Investigative Acid/Base/Neutral Extraction of a Three-Component Mixture

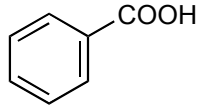
Organic Chemistry Lab

Revised 7/10/17

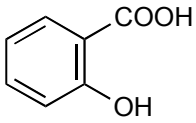
Some mixtures of organic compounds may be separated by exploiting differences in their acidic or basic properties. Read the discussion in your text describing this extraction strategy and explore the web site on this topic at the University of Alberta's organic labs web site: http://www.chem.ualberta.ca/~orglabs/Interactive%20Tutorials/separation/mastercopy/Extraction.htm. This website has great animation that will help you to visualize the chemistry that is going on in these extractions!

The experiment[1] that you will use has been adapted from an article in the *Journal of Chemical Education*. Over the course of two lab periods, we will separate a mixture of an acidic substance, a basic substance, and a neutral substance using acid-base reactions to change the solubility of these materials. The options for each of these kinds of materials are given below. Note that your mixture will contain only one of each type of material, and it will probably be different from others in your lab! Once the substances are separated you will identify which substances were in your mixture by color, mp, IR and proton NMR and quantify your recovery of each one.

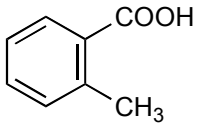
Acidic Substance Options:



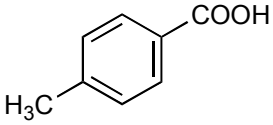
benzoic acid



salicylic acid

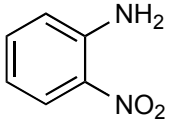


2-toluic acid

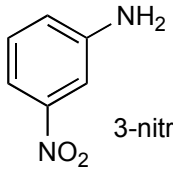


4-toluic acid

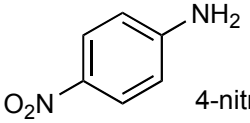
Basic Substance Options:



2-nitroaniline

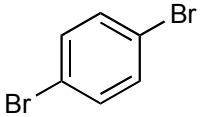


3-nitroaniline

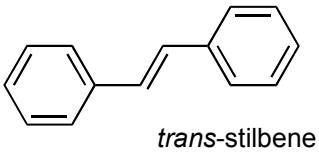


4-nitroaniline

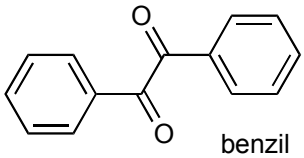
Neutral Substance Options:



1,4-dibromobenzene



trans-stilbene



benzil

Prior to the first lab period, using the experimental directions written below, you should write a step-by-step procedure as you usually would prior to lab. You should prepare a table of physical properties, some of which are included at the end of this lab. *During the lab*, you must also record notes and observations of the details of your experiment as you proceed, as usual.

Prior to the second lab period, you will also need to include a flow chart that outlines your procedure. During the first recitation for this lab, we will talk about constructing such flowcharts.

---

[1] Hobbs, G .D. ; Woodyard , J. D. *J. Chem. Ed.* **1982**, *59*, 386.

Experimental

Dissolve ~ 2 g (know exact quantity!) of your mixture of equal masses of your acidic, basic and neutral substances in 50 mL diethyl ether in an appropriately sized flask. Pour the mixture into a separatory funnel, and rinse the flask with a little extra ether to complete the transfer.

First extraction. Extract this mixture with three 15 mL portions of 10% aqueous NaOH solution. "Extract with three 15 mL portions" means to first add one 15 mL portion of 10% aqueous NaOH to the ether solution in the separatory funnel. Cap the separatory funnel with a glass stopper, invert, and shake or swirl the immiscible solutions together for at least 5 minutes. Carefully vent the funnel through the stopcock regularly during this process. Finally, with the stopcock closed, turn the funnel right side up, set it in a ring clamp, and remove the glass stopper from the top. Drain the bottom layer (is it aqueous or organic?) that separates into a clean flask. Repeat this process with the other two portions of aqueous base solution. Combine the aqueous extracts in a beaker, label it as "first extracts", and set it aside.

Second Extraction. Extract the remaining ether solution with three 15 mL portions of 3 M aqueous HCl. Use the same process described above. Combine these aqueous extracts in a beaker, label it as "second extracts", and set it aside.

Third Extraction with work-up. Pre-dry the remaining ether layer by extracting with three 15 mL portions of saturated aqueous NaCl, using the extraction procedure outlined above. Combine the aqueous portions and set aside for later disposal. (Be sure that you are setting aside the right solution!) Transfer the ether layer that remained in the separatory funnel through the top opening into an Erlenmeyer flask and dry it with solid anhydrous sodium sulfate by adding a scoop of this solid drying agent to the solution; it will not dissolve. Swirl the mixture and note that the solid drying agent clumps up; if it is all clumped, add more drying agent and swirl again. When some of the drying agent is not clumped, you have added enough. Leave the mixture to dry for about 10 minutes. After the solution is "dry", filter the solid drying agent using gravity filtration; rinse the filtered drying agent with a little ether (which you may add to your ether solution) to get all of the material. Allow the filtered ether solution to sit open in your hood at RT or use very gentle heat, so that the ether can evaporate from the solution and leave a solid in the flask. Recrystallize this material from ethanol. When these crystals are dry, note their color, take their mass and mp, and record their IR and proton NMR spectra. What is this material?

First extraction work-up. Carefully add 6 M hydrochloric acid until a pH of 1 is reached. (Most students need ~14 mL; once you have precipitated a good bit of solid, you can check the pH using pH indicator paper.) Allow the resulting solution to cool to room temperature, then cool further in ice, and collect the resulting precipitate. Recrystallize this precipitate from water. When the crystals are dry, note their color, take their mass and mp, and record their IR and proton NMR spectra. What is this material?

Second extraction work-up. Carefully add 10% aqueous NaOH until a pH of 10 is reached. (Most students need ~80 mL; once you have a good bit of precipitate, you can check the pH using pH indicator paper.) Allow the resulting solution to cool to room temperature, then cool further in ice, and collect the resulting precipitate. Recrystallize this precipitate from water. When the crystals are dry, note their color, take their mass and mp, and record their IR and proton NMR spectra. What is this material?

Cleanup. Three types of waste are generated in this lab.

- *Aqueous Waste*: Combine all aqueous layers, washes, and filtrates. Put this mixture directly into the aqueous hazardous waste bottle labeled for this lab.
- *Halogenated Organic Waste*: Diethyl ether must go in the halogenated hazardous waste container, since some of the mixtures could contain a halogenated substance.
- *Solid Organic Waste*: AFTER your samples are graded, if your instructor does that, then the solids go in the solid hazardous waste bottle.

Prior to turning in your lab notebook write-up, you must

- identify which substances were in your own mixture by using color, mp, IR and proton NMR spectroscopy,
- write the analysis of the IR and proton NMR spectra on the spectra and include them in your notebook,
- measure the mass of each of the recrystallized solids that you isolated and calculate the % recovery for each material, assuming that the initial mixture (of which you must know an exact mass) had exactly equal portions of the three materials,
- tabulate your results, including the ID of each type of substance, its recovered mass, its resulting % recovery, its experimental mp, and its color, and
- turn in all three isolated materials, which will be judged for purity.

Table of Physical and Hazardous Properties for Acidic, Basic and Neutral Materials.
(Record this table in your lab notebook!)

Chemical	*Mp (°C)*	*Color*	*Hazards*
Benzoic acid	121-125	white	Harmful if ingested, inhaled, or absorbed through skin
2-Toluic Acid	104	white	Irritant
4-toluic acid	177-180	white	Irritant
Salicylic acid	159	white	Irritant- dangerous if severely exposed
2-nitroaniline	71.5	orange	
3-nitroanaline	111-114	golden	Toxic if absorbed through skin. Environmental hazard. Harmful if swallowed
4-nitroanaline	148.5	Bright yellow	Irritant/slightly corrosive. Hazardous
Benzil	94-95	Pale yellow	Harmful if swallowed; irritant
1,4-dibromobenzene	87.3	White	Strong lung irritant, slightly skin irritant
Trans-stilbene	123-125	orange	Harmful if ingested or if it gets in eyes. Environmental hazard