EXPERIMENT 3

A COLORFUL EXTRACTION: USE OF ACID & BASE PROPERTIES TO SEPARATE ORGANIC COMPOUNDS

Reading Assignment: Pavia, sections 12.1 – 12.4, 12.8 – 12.11, Smith Chapter 2

Pre-lab Questions:
1) Questions #1, 2 and 8, Pavia p. 188 - 189.
2) Write a complete flow diagram for the extraction/separation procedure (write this in your duplicate notebook pages under “procedure.”
3) A compound distributes between water (phase 1) and benzene (phase 2) with $K_p = 2.7$. If one gram of the compound is dissolved in 100 mL water, how much compound would be extracted by three 10 mL portions of benzene? How much compound would be extracted by one extraction with 30 mL benzene?
4) Calculate the theoretical amount of 2.5 M NaOH (10%) solution needed to convert the benzoic acid to its water-soluble salt. Is the combined volume of NaOH used in the extractions sufficient for complete deprotonation of benzoic acid?

Chemicals: Mixture of benzoic acid, $m$-nitroaniline, and azobenzene (1:1:1)
diethyl ether
10% NaOH (aq.)
3 M sulfuric acid (aq.)
sat. NaCl (aq.)
conc. HCl
anhydrous MgSO₄

![Chemicals](benzoic_acid.png)

![Chemicals](azobenzene.png)

![Chemicals](m-nitroaniline.png)

In this experiment, a mixture of three compounds is separated into its components using their acid-base properties. Purification of the components is accomplished by recrystallization and identification is made by melting point.
The partitioning of the components is adjusted during this experiment by manipulation of the pH of the extraction phases, taking advantage of the pKa values for the functional groups. Be sure to include the approximate pKa values in your report.


**Experiment**

Transfer 1.5 g of the mixture of benzoic acid, *m*-nitroaniline, and azobenzene to a 100 mL Erlenmeyer flask. Add approximately 40 mL of ether to dissolve the sample (add more if necessary to dissolve all of the sample), and transfer the solution to a 125 mL separatory funnel.

Add 10 mL of the 10% NaOH solution and swirl to mix. Stopper the funnel and carefully shake it, with frequent venting. After the contents are thoroughly mixed, place the separatory funnel in a ring stand, allow the layers to separate, and drain the aqueous phase into a 100 mL beaker labeled "A". Repeat two more times with 10 mL 10% NaOH each time, adding each aqueous phase to the beaker A.

With the organic phase in the separatory funnel, add 10 mL of 3 M sulfuric acid solution, shake thoroughly as before, allow the layers to separate. **WATCH FOR EMULSIONS! If an emulsion forms, add saturated sodium NaCl solution (brine), and allow layers to separate.** Drain the aqueous phase into a 250 mL beaker labeled "B". Repeat two more times with 10 mL 3 M sulfuric acid solution, adding each aqueous phase to the beaker B.

To the remaining organic phase, add 30 mL of the saturated NaCl solution, shake thoroughly as before, and drain off and discard the aqueous phase (place in the aqueous/organic waste container.) Pour the organic phase into a 100 mL Erlenmeyer flask labeled "C", add anhydrous MgSO₄ until it no longer forms clumps and remains free-flowing. (about 3 g.) Do a vacuum filtration using a Büchner funnel, and evaporate the solvent using the rotary evaporator.

Obtain a weight and determine a crude yield. Submit your labeled product in a small vial to your TA.

Briefly heat the beaker labeled A to evaporate any remaining ether, cool in an ice bath, then cautiously add concentrated hydrochloric acid slowly until a pH of 1 is reached. Crystals should begin to fall out of solution. After approximately 15 minutes in the ice bath, filter the product using vacuum filtration and wash the crystals with a small amount of cold water. Allow crystals to dry.

Obtain a weight and determine a crude yield. Submit your labeled product in a small vial to your TA.
To the contents of beaker B, slowly add $\approx 70\text{mL}$ (more if necessary) of 10% sodium hydroxide until a pH of 10 is reached. Cool to room temperature, then transfer to a 250 mL separatory funnel, add 20 mL ether, and swirl to mix. Stopper the funnel and carefully shake it, with frequent venting. Drain the aqueous layer into an Erlenmeyer flask, and pour the ether layer into another 100 mL Erlenmeyer flask labeled B. Pour the aqueous phase back into the separatory funnel, and extract again with 10 mL ether. Drain the aqueous layer into a Erlenmeyer flask, and pour the ether layer into the Erlenmeyer flask labeled B. Pour the aqueous phase back into the separatory funnel, and extract again with 10 mL ether. Drain and discard the aqueous layer in the aqueous waste container, and pour the ether layer into the Erlenmeyer flask labeled B. Pour the combined contents of Erlenmeyer flask B back into the separatory funnel. Add 30 mL of the saturated NaCl solution, shake thoroughly, and drain off and discard the aqueous phase (place in the aqueous/organic waste container.) Pour the organic phase into a clean and dry 100 mL Erlenmeyer flask labeled B, then add anhydrous MgSO$_4$ until it no longer forms clumps and remains free-flowing. Do a vacuum filtration using a Büchner funnel, and evaporate the solvent using the rotary evaporator.

Obtain a weight and determine a crude yield. Submit your labeled product in a small vial to your TA.

**Cleanup**

Transfer all waste into the aqueous/organic waste container.

**Post-lab Questions:**
1) Write a balanced equation for the acid-base reaction between $m$-nitroaniline and HCl. Using a pK$_a$ table, predict which way the equilibrium is favored.
2) Write a balanced equation for the acid-base reaction between benzoic acid and KOH. Using a pK$_a$ table, predict which way the equilibrium is favored.
3) What would have happened if you switched the first two extractions of the original mixture (extracted the with 3 $M$ sulfuric acid first, followed by saturated 1.5 $M$ NaOH second?) Draw a flow chart using the style shown in Figure 12.10 in Pavia (page 184) to show where all of the three components of the mixture would be found following these two extractions.
4) Problem #4ac, Pavia, p.188.
5) Benzoic acid precipitated when the aqueous solution of sodium benzoate in beaker A was acidified. If benzoic acid failed to precipitate after acidification, how would you recover benzoic acid from beaker A?