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Chem 69A

Lab 2

### **Magnetic Nanoparticles: Ferrofluid Synthesis**

In this experiment we synthesized superparamagnetic nanoparticles via iron reduction and suspended them in kerosene, creating a ferrofluid solution.

#### **Experimental**

Materials:

- Oleic acid
- Ferric chloride solution
- Steel wool
- Distilled water
- Ammonia
- Kerosene

Procedure:

Day 1

1. Add 12.180 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  to beaker with 30 mL  $\text{dH}_2\text{O}$  – this creates the ferric chloride solution of about 1.5 M
2. Dilute 10 mL ferric chloride solution with 10 mL  $\text{dH}_2\text{O}$  then add about 3-5 cm steel wool and stir for about 30 min until solution turns green. During this time,  $\text{FeCl}_3$  is reduced to  $\text{FeCl}_2$ .
3. Cover  $\text{FeCl}_2$  beaker and remaining  $\text{FeCl}_3$  beaker and leave for 1 week.

Day 2

1. Filter  $\text{FeCl}_2$  solution into round bottom flask to remove excess steel wool
2. Add 20 mL  $\text{FeCl}_3$ , then slowly add 50 mL ammonia over 30 minutes. During this time, the ammonia acts as a base ( $\text{OH}^-$ ) in solution, and will form unstable complexes with the

$\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. These complexes are unstable in basic conditions, and will dehydrate to form  $\text{Fe}_3\text{O}_4$ , magnetic nanoparticles, leaving water and chloride ions in solution.

3. Next, submerge flask in water bath at  $90^\circ\text{C}$  and slowly add 5 mL oleic acid. The oleic acid acts as surfactant molecules, coating the magnetic nanoparticles with a hydrophobic outer layer. The ammonia will evaporate during heating, leaving coated molecules in aqueous solution. Solution should be heated slowly over 1.5 hours, but our heating setup malfunctioned and heating was stopped after 20 minutes (see Discussion for details).
4. Once solution has cooled, add 100 mL kerosene to flask. The hydrophobic particles should be pulled out of aqueous solution into the kerosene, leaving two distinct solution layers in the flask. Carefully decant the kerosene layer to isolate final product- magnetic nanoparticles suspended in solution- ferrofluid!

Observations:

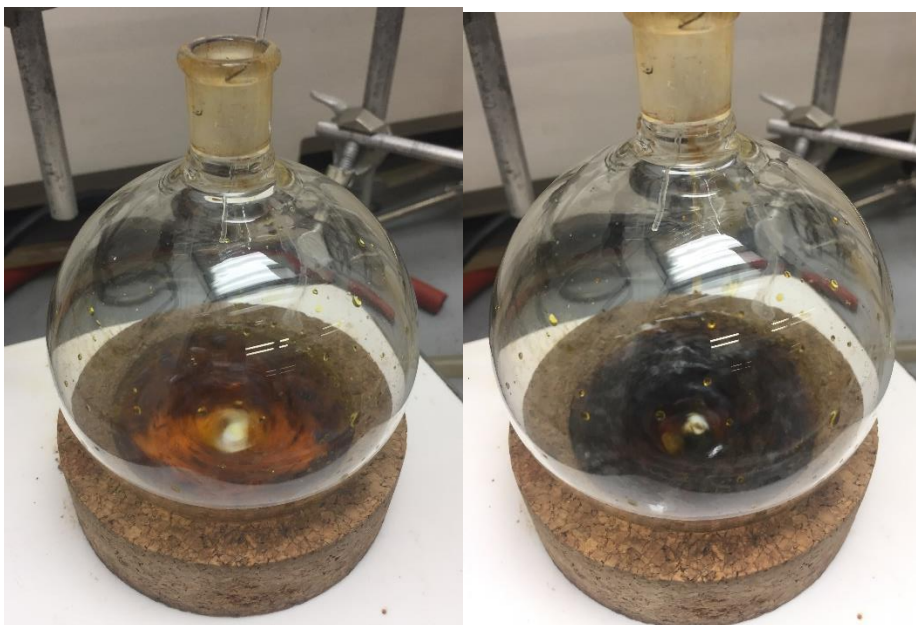
Day 1

1.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is a opaque, yellow solid with large crystalline flakes. Addition of water creates a clear, dark orange solution. When diluted, color is slightly lighter.
2. Addition of steel turns solution a dark, murky brown that is mostly opaque. Solution turned slightly more green as more steel was added and solution was stirred.

Day 2

1.  $\text{FeCl}_2$  solution looks the same after one week in lab- dark, murky brown/green. After filtering, solution is a clear and very light green.
2. The reserved  $\text{FeCl}_3$  solution also had no change in appearance after one week- remained clear, bright orange. Mixing the two liquids produced a clear, bright orange solution.

3. Addition of ammonia (a clear and colorless liquid) turned solution opaque black, with black specks of precipitate (nanoparticles).



4. Oleic acid is a viscous, clear, light yellow liquid. When added to Fe solution, no change was observed.



5. Flask overheated in water bath causing ammonia to boil too rapidly- solution was lost to water bath as it boiled over.



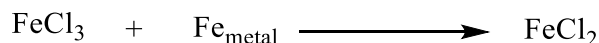
6. Addition of kerosene caused no color change. After swirling and waiting several minutes, two distinct layers formed in flask- the darker kerosene layer on top (with particles suspended), and the lighter aqueous layer on the bottom.
7. Final solution was opaque black and responded to magnet placed on outside of beaker.

## Results & Discussion

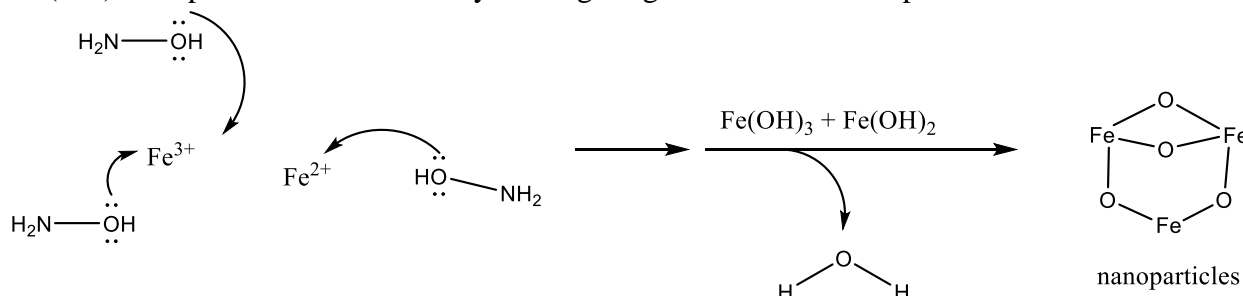
There were several sources of error in this lab that could have impacted the final product. First, when creating the  $\text{FeCl}_2$  solution from  $\text{FeCl}_3$  and steel wool, the solution did not turn a bright green as expected. This could indicate that less iron was reduced than expected, which might have been observed if the molar ratio of  $\text{FeCl}_3$  and steel wool was wrong. The most notable error occurred on Day 2 when heating the Fe-ammonia solution. Unfortunately, the flask containing solution was unable to be completely suspended in the water bath as it heated due to physical constraints of the clamping apparatus. This forced the bottom of the flask to be in direct contact with the bottom of the water bath glass, resulting in an overheating of solution which caused the ammonia to boil over. Because the flask could not be raised, it could not be taken out of the water bath as it was overheating, resulting in a large amount of solution lost to the water bath. Assuming all ammonia had boiled off, we stopped heating the solution after the ammonia stopped boiling over, cutting the heating time down from 1.5 hours to 30 minutes. This was

likely premature; later when adding the kerosene, it the aqueous layer was only slightly lighter in color than the organic layer, indicating that much of the iron nanoparticles remained in aqueous solution (likely in unevaporated ammonia, which is miscible with water).

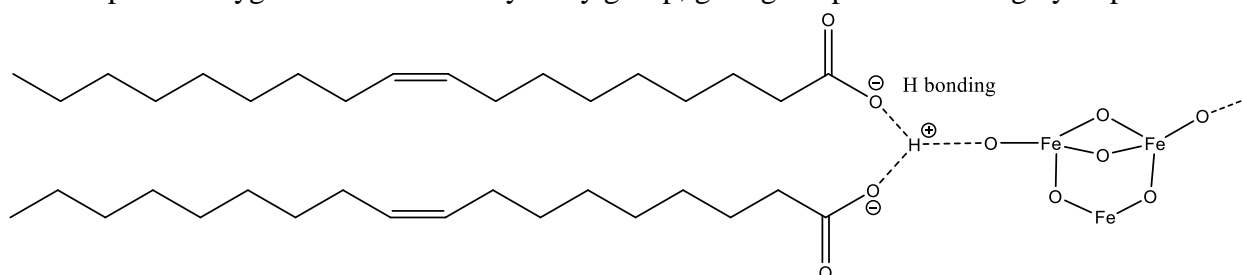
This synthesis was composed of several reactions. First, addition of Fe metal (steel wool) to aqueous  $\text{FeCl}_3$  caused the iron to reduce, forming  $\text{FeCl}_2$ .



The following week,  $\text{FeCl}_3$  and  $\text{FeCl}_2$  reacted with ammonia, first forming unstable  $\text{Fe}(\text{OH})_2$  /  $\text{Fe}(\text{OH})_3$  complexes which then dehydrated giving  $\text{Fe}_3\text{O}_4$  and  $\text{H}_2\text{O}$  as products.



The addition of oleic acid coated the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles, forming H bonds between the complexed oxygen and the acid's hydroxy group, giving the particles a long hydrophobic tail.



This allowed them to be removed from aqueous solution with the addition of kerosene, with Van der Waals forces attracting the two hydrophobic components. The  $\text{Fe}_3\text{O}_4$  demonstrates superparamagnetism, (ferrimagnetism) with  $3d_6 4s_2$  valence electrons. The difference in spin directions creates a magnetic field, while the mix of higher energy 3d electrons and the lower energy 4s electrons give the magnetite ferrimagnetic properties; the magnetic moments of these electrons are opposite direction but not of the same magnitude, creating spontaneous magnetization.

## Conclusion

This lab demonstrated the ease of synthesizing magnetic nanoparticles, which have a wide range of application in technology and biomedical fields. Because many biological functions are on the 'nano' scale (things such as organelles, proteins, etc.), nanoparticles have important applications for biotechnology. Magnetic nanoparticles can serve as multifunctional bionanomaterials, which are the basis of technology used in Recombinant DNA technology, antibody synthesis, biosensors, and more.