

SYNTHESIS AND RHEOLOGICAL PROPERTIES OF AN AQUEOUS FERROFLUID

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Ferrofluids are very stable colloidal dispersions of ultra-fine particles of a magnetic material, such as magnetite, in a liquid, which may be chosen to conform to a particular application. Since in future the applications of the ferrofluids will focus more toward the biological uses where the ultra-fine ferrophase is particularly important for the penetration of the cell structures. In these applications, it is proper to have a biocompatible solvent such as water at optimum pH, also. Ferrofluids containing superparamagnetic Fe_3O_4 nanoparticles have been prepared by a chemical precipitation method. The aggregation of the particles was prevented by using citric acid. Physical tests have been performed on two samples of the ferrofluid prepared by us (consisting mainly of Fe_3O_4 ultra-fine particles stabilized with citric acid and immersed in water). Physical tests have been performed on these samples.

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1. Introduction

Though known since decades the ferrofluids still represent modern advanced materials with consecrated technical applications and promising new utilizations in the life sciences. Since the magnetic fluids do not exist as natural materials the preparation of such stable magnetic colloids can be only the result of human activities, the continuous improving of the yielding protocol preoccupating more and more the specialized research teams. The control of magnetic particle size and distribution in the auto-catalysis reaction represents an actual technological challenge for all those interested to obtain metal oxide nanoparticles by using classical available chemical methods. The surface energy of metal oxide nanoparticles in suspension is in excess of 100 dyn/cm [1] meaning high surface to ratio volume, which results in the tendency to minimize the energy by particle aggregation. But large aggregates or particle chains potentially lead to precipitation, the magnetic dipole-dipole attraction contributing also to the colloidal suspension destabilization. Repulsive forces could be controlled by using convenient solvent and surfactant molecules only an adequate fitting of these two components being able to assure the thermodynamically stable magnetic colloids. The convenient coating of metal oxide cores of ferrofluid ferrophase results also in the protection against metal oxidization (which decreases the magnetic properties) within the carrier fluid as well as in the biocompatibility improvement in case of bio-medical uses. The water-ferrofluids based on magnetite cores are the basic products intended for the utilization in the medicine and biology; the ferrophase coating with high molecular weight molecules of acids or hydroxides favorize the repulsive forces action leading to either steric or electrostatics stabilization. Adsorption of different ligands as citric, tartaric, gluconic, glucuronic and 2,3 - dimercapto-succinic acid on maghemite is already studied using conductometric measurements [2-3]. The use of citrate

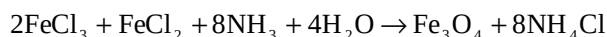
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shell around the magnetite or cobalt-magnetite ferrophase was investigated in several recent studies [4-7].

In this paper the authors present their results regarding the preparation and characterization of some microstructural and rheological properties of a water-ferrofluid prepared as an aqueous dispersion of magnetite core coated with citric acid.

2. Material and method

Ferrofluid preparation. Magnetite (Fe₃O₄) particles were prepared by chemical precipitation of FeCl₂ and FeCl₃ (1:2 molar ratio) by the addition of 25% ammonia solution [5]. In a typical reaction, 4.3 g FeCl₂ and 11.75 g FeCl₃ were mixed in 200 ml water and heated to 80 °C.



The volume of reaction mixture have been mixed under magnetic stirring during continuous slow addition by a syringe of 25 ml to 25% ammonia solution and the heating continued for thirty minutes. Magnetite, a black precipitate, was decanted in a variable magnetic field and washed with 500 ml distilled water. After that, 5g of citric acid (C₆H₈O₇) in 10 ml water was introduced and the temperature was raised to 90 °C. All reactives were pure Merck products. Further the magnetite was vigorously mechanically mixed with aqueous citric acid continued for an additional sixty minutes. The physical characterization carried out for two of the samples (L₁ and L₂) prepared following this procedure was further discussed (these two ferrofluid samples differ from the viewpoint of the mixing procedure: the L₁ sample was magnetically and non-magnetically mixed (for equal time durations of 20 minutes) while the L₂ sample was only non-magnetically mixed (for 40 minutes).

Rheological characterization. The ferrofluid density (picnometric method), viscosity (capillary method with an Ostwald viscosimeter) and surface tension (stalagmometric method) have been measured using standard methods. The electrical conductivity measurements on the ferrofluids samples were performed with a standard universal device LCR [2]. The pH measurements were carried out with universal indicative paper (Merck) [8].

Microstructural investigation. Transmission electron microscopy (TEM) infrared absorption spectra (IR) and thermal differential analysis (DTA) were the main investigation methods. For the assessing of the ferrophase particle size, a TESLA device with a resolution of 1.0nm (sample deposition of collodion sheet after 10⁻⁴ dilution) was used. Infrared absorption spectra have been recorded using a Perkin Elmer 580 device for the scanning of the ferrofluid dispersion in KBr after previous thermal treatment at 100 °C up to constant weight. The DTA investigation was accomplished using a Mettler device at a heating rate of 10 °C/min.

The box-plot statistical analysis of the distribution curves [9] was applied in order to compare ferrophase diameter histograms for the two ferrofluid samples prepared by us (L₁ and L₂).

3. Results and discussion

The ferrofluid macroscopic homogeneity was obvious following the visual inspection upon the reaction vial when submitted to the action of a relatively weak magnetic field. The values of the measurements carried out on the ferrofluid samples are presented in the next graphics in comparison with water (the carrier liquid). In Fig. 1 can be seen the values of density, viscosity, surface tension and electroconductivity for the ferrofluid samples in comparison with the same values for water (carrier liquid).

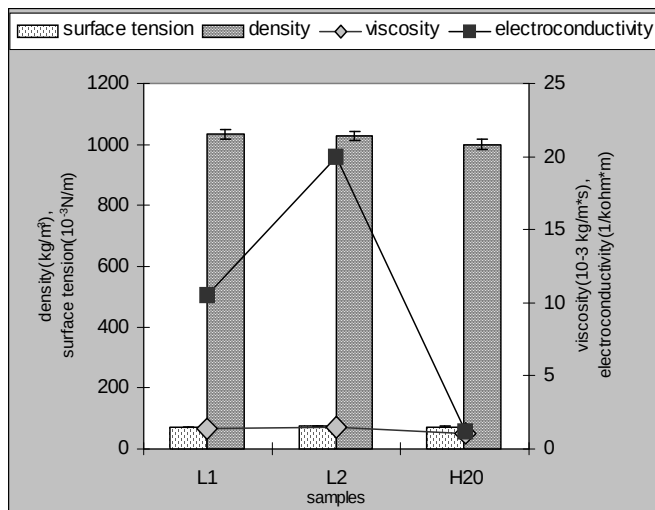


Fig. 1. The density, viscosity, surface tension and electroconductivity values for the ferrofluid samples and water (carrier liquid).

The highest viscosity was revealed for L_2 sample – which may suggest that the application of the non-magnetic mixing procedure is desirable (probably during the magnetic stirring certain perturbation of the colloid stability occurs resulting in some ferrophase precipitation remained on the reaction container walls). The electric conductivity is also higher in L_2 which also recommend this ferrofluid for further utilization. Both samples have convenient physiological pH values (6.5-7.0). TEM investigation revealed rather small particles (fig. 2) that are able to ensure the colloid stability in agreement with the theoretical consideration of Rosenweig [10] that found (from energy and forces equilibrium conditions) the $d < 7.8$ nm (d being the ferrophase physical diameter) in a good ferrofluid.

The statistical analysis of the diameter distribution in L_1 and L_2 is presented in Figs. 3 and 4. In Fig. 3 are given the histograms resulted from the measurements on the TEM pictures.

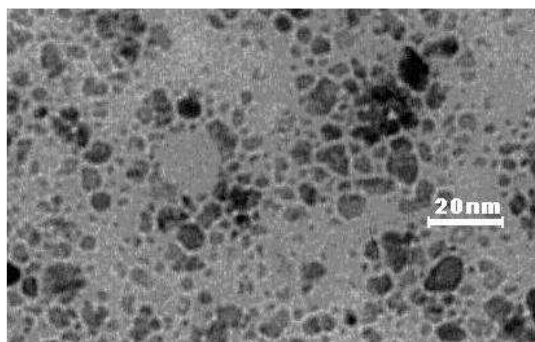


Fig. 2. TEM image for L_1 ferrofluid sample.

The maximum frequency values correspond to about 10.64 and 7.47 nm. Average values as well as exceptional large aggregates (still present in the samples) are presented by means of the box-plot representation (Fig. 4). The average values are 10.64 nm for L_1 and 7.47 nm for L_2 (while median values are 9.9 nm for L_1 and 7 nm for L_2). The L_2 box is shifted to smaller diameter values indicating a better distribution. Exceptionally large size particles ranged between 30 and 38 nm for both ferrofluid samples analyzed. In figure 6 is presented the histogram for L_1 ferrofluid sample. The

histogram to both ferrofluid samples have been transformed into a box for comparison picture (Fig. 7).

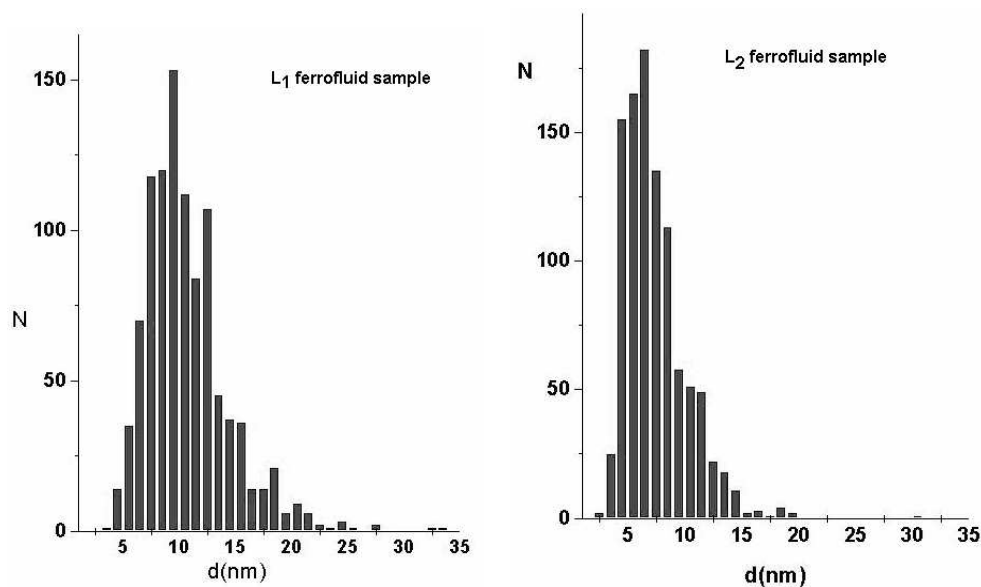


Fig. 3. The histogram picture for L₁ and L₂ ferrofluid samples.

The relatively small values of the box edges as well as of the median value confirm that the ferrophase is rather convenient for biological uses.

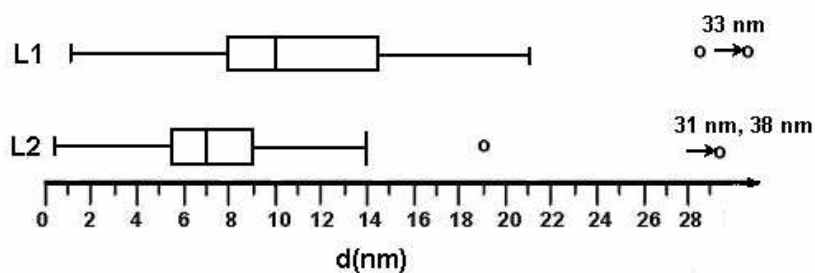


Fig.4. The box-plot representation for both ferrofluid samples.

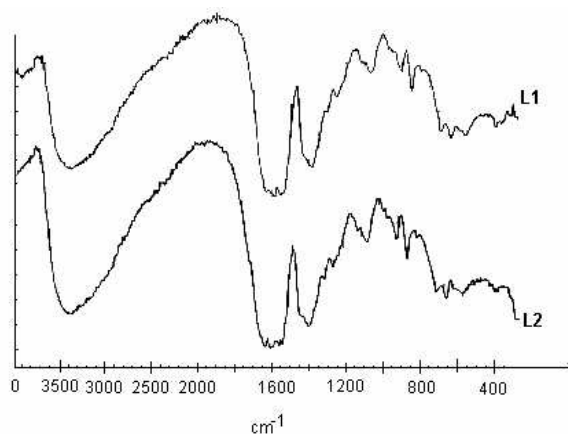


Fig. 5. The IR spectra for L₁ and L₂ ferrofluid sample.

The IR investigation was carried out on the range between 4000 cm^{-1} and 600 cm^{-1}) revealed the following:

- the large and intense band from 3450 cm^{-1} confirms the presence of hydrate H_2O while the absorption at $3200\text{--}3400\text{ cm}^{-1}$ suggests the non-dissociated OH groups of the citric acid.

- the intense band at 1600 cm^{-1} may be assigned to the symmetric stretching of OH from COOH group while the neighbor band at 1400 cm^{-1} to the asymmetric stretchings of CO from COOH group can be assigned.

- The free COOH groups are expected to contribute to the 1710 cm^{-1} absorption.

The ferrophase “skeleton” vibrations ranged between 800 cm^{-1} and 400 cm^{-1} .

The DTA investigation (Fig. 6) revealed two main thermal events: at about 230°C and close to 300°C which could be assigned to desorption of physical bonded citrate ions and, respectively, to the iron citrate elimination. The preliminary results are in agreement with the data reported in literature. Further investigation is designed aiming to reveal the magnetic properties of the colloid produced following this methodology.

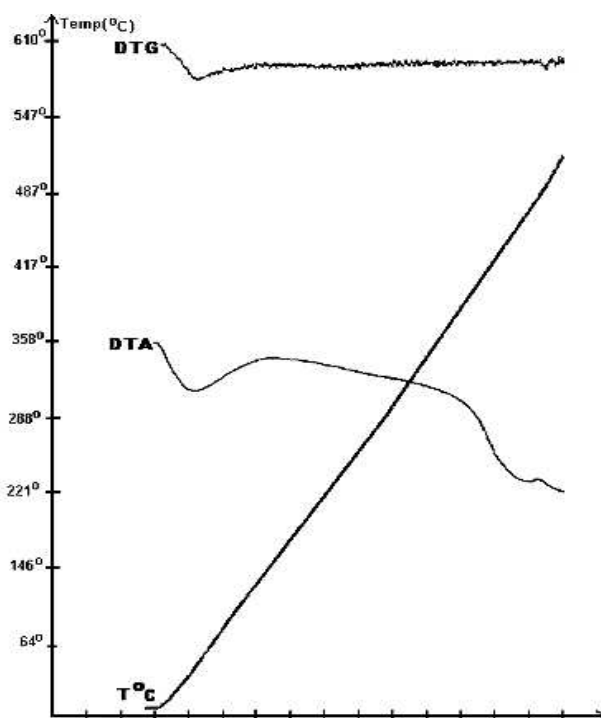


Fig. 6. The DTA investigation results.

4. Conclusions

Stable magnetic colloid, prepared by using the citric acid as stabilizer in water dispersion, was adjusted in order to get physical parameters in agreement with the literature data. Its future destination for living tissues applications will be accompanied by adequate measurements of the biological effects.

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