Magneto-optical properties of binar ferrocolloids

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Abstract. In this work, a new method for increasing optical anisotropy of a ferrocolloid through introducing the coiled polymer molecules or elongated nanosized non-magnetic particles is realized. Since the dimensions of structural elements comprising such a binary colloidal solution are small compared to the wavelength, the ferrocolloid remains optically homogeneous. Type I binary ferrocolloids are obtained by introducing polybutadiene molecules into a magnetic fluid (magnetite + kerosene + oleic acid). In this case, an increase in the double refraction (DR) is due to the deformation and stretching of the polymer coils along the magnetic field. In weak fields, double amplification of the signal was detected for the concentration of polymer molecules of about 0.5 %. A further increase in the concentration of impurity molecules weakens DR due to a disturbance of the sedimentation stability of the solution and precipitation of colloidal particles. Type II binary solution is synthesized on the basis of a magnetic fluid and rod-shaped impurity nanoparticles of goethite (α–FeOOH). The transverse dimension of the impurity particles (10 – 30 nm) was close to the average diameter of single-domain magnetite particles, and the longitudinal dimension was an order of magnitude larger. An increase in the DR occurs due to the orientation of long axes of impurity particles along the magnetic field caused by the difference in the "demagnetizing" coefficients along and across the axis of the particle. The magnetic double refraction has been studied depending on the concentration of magnetite and impurity particles and the strength of the magnetic field. For the first time, an experimental substantiation of the multiple amplification of the DR signal by impurity particles was obtained. In the fields (up to 10 kA/m) and for the volume fraction of impurity particles of the order of one percent, the DR signal is amplified by more than an order of magnitude. In stronger fields, the signal gain, associated with the influence of impurity particles, reaches saturation and, with further increase in the field strength, remains practically unchanged, while the total anisotropy of the solution continues to increase due to the orientation of the magnetite particles.

1. Introduction
Magnetic fluids, which are stable colloid suspensions of single-domain ferromagnetic nanoparticles with a characteristic dimension of ~ 10 nm, in the absence of the external magnetic field are optically homogeneous. However, when exposed to the external field they acquire properties of uniaxial crystal with very strong optical anisotropy. An abnormally large value of the Cotton-Mouton constant is the special feature that arouses keen researchers’ interest in the double refraction (birefringence) in magnetic fluids. This effect was investigated in a series of theoretical and experimental works [1]-[12]. Despite a high value of the Cotton-Mouton constant the integral effect of double refraction (DR) in magnetic fluids was found to be rather weak,
since due to a strong absorption of light, it is common practice to use in experiments either
dilute solutions or very thin (a few tenths or hundredths of a millimeter) layers of magnetic
fluid.

In [13] the authors describe a new method of increasing optical anisotropy of a ferrocolloid by
introducing the coiled molecules of a polymer into a suspension and present preliminary results.
Our work is an extension of the above study. Furthermore, it interprets the results of experiment
on the double refraction in the Type II binary solution, containing impurity particles in the form
of elongated nonmagnetic particles. Since the dimensions of structural elements comprising such
binary colloid solutions are small compared to the wavelength, the ferrocolloid remains optically
homogeneous. Hence, the focus of our study is the magnetic and optical properties of new
magnetizable media binary ferrocolloids, which differ from the ordinary magnetic fluids by high
values of the Cotton-Mouton constant.

2. Type I binary ferrocolloids
In all experiments, a magnetic fluid composed of magnetite particles dispersed in kerosene
and stabilized with oleic acid was used as a basis. It was obtained by a standard method
of chemical precipitation and subsequent removal of non-magnetic particles and free stabilizer
through repetization. Type I binary ferrocolloids were obtained by introducing polybutadiene
molecules into the magnetic fluid. An increase in the optical anisotropy of the solution was
achieved due to deformation and stretching of polymer coils along the magnetic field. The main
difficulty in obtaining binary colloids is associated with a strong influence of polymer molecules
on the aggregative stability of the solution.

To obtain information on the stability of magnetic liquids and binary solutions against
aggregation, the dynamic susceptibility of solutions was measured and cluster analysis was
carried out based on the expansion of the dynamic susceptibility into a series of the Debye
functions and the known relationship between the relaxation time of the magnetic moments of
particles (or clusters) and their volume. The method of cluster analysis is described in detail in
[14]-[16]. It was found that in magnetic fluids, even if they do not contain polymer molecules,
there are a great number of quasispherical aggregates with characteristic dimensions ranging
from 40 to 80 nm. The results obtained are in good agreement with the data of previous
papers [14]-[16], in which the same magnetic fluids were investigated. As an example, Figs. 1
and 2 show typical dispersion curves for the dynamic susceptibility of a magnetic fluid and the
temperature dependence of the average (hydrodynamic) diameter of aggregates. Clearly, the
average diameter of single particles does not depend on temperature. The fact that its value
practically coincides with the data of the magneto-granulometric analysis lends support to the
validity of the data obtained. According to the results of [12], nanosized aggregates have very
little effect on the optical properties of the solution, since the magnetic cores of the particles are
separated by a double layer of the stabilizer, and the contributions of these particles to the DR
signal do not change during aggregation.

The injection of polymer molecules into a colloidal solution can substantially change the
properties of the solution. At high impurity concentrations, it leads to the formation of large
aggregates, partial precipitation of colloidal particles, and a multiple decrease in the magnetic
susceptibility: with increasing impurity concentration, the solution loses its sedimentation
stability. Binary solutions are stable to aggregation only at low impurity concentrations
(approx. one percent). In this case, their magnetic susceptibility decreases insignificantly. In
the DL tests, only sedimentation-stable binary ferrocolloids were used.

A typical dependence of the signal of the measuring cell, assembled according to the standard
scheme [12], on the field strength and concentration of impurity molecules is shown in Fig. 3.
The signal from a photodiode, which measures the intensity of laser radiation with a wavelength
of 633 nm, passing through a thin layer of a magnetic fluid and a polarizer, is plotted on the
Figure 1. The real (upper) and imaginary (bottom) parts of the dynamic susceptibility of a magnetic fluid versus the frequency of the sounding field at temperature $T = 340$ K

Figure 2. The average diameter of aggregates (top) and single particles in a magnetic fluid as a function of temperature
Figure 3. The DR signal as a function of the magnetic field strength for binary ferrocolloids with different concentrations of polymer molecules

ordinate. The constant magnetic field is oriented perpendicular to the light ray. The angle between the plane of polarization of the incident ray and the magnetization vector was $\pi/4$. As expected, the intensity of light passing through the measuring cell increases as the fourth power of magnetic field strength (the difference between the indices of the ordinary and extraordinary rays grows according to a quadratic law). It can be seen from the figure that the injection of polybutadiene molecules into a magnetic fluid can lead to a significant enhancement of DR effect. The maximum (twofold) increase in the DR is observed in the case when the volume concentration of impurity molecules is about 0.5%.

3. Type II binary ferrocolloids
A binary solution of the second type is synthesized on the basis of a magnetic fluid and impurity nanoparticles of goethite ($\alpha$-FeOOH). The transverse dimension of the impurity particles (10 – 30 nm) was close to the average diameter of single-domain magnetite particles, and the longitudinal one was an order of magnitude larger. An increase in the DR was due to the orientation of the long axes of the impurity particles along the magnetic field caused by a difference in the "demagnetizing" coefficients along and across the long axis of the impurity particle. The magnetic birefringence was studied as a function of the concentration of the magnetic phase, impurity particles, and magnetic field strength. The main result of the study was the experimental substantiation of a multiple amplification of the DR signal by impurity particles, which was predicted in calculations made in [17]. For the sake of illustration, Fig.4 shows the DR signal for a binary solution and a base magnetic fluid as a function of the magnetic field strength. In weak fields and for a volume fraction of impurity particles of the order of one percent, the DR signal intensity is increased by one or two orders of magnitude. In the fields of about 10 kA/m, the signal gain, associated with the influence of impurity particles, reaches saturation and in the future practically does not change. The total optical anisotropy continues to increase due to the orientation of magnetite particles. A surprising result is that curve 2 in Fig. 4 (in contrast to curve 1 for a magnetic fluid) is close to a linear relationship, and there is
Figure 4. The DR signal in experiments with a binary ferrocolloid of the second type. 1 - magnetic fluid, 2 - solution with $\alpha$-FeOOH particles ($C = 0.6\%$).

no evidence that in weak fields the signal grows as the fourth power of the field strength. Most likely, the fields of a few kA/m, used in the experiment, can no longer be considered small for impurity particles. In this case, the range of parameters, in which the law $U \sim H^4$ is satisfied, is limited to the field strength of the order of 100 A/m and cannot be resolved in Fig. 4.

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