
**SMALL-ANGLE NEUTRON SCATTERING
BY WATER-BASED FERROFLUID MIXED
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A new approach in the contrast variation experiments (small-angle neutron scattering) is demonstrated with a complex water-based magnetic fluid, where magnetite nanoparticles (size about 10 nm) coated with sodium oleate are mixed with poly(ethylene glycol), PEG. The contrast variation is performed basing on the substitution of hydrogen with deuterium in the liquid carrier (water). Modified basic functions defined for the polydisperse multicomponent superparamagnetic system are analyzed. Two kinds of particles in the solution, which are fractal aggregates (size more than 120 nm) of magnetite nanoparticles coated with sodium oleate and micelles (radius about 2 nm) of free sodium oleate, are revealed. It is shown that PEG substitutes sodium oleate in the initial ferrofluid. Aggregates are formed because of its worse stabilizing properties with respect to nanomagnetite in water.

1. Introduction

Small-angle neutron scattering (SANS) is actively used for finding the distribution of the scattering length density (SLD) within nanoparticles in various colloidal solutions [1, 2]. Major advantages of SANS are connected with possibilities of the contrast variation in the studied systems by the hydrogen/deuterium substitution. Here, we consider experimental possibilities of this method with a complex water-based ferrofluid, where magnetite nanoparticles (size about 10 nm) coated with sodium

oleate are mixed with poly(ethylene glycol), PEG. Rather high polydispersity of particles in magnetic fluids, as well as the presence of the magnetic scattering, complicates the classical implementation of the contrast variation [3]. Nevertheless, recent developments of this technique, namely the basic functions approach for polydisperse and superparamagnetic systems [4], show that the scattering can be interpreted in the same manner in terms of some functions comprising information about the nuclear and magnetic SLD distributions within particles together with the particle size distribution.

Magnetic fluids have many prospects in actively developing medical applications such as drug targeting [5], magnetic resonance imaging (contrast medium) [6], magnetic hyperthermia for cancer treatment [7], etc. In biocompatible systems, the chemical composition of a surface is especially important to avoid the action of the reticuloendothelial system (RES), which is a part of the immune system, in order to increase the lifetime of magnetic nanoparticles in the blood stream. If magnetic particles are coated with neutral and hydrophilic compounds such as PEG, the lifetime increases from minutes to hours or days [8].

The purpose of the present experiments is to reveal the structural organization of nanoparticles in the studied ferrofluid.

2. Materials and Methods

The preparation of the studied ferrofluid was based on the co-precipitation method that involves the mixing of two solutions of 20 ml of 2M FeCl₂ and 20 ml of 1M FeCl₃ in an alkali aqueous medium (7.5 ml of 25% solution of NH₄OH). A black magnetite precipitate (1 g) was formed. The stabilization of the magnetite precipitate was achieved by adding 1 g of sodium salts of oleic acid (C₁₇H₃₃COONa) (as a surfactant to prevent the magnetic particles agglomeration), which leads to a hydrophilic surface due to the bilayer of the adsorbed surfactant on magnetic particles. The final volume of the suspension was adjusted to 10 ml of deionized water and stirred until the boiling point is reached. Then, 25 ml of PEG (10% w/w solution with M_w = 1000 g/mol), as a second stabilizer, were added to the magnetite – sodium oleate system. The mixture of the magnetic fluid and the water solution of PEG was stirred approximately for 3 h at a temperature of 50 °C. The last step is a centrifugation at 5000 rot/min during 30 min. The final ratio between components in the prepared fluid was estimated from the density measurements and constituted 0.73 g of sodium oleate and 2.5 g of PEG per 1 g of Fe₃O₄.

The magnetic fluid was investigated by small-angle scattering of non-polarized neutrons (SANS). The contrast variation with the H/D substitution was used to reveal features of the internal structure of the ferrofluid on the scale 1-100 nm. The initial sample (volume fraction of magnetite about 2%) was dissolved with the ratio 1:3 by different mixtures of light/heavy water to achieve the D₂O contents of 0, 10, 20, 30, 40, 50, 60, and 70% in the final fluid. The H₂O content in the initial solution was estimated to be 95% from the mass density measurements (1.02 g/ml). Pure H₂O/D₂O mixtures with the same D₂O contents as in the experimental samples were used as buffer solutions. The studied fluid shows the good stability in the absence of an external magnetic field. No significant changes in its properties were observed within the period of one year after the preparation.

Experiments were carried out on the SANS-1 small-angle instrument at the FRG-1 steady-state reactor of the GKSS Research Center (Geesthacht, Germany) [9]. No external magnetic field was applied to the samples. In this case, the differential cross-section, which is isotropic over the radial angle ϕ on the detector plane, per sample volume (scattering intensity) is obtained as a function of the momentum transfer $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident neutron wavelength and θ is

the scattering angle. Measurements were made at a neutron wavelength of 0.81 nm (monochromatization $\Delta\lambda/\lambda = 10\%$) and a series of sample-detector distances (SDD) within the interval of 0.7 ÷ 9.7 m (detector size 50 cm) to cover a q -range of 0.04 ÷ 2 nm⁻¹. A standard procedure to calibrate the cross-section on the water sample [10] together with the corrections on the background, container scattering, and incoherent background (subtraction of the scattering from the corresponding buffer) was performed. At large sample-detector distances (> 4.5 m), the calibrating patterns were obtained by the recalculation of the curves for H₂O at the SDD of 1.8 m with the corresponding distance coefficients. Samples and buffers were put into quartz cells (Hellma) of 1 mm thick and were kept at room temperature (25 °C) during the expositions. Experiments were also done at different temperatures (up to 70 °C) for the samples with H₂O to find out the temperature stability of the ferrofluid from the structure viewpoint.

The studied ferrofluid shows a complex multilevel and multicomponent structure. The experimental data were treated in terms of the approach given in [4] which takes into account these aspects in addition to the classical contrast variation technique [3]. The advanced basic function approach takes the following view:

$$I(q) = \tilde{I}_s(q) + \Delta\tilde{\rho}\tilde{I}_{cs}(q) + (\Delta\tilde{\rho})^2\tilde{I}_c(q), \quad (1)$$

where

$$\Delta\tilde{\rho} = \bar{\rho}_e - \rho_s \quad (2)$$

is the modified contrast, the difference between the effective mean scattering length density (SLD) of the particles, $\bar{\rho}_e$, and SLD of the liquid carrier, ρ_s . The modified basic functions $\tilde{I}_c(q)$, $\tilde{I}_s(q)$, and $\tilde{I}_{cs}(q)$ comprise information about the nuclear and magnetic SLD distributions within particles, as well as the polydispersity function [4]. Among three basic functions, the most transparent for interpretation is $\tilde{I}_c(q) = \langle I_c(q) \rangle$, the average of the scattering shape function $I_c(q)$ of the Stuhmann's type [3]. The corresponding term $(\Delta\tilde{\rho})^2\tilde{I}_c(q)$ prevails in the scattering intensity (1) at a sufficiently large contrast, so we can write

$$(\Delta\tilde{\rho})^2\tilde{I}_c(q) = I_N(q)|_{\Delta\tilde{\rho} \rightarrow \infty}, \quad (3)$$

where $I_N(q)$ denotes the nuclear scattering component in the system. Another basic function $\tilde{I}_s(q)$ describes the scattering at the effective match point ($\Delta\tilde{\rho} = 0$). It comprises both the residual nuclear scattering $I_N(q)$

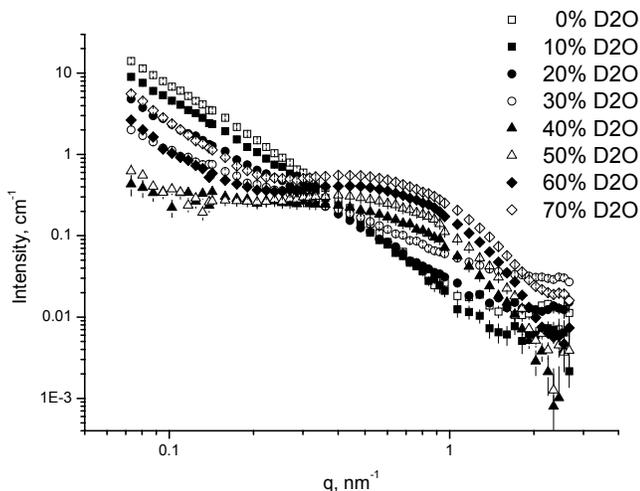


Fig. 1. Changes in the SANS curves with the contrast variation on the studied ferrofluid. Percent volume fraction of D₂O in the solvent is indicated. Volume fraction of dispersed magnetite in the samples, ϕ_m , is less than 0.5%)

and the magnetic scattering $I_M(q)$:

$$\tilde{I}_s(q) = I_N(q)|_{\Delta\bar{\rho}=0} + I_M(q). \quad (4)$$

Finally, the $\tilde{I}_{cs}(q)$ contribution is a cross-function. In the general case, in contrast to the other two basic functions, it can take negative values.

3. Results and Discussion

The experimental SANS curves at different D₂O contents in the carrier are presented in Fig. 1. The change in the character of the curves repeats that seen in similar experiments on a water-based ferrofluid with nanomagnetite sterically stabilized by a double layer of dodecylbenzenesulphonic acid [11] and mono-carboxylic acids [12]. Samples with the small content of D₂O in the solvent (below 30%) show the signal mainly from magnetite, because of the slight contrast between water and sodium oleate/PEG layer. The behavior of these curves differs from that in the case of the scattering by single separated nanoparticles and corresponds to rather large (characteristic size more than 120 nm) aggregates. A specific feature clearly appears at q -values above 0.5 nm⁻¹ at high D₂O contents (above 50%), which corresponds to significantly smaller particles consisting mainly from H-components of the ferrofluid.

Because of the large size of the mentioned aggregates, which is beyond the instrument limit, no specific Guinier regime can be resolved in the initial parts of the curves. In this case, the effective match point of the

system (content of D₂O, when the scattering is minimal) cannot be related to the forward scattering intensity as in the standard procedures [3,4] on the contrast variation. Nevertheless, as it was noted in [4], the choice of this parameter for polydisperse systems is entirely arbitrary. The contrast dependence of the scattering intensity is of parabolic type at any q -point. Examples of the corresponding treatment at various q -points are given in Fig. 2. Each minimum in Fig. 2 can be associated with the effective match point. If particles are homogeneous, the minima in such dependences should not change and correspond to the mean particle SLD. For inhomogeneous particles, they should move with q .

The full q -dependence of the effective match point is shown in Fig. 3. It is clearly seen that this parameter does not change much at $q < 0.2$ nm⁻¹. This means that the aggregates can be considered as homogeneous on the corresponding scale, > 30 nm. The effective match point ($\eta \sim 0.45$) for this region can be directly associated with the mean SLD of the aggregates. Using SLDs of light ($\rho_{\text{H}_2\text{O}} = -0.56 \times 10^{10}$ cm⁻²) and heavy ($\rho_{\text{D}_2\text{O}} = 6.34 \times 10^{10}$ cm⁻²) water, the mean SLD for the aggregates is calculated as

$$\rho = \eta\rho_{\text{D}_2\text{O}} + (1 - \eta)\rho_{\text{H}_2\text{O}}, \quad (5)$$

which gives $\rho = 2.55 \times 10^{10}$ cm⁻². From this value (taking into account the scattering length densities of magnetite, $\rho = 6.9 \times 10^{10}$ cm⁻², and surfactant/PEG, $\rho \sim 0 \times 10^{10}$ cm⁻²), we estimate the volume fraction of magnetite in the aggregates as 0.37. This value is close to that concluded for a water-based fluid with double DBS stabilization [11].

The second plateau ($\eta \sim 0.05$) at large q -values can be distinguished in Fig. 3. Since SLD of the surfactant and PEG is close to zero, we associate the discussed match point with possible magnetite-free aggregates of these molecules.

The conclusions made above are testified further by the analysis of the basic function $\tilde{I}_c(q)$.

In order to solve the system of equations of type (1), we define the modified contrast (2) through the solvent SLD, where the D₂O content dependence of the scattering intensity at $q = 0.09$ nm⁻¹ approaches its minimum. The found minimum gives the effective match point of 0.446 of the D₂O content (corresponding SLD 2.52×10^{10} cm⁻²). To find the basic functions from experimental curves obtained at different contrasts, the following functional was minimized [13]:

$$\chi^2 = \frac{1}{N-3} \times$$

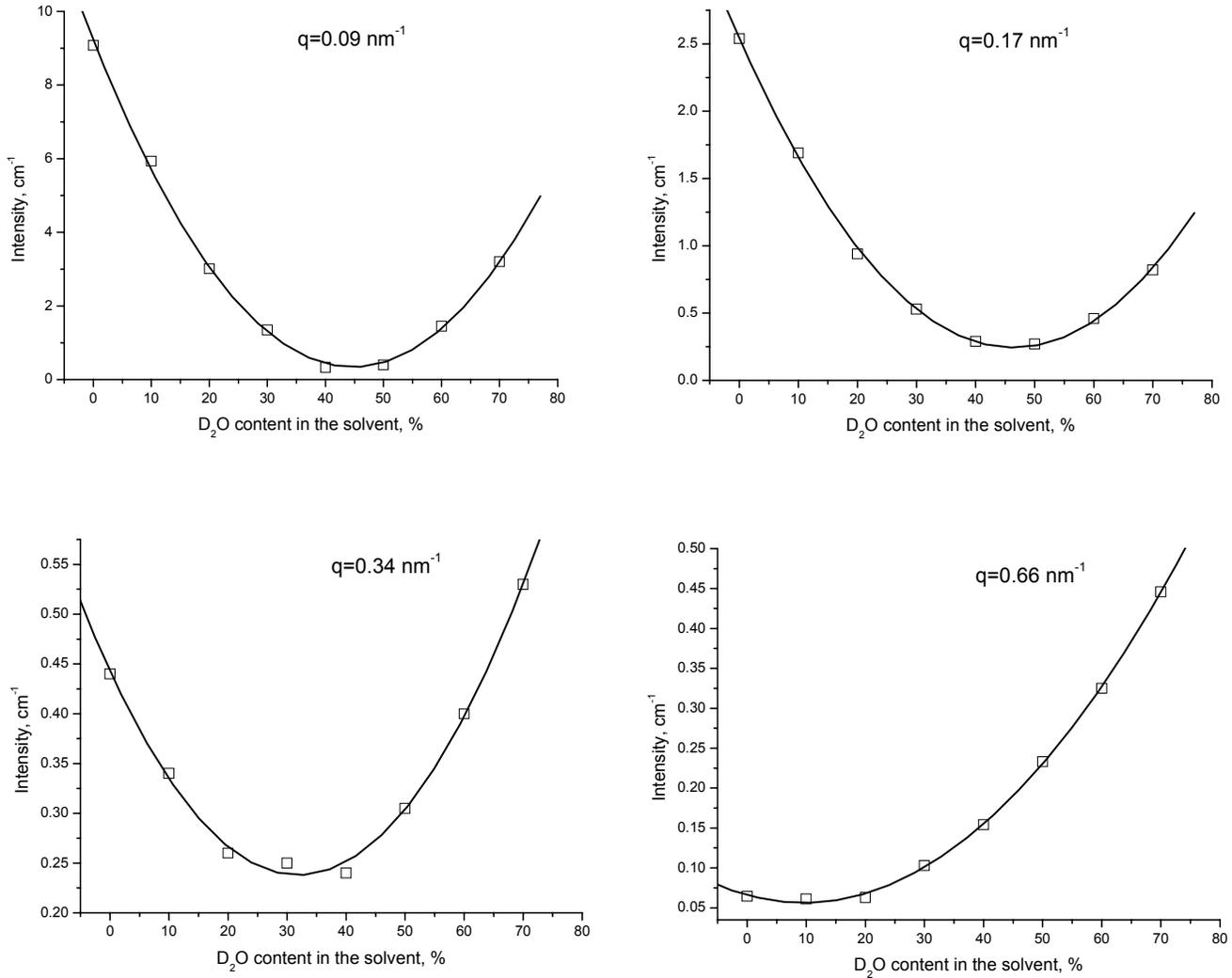


Fig. 2. Behavior of the scattering intensity for the studied magnetic fluid on the D₂O content in the solvent at different q -values)

$$\times \sum_k \frac{[I_k(q) - \tilde{I}_s(q) - \Delta\tilde{\rho}_k \tilde{I}_{cs}(q) - (\Delta\tilde{\rho}_k)^2 \tilde{I}_c(q)]^2}{\sigma_k^2(q)}, \quad (6)$$

where $I_k(q)$ and $\sigma_k(q)$ are the experimental intensity and error at a point q obtained for the k -th contrast; N is the number of contrasts in the experiment.

The resulting modified basic functions are given in Figs. 4-6. To check out the consistency of the given approach, we use the $\tilde{I}_s(q)$ basic function. As was mentioned above, it shows the residual scattering at the effective match point. This means that it should be close to the curves measured at the 40 and 50% D₂O contents, which is shown in Fig. 4. The cross-function function $\tilde{I}_{cs}(q)$ (Fig. 5) is difficult for interpretation in the case of polydisperse multicomponent systems [4]. Nevertheless,

it can be compared with the similar functions for water-based ferrofluids sterically stabilized by a double layer of monocarboxylic (lauric and myristic) acids [12]. In these fluids, large aggregates were also revealed. The specific difference is a strong oscillation of the $\tilde{I}_{cs}(q)$ function in Fig. 5 as compared to the previous work. We interpret this effect as a result of the superposition of two functions corresponding to different kinds of particles, as was assumed above. The first positive peak at small q -values repeats qualitatively the situation with the previous fluids, thus indicating that it corresponds to large aggregates. The new negative peak at higher q -values (smaller sizes) should be associated with new particles whose SLD significantly differs from that of large aggregates.

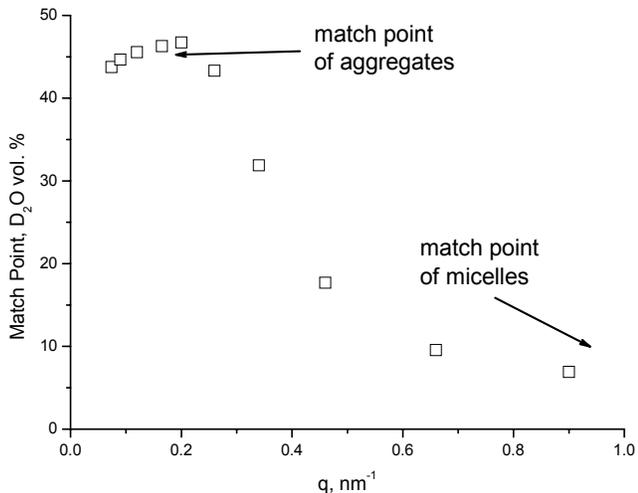


Fig. 3. Dependence of the effective match point on q for the studied magnetic fluid. Two specific regions are distinguished

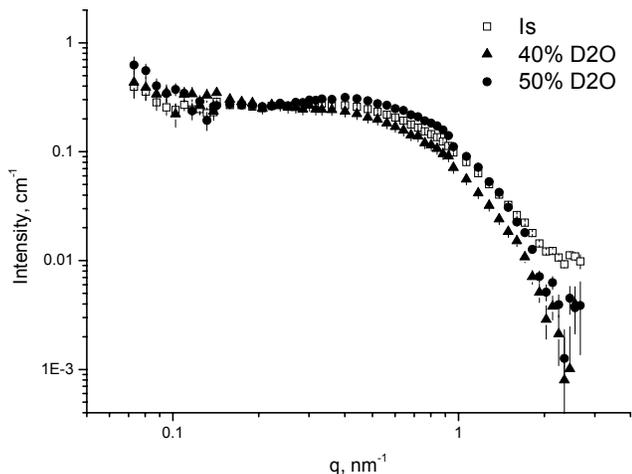


Fig. 4. Experimentally obtained $\tilde{I}_s(q)$ basic function is compared with the scattering curves at 40 and 50% D₂O in the carrier, which are close to the effective match point

As was claimed above, our main goal is the $\tilde{I}_c(q)$ basic function (Fig. 6). It clearly shows two different scattering levels. The first level (small q -values) reflects the power-law type scattering $\sim q^{-2.5}$, which is a linear dependence in the double logarithmic plot in Fig. 6. The obtained exponent (-2.5) indicates the presence of fractal aggregates with the dimension of 2.5 (mass fractals [14]). Their size, as was mentioned above, exceeds 120 nm, that is why their Guinier region is out of the instrument resolution. The second level (large q -values) shows the well-defined Guinier regime for

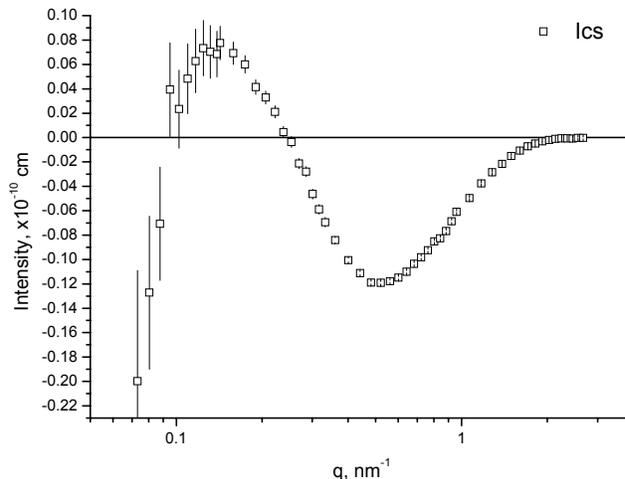


Fig. 5. Experimentally obtained $\tilde{I}_{cs}(q)$ basic function. Its oscillatory shape confirms the inhomogeneity of particles in the studied magnetic fluid

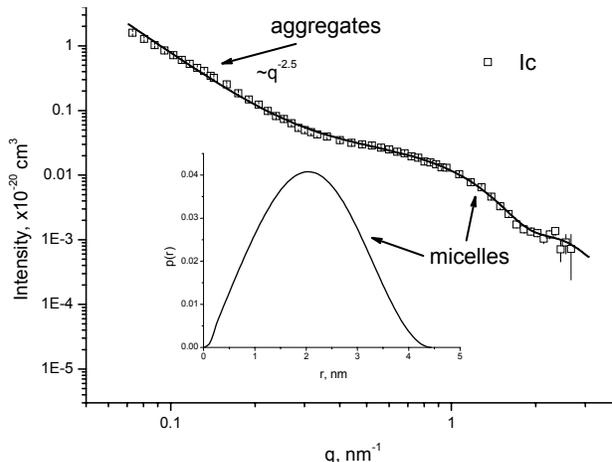


Fig. 6. Experimentally obtained $\tilde{I}_c(q)$ basic function. Different scattering levels corresponding to two different kinds of particles are indicated. The line shows a fit of the curve, which takes into account the power-law type scattering on aggregates (low q -values) and scattering on micelles (large q -values). Inset shows PDD for the “micelle part” of the scattering curve. Parameters of the IFT fit are $R_g = 1.59 \pm 0.05$ nm, $I(0) = (0.021 \pm 0.001) \times 10^{-20}$ cm³

significantly smaller particles:

$$\tilde{I}_c(q) = I_c(0) \exp(-q^2 R_g^2/3), \quad (7)$$

where $I_c(0)$ is the forward scattering intensity determined by the particle concentration n and the volume V :

$$I_c(0) = nV^2. \quad (8)$$

After the subtraction of the extrapolated power-law scattering at large q -values, the second level can be treated well by the Indirect Fourier Transform (IFT) procedure [15] to obtain the pair distance distribution (PDD) of small particles and, then, $I_c(0)$ and R_g . The resulting PDD is given in the inset in Fig. 6. Parameters of the IFT fit are indicated in the caption to Fig. 6. The radius of the discussed particles, R , calculated in accordance with the formula for spherical homogeneous particles, $R_g^2 = (3/5)R^2$, constitutes ~ 2.1 nm and correlates well with the length of sodium oleate, thus indicating that one deals with micelles of the free surfactant in the solution. The parameter $I_c(0)$ can be used to estimate the volume fraction ϕ of the surfactant which form micelles in the solution. From (8), we have $\phi = I_c(0)/V = 0.006$, which corresponds to a concentration of about 6 mg/ml. This value can be compared with the free surfactant concentration in the initial ferrofluid which is chosen close to its critical micelle concentration (CMC). For sodium oleate, CMC is equal to 2 mM which corresponds to the free surfactant concentration in the solution of about 0.6 mg/ml. Thus, for the studied sample, we can conclude about a significant increase in the free surfactant content as compared to that in the initial fluid, which results in a great increase in the micelle formation. The most reasonable origin of this surfactant seems to be a desorption of sodium oleate during the preparation and its substitution with PEG. As a result, PEG shells show worse stabilizing properties and cannot prevent the particle aggregation observed in the SANS experiments. It should be noted that the aggregates are stable with respect to the temperature increase. The additional experiments with the temperature increase up to 70 °C and its following decrease down to 25 °C for the H₂O-based sample did not show any significant change in the scattering (where it comes mostly from magnetite). If we assume that PEG fully substitutes oleate, its relative content in the aggregates (which follows from their match point) does not exceed 0.63. Taking into account the characteristic size of nanomagnetite of 10 nm and a polydispersity of about 50%, one can obtain that the thickness of the PEG shell around magnetite nanoparticles is not more than 3 nm to satisfy the mean SLD of the aggregates.

4. Conclusions

The structure of the water-based ferrofluid mixed with PEG is revealed by the contrast variation

technique in experiments on the small-angle neutron scattering. The possibilities of the new basic functions approach for polydisperse and superparamagnetic systems are demonstrated with the analysis of the complex multiscale structure. Two kinds of particles in the solution, which are fractal aggregates (size more than 120 nm) of magnetite nanoparticles coated with sodium oleate and micelles (radius about 2 nm) of free sodium oleate, are observed. The aggregates are assumed to be formed because of the substitution of sodium oleate in the initial ferrofluid with PEG, which shows worse stabilizing properties with respect to nanomagnetite in water.

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МАЛОКУТОВЕ РОЗСІЯННЯ НЕЙТРОНІВ ВОДНИМИ СИСТЕМАМИ ФЕРОФЛЮЇДІВ З ДОДАВАННЯМ ПОЛІЕТИЛЕНГЛІКОЛЮ

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Резюме

В рамках експериментальної методики варіації контрасту (малокутове розсіяння нейтронів) розроблено новий підхід для дослідження складних магнітних рідинних систем на основі води. Вивчено водні системи з додаванням поліетиленгліколю (ПЕГ)

та магнітних наночастинок (розміром порядку 10 нм), вкритих олеатом натрію. Варіація контрасту ґрунтується на заміщенні водороду дейтерієм у рідкому носії (воді). Було проаналізовано відповідні модифіковані базисні функції, які описують полідисперсні мультикомпонентні суперпарамагнітні системи. Встановлено, що у розчині присутні два типи частинок – фрактальні агрегати розміром, більшим за 120 нм, що складаються з магнітних наночастинок, вкритих олеатом натрію та міцели з чистого олеата натрію розміром близько 2 нм. Показано, що ПЕГ заміщує олеат натрію в вихідній магнітній рідинній системі. Через його гірші стабілізаційні властивості, по відношенню до наномагнетиту у воді, в магнітній рідинній системі формуються агрегати.