Structural analysis of aqueous ferrofluids with cobalt ferrite particles stabilized with lauric acid and sodium n-dodecyl sulphate

A -M Balasoiu-Gaina1,2,3, M Balasoiu4,*, O Ivankov1,5,6, D Soloviov1,5,6, S Lysenko7, C Stan8, N Lupu9, D Creanga10, A Kuklin1,5
1 Joint Institute for Nuclear Research, Dubna, Russia
2CMCF, Moscow State University, Moscow, Russian Federation
3West University of Timisoara, Timisoara, Romania
4“Horia Hulubei” National Institute of Physics and Engineering, Bucharest, Romania
5Moscow Technical Physics Institute, Dolgoprudnyi, Russia
6Institute for Safety Problems of Nuclear Power Plants of the Ukrainian NAS, Kyiv, Ukraine
7Institute of Technical Chemistry, Ural Branch of RAS, Perm, Russian Federation
8“Politehnica” University of Bucharest, Faculty of Applied Sciences, Romania
9National Institute of Research and Development for Technical Physics, Iasi, Romania
10Alexandru Ioan Cuza University, Iasi, Romania

*E-mail: balas@jinr.ru

Abstract. Small angle neutron scattering (SANS) experiment on CoFe2O4/lauric acid/sodium dodecyl sulphate/H2O ferrofluid was performed at the time-of-flight YuMO spectrometer. Concentration effects on the structure variation of the investigated ferrofluid are presented. Using the zero concentration approximation, the structure factors of samples with different concentration were determined. It was shown that the structure factor of values higher than 1 is present in samples with particle volume concentration equal and greater than 0.5%.

1. Introduction
Ferrofluids reveal a wide range of applications in many technical and industrial fields, as well as in medicine and biotechnology. Water-based ferrofluids present the most complex microstructural behaviour and their properties improvement represents an important challenge in this field [1-7]. Use of nano-ferrites in wide technical and biomedical areas, as for example, magnetic recording, permanent magnets, ferrofluids, drug delivery, hyperthermia, etc., make these materials very interesting to researchers for improving their properties, magnetization and coercitivity on one hand, and particle dimensions and shapes, on the other [8, 9].

Small angle neutron scattering is a well-known useful method for investigating such systems [10].

Preliminary results on the CoFe2O4/lauric acid/ sodium dodecyl sulphate/H2O ferrofluid sample of 3% particle volume concentration were reported earlier [11]. TEM images have revealed that the sizes and the geometrical forms are not uniform and even that some particles show rhomboidal shape. The size distribution is found to be lognormal with mean value of particle diameter 8.48 nm.
The model fit of SANS data gave triaxial ellipsoid and ellipsoidal shell, as objects characterizing the investigated system [11]. μSR technique [12, 13] was applied to the same sample and the results evidenced that the system is formed from monodomain nanoparticles of an average dimension about 85 Å and a high anisotropy coefficient [14]. Further, a multifractal approach [15] was applied to the TEM experimental data and the existence of multifractal properties in the sample was demonstrate [16].

In the present paper concentration effects on the structure variation of a non-ionic CoFe₂O₄/lauric acid/ sodium dodecyl sulphate/H₂O ferrofluid investigated by means of small angle neutron scattering are presented.

2. Experimental

2.1. Samples preparation
The ferrofluid was prepared by the coprecipitation method of Fe(OH)₃ and Co(OH)₂. Further step in the preparation was the adsorption of lauric acid on ferrite particles and peptisation of hydrophobic precipitate in aqueous solution with sodium n-dodecyl sulphate [11].

Before SANS measurements the sample was centrifuged in Biofuge 15R (Heraeus instruments) 2 times 6000 rot/min for 60 min. After that, the obtained sample of 3% particle volume concentration was diluted with double distillated water and obtained the following concentrations: 1%; 0.5%; 0.25%; 0.14%; 0.07%; 0.04%.

2.2. Neutron scattering experiment
Small angle neutron scattering (SANS) experiments were performed at the time-of-flight YuMO spectrometer [17] in function at the high flux pulse IBR-2 reactor, JINR Dubna. The Sonix+ software control system provides spectrometer operation [18]. 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÷0.2 Å⁻¹. The sample diameter and thickness in the beam were 14 mm and respectively 1 mm. The measured neutron scattering spectra are corrected relative to the transmission and thickness of the sample, background scattering due to the experimental cuvette and the vanadium reference sample using the SAS software [19], providing a neutron scattering intensity in absolute units of cm⁻¹.

2.3. 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. [20-23]), 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 [24, 25]:

\[ I(Q) = \phi P(Q)S(Q) \]  

(1)

where:
\( Q \) is the modulus of the scattering vector defined as \( Q = (4\pi/\lambda)\sin(\theta/2) \), with the scattering angle being \( \theta \); \( \phi = N/V_0 \) is the density of particles in the volume \( V_0 \) of the sample, \( P(Q) \) characterize a particle and is related to its form factor, \( F(Q) \), by the relation \( P(Q) = \left| F(Q) \right|^2 \) with

\[ F(Q) = \int_{\text{Volume of particle}} (\rho - \rho_0) \exp(iQ\cdot r) dV; \]

\( \rho \) and \( \rho_0 \) 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 centres of mass:

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

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

In case of materials with magnetic properties, the neutron scattering intensity contains a part representing the contribution of the magnetic scattering [23]:

$$I(Q) = I_n(Q) + I_m(Q)$$

It is known, that if the nanoparticles in ferrofluid are dispersed in $\text{H}_2\text{O}$, the nuclear contribution mostly dominates the magnetic one:

$$I_m(Q) \ll I_n(Q)$$

and in the case of non-polarized neutron scattering it is correct the following approximation:

$$I(Q) = I_n(Q) + I_m(Q) \approx I_n(Q)$$

Further analysis of the experimental results is based on this approximation.

### 3. Results and discussion

#### 3.1. Concentration series analysis

SANS data sets for 1%, 0.5%, 0.25%, 0.14%, 0.07% and 0.04% particle vol. concentration samples were obtained (Fig. 1).

![Fig.1 SANS experimental curves for 1%, 0.5%, 0.25%, 0.14%, 0.07% and 0.04% particle vol. concentration samples and the zero concentration approximation curve.](image-url)
For a qualitative analysis of a polydisperse system accounting particle interaction, a ratio between the scattering curves for concentrated and zero concentration diluted solutions can describe the effective structure-factor [26]:

$$S_\phi(Q) = \frac{I_\phi(Q)}{I_{\phi=0}(Q)}$$

In figure 2 the representations of these ratios for every volume particle concentration are given.

**Fig.2** Effective structure-factor in dependence on 1%, 0.5%, 0.25%, 0.14%, 0.07% particle volume concentration samples.

Values of structure factor higher than 1 are determined for volume particle concentrations equal and greater than 0.5%.

For the data processing, the PRIMUS software was used [27].

4. Conclusion
Small angle neutron scattering (SANS) experiments on CoFe2O4/lauric acid/DDS-Na/H2O ferrofluid samples of 1%, 0.5%, 0.25%, 0.14%, 0.07% and 0.04% particle vol. concentrations were performed at the time-of-flight YuMO spectrometer.

Using the zero concentration approximation the structure factor of the samples was determined. It was shown that the structure factor of values higher than 1 is present in samples with particle volume concentration equal and greater than 0.5%. In ferrofluid samples based on nonpolar and polar liquid base with magnetite particles it was determined that the structure factor value in not higher than 1 for volume particle concentration up to 1% [28].

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