Proceedings of the 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13–17, 2016

Generation of Fe_3O_4 Nanoparticle Aggregates in a Ferrofluid Driven by External Electric Field

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In the paper the experimental study of magnetic nanoparticle aggregation in a transformer oil based ferrofluid driven by an external electric field is reported. The studied ferrofluid was composed of the magnetite nanoparticles, oleic acid surfactant, and transformer oil. Generally, it is considered that superparamagnetic nanoparticles do not interact in the absence of external magnetic field. In the paper we present an experimental observation of the particle assembly formation in a direct current external electric field by optical microscopy. During the observation no external magnetic field was applied. A diluted low-polarity ferrofluid drop on a glass surface was exposed to the external static inhomogeneous electric field. It is assumed that induced dipole–dipole interaction and subsequent dielectrophoretic motion give rise to the electrohydrodynamic flow in the fluid after a certain time period. As a result, a visible particle chain was formed at the drop electrical equator. This demonstration is expected to contribute to the understanding of the streamer formation and electrical breakdown in transformer oil based ferrofluids.

DOI: 10.12693/APhysPolA.131.907

PACS/topics: 47.57.J–, 47.65.Cb, 77.22.Jp, 77.22.Ch, 82.70.Dd

1. Introduction

For decades, the ferrofluids (FFs) are in the center of scientific effort owing to the unique combination of magnetic and flow properties. In FFs based on a mineral oil, a magnetodielectric effect has been studied extensively [1]. Although there is high number of papers published on the topic of FFs, the interaction with an electrical field has not received sufficient attention yet from both experimental and theoretical approach [2–4]. The most peculiar phenomenon observed in mineral oil-based FFs is the increased breakdown voltage of the oil due to the presence of magnetic nanoparticles (MNP) [5, 6]. Based on the experimental investigation, this is associated with a reduced velocity of streamer propagation. Recently, a numerical simulation showed that magnetite MNP dispersed in a mineral oil can act as free electron (free electric charge) scavengers due to the short charge relaxation time constant of magnetite [7]. The reported trapping process thus converts fast electrons from field ionization to slow MNP charge carriers with effective mobility reduction. The proposed model considers the migration of small individual MNP, whereas any particle interactions are neglected. In this respect one can assume that a particle aggregation and structure formation will have a remarkable impact on the charge trapping performance and the mobility reduction in the electric field. From this point of view, it is desirable to investigate if the stabilized MNP in mineral oils can undergo external electric forces and form assemblies like those observed in different colloidal systems [8].

The MNP aggregation and chain formation in FFs have been intensively studied in external magnetic fields [9]. Similar effects in mineral oil-based FFs induced by an external electric field have been reported just recently [10, 11]. For that purpose, the method of dielectric spectroscopy and *in situ* small angle neutron scattering were applied. The experiments confirmed the electric field induced formation of reversible anisotropic aggregates of MNP. The electric dipole–dipole interactions, dielectrophoretic forces and related electrohydrodynamics (EHD) were considered on a qualitative basis to account for the observed assemblies. However, these methods do not allow the exact identification of the assembling mechanism.

It is known that induction of electric dipoles in colloidal particles and EHD flow is strongly dependent on a dielectric contrast between the particles and the carrier liquid [12]. In such systems, an external electric field can induce assemblies of the particles as it was practically demonstrated in various colloidal systems. An excellent example can be represented by recent works dealing with assembly and manipulation of colloidal particles on liquid droplets [13, 14]. It was shown that colloidal particles can be carried by EHD convective flow which finally concentrates the particles in a dense packed colloidal ribbon on the drop surface. Analogical behavior can be expected for a droplet of a mineral oil-based FF. Here we report our first *in situ* observation of the MNP aggregation in a single FF drop on a glass surface under an external electric field. We have found that the resulted aggregates tend to form an electrorheological chain oriented perpen-

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dicular to the electric field. This finding can be relevant for modeling and understanding the breakdown mechanism in FF and can be useful for fabrication of patterned thin films with magnetic and dielectric anisotropy.

2. Experimental

The magnetic fluid was prepared based on transformer oil and magnetite MNPs, with oleic acid as a surfactant. The paraffin inhibited oil used for the fluid preparation has a kinematic viscosity of 10 $mm^2\ s^{-1}$ at 40 °C (values has been taken from the product list). Generally, such kind of the oil is often used as insulating and cooling fluid in electrical power industry. The MNPs were prepared by means of coprecipitation from the aqueous solution of Fe^{3+} and Fe^{2+} [15]. The median of particle size distribution was 7.9 nm which was obtained from magnetic measurements (not included here). The FF was diluted to obtain a sample with the volume fraction of 0.95%, in order to match the concentration investigated by the neutron scattering method [10].

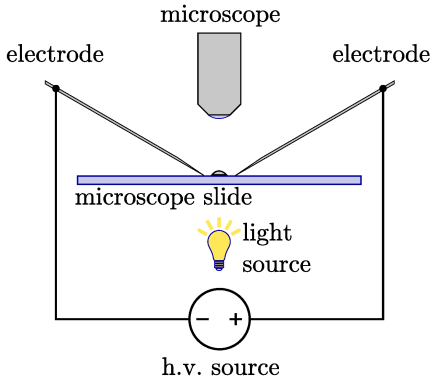

Fig. 1. Experimental setup for the observation of Fe_3O_4 aggregates formation in external electric field.

To investigate MNP aggregate formation in an electric field, a 2-electrode cell setup has been developed. The dc electric field of 2 kV/mm was created between the electrodes. In the present work, a pair of nickel electrodes (no particular reason for this material) has been employed as working electrodes. In order to generate and focus the non-uniform electric field on the investigated droplet, the electrodes were of needle-shape with dimensions as follows: length of 30 mm and the thickness of 0.5 mm. The radius of the tip was 0.1 mm. The tips were placed on a surface of a rectangular microscope glass slide. The inter-electrode distance of 2 mm was used in the experiments. Then, the investigated FF drop was placed between the electrodes. The approximate diameter of the drop was 700 μm. The setup configuration is depicted in Fig. 1.

3. Results and discussion

Herein, we present several stages of the interaction of the external electric field and the studied FF, see Fig. 2. The submillimeter-sized FF drop is set on the surface of the microscope glass slide. The magnetite nanoparticles are dispersed throughout the drop volume. In the upper row of the parts we present the development of the particle chain in five following time periods, whereas the lower row depicts a series of magnified areas showing more details in the chain formation process. The dc electric field with the intensity of 2 kV/mm was applied across the test cell. Usually, in colloidal drops containing microsized particles, the EHD circulation can be seen immediately after application of the electric field [13]. However, in our experiment the EHD circulation was not distinguishable from the steady state of the drop until approximately 200 s after application of the field. This can be associated with the nanometric size of the dispersed MNPs.

In this case, the immediate response of the free space charge represented by unreacted ions from coprecipitation and residual surfactant may engender very weak oil flow, which is apparently difficult to monitor by the applied optical setup. Before the appearance of the visible EHD flow, one can assume that the effective polarization of MNPs and their interface (surfactant and surrounding counter ions [11]) takes place during this time, leading to the induced electric dipole–dipole interactions supported by Van der Waals and magnetic interactions (as the MNPs possess permanent magnetic moments). This behavior happens on the nanoscale, far from the resolution of the optical microscopy.

Then, when the aggregates reach a certain critical size, they undergo stronger dielectrophoretic motion characterized with higher flow inertia, which induces stronger EHD flow in the drop. This can be a key point for the appearance of the delayed EHD flow visible by our optical setup. On the other hand, the start of the EHD flow in the drop with free space charge and individual MNPs can be initially hindered by the adhesive forces bounding the small drop to the glass surface.

The observed EHD motion in the drop exhibited unidentified flow, without any specific pattern which would resemble e.g. that predicted by Taylor [16]. However, Fig. 2i shows a formation of a visible solid chain in the middle of the drop, oriented perpendicular to the electric field direction. This chain appeared approximately 200 s after application of the field, whereas its thickness was increasing in time. It can be therefore concluded that the main mechanism of the visible chain formation is associated with the visible EHD flow. Owing to the orientation of the formed chain it is assumed that the EHD flow in the drop is characterized by a stagnation region, where the MNPs and their aggregates are guided by the flow. In this way, the MNPs and the aggregates form the large chain located at the electrical equator. However, from the conducted experiment and the obtained 2-dimensional pictures we cannot determine if the chain is located on the surface of the glass, or on the surface of the drop, or in the bulk volume of the drop. Finally, as a result of the ongoing EHD flow, the assembled chain breaks up into complex aggregates (Fig. 2j). When the electric field was switched off, these aggregates remained in a stable position and started to dissipate due to the thermal energy.

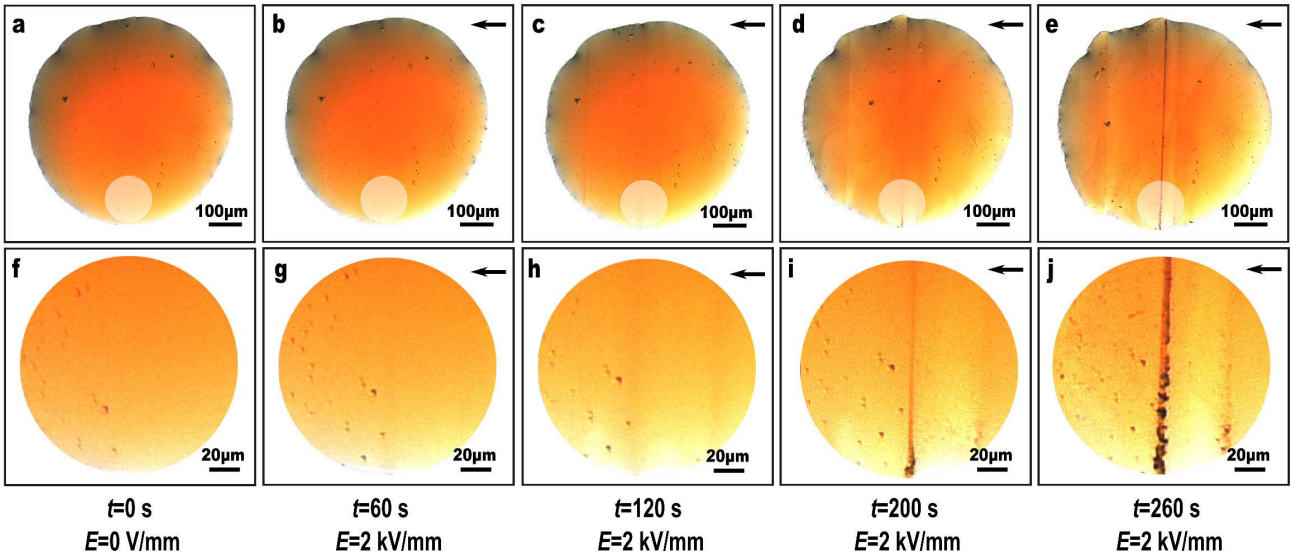

Fig. 2. Assembly of colloidal chain in a ferrofluid. A FF drop of radius 0.7 mm is initially set on the microscope slide surface. The arrows indicate the direction of the electrical field. Five upper parts (a–e) represent a timed aggregate formation in electrical field, while the five lower parts (f–j) are magnified views of the upper area as indicated by bright circles in the upper parts. The parts (a,f) show the situation without the electric field, and (b–e) and (g–j) after a dc electric field is applied. External magnetic field was not presented. The hydrodynamic circulation can be seen in the parts (d, e).

4. Conclusions

In the paper we have shown that dc electric field can induce structural assembly of the colloidal chain in the FF drop. The process of the Fe_3O_4 aggregates generation without external magnetic field interaction has been thus documented. Electrohydrodynamic flow was considered to be the main mechanism leading to the assembly of the chain. As the visible flow did not appear immediately after application of the electric field, particle polarization and dipole–dipole interaction probably take place first. Subsequently, dielectrophoretic motion of the aggregates induced the stronger flow. The time dependent assembly formation is in accord with our previous neutron scattering study. We propose that the magnetic particle aggregation in electric field lower than the field ionization threshold should be taken into account when explaining the peculiar breakdown mechanism in the transformer oil based FF. This can be relevant especially in the context of the currently discussed electron scavenging model.

Acknowledgments

Slovak Academy of Sciences and Ministry of Education, projects VEGA No. 1/0132/15, 1/0311/15, and 2/0141/16; Ministry of Education Agency for structural funds of EU projects No. 26220120003, 6220120046, and 26220120055. This work was supported by the Slovak Research and Development Agency under the contract No. APVV-15-0438.

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