# ***Synthesis of an Aqueous-Based Ferrofluid****

*This procedure replaces the procedure given on pages 11-13 in the laboratory manual. Please see the following website for a series of films demonstrating this new procedure:* http://www.mrsec.wisc.edu/EDETC/cineplex/ffexp/index.html

Ferrofluids are colloidal suspensions of magnetic particles in a liquid medium. The interest in ferrofluids arises from the fact that these liquids can be controlled directly by the application of a magnetic field. NASA was the first to develop and characterize ferrofluids in the 1960's. Since then, ferrofluids have been incorporated into a number of commercial and industrial processes.

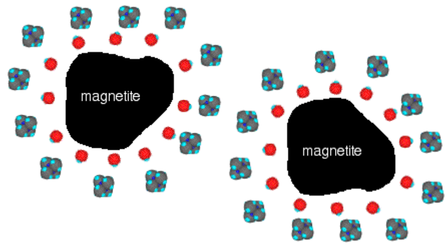
**Warnings:** Wear eye protection. Concentrated ammonium hydroxide should be used only in the hood. Tetramethylammonium hydroxide ¾ $N(CH_3)_4OH$¾ is a strong base. Ferrofluids can be messy. The particular ferrofluid you will prepare will permanently stain almost any fabric. If it gets on your skin, wash it off immediately. Do not let the ferrofluid come directly into contact with any magnet; any time you are holding a magnet near a ferrofluid, keep the two well separated.

There are two basic steps in creating a ferrofluid: synthesis of the magnetic solid, magnetite ($Fe_3O_4$), and suspension in water with the aid of a surfactant. The magnetic particles must be very small¾on the order of 10 nm (100 Å) in diameter¾so that the thermal energy of the particles is large enough to overcome the magnetic interactions between particles. If the particles are too large, magnetic interactions will dominate and the particles will agglomerate.

The magnetite will be synthesized by a precipitation reaction that occurs upon mixing $FeCl_2$ and $FeCl_3$ with ammonium hydroxide (an aqueous solution of ammonia, $NH_3$). The unbalanced equation for this reaction is as follows:

$$\_\_\ FeCl_3 + \_\_\ FeCl_2 + \_\_\ NH_3 + \_\_\ H_2O \rightarrow \_\_\ Fe_3O_4 + \_\_\ NH_4Cl$$

The surfactant used in this synthesis is tetramethylammonium hydroxide ($N(CH_3)_4OH$ ). The hydroxide ($OH^-$) ions formed in solution tend to bind to the iron sites on the magnetite particles, creating a net negative charge on each particle. The positively-charged tetramethylammonium ions will then associate with the negatively-charged magnetite particles, forming a kind of shell around each magnetite particle. This charged shell raises the energy required for the particles to agglomerate, stabilizing the suspension.




* This experiment is based on syntheses described in the following papers: (1) Palacin, S.; Hidber, P.C.; Bourgoin, J.; Miramond, C.; Fermon, C.; Whitesides, G. *Chem. Mater,* **1996**, *8*, 1316. (2) Jolivet, J.P.; Massart, R.; Fruchart, J. M. *Nouv. J. Chim.* **1983,** *7*, 325. (3) Enzel, P.; Adelman, N.B.; Beckman, K.J.; Campbell, D.J.; Ellis, A.B; Lisensky, G.C., *J. Chem. Educ.* **1999**, *76*, 943. We also thank Jonathan Breitzer for his modifications of the original procedure.

## ***Procedure***

Add 1.0 mL of 2M $FeCl_2$ solution and 4.0 mL of 1M $FeCl_3$ to a 100 mL beaker. Add a magnetic stirring bar and begin stirring. Use a 50 mL buret to add **dropwise** 50 mL of 0.7 M aqueous $NH_3$ solution. Magnetite, a black precipitate, will form. Continue stirring throughout the slow addition of the ammonia solution over a period of 5 minutes.

Turn off the stirrer and immediately use a strong magnet to work the stir bar up the walls of the flask. Remove the stir bar with gloved hands before it touches the magnet.

Let the magnetite settle for a few minutes, then decant (pour off) and discard the clear liquid without losing a substantial amount of solid. Transfer the solid to a weighing boat with the aid of a few squirts from a wash bottle.

Use a strong magnet to attract the ferrofluid to the bottom of the weighing boat. Pour off and discard as much clear liquid as possible. Rinse again with water from a wash bottle and discard the rinse as before. Repeat the rinsing a third time.

Add 2.0 mL of 25% tetramethylammonium hydroxide. Stir with a glass rod to suspend the solid in the liquid. Use a strong magnet to attract the ferrofluid to the bottom of the weighing boat. Pour off and discard the liquid. Move the strong magnet around and pour off any liquid.

Place a cow magnet under the remaining fluid and record your observations. Add ONE drop or less of distilled water if your ferrofluid does not spike easily.

Examine the starting $FeCl_2$ and $FeCl_3$ solids used to prepare magnetite (leave the solids in the sealed zip-loc bags.) How do they respond to a magnet?

Consider the refrigerator magnet provided. Where are the north and south poles? Try dragging the probe strip that is included with the refrigerator magnet over the back of it. Drag the probe along both perpendicular directions. The probe strip contains a small magnet that will help you determine where the poles are. What do the poles look like, and how are they arranged?  Use the probe to measure the distance between two poles in the magnet.

Now place a refrigerator magnet under the ferrofluid, and leave it there for a few minutes.  Does the pattern in the ferrofluid confirm what you found using the probe strip?  Use the ferrofluid to estimate the distance between the poles.

Add a grain of either solid potassium chloride, sodium chloride, or potassium bromide to the ferrofluid.  Stir with the glass rod to dissolve the salt and place the cow magnet under the weighboat.  What does the ferrofluid look like now?  Does it still spike?  Keep adding the salt until you notice a difference, and record how much you needed.  Pool your data with those of groups who tried the other two salts.  What happens if you then add water?  Is the magnetite still in suspension?

Magnetite has the inverse spinel crystal structure. Build or examine a model of a magnetite unit cell using the Solid-State Model kit. The spheres used in this model represent the following:

colorless = $O^{2-}$
blue = iron (II) in octahedral sites
pink = iron (III) in tetrahedral sites
blue spheres spray-painted red = iron (III) in octahedral sites

Show your work for the calculation of the empirical formula from the model structure.

What is the purpose of the surfactant? Explain chemically how the surfactant works. Based on the solid-state model, where do the hydroxides from tetramethylammonium hydroxide associate with the structure?