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## SENSITIVITY OF SMALL-ANGLE NEUTRON SCATTERING METHOD AT DETERMINING THE STRUCTURAL PARAMETERS IN MAGNETIC FLUIDS WITH LOW MAGNETITE CONCENTRATIONS

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*The capabilities of the small-angle neutron scattering (SANS) method for the research of various magnetic fluids with low magnetite concentrations ( $\sim 0.1$  vol.%), when the structural factor effect is absent, have been considered. The structural parameters of nanoparticles (the magnetic coherent scattering length density, thickness of a nonmagnetic layer on the surface of magnetic nanoparticles, and thickness of a stabilizing shell), which can be obtained from SANS experiments and the Guinier parameters for the scattering intensity, were analyzed in the framework of the “spherical core-shell” model. The model is found to be sensitive to a variation of the structural parameters of magnetic fluids if the particle polydispersity is taken into account. Experimental conditions for magnetite/oleic acid/benzene (a nonpolar carrier fluid) and magnetite/oleic and dodecyl-benzenesulphonic acids/pentanol (a polar carrier fluid) ferrofluids are selected and compared.*

*Keywords:* magnetic fluid system, small-angle neutron scattering, surfactant.

### 1. Introduction

Magnetic fluid systems (MFSs)—or ferrofluids—are colloids of magnetic nanoparticles about 10 nm in dimension covered with a surfactant layer, which is used to stabilize the fluid system. The nano-sized dimensions of particles correspond to their single-domain state of magnetization and are responsible for the MFS behavior close to the superparamagnetic one. The study of the structure in such systems is of high interest, from both the academic and application viewpoints [1–3].

The method of small-angle neutron scattering (SANS) has been actively used [2–5] while studying the nuclear and magnetic structures in MFSs. The presence of a homogeneous fluid medium (liquid carrier) gives ample opportunities for the contrast variation to be realized in the systems concerned with the use of solutions of deuterated and protonated fluid bases [6]. At the same time, magnetic nanoparticles dispersed in a carrier fluid are characterized by a considerable polydispersity, which complicates the analysis of experimental data. First of all, this is associated with the fact that there exists a substantial dipole–dipole magnetic interaction between particles in ferrofluids, which depends on the relative orientation of particle magnetic moments and results in

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deviations from the paramagnetic behavior. The indicated factors hamper a direct observation of one of the most interesting properties predicted for magnetic nanoparticles—the existence of a nonmagnetic surface layer about 1 nm in thickness, which could explain a decrease in the specific magnetization of magnetic nanoparticles as their dimensions diminish [2, 6] and improve the interpretation of the results of some experiments dealing with magnetization [7–10] and the Mössbauer effect [11, 12]. A numerical calculation of this phenomenon was made in a theoretical work by Kodama et al. [13]. It has to be noticed, however, that the effect of magnetic scattering reduction can be associated with reorientations of the magnetic moment vectors and the Brownian motion of particles [14]. As was demonstrated earlier [4], even in the case of low-concentrated MFSs the volume fraction of a magnetic material close to 1%, the influence of the structural factor gives rise to the effective growth of the observed dimensions of magnetic particles. If the scattering of nonpolarized neutrons by nonmagnetized MFSs in the absence of an external magnetic field is used for this purpose, the particle size growth manifests itself as a deviation of the model scattering curves calculated making no allowance for the interaction from the experimental data in the interval of small scattering vectors [15]. The dipole–dipole interaction can be reduced if we further decrease the particle concentration in the fluid system. However, this way gives rise to a reduction in the registered scattering intensity and, owing to a noncoherent background (especially in the case of completely protonated solvents), makes the analysis of scattering curves possible only in the Guinier region, where the roles of main substance characteristics are played by integrated parameters [16] such as the scattering intensity at the zero angle,  $I(0) = |\int \rho(\mathbf{r}) d\mathbf{r}|^2$ , and the squared gyration radius,  $R_g^2 = \int_V \rho(\mathbf{r}) r^2 d\mathbf{r} / \int_V \rho(\mathbf{r}) d\mathbf{r}$ , which are defined in terms of the scattering length density  $\rho(\mathbf{r})$ , the latter being equal to the length of coherent neutron scattering in a unit volume of the substance averaged over the chemical and isotopic compositions.

Earlier, we carried out calculations for strongly diluted nonpolar magnetic fluid systems in the monodisperse approximation [17]. The present work aimed at estimating the possibility of carrying out a SANS experiment for polar and nonpolar magnetic fluids in the polydisperse approximation and in the absence of an influence of the structural factor (the

volume fraction of a magnetic material is about 0.1%) and at finding such experimental conditions, which would allow us to estimate the magnetic properties of particles using the results obtained. For this purpose, we analyzed the sensitivity of the Guinier parameters to variations in the parameters of polydisperse MFS particles, including the thickness of a nonmagnetic layer in nanoparticles, by carrying out the corresponding simulation on the assumption that there is no magnetic interaction between the particles.

Expressions for the Guinier parameters—namely, the squared gyration radius,  $R_g^2$ , and the zero-angle scattering intensity,  $I(0)$ —were calculated in the framework of the “spherical core–shell” model for the profiles of nuclear and magnetic scattering length densities in polydisperse magnetite ( $\text{Fe}_3\text{O}_4$ ) particles. Two cases of polydisperse colloid systems were considered: with the typical average sizes of magnetic particles  $R_0 = 3$  and 8 nm; in both cases, the parameter of particle polydispersity was selected to equal  $S = 0.3$  for the log-normal distribution over particle dimensions. The quantities to vary were the nonmagnetic layer thickness  $h$ , the magnetic scattering length density  $\rho_m$ , the thickness  $\delta$  of the surfactant layer, and the neutron scattering length density  $\rho_1$  in it. Taking into account that the match points for the given model systems lie in a range 40–70 vol.% of the deuterated component in the fluid basis, the calculations were carried out for maximum SANS signals and a completely protonated or completely deuterated carrier fluid. Our purpose was to choose conditions for an experiment on varying the SANS contrast for a reliable (with an error less than 5%) determination of MFS particle parameters. The criterion of 5%-deviation was selected with regard for typical errors in real SANS experiments.

## 2. Description of the Model

In the case of magnetic spherical polydisperse particles and in the absence of an external magnetic field, when the magnetic moments of particles are oriented randomly, and the magnetic component of scattering is isotropic, the intensity of angular neutron scattering can be written down as a sum of nuclear and magnetic scattering terms [16],

$$I(q) = I_n(q) + (2/3)I_m(q), \quad (1)$$

where  $I_n(q)$  and  $I_m(q)$  are the nuclear and magnetic, respectively, contributions to the scattering. The coefficient  $2/3$  in the second term of formula (1) is associated with the fact that the magnetic coherent scattering length depends on the angle between the scattering vector and the magnetic moment of the atom. It emerges when the averaging is carried out over all disordered positions of magnetic moments inherent in magnetically noninteracting particles. The quantities in expression (1) can be written down as follows:

$$I_n(q) = n(\rho_0 - \rho_1)^2 \times \langle [V(r)F(qr) + \eta V(r + \delta)F(q(r + \delta))]^2 \rangle_r, \quad (2)$$

$$I_m(q) = n\rho_m^2 \langle [V(r - h)F(q(r - h))]^2 \rangle_r,$$

where  $n$  is the concentration of particles in the MFS;  $\eta = (\rho_1 - \rho_S)/(\rho_0 - \rho_1)$  is the parameter of neutron contrast, which depends on the coherent scattering length densities in the magnetic core,  $\rho_0$ , surfactant shell,  $\rho_1$ , and in the liquid medium,  $\rho_S$ ;  $\delta$  is the surfactant shell thickness;  $\rho_m$  is the magnetic scattering length density in the particle core;  $h$  is the thickness of a hypothetical nonmagnetic layer on the magnetite surface;  $V(r) = (4/3)\pi r^3$  is the volume of a sphere of radius  $r$ ; and  $F(qr) = 3(\sin(qr) - qr \cos(qr))/(qr)^3$  is the form factor of this sphere. In the second expression of system (2), the scattering magnetic particles with the effective volume  $V_m = (4/3)\pi(r - h)^3$  are assumed to be located in a nonmagnetic medium, and the notation  $\langle \dots \rangle_r$  means the averaging with a log-normal distribution function, which looks like

$$Dn(r) = \frac{\exp(-\ln^2((r/R_0)/2S^2))}{r\sqrt{2\pi S}}.$$

In the Guinier approximation region ( $qR_g < 1$ ), the corresponding approximation is used [16],

$$I(q) \simeq I(0) \exp(-(qR_g)^2/3), \quad (3)$$

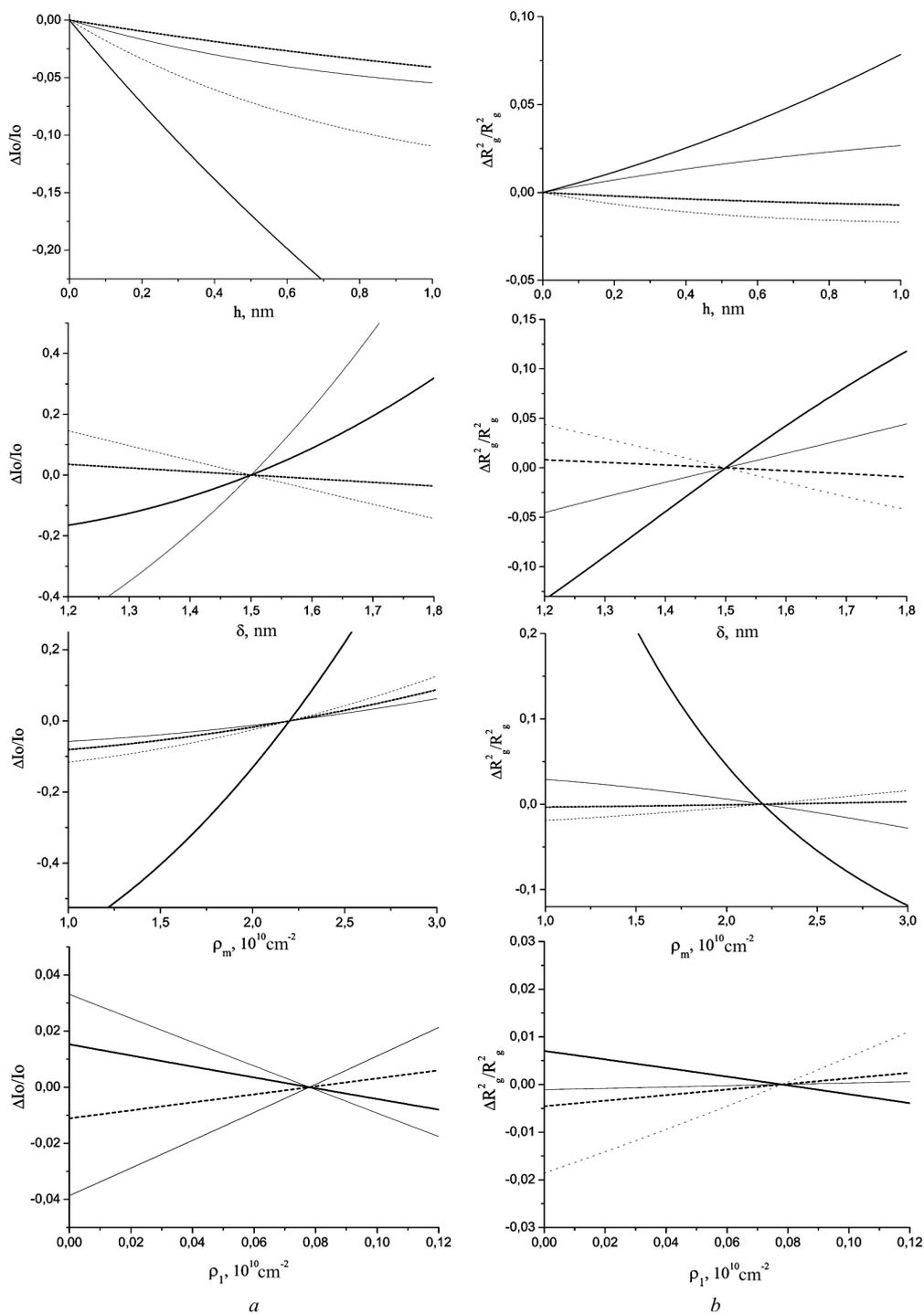
where  $I(0)$  is the intensity of zero-angle scattering, and  $R_g$  is the gyration radius of the particle. Using Eqs. (2) and (3) and introducing the notation  $\Delta\rho = \rho_0 - \rho_1$ , we obtain

$$I(0) = n(\Delta\rho)^2 \langle [V(r) + \eta V(r + \delta)]^2 \rangle_r + (2/3)n\rho_m^2 \langle V_m(r - h)^2 \rangle_r,$$

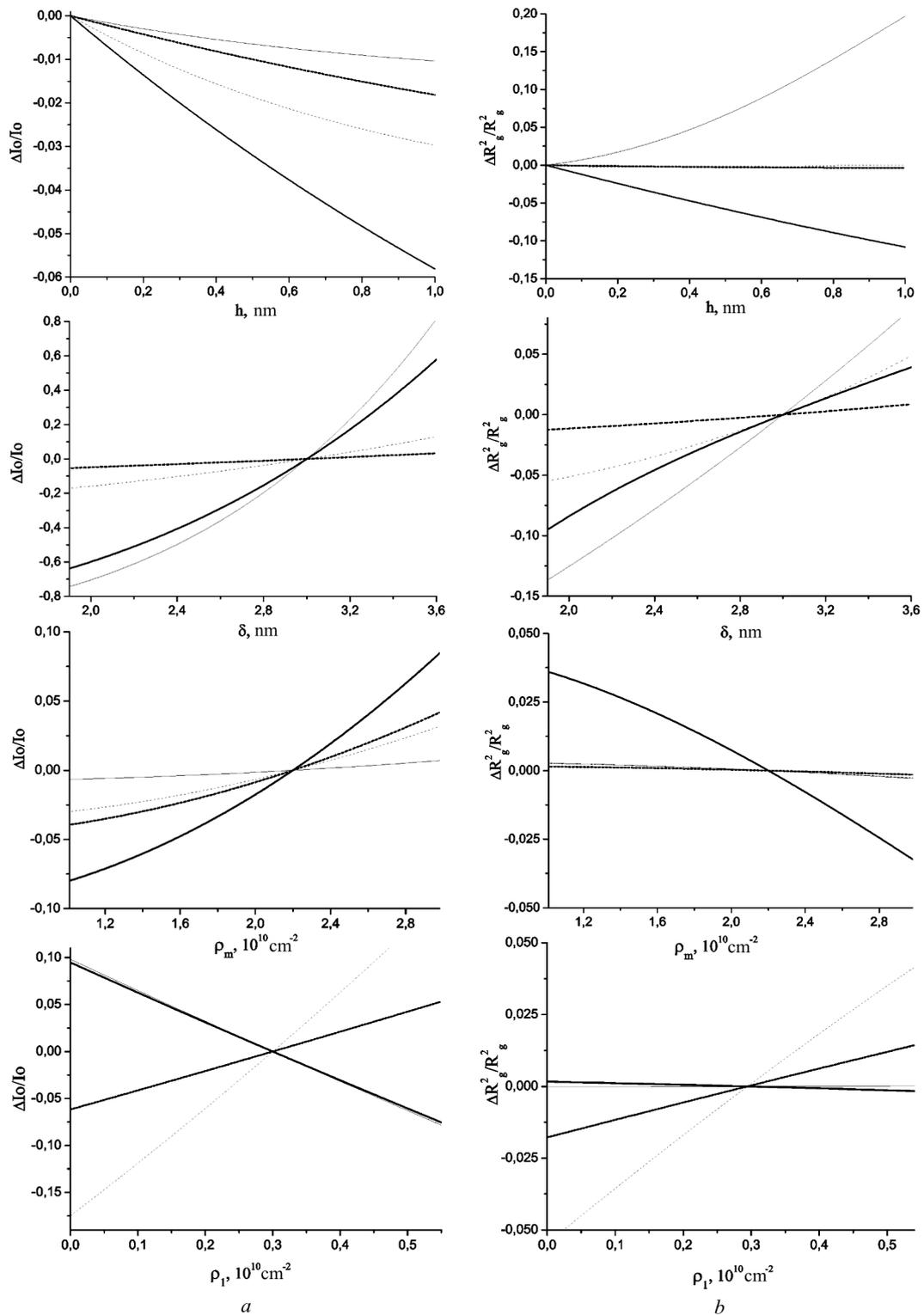
$$R_g^2 = (1/A) \langle [rV(r) + \eta(r + \delta)V(r + \delta) + (\eta\delta)^2 V(r)V(r + \delta)]^2 \rangle_r + (1/A)(2/3)(\rho_m/\Delta\rho)^2 \langle (r - h)^2 V_m(r - h)^2 \rangle_r, \\ A = \langle [V(r) + \eta V(r + \delta)]^2 \rangle_r + (2/3)(\rho_m/\Delta\rho)^2 \langle V_m(r - h)^2 \rangle_r. \quad (4)$$

The scattering length density in the solvent with volume fraction  $x$  of the deuterated component can be written down as  $\rho_S = x\rho_D + (1 - x)\rho_H$ , where  $\rho_D$  and  $\rho_H$  are the scattering length densities in the completely deuterated and protonated solvents, respectively; and the parameter  $x$  can vary in the interval from 0 to 1 (0–100%). We carried out calculations for two values of deuterated component fraction,  $x = 0$  and 1.

The relative changes of parameters in the Guinier approximation,  $\Delta R_g^2/R_g^2$  and  $\Delta I(0)/I(0)$ , were determined by varying the structural parameters of particles  $h$ ,  $\delta$ ,  $\rho_m$ , and  $\rho_1$ ; the other parameters were adopted to be constant. As a fixed starting point, we selected characteristic values for highly stable MFSs on the basis of nonpolar and polar organic solvents with magnetite ( $\rho_0 = 6.9 \times 10^{10} \text{ cm}^{-2}$ ) stabilized by monocarboxylic acids [15]. As a carrier fluid for the ferrofluid, we selected benzene (a nonpolar solvent,  $\text{C}_6\text{H}_6$ ) with  $\rho_D = 5.4 \times 10^{10} \text{ cm}^{-2}$  and  $\rho_H = 1.1 \times 10^{10} \text{ cm}^{-2}$ , and pentanol (a polar solvent,  $\text{C}_5\text{H}_{11}\text{OH}$ ) with  $\rho_D = 6.6 \times 10^{10} \text{ cm}^{-2}$  and  $\rho_H = -0.3 \times 10^{10} \text{ cm}^{-2}$ . The initial values for varied parameters were as follows:  $\delta = 1.5 \text{ nm}$  for a nonpolar MFS on the basis of benzene with a single surfactant layer, and  $\delta = 3 \text{ nm}$  for a polar MFS on the basis of pentanol with a double surfactant layer;  $\rho_1 = 0.08 \times 10^{10} \text{ cm}^{-2}$ ;  $h = 0 \text{ nm}$ ; and  $\rho_m = 2.2 \times 10^{10} \text{ cm}^{-2}$ . The choice of variation intervals for those parameters was based on the preliminary analysis of literature data [5, 15, 18–22]. For the parameter  $\delta$ , we selected the interval from 1.2 to 1.8 nm in the case of a nonpolar MFS and from 2.0 to 3.6 nm in the case of polar one, which corresponds to the probable effective thickness of a surfactant layer in a polar or nonpolar ferrofluid [15, 23]. The coherent scattering length density in the surfactant shell,  $\rho_1$ , was changed within an interval from 0



**Fig. 1.** Relative deviations of (a) zero-angle scattering intensity and (b) gyration radius at the variation of various parameters of the “core-shell” model in the polydisperse case for the MFS magnetite/oleic acid/benzene. Thick solid curves correspond to  $R_0 = 8$  nm, and thin solid ones to  $R_0 = 3$  nm in the case of deuterated carrier fluid; dotted curves correspond to the case of protonated carrier fluid



**Fig. 2.** The same as in Fig. 1, but for the MFS magnetite/oleic and dodecylbenzenesulfonic acids/pentanol

to  $0.12 \times 10^{10} \text{ cm}^{-2}$  to reflect the fact that, in the case of the preparation of a magnetic fluid on the basis of benzene, the solvent practically does not penetrate into the surfactant layer [23]. For a polar solvent, the scattering length density in the surfactant shell was varied within an interval from 0 to  $0.5 \times 10^{10} \text{ cm}^{-2}$ , because, in this case, the indicated magnitude is the averaged value ( $0.3 \times 10^{10} \text{ cm}^{-2}$ ) for two surfactant layers on the surface of magnetic particles, oleic ( $\text{C}_{17}\text{H}_{33}\text{COOH}$ ,  $\rho_1 = 0.078 \times 10^{10} \text{ cm}^{-2}$ ) and dodecylbenzenesulfonic ( $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{H}$ ,  $\rho_1 = 0.51 \times 10^{10} \text{ cm}^{-2}$ ) acids. The parameter  $h$  was varied within an interval from 0 to 1.0 nm, in accordance with the expected effect [8, 13]. For the magnetic scattering length density  $\rho_m$ , the variation interval amounted to  $(1.0 \div 3.0) \times 10^{10} \text{ cm}^{-2}$ .

It is known that, for an external stabilization layer to be formed in the case of polar MFSs, there must exist a certain excess of a surfactant in the bulk of a carrier fluid [5, 20]. In this case, nonadsorbed surfactant molecules may form micelles in the bulk of a polar solvent [24], the phenomenon being not observed in the case of a nonpolar solvent [25]. In this work, we did not consider the contribution to the neutron scattering by micelles, which can be formed in a polar ferrofluid only provided a surfactant excess.

### 3. Results and Their Discussion

In Figs. 1 and 2, we demonstrate the calculated dependences of relative variations for those quantities, which can be observed in SANS experiments while varying the parameters of nonpolar and polar ferrofluids indicated above. The Guinier approximation provides us with the squared gyration radius, so that we considered the variation  $\Delta R_g^2/R_g^2$ . The dotted curves correspond to the dependences obtained in the case of MFS with a completely protonated carrier fluid, and the solid curves to the case of completely deuterated carrier fluid. The thin curves correspond to MFSs with a small average particle size, and the thick ones to MFSs with a large average particle size.

Neglecting those curves in Fig. 1, for which the deviations exceed 5%, we may assert that the Guinier parameters for nonpolar MFSs are practically insensitive to the uncertainty of  $\rho_1$ , the scattering length density in the shell. By combining the corresponding information about other three parameters, we see that the most informative is the case of a completely

deuterated fluid system with large average particle dimension. It is a favorable factor for carrying out SANS experiments with very diluted MFSs on the basis of nonpolar carrier fluids. Moreover, the considerable substitution of a protonated solvent by a deuterated component additionally improves experimental conditions, because the background level of the noncoherent neutron scattering intensity in systems with a high content of the deuterated component is much lower than that in the case with protonated fluids. The data obtained for nonpolar ferrofluids in the polydisperse approximation qualitatively confirm the results of similar calculations, which were made earlier for the monodisperse case [15].

Generalizing the data obtained for MFSs on the basis of a polar carrier fluid (see Fig. 2), we come to a conclusion that, in the case of polar ferrofluid, the Guinier analysis remains valid for the determination of the thicknesses of the nonmagnetic layer and the stabilizing surfactant shell, if the concentration of a magnetic material substantially decreases. In this case, of two observed integrated parameters,  $R_g^2$  and  $I(0)$ , the latter is the most informative. However, in contrast to a low-concentration nonpolar MFS, the Guinier analysis in a polar fluid system becomes weakly sensitive to uncertainties of the parameter  $\rho_m$ . At the same time, the deviation of the parameter  $\rho_1$  from the expected value can be determined with a sufficient accuracy from the SANS experiment. Such a result is quite reasonable, because the presence of a stabilizing double layer on the nanoparticle surface simultaneously gives rise to a growth of the effective volume for the nuclear scattering and a relative reduction of the magnetic material volume, in which the magnetic scattering is observed.

### 4. Conclusions

Hence, while carrying out the small-angle neutron scattering experiments for the determination of a structure in magnetic fluid systems with low concentrations of magnetite, the most promising way is the variation of a contrast by changing the fraction of the deuterated component  $x$  in the interval of 0.75–1.0 for MFSs with relatively large average particle dimensions. On the one hand, the system is far enough from the effective match point. On the other hand, the indicated range allows one to obtain the curves of small-angle neutron scattering that are suitable for

the reliable determination of the following parameters. In the case of nonpolar MFS, these are the nonmagnetic layer thickness  $h$ , the magnetite magnetic scattering length density  $\rho_m$ , and the stabilizing shell thickness  $\delta$ ; in the case of nonpolar MFS, these are the nonmagnetic layer thickness  $h$ , the scattering length  $\rho_1$ , and the surfactant shell thickness  $\delta$ .

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ЧУТЛИВІСТЬ МЕТОДУ МАЛОКУТОВОГО РОЗСІЯННЯ НЕЙТРОНІВ ПРИ ВИЗНАЧЕННІ СТРУКТУРНИХ ПАРАМЕТРІВ МАГНІТНИХ РІДИННИХ СИСТЕМ З НИЗЬКОЮ КОНЦЕНТРАЦІЄЮ МАГНЕТИТУ

Резюме

У роботі розглядаються можливості методу малокутового розсіяння нейтронів при дослідженні магнітних рідинних систем різного типу з низькою концентрацією магнетиту (~0,1% за об'ємом), коли відсутній ефект структурного фактора. У рамках моделі "сферичне ядро-оболонка" проаналізовано структурні параметри наночастинок (густина довжини магнітного когерентного розсіяння, товщина немагнітного шару на поверхні магнітних частинок та товщина стабілізаційної оболонки), які можна одержати з експериментів малокутового розсіяння нейтронів та параметрів наближення Гінґе для інтенсивності розсіяння. За допомогою розрахунків встановлено чутливість указаної моделі до зміни структурних параметрів магнітної рідинної системи з урахуванням полідисперсності частинок. На прикладі магнітних рідинних систем магнетит/олеїнова кислота/бензол (на основі неполярної рідини-носія) та магнетит/олеїнова та додецил-бензолсульфонова кислоти/пентанол (на основі полярної рідини-носія) здійснено вибір та проведено порівняння умов виконання експерименту.