



SANS study of particle concentration influence on ferrofluid nanostructure

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Abstract

The effect of the magnetic particle concentration on the structure of the ferrofluid based on magnetite and oleic acid in deuterated benzene is investigated by means of small-angle neutron scattering. A significant decrease in the thickness of the surfactant layer with an increase in the magnetite concentration is observed. This points to the interlacing of surfactant tails in the layer caused by the interparticle interaction.

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1. Introduction

Structural parameters of colloidal particles in ferrofluids, in particular, the thickness of the surfactant layer, are responsible for the stability and aging process of the fluids in different conditions [1]. In the present work, the results of small-angle neutron scattering (SANS) experiments reflecting how the surfactant layer changes with the particle concentration in magnetite-based ferrofluids are discussed.

2. Materials and methods

The studied ferrofluid on the basis of magnetite and oleic acid in deuterated benzene was obtained [2,3] at the Laboratory of Magnetic Fluids, Timisoara Branch of Romanian Academy. The magnetite concentration c_m of

19 vol% was determined by the saturation magnetization value of 838 G. The content of the surfactant (oleic acid) was 21.5 vol% corresponding approximately to the magnetite/surfactant ratio 1:1. The density of the fluid was 1.724 g cm^{-3} . The type and parameters of the size distribution function of magnetite particles were obtained by the analysis of electron microscopy (EM) images. A lognormal distribution with $\langle R \rangle = 4.2$ and $\sigma_R = 1.3 \text{ nm}$ within an R -interval of 2.5–9.0 nm, was detected. The original fluid was diluted at room temperature to the magnetite concentration c_m of 9.5, 6.3, 3.8, 1.1 vol%.

SANS experiments in normal conditions (without applying magnetic field) were carried out on the small-angle diffractometer at the Research Institute for Solid State Physics and Optics at the Budapest Neutron Centre (BNC), Hungary. Measurements were made at the fixed neutron wavelength of 0.36 nm (resolution 13%) and two sample detector distances of 5.5 and 1.5 m covering a q -range $0.19\text{--}5 \text{ nm}^{-1}$. The calibration was made with H_2O [4] following the usual procedure [5]. Pure deuterated benzene was used as buffer.

The used model expression of SANS intensity of noninteracting polydisperse spherical homogeneous

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magnetic particles covered by a homogeneous shell has the form

$$I(q) = I(0) \frac{\int_{R_{\min}}^{R_{\max}} D_N(R_0) F(q, R_0) dR_0}{\int_{R_{\min}}^{R_{\max}} D_N(R_0) F(q, 0) dR_0} + B, \quad (1)$$

$$F(q, R_0) = ((\rho_0 - \rho_1)V_0\Phi(qR_0) + \rho_1 V_1\Phi(qR_1))^2 + \frac{2}{3}\rho_m^2 V_0^2 \Phi^2(qR_0), \quad (2)$$

$$\Phi(x) = 3 \frac{\sin(x) - x \cos(x)}{x^3}, \quad (3)$$

where q is the module of the scattering vector, $I(0)$ is the intensity in zero angle; B is the incoherent background remaining on subtraction of the buffer scattering; R_0 is the radius of the magnetite particle; $D_N(R)$ is the size distribution function of the magnetite particles with the minimal, R_{\min} , and maximal, R_{\max} , radii; ρ_0 is the contrast of the core (difference in the scattering density of the core and solvent); ρ_1 is the contrast of the shell; ρ_m is the magnetic scattering density of the magnetite core; $V_i = 4/3\pi R_i^3$ is the volume restricted by the radius R_i , $R_i = R_0 + \delta_1$, where δ_1 is the thickness of the shell. Eq. (1) assumes that the magnetic radius of the magnetite particle coincides with its nuclear radius.

Parameters $I(0)$, B , δ_1 , $\eta_1 = \rho_1/(\rho_0 - \rho_1)$ were varied at the fixed ρ_m value of $3.068 \times 10^{10} \text{ cm}^{-2}$ [6] and fixed parameters of $D_N(R)$ known from EM. The fits were performed taking into account the instrumental resolution function calculated according to [7].

3. Results

The experimental scattering curves are shown in Fig. 1. Eq. (1) was fitted to the experimental data and did not give stable fits with reliable parameters. We believe that the reason for this fact is connected with the difference between nuclear and magnetic radii of the magnetite particles, reported previously [6]. Along with this, if the term corresponding to the magnetic scattering in Eq. (2) is neglected, the model fits the data well (Fig. 1). The results of these fits are presented in Table 1. Modeling of the magnetic contribution independent of the nuclear one requires more parameters. The more correct way to take the magnetic scattering into account is to perform SANS experiments when samples are in a magnetic field, and the nuclear and magnetic scattering contribution can be separated. Experiments of such kind are in our plans. The fact that the model, when the magnetic scattering is neglected, works well points to a small systematic effect of the latter on the obtained parameters. Similarly, the interparticle interaction in the solutions has a small effect on the scattering curves in the studied q -interval, since Eq. (1) does not take it into account. To reveal the influence of the interparticle

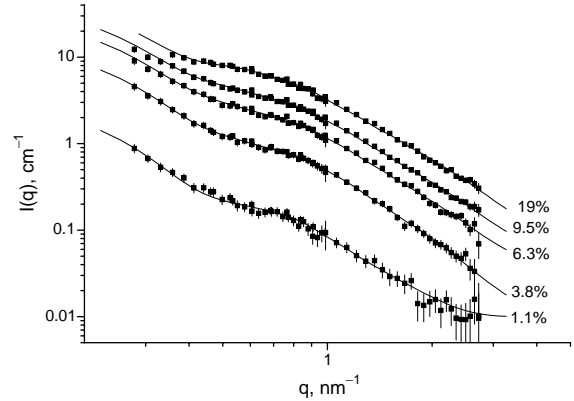


Fig. 1. Experimental (points) and model (lines) scattering curves at different magnetite concentrations indicated to the right of the graph. Magnetic scattering was not taken into account when fitting.

Table 1

Results of the fits at different magnetite concentration values c_m

| c_m (vol%) | $I(0)$ (cm^{-1}) | B (cm^{-1}) | δ_1 (nm) | η_1 |
|--------------|-----------------------------|--------------------------|-----------------|----------|
| 1.1 | 3.4 | 0.009 | 1.85 | -0.774 |
| 3.8 | 15.6 | 0.010 | 1.39 | -0.801 |
| 6.3 | 32.1 | 0.036 | 1.27 | -0.801 |
| 9.5 | 44.9 | 0.045 | 1.17 | -0.801 |
| 19.0 | 63.1 | 0.055 | 1.05 | -0.801 |

interaction on the obtained parameters, further experiments at smaller q -values are required.

It should be pointed out that the discussed fits are stable in respect to the parameters of the particle size distribution. If we vary parameters $\langle R \rangle$, σ_R , R_{\min} , R_{\max} in addition to parameters $I(0)$, B , δ_1 , η_1 starting with the values indicated in the previous chapter, despite a quite large number of free parameters the difference between their initial and final values does not exceed 5% in wide intervals of initial values of parameters $I(0)$, B , δ_1 , η_1 .

The obtained parameters δ_1 and η_1 (Table 1) give the information about the structural changes of the surfactant layer with the magnetite concentration. One can see that the thickness δ_1 of the surfactant layer decreases significantly with an increase in the magnetite concentration, which can be explained by the interlacing of surfactant tails on the surface of magnetite caused by the interparticle interaction. At the same time, parameter η_1 does not change with the magnetite concentration, except for the smallest c_m , which means that in spite of the decrease in the volume of the surfactant shell, the contrast of the latter remains constant. However, the smallness of the absolute scattering density of the surfactant ($0.077 \times 10^{10} \text{ cm}^{-2}$ in the bulk) along with a strong influence of the error in η_1 on the accuracy in ρ_1 does not allow us to conclude about the layer content, in

particular, to estimate the rate of solvent penetration into the layer by the η_1 values.

4. Conclusions

For the ferrofluid on the basis of magnetite and oleic acid in the nonpolar organic solvent the concentration effect on the thickness of the surfactant layer is well observed by means of SANS in a q -range $0.2\text{--}5\text{ nm}^{-1}$. The model of noninteracting spherical particles covered by a homogeneous shell fits experimental data well in the given q -interval at the magnetite concentration up to 19 vol% revealing a significant decrease in the thickness of the shell with an increase in the magnetite concentration. The analysis of the effect of interparticle interaction as well as magnetic scattering on the accuracy in the found thickness values and other parameters require additional SANS experiments.

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