CONCENTRATION AND PATH-LENGTH DEPENDENCE ON THE FARADAY ROTATION OF MAGNETIC FLUIDS BASED ON HIGHLY WATER-SOLUBLE Fe$_3$O$_4$/PAA NANOPARTICLES SYNTHESIZED BY A HIGH-TEMPERATURE HYDROLYSIS METHOD

ODVISNOST KONCENTRACIJE IN DOLŽINE POTI OD FARADAYEVEGA VRTENJA MAGNETNIH TEKOČIN NA OSNOVI VISOKOVODOTOPNIH NANODELCEV Fe$_3$O$_4$/PAA, SINTETIZIRANIH Z METODO VISOKOTEMPERATURNE HIDROLIZE

Serhat Küçükdermenci[1,5], Deniz Kutluay[2], Erdal Çelik[3,4], Ömer Mermer[1], İbrahim Avgın[1]

[1]Department of Electrical and Electronics Engineering, Ege University, Bornova 35100, Izmir, Turkey
[2]Department of Electronics and Communications Engineering, Izmir University, Uckuyular 35290, Izmir, Turkey
[3]Center for Fabrication and Applications of Electronic Materials (EMUM), Dokuz Eylul University, Tınaztepe Campus, 35160, Izmir, Turkey
[4]Department of Metallurgical and Materials Engineering, Dokuz Eylul University, Tınaztepe Campus, 35160, Izmir, Turkey
[5]Department of Electrical and Electronics Engineering, Balikesir University, Campus of Cagis 10145, Balikesir, Turkey
serhat.kucukdermenci@ege.edu.tr

In this study, highly water-soluble Fe$_3$O$_4$/PAA (polyacrylic acid) nanoparticles (NPs) were synthesized by a high-temperature hydrolysis method. We report the first demonstration of the concentration and path-length dependence on the Faraday rotation (FR) for a magnetic fluid (MF) synthesized by this novel method. Experiments were performed in the DC regime (0–6 × 10^{-2} T) at room temperature. Measurements were carried out with 5–3.33 mg/ml and 1.18 mg/ml samples in cells (2, 5, 7 and 10) mm. The maximum rotation was recorded as 0.96° cm^{-1} for the 3.33 mg/ml concentration in the cell 10 mm. It was found that the magnetic fluid behaves with a distinctive phenomenon in different sized cells although its concentration was the same. The role of the different parameters on the FR was discussed via spatial limitations imposed by the cells and a premature saturation term. This work provides a new insight for FR investigations of MFs including highly water-soluble magnetic NPs.

Keywords: magnetic fluids, water soluble Fe$_3$O$_4$/PAA-nanoparticles, Faraday rotation

V tej študiji so bili sintetizirani visokovodotopni Fe$_3$O$_4$/PAA (poliakrilna kislina)-nanodelci (NPs) z metodo visokotemperaturne hidrolize. Poročamo o prvih predstavitvah odvisnosti koncentracije in dolžine poti od Faradayevega vrtenja (FR) za magnetno tekočino (MF), sintetizirano po tej novi metodi. Preizkusi so bili izvedeni v DC-režimu (0–6 × 10^{-2} T) pri sobni temperaturi. Meritve so bile izvršene z vzorci 5–3,33 mg/ml in 1,18 mg/ml v celicah (2, 5, 7 in 10) mm. Maksimum vrtenja je bil ugotovljen kot 0,96° cm^{-1} pri koncentraciji 3,33 mg/ml v celici 10 mm. Ugotovljeno je bilo, da magnetna tekočina izkazuje značilne pojave v celicah različne velikosti, čeprav je bila njena koncentracija enaka. Vloga različnih parametrov na FR je bila razložena s prostorskimi omejitvami, ki jo povzročijo celice in z uvajanjem izraza za prezgodnjo prenasičenost. To delo zagotavlja nov vpogled v preiskave Faradayevega vrtenja (FR) magnetnih tekočin (MFs), vključno z visokovodotopnimi magnetnimi nanodelci (NPs).

Ključne besede: magnetne tekočine, vodotopni Fe$_3$O$_4$/PAA-nanodelci, Faradayevo vrtenje

1 INTRODUCTION

Magneto-optic (MO) effects occur in gases, liquids, and solids. In general, solids exhibit the strongest MO effects, liquids exhibit weaker effects, and gases exhibit the weakest effects.[1] FR in MFs has been demonstrated in the visible,[2] near-infrared[3,4] and mid-infrared[5] regimes. The wavelength dependence of FR and Faraday ellipticity was investigated by N. A. Yusuf and co-workers.[6] MO experiments were performed on size-sorted iron oxide (γ-Fe$_2$O$_3$) MFs.[7] Water-based MF samples were synthesized by the coprecipitation method followed by a size-sorting process. Davies and Llewellyn[8] have reported measurements on FR in highly diluted samples of Fe$_3$O$_4$ and CO particle MFs. From their results they concluded that FR is governed by magnetization. Yusuf et al.[9] have reported measurements on FR in a relatively concentrated sample.

The MO response of MFs depends on various parameters including particle size, the concentration of the particles, the externall applied magnetic field, temperature, and the kinds of particles, surfactants, and carrier fluids.[10] Due to the large variety of MFs, measurements of the MO effects of MFs have still not been reported so widely for novel ones and each new sample should be carefully analyzed.

In 2007, the Yin group synthesized novel superparamagnetic magnetite colloidal NPs which can self-assem-

ble into one-dimensional (1D) particle chains and exhibit excellent tunable photonic properties.[11,12] Since then, there has been a widespread interest in these NPs and their applications. Despite their tremendous potential in various applications, interesting fundamental questions which refer to their colloidal crystallization with and without a magnetic field remain unanswered. Therefore, in this paper we report the first demonstration of the concentration and path-length dependence on FR for MF based on these NPs. Here we report the results of an investigation of long-term stable MFs including highly water-soluble NPs showing FR in the DC regime (0–6 × 10^{-2} T) at room temperature. Water-based MF samples were synthesized by a novel high-temperature hydrolysis method.

The different relationships between the chain length and the concentration obtained by different workers may be attributed to the dependence of the chain length on other parameters such as the field, temperature and spatial limitations imposed by the cells used in containing the sample under investigation.[13–15] In our previous work[16] we measured the FR for 14 different concentrations from 1.8 mg/ml to 5 mg/ml in a cell 10 mm. It was observed that the FR increases for higher concentrations (from 1.18 mg/ml to 3.33 mg/ml). The maximum rotation was recorded as 0.96 °/cm for 3.33 mg/ml and this was named the critical concentration ($C_{CRITICAL}$). It was found that rotation tends to decrease when the concentration is higher than $C_{CRITICAL}$ (for 4 mg/ml and 5 mg/ml). We chose three samples and repeated the measurements for 2–5 mm and 7 mm cells additionally for observing the path-length dependence on the FR and investigating the spatial limitation factor on MO effects.

2 EXPERIMENTAL DETAILS

The synthesis of Fe_3O_4 NPs was explained in detail in our previous report[16] and is summarized here. For the synthesis, diethylene glycol (DEG, 99.9 %), anhydrous ferric chloride ($FeCl_3$, 97 %), sodium hydroxide (NaOH, 96%), and polyacrylic acid (PAA, M_w = 1800) were obtained from Sigma-Aldrich. Distilled water was used in all the experiments. All the chemicals were used as received without an further treatment and/or purification. For the synthesis of the Fe_3O_4 NPs a NaOH/DEG solution was prepared by dissolving 100 mmol of NaOH in 40 m of DEG at 120 °C under nitrogen for 1 h. Then, the light-yellow solution was cooled to 70 °C (stock solution A). Using a 100 ml three-necked flask equipped with a nitrogen inlet, a stirrer and a condenser, 10 mmol of $FeCl_3$ and 20 mmol of PAA were dissolved in 41 ml of DEG under vigorous stirring. In this method, DEG is not only a reducing agent but also a solvent in the reaction. The solution was purged with bubbling nitrogen for 1 h and then heated to 220 °C for 50 min (stock solution B). Subsequently, 20 ml of NaOH/DEG solution was injected rapidly into the above solution. The reaction was allowed to proceed for 2 h. The black color of the solution confirmed the formation of magnetite nanoclusters. The resultant black product was repeadedly washed with a mixture of ethanol and water and collected with the help of a magnet. The cycle of washing and magnetic separation was performed five times. A one-pot synthesis was conducted for the Fe_3O_4/PAA nanoparticles, and thus no extra separate process was needed for the surface modification. The polyol method is based on the theory that NPs will be yielded upon heating precursors in a high-boiling-point alcohol at elevated temperature. DEG is chosen here as the solvent inasmuch as it can easily dissolve a variety of polar inorganic materials due to its high permittivity (ε = 32) and high boiling point (246 °C). PAA is used as the capping agent, on which the carboxylate groups show strong coordination with Fe^{3+} on the Fe_3O_4 surface and the uncoordinated carboxylate groups extend into the water solution, rendering particles with a high water dispersibility.

Powder X-ray diffraction (XRD) analysis of the Fe_3O_4 NPs was performed on a Phillips EXPERT 1830 diffractometer with Cu K_α radiation. The XRD data were collected over the range of 10–80° (2θ) with a step interval of 0.02° and a preset time of 1.6 s per step at room temperature. Particle size distributions of the NPs were measured using a Zetasizer 4 Nano S dynamic light scattering (DSL, Malvern, Worcestershire, UK). The light-scattering measurements were carried out with a laser of wavelength 633 nm at a 90° scattering angle.

The magnetic measurements were carried out using a LakeShore 7400 (Lakeshore Cryotronics) vibrating-sample magnetometer (VSM) at 300 K. For the FR experiments we used a Thorlabs model HGR20 2.0 mW, 543 nm laser source, a GMW Electromagnet Systems model 5403 electromagnet, a Kepco power supply model BOP 20-5M, a LakeShore Model 455 DSP Gaussmeter, a Stanford Research Systems Model SR830 DSP lock-in amplifier, a New focus model 2051 photo detector, a ILX Lightwave model OMM – 6810B optical multimeter and a model OMH – 6703B silicon power head.

3 RESULTS

Figure 1 shows the XRD pattern of PAA-coated Fe_3O_4 NPs synthesized by the high-temperature hydrolysis method. Note that the (220), (311), (400), (422), (511), and (440) diffraction peaks observed for the curves can be indexed to the cubic spinel structure, and all the peaks were in good agreement with the Fe_3O_4 phase (JCPDS card 19-0629). It is clear from **Figure 2** that the average diameter of the Fe_3O_4/PAA NPs obtained from the DLS analysis is approximately 10 nm. The magnetic properties of the NPs were measured at 300 K using the VSM. As given in **Figure 3**, the saturation magnetization was determined as 38.8 emu/g. Worth nothing here is that the NPs showed no remanence
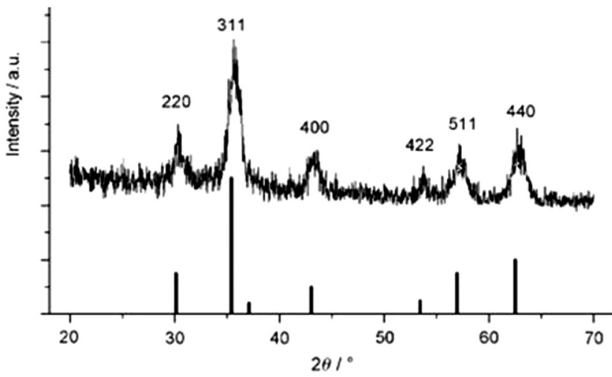
Figure 1: XRD pattern of PAA-coated Fe$_3$O$_4$ NPs synthesized by high-temperature hydrolysis
Slika 1: Rentgenska difrakcija (XRD) s PAA, prekritega z Fe$_3$O$_4$ nanodelci, sintetiziranimi z metodo visokotemperaturne hidrolize
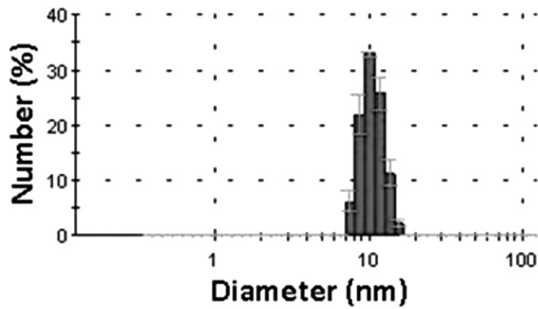

Figure 2: Particle size distribution of Fe$_3$O$_4$ NPs synthesized by high-temperature hydrolysis
Slika 2: Razporeditev velikosti nanodelcev Fe$_3$O$_4$, sintetiziranih z metodo visokotemperaturne hidrolize

or coercivity at 300 K, i.e., they exhibited superparamagnetic behavior.

The particle content is 20 mg for various concentrations with the addition of distilled water from 4 ml to 17 ml. The NPs kept dispersing well after the MF had been standing for more than 4 weeks and no sedimentation was observed for all the samples. Maintaining long-
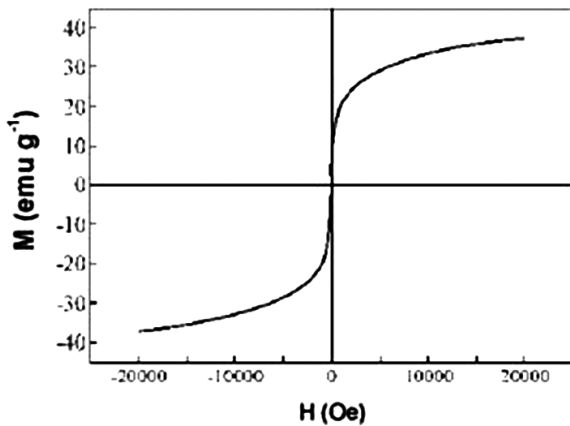

Figure 3: Hysteresis loops of superparamagnetic nanoparticles at room temperature
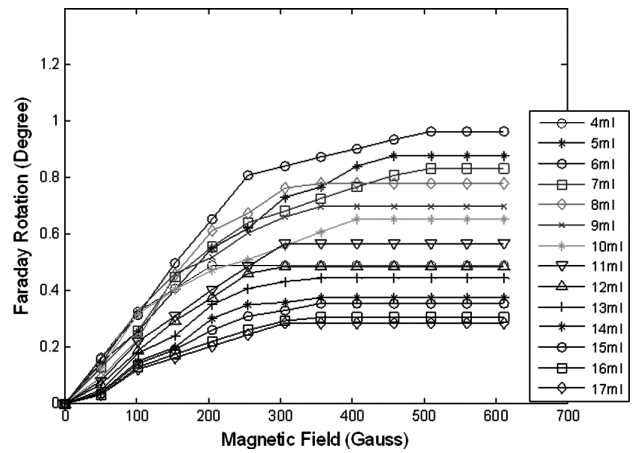**Slika 3:** Histerezna zanka super paramagnetnih nanodelcev pri sobni temperaturi

Figure 4: FR concentration dependence for 10-mm cell
Slika 4: Odvisnost FR od koncentracije pri celici 10 mm

term stability can make these kinds of MFs ideal candidates for optical devices.

The FR measurements for 14 different concentrations from 1.8 mg/ml to 5 mg/ml in a 10 mm cell were shown graphically in **Figure 4**. The maximum FR of these measurements was shown in **Figure 5**. We chose three concentrations for investigating the effect of cell size on the FR measurements. The chosen concentrations were: 3.33 mg/ml $C_{CRITICAL}$, for which we measured the maximum FR; 1.18 mg/ml, for which we measured the weakest FR before $C_{CRITICAL}$; and 5 mg/ml, for which we measured the lowest FR after $C_{CRITICAL}$. The measurements were repeated for 2–5 mm and 7 mm cells for these concentrations.

For sample 14 (**Table 1**) the FR was found to be less than 0.1 degree in the 2 mm thick cell. For the samples that have same concentration but in different cell sizes, the magnetization must be the same at a particular field since all have an equal magnetic dipole moment per unit volume. Therefore, if the FR is only governed by magnetization, it would be the same value for these samples. In order to explain the results, we can introduce terms to the
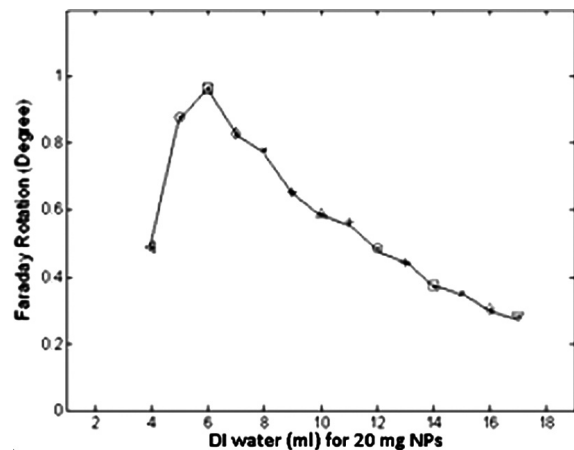

Figure 5: Maximum FR graph of samples for 10-mm cell
Slika 5: Predstavitev FR maksimumov vzorcev pri celici 10 mm

Table 1: Maximum FR of three different concentrated MF in four different cells
Tabela 1: Maksimum za FR pri treh različnih koncentracijah MF v 4 različnih celicah

Sample number	Concentration (mg/ml)	FR maximum degree (°/cm)			
		Cell size (mm)			
		2	5	7	10
1	5.00	0.3	0.36	0.43	0.49
2	4.00				0.87
3	3.33 (C_{CRITICAL})	0.15	0.37	0.6	0.96
4	2.86				0.83
5	2.50				0.78
6	2.22				0.70
7	2.00				0.65
8	1.82				0.56
9	1.67				0.48
10	1.54				0.44
11	1.43				0.37
12	1.33				0.35
13	1.25				0.30
14	1.18	<0.1	0.13	0.22	0.28

Faraday rotation which is due to the chain formation and is given by:

$$\phi_C(B) = VBl(B) \tag{1}$$

where $\phi_C(B)$ is the Faraday rotation due to the chain formation, B is the local field, $l(B)$ is the chain length at field B and V is the Verdet constant.

For a homogeneous colloidal system of single-domain fine ferromagnetic particles, the Faraday rotation is given by:

$$\phi_M(B) = C \frac{M(B)}{M_S} \tag{2}$$

in which $\phi_M(B)$ is the Faraday rotation at magnetic field B, $M(B)$ is the magnetization of the sample at magnetic field B, M_S is the saturation magnetization of the sample and C is a constant. Both the magnetization of the sample and the chain formation FR for the MFs can be expressed as shown below:

$$\phi(B) = C \frac{M(B)}{M_S} + VBl(B) = \phi_M(B) + \phi_C(B) \tag{3}$$

Here, C is a constant that can be found the at high field assuming that saturated chain length has no change.[14] This artificial saturation can be referred to as "premature saturation" and utilized to explain the different behavior of the same sample but in a different cell thicknesses.

Since samples 1 and 14 were less imposed effect of chain formation, their initial slopes in various cell thickness do not diverge too much in the $0–2 \times 10^{-2}$ T. Nevertheless, at the optimum concentration, sample 3 which has the maximum effect of chain formation, despite the same amount of NPs, the initial slope in different thickness cells is quite different.
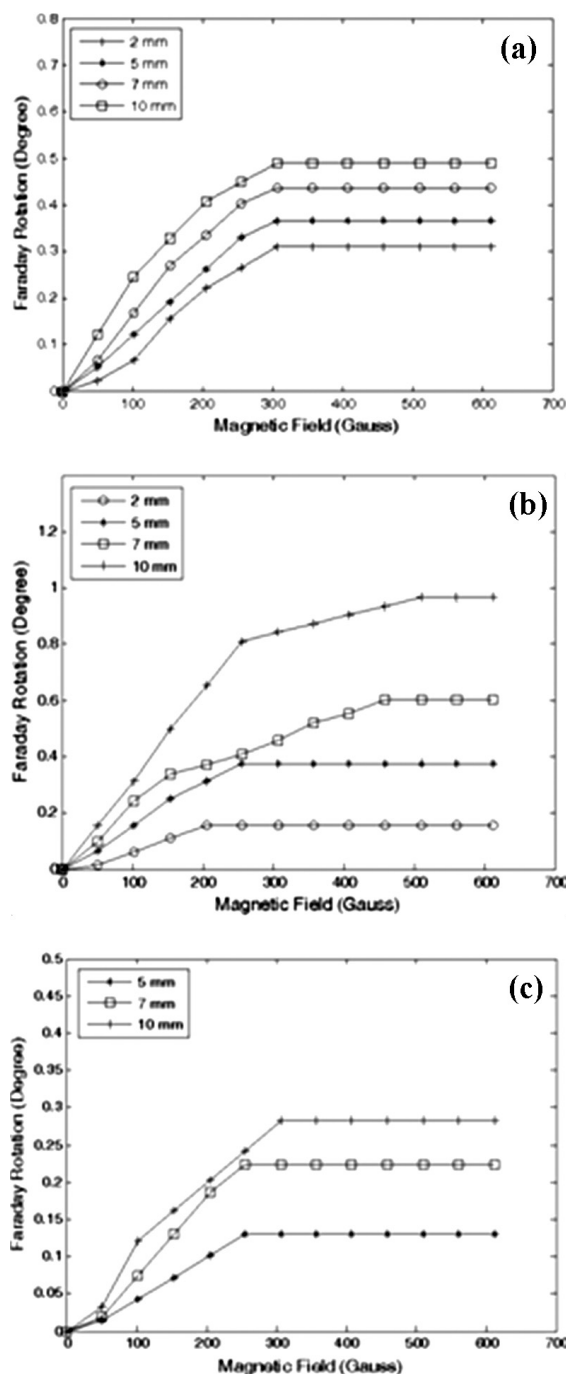

Figure 6: FR of three different concentrated MF in different size cells including: a) sample 1 (concentration: 20 mg/(4 ml)), b) sample 3 (concentration: 20 mg/(6 ml)) and c) sample 14 (concentration: 20 mg/(17 ml)). The dimensions of the cells are indicated on the figures.
Slika 6: FR treh magnetnih raztopin (MF) z različno koncentracijo pri celicah z različno velikostjo: a) vzorec 1 (koncentracija: 20 mg/(4 ml)), b) vzorec 3 (koncentracija: 20 mg/(6 ml)) in c) vzorec 14 (koncentracija: 20 mg/(17 ml)). Velikosti celic so označene na slikah.

We also observed that the FR of the same concentration fluids reached saturation at higher fields for a longer path length (**Figure 6**). This effect might be the result of premature saturation phenomena of the mean chain length in fluids. Notably, for samples 3 and 14, changing

of saturation values on FR with different cell size indicates premature saturation of the chain length.

4 DISCUSSION

The dipole-dipole interactions can be described as $F = 3\mu^2 (1 - 3 \cos^2 \alpha)/l^4$, where μ is the induced magnetic moment, α is the angle between the dipole and the line connecting the dipoles, and l is the center-center distance between two particles. When two dipoles are aligned head-to-end, the dipole interaction is an attraction $F_{ma} = -6(\mu^2/l^4)$. While they are aligned side by side, the interaction becomes a net repulsion $F_{mr} = 3(\mu^2/l^4)$. Along the magnetic field, the particles attract each other and form chains due to the head-to-end alignment of dipoles.[17]

The formed chain length varies with applied magnetic field and the concentration of the MF. The FR is not only governed by the magnetization of the fluid but also by the chain formation. The dimension of the cell in the field direction plays an important role in the length and number of chains formed in the sample. For short path length, a "spatial limitation" on the chain length is imposed, resulting in a "premature saturation" of the length. Jones and Niedoba[18] had a drop of undiluted fluid sandwiched between two parallel glass cover slips and placed normal to the optical axis of a microscope. The magnetic field was applied parallel to the axis of the microscope, i.e., perpendicular to the plane of the thin-film sample. In this experimental arrangement Jones and Niedoba observed the number of chains per unit volume, n, and found it increased rapidly with the applied field. The experimental set up used by Jones and Niedoba put a severe limitation on the length of the formed chains and led to premature saturation in the chain lengths, as was suggested by Fang et al.[19] It is worth mentioning that for thin samples, the chain length approaches the thickness of the sample at very low fields and saturates prematurely. Consequently, the chain length is not expected to increase any further with the field but rather an increase in the number of chains is observed.

If the Faraday rotation is only governed by the magnetization of the sample, then the saturation will take place at practically the same applied field for the same sample, regardless of the thickness of the sample. The difference in the saturation field is attributed to the chain formation in the sample. As was mentioned above, this chain formation may prematurely saturate in thin samples due to the physical limitation imposed on the sample.

5 CONCLUSIONS

In summary, high-quality Fe_3O_4/PAA NPs for MF formation were successfully synthesized. We report the first demonstration of the concentration and path-length dependence on the FR for MF synthesized using this novel method. We have demonstrated the FR of highly water-soluble MF measured in the $0–6 \times 10^{-2}$ in the DC regime. The effects of both spatial limitations imposed by the cells and the chain concentration were observed on the FR. We observed that the chain length is also determined by the physical dimensions of the sample. Four different cells were used for the path-length experiments. The FR of the same concentration fluids with shorter path lengths reached saturation at lower fields as a result of the premature saturation of an average chain length. The experimental results shed some light on the role of agglomeration and chain formation in the FR. Magneto-optical effects in the magnetic fluids have a promising potential for technological and industrial applications as well as their academic importance. These measurements can help to understand the MO behavior of the MFs, including highly water-soluble magnetic NPs.

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