Preparation and Properties of an Aqueous Ferrofluid

Patricia Berger
Department of Chemistry, Southern Oregon University, Ashland, OR 97520

Nicholas B. Adelman, Katie J. Beckman, Dean J. Campbell,†† and Arthur B. Ellis*
Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706; *ellis@chem.wisc.edu

George C. Lisensky
Department of Chemistry, Beloit College, Beloit, WI 53511

Introduction

Imagine the production and applications of a liquid that can be controlled by a magnetic field. Creating a strongly magnetic liquid is not as easy as melting a strongly magnetic solid, since magnetic solids lose much of their magnetism above what is known as the Curie temperature, as thermal energy overwhelms the tendency of their electrons to align in magnetic domains (regions of similarly oriented electron spins). The Curie temperature is well below the melting point for known magnetic materials (1–3). Ferrofluids, which are colloidal suspensions of magnetic material in a liquid medium, are an example of a liquid that responds to an external magnetic field. The coupling of liquid and magnetic behavior means that the liquid’s location may be manipulated by an applied magnetic field.

Ferrofluids were first developed and classified in the 1960s by Stephen Pappell at NASA as a method for controlling fluids in space (4). NASA initially used them as rotating shaft seals in satellites, and they now serve the same purpose in a wide variety of machines, ranging from centrifuges to computer hard disk drives (1, 2). They are incorporated into the voice coil gap of loudspeakers for damping undesired vibrations and for cooling. Ferrofluids have also been used in the separation of metals from ores by taking advantage of a density change that appears in the fluid under application of a magnetic field. One South African company has even been utilizing ferrofluids to separate diamonds from beach sand (5).

In medicine, a ferrofluidic actuator has been proposed for an implantable artificial heart (1). This actuator would be driven simply by applying an external magnetic field. It is possible to attach drugs to the surface of the magnetic particles and use magnetic fields to hold the drug at the site where it is needed (3). Aqueous magnetic fluids have successfully oriented biological assemblies such as the tobacco mosaic virus, enabling information concerning the helical structure of the virus to be obtained (6).

Recently, ferrofluids have been utilized in conjunction with microcontact printing and capillary filling to fabricate patterned structures of magnetic materials on the micron scale (7). The ability to produce patterns of ultrathin magnetic particles has important technological applications, since the information density on tapes, for example, is inversely proportional to the size of the particles. Research has been conducted exploring the use of ferrofluids as magnetic inks for ink jet printing (2). Magnetic inks are currently used in printing United States paper currency, as can be demonstrated by the attraction of a genuine dollar bill to a strong magnet (Fig. 1) (8).

Background

There are two major steps in synthesizing a ferrofluid. The first is to make the magnetic nanoparticles (~100 Å diameter) that will be dispersed in the colloidal suspension. These particles must be chemically stable in the liquid carrier. The magnetic particles in ferrofluid are generally magnetite, Fe₃O₄, although other magnetic particles have been used. The second synthetic step is the dispersion of the magnetic particles into a carrier liquid by utilizing a surfactant to create a colloidal suspension. Surfactants are dispersion agents for particles in a liquid that work by adhering to the particles and creating a net repulsion between them (steric and/or coulombic), raising the energy required for the particles to agglomerate, and stabilizing the colloid (Fig. 2) (3). Aqueous, oil-, and liquid-metal-based (mercury; gallium alloys) ferrofluids have been developed with the proper choice of surfactant (1). The magnetic properties of magnetite that make it a desirable component of ferrofluids are derived from its crystal structure. Magnetite crystallizes in the inverse spinel structure above 120 K (9). The inverse spinel structure consists of oxide ions in a cubic close-packed arrangement. Iron(II) ions occupy 1/4 of the octahedral holes, and the iron(III) ions are equally...
divided between 1/8 of the tetrahedral holes and 1/4 of the
octahedral holes. Electron spins of iron(III) ions in octahedral
holes are aligned antiparallel to those in tetrahedral holes;
therefore, no net magnetization is observed from these ions.
The iron(III) ions, however, tend to align their spins parallel
with those of iron(III) ions in adjacent octahedral sites, leading
to a net magnetization. This arrangement of antiparallel spins
throughout the solid that do not completely cancel is referred
to as ferrimagnetism. Ferrofluids are actually superparamag-
netic, meaning that a ferrofluid reacts to a magnetic field in
the same way as a ferromagnetic or ferrimagnetic solid, but
magnetizes and demagnetizes more rapidly because in a ferro-
fluid the magnetic domains are the same size as the actual
particles. Manganese and cobalt ferrites, MnFe₂O₄ and CoFe₂O₄,
respectively, also have the inverse spinel structure and have
been used in the preparation of ferrofluids (10).

The layer sequences for a conventional cubic unit cell and
for a smaller tetragonal unit cell for magnetite are shown in
Figure 3. The Fe₃O₄ cubic unit cell and the Fe₁₂O₁₆ tet-
ragonal unit cell both have the same empirical formula,
Fe₃O₄. Construction directions using the ICE Solid-State
Model Kit (11) are included in the Supplemental Material.
A cubic unit cell built with the kit is shown in Figure 4.

For magnetite to remain in suspension, its particle diam-
eters need to be on the order of 10 nm (100 Å) (2, 4b). At
room temperature, the thermal energy of these colloidal
particles is of the same order of magnitude as the gravitational
and magnetic attraction, ~4 × 10⁻²¹ J, and therefore the
particles remain suspended. The original ferrofluids developed
at NASA used finely divided magnetite, prepared by grinding
in a ball mill for several weeks to obtain particles of an appro-
priate colloidal size. Carrier liquid, surfactant and a dispersant
were added during the grinding process to prevent agglom-
eration of the nanoparticles. In an alternative procedure, as
used in this paper, magnetite is synthesized in solution and
precipitated as nanoparticles (2, 3).

Overview

This paper presents an easy, economical method for
preparing a ferrofluid that can be used in high school or college
science or engineering courses.¹ This ferrofluid may be prepared
in less than 2 h. The synthesis is based on reacting iron(II)
and iron(III) ions in an aqueous ammonia solution to form
magnetite, Fe₃O₄, as shown in eq 1.

$$2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_3 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} \ (1)$$

The magnetite is mixed with aqueous tetramethylammonio-
mium hydroxide, (CH₃)₄NOH, solution. This surfactant can
surround the magnetite particles with hydroxide anions and
tetramethylammonium cations (12) to create electrostatic
interparticle repulsion in an aqueous environment (Fig. 2).
This paper also includes a method for applying a ferrofluid-
resistant coating to objects and describes a dramatic classroom
demonstration of the attraction of ferrofluid to magnets.

Synthesis

Safety

CAUTION: Gloves and goggles must be worn at all times.
Hydrochloric acid and aqueous ammonia are corrosive and
should be handled with care. FeCl₃ is toxic, corrosive, and a
mutagen. FeCl₂ is corrosive. Tetramethylammonium hydroxide

Figure 2. Idealized illustration of an aqueous ferrofluid stabilized by a tetramethylammonium hydroxide surfactant. Surfactant
cpecies adhere to the surface of magnetite particles, creating a net repulsion between the particles and stabilizing the colloid.
Tetramethylammonium hydroxide can coat the magnetite particles with hydroxide anions, which attract tetramethylammonium
cations, forming a diffuse shell around each particle and creating repulsion between particles. The drawing is not to scale.

Figure 3. The layer sequence of magnetite (see ref 4b, Chapter 3, for a discussion of layer sequences). The larger gray square represents the crosssection of the conventional cubic unit cell; the smaller, black-outlined square represents the crosssection of an alternate, smaller tetragonal unit cell. The arrangement of the atoms is the same in both. Fe³⁺ is represented by
circles of different sizes: large circles represent iron in octahedral coordination, small circles represent iron in tetrahedral coordination.
Cease stirring and allow the precipitate to settle for 5–10 min, then decant and dispose of most of the liquid. Stir the remaining solution and centrifuge the solution for 1 min at 1000 rpm. (In general, at least 15–20 mL of liquid should be centrifuged in order to obtain an adequate amount of solid magnetite for preparing a ferrofluid sample; one or more centrifuge tubes can be used for this step, depending on the centrifuge available.)

**Special Materials Required**

- Cow magnet (0.5 in. diameter × 3 in.), available from farm supply stores or from Edmund Scientific, Barrington, NJ.
- Strong neodymium-iron-boron (Nd₂Fe₁₂B) magnet, available from Edmund Scientific, Barrington, NJ, or Magnet Sales and Manufacturing Company, Culver City, CA.
- Benchtop centrifuge, such as an International Clinical Centrifuge from the International Equipment Company, Boston, M.A.
- 2.0 M FeCl₂ in 2 M HCl (39.76 g of FeCl₂ · 4H₂O in 100 mL of 2 M HCl).
- 1.0 M FeCl₃ in 2 M HCl (67.58 g of FeCl₃ · 6H₂O or 40.55 g of FeCl₃ in 250 mL of 2 M HCl).
- 0.7 M aqueous NH₃ (48 mL of concentrated aqueous NH₃ diluted to 1 L with H₂O).
- 25% aqueous (CH₃)₄NOH solution, available from Aldrich, Milwaukee, WI.

**Procedure**

Combine 1.0 mL of stock FeCl₂ solution and 4.0 mL of stock FeCl₃ solution. Place a magnetic stirring bar in the flask and begin stirring vigorously. Add dropwise by pipet or buret 50 mL of 0.7 M aqueous NH₃ solution into the flask. We have found that the slow rate of addition is critical, and a pipet or buret is a convenient means of slowing the addition rate. Magnetite, a black precipitate, will form immediately. Stir throughout the addition of the ammonia solution. Cease stirring and allow the precipitate to settle (5–10 min),

is a strong base that is corrosive and flammable. Caution must be exercised when handling any of these materials. Wash immediately with water in case of skin contact.

Ferrofluids can be messy. This particular ferrofluid will permanently stain almost any fabric and it has a high pH. It is also very difficult to remove from magnets.

**NOTE:** Stoichiometry of the reaction is important. The solids are hygroscopic and previously unopened reagents will work better. It is absolutely essential that there is no undissolved material in the solutions. Prepare the iron chloride solutions by adding the solid iron chlorides to the 2 M HCl solution. The acidic conditions prevent formation of iron hydroxides. The iron(II) solution is susceptible to air oxidation and should be used within a week of preparation. Both the ammonia and (CH₃)₄NOH solutions should also be free of undissolved solids.

**NOTE:** We have also found that we can synthesize high-quality ferrofluid using 1 M tetra-n-butylammonium hydroxide, also available from Aldrich, in place of tetramethylammonium hydroxide. The ferrofluid spikes are about the same size for both surfactants, but tetramethylammonium hydroxide is less expensive.

Figure 5. The final ferrofluid preparation step. Remove the magnetite from both ends of the stirring bar by grasping the bar in the center, touching each end in turn to the weighing boat above the strong magnet, and rotating the stirring bar until all of the magnetite adheres to the weighing boat through attraction to the strong magnet beneath the boat.
The lab is to assign different stoichiometric ratios to different student data is shown in Figure 7. An alternate format for spiked) as a function of precursor solution ratios for the pooled iron(II) stoichiometric ratio that is known to work, as well as a second synthesis using a different stoichiometric ratio. The students to perform the synthesis with the 2:1 iron(III)/ iron(II) stoichiometric ratio that is known to work, as well as a second synthesis using a different stoichiometric ratio.

A graph of the percent of successful syntheses (ferrofluids that are due to surface instability of the suspended particles. The surface instability associated with the ferrofluid causes small waves to be constantly present on the surface of the liquid (2). When a magnetic field is applied, the amplitude of the waves increases until they begin to form peaks. If the magnetic field is large enough to dominate the forces of surface tension and gravity, the spikes appear. The spikes increase in size as the magnetic field is increased. By far, this is the easiest and most fascinating test for a high-quality ferrofluid. However, if the magnetic field becomes too great, the magnetic particles will become too dilute and will not spike. If the ferrofluid is too dilute, hold the strong magnet under the weighing boat, then tilt the weighing boat so that the excess liquid runs off.

Results and Discussion

A fascinating physical property of a ferrofluid is the unusual distortion that the fluid experiences when exposed to a magnetic field. When a high-quality ferrofluid is brought into contact with a moderate magnetic field, such as that from a cow magnet, it develops spikes on its surface (Fig. 6). These spikes, which may adopt a close-packed hexagonal pattern, are due to surface instability of the suspended particles. The surface instability associated with the ferrofluid is most likely due to the presence of a moderate magnetic field (Fig. 6) (a more detailed description of ferrofluid spiking is given in the Results and Discussion section). If the fluid does not spike, or the spikes are small, remove the cow magnet, add one drop of distilled water, stir well with the glass rod, and again check for spiking with the cow magnet. If spikes are still not seen, try adding one or two more drops of water. It should not take more than a few drops to obtain a good spiking effect. If too much water is added, the ferrofluid will become too dilute and will not spike. If the ferrofluid is too dilute, hold the strong magnet under the weighing boat, then tilt the weighing boat so that the excess liquid runs off.

% of successful syntheses (ferrofluids that are due to surface instability of the suspended particles. The surface instability associated with the ferrofluid causes small waves to be constantly present on the surface of the liquid (2). When a magnetic field is applied, the amplitude of the waves increases until they begin to form peaks. If the magnetic field is large enough to dominate the forces of surface tension and gravity, the spikes appear. The spikes increase in size as the magnetic field is increased. By far, this is the easiest and most fascinating test for a high-quality ferrofluid. However, if the magnetic field becomes too great, the magnetic particles will reversibly precipitate from the solution (3).

The synthetic procedure described above can be carried out with varying mole ratios of FeCl₂ to FeCl₃ in order to demonstrate the effect of stoichiometry. About 250 pairs of undergraduates in an introductory chemistry lab performed the synthesis with varying ratios of the precursor iron chloride solutions. There was time during the three-hour lab period for the students to perform the synthesis with the 2:1 iron(III)/iron(II) stoichiometric ratio that is known to work, as well as a second synthesis using a different stoichiometric ratio.

A graph of the percent of successful syntheses (ferrofluids that spiked) as a function of precursor solution ratios for the pooled student data is shown in Figure 7. An alternate format for the lab is to assign different stoichiometric ratios to different groups of students at the beginning of the lab. After the first synthesis is complete, the resulting fluids can be checked for spiking with a magnet. The stoichiometric ratio that results in the “best” ferrofluid (the one that responds most dramatically to a magnet) can then be assigned to the entire class for a second ferrofluid synthesis, allowing everyone to prepare a high-quality ferrofluid.

The structure of the synthesized magnetite particles can be identified by X-ray powder diffraction. The average particle diameter for the crystalline precipitate can be determined by Scherrer’s formula, eq 2, using the half-widths of the most intense X-ray diffraction peaks (3, 13).

\[
t = \frac{(0.9 \lambda)}{(B \cos \theta)}
\]

In this formula, \(t\) is the particle diameter in Å, \(\lambda\) is the wavelength of the X-ray radiation in Å, \(\theta\) is the Bragg angle (°) of the peak, and \(B\) is the peak broadening. Peak broadening is a measure of the size of the nanoparticles with respect to reference particles. The reference particles must have a crystal thickness greater than ~2000 Å, which gives relatively narrow peaks (Fig. 8A). A commercially manufactured sample of magnetite has particles that are sufficiently large to serve as a reference. The peaks for the colloidal sample are typically broader (Fig. 8B). The peak broadening, the difference between the sample and reference peak widths, is given by the Warren formula (eq 3) (14).

\[
B^2 = B_{\text{colloid sample}}^2 - B_{\text{bulk material}}^2
\]

\(B\) is the peak width (in radians) that is measured at half the maximum peak intensity. The data for the bulk material may be obtained from JCPD files (15) or from a diffraction pattern of commercial Fe₃O₄ (available from Aldrich, Milwaukee, WI) having an average crystal size greater than ~2000 Å (13). Using the peak at 2\(\theta\) = 35.6° (Miller indices, (311)), the average size of magnetite particles synthesized by the method described in this paper is ~14 nm. Two magnetite particles are small enough to sustain a colloidal suspension, and a good ferrofluid can be produced.
A Ferrofluid-Resistant Coating

Many water- and oil-based ferrofluids tend to stain (sometimes permanently) materials with which they come into contact. This procedure outlines a method to affix a ferrofluid-resistant coating to a container. (The container should be able to withstand temperatures in the range of 120–180 °C.) Scotchgard Fabric Protector FC-247 is a concentrated aqueous suspension of fluoroaliphatic resin; it can be obtained from 3M Specialty Chemicals Division, St. Paul, MN. Avoid eye and prolonged skin contact with this suspension. Thoroughly coat the surface of the container that will contact the ferrofluid with the Scotchgard; rotate the vessel or use a spray-bottle to evenly coat it, then pour out the excess liquid. (The excess can be poured back into its storage bottle to be reused.) Allow the container to dry for approximately an hour in open air, then place it in a 120–180 °C oven for 30 min. Let the vessel cool to room temperature before allowing ferrofluid to contact the treated surface. We have found this coating to resist wetting and staining by ferrofluid for a period of several weeks.

This coating can be removed by soaking in hot soapy water or a KOH/isopropanol base bath. Scotchgard fabric protector, sold in spray cans, provides a more limited resistance to ferrofluid.

The “Leaping Ferrofluid” Demonstration

The following describes a demonstration (Fig. 9) that uses magnets to force a ferrofluid to leap into the air, providing a dramatic demonstration of the effects of magnetic fields on ferrofluid.

Using a cork borer, bore a hole slightly smaller than the diameter of an 18 × 130-mm test tube (~17 mm) in a #13 rubber stopper, then push the test tube through the hole until the stopper is about a third of the way from the bottom of the tube. This stopper will prevent ferrofluid from following the magnets all the way up the test tube. Attach a 3-fingered clamp near the bottom of a ring stand and place the test tube vertically in the clamp, leaving about 3 cm clearance under the end of the test tube.

Stack small strong magnets so the poles are at the ends of the stack. N@$\text{_{12}}$Fe@$\text{_{14}}$B magnets, such as those available from Edmund Scientific Corporation, Barrington, NJ, or Magnet Sales and Manufacturing Company, Culver City, CA, work well, as long as they are sufficiently small to fit easily into the test tube. Tie the end of the string around one of the magnets. Place the tied magnet on one end of the stack, using broken magnet pieces (broken with a hammer) as spacers to give more stability to the gap caused by the string (Fig. 10). Attach a ring clamp near the top of the stand, thread the string through a one-hole #1 rubber stopper that will be placed in the open end of the test tube (small side of the stopper toward the magnets) and through the ring clamp ring, and tie the other end to a ~100-g weight. The weight should be slightly heavier than the magnets, so that when it is released it will hold the magnets in the “up” position, away from the ferrofluid that will be placed below the test tube.

Place the magnets in the test tube and fill the tube with mineral oil to about 2 cm from the top. The viscous oil decreases the descent rate of the magnets, preventing splashing of the ferrofluid from the external walls of the glass tube. Apply silicone caulk to the mouth of the tube and to the sides of the small stopper, then insert the stopper and cure for 24 h. A watch glass with a small amount of ferrofluid (a few milliliters of either a commercial oil-based ferrofluid from Ferrofluidics Corporation, Nashua, NH, or the water-based ferrofluid synthesized using the procedure given in this paper) can then...
The synthesis and properties of ferrofluids would fit into a means for introducing nanoscale materials and preparation. The small size of the particles also provides a variety of chemical and physical concepts, including stoichiometry, crystal structure, colloidal properties, oxidation states, and magnetism. The demonstration may be repeated many times successively and presented in a large lecture hall using a video camera.

Conclusions

Ferrofluids are fascinating materials. They are easy to synthesize and the preparative procedures illustrate a wide variety of chemical and physical concepts, including stoichiometry, crystal structure, colloidal properties, oxidation states, and magnetism. The small size of the particles also provides a means for introducing nanoscale materials and preparation. The synthesis and properties of ferrofluids would fit into the curriculum of many types of introductory science and engineering laboratory courses.

Acknowledgments

We would like to thank the National Science Foundation's REU Program and the Materials Research Science and Engineering Center for Nanosstructured Materials and Interfaces (DMR-9632527) for generous support of this research. We also thank Judith Burstyn for use of her supercentrifuge, Joel Miler for informing us of the magnetic inks in paper currency, and John Zhang and David Larbalestier for helpful discussions of magnetic phenomena. We thank Karen Nordell and S. Michael Condren for help with the synthesis, and Lawrence F. Dahl, Douglas R. Powell, and Mikhail Khoudiakov for assistance in the X-ray diffraction measurements. We are grateful to Patrick Doolan, the UW-Madison General Chemistry staff, and the 1997 U-W-Madison Chemistry 109 class for assistance in refining the ferrofluid synthesis.

Notes

**1**Supplementary materials for this article are available on JCE Online at http://chemed.chem.wisc.edu/journal/issues/1999/jul/ab943.html and can be downloaded from this site. fsfup is a Microsoft Word 6.0 document of instructions for building the solid state model of the magnetite structure and the student laboratory synthesis of ferrofluid. Images and movies of these and other experiments are available at the Materials Research Science and Engineering Center for Nanosstructured Materials and Interfaces Education and Outreach Web site, http://mrsec.wisc.edu/edetc/.


2. Experimental conditions for powder diffraction: Scintag PAD V diffractometer, Scintag Inc., Cupertino, CA; X-ray source: λ = 1.540562 Å (Cu Kα1KαII); steptime: 0.600 s; stepwidth: 0 = 0.020°; 2θ = 0.040°; 2θ range: 20°–70°; scan rate: 20/min.

**Literature Cited**

5. Ogden, F. The Last Book You'll Ever Read; MacFarlane, Walter, and Ross: Toronto, 1993; p 206.
15. JCPDS file 1629; Joint Committee on Powder Diffraction; Swarthmore, PA.