Synthesis of Cadmium Sulfide Nanoparticles
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I. Abstract

This experiment is an introductory study of Cadmium sulfide nanoparticles. The Cadmium sulfide nanoparticles are inverse phase micelles.[2] Micelles are an aggregate of surfactant molecules dispersed in a liquid colloid[1], and are used in a wide variety of different biochemical and industrial applications. Specifically, this lab studies the shift in the absorption spectrum from the bulk sample of CdS to the micelle CdS absorption spectrum. This shift in absorption can aid in calculating the micelle radius. The experimentally obtained average shift is 71nm. Using this average the micelle radius was found to be 2.15nm.

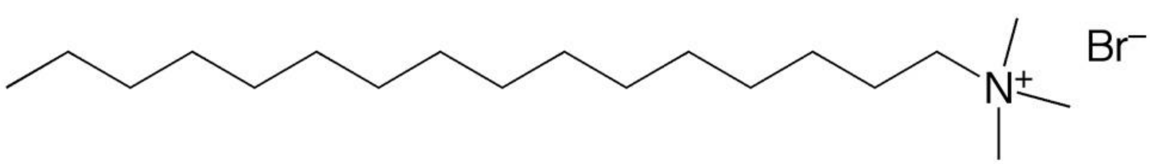
II. Learning Objectives

1) Interpret UV-Vis absorption spectra
2) Apply the concept of polarity to Micelle formation

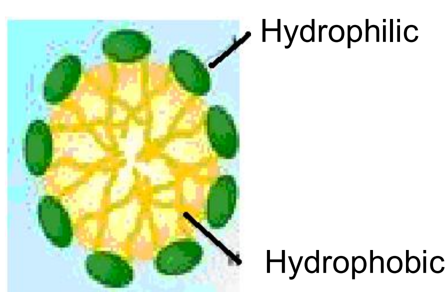
III. Introduction

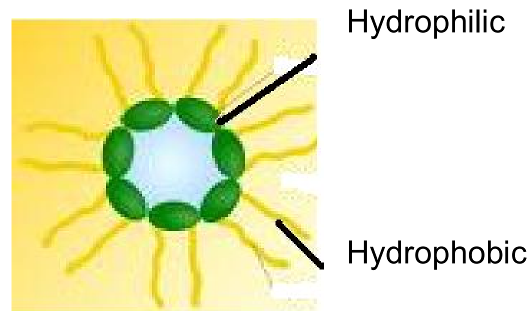
A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. Surfactant molecules are organic compounds that are amphiphilic. Amphiphilic means that they have both a polar (hydrophilic) end and a non-polar (hydrophobic) end. Through this understanding a micelle can be defined as a nanoparticle of an organized organic molecule in a particular solvent.

In the synthesis of cadmium sulfide (CdS) nanoparticles we will be using hexadecyltrimethylammonium bromide as the surfactant molecule. This molecule does not dissolve well in aqueous or organic solvents, but it is essential in making the micelle. The hexadecyltrimethylammonium bromide structure is shown below:



There are different types of micelle phases. The two phases that will be focused on are the normal and inverse cylindrical phases. The normal phase micelle is produced when it is in a polar solution and the polar end of the surfactant is attracted to the polar solvent. The hydrophobic non-polar hydrocarbons form the core of the micelle, and the polar end of the surfactant forms the outer layer of the micelle. This is also known as the oil-in-water micelle. The inverse cylindrical phase is formed in just the opposite environment. The solvent is non-polar. In this way the hydrocarbons make the outer layer and the polar end makes the core of the micelle. This is known as the water-in-oil micelle.

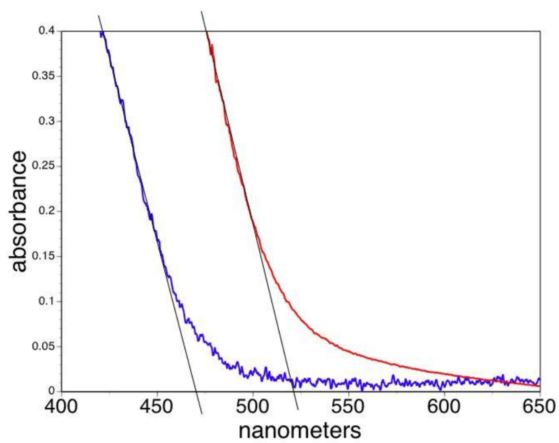




Aqueous Solvent Organic Solvent

In order to form the cadmium sulfide micelles, hexadecyltrimethylammonium bromide will be mixed with pentanol in a hexane solution. Pentanol is a cosurfactant that has two mainfunctions. The first function of pentanol is that in relative amounts it controls the size of the micelles. Pentanol is also used as a capping agent to stabilize the CdS particles.

Cd+ micelles are made and mixed with S- micelles which produce CdS particles. CdS is found in the core of the micelle. The aqueous solution serves as a nanoreactor and the particles cannot grow bigger than the micelle. This phenomenon has an effect on the quantum size of the micelle. Since there is a difference in size from the bulk CdS and the micelle the absorption spectrum can be taken for each and than compared. There will be a shift of wavelength based on size. This change in wavelength can be calculated and used to find the radius of the CdS micelle. An example of the shift phenomenon and equation is shown below.



$\lambda^{bulk} = 512$ nm
$E_g = h\ c\ /\ \lambda$

The x-intercept of the linear portion of the absorbance as a function of wavelength graph is a measure of E_g.

$$E_g^{nano} = E_g^{bulk} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r}$$

$e = 1.60\text{x}10^{-19}$ C
$\varepsilon_0 = 8.85\text{x}10^{-12}$ $C^2/N/m^2$
$\varepsilon = 5.7$
$h = 6.63\text{x}10^{-34}$ J s
$c = 2.998\text{x}10^{8}$ m/s
$m_e^* = 1.73\text{x}10^{-31}$ kg
$m_h^* = 7.29\text{x}10^{-31}$ kg

$$r = \frac{-\left(\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right) + \sqrt{\left(\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right)^2 + \left(E_g^{nano} - E_g^{bulk}\right)\frac{h^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)}}{2\left(E_g^{nano} - E_g^{bulk}\right)}$$

culation

λnano= 495nm
Eg nano= hc/λ
Eg nano=
(6.63E-34)(3.0E8)/495E-9m
Eg nano= 4.018E-19J

λbulk= 550nm
Eg bulk= hc/λ
Eg bulk=
(6.63E-34)(3.0E8)/550E-9m
Eg bulk= 3.616E-19J

$$r = \frac{-\left(\frac{(1.8)(1.60E\text{-}19)^2}{4\pi(5.7)(8.85E\text{-}12)}\right) + \sqrt{\left(\frac{(1.8)(1.60E\text{-}19)^2}{4\pi(5.7)(8.85E\text{-}12)}\right)^2 + \left(4.018E\text{-}19 - 3.616E\text{-}19\right)\frac{(6.62E\text{-}34)^2}{2}\left(\frac{1}{1.73E\text{-}31} + \frac{1}{7.29E\text{-}31}\right)}}{2\left(4.018E\text{-}19 - 3.616E\text{-}19\right)}$$

r = 2.34nm

IV. Materials

*0.012M $CdCl_2$ (0.110g in 50mL distilled water)
*0.012M Na_2S (0.144g in 50mL distilled water)
0.20g hexadecyltrimethylammonium bromide
4mL Heptane
1mL Pentanol
Mortar and pestle
2 test tubes

2 small magnetic stir bars
Magnetic Stirrer
Plastic Cuvetts
Volumetirc pipets, 1 1mL, 2 5mL

* pre-made

V. Procedure

1) Turn on the UV-Vis, and connect it to the computer. It will take a little time. Go onto the other steps.
2) Obtained about 5 ml each of the $CdCl_2$ solution and the Na_2S solution in separate, small vials.
3) Test the reagents $CdCl_2$ and Na_2S by adding a drop of each together. If a yellow color appears this shows that the Na_2S solution is good. If the mixture stays clear, remake the Na_2S solution.
4) Returning back to the UV-Vis, it should be connected. Take a baseline.
5) Place equal amounts of $CdCl_2$ and Na_2S into a cuvet, mix gently with pipet (do not make bubbles).Immediately obtain a visible absorption spectrum, using an empty cuvet as the blank. Visually note the change in color before and after adding the Na_2S to the $CdCl_2$.
6) Set up two clean test tubes over two separate magnetic stirrers.
7) Place 0.20g of hexadecyltrimethylammonium bromide to test tube one. Add a small stir bar to each test tube.
8) Add 4.0mL of Heptane and 1.0mL of 1-Pentanol into test tube one. Note: Remember that the amount of pentanol is the capping agent and changes the size of the micelle. Make sure that the pentanol doesn't get stuck on the side of the test tube. Stir to give a suspension.
9) With volumetric pipet transfer a little over 2.5mL of the suspension into the second test tube.
10) To test tube one, add 0.1mL (3 drops) of 0.012M of $CdCl_2$. Add the solution drop-wise until the suspension in the test tube clears, don't add more than 3 drops.
11) Add 0.1mL (3 drops) of 0.012M Na_2S to test tube 2. Add the solution drop-wise until the suspension in the test tube clears. IF THE SOLUTION CLEARS BEFORE ADDING ALL THREE DROPS DON'T ADD MORE.
12) Place the solution from test tube two into test tube one. Solution could either have a light yellow hue or be clear.
13) Record the visible absorption spectrum in either a glass or plastic cuvet.

VI. Questions

1) What is a micelle? State it in your own words. Draw a diagram and label its parts.

2) What is the difference between a normal and reverse phase micelle? What micelle phase does the Cadmium Sulfide nanoparticle form into?

3) What part does pentanol play in forming the micelle?

4) What two changes occur between in the absorption spectra of the CdS solution and the CdS micelles? Talk about the difference in absorbance and shift in wavelength.

5) When the formation of the micelle has occurred, where is the location of the CdS salt? What is the other salt byproduct that is formed?

6) If there was a shift in the absorption spectra from 575cm-1 to 480cm-1, would the micelle be smaller or bigger than the original sample?

7) What are two practical uses for micelles?

8) What was the radius of your micelle

VII. References

Images of Normal and Inverse Phase Micelles. (2007). Retrieved April 19,2008.
Website: http://en.wikipedia.org/wiki/Micelle

Linsensky, George and Hansen, Paul.(2005). “Synthesis of Cadmium Sulfide Nanoparticle.” Retrieved on March 24, 2008.
Website: http://mrsec.wisc.edu/Edetc/nanolab/CdS/text.htm

Pre-made Materials

0.012 M Na_2S solution

1. Weigh out 0.144g of the powder Na_2S, place in a mortor and grind into a find powder.
2. Place the powdered Na_2S in a 50mL graduated flask and fill it with the deionized water to the mark.

0.012 M $CdCl_2$ solution

1. Weigh out 0.110g of $CdCl_2$ into a 50 ml graduated flask, and fill the flask up to the line. Swirl mixture until all the dissolves.

VIII. Answers

1) A micelle is clusters of organized surfactant, organic compounds that have a polar and non-polar head, that form in a heterogeneous mixture. Main definition: A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid.
2) A) Normal phase: The polar region is in contact with the solvent. (Polar head, Polar solvent) B)Reverse phase: The non-polar chain region is in contact with the solvent. (Non-polar chain, Non-polar solvent) CdS micelles are reverse phase.
3) The pentanol controls the size of the micelle, it also acts as a capping agent to stabilize the CdS particles.
4) Absorbance: In the solution the CdS is dilute in the micelle solution. Shift: The size of the particles determines the shift in wavelength.
5) A) CdS is located in the core of the micelle. B) NaCl.
6) Smaller
7) Answer Dependant
8) Based off of data.

IX. Conclusions and Placement

This lab is very interesting, but not for general chemistry students. There is some difficulty in creating the micelles and the calculation might be a little difficult to understand. The suspensions in the test tubes will not always clear, but will still form micelles that have the appropriate absorption shift. This lab might be good for analytical chemistry because it is dealing with absorption, concentration and pH, but doesn't focus on titration. This will give the students a break from titration, but leads to the same types of concepts. Further calculations can be done on the concentration of micelles based off of absorption (Beers Law). Applications of micelles can also be discussed (for example in biochemistry and industry) during analytical chemistry to make the topic interdisciplinary. The absorption spectra are in the laboratory notebook.

Chemicals

CdO

Oleic Acid

Selenium

Trioctylphosphine

Technical Grade Octadecene (ODE)

Supply List for 10 Students

100 Small test tubes

10 Test tube racks

10 tubes for ice (big enough to fit the test tube rack into)

Ice

10 Heating mantles

10 Variacs

10 Thermometers capable of measuring 225 ^{o}C

10 Round bottom flasks (each)

- 10 ml
- 25 ml

10 Syringes (capable of delivering 0.4 ml) and medium size needle (≥ 10 cm long).

10 Glass Pipettes

10 Volumetric pipettes (each)

- 1 ml
- graduated 1ml to deliver 0.6ml
- 10 ml
- 5 ml