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Feoktystov, A.; Avdeev, M.V.; Aksenov, V.L.; Petrenko, V.I.; Bulavin, L.A.;
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In: Solid State Phenomena, Magnetism and Magnetic Materials (2009)

Trans Tech Publications

DOI: [10.4028/www.scientific.net/SSP.152-153.186](https://doi.org/10.4028/www.scientific.net/SSP.152-153.186)

Contrast Variation in Small-Angle Neutron Scattering from Magnetic Fluids Stabilized by Different Mono-Carboxylic Acids

A.V. Feoktystov^{1,2,5,a}, M.V. Avdeev^{1,3}, V.L. Aksenov^{3,1}, V.I. Petrenko^{1,2},
L.A. Bulavin², D. Bica⁴, L. Vekas⁴, V.M. Garamus⁵, R. Willumeit⁵

¹ Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Joliot-Curie 6, 141980 Dubna, Moscow region, Russia

² Taras Shevchenko Kyiv National University, Physics Department, Glushkova prosp. 6, k.I, 03022 Kyiv, Ukraine

³ Russian Research Center "Kurchatov Institute", Akademika Kurchatova pl. 1, 123182 Moscow, Russia

⁴ Laboratory of Magnetic Fluids, CFATR, Romanian Academy, Timisoara Division, Mihai Viteazul blvd. 24, 300223 Timisoara, Romania

⁵ GKSS Research Centre, Max-Planck-Str.1, 21502 Geesthacht, Germany

^afeoktystov@gmail.com

Keywords: magnetic fluids, small-angle neutron scattering, contrast variation, basic functions.

Abstract. Contrast variation method in small-angle neutron scattering (non-polarized neutrons) is applied to magnetic fluids (MFs) with magnetite dispersed in benzene and coated with myristic or oleic acid in zero external magnetic field. The basic functions approach for polydisperse superparamagnetic systems is used to get structure parameters of particles in MFs.

Introduction

Synthesis of new types of magnetically controllable fluids, liquid dispersions of magnetic nanoparticles, in various carriers is of current interest. Oleic acid (OA), $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, a non-saturated mono-carboxylic acid, is a classical stabilizing agent used for coating magnetic nanoparticles in non-polar organic MFs [1]. The reason for high stabilization efficiency of oleic acid (OA) is associated with its non-saturated bond, which results in a kink in the middle of the molecule. Recently, it was found [2] that saturated linear mono-carboxylic acids with short chain length like myristic acid (MA), $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$, can be used for producing highly stable MFs, but with smaller mean size and polydispersity of magnetic particles and almost the same thickness of the surfactant layer. Particularly, this conclusion comes from the analysis of the small-angle scattering of polarized neutrons (SANSPOL) from the low-concentrated samples under saturated magnetic field [2]. Here, the contrast variation technique in the small-angle neutron scattering (SANS) was applied for obtaining independently the information about the particle size distribution with respect to the whole particles including magnetite core and surfactant shell in unmagnetized MFs. For this purpose the recently developed [3] basic functions approach for polydisperse superparamagnetic systems was used.

Materials and Methods

Initial concentrated MFs in D-benzene (D-content 99 %) were prepared at the Laboratory of Magnetic Fluids, CFATR (Timisoara, Romania), as described in [4]. For changing scattering length density (SLD) of the solvent MFs were diluted with different mixtures of D- and H-benzene, so that the D-benzene content in the final solution was varied within interval 10 – 100 % (10-12 points). In the MA stabilized samples the initial volume fraction of magnetite $\varphi_m = 6$ % was decreased down to 0.8 %, and the initial OA sample was diluted from $\varphi_m = 10$ % down to 0.7 %.

SANS experiments were performed on the SANS-1 diffractometer at the GKSS. The differential cross-section per sample volume, I (scattering 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 and θ is the scattering angle, over the q -interval of 0.06-2.5 nm⁻¹. Experimental details are described in [5].

The contrast variation method in the SANS experiment is based on detecting changes in the scattering from the system when varying the contrast, a difference between mean scattering length densities (SLDs) of the particles and the carrier. In the classical generalized approach for monodisperse non-magnetic particles [6] the SANS intensity is analyzed in terms of the basic functions (q -dependent coefficients in the expansion of I over the contrast). For polydisperse and magnetic particles the scattering can be treated [3] in similar manner after some modifications in definitions of the contrast and basic functions. As a consequence, dependences of the scattering parameters (e.g. parameters of the Guinier approximation) on the modified contrast take specific forms.

Here, together with analysis of the modified basic functions found from the experimental curves the parameters of the Guinier approximation (intensity at zero angle, $I(0)$, and radius of gyration, R_g) were considered. Following [3], first, the minimum of $I(0)$ as a function of the C₆D₆ content in the carrier was associated with the effective match point. Then, the modified contrast, $\Delta\tilde{\rho} = \tilde{\rho}_e - \rho_s$, was introduced as a difference between SLDs corresponding to the effective match point, $\tilde{\rho}_e$, and the solvent, ρ_s .

The SANS intensity was treated in accordance with the expression [3]:

$$I(q) = \tilde{I}_s(q) + \Delta\tilde{\rho}\tilde{I}_{cs}(q) + (\Delta\tilde{\rho})^2\tilde{I}_c(q), \quad (1)$$

where the modified basic functions $\tilde{I}_c(q)$, $\tilde{I}_s(q)$, $\tilde{I}_{cs}(q)$ comprise information about the nuclear and magnetic SLD distributions within particles, as well as the polydispersity function. The term $(\Delta\tilde{\rho})^2\tilde{I}_c(q)$ prevails in the scattering intensity at sufficiently large contrast and corresponds to the average particle shape. The contrast independent term $\tilde{I}_s(q) = I_N(q)|_{\Delta\tilde{\rho}=0} + I_M(q)$ comprises the residual nuclear scattering $I_N(q)$, at the effective match point because of the polydispersity and magnetic scattering contribution, $I_M(q)$, which is determined by the magnetic SLD of the particles.

Parameters of the Guinier approximation were analyzed according to equations [3]:

$$I(0) = n \langle V_c^2 \rangle (\Delta\tilde{\rho})^2 + n \langle V_c^2 \rangle D, \quad (2a)$$

$$\tilde{R}_g^2 = \left(\frac{\langle V_c^2 R_c^2 \rangle}{\langle V_c^2 \rangle} + \frac{A}{\Delta\tilde{\rho}} - \frac{B}{(\Delta\tilde{\rho})^2} \right) / \left(1 + \frac{D}{(\Delta\tilde{\rho})^2} \right). \quad (2b)$$

Here, R_c and V_c are the radius of gyration and volume corresponding to the particle shape, respectively; n is the particle number density. Parameters $\langle V_c^2 R_c^2 \rangle / \langle V_c^2 \rangle$, A , B , D were determined by fitting Eqs. 2a, 2b to experimental contrast dependences. Explicit expressions of parameters A , B , D related to the polydispersity function can be found in [3].

Results and Discussions

SANS curves with different D-benzene content for two kinds of diluted MFs are given in Fig. 1. Several contrasts are shown to follow main changes with the contrast variation. One can see a significant difference in the character of these changes in the MA and OA samples as a consequence of different size distribution for dispersed magnetite. Some amount of aggregation in OA fluid was detected with the effect on the scattering at $q < 0.1$ nm⁻¹. This region was not involved in the

Guinier treatment. Resulting dependences of $I(0)$ on the C_6D_6 content in the solvent are shown in Fig. 2. The effective match points were determined from parabolic fitting as $34.2 \pm 0.4 \%$ and $63 \pm 3 \%$ of the D-benzene content for MA and OA fluids, respectively. The corresponding SLD values are $(2.64 \pm 0.03) \times 10^{10} \text{ cm}^{-2}$ and $(3.86 \pm 0.15) \times 10^{10} \text{ cm}^{-2}$, which were used for defining the modified contrasts $\Delta\tilde{\rho}$ at different D-benzene content. Dependences in Fig. 2 were re-plotted in the form of Eq. 2a to find out the D values, $(1.81 \pm 0.02) \times 10^{19} \text{ cm}^{-4}$ (MA) and $(2.87 \pm 0.01) \times 10^{19} \text{ cm}^{-4}$ (OA).

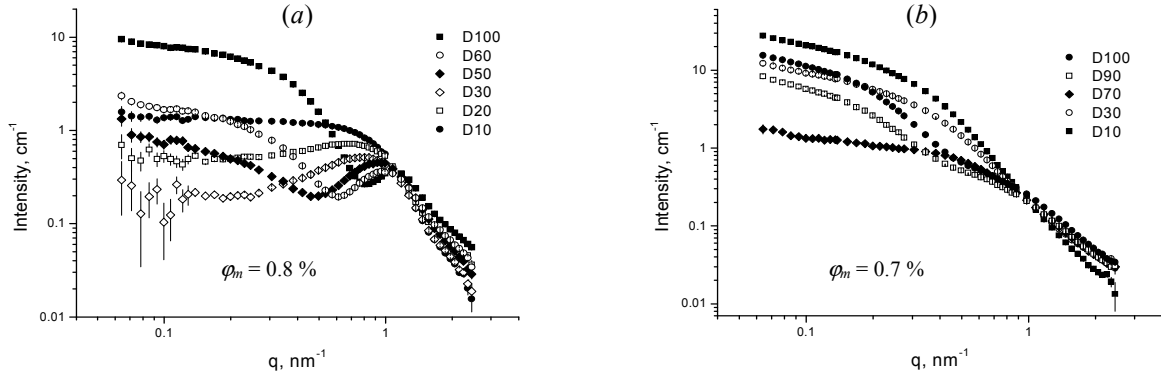


Fig. 1. SANS contrast variation for MFs with MA (a) and OA (b) stabilization. Percent volume fraction of C_6D_6 in the solvent is indicated in the sample names. Volume fractions of dispersed magnetite in the samples, ϕ_m , are indicated.

The apparent squared radius of gyration versus the inversed modified contrast is shown in Fig. 3. Equation Eq. 2b was fitted to this dependence with D fixed at the values found from the contrast dependence of $I(0)$. Resulting parameters are given in the caption to Fig. 3. The intersection of $\tilde{R}_g^2(\Delta\tilde{\rho}^{-1})$ with axis of ordinates corresponds to the infinite contrast, i.e. the scattering from the shape of colloidal particle (magnetite core plus surfactant shell). Taking into account the quasi-spherical shape of particles in MFs one obtains for the characteristic radius of the whole particle, $(\langle R_c^2 V_c^2 \rangle / \langle V_c^2 \rangle)^{1/2}$, values of $5.0 \pm 0.1 \text{ nm}$ (MA) and $10.3 \pm 0.1 \text{ nm}$ (OA). In last estimates the relation between the radius of gyration and particle radius, $R_c^2 = (3/5) R^2$, was used. Thus, the characteristic particle size, which comprises both the mean size and polydispersity, in OA fluid is twice larger as compared to MA fluid.

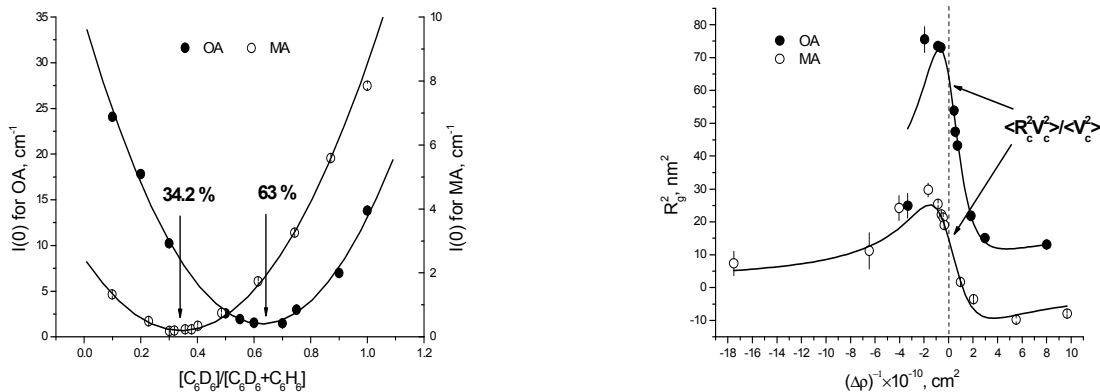


Fig. 2. Experimental points of intensity at zero angle with different contents of D-benzene in the solvent. Solid lines show best parabolic fits.

Fig. 3. Apparent squared radius of gyration versus the inversed modified contrast. Solid lines show the best fits to the dependence according to Eq. 2b. Resulting parameters are for MA sample: $\langle V_c^2 R_c^2 \rangle / \langle V_c^2 \rangle = 15.1 \pm 0.1 \text{ nm}^2$, $A = (-1.34 \pm 0.01) \times 10^{-3}$, $B = (-1.4 \pm 0.4) \times 10^5 \text{ cm}^{-2}$, $D = 1.81 \times 10^{19} \text{ cm}^{-4}$ (fixed); for OA sample: $\langle V_c^2 R_c^2 \rangle / \langle V_c^2 \rangle = 64.4 \pm 0.7 \text{ nm}^2$, $A = (-22.3 \pm 0.7) \times 10^{-3}$, $B = (-5.7 \pm 0.3) \times 10^5 \text{ cm}^{-2}$, $D = 2.87 \times 10^{19} \text{ cm}^{-4}$ (fixed);

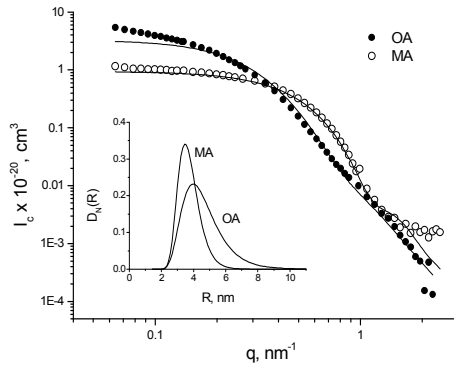


Fig. 4. $\tilde{I}_c(q)$ for two fluids. Lines show curves calculated with particle parameters from [2]. Inset shows model $D_M(R)$ functions for the particle size.

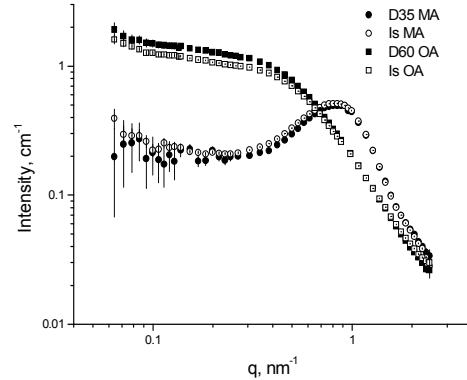


Fig. 5. $\tilde{I}_s(q)$ for two fluids are compared with experimental curves obtained in the vicinity of the match points.

Basic functions $\tilde{I}_c(q)$ obtained as a result of solution of the system of equations of type Eq. 1 with different contrasts are shown in Fig. 4. The correctness of this solution is supported by the fact that the other basic function $\tilde{I}_s(q)$ is quite close to the experimental curve obtained in vicinity of the effective match point (Fig. 5). The shape basic functions $\tilde{I}_c(q)$ in Fig.4 testify large difference in the particle structure of the two fluids. They are compared with calculations based on results of [2], where the scattering of polarized neutrons from magnetite with OA and MA shells in cyclohexane was treated by the model of polydisperse core-shell particles. Here, the shape function $\tilde{I}_c(q)$ is determined by the scattering from polydisperse spheres with radius $R = R_0 + h$, where R_0 is the radius of magnetite core and h is the effective thickness of the surfactant shell. The log-normal size distribution of magnetite core, $D_M(R_0)$, in the given case is replaced by $D_M(R - h)$. The consistency of the data in Fig. 4 with calculations is quite good. Deviations in the initial parts of the curves are related to aggregates mentioned above.

So, the data of the SANS contrast variation for the studied MFs agree well with the SANSPOL results obtained for the samples under the saturating magnetic field. This proves that the field does not take any significant effect on the particle structure of MFs at $\phi_m < 1$ %. The used approach allows one to separate the nuclear scattering from magnetic scattering of neutrons for unmagnetized MFs, thus providing independent structural information complementary to methods using magnetic field. In comparison with earlier works [7] on such type of separation by the SANS contrast variation, in the given approach better understanding of the dependence of the scattering parameters on the contrast was achieved.

The work is done in the frame of the project RFBR-Helmholtz (HRJRG-016) and partially supported by the Nat. Authority for Scientific Research through the CEEX (nr. 83/2006 *NanoMagneFluidSeal*).

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Magnetism and Magnetic Materials

doi:10.4028/3-908454-13-1

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doi:10.4028/3-908454-13-1.186