

INTERACTION EFFECTS IN NON-POLAR AND POLAR FERROFLUIDS BY SMALL-ANGLE NEUTRON SCATTERING

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Abstract. Small-angle scattering of non-polarized neutrons is applied to reveal the character of the interparticle interaction in ferrofluids. Scattering curves obtained at the SANS diffractometer of the Budapest Neutron Center are analyzed with respect to the scattering structure-factor reflecting this interaction. Two types of ferrofluids which are magnetite stabilized sterically in non-polar (benzene) and polar (pentanol) carriers, are considered. A principle difference between the two types of non-magnetized samples is observed. In the non-polar fluids the interaction effect on the scattering is small even for a comparatively high volume fraction of magnetite ($> 5\%$), while in polar fluids it starts to be visible since 1%, which can be explained by the observed difference in the characters of the interaction potential.

Key words: ferrofluids, magnetic fluids, interaction, small-angle neutron scattering.

1. INTRODUCTION

At present, ferrofluids (magnetic fluids), stable dispersions of magnetic materials in liquids, are widely used systems in different applications including technical, industrial and biomedical fields [1,2]. The most stable ferrofluids are formed in organic non-polar solvents, where the highest volume fractions of magnetic material, φ_m , can achieve 25% [3]. The stabilization of these fluids takes place after a single layer of surfactants covers the surface of the magnetic particles, which is enough to avoid the particle aggregation in various external conditions including magnetic fields and temperature effects. However, modern needs require the continuous development of the methods for synthesizing new classes of ferrofluids, especially in the case of polar carriers. Stabilization of ferrofluids based on polar carriers is a more complicated problem, and a single surfactant layer

around the magnetic particles providing only sterical repulsion between particles in the fluids is not enough. Recently, methods of double sterical stabilization were developed for several classes of polar carriers [4,5]. The technique implies that after the surfactant of one type is adsorbed on the particle surface through chemical adsorption, the surfactant of the same or another type (depending on the adsorption properties) is adsorbed on the previous layer through physical adsorption. As a whole, the stability of these fluids is less than that of organic non-polar ferrofluids. Nevertheless, there are samples of the highest stability, which also allows large values of φ_m up to 20%. One of such samples is the ferrofluid based on pentanol. In the stabilization process the combination of oleic acid and dodecylbenzenesulphonic acid is used.

The aim of the current work is to compare this ferrofluid with that based on non-polar carrier (benzene) and stabilized with a single surfactant layer (oleic acid) with respect to the interaction character between colloidal particles in the samples. We do this with the help of small-angle neutron scattering (SANS), which is actively used now for revealing features of ferrofluids at a nanoscale of 1-100 nm [6-23]. The study of the interaction effect in ferrofluids is quite difficult, since one deals with the system of polydisperse and multicomponent particles, whose magnetic interaction is orientation dependent. However, the analysis of the concentration effect on the scattering curves makes it possible to compare qualitatively different classes of ferrofluids and shows principle differences in the interparticle interaction for the studied systems.

2. EXPERIMENTAL

Studied ferrofluids were produced at the Center of Fundamental and Advanced Technical Research, Timișoara Branch of RAS, Romania. Magnetite obtained by the chemical condensation reaction was dispersed into benzene and pentanol up to volume fractions of about 15 and 20%, respectively, found from the magnetization saturation. Details of the preparation procedure are fully covered in previous works [3, 4]. The studied ferrofluids showed excellent stability both in the absence and presence of external magnetic field. To follow the concentration effect, the initial samples were dissolved by pure solvents to several values of volume fraction of magnetite in the φ_m -range from 0.6 to 20%, so that the ratio between magnetite and the surfactants remained the same.

The small-angle neutron scattering (non-polarized neutrons) experiments were performed at the Research Institute for Solid State Physics and Optics at the Budapest Neutron Centre (BNC), Hungary, diffractometer "Yellow Submarine". The use of neutron wavelength of 0.4 (resolution 18%) and SD distances of 1.3 and 5.5 m resulted in the covered q -interval of $0.1\div 4 \text{ nm}^{-1}$. The data were calibrated on water.

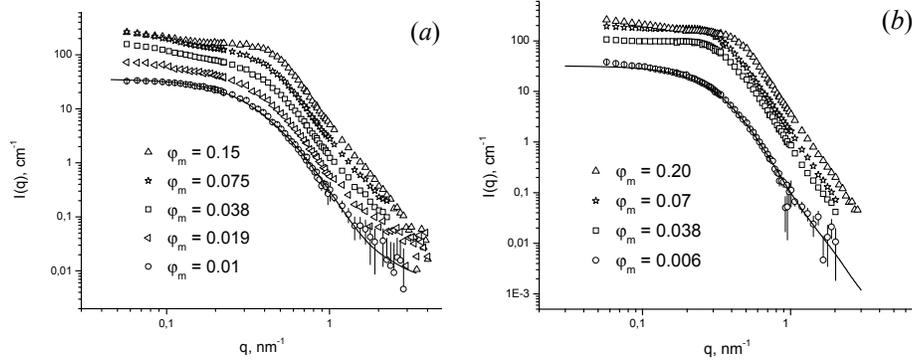


Fig. 1 – Experimental scattering curves (points) obtained at different volume fraction of magnetite for ferrofluids based on benzene (a) and pentanol (b). Lines correspond to modeling curves at the lowest values of φ_m : (a) fit of the core-shell model according to Eqs. 1a-1d; resulting parameters are $R_0 = 2.38$ nm; $S = 0.46$; $R_{min} = 1.0$ nm; $R_{max} = 11.0$ nm; $h = 1.0$ nm; $\eta_1 = -0.14$; $I(0) = 36$ cm⁻¹; (b) fit of the spherical model according to Eqs. 3a-3b; resulting parameters are $R_0 = 3.4$ nm; $S = 0.38$; $R_{min} = 1.0$ nm; $R_{max} = 11.0$ nm; $I(0) = 32$ cm⁻¹.

3. RESULTS AND DISCUSSION

Experimental scattering curves at different φ_m -values for two studied types of ferrofluids are given in Fig. 1. The curves corresponding to the smallest φ_m -values fit well the model of non-interacting particles (Fig.1). For the benzene-based ferrofluid the model describes spherical core-shell particles with quite small scattering contrast between the shell (scattering length density $\rho \sim 0.1 \times 10^{-10}$ cm⁻²) and carrier ($\rho \sim 1.2 \times 10^{-10}$ cm⁻²). The formula for the scattering intensity (differential scattering cross-section per sample volume) in this case is the following:

$$I(q) = \frac{I(0)}{\langle (V(R) + \eta_1 V(R+h))^2 \rangle_R} \times \int_{R_{min}}^{R_{max}} D_N(R) \{V(R)\Phi(qR) + \eta_1 V(R+h)\Phi(q(R+h))\}^2 dR + B \quad (1a)$$

$$I(0) = n(\rho_0 - \rho_1)^2 \langle (V(R) + \eta_1 V(R+h))^2 \rangle_R, \quad (1b)$$

$$V(R) = (4/3)\pi R^3, \quad (1b)$$

$$\eta_1 = (\rho_0 - \rho_1)/(\rho_1 - \rho_s), \quad (1c)$$

$$\Phi(x) = 3 \frac{\sin(x) - x \cos(x)}{x^3}. \quad (1d)$$

Here, R is the magnetic particle radius, h is the surfactant layer thickness; n is the particle concentration; ρ_0 , ρ_1 , ρ_s are the scattering length densities of the magnetic core, surfactant shell and the carrier, respectively; B is the remained incoherent background after correction on the solvent scattering; brackets $\langle \dots \rangle_R$ denote the average over the magnetic particle size distribution, $D_N(R)$, defined at the interval of $R_{\min} - R_{\max}$. For the $D_N(R)$ function the lognormal distribution with the most probable radius R_0 and the mean logarithmic squared deviation S was used:

$$D_N(R) = \frac{1}{\sqrt{2\pi}SR} \exp\left(-\frac{\ln^2(R/R_0)}{2S^2}\right). \quad (2)$$

For the other ferrofluid the contrast between the surfactant shell and the carrier is virtually zero, since for pentanol $\rho \sim 0.11 \times 10^{-10} \text{ cm}^2$, so the simpler model of spherical particles was used:

$$I(q) = \frac{I(0)}{\langle V^2(R) \rangle_R} \int_{R_{\min}}^{R_{\max}} V^2(R) D_N(R) \Phi^2(qR) dR + B, \quad (3a)$$

$$I(0) = n(\rho_0 - \rho_s)^2 \langle V^2(R) \rangle_R \quad (3b)$$

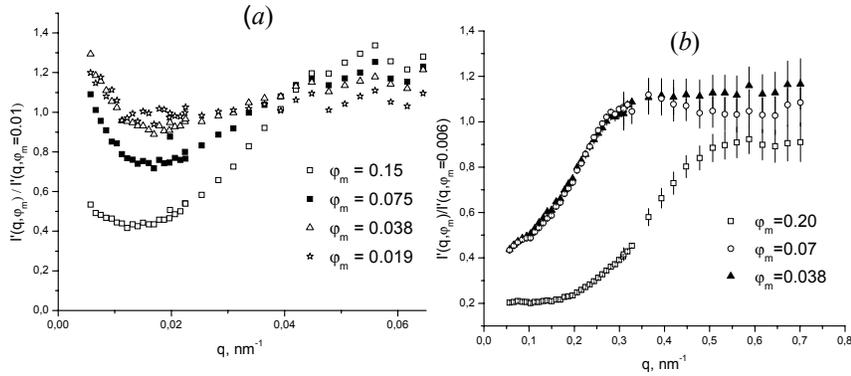


Fig. 2 – Pseudo structure-factors for ferrofluids based on benzene (a) and pentanol (b) as ratios between intensities, I' , referred to one magnetite concentrations. In (a) errors (up to 10 % at large q -values) are not shown to avoid cumbersome view.

With the increase in the magnetite concentration the effect of interparticle interaction on the scattering curves starts to be significant, which is reflected in the deviation of the curves from the model of non-interacting particles at the smallest registered q -values. In a particular case of monodisperse particles interacting in an isotropic way this effect is factorized, so that it is described as an additional factor,

structure-factor, in the expression for the differential scattering cross-section. The structure-factor is a Fourier transform of the so-called radial distribution function in the theory of liquids. It can be easily obtained through dividing a scattering curve by that where the effect is insignificant. For more complex systems with polydispersity and dependence of the interaction on the particle orientation (these two features take place in ferrofluids) such factorization is no more possible, and it is highly difficult to take the interaction effect into account when treating the scattering curves. The analysis of some approximations at small particle concentrations for pentanol-based ferrofluid can be found in [23]. Despite the emphasized difficulty, the interaction effect for ferrofluids can be followed qualitatively in the same manner as in the usual case of monodisperse and isotropic system. Still, such pseudo structure-factor shows the character of the interaction. It is done for the studied ferrofluids in Fig. 2, where the obtained scattering curves are divided by the curve corresponding to the minimal particle concentration, where the interaction effect, as one can see, is insignificant. A principle difference in the behaviour of the pseudo structure-factors can be seen for the two types of ferrofluids. For the benzene-based ferrofluids (Fig. 2, *a*) we observe clearly the structure-factor corresponding to the case of the so-called attractive potential with repulsion at the particle surface. The attractive character of the interaction determines the increase in the cross-section at low q -values, while the peak at higher q -values is a result of repulsion. It reflects well the general concept of the behavior of the particles in ferrofluids. They attract each other due to the magnetic interaction and repulse only when contacting (purely sterical repulsion). For this reason the effect of the structure-factor on the scattering curve is not so significant for this class of ferrofluids up to $\varphi_m = 10\%$ which was revealed previously [20, 23]. In the case of pentanol-based ferrofluid (Fig. 2, *b*) two specific features can be distinguished. First, the interaction potential is softer than in the previous case, there is no sharp particle boundary in the system. This follows from the absence of the explicit repulsion peak in the structure-factor in contrast to benzene-based ferrofluid. The reason for this is the structure of the second surfactant layer which differs much from the single chemically adsorbed layer and allows interpenetration of the particles. Second, there is no attraction part in the structure-factor at the smallest q -values like in benzene-based ferrofluid. This means that the system is close to that of non-interacting particles. However, the softness of the interaction smears the structure-factor so that no specific peak usual for monodisperse non-interacting particles is observed.

4. CONCLUSIONS

By means of small-angle neutron scattering a principle difference in the interparticle interaction for ferrofluids stabilized sterically by single and double surfactant layers is demonstrated. In the first class of ferrofluids based on non-polar

carriers the attractive potential between particles with repulsion at their surface is revealed, while for the second class of ferrofluids based on polar carriers it is close to that of non-interacting polydisperse particles. This fact correlates with the features of the structure of colloidal particles in the fluids and explains the effectively small influence of the structure-factor on the scattering in the case of non-polar ferrofluids up to a comparatively high volume fraction of magnetic materials ($\varphi_m = 10\%$).

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