

SELF-STABILIZED AQUEOUS FERROFLUIDS PROPERTIES AND CHARACTERISTICS

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INTRODUCTION: Ferrofluids are very stable colloidal dispersions of ultra-fine particles of a magnetic material, such as magnetite, in a liquid, which may be chosen to conform to a particular application. A stabilizer or surfactant is usually added at the time of preparation to prevent aggregation of the nanoscale particulate. As a result of their composition, magnetic fluids possess a unique combination of fluidity and the capability to interact with a magnetic field. For magnetic carrier applications, ferrofluids may be thought of as being bi-functional materials with both a magnetic particle and magnetic fluid component.

PERSPECTIVE: S. S. Papel made the first ferrofluids by grinding magnetite in a ball mill in the presence of oleic acid (surfactant) and kerosene (U. S. Patent 3,215,572, 1965). The preparations required many months of milling and commercial ferrofluids soon followed. Their development and eventual understanding were pioneered by such researches as R. E. Rosensweig, then at Exxon Corp, and K. Raj, then at Ferrofluidics Corp.

The early preparations followed a “top down” strategy starting with the grinding of micron or sub-micron sized magnetite in the presence of a hydrocarbon and a small amount of surfactant. The grinding usually lasted in excess of six months. Rapid recombination of the nascent nanoscale particles probably contributed to the very long grinding times.

Significant advances in the preparation of ferrofluids, and thus in the understanding and creation of new ferrofluids, came when researchers realized that magnetic fluids could be made from a “bottom up” rather than “top down” strategy. Thus, precipitation reactions to produce magnetic nanoparticles in the presence of a stabilizing agent led directly to the formation of ferrofluids and eliminated the need to mill. The new approach decreased the preparation time from months to days.

The technological development of the hydrocarbon ferrofluids outpaced that of the water based ferrofluids, partly as a result of practical need, and partly as a result of the extraordinary stability of the former and instability of the latter. In non-polar

carrier liquids, such as the hydrocarbons, the particulate is stabilized by steric repulsion.

It wasn't until ionic stabilization was introduced by R. Massart that water based fluids took hold [1]. The electrostatic repulsion was achieved by the preferential adsorption of ions of one type on the magnetic particles and resulted in a relatively stable water-based fluid.

In general, practical ferrofluids are black or very dark brown liquids and are not very suitable for optical applications. Some of the more important uses of ferrofluids today are for heat exchange and mechanical damping in loudspeakers, as seals in hard disk drives and as vacuum seals in general.

To date, applications of ferrofluids in the biomedical and biotech communities have been driven mainly by the diverse and specific needs of those communities. Many excellent examples of applications can be found in the published proceedings of former conferences such as the present one, *Scientific and Clinical Applications of Magnetic Carriers*, and the *International Conference on Magnetic Fluids*.

Although ferrofluids involve nanoscale materials, their community and technologies evolved long before the emergence of nanoscience and nanotechnology. In an academic sense, the study of ferrofluids would qualify as a subset of the later and present a research area rich in challenges for the newcomer. Interdisciplinary research on ferrofluids as nanomaterials could lead to more ‘user-friendly’ ferrofluid designs that may in turn help drive the biomedical and biotechnical applications. Two such series of water-based ferrofluids will be discussed in the present talk along with their properties, characteristics and unusual effects.

SULFONATED POLYSTYRENE AS MATRIX:

One series of ferrofluids is formed by a technique of matrix milling a nanocomposite containing maghemite, $\gamma\text{-Fe}_2\text{O}_3$, in water or a water miscible solvent. In this case, a solid matrix, a DVB cross-linked sulfonated polystyrene, is used to synthesize the nanoparticles and keep them isolated to prevent aggregation [2]. The composite is then milled for a few hours to yield the ferrofluid.

In order to increase the magnetization (M) of the ferrofluids after centrifugation, the fluids are subjected to ultrafiltration, which effectively increases the volume fraction of the maghemite. Volume reductions of between 80% and 96% result in stable ferrofluids containing between 15% and 55% by weight solids, as determined by oven drying the fluids at 110 C.

Analysis of the solids showed that the iron oxide to polymer ratio was not constant. The mass ratio increased from 1:1 for the pre-concentrated ferrofluids to about 6:1 for the most concentrated ferrofluids, demonstrating that only a portion of the original polymer was necessary for colloidal stabilization of the nanocrystalline γ - Fe_2O_3 . Moreover, there was no apparent effect on the stability of the ferrofluids over this mass ratio range, unlike that reported for aqueous ferrofluids of magnetite, Fe_3O_4 , stabilized with sodium oleate. In the latter case, deviation on either side of the optimal magnetite-to-stabilizer ratio, 7:5, resulted in a drastic reduction of either the magnetic properties of the fluid or its stability.

Capillary electrophoretic analysis (see below) established that ultrafiltration served not only to concentrate the ferrofluids by carrier loss but also to purify them by removal of non-bonded or degraded polymer with both losses contributing to the increase in magnetization.

Zeta potential determinations on the particulate in the diluted ferrofluids yielded values of from -65 to -85 mv. Solution studies of the hydrodynamic particle size by quasi-elastic light scattering techniques and by SAXS measurements suggested particles of a very narrow size distribution with diameters of either 47 or 100 nm. The particle size analyses and general behavior of the ferrofluids suggest a solvent swollen, three-dimensional polymer network stabilizing the nanocrystalline γ - Fe_2O_3 . The behavior of the particles appears to mimic the comb-like grafted hydro gels that show rapid de-swelling response to temperature changes or to gels as described earlier by Y. Li and T. Tanaka. For the most part, the present ferrofluids, which are water-based, are stabilized by steric repulsion.

MAGNETIC AND OPTICAL PROPERTIES:

Room temperature magnetization values (M) for the present ferrofluids range from <2 to 52 kA/m, depending on the preparative history of the sample and the applied field. In general, the magnetization of the fluids increases proportionally with the mass

loading of iron oxide. A representative ferrofluid at 300 K in the present series is nearly saturated with a magnetization 35.8 kA/m in an applied field of 800 kA/m. The magnetic remanence and coercivity are zero, consistent with superparamagnetic behavior and the nanoscale dimensions of the particles. Below 50 K, a small hysteresis loop appears. At 10 K, the ferrofluid has a sizable coercive field of 22 kA/m. The hysteresis loop appears symmetric about the center for both the field-cooled and zero field cooled cases. Superparamagnetic behavior was observed for all of the ferrofluids in the present series, as well as for the solid nanocomposite parent.

One of the magnetically strongest ferrofluids in the present group is a very viscous fluid with a saturation magnetization of 52.3 kA/m in an applied field of 800 kOe. Magnetization versus applied field curves at 300 K showed virtually no hysteresis consistent with superparamagnetic behavior. The fluid contained 53% by weight solids and had a density of 1.55 g/cc.

In the proximity of a one Tesla permanent magnet, the ferrofluids with an M of about 12 kA/m and higher show the familiar spiking or tooth pattern that represents the surface structure of a ferrofluid in the presence of a magnetic field. The surface instability results from the interaction of magnetic, gravitational and viscous forces and the surface free energy of the ferrofluid. Spike heights in the strongest ferrofluids can reach several centimeters.

Optical data on bulk ferrofluids has been quite limited. Magnetite-base ferrofluids, for example, are black and opaque except in very thin layers. Optical data for the present ferrofluids were identical to those reported for the solid nanocomposite [2], consistent with our observation of no detected physical or chemical change in the crystallite after milling. As a result, the ferrofluids have a color similar to that of the solid composite parent and appear amber or amber red in color except for the strongest fluids. Because of their relative transparency, the ferrofluids may be used as an optical diagnostic tool in fluid dynamic and fluid mechanical studies. For example, use of the present fluids aboard MIR has enabled the first observation and study of convection currents *inside* of a suspended drop of ferrofluid in microgravity experiments using simple optical diagnostic techniques. In the presence of an applied field, the stronger ferrofluids exhibit optical birefringence.

Changing the alkali metal hydroxide used in the preparation of the starting material can significantly

change the color of the ferrofluids. The use of Li, K, Rb, Cs and ammonium hydroxides instead of NaOH causes the ferrofluids to go from lighter to darker red through a significant shift in the optical absorption edge of the nanocrystalline γ -Fe₂O₃. The role of the cation in changing the optical properties of the mesoscopic oxide appears to be more complex than a simple doping phenomenon since K, Rb and Cs cations presumably do not fit into a normal γ -Fe₂O₃ lattice. The observed shifts support the possible effects of the pressure hypothesis as suggested earlier [2] involving different size cations located between the sulfonated resin and the Fe₂O₃ particles.

The optical transparency of the nanocrystalline γ -Fe₂O₃ along with the relatively high initial permeability, magnetization and stability of the ferrofluids also enables the existence of machine-usable colored magnetic inks at room temperature. To our knowledge, nanotechnology has been the only approach to successfully provide simultaneous color and magnetism in the same material at room temperature.

ALGINATE AS MATRIX: Alginate is a naturally occurring polysaccharide that finds heavy use in the pharmaceutical and food industries. The availability of magnetic forms of the polysaccharide can offer new avenues for materials management and control.

In the form of alginic acid, alginate forms cross-linked gels in the presence of various cations. Magnetic forms of alginate have been made by incorporating micron scale iron oxides into the calcium cross-linked gel. Magnetic gels are the subjects of current research for applications in medical diagnostics, drug delivery and cell sorting systems.

We have produced alginate based ferrofluids by first forming the magnetic gel [3]. This was accomplished by using Fe as the cross-linking ion and using it as the reaction center for the in situ formation of nanocrystalline iron oxides.

Two mm diameter Fe(II) cross-linked beads were formed by dropping an aqueous solution of sodium alginate at room temperature through a 17-gauge stainless steel needle into a degassed solution of iron(II) chloride. Excess ferrous ions were removed by washing with 1:1 MeOH/water solutions under nitrogen. The beads, which were kept in the MeOH/water mix and under nitrogen, were then treated with a sodium hydroxide solution to effect the conversion of Fe(II) ion to γ -Fe₂O₃. This two-

step synthesis was repeated up to four times to increase the loading of iron oxide in the gel. This technique led to gels that on a dry basis contained between 10 and 50% iron.

Aqueous alginate ferrofluids were then formed by oxidative depolymerization of the beads in water with air bubbled through the suspension to evaporate the methanol, which acts as an inhibitor to the depolymerization of the alginate.

The physical properties of the alginate ferrofluids are similar to those of the sulfonated polystyrene fluids. Gels obtained after five consecutive loading cycles and then dehydrated have a room temperature saturation magnetization of 30 kA/m at 20 kOe. Magnetization curves of M vs. applied field and temperature (4.2 K to 300 K) suggest superparamagnetic behavior consistent with the small size of the iron oxide.

ANALYSIS: The effective characterization of water-based ferrofluids is as important as their design. Conventional methods of analyzing these materials include transmission electron microscopy and quasi-elastic light scattering techniques for particle size. Microelectrophoresis is also used and yields data on the *average* electrophoretic mobility and the zeta-potential of the colloid. None of these methods allows for the fast detection of impurities. Methodology reported by Morneau et al. [4] on the application of capillary electrophoresis (CE) to the analysis and characterization of magnetic fluids will also be discussed. In the study, CE was coupled with diode array UV-visible detection to provide a new, efficient and sensitive method to characterize water-based ferrofluids in terms of surface charge, electrophoretic mobility and the level of purity. The method has also proved useful in quality control of ferrofluid production.

REFERENCES: ¹See, for example, S. W. Charles (1992) *Magnetic Fluids (Ferrofluids)* in *Magnetic Properties of Fine Particles* (eds J. L. Dormann and D. Fiorani) North-Holland Elsevier, pp 267-374. ²R. Ziolo, et al. (1992) *Science* **33**:1471-77. ³E. Kroll, et al. (1996) *Chemistry of Materials*, **8**:1594-1596. ⁴A. Morneau, et al. (1999) *Colloids & Surfaces A: Physicochemical & Engineering Aspects* **154**:295-301.

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