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On the adsorption properties of magnetic fluids: Impact of bulk structure

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ABSTRACT

Adsorption of nanoparticles from magnetic fluids (MFs) on solid surface (crystalline silicon) was studied by neutron reflectometry (NR) and related to the bulk structural organization of MFs concluded from small-angle neutron scattering (SANS). The initial aqueous MF with nanomagnetite (co-precipitation reaction) stabilized by sodium oleate and MF modified by a biocompatible polymer, poly(ethylene glycol) (PEG), were considered. Regarding the bulk structure it was confirmed in the SANS experiment that comparatively small and compact (size~30 nm) aggregates of nanoparticle in the initial sample transfer to large and developed (size > 130 nm, fractal dimension 2.7) associates in the PEG modified MF. This reorganization in the aggregates correlates with the changes in the neutron reflectivity that showed that a single adsorption layer of individual nanoparticles on the oxidized silicon surface for the initial MF disappears after the PEG modification. It is concluded that all particles in the modified fluid are in the aggregates that are not adsorbed by silicon.

1. Introduction

Structural characterization of ferrofluids (MFs) (colloidal solutions of magnetic nanoparticles with a characteristic size of about 10 nm which are usually covered by surfactant molecules to prevent aggregation and sedimentation) are important from both the fundamental and applied points of view. Such type of information is necessary for understanding stabilization mechanisms of these systems and their behaviour in different conditions. The latter determines the possibilities for practical applications of magnetic fluids in different fields (e.g., [1,2]). Mainly the works on the structure characterization of MFs are devoted to the structural organization of bulk solutions, which is, in particular, well observed by small-angle X-ray (SAXS) and neutron (SANS) scattering (e.g., see reviews in [3,4]). At the same time, because of specific adsorption properties, the behaviour of magnetic nanoparticles and surfactants in MFs at interfaces with solids can be different from that in bulk, which is to be also considered with respect to application purposes. A number of recent works [5–9] involving various methods are devoted to the study of formation and structural characterization of magnetic nanoparticles (MNPs) assembling into a monolayer. Self-assembly of the nanoparticles occurs during the solvent evaporation, therefore interaction between the film and a substrate plays an important role in the ordering. An additional point is that a possible difference in the stability of MFs in bulk and at interfaces should be taken into account in the requirements for the stabilization of these systems with respect to their storage, namely to the interaction of the MF particles with container walls under different conditions.

Thus, some kind of ordering into layered structures at the interface with silicon was reported [10] for highly concentrated water-based MF (nanomagnetite coated by double layer of sodium oleate in heavy water) with the volume fraction of magnetic material φ_m~10%. It was observed in the neutron reflectometry (NR) experiments with horizontal sample plane when analyzing total specular reflection enhanced by the use of deuterated liquid carrier. In a similar way, less concentrated analogue of the water-based MF (φ_m~1%) was compared [11] with the highly stable MF based on organic non-polar liquid carrier (nanomagnetite coated with oleic acid in deuterated benzene). In both cases, the formation of only one well-defined adsorption layer of nanoparticles on silicon surface was concluded.

An interesting question is at what extent the bulk structure of MFs influences their adsorption properties. To clarify this point, in the given

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work we have performed similar kind of NR experiments applied to the water-based MF (nanomagnetite coated by double layer of sodium oleate in heavy water, φ_m~0.8%) and to this aqueous MF but after poly(ethylene glycol) (PEG) modification. Previously, it was reported [12,13] that the introduction of PEG into the structure of the considered water-based MF can result in its strong structure reorganization, namely the appearing of large fractal aggregates. These studies were motivated by the fact that the system is of current interest regarding biomedical applications, since it is often used [13,14] as a precursor for PEGylation (coating modification using polyethylene glycol to increase the biocompatibility). The characterization of the bulk structure of the MFs in the given work was done by SANS. The correlation of the interface properties of the two (without and with PEG) aqueous MFs with their bulk structures is analyzed. The effect of gravity on the interface properties is considered as well.

2. Experimental

Preparation of initial aqueous magnetic fluid was based on the co-precipitation reaction to produce nanomagnetite. MF was synthesized at the Institute of Experimental Physics, Slovak Academy of Sciences (IEP SAS), Slovakia, in accordance with the procedure described in [12]. To avoid aggregation between the magnetite particles they were covered with a double layer of sodium oleate ($C_{17}H_{33}COONa$, surfactant/magnetite mass ratio 0.73 to 1). The volume fraction of magnetite, φ_m=0.8%, in the fluid was found by the static magnetization analysis (MPMS SQUID magnetometer, IEP SAS).

Poly(ethylene glycol) with average mass M_w=1000 g/M was chosen for further MF modification in order to improve biocompatibility of the prepared MF. The previous studies showed [12,13] that the observable influence of PEG on the bulk structure and stability of the MF starts at the PEG/magnetite weight ratio of 1. Here, a defined amount of PEG aqueous solution was added to the initial MF with PEG/magnetite weight ratio of 1.5. The mixture was stirred thoroughly and shaken for 72 h. Afterwards, the sample was lyophilized and the obtained powder was redispersed in D_2O.

Solutions for SANS experiments were placed in 2-mm thick quartz cells (HELMA). The SANS measurements were performed on the Yellow Submarine small-angle instrument at the steady-state reactor of the Budapest Neutron Centre (BNC), Hungary. The isotropic differential cross-section per sample unit volume (hereafter called scattered intensity) was obtained as a function of the momentum transfer module, $q=(4\pi/\lambda)\sin(\theta/2)$, where λ is the incident neutron wavelength (fixed at 0.39 nm and also at 1.17 nm) and θ is the scattering angle (scanning over 64×64 cm^2 detection area of a position-sensitive detector placed at 1.5 m and 5.5 m behind the sample), in a q-range of 0.05–4 nm^{-1}. The calibration with a 1-mm water sample was performed in a standard way [15] after making corrections for the background, buffer and an empty cell.

A principal scheme of the NR experiments with a solid-liquid interface was similar to that in our previous works [11,16]. The plane neutron beam penetrated the silicon monocrystalline block through its face (height 1.5 cm) to meet the silicon-MF interface. MF was held in a hermetic Teflon container which provided the contact of the MF layer (width 2.5 mm) with polished (roughness less than 1 nm) and specially cleaned silicon block with hydrophilic (because of silicon oxide) surface. The NR experiments were performed at the NREX reflectometer (Max-Planck-Institut for Solid State Research, FRM-II reactor, Germany) and at the GRAINS reflectometer (Joint Institute for Nuclear Research, IBR2 reactor, Russia) both with vertical scattering plane. At NREX, the monochromized neutron beam (wavelength 0.43 nm) was used in the θ-2θ scanning mode. Experiments at the GRAINS reflectometer were conducted in TOF (time-of-flight) mode with neutron wavelength range of 0.05–0.7 nm [17]. The experiments were done in two kinds of MF/Si geometries, namely Si block on bottom and the inverse geometry with Si on top. The reflected neutrons were registered by the 2D position-sensitive detector. The measurements were carried out at room temperature.

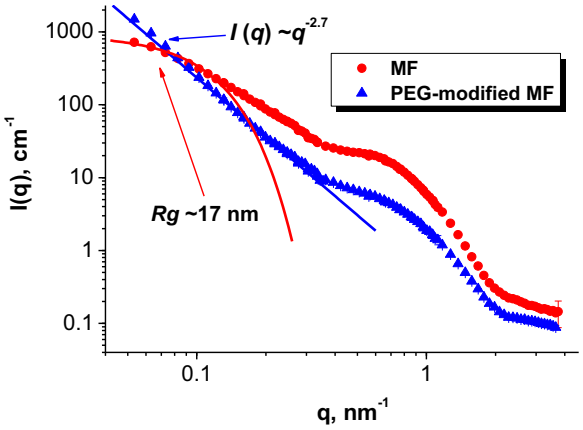

Fig. 1. Experimental SANS curves for the initial MF (red circles) and PEG-modified MF (blue triangles). Solid lines follow the Guinier approximation with Rg=17 nm and the power-law dependence, ~$q^{-2.7}$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Experimental SANS curves for the two kinds of aqueous MFs are presented in Fig. 1. Since the studied MFs are based on heavy water, a contribution from hydrogen-containing components is significant. Thus, the broad band in the curves around q~0.7 nm^{-1} is attributed to the scattering from surfactant which forms a stabilizing shell around magnetite particles, as well as micelles in the solution [18,19]. Different behaviour can be seen in the initial part of the curves. The scattering from the initial aqueous MF corresponds to the scattering from compact particles, which is reflected in the existence of the so-called Guinier regime at low q-values with the radius of gyration, Rg =17 nm. This value exceeds that expected for separated particles, so there is some fraction of compact and structurally stable aggregates in the initial MF. The corresponding Guinier plot is given in Fig. 1. In the aqueous MF after PEG modification, a degree of aggregation increases and affects the curves, so that they are comparable with those observed for water-based ferrofluids with double steric stabilization [20–22]. This is concluded from the power-law behaviour of the scattering, $I(q)$ ~$q^{-2.7}$, at low q values, which indicates now a fractal-type organization of the aggregates with mass fractal dimension, D=2.7 [23]. The Guinier regime is not observed in the initial parts of the curves for these fractal aggregates, which means that the aggregate size, $D > 130$ nm (the estimate is derived from the minimum measured q-value in accordance with the rule $D=2\pi/q$), is beyond the instrumental limit. The observations are in full agreement with the previous SANS studies of similar MFs [12,13].

The experimental reflectivity, R, for D_2O/Si and two kinds of MF/Si interfaces are represented (Fig. 2) as $R\,Q_z^4$ to enhance the differences in the data from the samples under study and demonstrate the quality of the fits. It should be mentioned that in NR experiments in addition to specular reflection for both studied MFs samples a strong off-specular (diffuse) scattering was detected, which is a consequence of small-angle scattering from nanoparticles and their aggregates. This type of the scattering also makes an additional contribution to the channel of the specular reflection. It is indicative of the fact that the aggregates are present in the close-to-surface region for the studied MFs. The diffuse scattering background from MFs was subtracted according to the procedure describe in [16] to get purely specular reflectivity curves.

The found reflectivity curves given in Fig. 2 do not show any ordering effects at the interface like in [10]. The reflectivity curves for

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