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

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Ядерная и магнитная структура неполярных феррожидкостей
по данным малоуглового рассеяния нейтронов

Малоугловое рассеяние неполяризованных и поляризованных нейтронов является информативным методом для изучения особенностей ядерной и магнитной структуры в феррожидкостях в нанометровом масштабе. Представлены последние результаты по использованию метода для сравнительного анализа неполярных феррожидкостей на основе дейтерированного циклогексана, стабилизированных разными поверхностно-активными веществами (ПАВ), а именно олеиновой и миристиновой кислотами. Обсуждаются качественные различия, наблюдаемые как в ядерной, так и в магнитной структуре исследуемых жидкостей в зависимости от используемого ПАВ.

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Nuclear and Magnetic Structures of Nonpolar Ferrofluids by
Small-Angle Neutron Scattering

Small-angle scattering of nonpolarized and polarized neutrons has proved to be a powerful technique for studying features of nuclear and magnetic structures of ferrofluids at nanoscale. The paper presents our recent results on application of the technique for comparative analysis of nonpolar 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.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

INTRODUCTION

Our recent experiments on ferrofluids (fine dispersions of magnetic materials in liquids stabilized by surfactants) showed that the small-angle scattering of nonpolarized 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 nonpolar 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 $C_{17}H_{33}COOH$) and myristic (MA, chemical formula $C_{13}H_{27}COOH$) 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.

1. EXPERIMENT AND DATA TREATMENT

The studied samples were synthesized at the Center of Fundamental and Advanced Technical Research, Timisoara 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 nonpolarized neutrons were carried out on the YuMO small-angle time-of-flight diffractometer [7, 8, 9] at the IBR-2 pulsed reactor of the 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 13 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 like 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 to 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) [10]. 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 × 55 cm^2 and pixel size of 0.8 × 0.8 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 0.04–2 nm^{-1}. H_2O was used to calibrate the curves. At large sample-detector distances (> 4 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:

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

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

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 $\langle\ldots\rangle_R$ 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 °C results in four equations which are used to determine scattering contributions $\langle F_N^2(q)\rangle_R$, $\langle F_M^2(q)\rangle_R$, $\langle F_N(q)F_M(q)\rangle_R$.

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2. 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

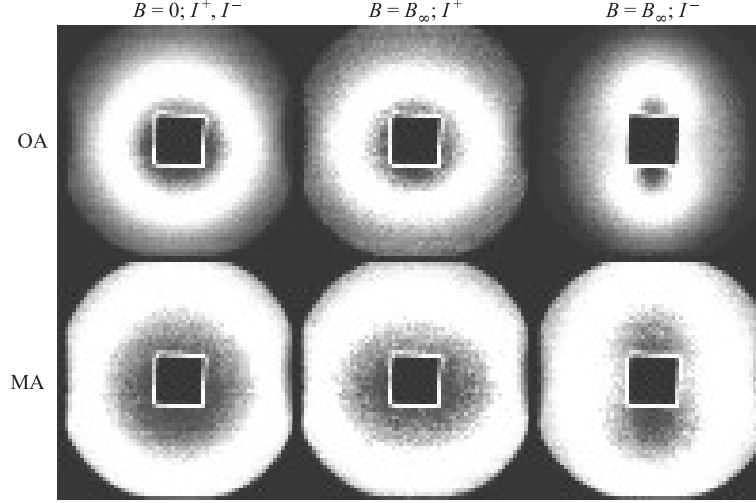$B = 0; I^+, I^-$ $B = B_\infty; I^+$ $B = B_\infty; I^-$

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 1.8 m

orientation of magnetic moments in the systems, so the scattering is isotropic over the φ angle on the detector and both beam polarization results in 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 seem more transparently when the data are transformed into one-dimensional scattering curves by simple averaging over the whole φ angle (Fig. 2). The observed intersection of the curves $\langle I^+ \rangle_\varphi$ and $\langle I^- \rangle_\varphi$ indicates that the sign of the cross-term $\langle F_N(q)F_M(q) \rangle_R$ changes within the registered q interval. The appearance of the pronounced peak in the scattering curve for the case of stabilization with MA tells us that the characteristic particle size, as well as the polydispersity of the particles are significantly smaller than in the case with OA. The more precise analysis of the nuclear structure of the particles in the ferrofluids are 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 colloidal particles in stable single-layered ferrofluids, the core-shell model is applied for
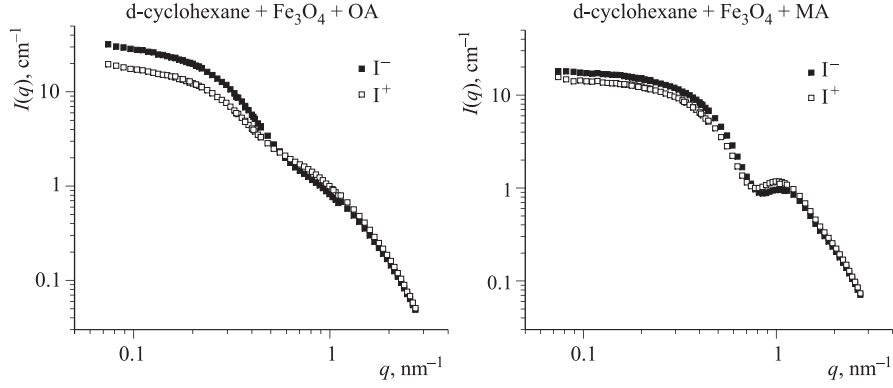
3

Fig. 2. 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%
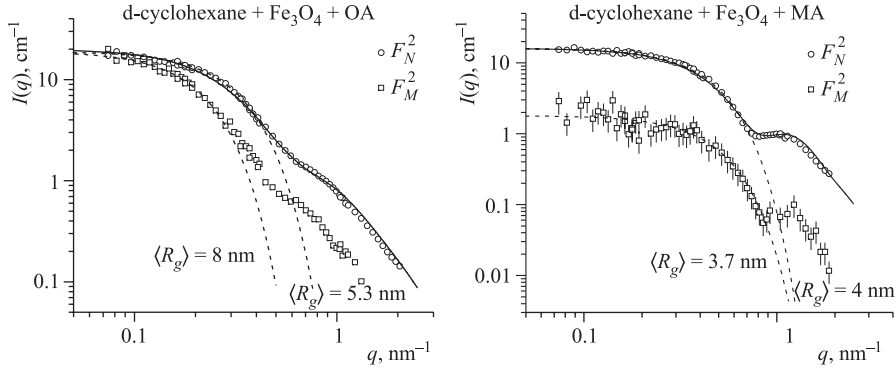

Fig. 3. Separation of the nuclear ($\langle F_N^2 \rangle_R$) and magnetic ($\langle F_M^2 \rangle_R$) scattering contributions for the studied ferrofluids from the scattering of polarized neutrons. Solid lines correspond to the core-shell model calculations for the nuclear structure. The log-normal particle size distribution (parameters R_0, S) was used. 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. Results of fits are the following. OA: $R_0 = 3.0$ nm; $S = 0.38$; $\eta = -0.82$; $h = 1.38$ nm. MA: $R_0 = 2.3$ nm; $S = 0.28$; $\eta = -0.67$; $h = 1.35$ nm. Dashed lines represent the Guinier approximations for both contributions (the corresponding mean radii of gyration are indicated)

the nuclear contributions in Fig. 3. From the fits one can conclude that the use of myristic acid results in the less size of stable particles and smaller polydispersity

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in the corresponding fluid, as it was mentioned above. It is also seen from the Guinier approximations given in the same figure according to the expression

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

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 made, 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 (the less length of the surfactant results in less stable size), we are inclined to believe that this length is not a key parameter in respect to the characteristic stable size. This is followed 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 independent magnetic moments oriented by the external magnetic field in one directions. 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 the magnetic field close to the saturation. It should pointed out that the discussed magnetic correlation takes place in the absence of any significant correlation in location of the particles themselves, which is followed 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 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.

CONCLUSIONS

So, a strong effect of the stabilizing surfactant on the structural characteristics of 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 adsorption properties of the surfactant. While complex magnetic correlations take place in both studied ferrofluids, still these correlations differ qualitatively for them.

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