

Extinction and Scattering of Light by Magnetic Colloidal Nanoparticles

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The peculiarities of scattering and extinction of light by colloids with different concentrations of magnetite nanoparticles are investigated. The light absorption effect on spectral dependencies of optical density of magnetic colloid are observed. According to dynamic light scattering experiments, particle size distributions for samples with different concentration of nanoparticles are defined.

Keywords: Magnetic fluid, Light extinction, Dynamic light scattering, Particles size distribution, Aggregate of nanoparticles.

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1. INTRODUCTION

In magnetic fluids different optical effects [1] such as extinction and scattering of light, birefringence, dichroism, and others can observe. Due to the presence of a magnetic dipole-dipole interaction between the particles of magnetic fluids tend to form aggregates of various shapes, as well as the ordered structures of nanoparticles and aggregates. The optical effects in colloidal nanosystems are extremely sensitive to particle size [2, 3] (usually magnitude of the effect is proportional to the cube of the particle volume), so these effects are most useful for assessing the aggregate stability of magnetic fluids, as are capable of detecting even small aggregates of a few nanoparticles [4].

The most popular optical methods for determining the size of the colloidal particles are dynamic and static light scattering. In the method of static light scattering the angular dependence of the scattered light intensity is usually measured and compared with the theoretical calculation of the Mie theory or different approximations (Rayleigh-Gans, anomalous diffraction, etc.) for particles of a certain size. In the method of dynamic scattering the correlation function of the intensity of light scattered by a small volume of sample is measured. According to this data it is determined by translational diffusion coefficient of the particles associated with their size by the Stokes-Einstein equation [5].

Modern data processing techniques make it possible to build a dynamic scattering particle size distribution based on the solution of the inverse scattering problem by various methods of regularization.

To study the various classes of disperse systems widely used method of turbidity spectrum [6], which is to study the dependence of the optical density D of the colloid on the wavelength λ . In a wavelength dependence of $D(\lambda)$, built in double logarithmic scale is nearly linear. On the slope of this relationship can be estimated particle size of the colloid.

2. EXPERIMENT

We have investigated the optical effects of extinction and scattering of light in the colloidal solutions of magnetite in kerosene stabilized by oleic acid with concentra-

tion of solids in the range from 0.1 vol. % to 0.0001 vol. %. This concentration was obtained by diluting the initial magnetic fluid (from the Research and Production Institute of Gas Processing, Krasnodar, Russia) with a concentration of about 13 % by purified kerosene.

Measurement of the spectral dependence of the optical density was performed using spectral ellipsometric apparatus "Ellipse 1891" in the mode of the spectral photometer. The test sample was placed into the rectangular optical quartz glass cuvette different thicknesses. The weakening of the light transmitted through the sample was detected by a photodetector, and the received data is automatically calculated dependence of $D(\lambda)$ (see. Fig. 1).

As is well known [7], the extinction of light when passing through the dispersion, subject to single scattering of light (i.e., not a very large concentration of particles) is described by Bouguer-Lambert law:

$$I = I_0 \exp(-\sigma Nl), \quad (1)$$

where σ is cross-section of light extinction, l is the radiation path length in a cell, N is numeric concentration of particles, and I_0 is the intensity of the incident radiation. By definition, the optical density of the medium is:

$$D = \log \frac{I_0}{I} = 0.43\sigma Nl. \quad (2)$$

Since the measurement samples of varying concentrations produced in cells of different length, which is not to represent the concentration dependence of the optical density and the attenuation coefficient $\chi = 2.3D/l$, which is determined by the concentration of individual particles and particle characteristics – cross section of light extinction $\chi = \sigma N$. Fig. 2 shows that a wide range of concentration dependence $\chi(C_V)$ is linear. This indicates light extinction constant sectional particles, i.e. their uniform sizes. Deviations from linearity are observed for low concentrations (about 0.0001 %), due, apparently, to the significant role of aggregates of particles in the low-concentration magnetic colloids.

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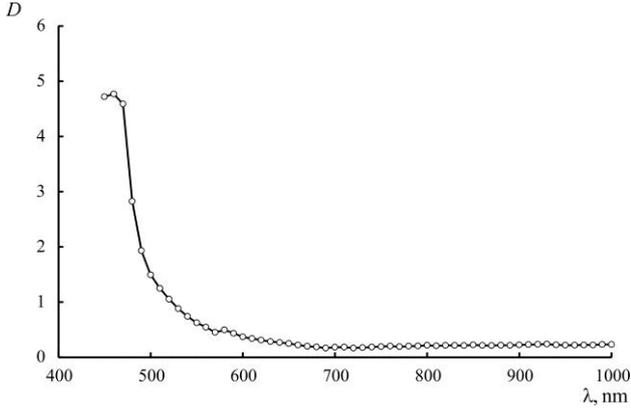


Fig. 1 – Optical density spectrum for the sample with concentration 0.001 % (optical path is 51 mm)

Fig. 3 shows the dependence on a double logarithmic scale in the wavelength range 400-600 nm for all the samples. The figure shows that the dependence is close to linear and have the same within experimental error, the inclination angle (with the exception of the sample at a concentration of 0.0001 %, for which the angle of inclination is substantially less). This suggests that the size of the magnetite particles in the samples with a concentration of 0.1 % to 0.001 % not significantly different and in the dilution of the initial sample relatively large aggregates is not formed.

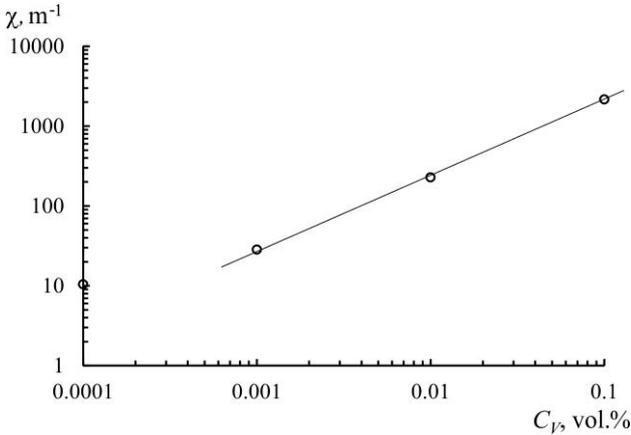


Fig. 2 – Concentration dependence of coefficient of extinction by colloidal solution of magnetite

Our experimental devices for dynamical light scattering the autocorrelation function of the photocurrent is determined [5]:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I^2 \rangle} = \frac{1}{\langle I^2 \rangle} \lim_{N \rightarrow \infty} \sum_{i=0}^N I(t_i)I(t_i + \tau) \quad (3)$$

To calculate the particle size a is necessary to determine the autocorrelation function of the light field $g^{(1)}(t)$ which is determined by the configuration of the optical experiment (wavelength, scattering angle) and the constant of translational diffusion $D_t = kT / 6\pi\eta a$. In the case of a polydisperse system the autocorrelation function has the form [5]:

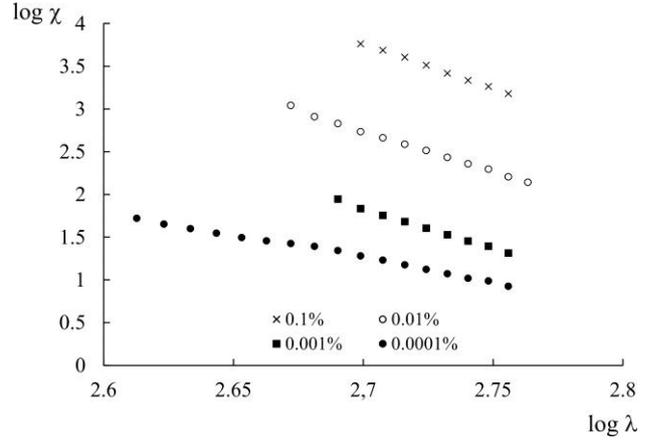


Fig. 3 – Spectra of coefficients of extinction in double logarithmic scale

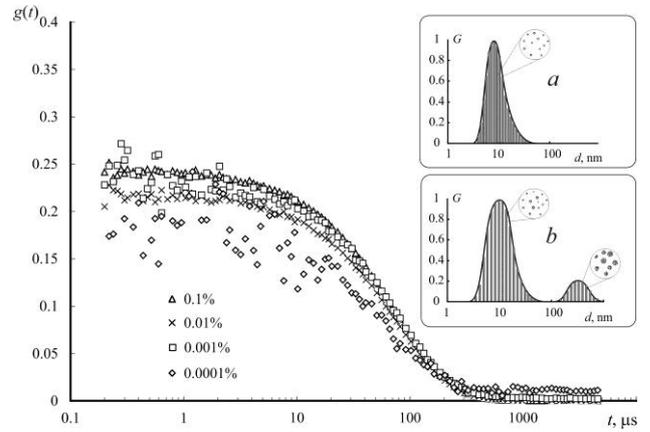


Fig. 4 – Autocorrelation functions of dynamic light scattering and particles size distributions (a – 0.1 %; b – 0.0001 %)

$$g^{(1)}(t) = \int_0^{\infty} G(\Gamma) \exp(-\Gamma t) d\Gamma, \quad \Gamma = q^2 D_t, \quad q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}. \quad (4)$$

This is Fredholm's equation but with a fairly simple exponential kernel. For recovery of the distribution function of particles disperse systems in size according to the dynamic light scattering there is a set of special methods.

Dynamic light scattering experiments is carried out on spectrometer Photocor Complex (Fig. 4). Studies have shown that the average diameter of the magnetite particles in all the samples is about 14 nm, ranging in size from 8-10 nm to 40-60 nm, the distribution width in the more concentrated samples is smaller (10-18 nm) than the diluted (8-60 nm).

3. DISCUSSION

Let us to consider the contribution of light extinction and scattering by magnetic colloids in the spectral dependence of the optical properties. The cross section of the light extinction is made up of the scattering cross section σ_{sca} and absorption cross section σ_{abs} :

$$\sigma = \sigma_{sca} + \sigma_{abs} \quad (5)$$

For particles that are small compared with the wavelength of light, the approximation of Rayleigh

[7, 8] and the expressions for the cross sections are of the form:

$$\sigma_{sca} = \frac{8}{3} \left(\frac{2\pi a}{\lambda} \right)^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \quad (6)$$

$$\sigma_{abs} = \frac{8\pi a}{\lambda} \operatorname{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 \quad (7)$$

Where a , m – are the size of particles and relative index of refraction respectively. It follows from (6), the spectral dependence of the optical density in the double logarithmic scale is linear with a slope (wavelength exponent):

$$w = \frac{\partial(\log D)}{\partial(\log \lambda)} \quad (8)$$

Wavelength exponent for non-absorbing particles is $|w| \leq 4$ and for particles whose absorption is dominated over scattering (formula (7)) $|w| \approx 1$.

Determination of the slope of the spectral dependence of the optical density (Fig. 3) shows that the experimental values are much higher than these estimates, in the order $w \approx 8-10$.

It should be noted that the expressions (6) and (7) are valid for the case when the dispersion of the refractive index of the particles can be neglected [7, 8]. However, the magnetite particles in the visible region, this assumption requires further confirmation. For this was an experimental study of the dispersion of the real and imaginary parts of the refractive index of the dried on a flat substrate, the source of the magnetic fluid by means of reflection ellipsometrical techniques on the instrument "Ellipse 1891".

The experiment showed that the real and imaginary part of the complex refractive index ($m = n - ik$) of the magnetite particles vary significantly in the wavelength range 400-700 nm. The change of imaginary part is the very significant (almost three times). This

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means that in the calculation of the formulas (5-8) should be considered depending on $n(\lambda)$ and $k(\lambda)$.

Consideration of these relationships when calculating tangent angles of the logarithm of the optical density shows that the wavelength exponent in this case may significantly exceed the value of $w = 4$, which is confirmed experimentally. In addition, the calculations show that the important role of effects absorption of light by magnetic colloidal particles in the short-wavelength region (400-500 nm).

4. CONCLUSION

Optical density spectra of samples of different concentrations of magnetic colloids are similar in nature to the rapid decline of the optical density in the range of 400-550 nm and maximum transparency in the near infrared region of 800-900 nm. The study of the concentration dependences of the spectra confirms the applicability for magnetic colloids Bouguer-Lambert law in a wide range of concentrations (0.1 %-0.001 %).

Applying a magnetic colloid turbidity spectrum method shows that the extinction of light in magnetic fluids is significantly affected by the absorption by nanoparticles. Adequate values of the wavelength exponent can be obtained only on the basis of the spectral dependence of the complex refractive index of the magnetite particles, which has strong dispersion in the wavelength range 400-600 nm.

The data of dynamic and static light scattering show that the solutions of moderate concentrations (0.01 %-1 %), the maximum size of the aggregates usually not exceed 50-70 nm. Light scattering in such samples differs little from Rayleigh. In very dilute solutions (with a concentration of 0.001 % or less) are observed much larger aggregates with a size up to 600 nm.

ACKNOWLEDGMENTS

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