Microstructure investigation of a $CoFe_2O_4$/lauric acid/DDS-Na/H_2O ferrofluid

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Preliminary microstructural results on a new $CoFe_2O_4$/lauric acid/DDS -Na/H_2O ferrofluid by means of small angle neutron scattering (SANS), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) are presented. The ferrofluid was prepared by coprecipitation of $Fe(OH)_3$ and $Co(OH)_2$, ferritisation of hydroxide mixture in 1M alkali aqueous solution, adsorption of lauric acid on ferrite particles and peptisation of hydrophobic precipitate in aqueous solution with sodium n-dodecylsulphate. TEM images reveals that though the sizes and the geometrical forms are not uniform, the particles, partially shows rhomboidal shape. The model fit of SANS data gives triaxial ellipsoid and ellipsoidal shell, as objects characterizing the investigated system. Both techniques confirm the simultaneous presence of particles and surfactant. The synthesis procedure of the water suspension of the $CoFe_2O_4$ nanoparticles used in the present work appears to be very promising from the aspect of the stability properties and rather high particle concentration improvements.

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1. Introduction

Ferrofluids, ultrastable dispersions of magnetic nanoparticles in liquids [1,2], find a wide range of applications in many technical and industrial fields [3-10], as well as in medicine and biotechnology [11-17].

Nowadays researches on developing ferrofluids with new types of particles [18-25], new synthesis methods [26-30], increased particle concentration [31-36], using different stabilization methods [37-41] and compounds [42-46] are in progress. Water-based ferrofluids present the most complex microstructural behavior and their properties improvement represents an important challenge in this field [29, 47-55].

The knowledge about the microstructure of ferrofluids is very important to understand and control the mechanisms of their stabilization. The non-ionic ferrofluids in contrast to the ionic ones [56, 57, 58], often show the presence of aggregates in their structure even at low particle concentration and in the absence of the magnetic field [59, 60, 61, 62]. These factors diminish the long-term stability of the ferrofluids.

Cobalt ferrite nanoparticles ($CoFe_2O_4$) have received increasing attention for the combination of their bulk magnetic properties (high coercivity at room temperature, moderate saturation magnetization) with the magnetic properties typical of nanoparticles (superparamagnetism) that make them ideal materials for technological and medical applications [63, 64]. $CoFe_2O_4$ is shown as a promising material for high-density recording, due to its excellent electrical and magnetic properties [65, 66, 67] and catalysis [68].

There is continuing interest in magnetic nanoparticles, especially because of their applications in the fields of imaging and therapy [69, 70]. Among these applications, the treatment of tumours by hyperthermia has been recognized as very promising, and the efficiency of cobalt ferrite, $CoFe_2O_4$, nanoparticles has been established [71-73]. Recently emerged a growing interest for investigating effects of magnetic cobalt ferrite nanoparticles on biological and artificial lipid membranes [74], on microorganism cells [75] and for targeted delivery of DNA into tissues and cells [76].

Several $CoFe_2O_4$, nanoparticles synthesis processes have been proposed, such as the sol–gel method [77], chemical coprecipitation [73,78,79,80], spraying coprecipitation [81], forced hydrolysis in a polyol medium [82,83], forced hydrolysis and combustion method [84], synthesis in oil-in-water micelles [85], synthesis in reverse micelles [86] or thermal decomposition of amixed Co2+–Fe3+ oleate complex [87,88], hydrothermal preparation [89].

In the present paper results on the structure of a new non-ionic $CoFe_2O_4$/lauric acid/DDS-Na/H_2O ferrofluid investigation by means of small angle neutron scattering

(SANS), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) are presented.

2. Experimental

The ferrofluid was prepared at the Institute of Technical Chemistry (Perm) [90,91] by the coprecipitation of $Fe(OH)_3$ and $Co(OH)_2$, ferritisation of hydroxide mixture in 1M alkali aqueous solution, adsorption of lauric acid on ferrite particles and peptisation of hydrophobic precipitate in aqueous solution with sodium n-dodecyl sulphate.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis were carried out on a LEO 912 AB OMEGA transmission electron microscope with an accelerating voltage of 120 kV (Advanced Technology Centre, Moscow). One droplet of water dispersion of $CoFe_2O_4$ nanoparticles was dropped on a carbon-coated copper grid and then dried naturally before recording the micrographs.

Small angle neutron scattering (SANS) experiments were performed at the time-of-flight YuMO spectrometer in two detector mode [92] at the high flux pulsed IBR-2 reactor, JINR Dubna. The Sonix+ software system accomplishes the control of the spectrometer [93]. The experiments were carried out at a sample-to-detector distances of 5.28 m and 13.04 m, resulting in a Q range of 0.007÷0.3 A^{-1}. The sample diameter and thickness in the beam were 14 mm and respectively 1 mm. The measured neutron scattering spectra were corrected for the transmission and the thickness of the sample, background scattering on the experimental cuvette and on vanadium reference sample using the SAS software [94], providing a neutron scattering intensity in absolute units of cm^{-1}.

3. Small angle neutron scattering method

Small-angle neutron scattering (SANS) has been shown to be a valuable technique for studying the properties of magnetic fluids (e.g. [62, 95-109]), which characteristic structural features lies mostly in the interval of 1-100 nm.

The scattered intensity on an absolute scale for any interacting particulate systems of scatters can be expressed as [110]:

$$I(Q) = \phi P(Q) S(Q) \tag{1}$$

where: Q is the modulus of the scattering vector defined as $Q = (4\pi/\lambda)\sin(\theta/2)$, with the scattering angle being θ; $\phi = N/V_0$ is the density of particles in the volume V_0 of the sample, $P(Q)$ concerns each particle and is related to its form factor, $F(\vec{Q})$, by

$$P(Q) = \left\langle \left| F(\vec{Q}) \right|^2 \right\rangle$$

with

$$F(\vec{Q}) = \int_{\text{Volume of particle}} (\rho - \rho_0) \exp(i\vec{Q}.\vec{r}) dV$$

ρ and ρ_0 are the coherent lengths densities of the particle and respectively of the polymer matrix.

$S(Q)$ is the interparticle term-the structure factor-related to the spatial distribution of the centers of mass.

$$S(\vec{Q}) = \left\langle \sum_{\alpha,\beta} \exp i\vec{Q}(\vec{R}_\alpha - \vec{R}_\beta) \right\rangle$$

$\langle .... \rangle$ denotes a statistical average and is taken over the available positions and orientations of the particles.

In this work, small-angle neutron scattering (SANS) is applied to a new water based ferrofluid to reveal its structural features.

4. Results

4.1. Transmission electron microscopy and selected area electron diffraction

The morphology and microstructure of the $CoFe_2O_4$/lauric acid/DDS-Na/H_2O ferrofluid sample, preliminary treated in Biofuge 15R (Heraeus instruments) 2 times 6000 rot/min for 60 min., was examined using TEM, SAED, as shown in Fig. 1 and Fig. 2. The micrographs show fine particles, mostly nonagglomerated. The TEM micrograph in Fig.1a reveals that though the sizes and the geometrical forms of the particles are not uniform, a part of the particles shows clearly a rhomboidal shape (Fig.1b).

(a)

(b)

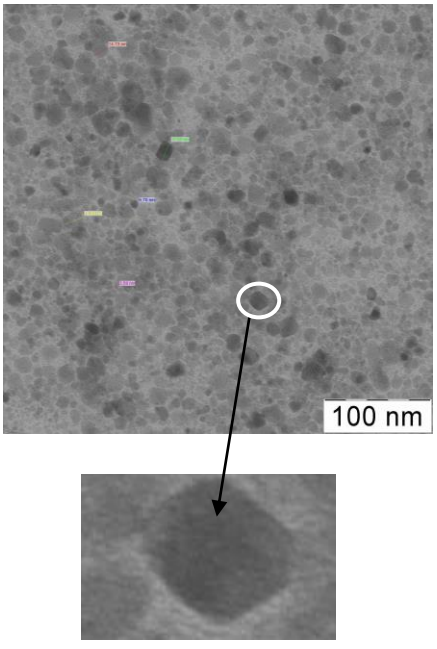


Fig.1 TEM image of: (a) 3% particle vol. concentration $CoFe_2O_4$/lauric acid/DDS-Na/H_2O ferrofluid; (b) a rhombohedra particle.

In between the particles, very small objects of low contrast could be surfactant remains.

The size of the nanoparticles physical diameter was determined from the TEM micrographs using powerful image analysis software [ImageJ] [111].

The program Python 2.7.5 performed the data processing of the size distribution. Forming and mapping of the normed histogram was implemented by the built-in library matplotlib.pyplot.

Forming of the histogram fitting function was carried out using the scipy.optimize built-in libabry. Built-in libraries math and numpy were used for performing some of the intermediate calculations.

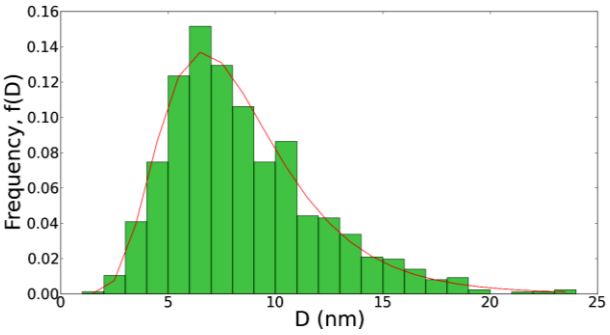


Fig.2. The size distribution histogram of $CoFe_2O_4$ particles from TEM image.

Lognormal distribution with the following parameters is obtained as the histogram fitting function:

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma D} \exp\left(-\frac{\ln^2 (D/\mu)}{2\sigma^2} \right),$$

where $\mu = 2.056$ and $\sigma = 0.164$

Mean value of D respectively equals to: $\bar{D} = 8.48nm$

The selected-area electron diffraction (SAED) pattern of $CoFe_2O_4$ clearly shows the crystalline nature of the product, indexed to (111) (220), (311), (400), (422), (511), and (440), respectively, for the diffraction rings. The electron diffraction rings indicate the nature of single-phase crystallite with $CoFe_2O_4$.

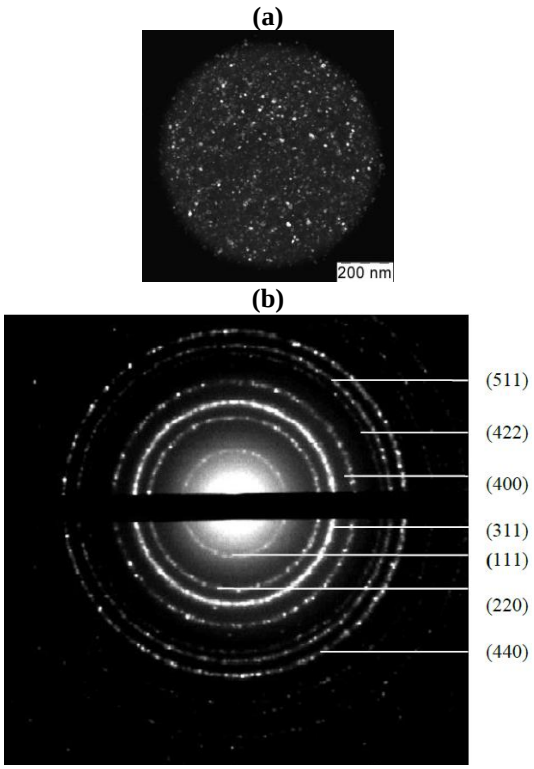


Fig.3 Selected aria electron diffraction (SAED) pattern of $CoFe_2O_4$ particles: (a) image of the sample selected area; (b) electron diffraction pattern.

4.2 Small angle neutron scattering

The evolution (in a log-log plot) of the scattered intensity vs. the scattering vector for the 3% $CoFe_2O_4$/lauric acid/DDS-Na/H_2O particle vol. concentration ferrofluid sample is shown in Fig.4.

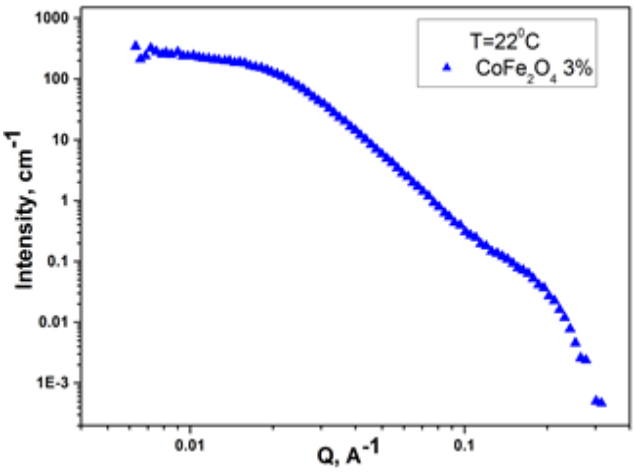


Fig.4 SANS experimental curve of 3% $CoFe_2O_4$/lauric acid/DDS-Na/H_2O particle vol. concentration ferrofluid sample.

Determination of invariants for small-angle scattering curves allows one to analyze the structure of the particles under study. Upon the first step of this analysis, the particle form is approximated by simple geometrical bodies: ellipsoids, cylinders, prisms.

Detailed information on SANS intensity expression for different scattering model objects is available in [112].

Using the FITTER program [113] to model the experimental curve, there were obtained two models:

(i) For the range of 0.07 Å^{-1}≤ Q ≤0.8 Å^{-1} it was found for form factor a triaxial ellipsoid model described by the expression:

$$P(Q) = A\int_0^1\int_0^1 \Phi\left[Q\sqrt{\left[(a^2\cos^2\frac{\pi}{2}x + b^2\sin^2\frac{\pi}{2}x)(1-y^2) + c^2y^2\right]}\right]^2 dxdy + B$$

$$\text{where } \Phi(t) = 3\frac{\sin t - t\cos t}{t^3}$$

(ii) In the range of 0.8 Å^{-1}≤ Q ≤0.3 Å^{-1} is determined a triaxial ellipsoidal shell model described mathematically as follows

$$I(Q) = \mathrm{A}\int_0^1\int_0^1 [V_t\Phi\left(Q\sqrt{\left((a+t)^2\cos^2\frac{\pi}{2}x + (b+t)^2\sin^2\frac{\pi}{2}x\right)(1-y^2) + (c+t)^2y^2}\right)$$

$$-V_c\Phi\left(Q\sqrt{\left(\left(a^2\cos^2\frac{\pi}{2}x + b^2\sin^2\frac{\pi}{2}x\right)(1-y^2) + c^2y^2\right)}\right)]^2 dxdy + B$$

$\Phi(t) = 3\frac{\sin t - t\cos t}{t^3}$; $V_c = \frac{4}{3}\pi abc$, volume of core; $V_t = \frac{4}{3}\pi(a+t)(b+t)(c+t)$, volume of core with shell.

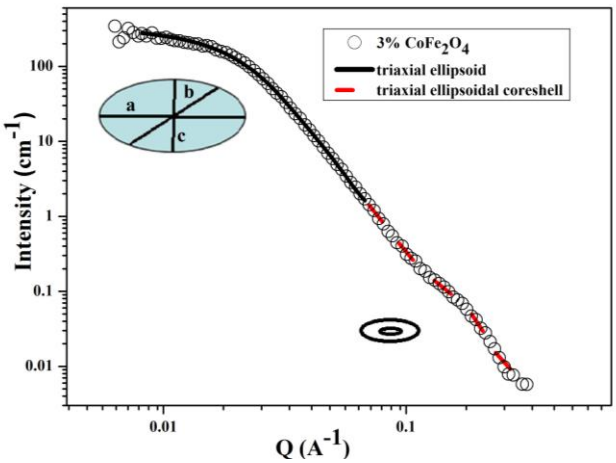


Fig.5 Model curve fitting the experimental data of 3% $CoFe_2O_4$/lauric acid/DDS-Na/H_2O particle vol. concentration ferrofluid sample with FITTER program.

The model curve fitting of the sample experimental data (see Fig.5) gives the following parameters for the determined structural objects:

(i) Triaxial ellipsoid with half axes (schematic figure in the upper side of Fig.5):

$$a = (15.2 \pm 0.4)nm$$

$$b = (10.85 \pm 0.2)nm$$

$$c = (5.0 \pm 0.1)nm$$

(ii) Triaxial ellipsoidal shell (schematic figure in the lower part of Fig.5):

$$a_{core} = (1.5 \pm 0.02)nm$$

$$b_{core} = (3.2 \pm 0.02)nm$$

$$c_{core} = (5.2 \pm 0.2)nm$$

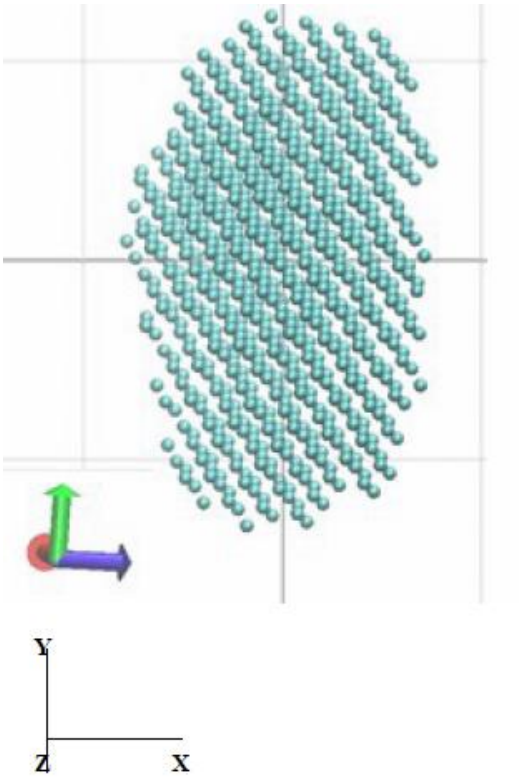
$$t_{shell} = (3.3 \pm 0.1)nm$$

The triaxial ellipsoid model with the obtained half axes values fits the big mono and double particles shape, while the determined triaxial ellipsoidal shell object correspond to micelles description.

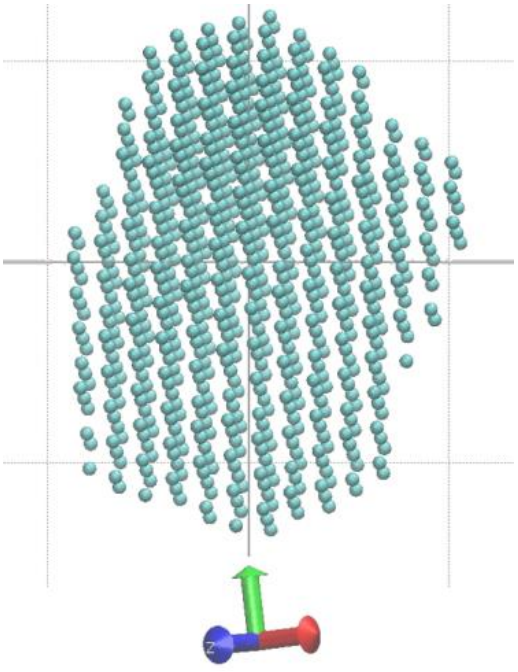
Further, the scattering curve was analyzed using model calculations included in ATSAS Package (GNOM, DAMMIN, DAMAVER) program [114].

It was accomplished the ab initio analysis aiming the recovering of three-dimensional structure from one-dimensional scattering curve. The program DAMMIN implements a method to restore ab initio low-resolution shape of randomly oriented particles in solution [115],

while DAMAVER is a set of programs to align ab initio models, select the most typical one and build an averaged model [116].



(a)



(b)

Fig.6 Ab initio reconstruction of overall $CoFe_2O_4$ nanoparticles shape, clockwise rotation around Y-axis by 90^0 (a,b).

The overall shape of the particles represented in two position upon the clockwise rotation around Y-axis is presented in Fig.6 (a, b).

The identified elongated 3D object resembles quite closely the triaxial ellipsoid model obtained with FITTER program. As any other method that generates 3D structures from the 1D scattering data, the resulting pattern is not unique and might be optimized with supplementary experimental data.

5. Conclusions

A novel ferrofluid was prepared by coprecipitation of $Fe(OH)_3$ and $Co(OH)_2$, ferritisation of hydroxide mixture in 1M alkali aqueous solution, adsorption of lauric acid on ferrite particles and peptisation of hydrophobic precipitate in aqueous solution with sodium n-dodecyl sulphate.

TEM images reveal that though the sizes and the geometrical forms are not uniform, the particles partially show rhomboidal shape. The model fit of SANS data gives triaxial ellipsoid and ellipsoidal shell, as objects characterizing the investigated system. Both techniques confirm the simultaneous presence of particles and surfactant.

The same time, while the results are in general agreement, this study has shown that significant differences are measured by the two methods in the sample microstructure. For instance, the size mean value of the magnetic particles obtained from TEM differs from the parameters resulted from SANS.

Based on our comparison between *in situ* (SANS) and *ex situ* (TEM) experimental techniques, we suggest that this discrepancy appears mainly because of the non-negligible amount of surfactant, which it is less discernable by TEM. Whereas, from our SANS data analysis we are able to observe a high amount of surfactant micelles.

Another possible contribution to the determined discrepancies of the results could be the fact that, TEM gives information on the system in a 2D plan section, while SANS supplies data simultaneously from a 3D sample volume.

During the sample preparation procedure for TEM analysis, a flattening of the sample occurs, In fact, the original ferrofluid system is artificially subjected to a convolution from 3D to 2D, inducing a distortion of experimental data in comparison to those obtained by SANS technique.

The presented results also highlight the advantages of using a variety of complementary techniques to better characterize the scale and nature of the investigated microstructure.

The synthesis procedure of the water suspension of the $CoFe_2O_4$ nanoparticles used in the present work appears to be very promising from the aspect of the stability properties and rather high particle concentration improvements. Further investigations of the sample properties are in progress.

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