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Aggregation in non-ionic water-based ferrofluids by small-angle neutron scattering

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Abstract

Small-angle neutron scattering was applied for detecting structural changes in non-ionic water-based ferrofluids when they were put in a magnetic field and then, after some period, returned to normal conditions. The observed changes in the scattering reflect the formation of elongated chain-like complexes stimulated by the magnetic field. The growth of these complexes takes place long after the magnetic field is turned off.
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1. Introduction

The aggregation stability both in a magnetic field and in normal conditions is an important characteristic of ferrofluids. In the present work, we studied the aggregation in non-ionic water-based ferrofluids. In contrast to ionic water-based ferrofluids [1,2], these fluids often show the presence of aggregates in their structure even in the absence of the magnetic field [3,4]. In the magnetic field, the elongated chain-like complexes are formed [5]. Our interest concerned the changes in aggregation after the ferrofluids placed in the magnetic field for a comparatively short time returned to normal conditions. For this purpose, the small-angle neutron scattering (SANS) was used. The aim of the work was to reveal how the nuclear and magnetic parts of the scattering in the ferrofluids vary in time. The previous magnetic and magnetorheological studies [3,6] pointed to the formation of aggregates in analogous systems during the magnetization and demagnetization.

2. Materials and methods

Samples were prepared [7] by dispersing Fe_3O_4 and $CoFe_2O_4$ nanoparticles in water by ultrasonication with double layer sterical stabilization using a number of surfactants including oleic (AO), lauric (AL) and dodecylbenzenesulphonic (DBS) acids:

Sample I: $H_2O/Fe_3O_4/AL+DBS$, concentration of magnetic particles $c_m = 6.5$ vol%, saturation magnetization $M_s = 280$ G.

Sample II: $H_2O/CoFe_2O_4/AL+AL$, $c_m = 2$ vol%, $M_s = 80$ G.

The ratio between contents of the surfactant and magnetic material was about 1.7 in both samples. In the case of sample I, experiments were repeated for the fluid diluted down to c_m of 4.2 vol%, $M_s = 180$ G.

The SANS experiments 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, in a q range 0.19–5 nm^{-1}. For each sample the measurements were made consequently in conditions "no field" (1200 or 600 s), "field on" (1200 or 600 s), "field off" (several expositions, 1200 or 600 s each). The exposition time was chosen to achieve the

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necessary statistics. The strength of the applied magnetic field was 1.2 T, at which the saturation magnetization in the samples takes place. The time of increase and decrease of the magnetic field was about 1 s. The temperature was maintained at 20°C.

The possible anisotropy in the 2D scattering patterns was analyzed according to the expression

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

where φ is the angle between the direction of the applied magnetic field and scattering vector. In the absence of the magnetic field, the magnetic scattering like the nuclear scattering is isotropic and $B(q) = 0$. At the saturation magnetization, the $A(q)$ and $B(q)$ functions correspond to nuclear and magnetic scattering in the system, respectively.

Both the nuclear and magnetic scattering from the possible aggregates in the fluids can be expressed as

$$F(q) = c_m(\Delta\rho)^2 \langle V^2 P^2(q)\rangle S(q)/\langle V\rangle, \quad (2)$$

where respectively to nuclear or magnetic scattering, $(\Delta\rho)^2$ is the contrast between aggregates and solvent, V is the aggregate volume, $P^2(q)$ is the form-factor of the aggregate, $S(q)$ is the structural factor reflecting the interparticle space correlation, and $\langle \ldots \rangle$ means averaging over all aggregates. Neglecting the polydispersity of the aggregates and their interparticle correlation one can write for elongated particles:

$$F(q) \sim c_m(\Delta\rho)^2 R^2 L P^2(q), \quad (3)$$

where R is a cross and L is a linear characteristic size of the aggregates. The experimental mean scattering intensity over a q-interval 0.2–0.8 nm^{-1} were compared with the averaged Eq. (3) using for $P^2(q)$ form-factors of cylinder and ellipsoid of revolution.

A comparison of the scattering from the present water-based ferrofluids with a highly stable pentanol-based ferrofluid (Fe_3O_4/penthanol/AO + DBS, $M_s = 280$ G) was made. The preceding analysis of the magnetization curve of this fluid (below sample REF) did not show any significant aggregation effect.

3. Results and discussion

Typical changes in the radially averaged scattering from the diluted sample I are shown in Fig. 1. The analysis of anisotropy results in $B(q) \approx 0$ for all scattering patterns from the water-based ferrofluids. Thus, we interpreted the changes in the scattering as a reflection of formation and changes in the aggregation in the systems. The aggregation effect on the scattering in the studied q-range is significantly greater than the effect of magnetic structure of the fluids.

As in our previous study [8] of the water-based ferrofluid (D_2O/Fe_3O_4/DBS + DBS), the simple model

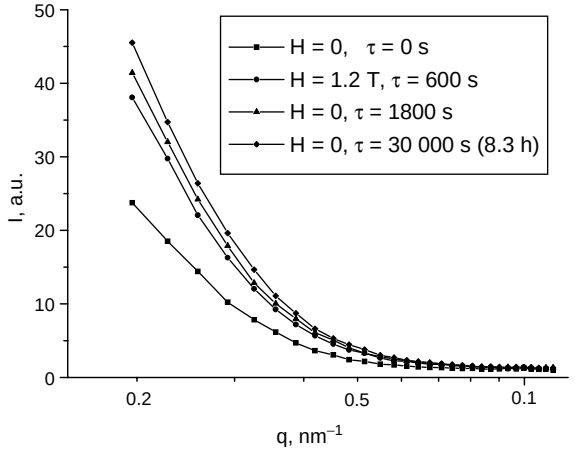

Fig. 1. Radially averaged scattering curves for the diluted sample I at different moments. Experimental errors do not exceed 5%. The solid lines are to guide the eyes.

of the uniform magnetic core and surfactant shell does not fit the obtained scattering curves. However, at small q-values of 0.2–0.6 nm^{-1} there are indications of the presence in the fluids of elongated particles. This q-interval corresponds mainly to the scattering from the shape of the particles. To follow the changes in this shape the mean intensity as a function of time (Fig. 2) was considered. The averaged Eq. (3) was fitted to the experimental data (Fig. 2a and b) assuming the growth of the aggregate length to be linear in time and neglecting changes in the cross size of the aggregates. Taking into account all the simplifications made, one can see that the model describes well the behavior of the experimental graphs in Fig. 2 revealing that essentially the elongation continues to increase after the magnetic field is turned off. The insignificance of the change in the R size is confirmed by the fact that the character of the experimental graphs in Fig. 2 does not vary much when the averaging interval is changed, while it follows from the model calculations that the mean intensity as a function of R is very sensitive to this interval. Eq. (3) as a function of L is almost constant for large L values and cannot give the information about how the length of the aggregates changes at $\tau > 10,000$ s (Fig. 2). By the same reason, we cannot say exactly what type of the aggregate growth in time is realized. Models with different power law dependence $L(\tau)$ fit well the experimental graphs at $\tau < 10,000$ s. Nevertheless, these models result in common conclusions.

First, the cross radius of the aggregates is the same in different cases and is about of 5 nm, which coincides with the mean radius of the particles in initial ferrofluids [7].

Second, the use of the form-factor of cylinder is more preferable, since in contrast to the form-factor of

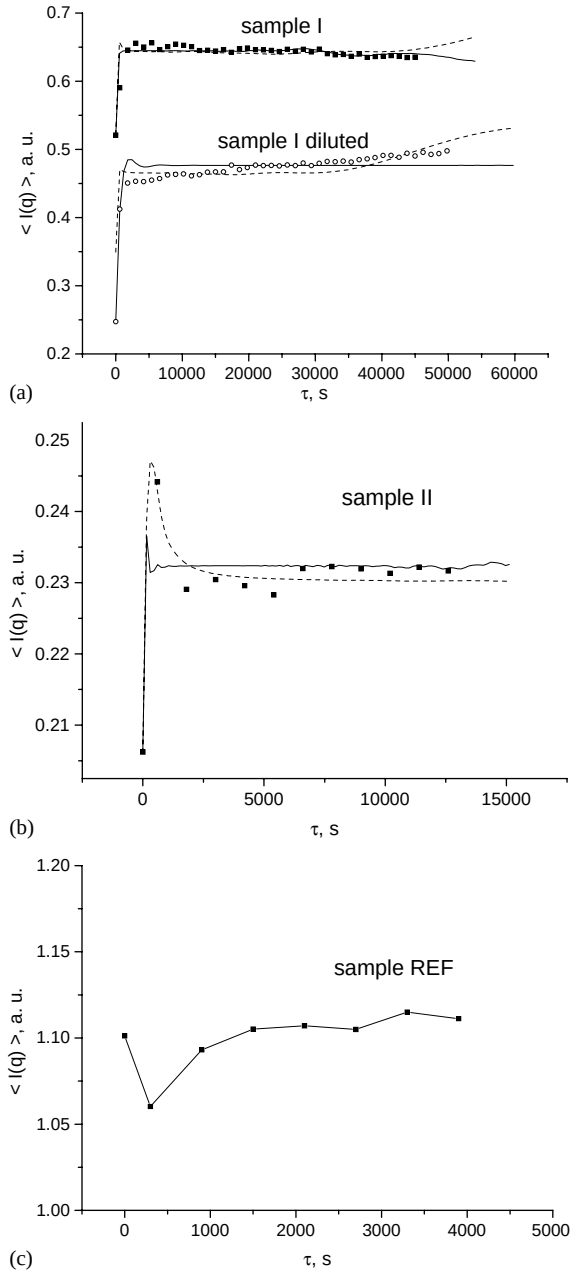

Fig. 2. Mean intensity $\langle I \rangle$ (points) as a function of time τ for sample I (a), sample II (b) and REF sample (c). For graphs (a) and (b): at $\tau = 0$ s, $H = 0$ T; at $\tau = 600$ s, $H = 1.2$ T; at $\tau \geqslant 1200$ s, $H = 0$ T. For graph (c): at $\tau = 0$ s, $H = 0$ T; at $\tau = 300$ s, $H = 1.2$ T; at $\tau \geqslant 600$ s $H = 0$ T. In graphs (a) and (b) solid and dash lines correspond to best models with form-factors of cylinder and ellipsoid of revolution, respectively. In graph (c) the solid line is to guide the eyes.

ellipsoid of revolution it describes better the ratio between the initial scattering and the scattering in the stages "field on" and "field off". In particular, it reveals a small aggregation in undiluted samples I and II at $\tau = 0$ s (case "no filed") giving the length values of about 6 and 7 nm, respectively. Also, it gives the reliable values of the speed of the growth in accordance with the statement "the more concentration the more the speed of the aggregate growth" in the case of sample I (0.04 and 0.006 nm s^{-1} for initial and diluted sample I, respectively). For sample II, despite the small concentration in comparison with sample I, the speed of the growth is higher, 0.06 nm s^{-1}, which can be explained by the stronger interaction between magnetic particles. The latter is also confirmed by the fact that for diluted sample I, additional mechanisms of aggregate growth besides the elongation are observable, which follows from the difference between the model and experimental graphs (Fig. 2a), while for sample II (magnetic particle concentration twice less than for diluted sample I), no significant additional aggregation but the elongation is seen (Fig. 2b).

Finally, an increase in the length of the aggregates continues after the magnetic field is turned off during the time for a minimum 10,000 s up to the values of more than 400 nm for undiluted samples I and II and 50 nm for diluted sample I.

For comparison the time dependence of the mean intensity for sample REF without large aggregation is presented in Fig. 2c. In the stage "field on" the non-zero anisotropic part $B(q)$ in 2D scattering patterns can be extracted in this case and comprises up to 40% of the isotropic part $A(q)$ at a minimal experimental q-value. One can see in Fig. 2c that the scattering returns to the initial value for the time of about 1000 s and does not show any significant aggregation effect. It should be pointed out that despite the high stability of sample REF, the core-shell scattering model mentioned above in respect to the water-based ferrofluids does not work in this case either.

4. Conclusions

The aggregation effect stimulated by a magnetic field in non-ionic water-based ferrofluids is observed by means of small-angle neutron scattering revealing the formation of elongated chain-like aggregates. The growth of such aggregates, essentially of their length, continues long after the magnetic field applied for a comparatively short time is turned off. No observable influence of the magnetic structure of the fluids in the studied q-range on the scattering against the background of the aggregation effects was found.

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