

NUCLEAR AND MAGNETIC STRUCTURES OF NON-POLAR FERROFLUIDS BY SMALL-ANGLE NEUTRON SCATTERING

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(Received March 14, 2006)

Abstract. Small-angle scattering of non-polarized and polarized neutrons has proved to be a powerful technique for studying the features of nuclear and magnetic structures of ferrofluids at nanoscale. The paper presents our recent results on the application of the technique for comparative analysis of non-polar ferrofluids (d-cyclohexane) stabilized by different surfactants, which are oleic and myristic acids. Qualitative difference both in nuclear and magnetic structural organization is observed and discussed.

Key words: ferrofluids, magnetic fluids, small-angle neutron scattering, polarized neutrons.

1. INTRODUCTION

Our recent experiments on ferrofluids (fine dispersions of magnetic materials in liquids stabilized by surfactants) showed that the small-angle scattering of non-polarized and polarized neutrons is a quite informative technique in respect to features of both nuclear and magnetic structures of the studied systems at nanoscale of 1–100 nm [1-5]. In particular, the method was applied for a class of ferrofluids based on organic non-polar carrier (benzene, cyclohexane) and stabilized by a single layer of various surfactants (oleic, stearic and myristic acids) [1,3,4]. Different structural organizations of colloidal particles in the fluids were revealed depending on the surfactant used.

The given work is the continuation of this study, where the nuclear and magnetic structures of two different ferrofluids are compared by means of small-angle neutron scattering. The fluids are dispersions of magnetite in deuterated cyclohexane (d-cyclohexane) stabilized by oleic (OA, chemical formula

C₁₇H₃₃COOH) and myristic (MA, chemical formula C₁₃H₂₇COOH) acids. The given surfactants differ significantly in their length (by four carbon groups), as well as in their structures, because of the presence of the double bond in the OA molecule. Nevertheless, both fluids show high stability in various conditions.

2. EXPERIMENT AND DATA TREATMENT

The studied samples were synthesized at the Center of Fundamental and Advanced Technical Research, Timișoara Branch of RAS, Romania. Magnetite was obtained by the chemical condensation reaction and dispersed into d-cyclohexane. The deuterated carrier was used to avoid the strong effect of the incoherent scattering from hydrogen in the course of neutron scattering experiments. The volume fraction of magnetite in both samples, $\varphi_m = 2.8\%$, was found from the density measurements. Details of the preparation procedure of the studied class of ferrofluids can be found in [6].

Experiments on small-angle scattering of non-polarized neutrons were carried out on the YuMO small-angle time-of-flight diffractometer [7,8] at the IBR-2 pulsed reactor, Joint Institute for Nuclear Research, Dubna, Russia. The differential cross-section per sample volume (scattering intensity) isotropic over the radial angle φ on the detector was obtained as a function of the module of momentum transfer, $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident neutron wavelength and θ is the scattering angle. The neutron wavelengths within an interval of 0.05-0.5 nm and the sample-detector distances (SD) of 4 and 16 m were used to obtain scattering curves in a q -range of 0.08-5 nm⁻¹. The wavelength of the scattered neutrons registered by the detector was determined according to the time-of-flight method. The calibration procedure was made using vanadium [7]. The experiments concerned the choice of the conditions in the next time-consuming experiments with polarized neutrons. The effects of concentration and external magnetic field were checked out. The ferrofluids on d-cyclohexane with OA showed similar behavior to the fluids on d-benzene with OA studied earlier [1,3]. The character of the scattering from the ferrofluid with MA differed much from that of the previous case, which determined the interest in the study of this system by means of scattering of polarized neutrons regarding the study of nuclear and magnetic structures and their comparison with other types of ferrofluids. In the given experiments the two samples showed excellent stability both in the absence and presence of external magnetic field.

Experiments on the small-angle scattering of polarized neutrons were performed at the SANS-1 instrument at the FRG-1 steady-state reactor of the GKSS Research Center, Geesthacht, Germany [9]. Measurements were made at a neutron wavelength of 0.81 nm (monochromatization $\Delta\lambda/\lambda$ 10%). Two-dimensional

scattering patterns for two polarization states of neutrons along, I^- , and opposite, I^+ , to the external saturating magnetic field applied to the samples (2.5 T) were registered by the position-sensitive detector with area of $55 \times 55 \text{ cm}^2$ and pixel size of $0.8 \times 0.8 \text{ cm}^2$. The patterns were obtained at a series of sample-detector distances within the interval of 1-9 m. The corresponding q -range covered in the experiments was $0.04\text{-}2 \text{ nm}^{-1}$. H_2O was used to calibrate the curves. At large sample-detector distances ($> 4 \text{ m}$) the calibrated curves were obtained by the recalculation of the curves for H_2O obtained at SD of 2 m with the corresponding distance coefficient. The scattering signals corresponding to the nuclear and magnetic structures were separated according to the equations:

$$I^+(q, \varphi) = \langle F_N^2(q) \rangle_R + (\langle F_M^2(q) \rangle_R - 2P \langle F_N(q)F_M(q) \rangle_R) \sin^2 \varphi, \quad (1a)$$

$$I^-(q, \varphi) = \langle F_N^2(q) \rangle_R + (\langle F_M^2(q) \rangle_R + 2P \varepsilon \langle F_N(q)F_M(q) \rangle_R) \sin^2 \varphi, \quad (1b)$$

where $I(q, \varphi)$ is the two-dimensional scattering image on the position-sensitive detector; P is the beam polarization (100% at the given instrument); ε is efficiency of the spin-flipper which provides the opposite neutron polarization (95%); brackets $\langle \dots \rangle_R$ denote the average over the particle size distribution function. The averaging of the signals (1a), (1b) in vicinities of the radial angles φ of 0, 90, 180 and 270° results in four equations which are used to determine scattering contributions $\langle F_N^2(q) \rangle_R$, $\langle F_M^2(q) \rangle_R$, $\langle F_N(q)F_M(q) \rangle_R$.

3. RESULTS AND DISCUSSION

Two-dimensional scattering patterns for two types of the studied ferrofluids are shown in Fig.1. In the absence of the external magnetic field there is no orientation of magnetic moments in the systems, so the scattering is isotropic over the φ angle on the detector and both beam polarizations result in a similar picture. Under saturation field the magnetic scattering contribution is fully anisotropic, which is reflected in Fig. 1. In accordance with (1a), (1b), the anisotropy of the signals $I^+(q, \varphi)$ and $I^-(q, \varphi)$ is different. Also, the scattering differs much in respect to the used surfactant. It is seen more transparently when the data are transformed into one-dimensional scattering curves by simple averaging over the whole φ -angle (Fig. 2). As one can see, the cross-term $\langle F_N(q)F_M(q) \rangle_R$ in (1a), (1b) is proportional to the nuclear and magnetic scattering amplitudes, so, in contrast to the scattering cross-section, it can be both positive and negative. The observed intersection of the curves $\langle I^+ \rangle_\varphi$ and $\langle I^- \rangle_\varphi$ in Fig. 2 indicates that the sign of the cross-term changes within the registered q -interval. The appearance of the pronounced peak in the scattering curve for the case of stabilization with MA comes from a stronger scattering effect of the surfactant shell in comparison with the fluid stabilized by

OA. Two reasons for this can be given. First, the characteristic magnetic particle size is less in the MA-fluid, so that the effect of the surfactant shell is higher. Second, the polydispersity of the magnetic particles is less in the MA-fluid, so that specific features of the scattering curves are less smeared. A more precise analysis of the nuclear structure of the particles in the ferrofluids shows that both factors are significant. Such analysis is given in Fig. 3 where the separated nuclear and magnetic scattering contributions are presented together with the fits of different models. Taking into account the general concept of the structure of the colloidal particles in stable single-layered ferrofluids, the core-shell model is applied for the nuclear contributions in Fig. 3. The log-normal particle size distribution (parameters R_0 , S) was used. The free parameters are parameters of the particle size distribution, R_0 , S ; surfactant shell thickness, h ; and the ratio $\eta = (\rho_1 - \rho_s) / (\rho_0 - \rho_1)$, where ρ_0 , ρ_1 , ρ_s are scattering length densities of the magnetite core, surfactant shell and solvent, respectively. The results of fits are the following. For the OA-fluid: $R_0=3.0$ nm; $S=0.38$; $\eta=-0.82$; $h=1.38$ nm; for the MA-fluid: $R_0=2.3$ nm; $S = 0.28$; $\eta=-0.67$; $h=1.35$ nm. From the fits one can conclude that the use of myristic acid results in the less size of the stable particles and smaller polydispersity in the corresponding fluid, as was mentioned above. It is also seen from the Guinier approximations given in the same figure according to the expression:

$$I(q) = I(0) \exp(-q^2 \langle R_g^2 \rangle_R / 3), \quad (2)$$

where $\langle R_g^2 \rangle_R$ is the size-averaged radius of gyration of the whole particles including the surfactant shell.

From the comparison of the results obtained for two types of ferrofluids an important conclusion can be drawn, namely, the type of surfactant regulates the size distribution of the stabilized particles. While the final size distribution of the stable particles correlates with the length of the surfactant (lesser length of the surfactant results in a lesser stable size), we are inclined to believe that this length is not a key parameter in respect to the characteristic stable size. This follows from the found values of the surfactant shell thickness which are close in both fluids. Most likely, the difference in the adsorption properties of the surfactants as a consequence of their structural difference (double bond in the middle of the OA molecule) is responsible for the observed change in the nuclear structure of the colloidal particles when OA is replaced by MA. The character of the magnetic scattering contribution in both cases reflects a complicated spatial magnetization in the fluids. It is far from that corresponding to the scattering of the independent magnetic moments oriented by the external magnetic field in one direction. The reason for this is unclear for the moment. Apparently, a specific magnetic correlation between large particles, as well as a correlation between large and small particles in the system take place even at a magnetic field close to saturation.

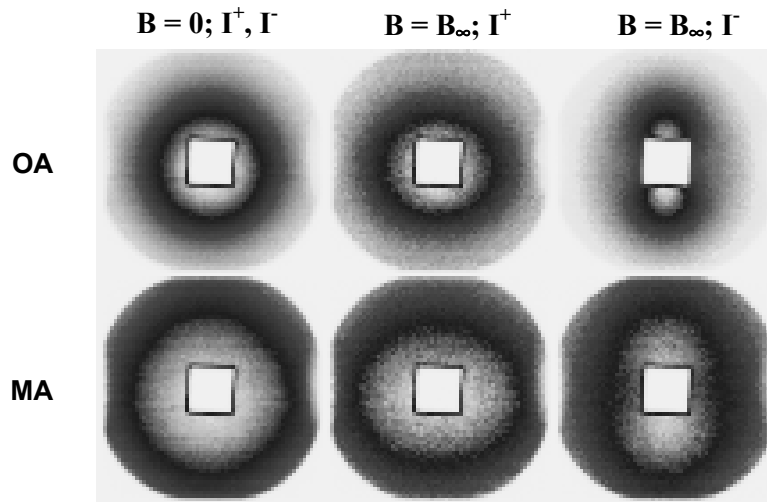


Fig. 1 – 2D scattering patterns obtained for ferrofluids based on d-cyclohexane and stabilized with oleic (OA) and myristic (MA) acids. Volume fraction of magnetite in both samples is 2.8%. Sample-detector distance is 4.5 m.

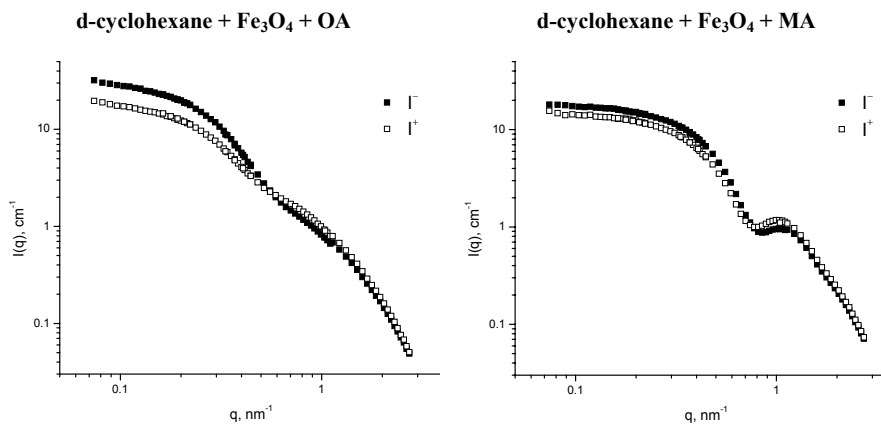


Fig. 2 – Radially averaged scattering patterns for two polarization states of the incident neutrons from the studied ferrofluids based on d-cyclohexane and stabilized by oleic (OA) and myristic (MA) acids. Physical volume fraction of magnetite in both samples is about 2.8%.

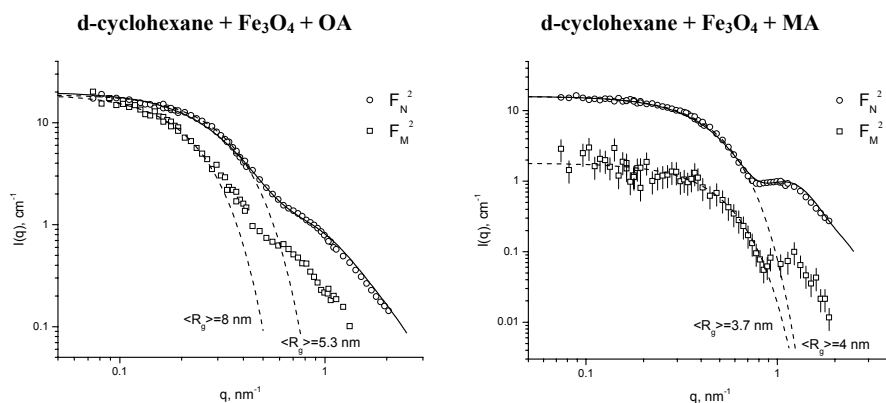


Fig. 3 – Separation of the nuclear ($\langle F_N^2 \rangle_R$) and magnetic ($\langle F_M^2 \rangle_R$) scattering contributions for the studied ferrofluids from the scattering of polarized neutrons. Solid lines correspond to the core-shell model calculations for the nuclear structure. Dashed lines represent Guinier approximations for both contributions (the corresponding mean radii of gyration are indicated).

It should be pointed out that the discussed magnetic correlation takes place in the absence of any significant correlation in location of the particles themselves, which follows from the good fit of the model of non-interacting particles to the experimental curves. Some speculations about the features of the magnetic structure can be found in [3], where the same situation was observed for the benzene-based ferrofluid with OA. Here, one can see that the type of surfactant has a significant effect on the magnetic scattering (Fig. 3). The behavior of the magnetic scattering curves regarding the nuclear ones differs much for the two cases. The magnetic scattering contribution is significantly smaller for the fluid with MA in comparison with that containing OA. Presumably, this is connected with the significant difference in the particle size distributions of the stable particles revealed above from the analysis of the nuclear scattering.

4. CONCLUSIONS

Features of nuclear and magnetic structures of non-polar organic ferrofluids stabilized by two different surfactants are compared by data of small-angle scattering of non-polarized and polarized neutrons. A strong effect of the type of surfactant on the structural characteristics of the stabilized colloidal particles in ferrofluids is observed. Effectively, the surfactant used in the preparation of ferrofluids regulates the final particle size distribution, which is determined mainly by the adsorption properties of the surfactant. Complex correlations between the magnetic moments of the particles are detected in both studied ferrofluids. Still these correlations differ qualitatively for the two samples.

Acknowledgements. We acknowledge the assistance of the Fundamental Researches CERES Project of the Romanian National Research and Development Programmes Nos. 4-36/2004-2006; and the grant of the Romanian Governmental Representative in JINR.

M.V.Avdeev acknowledges the support from the INTAS Fellowship Grant for Young Scientists, Ref. N. 04-83-2582.

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