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Abstract. The structure of magnetic fluids (magnetite in decahydronaphtalene) stabilized with saturated mono-carboxylic acids of different chain lengths (lauric, myristic, palmitic and stearic acids) is studied by means of magnetization analysis and small-angle neutron scattering. It is shown that magnetite nanoparticles are dispersed in the carrier approximately with the same size distribution whose mean value and width are significantly less as compared to the classical stabilization with non-saturated oleic acid. The found thickness of the surfactant shell around magnetite is analyzed with respect to stabilizing properties of mono-carboxylic acids.

Introduction

Colloidal stability of magnetic fluids (MFs), especially at a high volume fraction of magnetic nanoparticles, φ_m, is a complex issue connected to the synthesis procedure, including the nature of surfactant(s) and carrier liquids used. In this work we report our recent results on structural studies of stabilization factors in MFs based on non-polar organic carriers.

It is well known [1] that one of the best molecules for stabilizing magnetite nanoparticles in organic non-polar liquids is oleic acid (OA), a non-saturated mono-carboxylic (fatty) acid, which has a C_{18}–tail with a double bond kink in the middle. Despite wide use of this surfactant in stabilization procedures of magnetic fluids, still there is no full understanding what factors responsible for the resulting stabilization distinguish oleic acid from its straight-chain saturated analogue, stearic acid, which is always considered as a poor stabilizer. Here, we investigate the structure of magnetic fluids based on decahydronaphtalene (DHN) and stabilized by various chain length molecules from a series of saturated and straight carboxylic acids, namely lauric (LA), myristic (MA), palmitic (PA) and stearic (SA) acids with C_{12}, C_{14}, C_{16}, C_{18}- tails, respectively, and compared them with the classical fluid stabilized by OA. Magnetization analysis and small-angle neutron scattering are used to find out and compare the particle size distribution in the studied MFs and the effective thickness of the surfactant (acid) shell. This work is a continuation of [2].

Materials and methods

All studied fluids were prepared by the same procedure [3,2] standard for OA stabilization. Magnetite nanoparticles, Fe_3O_4, were obtained by the co-precipitation in aqueous solution of Fe^{2+} and Fe^{3+} ions (salts $FeSO_4.7H_2O$; $FeCl_3.4H_2O$) in the presence of NH_4OH sol. 25% (temperature 80-82°C). A surfactant from the above mentioned series with a significant excess (30 vol. %) was

added to the system right after the co-precipitation starts following its chemisorption on the magnetite surface. Then, several steps including washing with magnetic decantation, flocculation, re-dispersion in light hydrocarbon and filtration were performed to remove residues of salts, free surfactant in solution and large aggregates of non-dispersed magnetite particles, respectively. Finally, magnetite particles coated with a single surfactant layer were extracted by flocculation with acetone and, then, re-dispersed into the required carrier, DHN (Merck, chemically pure). The particle concentration in the MF strongly depends on the acid used. Despite the fact that exact quantitative analysis of the dispersing efficiency is quite a difficult topic for colloidal solutions, qualitatively we conclude that as compared to OA such efficiency is just several times less for MA, and more than 10 times less for other saturated acids (LA, PA, SA). Again, qualitatively, SA is the worst stabilizant among the considered saturated acids. Repeating the above procedure in the case of saturated acids several times (depending on dispersing efficiency) we succeeded in concentrating the samples up to φ_m within 6 - 10 %. It is important that the final flocculation-redispersing cycle was additionally performed until free surfactants were completely removed from the fluids. The ratio between volume fractions of magnetite and covering surfactants was determined from the density measurements and constituted ~1:1 for OA sample and between 1:2 and 1:3 for samples with saturated acids. All of the fluids were stable at least a year after preparation.

The magnetization analysis was performed on the MFs diluted down to $\varphi_m \approx 1.5$ %. The magnetization curves were obtained at the VSM 880 magnetometer with vibrating sample (DMS/ADE Technologies-USA) of the LMF CFATR, the maximal applied field of 800 kA/m.

For SANS experiments two kinds of samples were prepared from the initial MFs, which were diluted down to $\varphi_m < 1$ % with usual and deuterated DHN (d-DHN, 99 %, Deutero Gmbh), respectively. The d-DHN content in all samples of the second kind was 90 %.

SANS experiments (non-polarized mode, no magnetic field at the sample) were performed on the small-angle instruments SANS-1 (GKSS Research Centre) and "Yellow Submarine" (Budapest Neutron Center). The differential cross-section per sample volume was obtained as a function of the momentum transfer module, $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident neutron wavelength and θ is the scattering angle, over the q-interval of 0.06-2.5 nm^{-1}. Details are described in [4].

Results and discussion

The main structural difference revealed for the fluids with saturated acids as compared to the OA case concerns the size distribution function of the stabilized magnetite nanoparticles. First, it was judged from the magnetization curves (Fig.1). They were treated in terms of the polydisperse Langevin approximation [5] with the log-normal distribution of the magnetite core radius R:

$$D_N(R)=(1/(2\pi)^{1/2}SR)\exp[-\ln^2(R/R_0)/(2S^2)], \qquad (1)$$

where R_0, S are the varied parameters. Because of the low volume fraction of magnetite both the concentration effect and the magnetic interparticle interaction were not taken into account.

The SANS curves from solutions in DHN are given in Fig.2. In this case the scattering from the surfactant layer is almost matched, because the values of the mean scattering length density for the surfactants and carrier are close [4]. Also, the nuclear scattering dominates strongly over the magnetic part, which is a result of the large contrast between magnetite and carrier [4]. So, the curves in Fig.2 correspond to the nuclear scattering from magnetite and are treated in the frame of the model of homogeneous polydisperse spheres [4] with $D_N(R)$ as in Eq.1.

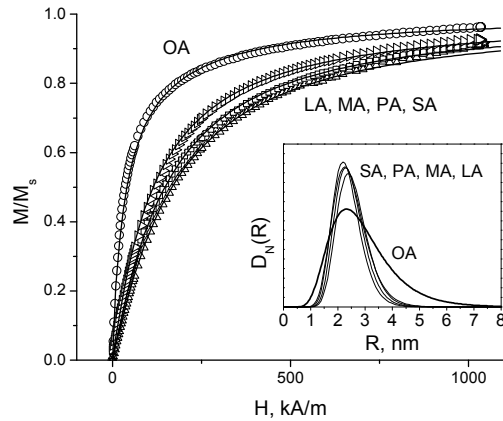The difference in the data of magnetization analysis and SANS can be seen for $D_N(R)$. It is most

Figure 1. Magnetization curves (points) for magnetic fluids stabilized by various mono-carboxylic acids in DHN, $\varphi_m = 1.5$ %. Lines are results of polydisperse Langevin approximation. Inset shows corresponding particle size distributions of magnetite (magnetic size).
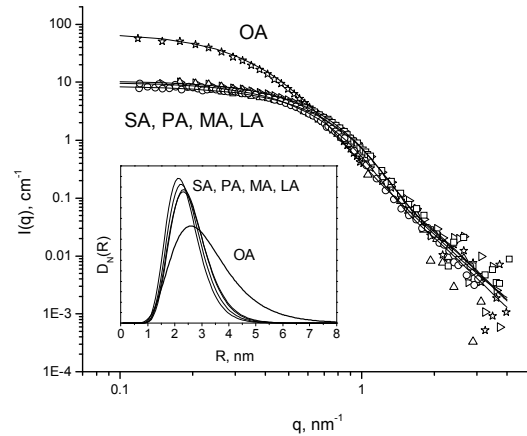
Figure 2. Experimental (points) SANS curves for MFs in DHN normalized to $\varphi_m = 1.5$ %. Lines are the results of approximation by the model of poly-disperse independent spheres. Inset shows the corresponding particle size distributions of magnetite (atomic size).

significant for the case of the OA stabilization. In [2] this difference was related to the size dependence of the thickness of the non-magnetic layer. However, there is no clear reason for such effect. The discussed difference can also reflect the magnetic interaction effect, which concerns both the magnetization analysis and SANS. In the first case, it influences the used Langevin approximation. The larger the particles dispersed in the liquid (OA sample), the stronger the interaction; hence, a larger deviation in the parameters of the Langevin approximation can take place. In SANS the attraction between particles results in appearance of the structure-factor increasing the apparent atomic size of the particles and making it different from the magnetic size.

The thickness of the surfactant layer around magnetite can be deduced from SANS data for 90% d-DHN solutions in Fig.3. In this case, due to a significant contrast the scattering from the layer contributes much in the curves making their behavior quite different from the previous case with usual DHN. Again, the curve for the fluid with the OA stabilization in Fig.3 shows qualitatively different behavior as compared to saturated acids. In Fig.3 all curves are fitted to the core-shell model for particles with poldisperse cores [4,6]. Here, the magnetic scattering contribution is neglected. Because of complex magnetic correlations its effect is significant only at small q-values [7,6,8]. This results in a systematic deviation of the initial parts of the experimental curves in Fig.3 from the model. The found effective thickness of the surfactant layer, h, (Table 1) correlates with the surfactant length, L, calculated according to Tanford's formula [9]. Taking into account the fact that saturated fatty acids of various chain lengths stabilize magnetite nanoparticles with approximately the same $D_N(R)$, one can conclude that this $D_N(R)$ is not determined by the acid length, but rather the acid organization on magnetite surface. Our data show that a stabilizing layer of a saturated acid possesses worse elastic properties than the layer of OA. The other reason, which can affect the stabilized particle size distribution, as well as the dispersing efficiency of the acids, is connected with chemical factors during the preparation. Thus, the possible micelle formation in intermediate water solutions can decrease the number of free surfactant molecules required for full coating of magnetite surface. The critical micelle concentration is inversely proportional to the molecule length, which correlates with the worst dispersing efficiency of the longest SA. Also, the addition of the surfactants during the synthesis of the studied MFs is performed using concentrated solutions of the acids in light hydrocarbon. The nematic interaction between the elongated acid molecules can affect the number density of free surfactant in solution. The careful consideration of these two points is the subject of our further research.
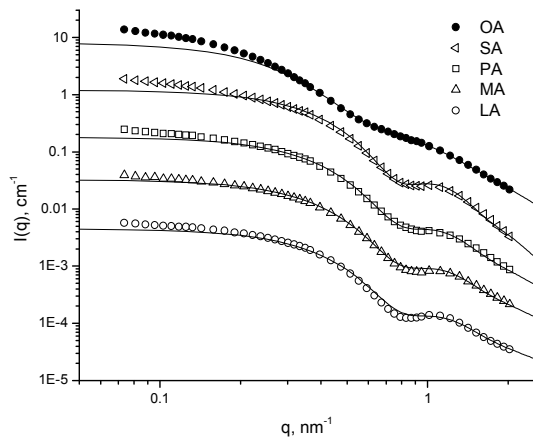
Figure 3. Experimental (points) SANS curves for MFs in 90 % d-DHN, normalized to $\varphi_m = 0.6$ %. Lines show approximations by the model of independent core-shell particles with polydisperse core; for convenient view the curves are additionally divided by factors of 10 (SA), 50 (PA), 200 (MA), 1000 (LA).

Table 1.

Sample	R_0 (nm)		S		h (nm)	L (nm)
	magnetization	scattering	magnetization	scattering	(scattering)	
OA	2.70	3.40	0.39	0.38	1.40	2.3
SA	2.50	2.55	0.22	0.28	1.85	2.3
PA	2.40	2.48	0.22	0.28	1.55	2.1
MA	2.40	2.65	0.22	0.28	1.35	1.8
LA	2.30	2.51	0.22	0.28	1.25	1.6

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