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NEUTRON STUDIES OF THE STRUCTURE OF NON-POLAR MAGNETIC FLUIDS WITH SURFACTANT EXCESS

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Non-polar magnetic fluid systems with an excess of surfactants have been studied with the use of the small-angle neutron scattering technique. Two types of highly stable ferrofluids, magnetite/oleic acid/decalin and magnetite/myristic acid/decalin, with a low (of about 1 vol.%) magnetite content and various acid fractions (up to 25 vol.%) are examined. The aggregation of magnetic particles and surfactant molecules is shown not to occur in the indicated concentration range of the acid molecule excess. The experimental results testify to a change of the interaction between the molecules of oleic and myristic acids in the free (non-adsorbed) state, when they are dissolved in magnetic fluids, and in their solutions in decalin without magnetic particles.

Keywords: magnetic fluids, ferrofluids, small-angle neutron scattering, decalin.

1. Introduction

Magnetic fluids (MFs) are colloid suspensions of magnetic particles about 10 nm in dimensions stabilized with the help of surfactants. The research of the structure of such systems has both fundamental and practical meanings [1–3].

On the one hand, the nanometer size of particles in MFs is responsible for their sedimentation stability [4, 5]. On the other hand, it provides the one-domain state of their magnetization, which results in the super-paramagnetic behavior of such fluid systems from the viewpoint of their magnetic properties. The magnetic and van der Waals interactions between particles favor their aggregation, so it is necessary to stabilize MFs, which is usually performed by means of the adsorption of surfactant molecules on the surface of magnetic nanoparticles. The aggregation stability of MFs is mainly governed by the interaction

between the surfactants and the fluid basis of a system. Therefore, one of the major factors that affect the MF stability is the concentration of surfactant molecules in the fluid system. In the course of the preparation of ferrofluids, an optimal amount of surfactants in the fluid system is chosen, at which the highest stability of the colloid system with respect to the aggregation is observed. This work continues our regular research concerning the influence of the surfactant excess (with respect to this optimum) on the structure of MFs belonging to different types [6–10].

The work aims at studying the influence of the surfactant excess on the stability of MFs created on the basis of a non-polar solvent with the help of the small-angle neutron scattering (SANS) technique. In our research, we used the magnetite/oleic acid/decalin and magnetite/myristic acid/decalin systems with various excesses of surfactants (oleic and myristic acids). If the volume ratio between magnetite and oleic (OA) or myristic (MA) acid is optimal, those fluid systems are a classical example of highly stable MFs. For the neutron contrast between acid and

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fluid (carrier) molecules to be maximum, we used deuterated decalin, which simultaneously made the level of non-coherent background obtained from the fluid basis lower. In this work, we analyze experimental SANS data obtained for OA and MA in the MF volume and in decalin in order to extract information on possible aggregation of surfactant molecules in corresponding systems and determine the character of interaction between acid molecules in those systems.

2. Experimental Part

Magnetic fluid systems magnetite/oleic acid/decalin and magnetite/myristic acid/decalin with the content of magnetic material $\varphi_m = 7$ vol.%, as well as chemically pure oleic and myristic acids, were supplied by the Center of Fundamental and Advanced Technical Research (Timisoara Branch of the Romanian Academy of Sciences). When the MF of the given type is synthesized, almost all surfactant molecules in the fluid system are adsorbed onto the surface of magnetic nanoparticles; i.e. the concentration of free, non-adsorbed surfactant in the MF volume is very low [11, 12].

Specimens with a surfactant excess were prepared for the experimental research by adding the corresponding amount of acid (the stabilizer) and deuterated decalin (D-decalin, $C_{10}D_{18}$) to the initially concentrated MFs. The final content of D-decalin in the fluid basis was about 90%. In such a way, we obtained specimens with a surfactant excess in the OA concentration interval of 5–25 vol.% and the MA concentration interval of 3–12 vol.%. To avoid the influence of the structural factor, the concentration of the magnetic material was taken $\varphi_m = 0.75$ vol.% in all specimens under study. The OA and MA solutions free of magnetic particles were obtained by dissolving the acids in deuterated decalin under the ultrasound action. The concentration of surfactants in decalin solutions amounted to 5–30 vol.% for OA and 3–10 vol.% for MA.

SANS experiments with MFs were carried out on an SANS-II installation at the Laboratory of Neutron Scattering (the Paul Scherrer Institute, Villigen, Switzerland). The SANS spectra of OA and MA solutions in D-decalin were obtained on an installation “Yellow Submarine” at the Budapest Neutron Center (the Wigner Research Centre for Physics, Budapest, Hungary). The differential scattering cross-

section per specimen volume unit (the scattering intensity $(d\sigma/d\Omega)/V_{\text{sample}} = I(q)$) was measured as a function of the absolute value of scattering vector, $q = (4\pi/\lambda) \sin(\theta/2)$, where λ is the neutron wavelength, and θ is the scattering angle. The measurements were carried out at a temperature of 25 °C. The background scattering signal from the buffer solution (D-decalin or its mixture with the acid) and the empty cuvette was subtracted from the primary experimentally registered curves. Changing to the absolute values was made by normalizing the intensity of scattering with respect to that from a 1-mm cuvette with water.

The experimental SANS dependences obtained for the MFs with the surfactant excess were approximated by the formula

$$I(q) = I(0) \times \frac{\int_{R_{\min}}^{R_{\max}} D_n(r) [V(r)F(qr) + \eta V(r+\delta)F(q(r+\delta))]^2 dr}{\int_{R_{\min}}^{R_{\max}} D_n(r) [V(r) + \eta V(r+\delta)]^2 dr} + I_S(0) \exp\left(-\frac{q^2 R_g^2}{3}\right) + I_{bkg}. \quad (1)$$

Here, the first term corresponds to the scattering by magnetic particles in the ferrofluid, $I(0) = n(\rho_0 - \rho_1)^2 \langle V^2 \rangle$ is the intensity of scattering at the zero angle, n is the concentration of particles in the MF; the parameter $\eta = (\rho_1 - \rho_S)/(\rho_0 - \rho_1)$ is determined by the scattering length density of the magnetic core, ρ_0 , the surfactant shell, ρ_1 , and the fluid medium, ρ_S ; $V(r) = (4/3)\pi r^3$ is the volume of the sphere of radius r ; δ is the effective thickness of the surfactant stabilization shell;

$$F(qr) = 3(\sin(qr) - qr \cos(qr))/(qr)^3$$

is the form factor of the sphere of radius r ;

$$D_n(r) = \exp(-\ln^2((r/R_0)/2S^2))(r\sqrt{2\pi S})^{-1}$$

is the function of the log-normal distribution over dimensions with the characteristic radius R_0 and the standard deviation S ; R_{\min} and R_{\max} are the minimum and maximum sizes of magnetite particles in the fluid. The second term in formula (1) corresponds to

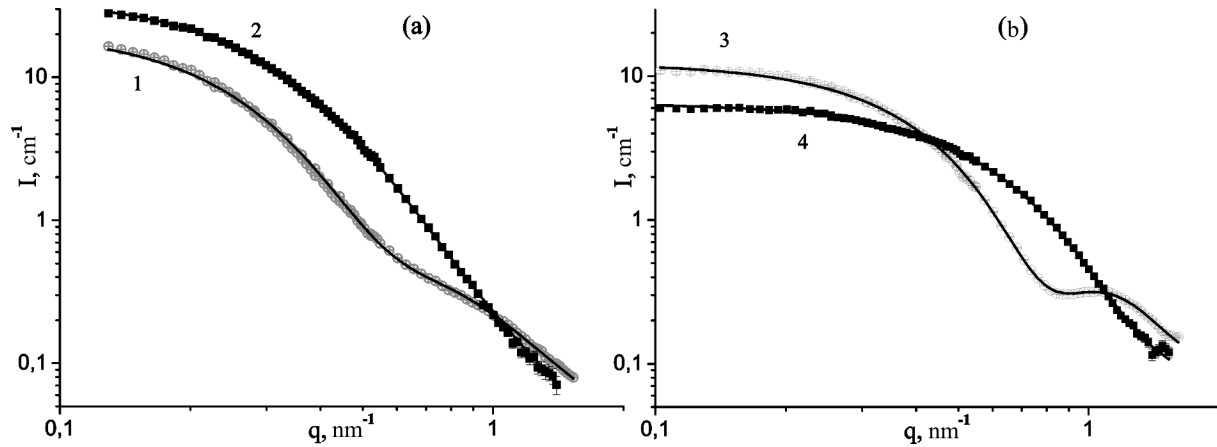


Fig. 1. Experimental SANS curves for MFs stabilized with the molecules of oleic (a) and myristic (b) acids with no surfactant excess in the system. Curves 1 and 3 correspond to ferrofluid specimens prepared on the basis of deuterated decalin (90% D-decalin), and curves 2 and 4 to specimens with a D-decalin content of 10%. Solid curves are the approximation of experimental data by formula (1) with the omitted second term

the scattering by free non-adsorbed surfactant molecules in the system; here, $I_S(0)$ is the intensity of scattering at the zero angle for free acid molecules in the fluid, R_g is the radius of inertia of a surfactant molecule in decalin, and I_{bkg} is the intensity of residual non-coherent background. In expression (f1), the first term describes the scattering by polydisperse spherical nanoparticles with the structure “core–shell”, and the second one corresponds to the scattering by free OA or MA particles in the MF volume. According to small dimensions of the molecules (about 2 nm), we used the Guinier formula for the latter term. As the first approximation, the magnetic scattering in formula (1) was neglected.

Experimental data obtained for MF specimens with no excess of OA and MA (Fig. 1) were approximated by expression (1), in which the second term was omitted. In this case, only the parameters R_0 and S in the size distribution, the surfactant shell thickness δ , and some other parameters of the “core–shell” model (these are $I(0)$, I_{bkg} , and η) were determined. For ferrofluids with a certain excess of acids in the MF volume, the first three indicated parameters were fixed, and the integral parameters of OA and MA molecules (these are $I(0)_S$ and R_g) were determined together with other parameters.

For the interpretation of SANS data obtained for the OA and MA solutions in decalin in the absence of magnetic particles in the fluid, the Guinier approxi-

mation was used,

$$I(q) = I(0) \exp(-q^2 R_g^2/3) + I_{bkg}. \quad (2)$$

From the analysis of the concentration dependences of the integral parameters (the intensity of scattering at the zero angle and the inertia radius) obtained for free acid molecules in the MF volume and in the solvent (decalin), it is possible to estimate the character of the effective interaction between OA and MA molecules, respectively. As was shown earlier [13–15], in the case of small molecules in solutions, the concentration dependence of the intensity of scattering at the zero angle can be written down in the form

$$I(0)/\Phi \approx C(1 + \Phi B), \quad (3)$$

where Φ is the volume fraction of molecules in the solution, C is a constant related to the effective volume of particles, $B = (1/v) \int (g(r) - 1) dV$ is a dimensionless analog of the second virial coefficient in the pair interaction potential, v is the volume occupied by a particle in the solution, and $g(r)$ is the pair radial distribution function. The sign of the parameter B testifies to the interaction character: this is attraction if $B > 0$, and repulsion if $B < 0$. For example, for the hard-sphere potential, $B = -8$ (pure repulsion) [13]. A similar expression for the concentration dependence of the experimentally apparent radius of inertia looks like

$$R_g^2 \approx R_{g0}^2 + \Phi B L^2 / (1 + B\Phi), \quad (4)$$

where R_{g0} is the true radius of inertia, and L is the correlation distance between two particles in the solution.

3. Results and Their Discussion

Experimental curves for initial MF specimens with no surfactant excess in the system volume and with a magnetite content of 0.75% are shown in Fig. 1 for the magnetite/oleic acid/decalin (panel *a*) and magnetite/myristic acid/decalin (panel *b*) systems. The scattering spectra from the mentioned ferrofluids were obtained for two different neutron contrast lev-

els, when the fluid basis of the systems was prepared by adding D-decalin in such a manner that its content amounted to 90 and 10% with respect to H-decalin.

In addition, the isotopic substitution in the solvent made it possible to determine the parameters R_0 and S in the distribution function over the size and the effective thickness of the stabilization shell δ more precisely: for the MF stabilized with OA molecules, $R_0 = 3.8(3)$ nm, $S = 0.36(1)$, and $\delta = 1.4(3)$ nm; and for the MF stabilized with MA molecules, $R_0 = 2.8(1)$ nm, $S = 0.26(1)$, and $\delta = 1.4(2)$ nm. The

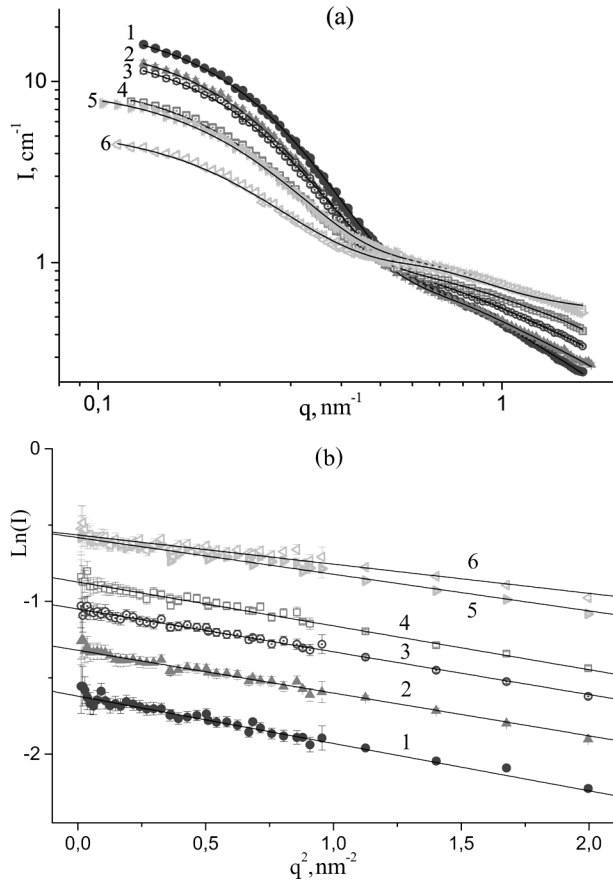


Fig. 2. (a) Experimental SANS curves for the fluid system magnetite/oleic acid/decalin with various excesses of OA molecules (symbols) and their approximations by formula (1) (solid curves). Curves 1 to 6 correspond to the excess OA content with concentrations of 5, 7, 10, 15, 20, and 25 vol.%, respectively. (b) SANS spectra for the OA solutions in decalin and their Guinier approximations (formula (2)) on the logarithmic scale. Curves 1 to 6 correspond to the solutions with various concentrations of oleic acid: 5, 7, 10, 12, 20, and 30%, respectively

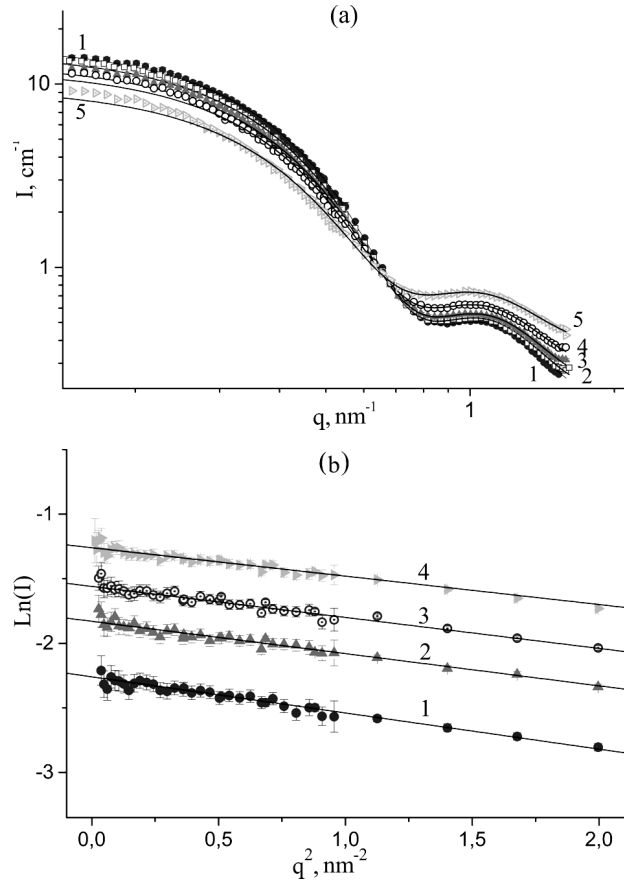


Fig. 3. (a) Experimental SANS curves for the fluid system magnetite/myristic acid/decalin with various concentrations of excess MA molecules (symbols) and their approximations by formula (1) (solid curves). Curves 1 to 5 correspond to the excess MA content with concentrations of 3, 5, 7, 10, and 12 vol.%, respectively. (b) SANS spectra for the MA solutions in decalin with various concentrations and their Guinier approximations (formula (2)) on the logarithmic scale. Curves 1 to 4 correspond to the solutions with various MA concentrations: 3, 5, 7, and 10 vol.%, respectively

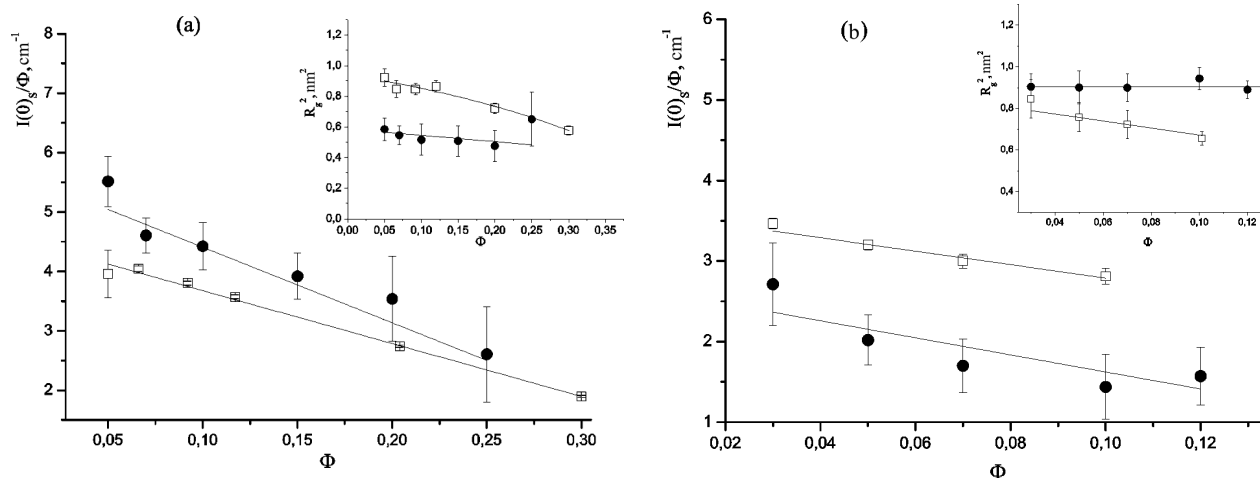


Fig. 4. Dependences of the intensity of scattering at the zero angle normalized by the concentration on the concentrations of excess oleic (a) and myristic (b) acids in the corresponding magnetic fluid (solid circles) and decalin (hollow squares). The insets demonstrate the concentration dependences of the squared radius of inertia of OA (a) and MA (b) molecules in the corresponding MF and decalin

averaging over the dimensions was carried out within the interval from 1 to 14 nm. In what follows, those parameters of model (1) were fixed. The parameters of the distribution function over magnetite particle dimensions, which were obtained in both cases, coincided with the corresponding parameters for similar MFs obtained earlier [16].

In Figs. 2 and 3, the experimental SANS data obtained for the magnetic fluid systems with various excess volume contents of OA and MA, respectively, are depicted. The exhibited dependences were approximated by formula (1). In general, the approximations demonstrate a good correspondence between the theoretical curves and the experimental data. The obtained structural parameters of MFs completely reproduce the results obtained in our previous work [16]. Figures 2,b and 3,b demonstrate the SANS data obtained for the specimens of the solutions of corresponding monocarboxylic acids with various concentrations in deuterated decalin. The deuterated solvent was used to enhance the neutron contrast between the OA and MA molecules, on the one hand, and the solvent molecules, on the other hand, as well as to reduce the intensity of non-coherent background scattering.

The values of integral parameters $I(0)$, S , and R_g^2 , which were obtained for non-adsorbed molecules of the acids concerned by approximating the experimental data shown in Figs. 2 and 3, were used to plot the

dependences in Fig. 4 according to formulas (3) and (4). The values of the dimensionless analog of the second virial coefficient amounted to $B = -1.95$ and -2.2 for the OA solutions in decalin and MF, respectively, which is much larger than $B = -8$ for the hard-sphere potential. In the cases of the MA excess in the MF volume and the MA solution in decalin, the coefficient values are as follows: $B = -2.5$ and $B = -2.3$, respectively. From whence, we may draw a conclusion that the attraction forces play a considerable role in the pair interaction potential between OA and MA molecules. The dependences depicted in Fig. 4 testify that the interactions between acid molecules in decalin and MF do not differ substantially. However, the acid molecules in the MF reveal the additional repulsion, which is evidenced by a lowered value of dimensionless coefficient B . This phenomenon can be associated with the so-called “depletion attraction” [17], when the effective attraction arises in the system owing to the removal of relatively small surfactant molecules from the space between relatively large magnetic particles.

4. Conclusions

Non-polar magnetic fluids with an excess of monocarboxylic acids are studied with the help of the small-angle neutron scattering technique. The results of our experiments allow us to draw a conclusion that all MFs with an excess of the surfactant content in

the considered concentration interval remain stable with respect to the aggregation. According to the plotted concentration dependences of the integral parameters for the molecules of oleic and myristic acids, the character of the interaction between them is estimated. It is shown that a reduction of attraction forces between the surfactant molecules in the fluid systems takes place, which is associated with the presence of magnetic particles, in contrast to the solutions of corresponding acids in the fluid basis, decalin. An enhancement of the attraction forces between non-adsorbed OA molecules in the magnetic fluid is observed in comparison with the MF stabilized by MA. Thus, from the viewpoint of MF microstructure, it is demonstrated that the interaction between the fluid and the surfactant plays an important role in the stabilization of the given fluid systems with an excess surfactant content.

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НЕЙТРОННІ ДОСЛІДЖЕННЯ СТРУКТУРИ НЕПОЛЯРНИХ МАГНІТНИХ РІДИННИХ СИСТЕМ З НАДЛИШКОМ ПОВЕРХНЕВО-АКТИВНИХ РЕЧОВИН

Резюме

У роботі представлено результати дослідження структури неполярних магнітних рідинних систем з надлишком поверхнево-активних речовин, які отримані методом малокутового розсіяння нейтронів. У ролі магнітних рідинних систем було вибрано високо стабільні ферофлюїди магнетит/олеїнова кислота/декалін та магнетит/мірїстинова кислота/декалін з низьким вмістом магнетиту (~1% за об'ємом) за різних значень надлишку кислот (до 25% за об'ємом). Показано, що у досліджуваному діапазоні концентрацій надлишку молекул кислот, агрегація магнітних частинок та молекул стабілізатора не відбувається. У результаті додаткового порівняння зроблено висновки щодо зміни у взаємодії між вільними (не адсорбованими) молекулами олеїнової та мірїстинової кислот у магнітних рідинних системах та їх розчинах у декаліні.