THE STUDY OF THE MAGNETO-BIREFRINGENCE RELAXATION FOR AN AQUEOUS FERROFLUID ON THE POLYVINYL ALCOHOL BASE

G. APREOTESEI[1], R. BĂDESCU[1], L. E. UDREA[2], O. ROTARIU[2]

[1] Technical University "Gh. Asachi", Department of Physics, Iasi, Romania, gabiap03@yahoo.com
[2] National Institute of Research and Development for Technical Physics, Iasi, Romania

Received March 13, 2007

Our work presents some results on the magnetic birefringence relaxation for aqueous ferrofluids. The water-based ferrofluids were prepared by precipitation of magnetite in presence or absence of poly(vinylalcohol). The time evolution of the birefringence of the prepared ferrofluids is analysed as depending on the intensity of the applied magnetic field.

Key words: birefringence, relaxation, aqueous ferrofluid, *in-situ* precipitation.

1. INTRODUCTION

Ferrofluids are colloidal suspensions of superparamagnetic nanometer sized particles in a suitable liquid carrier [1, 2]. The recent development of biocompatible functionalized ferrofluids led to a range of new biomedical and diagnostic applications [3–6]. A lot of research was conducted to develop carriers for drug delivery and drug targeting designed for in vivo usage.

For the successfully guidance of magnetic carriers through capillary vessels and tissues by using magnetic fields applied from the exterior, it is important to prevent the particles' spatial structuring.

Various surfactants are usually used to enhance dispersibility of magnetic nanoparticles in aqueous medium [7, 8]. Poly(vinylalcohol) (PVA) often serves as a protective agent to stabilize colloidal dispersions of magnetite particles as magnetic carriers [9]. Due to their high functionality and hydrogel-like properties, PVA magnetic composites appear to be successfully applied in many biomedical areas. However, there is a major difficulty to obtain uniform distributed magnetic materials because of the aggregation process of particles. Precipitation of inorganic particles in a cross-linking polymer matrix often prevents coagulation of particles. For obtaining adequate ferrofluids for drug delivery and drug targeting, the magnetite is precipitated in the presence of PVA at the moment of precipitation, in contrast to the subsequent addition of PVA

after precipitation. The magnetite precipitates along the unfolded polymer strands [10], this process giving rise to monodisperse particles. The resulting organic-inorganic composites form stable aqueous suspensions.

In the presence of magnetic field the ferrofluids becomes anisotropic. Their anisotropy is manifested on the dependence of the mechanic, electric, magnetic and optical properties on the direction and the intensities of the magnetic field applied. The analysis of the magnetooptical properties (linear dichroism and linear birefringence) in the ferrofluids is a way to emphasize and evaluate the structuring of ferrofluids in the presence of magnetic field [11–13].

In this work we present the method of preparation of some aqueous ferrofluids by precipitating magnetite *in-situ* within a PVA solution, or in the absence of PVA. Also we show why the analysis of birefringence phenomena is suitable to assess the texturing of the prepared ferrofluids in the presence of an applied magnetic field.

2. EXPERIMENTAL

2.1. GENERAL COMMENT

Two sorts of ferrofluids were prepared. For *sort* 1 the magnetite particles were prepared by precipitation of Fe(II) and Fe(III) ions in the presence of PAV and for *sort* 2 the particles were precipitated in the absence of PAV.

2.2. *IN-SITU* PRECIPITATION OF MAGNETITE PARTICLES

25.0 mL of $FeCl_2$ 4 H_2O solution (1.5 M) and 25.0 mL of $FeCl_3$ 6 H_2O (3.0 M) solution were added into 300.0 mL of 3.0 M PVA (72000 polymer basic units, $> 98\%$ acetylation degree) solution and stirred at 50°C until well dispersed. An approximately equal volume of 3.0 M NaOH solution was dropped into the mixed solutions under stirring at 65°C (until pH 8.0 ± 0.2 was attained). The mixture was allowed to stand at room temperature and then dialyzed with distilled water using a cellulose dialysis membrane until neutrality was attained. The precipitates were separated by centrifugation at 10,000 rpm for 30 min. The clear supernatant was then collected for analysis.

2.3. PRECIPITATION OF MAGNETITE IN ABSENCE OF PVA

A suspension of magnetite particles was also prepared in the same way as described above, except that the precipitating solution contained no polymer. The obtained suspension was washed repeatedly and the magnetite particles

resuspended in an aqueous solution of 3.0 M PVA. The mixture was then ball-milled for 100 h. The centrifugation and separation of supernatant follow the same steps as above.

2.4. FERROFLUIDS CHARACTERIZATION

The size distributions of particles in the supernatant fluids were determined by a dynamic light scattering method (DLS) and by analyzing the magnetization curves of ferrofluids [14, 15]. The magnetization curves were obtained using a balance force method.

2.5. MAGNETOOPTICAL ANALYSIS TECHNIQUE

Elliptically polarized transmitted light results when a linearly polarized light is incident normally to a ferrofluid film subjected to an external magnetic field parallel to the plane of the film. This phenomenon is a result of linear birefringence and is known as the Cotton-Mouton (C-M) effect. Also, as a result of linear dichroism, the transmission axis of the transmitted light is rotated by an angle with respect to that of the incident light, phenomenon known as the C-M rotation.

For a qualitative analysis of the two effects we have adopted a method relied on the measurement of the azimuthal distribution of the transmitted light intensity through a homogenous ferrofluid film magnetized parallel to its plane by an external continuous magnetic field [16, 17]. The experimental set-up is shown in Fig. 1. 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 and applied to the ferrofluid film perpendicular to the propagation direction of the light. The angle β_1

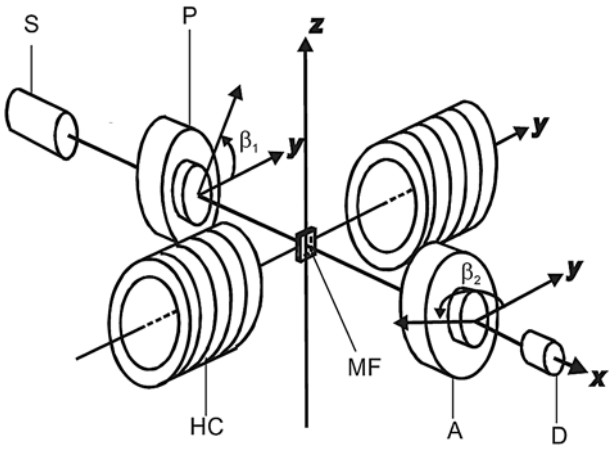

Fig. 1 – The experimental set-up for the study the azimuthal distribution of the transmitted light intensity.

between the transmission axis of the polarizer and the applied magnetic field can be adjusted by rotating the Helmholtz coils. The analyzer A is used to examine the polarization state of the transmitted light through the ferrofluid film. The azimuthal angle $\eta = \beta_2 - \beta_1$ (the angle between the two transmission axis of the analyzer and the polarizer) is modified rotating the transmission axis of the analyzer with the aid of a stepping motor, driven by a PC with a step angle of 2′. Finally, a receiving photodiode (D) is used to detect the intensity I of the transmitted light through the sample. The signals from photodiode are transmitted to a data acquisition board in a PC for storage and processing.

In this work the I–η curves were measured at $\beta_1 = 45°$ and various H's. Under zero field, the symmetric I–η curves exhibits a relative maximum intensity at $\eta_{I = max} = 0$ and zero intensity at $\eta_{I = min} = 90°$ and $–90°$. The symmetric I–η curves under $H \neq 0$ were also obtained with a translational shift $\Delta\eta$ with respect to the zero field curve. 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_{min} occurred at $\eta_{I = min}$ is non-zero under $H \neq 0$. This $I_{min} \neq 0$ implies that the transmitted light is not linearly but elliptically polarized, and it is considered a qualitative measure of birefringence.

For studying the relaxation of birefringence, the analyzer is turned round in the position $\eta_{I = min}$, which corresponds to the applied magnetic field. Then the magnetic field is suddenly cancelled and I_{min} is measured as depending on time.

3. RESULTS AND DISCUSSION

3.1. FERROFLUIDS SYNTHESIS AND CHARACTERIZATION

The magnetizations of saturation for the two sorts of ferrofluids depend on the volume fraction of the magnetite which remains in suspension after the dialysis process. Usually, the ferrofluids obtained after dialysis were concentrated by evaporation under vacuum at room temperature and the density of the new products had similar values with the supernatants obtained after centrifugation.

The magnetization of saturation obtained from the magnetization curve is 140 Gs (11.2 kA/m) for the *sort 1* ferrofluid and 98 Gs (7.84 kA/m) for the *sort 2* ferrofluid, respectively. The *sort 1* ferrofluid was very stable, being homogenous for >100 days. The *sort 2* ferrofluid had poor stability and became non-homogenous within few days.

Fig. 2 presents the particle size distribution obtained by DLS for the *sort 1* ferrofluid. The average size of the magnetic particles from suspension is ~350 nm. The magneto-granulometric analysis for the same ferrofluid is presented in Fig. 3. The particle size distribution is a lognormal function and the average size of the particles which states the magnetization of ferrofluid is 8.9 nm.

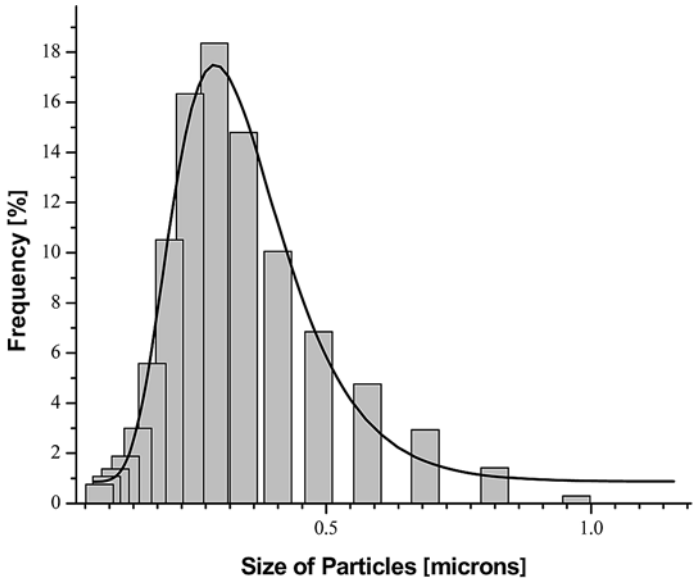

Fig. 2 – Particle size distribution determined by DLS for the sort 1 ferrofluid.

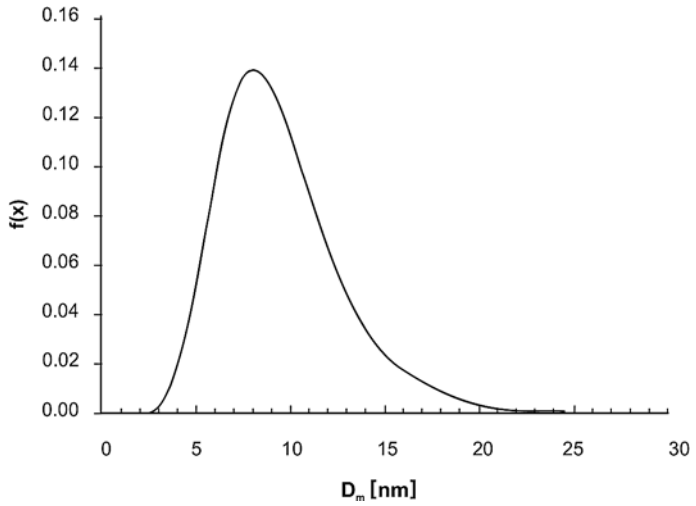

Fig. 3 – The function of distribution of particle size for the sort 1 ferrofluid determined by magnetogranulometric analysis of magnetization curve.

The huge difference between the two results can be explained by the fact that the DLS method measures the size of the scattering centers given by the polymer unfolded strands within which the magnetite is precipitated, but magneto-granulometric analysis gives the size of the magnetite which contribute to the ferrofluid magnetization and which are embedded within the three-spatial PVA network. The average size of the strands is consistent with the molecular weight of the polymer used (200 to 400 nm).

Fig. 4 presents the size distribution of the particles from the *sort 2* ferrofluid. The average size of the magnetite obtained in this particular case is ~ 26 nm, although the same amount of PVA was added in the dispersing medium. The larger average size determined by DLS for the *sort 2* ferrofluid is a consequence of the faster flocculation of particles after centrifugation. When repeated measurements for the same sample were carried out after few hours, the particle size increased to ~ 100 nm. It is evident that the magnetite particles precipitated outside the PVA matrix flocculate rapidly and this process determines the instability of the *sort 2* ferrofluid.

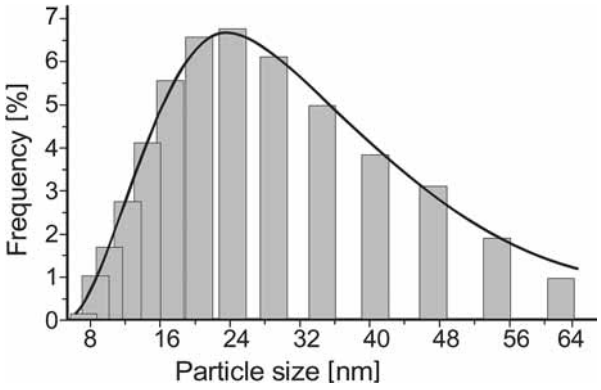

Fig. 4 – Particle size distribution determined by DLS for the sort 2 ferrofluid.

3.2. AZIMUTHAL DISTRIBUTION OF TRANSMITTED LIGHT INTENSITY

As we emphasized above, to obtain the most significant variation in the polarization of the incident light through the ferrofluid, the angle θ between H and the polarization of the incident light is set to be 45°. For $H = 0$, the I–η curve was symmetric with zero intensity at $\eta = 90°$ and –90°. The symmetric I–η curves were also obtained with a translation shift by a $\Delta\eta$ $\left(\equiv \left|\eta_{I=\min}(H) - \right.\right.$ $\left.\left. -\eta_{I=\min}(H=0)\right|\right)$ with respect to the zero field curve.

In Fig. 5 are shown the I–η curves for the *sort* 1 ferrofluid. To decide the $\Delta\eta$ precisely the I–η curves at η around –90° were enlarged. When a magnetic field of intensity H = 125 Öe (10 kA/m) is applied, $\eta_{I = min}$ is moved by an angle

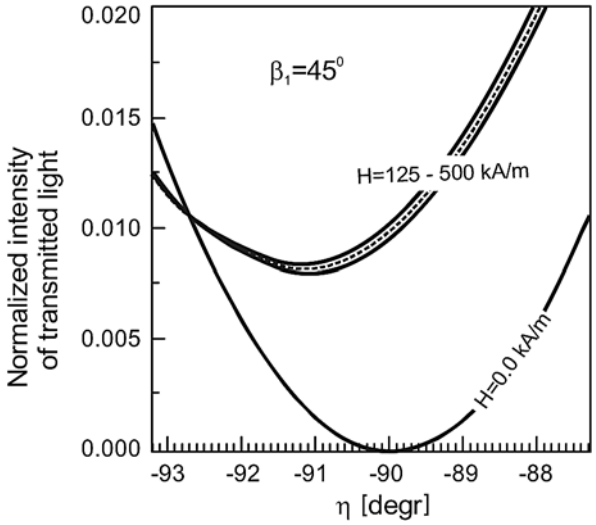

Fig. 5 – Azimuthal distribution of the transmitted light intensity for the sort 1 ferrofluid.

$\Delta\eta = 1.08°$ and I_{min} is nonzero. Increasing the intensity of field up to 650 Öe (52 kA/m), the I–η curves remain approximately in the same position. This behavior can be explained by the optical anisotropy of the ferrofluid which appears only by the alignment of the unfolded polymer strands carrying the nanometer sized magnetite particles, and not by association of these in long structural formations.

In Fig. 6 are shown the I–η curves for *sort* 2 ferrofluid. The value of $\Delta\eta$'s, which were indicated by arrows, increased gradually up to 2.14° as H increased to 500 Öe (40 kA/m) and then remains almost constant as $H > 550$ Öe (44 kA/m). A similar behaviour is observed for I_{min}. The fact that I_{min} depends

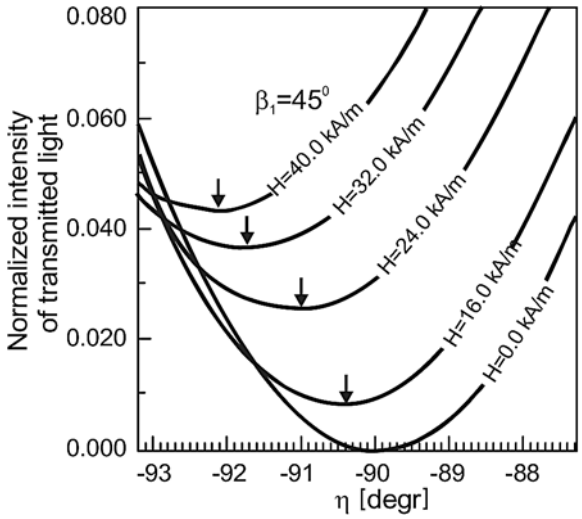

Fig. 6 – Azimuthal distribution of the transmitted light intensity for the sort 2 ferrofluid.

on the magnetic field intensity implies that the configuration of the elliptical polarized transmitted light is affected by the applied magnetic field. Long chains of particles are formed in the ferrofluid film plane. Increasing the field intensity, these long chains move closer to each other, thus changing the spatial anisotropy of ferrofluid film.

3.3. RELAXATION OF BIREFRINGENCE

In Fig. 7 is presented the time evolution of I_{min} for the *sort* 1 ferrofluid, after the magnetic field with intensity of 500 Öe (40 kA/m) is suddenly cancelled. It is observed a decrease of I_{min} in a very short time (< 0.1 sec) and after that the intensity of the transmitted light remains constant in time. The relaxation of birefringence in the ferrofluid *sort 1* may be associated with the relaxation of polymer strands from the parallel orientation with the applied magnetic field to a chaotic orientation.

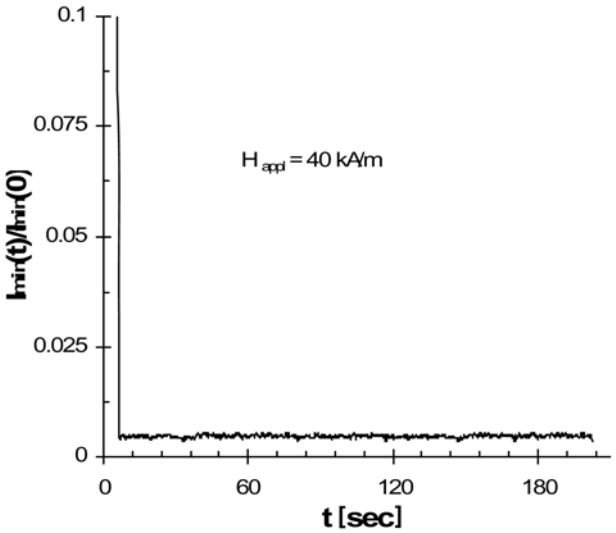

Fig. 7 – The time evolution of I_{min} for sort 1 ferrofluid after suddenly cancel of applied magnetic field.

In the Fig. 8 is presented the time evolution of I_{min} for the *sort* 2 ferroluid, after the magnetic field with intensity of 500 Öe (40 kA/m) is suddenly cancelled. In this case two stages are distinguished for the relaxation process. In the first stage I_{min} suddenly decreases with approximately 25% from the value it had in the presence of magnetic field. After that, I_{min} continuously decreases in a way which cannot be fitted by a simple exponential curve. The fit of the relaxation curve of I_{min} (for birefringence) can be approximate with a sum of exponential functions with various amplitudes and time constants. This behavior can be explained by the cumulating of some diffusion processes that finally conduct to the disintegration of the columnar structures formed in the presence of the magnetic field. These processes are characterized by the different

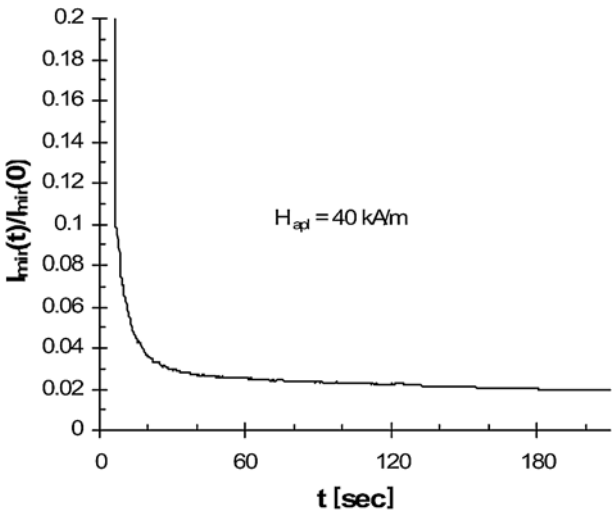

Fig. 8 – The time evolution of I_{min} for sort 2 ferrofluid after suddenly cancel of applied magnetic field.

diffusion coefficients (translation and rotation) depending on the structure and the thickness of the resulted structural elements. If the number of the terms taken into acount for the fitting of the relaxation curve is high, the structure of the ferrofluid in the presence of the magnetic field was more complex [18].

4. CONCLUSIONS

In this paper we have presented some recent efforts devoted to the preparation and characterization of magnetic carriers for drug delivery and targeting.

The relaxation of birefringence in ferrofluids was adopted as a tool for testing the spatial structure in the presence of an applied magnetic field. The results obtained in this context are presented reffering to the aqueous ferrofluids stabilized with poly(vinylalcohol).

Acknowledgements. This work was supported by the Nucleu Program-2006 of the National Authority for Scientific Research, Romania.

REFERENCES

1. R. E. Rosensweig, Ferrohydrodynamics, Dover Publications Inc., Mineola, New York, 1997, p. 344.
2. B. Berkovski, V. Bashtovoi, (Ed.), Magnetic Fluids and Applications Handbook, Begel Haouse, New York, 1996, p. 395.
3. U. Häfeli, W. Schütt, J. Teller, M. Zborowski, Scientific and Clinical Applications of Magnetic Microspheres, Plenum Press, New York, 1997, p. 628.
4. A. Halbreich, J. Roger, J. N. Pons *et al.*, Biomedical applications of maghemite ferrofluid, Biochimie **80**, 379–390 (1998).

5. J. Roger, J. N. Pons, R. Massart *et al.*, Some biomedical applications of ferrofluids, Eur. Phys. J. AP **5**, 321325 (1999).
6. A. S. Lübbe, C. Bergemann, W. Hunt *et al.*, Preclinical Experiences with Magnetic Drug Targeting: Tolerance and Efficacy, Cancer Res. **56**, 4694–4701 (1996).
7. J. F. Scamehorn, R. S. Schechter, W. H. Wade, Adsorption of surfactants on mineral oxide surfaces from aqueous solutions I: Isomerically pure anionic surfactants, J. Colloid Interface Sci **85**, 463–478 (1982).
8. A. Wooding, M. Kilner, D. B. Lambrich, Studies of the double surfactant layer stabilization of water-based magnetic fluids, J. Colloid Interface Sci. **144**, 236–242 (1991).
9. R. K. Iler, Coacervates of polyvinyl alcohol and colloidal silica, J. Colloid Interface Sci. **51**, 388–393 (1975).
10. H. Pardoe, W. Chua-anusorn, T. G. St. Pierre, J. Dobson, Structural and magnetic properties of nanoscale iron oxide particles synthesized in the presence of dextran or polyvinyl alcohol, J. Magn. Magn. Mat **225**, 41–46 (2001).
11. S. Chikazumi, S. Taketomi, M. Ukita *et al.*, Physics of magnetic fluids, J. Magn. Magn. Mat. **65**, 245–251 (1987).
12. J. P. Llewellyn, Form birefringence in ferrofluids, J. Phys. D: Appl. Phys. **16**, 95–104 (1983).
13. B. R. Jennings, M. Xu, P. J. Ridler, Structure in magneto-rheological fluids: a theoretical analysis, J. Phys. D: Appl. Phys. **34**, 1617–1623 (2001).
14. R. W. Chantrell, J. Popplewell, S. W. Charles, Measurements of Particle Size Distribution Parameters in Ferrofluids, IEEE Trans. Magn. **MAG-14**, 975–977 (1978).
15. L. Vekas, M. Rasa, D. Bica, Physical Properties of Magnetic Fluids and Nanoparticles from Magnetic and Magneto-rheological Measurements , J. Colloid Interface Sci. **231**, 247–254 (2000).
16. H. E. Horng, S. Y. Yang, S. L. Lee *et al.*, Evidence of birefringence due to two phases in the magnetic fluid film, Magnitnaia Gigrodinamica **36**, 39–46 (2000).
17. G. Fosa, R. Bădescu, Gh. Călugăru, Some new experimental results on magneto-optical effects in ferrofluids, Rom. J. Phys. **49**, 312–315(2004).
18. E. Fredericq, C. Houssier, Electric Dichroism and Electric Birefringence, Calderon Press, Oxford, 1973, p. 219.