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6. AUTHOR(S)
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14. ABSTRACT
During the reporting period the development of the ionic liquid ferrofluid (ILFF) based on EMIM-NTf2 was continued. The stabilizer anchoring group was changed from the bulky poly acryloxyethylphosphate to a less bulky poly acrylic acid based group, simplifying the synthesis and allowing the overall polymer content of the ILFF to be reduced. Supply of this ILFF was maintained to Brad King at Michigan Tech. We have also extended our collaboration to include Professor Juan Fernandez de la Mora of Yale University, for whom we designed and prepared an ethylammonium nitrate (EAN) miscible ferrofluid based on the high-boiling-point solvent sulfolane. As part of this collaboration we have also been investigating new ferrofluids based on other high-boiling solvents.

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Final Report for AOARD Grant 144062

"**The Colloidal Stability of Magnetic Nanoparticles in Ionic Liquids**"

Date: 08/03/2015

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Abstract: During the reporting period the development of the ionic liquid ferrofluid (ILFF) based on EMIM-NTf2 was continued. The stabilizer anchoring group was changed from the bulky poly acryloxyethylphosphate to a less bulky poly acrylic acid based group, simplifying the synthesis and allowing the overall polymer content of the ILFF to be reduced. Supply of this ILFF was maintained to Brad King at Michigan Tech. We have also extended our collaboration to include Professor Juan Fernandez de la Mora of Yale University, for whom we designed and prepared an ethylammonium nitrate (EAN) miscible ferrofluid based on the high-boiling-point solvent sulfolane. As part of this collaboration we have also been investigating new ferrofluids based on other high-boiling solvents.

Introduction: To the best of our knowledge, at the time of writing, our group is still the only group to have demonstrated an ability to prepare a spiking ferrofluid based on a hydrophobic ionic liquid. We have continued to supply Brad King at Michigan Tech. University with ILFFs based on EMIM-NTf2 and have endeavored to improve and modify the material as required. We have also responded to the need of Juan Fernandez de la Mora of Yale University to have a ferrofluid that is basically non conducting but that is capable of having ions added to increase the conductivity above the essentially non-conducting baseline. To this end we prepared a ferrofluid based on sulfolane that could be blended with EAN. Both Sulfolane and EAN are somewhat more hydrophilic than ideal and work has commenced on more hydrophobic alternatives.

Experiment: The preparation of a ferrofluid in sulfolane is described below:

Synthesis of the sterically stabilized magnetic nanoparticles:

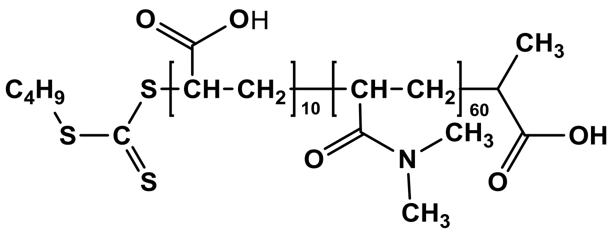
Magnetic nanoparticles with an average core diameter of 25 nm used in this work were obtained from Sirtex Medical limited, Sydney, Australia. Sterically stabilized iron oxide nanoparticles (SPIONs) were prepared by coating the iron oxide core with the block copolymer poly(acrylic acid)10 -block-poly(dimethylacrylamide)60.1-3 Scheme 1 shows the structure of the block copolymer used in this work.

Preparation of a poly(acrylic acid)10 -block-poly(dimethylacrylamide)60 macro-RAFT agent using 2-{[(butylsulfanyl)-carbonothioyl]sulfanyl}propanoic acid (RAFT-AA10 –DMAm60) (Scheme 1).

A solution of RAFT-COOH (0.26 g, 1.1 mmol), 4,4'-azobis(4-cyanovaleric acid) (0.03 g, 0.1 mmol), and dimethylacrylamide (6.45 g, 65.2 mmol) in dioxane (10 g) and water (10 g) was prepared in a 100 mL round bottom flask. This mixture was then stirred magnetically, purged with nitrogen for 15 minutes, and the reaction carried out at 70°C for 8 h. The homopolymer solution obtained, acrylic acid (0.78 g, 10.9 mmol), and 4,4'-azobis(4-cyanovaleric acid) (0.03 g, 0.1 mmol) were added to a 100 mL round bottom flask. The mixture was deoxygenated by purging with nitrogen for 15 min, and the flask stirred in a 70°C oil bath for 2 h. The copolymer solution, at 27% solids, was then diluted with MQ water to 1.2 wt%. The pH of the diluted copolymer solution was adjusted to 5 with 0.1 M NaOH.

Preparation of ferrofluid in Sulfolane

Ferrofluid in sulfolane was obtained by exchanging the solvent water from the aqueous dispersion of sterically stabilized iron oxide nanoparticles with sulfolane. In a typical process, a solution of 3.4 g dispersion of SPIONs (0.125 g) at 3.7% solids, sulfolane 0.38 g and absolute ethanol 5 g was prepared in 50 ml RBF. The water and ethanol were removed from the mixture by distillation at 40°C under reduced pressure using Rotary evaporator. At the end of this step, the SPIONs were successfully transferred into sulfolane and resulted in a very homogenous one-phase liquid (sulfolane based ferrofluid). Final trace of water was removed by heating the ferrofluid in an oil bath at 90°C under nitrogen flow for 30 min. Ferrofluid in Sulfolane had an iron oxide concentration of 26% (w/w).



(RAFT-AA_{10} –$DMAm_{60}$)

Scheme 1, block copolymer used in this study

References:

1. **Jain N, Wang Y, Jones SK, Hawkett BS, Warr GG. Optimized Steric Stabilization of Aqueous Ferrofluids and Magnetic Nanoparticles. *Langmuir.* 2010/03/16 2010;26(6):4465-4472.**
2. **Bryce NS, Pham BTT, Fong NWS, et al. The composition and end-group functionality of sterically stabilized nanoparticles enhances the effectiveness of co-administered cytotoxins. *Biomaterials Science.* 2013;1(12):1260-1272.**
3. **Jain N, Zhang X, Hawkett BS, Warr GG. Stable and Water-Tolerant Ionic Liquid Ferrofluids. *ACS applied materials & interfaces.* 2011/03/23 2011;3(3):662-667.**

Results and Discussion:

Juan Fernandez de la Mora of Yale University asked for a ferrofluid in sulfolane that could be mixed with ethyl ammonium nitrate to facilitate his contribution to Brad King's project. We formulated the required ferrofluid according to the approach described in the previous section. The new fluid was designed to allow him to vary the conductivity of the fluid at will so that he could examine the impact of low concentration of ions on the electrospray properties of an uncharged fluid. However, sulfolane was found to be quite hygroscopic and, if dry, had quite a high viscosity and melting point. We have now started working with a series of glycol diethers known as glymes to see if they can better serve the purpose.

As follow on projects we propose to continue to design ferrofluids and ionic liquid ferrofluids for the space propulsion project and get a better understanding of their use as propulsion media.

We also propose to team with Brad King's group at Michigan Tech to study composite materials that can be prepared by electrospinning. Electrospinning allows the preparation of sub-micron composite fibers. The fibers are formed when a solvent is evaporated from jets of poly composite solution sprayed into an electric field from various configurations of nozzle. The jet of material is unstable in the electric field and whips around in the air. It is proposed that the stream of fluid can be stabilized by the superposition of a magnetic field.

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

a) The previously foreshadowed Langmuir paper was published:

Lyon King, Edmond Meyer, Mark Hopkins, Brian Hawkett and Nirmesh Jain. Self-assembling array of magneto-electrostatic jets from the surface of a superparamagnetic ionic liquid. Langmuir 2014, 30(47), 14143-14150.

f) A new collaboration with Professor Juan Fernandez de la Mora of Yale University has been initiated.

Attachments: Publication in Langmuir

DD882: As a separate document, please complete and sign the inventions disclosure form.