The Cotton-Mouton effect in ferrofluids containing rod-like magnetite particles

V Badescu¹, LE Udrea¹, O Rotariu¹, R Badescu² and G Apreotesei²

¹ National Inst. of R-D for Technical Physics, 47 Mangeron Blvd., Iasi, 700050, RO
² Technical Univ. “Gh. Asachi”, Dept. of Physics, 67 Mangeron Blvd., Iasi, 700050, RO

E-mail: bav08@physiasi.ro

Abstract. Ferrofluids with rod-like nano-sized magnetite particles were prepared by precipitation from aqueous solutions of ferrous hydroxide and aging them in the presence of a magnetic field. We studied the Cotton-Mouton effect measuring the azimuthally distribution of the transmitted light intensity and obtained that its magnetic field dependence differs considerably for ferrofluids containing rod-like and spherical magnetic nanoparticles, respectively. After switching off the magnetizing field, the relaxation of the birefringence was observed, measured and analysed.

1. Introduction
Ferrofluids are very stable colloidal suspensions of ultrafine single domain magnetic particles in a suitable liquid carrier [1, 2]. They have a range of interesting physical properties, from which the magneto-optical properties may provide a basis for numerous applications. The main optical effects studied in ferrofluid films under parallel magnetic fields are linear dichroism and birefringence [3 - 9].

Some recent biomedical applications of ferrofluids require avoiding of field induced chain forming or aggregation of magnetic nanoparticles in suspension. From these we noticed the using of ferrofluids in monitoring of biological binding reactions, particularly by magnetooptical relaxometry [10 - 12].

To enhance the birefringence signal implicated in magnetooptical relaxometry we prepared a ferrofluid containing in suspension rod-like nano-sized magnetite particles with axial ratios >2. This non-typical morphology of particles is the key of our work. For such ferrofluids and at low concentrations the magnetic induced birefringence origin is dominated by form anisotropy of nanocrystallites in suspension. Furthermore, the birefringence relaxation takes place only by rotational diffusion of nanorods about some axis perpendicular to theirs cylindrical axis.

Within the scope of our work were to prepare the ferrofluid containing magnetite particles with above mentioned non-typical morphology, to characterize them and to measure the Cotton-Mouton (C-M) effect both in stationary and transitive regime.

2. Materials and methods
For our studies we prepared ferrofluids having octane as liquid base and oleic acid as stabilizing agent. The magnetic fraction was magnetite, prepared by two synthesis routes introduced by Khalafalla and Reimers [13] and Sugimoto and Matijević [14], respectively. The first route is based on the coprecipitation of Fe(OH)₂ and Fe(OH)₃ from an aqueous solutions mixture under the action of a strong alkali, followed by the fast aging of those. The obtained nanoparticles were transferred into the octane, resulting a ferrofluid with a magnetite volume content of 0.6%, named further on sort I ferrofluid.
The second procedure was analogous to that followed by Zhang et al. [15] and by Vereda et al. [16] with some minor modifications. The process consist in the precipitation of Fe(OH)$_2$ also in aqueous media and the slow aging of that gel in the presence of NO$_3^-$. For this aging the reaction system was placed in a hot oil bath preheated to 90°C and mounted in the cylindrical gap of an electromagnet with closed iron circuit. The solution was slightly stirred for 2 h with the axis of agitator parallel to force lines of the magnetic field. Test probes were extracted from the flask after 0.5 h, 1 h and 1.5h. This stage was repeated at different magnetic field intensities of 80 kA/m, 160 kA/m, 240 kA/m, 320 kA/m and 400 kA/m. The obtained probes of magnetite were cured with oleic acid and dispersed in octane to obtain some ferrofluids with a volume content of magnetite of 0.6%, named further on sort II ferrofluids.

The magnetizations of the two sorts of ferrofluids were measured with a vibrating sample magnetometer. In figure 1 are presented the magnetic properties for one sort II ferrofluid, the time of aging being 1 h and the intensity of the curing applied magnetic field being 160 kA/m. The measurement showed that the obtained ferrofluid have a superparamagnetic comportment.

\[
\begin{align*}
\text{Figure 1. The magnetic properties for a sort 2 ferrofluid.} \\
\text{Figure 2. The set-up for the study the azimuthal distribution of the transmitted light intensity.}
\end{align*}
\]

For a qualitative analysis of the birefringence effect in the prepared ferrofluids we adopted a method relied on the measurement of the azimuthally distribution of the transmitted light intensity through a ferrofluid film magnetized parallel to its plane by an external continuous magnetic field [17, 18]. The experimental set-up is shown in figure 2. A He-Ne laser beam (\(\lambda=632\) nm) is linearly polarized by the polarizer P and then is incident normally to the ferrofluid film MF. The magnetic field is generated by a pair of Helmholtz coils (HC). The angle \(\beta_1\) between the transmission axis of the polarizer and the magnetic field is adjustable. The analyzer A is used to examine the polarization state of the transmitted light. The azimuthal angle \(\eta = \beta_1 - \beta_2\) is modified rotating the analyzer. Finally, a receiving photodiode (D) is used to detect the intensity \(I\) of the transmitted light. In this work the \(I-\eta\) curves were measured for the prepared ferrofluids at \(\beta_2 = 45^0\) and various H’s. Under zero field, the symmetric \(I-\eta\) curves exhibits a relative maximum intensity at \(\eta_{I_{\text{max}}} = 0\) and zero intensity at \(\eta_{I_{\text{min}}} = 90^0\) and - 90°. The symmetric \(I-\eta\) curves under \(H \neq 0\) are also obtained with a translational shift \(\Delta \eta\) with respect to the zero field curves. This shift implies that the transmission axis of the transmitted light was rotated by an angle \(\Delta \eta\) with respect to that of the incident light (i.e. C-M rotation), and it is considered as a qualitative measure of the linear dichroism. On the other hand, the minimum intensity \(I_{\text{min}}\) occurred at \(\eta_{I_{\text{min}}}\) is non-zero under \(H \neq 0\). This \(I_{\text{min}} \neq 0\) implies that the transmitted light is not linearly but elliptically polarized, and it is considered a qualitative measure of birefringence.

Fixing the analyzer at \(I_{\text{min}}\) and switching off the magnetizing field, a relaxation of the birefringence can be observed. Assuming that the magnetic nanoparticles in suspension are cylindrical,
the birefringence relaxation is determined by a single exponential term

\[ \Delta n = \Delta n_0 \exp(-6D_r t) \],

where \( \Delta n_0 \) is a function of the applied field before its turning off and \( D_r \) is the rotational diffusion constant about an axis perpendicular to the cylindrical axis. The \( D_r \) can be written as [19]

\[ D_r = \frac{3kT}{\pi \eta L} \left( \ln \frac{L}{d} - \gamma \right), \]

where \( k \) is Boltzmann’s constant, \( T \) is temperature, \( \eta \) is the viscosity of the medium, \( L \) the length of the cylinder, and \( d \) the width. The parameter \( \gamma \) refers to end effects and depends upon the aspect ratio \( L/d \). For sufficiently large \( L/d \), the \( \gamma \) becomes inconsequential; for small \( L/d \), [20]

\[ \gamma = 0.662 - 0.92\left(\frac{d}{L}\right). \]

With known values for the viscosity \( \eta \) of the ferrofluid, the temperature \( T \), Boltzmann's constant \( k \) and \( D_r \), determined from the magnetobirefringence relaxation measurement it is possible to calculate the aspect ratio \( L/d \) of the particles.

3. Results

In figure 3 are shown the \( I - \eta \) curves for the sort 1 ferrofluid. When a magnetic field of \( H = 10 \) kA/m is applied, \( \eta \) is moved by an angle \( \Delta \eta = 1.08^0 \) and \( I_{\text{min}} \) is nonzero. Increasing the field up to 50 kA/m, the \( I - \eta \) curves remain approximately in the same position. This behavior can be explained by a low optical anisotropy of the ferrofluid containing nanoparticles with small form anisotropy.

[Figure 3. Azimuthally distribution of the transmitted light intensity for the sort 1 ferrofluid.]

In figure 4 are shown the \( I - \eta \) curves for sort 2 ferrofluid, magnetically characterized above. The value of \( \Delta \eta \)'s increased gradually up to 2.14\(^0\) as \( H \) increased to 40 kA/m and then remains almost constant as \( H > 44 \) kA/m. A similar behavior is observed for \( I_{\text{min}} \). The fact that \( I_{\text{min}} \) depends on the magnetic field intensity implies that the configuration of the elliptical polarized transmitted light is affected by the applied magnetic field. We thought this effect as a consequence of the induced orientational order of the independent colloidal magnetic nanoparticles with large axial ratios. This result is in accord with those from references [15] and [16].

[Figure 4. Azimuthally distribution of the transmitted light intensity for the sort 2 ferrofluid.]

Figure 5 shows the time evolution of \( I_{\text{min}} \) for the sort 1 ferrofluid, after the magnetic field with intensity of 40 kA/m is suddenly cancelled. It is observed a decrease of \( I_{\text{min}} \) in a very short time (< 0.1 sec) and after that the intensity of the transmitted light remains constant in time.

Figure 6 shows the time evolution of \( I_{\text{min}} \) for the sort 2 ferrofluid, after the magnetic field with intensity of
(40 kA/m) is suddenly cancelled. In this case two stages are distinguished for the relaxation process. In the first stage $I_{\text{min}}$ suddenly decreases with approximately 25% from the value it had in the presence of magnetic field. After that, $I_{\text{min}}$ continuously decreases in a way which cannot be fitted by a simple exponential curve.

The fit of the relaxation curve of $I_{\text{min}}$ can be approximated with a sum of exponential functions with various amplitudes and time constants. This behavior can be explained by the cumulating of some diffusion processes with different rotation diffusion coefficients, depending on the aspect ratios of nanoparticles in the ferrofluid.

### 4. Conclusions

For enhancing the birefringence signal implicated in magnetooptical relaxometry we prepared a ferrofluid containing in suspension rod-like nano-sized magnetite particles. At low concentrations these ferrofluids presented a superparamagnetic behaviour. The induced orientational order of the independent nanoparticles with large axial ratios in prepared ferrofluids lead to a clearly C-M effect. Since the time constants for the transitive regime depends on the hydrodynamic size of the particles, we will focus our future work on applying these ferrofluids for the monitoring of binding biological reactions.

### References

[1] Rosensweig R E 1997 Ferrohydrodynamics (Mineola, New York: Dover)

[2] Odenbach S 2003, *Colloids Surf. A* 217 171

[3] Martinet A 1974 *Rheol. Acta* 13, 260

[4] Skibin Yu N and Chekanov V V 1977 *Magnetohydrodynamics* 13 249

[5] Scholten P C 1980 *IEEE Trans.s Magn.* MAG-16 221

[6] Davies H W and Llewellyn J P 1980 *J. Phys. D: Appl. Phys.* 13 2327

[7] Taketomi S 1983 *Jpn. J. Appl. Phys.* 22 1137

[8] Xu M and Ridler P J 1997 *J. Appl. Phys.* 82 326

[9] Hasmonay E, Dubois E, Bacri J –C, Perzynski R et al. 1998 *Eur. Phys. J. B* 5 859

[10] Romanus E, Groß C, Kötitz R, Prass S, Lange J et al. 2001 *Magnetohydrodynamics* 37 328

[11] Wilhelm C, Gazeau F, Roger J, Pons J N et al. 2002 *Phys Rev E* 65 031404

[12] Glöckl G, Brinkmeier K, Aurich K, Romanus E et al. 2005 *J. Magn. Magn. Mater.* 289 480

[13] Khalafalla S E and Reimers G W 1980 *IEEE Trans. Magn.* 16 178

[14] Sugimoto T and Matijević E J 1980 *J. Colloid Interface Sci.* 74 227

[15] Zhang Y, Shi O H, Xiong H Q and Zhai Y 2005 *Int. J. Mod. Phys.B.* 19 2757

[16] Vereda F, de Vicente J and Hidalgo-Álvarez R 2007 *Langmuir* 23 3581

[17] Horng H E, Yang S Y, Lee S L, Wu J M et al. 2000 *Magnetohydrodynamics* 36 39

[18] Fosa G, Bădescu R and Călugăru Gh 2004 *Rom. J. Phys.* 49 312

[19] Elias J G and Eden D 1981 *Biopolimers* 20 2369

[20] Tirado J G and Eden D 1980 *J. Chem. Phys.* 73 1986