size ferrophase is essential not only for homogeneity of the magnetic colloid but also for the efficient penetration of biological structures. Initially produced by milling large particles in suitable organic solvents [2], ionic ferrofluids are now prepared chemically, mostly by following the Massart's method [3]. In recent years, researchers have prepared new ferrofluids and ferrofluid products with biomedical purposes [4-5]. Colloidal stability is assured by coating the particle with a shell of nonmagnetic molecular surfactants which prevent close approach of the nanomagnetic cores thereby reducing the possibility of aggregation via van der Waals or magnetic attractions. The magnetic colloidal particles usually have a small diameter, in the range of 10nm that reduce the effect of the attractive interactions between the particles. Ferrofluid stability is the main characteristic that determines the possibility to exploit ferrofluids in different industrial and biomedical applications.

In the present work, we start a comparative dimensional study of ferrofluids with nanoparticles synthesized in our laboratory, by the same method, but coated with different molecules, such as citric acid and tetramethylammonium hydroxide.

## 2. Experimental

The synthesis of magnetic nanoparticles has been carried out via a controlled chemical precipitation approach, at room temperature, as described in [6]. Aqueous mixture of ferric and ferrous salts and $NH_3$ as an alkali source were prepared as stock solutions. The stock solutions of ferric and ferrous salts were prepared in presence of 2M HCl solution since the acidic conditions prevent formation of iron hydroxides. 1ml of 2M stock $FeCl_2$ solution and 4ml of 1M stock $FeCl_3$ solution were mixed under vigorous and continuous magnetic stirring with 50mL of 0.7M aqueous $NH_3$ solution, dropwise added. The resulted magnetite was decanted in an inhomogeneous magnetic field and then filtration was carried out to separate the supernatant. The magnetite was washed several times with deionized water. The obtained ferrophase (2g) was vigorously mechanically mixed with 6ml 25% aqueous solution of citric acid ($C_6H_8O_7$) for CA-FF sample and respectively tetramethylammonium hydroxide ($N(CH_3)_4OH$) for TMA-FF sample. All reactives were pure Merck products.

Both systems are designed to assure the colloidal suspension stability by electrostatic repulsion based on the charges of hydrosoluble citrate and respectively, the

tetramethylammonium cations adsorbed on the magnetite core.

Microstructural investigation was accomplished by means of AFM and TEM techniques. AFM device was provided with commercial standard silicon nitride cantilevers (NSC21) having a force constant of 17.5 $Nm^{-1}$, 210 kHz resonance frequency and tips with radii between 10 and 20 nm (intermittent contact, tapping mode cantilevers). The AFM images cover a range of areas, from 50 × 50 to 3 × 3μm. The ferrofluid dispersion (both diluted and non-diluted samples) was deposited on mica substrate.

Particle size distribution was studied using transmission electron microscopy (TEM). TEM photographs were made on a TESLA device with a resolution of 1.0 nm (sample deposition on collodion sheet after $10^{-4}$ dilution).

Magnetic susceptibility and magnetization measurements were carried out by Gouy method. Magnetic field intensity was measured by means of Walker Scientific MG 50D Gaussmeter with Hall probe. For sample weight an electronic balance ACULAB-200 with $10^{-4}$g accuracy was used. The measurements were performed at constant temperature (22.0 ± 0.1°C) using in all cases the same air-tight nonmagnetic cylindrical sample holder with 3mm diameter and 25cm length, placed perpendicular to the magnetic field. Using magnetization data, the average sizes of magnetic diameter was calculated following Langevin's equation. The size of large particles, which are influenced by low magnetic field, assuming a spherical particle shape, can be calculated with $d_M^3 = \frac{18k_BT}{\pi\mu_0 M_s \cdot m_s}\left(\frac{dM}{dH}\right)_{H\to 0}$ equation, 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, $\mu_0$ is the permeability of vacuum, and for the $m_s$ value of bulk magnetite was utilized $0.48 \cdot 10^6$ A/m [7].

The box-plot technique, proposed by Koopmans [8], was applied to get comparative picture of these ferrofluid size distribution and some other similar products. The box-plot graphical method is able to represent a distribution curve by means of a draw box, being recommended for both large and small data series, since practically all the values are shown. This representation method is consistent with the transformation of any distribution curve into a "box" provided with two "tails" and certain "outliers". In order to do this the range of experimental data is divided into three subintervals defined as follows.

First subinterval is given by the box length and is limited by the box edges, Q1 and Q3, corresponding to cumulative percentile frequencies of 25% and respectively 75%. This main subinterval contains about 50% of the total data points of the studied series.

The second subinterval is defined by the box tails, A1 and A3 calculated as Q1-1.5(Q3-Q1) and respectively Q3+1.5(Q3-Q1): about 80% of the total data points in the studied series can be found within the box tails, which includes the box length. A "median", corresponding to the cumulative percentile frequency of 50%, is plotted as a vertical line within the box. For symmetrical curves, this line overlaps the average value. In other cases, the "median" is able to indicate curve asymmetry, as do the box tail length too. Also, it was calculated the exceptionally large (>A3) or small (<A1) values (which are represented as white circles placed near the box).

Comparisons between related or similar data series can be successfully carried out by this suggestive visual representation, no matter if symmetrical or nonsymmetrical, monomodal or multimodal, comprising either few or many data points.

## 3. Results

Fig. 1 shows a TEM image of the magnetite particles coated with tetramethylammonium hydroxide. Mostly round particles for both aqueous ferrofluids were noticed but also some large aggregates and particle chains, especially for CA-FF sample, have been also observed.

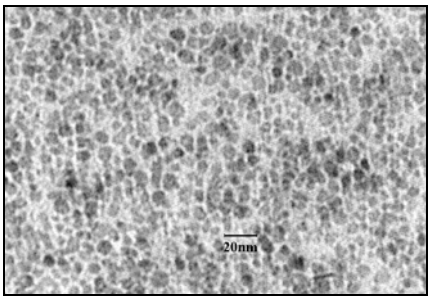


*Fig. 1. TEM image for ferrofluid coated with tetramethylammonium hydroxide*

The AFM images (2-D and phase recordings) are presented in Fig. 2 as 2-D and phase recordings carried out on 3 μm x 3 μm areas.

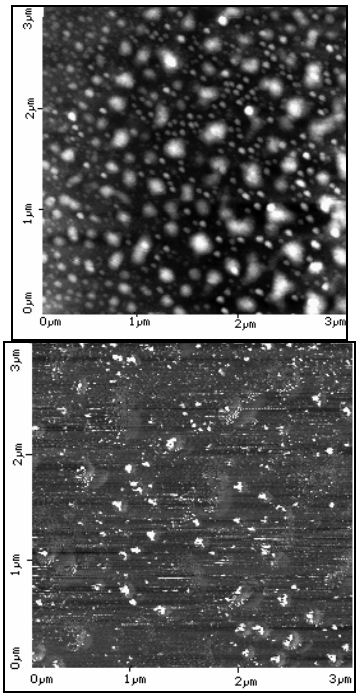


*Fig. 2. 2-D image (left) and phase recording (right) of magnetite-citrate colloidal particles; images size: 3μm x 3μm.*

In Fig.3 are presented the magnetization curves of aqueous ferrofluids batches synthesized in our laboratory. The saturation magnetization was obtained from magnetization versus $1/H$ curves, by extrapolating to $1/H = 0$. The initial susceptibility $\chi_i$ was determined from the susceptibility curve registered by extrapolating the initial linear curve to $H = 0$. Magnetic susceptibility value for the analyzed ferrofluids was of 0.17 for CA-FF sample and 0.3 for TMA-FF sample. The low values of the initial susceptibility for ferrofluids show small diameters and high densities of dispersed particles.

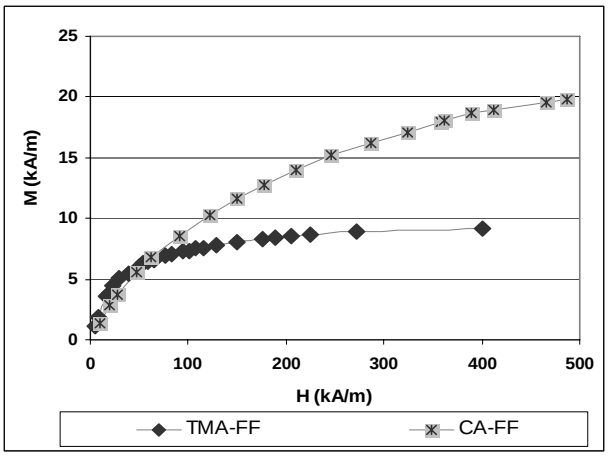


*Fig. 3. Magnetization curves of ferrofluids vs. applied field at room temperature. TMA-FF –coated with tetramethy lammonium hydroxide. CA-FF –coated with citric acid.*

Using magnetization data, the average magnetic diameter of ferrofluid nanoparticles was calculated according to Langevin's equation.

## 4. Discussion

The analysis of all TEM pictures measurements (Fig. 1) resulted in physical diameter distribution histograms (Fig. 4).

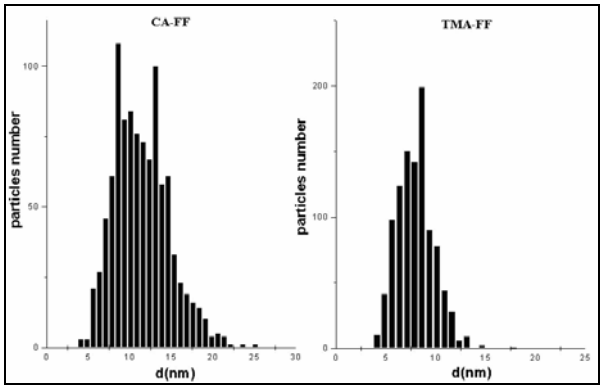


*Fig. 4. Diameter histograms for the analyzed ferrofluids.*

The maximum frequency corresponds to about 10.9nm in CA-FF sample and 8.1nm in TMA-FF sample.

The measurements carried out on the 2-D images and phase recordings in AFM tapping mode evidenced small particles but also particle agglomerations. Since the AFM tip radius was ranging between 5 and 10 nm the main reliable information provided following the dimensional analysis of data from Fig. 2 is concerning the large aggregates or particle short chains, confirming the TEM data regarding low percentage of more than 20 nm size structures in the CA-FF ferrofluid.

The interpretation of the magnetization measurements (Fig. 3) revealed that for the ferrofluid stabilized with citric acid (CA-FF) the saturation magnetization value is 23 kA/m, while for the ferrofluid coated with tetramethylammonium hydroxide (TMA-FF) the corresponding value is of 10 kA/m. For TMA-FF nanoparticles magnetic diameter of 7.9nm while for CA-FF nanoparticles of 5.9 nm were obtained. Differences evidenced between particle diameter values determined by TEM measurements and those provided by magnetization data, can be assigned to the surfactant layer on $Fe_3O_4$ nanoparticles surface. In Fig. 5 the box-plot diagram is presented for comparative discussion of dimensional distributions of ferrophase physical diameter in the water based ferrofluids synthesized by us with other aqueous ferrofluids presented in literature.

The comparison between TMA-FF and CA-FF samples and other aqueous ferrofluids reported in literature: S1-FF – stabilized with carboxidextran [5], S2-FF – stabilized with polyvinylic alcohol [9] and S3-FF – stabilized with dodecanoic acid [10], led to the results discussed below.

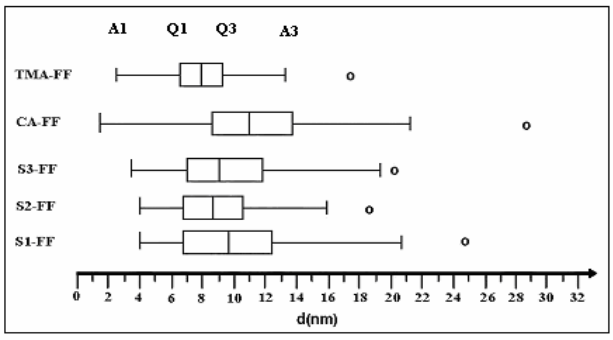


*Fig. 5. Box-plot diagram for dimensional distribution.*

From the box-plot data comparison (Fig. 5) one might see that the smallest size of colloidal particles and the most symmetrical box was obtained for TMA-FF ferrofluid batch synthesized in our laboratory. Indeed, the box corresponding to TMA-FF is small (2.70 nm) and situated toward the smaller diameter values, the median (about 7.8 nm) is symmetrically placed between the box edges Q1 and Q3 while the tails (Q1-A1 and Q3-A3) are equal (4.08 nm accordingly to Table I). In contrast, the CA-FF prepared by us is characterized by higher values of the box parameters in comparison to the other water based ferrofluids analyzed here, i.e. larger box length (5 nm),

median value (11 nm), larger tails (5.0 nm) and exceptionally large diameter (28 nm). This is not surprising since the other physical data presented above had already suggested that the best ferrofluid batch prepared by us is that stabilized with tetramethylammonium hydroxide. For both our ferrofluids exceptionally large size particles ranged between 17 and 28nm. In the Table I are presented also the box length values, right and left tail values for the aqueous ferrofluids presented in literature: S1-FF, S2-FF and S3-FF, which have larger box lengths (3.65, 5.63 and 4.88 nm) and larger right tail values (8.44, 5.47 and 7.30 nm) when compared to our TMA-FF. Regarding the acidic conditions of the chemical co-precipitation reactions resulting in ferrophase yielding we need to do a specific comment inhere.

*Table 1. Box-plot parameters.*

| Ferrofluid sample | Box length (nm) | Left tail (nm) | Right tail (nm) |
|---|---|---|---|
| TMA-FF | 2.70 | 4.08 | 4.08 |
| CA-FF | 5.00 | 7.5 | 7.5 |
| S1 | 5.63 | 2.64 | 8.44 |
| S2 | 3.65 | 2.73 | 5.47 |
| S3 | 4.88 | 3.64 | 7.30 |

Our preoccupation for the yielding of magnetite core - citric acid shell colloid has resulted previously in other ferrofluid samples prepared with neutral ferric and ferrous stock salt solutions accordingly to Goodarzi *et.al.* [11]. But the dimensional analysis showed particle agglomerations [12] considerably larger than in the present batch (up to 38 nm). Consequently, even if the CA-FF discussed inhere is characterized by still large distribution of particle diameter, however the acidic conditions allowed the avoiding of very large aggregate presence, further improving of preparation protocol remaining in our future plans.

## 5. Conclusion

In this study, the microstructural properties of two batches of aqueous ferrofluids prepared from acidic solutions of iron salts were analyzed. The stabilization of magnetic nanoparticles for biological uses was accomplished by coating the magnetite with citric acid and respectively tetramethylammonium hydroxide shell. As shown by TEM and AFM techniques, the suitability for biological purposes is assured by the fine ferrophase diameter, mainly for the TMA-FF ferrofluid, while the high magnetic properties are suggested also, mainly for CA-FF ferrofluid. The box-plot representation method seems to be a convenient analytical method for the comparative study of ferrophase dimension regarding the special importance of this ferrofluid feature in the assurance of stability and biocompatibility. Deeper physical investigations are intended in order to improve the yielding protocol while biological applications in plant biotechnology are planned also.

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*Corresponding author: mracuciu@yahoo.com