SANS study of concentration effect in magnetite/oleic acid/benzene ferrofluid

V. Aksenov[1], **M. Avdeev**[1,*], **M. Balasoiu**[1,3], **L. Rosta**[2], **G. Török**[2], **L. Vekas**[4], **D. Bica**[4], **V. Garamus**[5], **J. Kohlbrecher**[6]

[1] Frank Laboratory of Neutron Physics, JINR, 141980 Moscow region, Dubna, Russia
[2] Research Institute for Solid State Physics and Optics, KFKI, 1525 Budapest, Hungary
[3] Institute of Space Sciences, 76900 Bucharest, Romania
[4] Center of Fundamental and Advanced Technical Research, Timisoara Branch of RAS, Timisoara-1900, Romania
[5] GKSS Research Centre, 21502 Geesthacht, Germany
[6] Paul Scherrer Institut, 5232 Villigen, Switzerland

Abstract. The effect of the colloidal particle concentration on the structure of the magnetite/C_6D_6 ferrofluid stabilized by oleic acid is investigated by small-angle neutron scattering (SANS). A significant decrease in the thickness of the surfactant layer with increase in the magnetite concentration is observed. This points to the fact that the interparticle interaction increasing with the concentration presses the surfactant tails in the layer closer against the magnetite surface. The influence of magnetic scattering on the SANS curves is considered.

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Ferrofluids or magnetic fluids, colloidal solutions of magnetic materials stabilized by adding surfactants, are of current interest. Specific properties in a magnetic field, as well as the possibility of controlling these properties by a magnetic field determine a wide use of ferrofluids in different industrial applications [1].

Structural parameters of colloidal particles in ferrofluids, in particular, the thickness and composition of the surfactant layer, affect the stability of ferrofluids [2]. In the present paper, small-angle neutron scattering (SANS) is used to follow possible changes in these parameters with the particle concentration [2] in the magnetite/oleic acid/benzene ferrofluid.

1 Experimental

The studied ferrofluid based on deuterated benzene was produced at the Laboratory of Magnetic Fluids, CFATR, Timisoara, Romania [3]. The size distribution function $D_N(R)$ of magnetite particles was obtained by the analysis of electron microscopy (EM) images and is well described by lognormal distribution ($<R> = 4.2$ nm, $\sigma_R = 1.3$ nm). The original fluid with the magnetite concentration $c_m = 19.0$ vol. % and the surfactant/magnetite volume concentration ratio 1:1 was diluted at room temperature to several c_m values from 19 to 0.5 vol. %.

*Corresponding author.
(Fax: +7-096/2165484, E-mail: avd@nf.jinr.ru)

SANS experiments in normal conditions in a q-range $0.2 \div 5$ nm^{-1} were carried out on the small-angle diffractometer at the Research Institute for Solid State Physics and Optics at the Budapest Neutron Centre, Hungary. Scattering curves for q-values down to 0.03 nm^{-1}, as well as scattering patterns from the samples in a magnetic field up to 10 kOe were obtained at the SANS diffractometer at the SINQ neutron source of the Paul Scherrer Institute, Villigen, Switzerland [4].

Scattering curves were treated using the model of non-interacting polydisperse two-shell particles [5]. The intensity in zero angle $I(0)$, background B, thickness of the surfactant layer δ_1 and ratio $\eta_1 = (\varrho_1 - \varrho_s)/(\varrho_0 - \varrho_1)$, where ϱ_0, ϱ_1, ϱ_s are the scattering length densities of the magnetite core, surfactant shell and solvent, respectively, were varied at fixed parameters of $D_N(R)$ taking into account the resolution effect [6]. To reveal the influence of magnetic scattering on the resulting parameters of the fits, measurements when samples were in a magnetic field were performed. The isotropic $A(q)$ and anisotropic $B(q)$ contributions to two-dimensional scattering patterns were separated according to the expression:

$$I(q, \varphi) = A(q) + B(q) \sin^2 \varphi , \tag{1}$$

where φ is the angle between the direction of the applied magnetic field and scattering vector.

2 Results and discussion

SANS curves in a q-range $0.2 \div 5$ nm^{-1} [5] are shown in Fig. 1. Despite the fact that the possible magnetic scattering in the system is not taken into account the fits are quite good. This is indicative of little effect of magnetic scattering in a given q-interval. The fits result in a significant decrease in the thickness of the surfactant layer with an increase in the magnetite concentration, which is presented in Fig. 2. This may be explained by the effect of interparticle interaction, which increases with the particle concentration and presses the surfactant tails in the layer closer against the magnetite surface. Another structural parameter η_1 reflecting the rate of the penetration of the solvent into the surfactant shell does
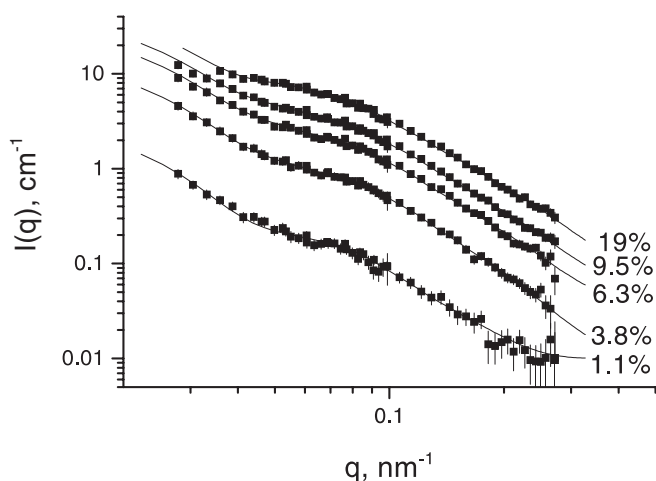
Fig. 1. Experimental (*points*) and model (*lines*) SANS curves at different magnetite concentrations indicated to the *right* of the graphs
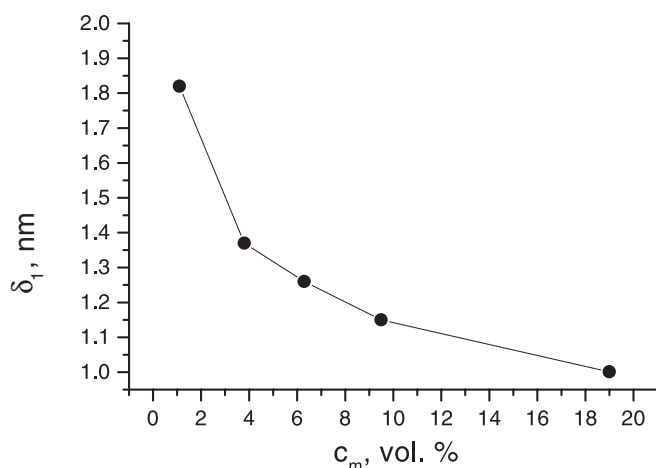

Fig. 3. $A(q)$ function at $c_m = 5$ vol. %. Results of fits are $I(0) = 13.2$ cm^{-1}, $B = 0.027$ cm^{-1}, $\delta_1 = 1.34$ nm, $\eta_1 = -0.779$ ($H = 0$) and $I(0) = 10.1$ cm^{-1}, $B = 0.018$ cm^{-1}, $\delta_1 = 1.19$ nm, $\eta_1 = -0.778$ ($H = 10$ kOe)

stant with a change in the layer thickness is more reliable, which means that one still has a significant systematic error in η_1. We note here that the contrast variation with changing the solvent scattering length density in ferrofluids [7, 8] also does not give conclusions about the structure of the surfactant layer. We believe that an increase in the scattering length density of the layer using deuterated surfactants will help to solve this problem.

Fig. 2. Thickness of surfactant layer δ_1 as a function of magnetite concentration

not change with the magnetite concentration and equals to -0.800. However, the precision in η_1 is not enough to conclude about the shell composition because of the smallness of the absolute scattering length density of the surfactant.

Figure 3 reflects how the width of the q-interval, as well as the magnetic scattering in the system affect the resulting parameters of the previous fits. The $A(q)$ function in the magnetic field $H = 10$ kOe corresponds to the nuclear scattering only, since the plateau on the plots of integrals of $A(q)$ and $B(q)$ over a q-range $0.05 \div 1$ nm^{-1} against H is observed for H of more than about 5 kOe. One can see that the width of a q-interval has a minor influence on δ_1, while the magnetic scattering at zero magnetic field results in 13% shift to upper values. And vice versa, the η_1 parameter is quite sensitive to the q-range and does not change when magnetic scattering is taken into account. It should be pointed out that new η_1 values are significantly closer to the value of -0.777 calculated using the bulk density of the surfactant and in assumption that the solvent does not penetrate into the surfactant shell. The latter, however, cannot be realized if the thickness of the surfactant layer changes. So, the case when the solvent penetration into the layer takes place and its rate remains con-
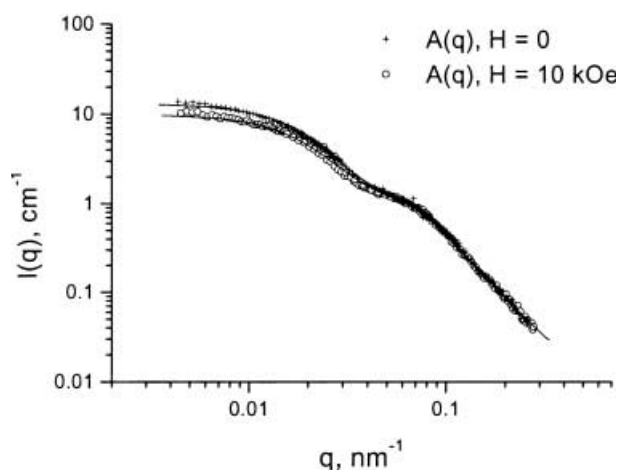
3 Conclusions

A significant change in the thickness of the surfactant layer with the particle concentration in magnetite/oleic acid/C_6D_6 ferrofluid is observed in SANS experiments. The thickness of the surfactant layer can be determined with a good precision (about 5%) by a direct fit to SANS curves of the model of noninteracting polydisperse two-shell particles in a q-range $0.1 \div 5$ nm^{-1}. It is necessary to take the magnetic scattering into account and perform additional measurements in a magnetic field of more than 5 kOe. To solve the problem of the inner structure of the surfactant layer further experiments with deuterated surfactants are required.

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