Electrospray Patterns of Oil-based Ferrofluids

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***Abstract*— We investigate the influence of superparamagnetic ferric oxide (10 nm nominal size) particulates making an oil-based ferro-fluid in the electrospray patterns of a transitory regime. Ferrofluids are electrosprayed in air at atmospheric pressure. A needle-plate configuration is used with a variable gap. Spray development and patterns were observed under positive polarity and recorded. The patterns are recorded at the grounded counter-electrode offering a visual spatial distribution of the spray droplets. Spray development is compared to those of the ferrofluid carrier-liquid, water-based ferrofluids, and water. For specific spray parameters the electrospray of the ferrofluid generates lobes in a sequential form not matched by the carrier-liquid. Although water-based ferrofluids were also tested, the lobing spray regime was observed only with the oil-based ferrofluids. Transitions from one lobe to another are taking place spontaneously due to instabilities in the spray. A relationship between nanoparticle concentration and spray patterns was observed but not specifically investigated. The lobing regime was also observed under the influence of the magnetic field of a permanent magnet. The distance between needle and counter-electrode for obtaining the regime was reduced in this case and the lobing pattern confined.**

I. INTRODUCTION

Electrosprays (ES) are generated by applying high voltage to a fluid (usually for a small opening) that leads to dispersing the fluid into small droplets. The atomization phenomenon is mainly due to the interplay of electrostatic forces and surface tension forces on the droplets. The maximum charge before coulomb fission was estimated for the first time by Rayleigh [1]. The resulting spraying is a complex electrohydrodynamic process. There was considerable effort directed to classifying various spraying modes that could be induced depending on the experimental parameters such as applied voltage, flow rate, liquid properties, etc. [2-4]. Yet, a thorough description of the spraying modes was likely not achieved due to the complexity of the phenomenon. Microscopic details of the droplet ejection at the nozzle associated to various regimes were also captured recently using high speed imaging techniques [5-6]. ES of nano-colloids have also become of interest lately [7]. Using the electrospinning technique nanoparticles can be incorporated in fibers creating new materials with properties that can be engineered [8]. Ferrofluids (FF) contain a liquid carrier along with nanoscale ferromagnetic, or ferromagnetic (often iron oxides) particles; nano-particles are coated with a thin layer of surfactant so that magnetic particles do not stick together in the liquid carrier [9]. External magnetic fields are able to magnetize the nanoparticles. Although the ES of FF were occasionally used in conjunction with mass spectrometers, there is scarce information about the study of the electrospray of such colloids. A special spraying regime was identified for oil-based FFES in which lobe patterns are observed at the counter-electrode. In this paper we aim at characterizing this transitory regime by revealing its patterns.

II. EXPERIMENTAL

A. Experimental setup

The experimental setup is given in Fig. 1. The electrospray is generated using a capillary nozzle fed with ferrofluid from a plastic syringe driven by a syringe pump. The capillary nozzle is a blunt needle (with luer hub) 25G (ID 0.241 mm, OD 0.508 mm).

The needle is attached to a 10 mL Kendall Monoject oral syringe. Vinyl tubing was used to connect the syringe to the needle placed in the wooden nozzle holder above the circular grounded counter-electrode. The position of the needle is adjustable both vertically and horizontally. The counter-electrode is a metal plate 35.56 cm in diameter, 1.9 cm thick, and with a 2.54 cm center hole, coaxial to the needle. The nozzle was connected either to a high voltage power supply (HVPS) (Spellman HVPS, RHR40PN60, positive 0-40 kV 1.5 mA) or a negative one (Glassman HVPS, 0-10 kV 30mA, PS/ER10R30-DM22).

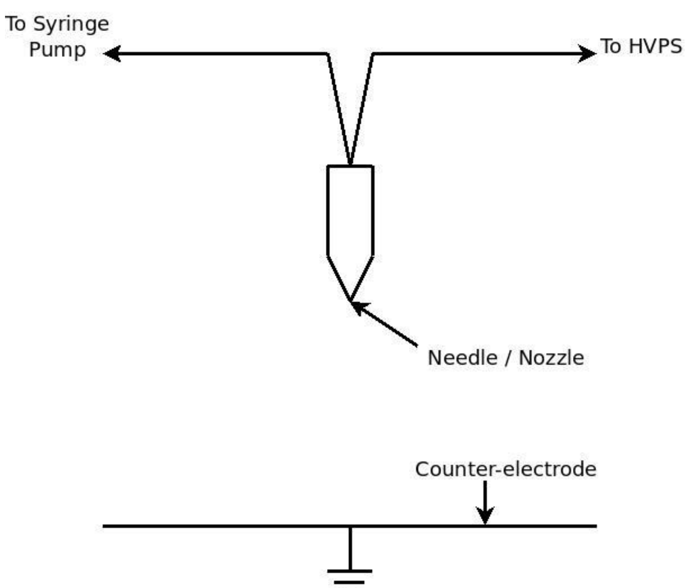


Fig. 1. Schematics of the experimental setup.

A syringe filled with the fluid to be electrosprayed was placed in a custom holder so that a syringe pump (Harvard Apparatus Model 44) could be used to control the spray flow rate. The needle was placed vertically above the ground electrode. The experimental apparatus allowed for needle-to-plate distance adjustments from 0 cm up to around 50 cm. Sheets of thin white paper were placed on the ground electrode so that the spray pattern could be recorded. Permanent magnets could be placed on or around the ground plate to test their influence. The same procedures were used with a fluid consisting of water and food coloring to test if this control-fluid also produced a lobed pattern. Different syringes (of the same type and characteristics) and tubes were used for each of the ferrofluids in order to control fluid samples and to prevent contamination. Electrospraying was generated in air in ambient conditions.

B. Fluids tested

The oil-based ferrofluids tested were acquired from Ferrotec Inc.: EMG900, EMG905 and EFH1. The nominal size of the magnetic particles in all the fluids is 10 nm. The nanoparticles contain mixtures of magnetite (Fe_3O_4 about 80%), with some maghemite (Fe_2O_3 about 20%). In addition, the paraffinic hydrocarbon used as carrier liquid for the acquired ferrofluids was also tested. A brief description of the tested ferrofluids was provided by the supplier.

EMG900: carrier liquid - paraffinic hydrocarbon, viscosity at 27^{o}C - 60 mPa.s, saturation magnetization - 99 mT, initial magnetic susceptibility - 0.85 (emu/g)/Oe, density - 1.74 x 10^3 kg/m^3, magnetic particle concentration 17.7 % by volume.

EMG905: carrier liquid - paraffinic hydrocarbon, viscosity at 27^{o}C - 3 mPa.s, saturation magnetization - 40 mT, initial magnetic susceptibility - 0.85 (emu/g)/Oe, density - 1.2 x 10^3 kg/m^3, magnetic particle concentration 7.8 % by volume.

EFH1: carrier liquid - paraffinic hydrocarbon, viscosity at 27^{o}C - 60 mPa.s, saturation magnetization - 44 mT, initial magnetic susceptibility - 0.17 (emu/g)/Oe, density - 1.21 x 10^3 kg/m^3, magnetic particle concentration 7.9 % by volume.

Carrier liquid: paraffinic hydrocarbon (petroleum distillate, NOS, clear, combustible liquid, UN 1268, III), viscosity at 27^{o}C is below 3 mPa.s, density – 0.79 x 10^3 kg/m^3, boiling point 424-495^{o}F………………...

The color of the ferrofluids is dark black-brown, which made it easy to visualize it on a white sheet of paper. This property was used for obtaining the patterns of *droplet distributions* at the counter-electrode.

III. Results and Discussion

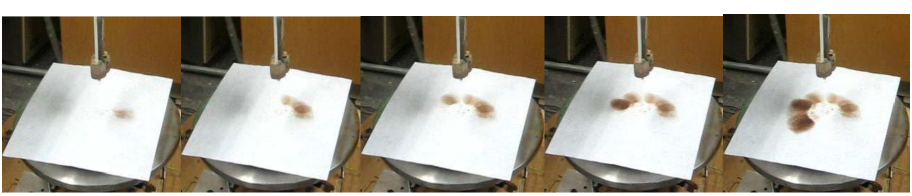
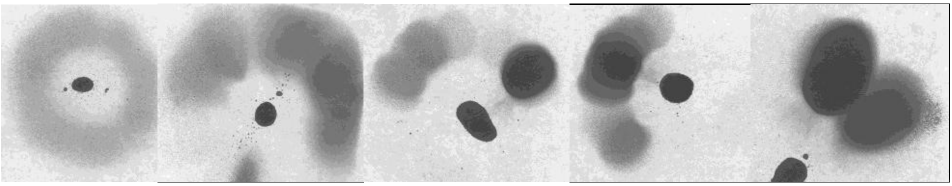


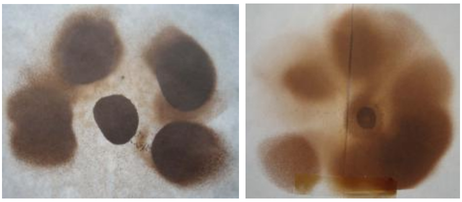
Fig. 2 Sequential generation of lobes for an oil-based ferrofluid.

It was observed that the oil-based FF has an unstable spraying transient regime in which the patterns generated at the counter-electrode appear as a sequence of lobes. Fig. 2 gives the sequential generation of the spray for about 15 seconds for an EFH1 type FF. The spray jet moved counterclockwise generating "lobes". The number of lobes is variable and they can partially overlap. The lobes can approximately be generated in a circle concentric to the nozzle axis or they may fill only part of the circle. The patterns are obtained only within specific voltage ranges and nozzle-counter-electrode gaps. Fig. 2 shows patterns obtained for EFH1 FF for various parameters. In all cases positive polarity high voltage, a flow rate of 0.1 ml/min, and a 25 gauge blunt needle were used. For a gap distance of about 11.5 cm a "lobing" regime can be obtained if the voltage is large enough. Fig. 2a shows that for a low voltage (+8 kV in this case) no lobes are generated and a circular pattern is obtained instead. At 12 cm and 14 kV (Fig. 2b) lobes appear to be generated simultaneously. The dark irregular spot in the middle of the pattern is created by the initial or final drop of FF unrelated to the spray (however, it marks the axis of the needle in all the photos). In Fig. 2c the gap is 12.5 cm, the spray jet moves progressively clockwise and it sets on the darker lobe. The jet moves predominantly in one direction but it often moves temporarily in the opposite direction as well. In Fig. 2d the gap is 12.5 cm at 14 kV and the lobes are more overlapped. At 15 cm and 14 kV (Fig. 2e) there are only two lobes created, while at 16 cm and the same voltage the lobing pattern disappears. Another pattern observed for the EFH1 was the sequential generation of the lobes around the nozzle axis followed by generation of an axial lobe such as in Fig 4b. The patterns showed in Fig. 4a and 4b were generated by an unforced spray of EFH1 (three years old). Ferrotec recommends using the ferrofluid within the first three months in order for it to be free of nanoparticle agglomerates.



(a) (b) (c) (d) (e)

Fig. 3 Spray patterns for EFH1, 25 G needle, flow rate 0.1 ml/min: (a) 11.5 cm, 8kV, (b) 12 cm, 14kV (c) 12.5 cm, 14kV, (d) 13 cm, 14kV (e) 15 cm, 14kV



(a) (b)

Fig. 4 Spray patterns for EFH1, 25 G needle, unforced sprays

In a similar manner, Fig. 5 shows the creation of lobes for EMG905 FF. The lobe pattern is essentially lost at 16 cm gap and the same 14 kV voltage. However, using a cylindrical magnet under the metal counter-electrode allows for the lobe pattern to be created at lower distances than in the absence of a magnetic field (Fig. 5d). The structure of the magnetic field above the counter-electrode is shown in Fig. 6. The axis of the magnet was aligned with the axis of the needle. Fig. 6 shows the variation of the field from the axis of the nozzle/needle (the zero point) within two cross-sections parallel to the counter-electrode.

(a) (b) (c) (d)

Fig. 5 Spray patterns for EMG905, 25 G needle, flow rate 0.1 ml/min: (a) 11.5 cm, 14kV, (b) 14 cm, 14kV (c) 16 cm, 14kV, (d) 8.5 cm, 14kV with magnetic field

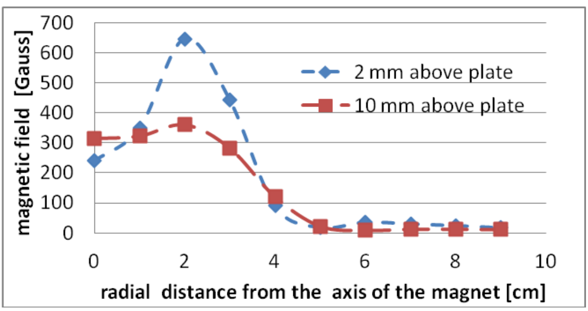


Fig. 6 Magnetic field structure

Preliminary testing was performed on the EFH1 type (oil-based) which provided us with the lobe patterns within certain range for the spray parameters. In order to test the hypothesis that the lobing regime may be associated with the ferromagnetic nanoparticles present in the FF, we also tested water-based ferrofluids. Nevertheless, we were never close to generating the lobing pattern that was observed for oil-based FF irrespective of the spray parameters of nanoparticle concentration in the FF (lower than 7.8% by volume). The spray patterns observed were rather close to those observed for water. In addition, we tested the liquid carrier for the oil-based FF (paraffinic hydrocarbon). Spraying patterns with three spots, irregularly displayed relative to the nozzle axis, were obtained for certain parameters. However, the “lobe” generation, spatial distribution, and size does not resemble the one observed for the oil-based FF. Although more testing of the liquid carrier may be needed, in our tests no lobing regime of the type observed for the oil-based FF was obtained.

IV. CONCLUSION

A transitory lobing spray regime was observed and characterized for oil-based ferrofluids. Positive polarity was applied to the nozzle when the regime was observed. Spontaneous transitions from one lobe to another are likely caused by instabilities in the spray, less characterized in the literature. This transitory regime does not appear to be caused by the nanoparticles present in the fluid. No lobes were obtained either for the water-based FF or for water electrosprays. At the same time, we were not able to obtain a similar regime for the FF carrier liquid itself, although some significant instabilities were observed resulting in favorite spraying spots. However, the sequence generation, shape, and irregular spatial arrangement were different from the patterns observed for oiled-based FF. It appears that the transitory regime described here is a combination of the paraffinic hydrocarbon properties enhanced by the presence of ferric oxide nanoparticles and agglomerates. Although we observed that the spraying regime varies with the concentration of the ferric oxide, a systematic analysis was not currently performed. The lobe regime is generated only at certain needle-counter-electrode gaps and voltage ranges that need to be investigated in a systematic manner. Spraying the ferrofluids in magnetic field influences the parameters needed for obtaining the regime as the fluid is almost superparamagnetic. A Lorentz force and a magnetic force due to the magnetization of the fluid will act on the droplets in addition to the gravitational and electrical forces. In our experiments we noticed the generation of the regime at a smaller nozzle-counter-electrode distance than in the absence of magnetic field and the lobing pattern confined.

V. ACKNOWLEDGEMENTS

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REFERENCES

[1] Rayleigh, "On the Equilibrium of Liquid Conducting Masses charged with Electricity," *Phil. Mag.*, vol. 14, pp. 184–186, 1882.

[2] R. Juraschek and F. W. Rollgen, “Pulsation phenomena during electrospray ionization,” *Int. J. Mass Spectrom*, vol. 177 no. 1, pp. 1-15, 3 August 1998.

[3] A. Jaworek and A. Krupa, “Classification of the modes of EHD spraying,” *J. Aerosol Sci*., vol. 30 no. 7, pp. 873-893, August 1999.

[4] I. Marginean, P. Nemes, and A. Vertes, “Astable regime in electrosprays,” *Phys. Rev*., vol. 76 no. 2, Art. No. 026320, Part 2, August 2007.

[5] Hyun-Ha Kim, Atsuchi Ogata, and Jong-Ho Kim, “High Speed Camera Observation of Electrospray,” *Proceedings of the Electrostatics Joint Conference*, P2. 21, 2009.

[6] Hyun-Ha Kim, Jong-Ho Kim, and Atsushi Ogata, “Time-resolved high-speed camera observation of electrospray,” *Journal of Aerosol Science*, vol. 42 no. 4, pp. 249-263, 2011.

[7] Ke Wang and John P.W. Stark, “Voltage effects on the nanoelectrospray characteristics in fully voltage-controlled atomisation of gold nanocolloids,” *Analytica Chimica Acta*, vol. 679 nos. 1-2, pp. 81-84, 2010.

[8] A. Jaworek, A. Krupa, M. Lackowski, A. T. Sobczyk, T. Czech, S. Ramakrishna, S. Sundarrajan, and D. Pliszka, “Electrostatic method for the production of polymer nanofibers blended with metal-oxide nanoparticles,” *Journal of Physics: Conference Series*, vol. 146 no. 1, doi: 10.1088/1742-6596/146/1/012006.

[9] . Jain Nirmesh, Yanjun Wang, Stephen K. Jones, Brian S. Hawkett, and Gregory G. Warr, “Optimized Steric Stabilization of Aqueous Ferrofluids and Magnetic Nanoparticles,” *Langmuir*, vol. 26 no.6, pp. 4465–4472, 2010.