The Analysis of the Structural Parameters of Magnetic Fluids with SAXS and MGA Techniques

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Purpose – to study the structural parameters of the magnetite particles surrounded by the surfactant in the various carrier liquids using SAXS and based on the magnetization curve obtained applying ballistic method. The samples of the magnetite magnetic fluid based on water, engine oil and kerosene were investigated in this paper. Methodology – three samples of magnetic fluid were chosen for studying. Samples No 1 and No 2 were obtained at the UNESCO department of "Energy Conservation and Renewable Energy Sources", Belarusian National Technical University. Sample No 3 was obtained in the Fundamental Scientific Research Laboratory of Applied Ferrohydrodynamics of Ivanovo State Power Engineering University. SAXS experiment was conducted using Anton Paar SAXSess mc² analyzer at the Regional Centre of Nanotechnology of Southwest State University. Originality / value – The value of this work is to obtain new data on the physical parameters of the magnetic fluid samples. Findings – the derived surfactant shell width, which for the samples No 2, 3 was 1,8-1,9 nm, for the sample No 1 surfactant shell width was 3.5 nm, the excess of the calculated width of the surfactant layer can be explained due to the presence of a double layer of stabilizer.

Keywords: Magnetic fluid, Magnetite nanoparticles, Stabilizer, SAXS, Magnetization curve.

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1. INTRODUCTION

Magnetic fluid (MF) is a nanodisperse colloidal system, which is formed on the basis of magnetite particles with sizes of 10 nm and a carrier liquid. Magnetic fluid is stabilized with surfactants to get aggregative stability [1-2].

The objective of the work is to study structural parameters of the magnetite particles surrounded by a surfactant in different carrier liquids on the basis of small angle X-ray scattering (SAXS) data and the magnetization curve obtained applying ballistic method. The samples of magnetite MF based on water, engine oil and kerosene were examined in the paper.

2. MAIN PART OF THE STUDY

Three magnetic fluids were chosen as the samples for the study. Samples No 1 and No 2 were obtained at the UNESCO department of "Energy Conservation and Renewable Energy Sources" of Belarusian National Technical University. Sample No 3 was obtained in the Fundamental Scientific Research Laboratory of Applied Ferrohydrodynamics of Ivanovo State Power Engineering University. Samples characteristics are presented in Table 1.

All the samples were obtained using chemical condensation method from the liquid with surfactants. For sample No 1 a double layer of surfactant was used because the carrier liquid is polar [3].

Magnetic parameters of the samples given in Table 1 are obtained from the magnetization curves applying ballistic method in the Nanoscale acoustics laboratory of Southwest State University. Initial magnetic susceptibility is calculated according to the extrapolation of the initial segment of the dependence $M(H)$; the saturation magnetization is calculated according to the ex-

trapolation of the final segment of the dependence $M(1/H)$.

Table 1 – MF samples characteristics

№	Carrier liquid	Magnetite concentration ϕ, vol. %	Saturation magnetization M_S, kA/m	Initial magnetic susceptibility χ_L
1	Water	6,3	28,9	0,96
2	Engine oil	12	35,6	0,93
3	Kerosene	10,6	32,2	2,76

Surfactant of the sample No 1 is oleinic acid + sodium oleate, the sample No 2,3 – oleinic acid.

3. EXPERIMENTAL TECHNIQUES

The first part of the work was to study MF structural parameters using small angle X-ray scattering method (SAXS).

SAXS experiment was carried out using Anton Paar SAXSess mc² analyzer at the Regional Centre of Southwest State University. The function of scatterin $I_{\exp}(q)$ depending on the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ was obtained, where λ is the X-ray wavelength, θ is the scattering angle. The measurements were carried out at a constant temperature equal to 20 °C; the sample was dropped onto the cover glass and then it was fixed in the holder and exposed to radiation for 15 minutes in vacuum at pressure o $p \leq 4$ mbar and wavelength equal t $\lambda = 0{,}1542$ nm. The background curve of the cover glass and of the solvent, as well as the dark background were subtracted from the resulting dispersion curve [4].

The resulting curve is processed using GIFT software package. The experimental curve was approxi-

mated by the function [4]:

$$I(q) = <F^2(q)> S(q) \qquad (1)$$

In this expression $<F^2(q)>$ is the averaged square of the particle form factor, $S(q)$ is the particle structure factor. To describe the type of interaction of nanoparticles of magnetite in MF the form factor of solid ball-shaped particles and structure factors based on the PY-approximation were chosen [4].

The paired correlation function $p(r)$ was determined using the formula [5]:

$$I(q) = \int_{r=0}^{r_{max}} p(r) \frac{\sin(qr)}{qr} dr \qquad (2)$$

The evaluation of the accuracy of calculation of the function $p(r)$ was performed applying the Monte Carlo method by multiple payroll of the function $p(r)$ with the addition of random errors to the experimental curve. Then the results were averaged to obtain the lowest mean deviation of the theoretical scattering function $I(q)$ from the experimental scattering function $I_{exp}(q)$.

The nanoparticle size volume distribution was calculated using the same method by the formula [5]:

$$I(q) = \int_{r=0}^{r_{max}} D_V(r) V^2(r) F(qr) dr, \qquad (3)$$

where $V(r)$ is the particle volume, $F(qr)$ is the given form factor of the particle.

The structural parameters of the MF particles were also calculated on the basis of the analysis of the samples magnetization curves applying ballistic method $M(H)$.

The flow diagram of the experimental setup and the experimental techniques are described in detail in [6], [7]. The maximum value of the external magnetic field strength in the experiment was 600 kA/m.

The resulting field dependence of the magnetic flux $\Phi(B)$ was transferred / changed to the dependence $M(H)$ by the formula [6]:

$$M = \frac{2\Phi}{\pi\mu_0 d^2 N(1 - N_d)}, \qquad (4)$$

where d is the inner diameter of the capsule with a sample, N is the number of turns in the coil, N_d is the demagnetization factor for the chosen capsule.

The obtained curve was approximated by the Langevin function, which describes the process of the magnetization of low-concentration MF:

$$M(H) = M_S L(\xi), \ L(\xi) = \mathrm{cth}\,\xi - \frac{1}{\xi}, \qquad (5)$$

where $\xi = \mu_0 m_* H / k_0 T$ is the Langevin parameter, which is the ratio of the magnetic energy of the particle to its heat energy; M_S is the MF saturation magnetization.

The assumption of the gamma distribution of the magnetite nanoparticles in size leads to the following calculation expressions [8]:

$$M_{teor}(H) = M_S \int f(r, \alpha, x_0) L(\xi V) dr,$$
$$\xi = M_{SO} H / kT, \qquad (6)$$
$$f(r, \alpha, x_0) = r^\alpha \frac{\exp(-r/x_0)}{x_0^{\alpha+1} \Gamma(\alpha+1)},$$

where $M_{SO} = 477,7 \ kA/m$ is the magnetite saturation magnetization [7], $V = 4\pi r^3/3$ is the nanoparticle volume in the assumption that it is ball-shaped and has the radius r; $f(r, \alpha, x_0)$ is the function of the gamma distribution with the parameters α, x_0; $\Gamma(\alpha+1)$ is the Euler gamma function.

To determine the parameters of the size distribution of MF-particles taking into account the interparticle interactions the following system of equations can be written down [6], [8]:

$$x_0^3 = \frac{6\langle m_* \rangle}{\pi M_{SO}(\alpha+1)(\alpha+2)(\alpha+3)}, \quad \langle m_* \rangle = M_S/n,$$
$$\frac{(\alpha+5)^3 - \alpha - 5}{(\alpha+2)^3 - \alpha - 2} = \frac{\langle m_*^2 \rangle}{\langle m_* \rangle^2}, \quad \langle m_*^2 \rangle = 3kT\chi_L/\mu_0, \qquad (7)$$

where $\langle m_* \rangle$ is the average magnetic moment of the particle; $\langle m_*^2 \rangle$ is the average square of the magnetic moment of the particle; M_{SO} is the magnetite saturation magnetization; M_S is the MF saturation magnetization; χ_L is the MF initial magnetic susceptibility; n is the quantitative concentration of magnetic particles.

In this case it is assumed that the magnetic moment of magnetite nanoparticles is equal to the product of their volume by the specific saturation magnetization of magnetite.

4. DISCUSSION OF THE RESULTS

Applying the two described above methods the functions of the MF nanoparticle size distribution, the values of the average diameter of the magnetite particles and of the diameter of the prevailing in number particles were obtained (see Table 2 and Fig. 1).

Table 2 – Structural parameters of MFs

Sample No	Average diameter of nanoparticles, nm		The diameter of the prevailing nanoparticles, nm	
	Ballistic method	SAXS	Ballistic method	SAXS
1	5,9	6,1	3.7	7.2
2	6,4	5,7	4	7.5
3	9,4	7,7	6	7.8

The calculated average particle sizes using above-noted methods differ from each other in the range of 3 % to 18 % which can be explained by the sensitivity of the methods to different factors determining the final result of the measurements. The size of the prevailing nanoparticles obtained applying the SAXS method ex-

ceeds the size of prevailing nanoparticles calculated according to the ballistic method.

a

b

c
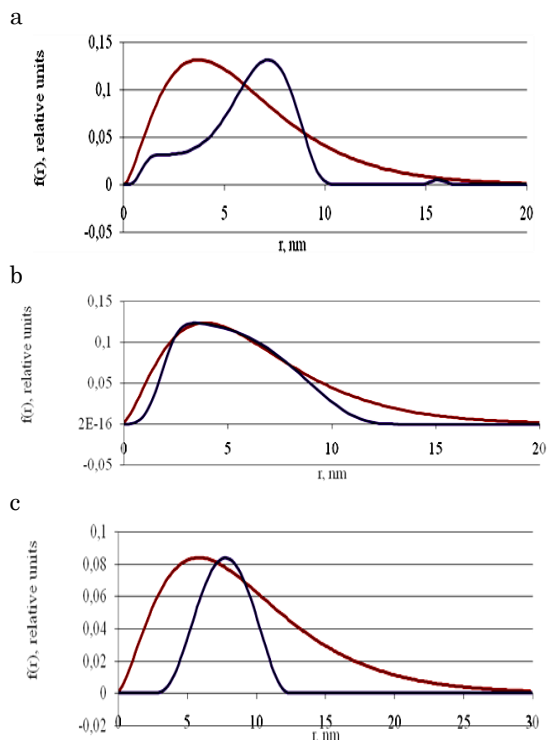
Fig. 1 – Nanoparticles size distribution, obtained by the ballistic method and by the SAXS method: a) for sample No 1; b) for sample No 2; c) for sample No 3. The dotted line –ballistic method; the full line – SAXS

This can be explained the following characteris tic features of the methods:

The method of determining the structural parameters of magnetic nanoparticles according to the magnetization curve is based only on the analysis of the magnetic properties of ferromagnetic cores of the particles, so it does not give any information concerning the surfactant shells.

The SAXS method provides information on the structural parameters of the surfactant shell due to the X-rays scattering on the gradient of the electron density created by a shell [9].

These facts allow evaluating the size of the shells of surfactant nanoparticles for magnetic fluids with different bases. The results are presented in Table 3.

Table 3 – Evaluation of the structural parameters of surfactant shells

Magnetic fluid	Carrier liquid	Surfactant	Surfactant shell width, nm
1	Water	Oleinic acid + sodium oleate	3,5
2	Engine oil	Oleinic acid	1,9
3	Kerosene	Oleinic acid	1,8

The data for samples No 2 and No 3 are consistent with the effective sizes of a molecule of oleinic acid (about 2 nm) given in [6], [11]. In sample No 1 the excess of ~ 1.8 times of the calculated width of the surfactant shell can be explained due to the presence of a double layer of the stabilizer.

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