Preparation and Properties of an Aqueous Ferrofluid W

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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 ultrafine 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

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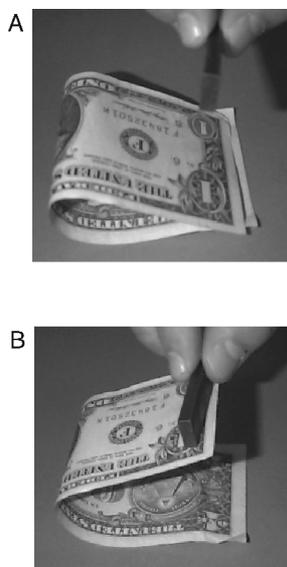
Figure 1. Magnetic inks are printed onto paper money for identification purposes. When a strong magnet is brought near a dollar bill (A), the bill is attracted to the magnet (B).

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, Fe_3O_4, 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(II) 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 superparamagnetic, 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 ferrofluid the magnetic domains are the same size as the actual particles. Manganese and cobalt ferrites, $MnFe_2O_4$ and $CoFe_2O_4$, 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 $Fe_{24}O_{32}$ cubic unit cell and the $Fe_{12}O_{16}$ tetragonal unit cell both have the same empirical formula, Fe_3O_4. 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 diameters 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, $\sim 4 \times 10^{-21}$ 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 appropriate colloidal size. Carrier liquid, surfactant and a dispersant were added during the grinding process to prevent agglomeration 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, Fe_3O_4, as shown in eq 1.

$$2FeCl_3 + FeCl_2 + 8NH_3 + 4H_2O \rightarrow Fe_3O_4 + 8NH_4Cl \quad (1)$$

The magnetite is mixed with aqueous tetramethylammonium hydroxide, $(CH_3)_4NOH$, 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. $FeCl_2$ is toxic, corrosive, and a mutagen. $FeCl_3$ is corrosive. Tetramethylammonium hydroxide
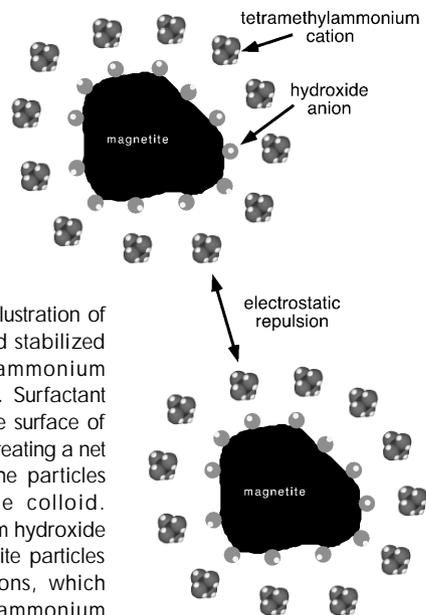
Figure 2. Idealized illustration of an aqueous ferrofliud stabilized by a tetramethylammonium hydroxide surfactant. Surfactant species adhere to the surface of magnetite particles, creating a net repulsion between the particles and stabilizing the colloid. Tetramethylammonium hydroxide can coat the magnetite 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.
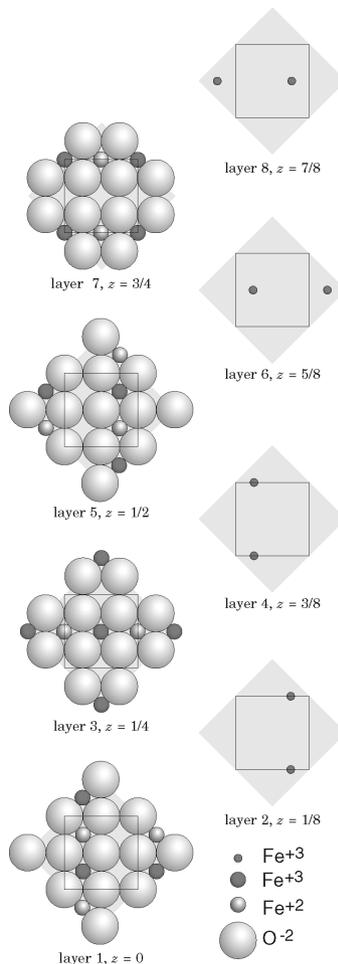
Figure 3. The layer sequence of magnetite (see ref 4b, Chapter 3, for a discussion of layer sequences). The larger gray square represents the cross-section of the conventional cubic unit cell; the smaller, black-outlined square represents the cross-section of an alternate, smaller tetragonal unit cell. The arrangement of the atoms is the same in both. Fe^{3+} is represented by circles of different sizes: large circles represent iron in octahedral coordination, small circles represent iron in tetrahedral coordination.

Figure 4. Model of the cubic unit cell of Fe_3O_4, built with the ICE Solid State Model Kit (*11*).
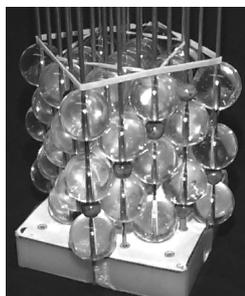
is a strong base that is corrosive and flammable. Caution must be exercised when handling any of these materials. Wash immediately with water in case of skin contact.

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.

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 ($Nd_2Fe_{12}B$) 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, MA.
>
> 2.0 M $FeCl_2$ in 2 M HCl (39.76 g of $FeCl_2$·$4H_2O$ in 100 mL of 2 M HCl).
>
> 1.0 M $FeCl_3$ in 2 M HCl (67.58 g of $FeCl_3$·$6H_2O$ or 40.55 g of $FeCl_3$ in 250 mL of 2 M HCl).
>
> 0.7 M aqueous NH_3 (48 mL of concentrated aqueous NH_3 diluted to 1 L with H_2O).
>
> 25% aqueous $(CH_3)_4NOH$ solution, available from Aldrich, Milwaukee, WI.

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 $(CH_3)_4NOH$ 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.

Procedure

Combine 1.0 mL of stock $FeCl_2$ solution and 4.0 mL of stock $FeCl_3$ 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 NH_3 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),

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.) Decant the supernatant after centrifugation. The dark, sludgelike solid at the bottom of the tube is magnetite.

Divide 8 mL of 25% tetramethylammonium hydroxide ($(CH_3)_4NOH$) solution among however many centrifuge tubes were used during the centrifugation and stir with a thin glass rod until the solid is completely suspended in the liquid. Pour the contents of all of the tubes into a vacuum filtration flask, add a magnetic stirring bar, and stopper the flask. Magnetically stir the solution under aspirator vacuum for 30 min to remove excess ammonia from the solution.

After stirring, slowly pour the liquid into a beaker. The magnetic stirring bar that remains in the filtration flask should be covered with a black sludge, which may or may not exhibit spikes at the ends of the magnet. Gently pour the stirring bar and attached sludge into a plastic weighing boat. Remember that ferrofluids are messy and can easily and permanently stain any fabric. *Carefully and slowly* hold a strong, block-shaped magnet (preferably a $Nd_2Fe_{12}B$ magnet—see above for suppliers) up to the bottom of the plastic weighing boat, keeping it underneath the weighing boat. Using *gloved* fingers, grasp and rotate the stirring bar about its axis to remove the magnetite adhering to it by allowing the magnetite to be more strongly attracted to the stronger magnet held beneath the weighing boat (Fig. 5). Make sure the magnetite is removed from *both* ends of the stirring bar. Pull the now-clean magnetic stirring bar out of the weighing boat, being careful not to let it slip back into the weighing boat, where it could cause splashing. With the strong magnet still underneath the weighing boat, pour off any excess water. Finally, carefully remove the strong magnet from the bottom of the weighing boat.

Hold a cow magnet up to the bottom of the weighing boat to check whether the ferrofluid forms spikes in the
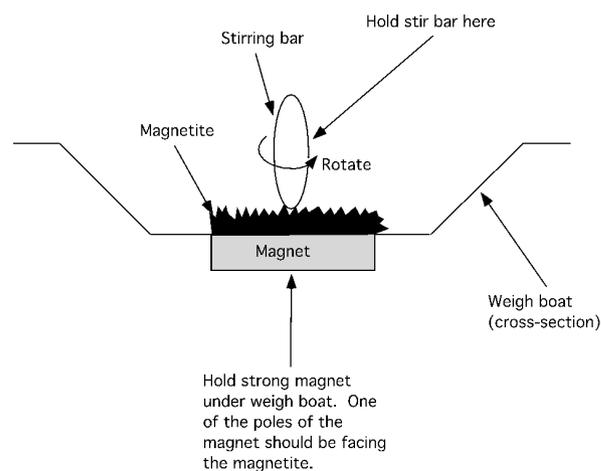
Figure 5. The final ferrofluid preparation step. Remove the magnetite from both ends of the stirring bar by grasping the bar in the center, touching each end in turn to the weighing boat above the strong magnet, and rotating the stirring bar until all of the magnetite adheres to the weighing boat through attraction to the strong magnet beneath the boat.

Figure 6. A side view of the spiking effect of an aqueous-based ferrofluid in the presence of a cow magnet, which is placed underneath a weighing boat.

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.

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 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 force 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 $FeCl_2$ to $FeCl_3$ 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*).

$$t = (0.9\,\lambda)/(B\cos\theta_B) \qquad (2)$$

In this formula, t is the particle diameter in Å, λ is the wavelength of the X-ray radiation in Å, θ_B is the Bragg angle (θ) 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*).

$$B^2 = B^2_{colloid\ sample} - B^2_{bulk\ material} \qquad (3)$$

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 JCPDS files (*15*) or from a diffraction pattern of commercial Fe_3O_4 (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.[2] These magnetite particles are small enough to sustain a colloidal suspension, and a good ferrofluid can be produced.
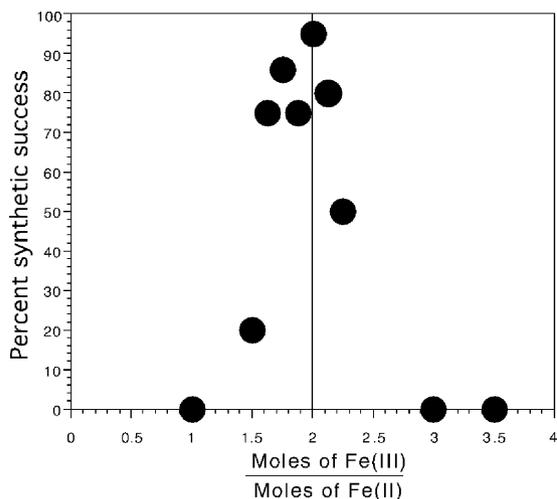
Figure 7. Percent success of the ferrofluid synthesis as a function of iron chloride solution mole ratios for a group of ~250 pairs of undergraduates performing the experiment during the third week of class. Most of the trials were conducted with the 2:1 Fe^{3+}/Fe^{2+} ratio.

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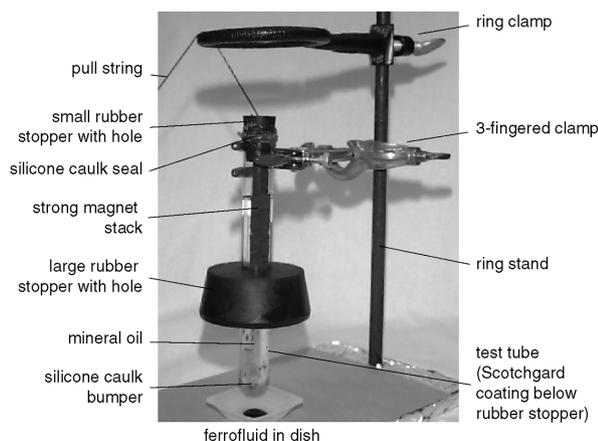
This coating can be removed by soaking in hot soapy water or a KOH/isopropanol base bath. Scotchgard fabric protector, sold in spray cans, provides a more limited resistance to ferrofluid.

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. $Nd_2Fe_{12}B$ 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

Figure 8. (A) X-ray powder diffraction pattern of commercially available magnetite. (B) X-ray powder diffraction pattern of the magnetite synthesized by the technique outlined in this paper. Using eqs 2 and 3, the average particle size is about 14 nm. The peak used in the calculations was at 2θ = 35.6° (Miller indices, (311)). The asterisk indicates an impurity peak.

Figure 9. Construction of the "leaping ferrofluid" demonstration.

Figure 10. Construction of the magnet stack used in the "leaping ferrofluid" demonstration.

Figure 11. The leaping ferrofluid demonstration. (A) The magnets are in the raised position. (B) The magnets are in the lowered position. (C) Ferrofluid spiking at the end of the test tube, which occurs when the magnets are in the lowered position.

be placed under the test tube. An option to prevent staining and to aid draining of ferrofluid off of the tube is to treat the contact surface of the test tube (that below the large rubber stopper) and of the watch glass with Scotchgard (see above).

When the weight is lifted, lowering the magnets through the oil, the ferrofluid leaps to the surface of the test tube, displaying its dramatic spiking (Fig. 11). When the weight is lowered, the magnets are raised, pulling the ferrofluid along with them until they are prevented from following any farther by the barrier of the large rubber stopper. At this point the ferrofluid drains off the test tube back into the watch glass. If the ferrofluid does not leap to the magnets, the test tube should be moved closer to the ferrofluid. The demonstration may be repeated many times successively and presented in a large lecture hall using a video camera.

Conclusion

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

Notes

[W]Supplementary materials for this article are available on *JCE Online* at *http://jchemed.chem.wisc.edu/Journal/issues/1999/Jul/abs943.html* and can be downloaded from this site. ffsup 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 Nanostructured Materials and Interfaces Education and Outreach Web site, *http://mrsec.wisc.edu/edetc/*.

1. A classroom kit (The Ferrofluidic Adventure Science Kit) is available from Ferrofluidics Corp., 40 Simon St., Nashua NH 03061; phone: 603/883-9800; fax: 603/883-2308; *www.ferrofluidics.com*.

2. Experimental conditions for powder diffraction: Scintag PAD V diffractometer, Scitag Inc., Cupertino, CA; X-ray source: $\lambda = 1.540562$ Å (Cu α_1KL_{III}); steptime: 0.600 s; stepwidth: $\theta = 0.020°$, $2\theta = 0.040°$; 2θ range: 20−70°; scan rate: 20/min

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