



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 $\varphi_m \sim 10\%$. 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 ($\varphi_m \sim 1\%$) 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, $\varphi_m \sim 0.8\%$) 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 coprecipitation 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, $\varphi_m = 0.8\%$, 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 cm² 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 für 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

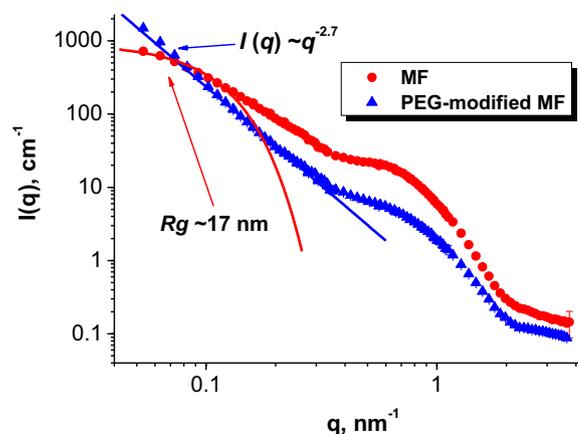


Fig. 1. Experimental SANS curves for the initial MF (red circles) and PEG-modified MF (blue triangles). Solid lines follow the Guinier approximation with $R_g = 17$ nm and the power-law dependence, $\sim q^{-2.7}$, respectively. (For interpretation of the references to color in this figure legend, the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

were registered by the 2D position-sensitive detector. The measurements were carried out at room temperature.

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 $q \sim 0.7$ 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, $R_g = 17$ 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, $I(q) \sim q^{-2.7}$, 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

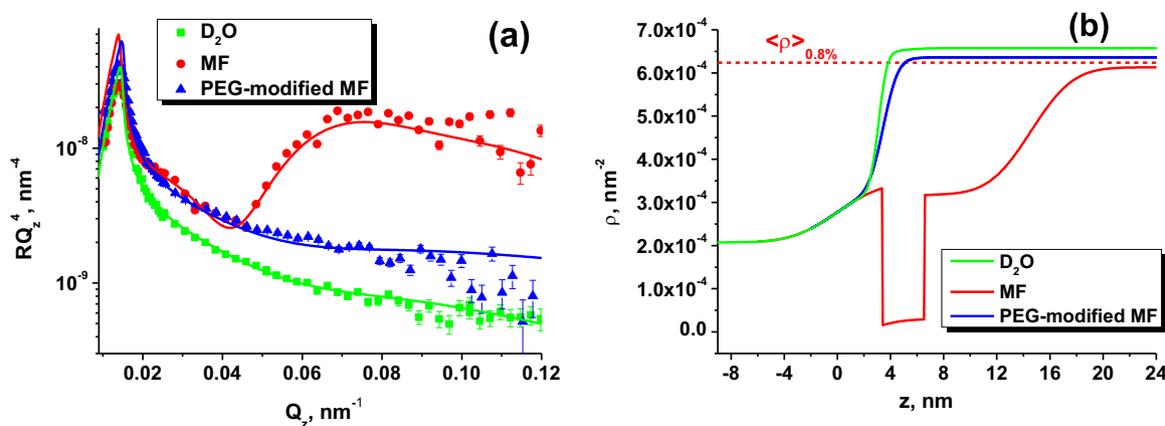


Fig. 2. (a) Experimental reflectivity curves (points) together with fits (solid lines) for pure D₂O (green squares), initial aqueous magnetic fluids (red circles) and PEG-modified MF (blue triangles); (b) found from experimental data SLD profiles for three studied kinds of solid/liquid interfaces. The calculated mean SLD for the initial MF (concentration 0.8%) is shown (dashed line) for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

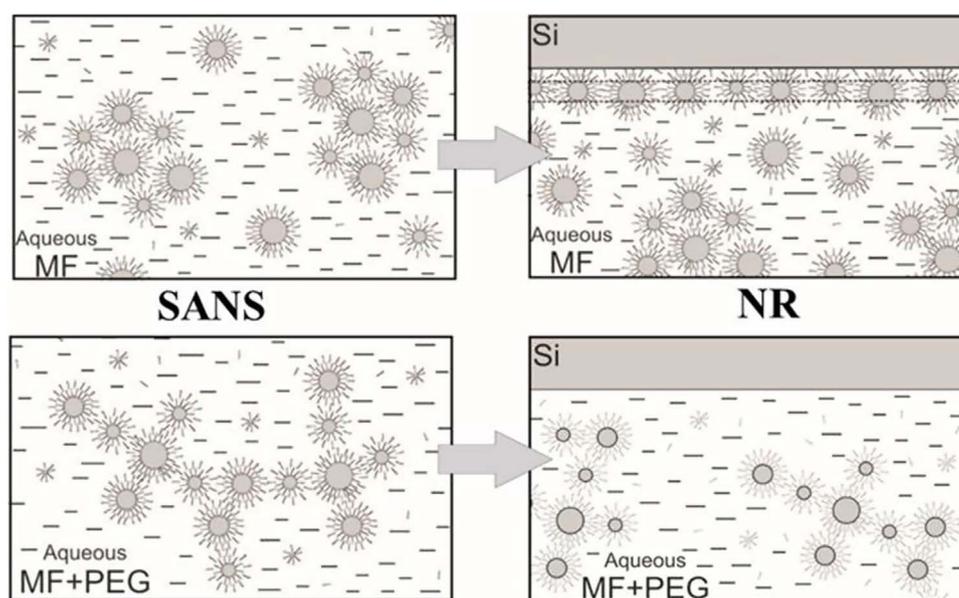


Fig. 3. Schematic representation of the discussed effect: bulk structure of ferrofluids with respect to the aggregate organization according to SANS data (on the left) and its influence on the structure of the interface with silicon according to NR data (on the right).

D₂O and D₂O-based MF modified by PEG are well described by the well-known Fresnel law (solid lines in Fig. 2a) for the interface between two infinite and purely homogeneous media. It means that there is no adsorption on Si surface from the PEG-modified MF and it looks like homogeneous medium in the NR experiments. The deviations of the NR curve for the initial D₂O-based MF from the Fresnel law indicate that there are some layer formations at the interface caused by adsorption of particles from MF. The curve for this interface was treated in the frame of the Parrat formalism [24]. The best fit (solid lines in Fig. 2a) was obtained using a two layer model on the silicon substrate. The corresponding scattering length density (SLD) profiles along the surface normal are shown in Fig. 2b, where they are compared with the mean SLDs of magnetic fluids under study, calculated from the known compositions. The revealed two layers with significantly different SLDs can be considered as two sub-layers of one layer of colloidal core-shell particles adsorbed on the silicon substrate, which is schematically shown in Fig. 3. The width (~4 nm) and SLD (~0 nm⁻²) of the first sub-layer are close to the corresponding parameters of the surfactant shell (sodium oleate) around magnetite in MFs, while the width of the second sub-layer is well associated with the mean diameter of magnetite nanoparticles, $D \sim 8$ nm. The mean SLD of this sub-layer is significantly lower than that of magnetite

($\rho = 6.9 \times 10^{-4} \text{ nm}^{-2}$) because of the large fraction of surfactant in it. It should be mentioned that such layer formation is similar to the previous results for sterically stabilized non-polar MF with stabilization by oleic acid and D₂O-based ferrofluids stabilized by sodium oleate [11]. Also, similar layer of MNPs were recently observed in aqueous MF (magnetic particles with average diameter of 11 nm surrounded by a 4 nm thick bilayer of carboxylic acid) with steric repulsion, $\phi_m = 5\%$ [25]. The difference in the SLD values at the interface and bulk of the initial MF is a consequence of the difference in the particle distributions at the interface and bulk. The lower SLD-value for MF at the interface means that the relative fraction of the surfactant (a component with zero SLD) is higher at the interface, which is explained by adsorption properties of the silicon substrate. In organic non-polar MFs the similar effect was interpreted [11] as a result of higher concentration of magnetic nanoparticles coated with surfactant whose mean SLD is lower than that of deuterated carrier. Here, in addition to the complex (magnetite plus surfactant) particles there is some fraction of free (non-adsorbed on magnetite) surfactant which also is attracted to the surface and contributes to the mean SLD of the suspension.

To check up the impact of gravity against the surface attraction at the interface, the NR experiments for MFs were performed in two geometries with silicon above the fluid ('beam from top') and silicon on

bottom of the fluid ('beam from bottom'). The change in the geometry showed just a slight shift in the critical Q_z for the full total reflection, which corresponds to a difference between the mean SLD of the same sample in different geometries. From the obtained SLD values, it was estimated that the particle concentration in MFs at the interface is about 10% higher for the 'beam from bottom' configuration as compared to the 'beam from top' configuration because of the gravitation effect with respect to the aggregates of magnetic nanoparticles. This is consistent with the previously reported [26] influence of gravity on ferrofluids with relatively large particles leading to the variation in shape and size of the diffraction patterns along the sample height. According to the thermodynamic calculations [27], which take into account the dipole-dipole interaction in ferrofluids, one can expect a significant modulation in the particle number density along the sample height under the effect of gravity for the magnetite particles with size higher than 10 nm.

From the comparison of the bulk and solid/liquid interface structures of MFs one can conclude about clear correlation between the bulk structure of MFs and adsorption properties of the interface. Thus, the attraction between hydrophilic silicon oxide layer on the Si surface and non-aggregated nanoparticles in the initial aqueous MF leads to the formation of a single MNP layer, which disappears after the PEG modification. The latter is explained by the fact that all particles in the modified MF aggregate and form new kind of developed clusters as compared to the initial MF, so no free individual particles are available to form the adsorption layer. A schematic representation of the observed effect for the two kinds of D₂O-based MFs with respect to their bulk structure (compact aggregates in initial MF and branched aggregates in PEG-modified MF) and structure at MF/Si interfaces (individual nanoparticles adsorption on the silicon surface from initial MF and no any adsorption of nanoparticles in the ferrofluid with PEG addition) are summarized in Fig. 3.

4. Conclusions

Different structural organizations of MFs at interface with silicon were concluded from NR experiments for two aqueous MFs with various bulk structures revealed by SANS. It was obtained that individual non-aggregated nanoparticles are preferably adsorbed on the oxidized silicon surface from the initial aqueous MF to form a single adsorption layer. The reorganization of the cluster structure in bulk after the modification of MF with PEG results in disappearing of the adsorption layer, which is correlated with the fact that as compared to the initial MF all nanoparticles in the PEG modified MF compose large developed aggregates that are not adsorbed by the surface. The gravity effect showed less than 10% difference in the mean SLD for the two configurations of the MF/Si interface with Si substrate above and below MF caused by a corresponding increase in the particle and aggregate concentration at the interface in the second case. The conclusions of the given work justify our further extended research of the behaviour of ferrofluids with different bulk properties (with respect to particle concentration, stabilization type, rate of aggregation, etc.) at various interfaces with solids, which is in progress.

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