Lab 2. Go Their Separate Ways: Separation of an Acid, Base, and Neutral Substance by Acid-Base Extraction

How can I use an acid-base reaction to separate an acid-base-neutral mixture?

Objectives
1. use acid-base reactions to separate an acid-base-neutral mixture
2. predict product of acid-base reactions
3. predict solubility of acids and bases in organic solvents


Introduction

Acids and bases are a very important class of compounds. Inorganic acids and bases are used extensively in the chemical and the electronics industry. For example, sulfuric acid is the most produced chemical in this country. Organic acids and bases are also very important. A very common organic acid is probably in your kitchen, vinegar which is 5% acetic acid. We can distinguish between acids and bases with various tests (name three test you can use to identify an acid or base). We can also look at the strength of an acid or base (name one lab test you can use to distinguish between a strong acid and weak acid). Another property of acids and bases is that they react with each other. The organic $pK_a$ table is a useful reference to help us determine which acid reacts with which base.

In this lab, you will prepare a mixture of an organic acid, base, and neutral substance. Then, you will separate the mixture into its components by an acid/base extraction. Once you have isolated each component of the mixture, you purify each substance by recrystallization, and then identify and determine the purity by melting point determination.

Materials

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>Neutral</th>
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</thead>
<tbody>
<tr>
<td>benzoic acid</td>
<td>4-tert-butylphenol</td>
<td>dimethoxybenzene</td>
</tr>
<tr>
<td>tert-butyl methyl ether</td>
<td></td>
<td></td>
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<tr>
<td>0.1 M solutions of HCl, NaOH, NaHCO₃</td>
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<td></td>
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<tr>
<td>saturated NaHCO₃ (aq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 M HCl</td>
<td>3 M NaOH</td>
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</table>

Procedure

While you are doing this experiment, try to determine the purpose of each step in the procedure, e.g.,

- Is this reagent reacting with one of the acid, base, or neutral? If so, write a chemical equation that represents the reaction. Is this reagent the limiting reactant or excess reactant?
- If the solvent I just added formed two layers, is the solvent extracting something? Which substance is being extracted?
- What is the reason for heating or cooling?

Record the purpose of each step in your notes.

0. a. Measure about 0.36 g of the solid mixture of benzoic acid (acid), 4-tert-butylphenol (base) and dimethoxybenzene (neutral). You need to know the exact mass because ______. Record the mass of each component of your mixture before you start so you can determine the % recovery of each component. Assume the solid mixture is 1/3 benzoic acid, 1/3 4-tert-butylphenol, and 1/3 dimethoxybenzene.

b. Dissolve your solid mixture in 2 mL of tert-butyl methyl ether in a reaction tube (Tube 1).

1. Separate benzoic acid (acid) from the 4-tert-butylphenol (base) and dimethoxybenzene (neutral) by acid-base extraction.

Make a flow chart of this procedure while you are doing this experiment. See Fig. 1 for the start of your flow chart.

b. Add 2 mL of saturated aqueous sodium bicarbonate. Use the graduations on the side of the tube to measure the amounts.

NaHCO₃ is a base and reacts with benzoic acid and not the 4-tert-butylphenol because ______. (Hint: see $pK_a$ table.) Write a chemical equation that represents the reaction that occurs.

Mix the two layers thoroughly by pulling the two layers into a Pasteur pipet and squirting the layers back into the tube. Repeat this mixing for a few minutes.

c. Allow the layers to separate completely.
Separate the layers by pushing the tip of a Pasteur pipet to the bottom of the test tube and pulling the lower layer into the pipet. (Normally, the lower layer is removed from the mixture because it is easier to make a clean separation this way.) Transfer the lower layer into another reaction tube (Tube 2). The lower layer is the aqueous layer because ______.

Is benzoic acid or benzoate ion (the conjugate base of benzoic acid) dissolved in the lower layer? Draw the structure of this substance.

Fig. 1. Start of flow chart for Lab 2.

d. Extract the ether layer (Tube 1) with an additional 0.3 mL of saturated NaHCO₃ (aq) and combine this extract (which layer, top or bottom?) with the first aqueous extract (Tube 2). (Make sure you mix the layers thoroughly and then allow the layers to completely separate.) You are adding the saturated NaHCO₃ (aq) to the ether layer to make sure any unreacted benzoic acid has _____ and separated from _____.

What substance is in the ether layer? What substance is in the aqueous layer?

e. Extract the combined aqueous extracts (Tube 2) with 0.4 mL tert-butyl methyl ether. This is called backwashing and is used to remove any organic compound that may contaminate the aqueous layer. Discard the ether layer. The ether layer is the top layer because _____.

Tube 2 contains _____ ml of saturated NaHCO₃ (aq) solution and should contain the conjugate base of benzoic acid. Benzoic acid is the _____ (acid, base, or neutral compound).

f. Calculate the volume of concentrated (12 M) HCl is needed to neutralize the NaHCO₃ (aq).
What observation tells you the HCl reacts with NaHCO₃?

Dropwise add this volume of 12 M HCl to Tube 2. Be careful so the CO₂ (g) produced won’t bubble the product over the top of the tube.
Test the solution with litmus paper.
What color do you want the litmus paper to be?

Once you’ve neutralized the NaHCO₃, add one extra drop of HCl. You should see a solid form.
Benzoate ion + HCl -->

Is this solid the conjugate base of benzoic acid or benzoic acid? Hint: which substance, benzoate ion or benzoic acid, is soluble in water?

g. Using a boiling stick, heat the contents of Tube 2 until most of the solid has dissolved. Remove the tube from the heat source and cool the tube slowly to room temperature and then in an ice bath. You should see a solid form because benzoic acid is ____ soluble in hot water than in cold water.

Remove the solvent with a Pasteur pipet. Squeeze the pipet bulb and push the tip of the Pasteur pipet to the bottom of the test tube and carefully suck solvent into the pipet while leaving the solid behind in the test tube.

h. Purify the crude benzoic acid.
Recrystallize the solid benzoic acid from boiling water (this is a single solvent recrystallization).
Prepare a hot water bath. The temperature of the warm water bath is slightly below the boiling point of the recrystallization solvent.

Make a saturated solution of benzoic acid: Place the crude solid in a test tube in the hot water bath. Add the hot water dropwise to the crude solid until all of the solid dissolves. Then, allow the solution to cool slowly to room temperature and then cool in an ice bath.

i. Separate the crystals from the liquid.

What piece of equipment will you use to do this?

Wash the crystals with ice cold water.

Dry the crystals.

How will you dry your crystals?

j. (i) Determine the % recovery of benzoic acid.

(ii) Measure the melting point range.

Record your % recovery and m.p. in Table 2.

2. Separate the 4-tert-butylphenol (base) and dimethoxybenzene (neutral) by acid-base extraction. Tube 1 should contain the 4-tert-butylphenol (base) and dimethoxybenzene (neutral). (Where is the acid compound?)

a. Add 2.0mL of 3 M NaOH (aq) to Tube 1.

NaOH is a base and reacts with 4-tert-butylphenol (base) and not the dimethoxybenzene (neutral) because ____. (Hint: see pKₐ table.)

Write a chemical equation that represents the reaction that occurs.

Shake the mixture thoroughly and allow the layers to separate. Draw off the lower layer with a Pasteur pipet and place it into Tube 3. The lower layer is the aqueous layer because _____.

b. Extract Tube 1 (the ether layer) with two 0.3 ml portions of water, and add the extract to Tube 3. (Mix the layers thoroughly.)

The extract is the bottom layer because ______.

You've separated the 4-tert-butylphenol (base) from the dimethoxybenzene (neutral).

Tube 3 should contain water, unreacted NaOH, and ______. You (or your lab partner) will work with Tube 3.

Tube 1 should contain ether and dimethoxybenzene (neutral). Your lab partner (or you) will work with Tube 1.

3. Separation, isolation, and purification of dimethoxybenzene (neutral).

a. To Tube 1 (the ether layer which contains______), add saturated NaCl (aq) and mix.

You add saturated NaCl (aq) to remove water from the ether solution. (Mix the layers thoroughly.)

Remove the aqueous layer. The aqueous layer is the bottom layer because _____.

b. Add CaCl₂ pellets to the ether layer.

The ether layer contains ____ (benzoic acid (acid), 4-tert-butylphenol (base), or dimethoxybenzene (neutral)?). CaCl₂ pellets are used to remove _____. If the CaCl₂ clumps together, this means the ether solution is still ____ so add more CaCl₂.

Remove the ether layer with a Pasteur pipet. (In other words, separate the ether liquid from the solid drying agent. Squeeze the pipet bulb and push the tip of the Pasteur pipet to the bottom of the test tube and carefully suck solvent into the pipet while leaving the solid behind in the test tube.)

Wash the drying agent two times with ether.

Why should you wash the drying agent?

What should you do with the ether wash?

c. In the hood, evaporate the ether solvent under reduced pressure. Pour your dry ether solution into a small filter flask. Stopper the flask. Attach vacuum tubing to the filter flask sidearm and vacuum line. Turn on the vacuum. You should see the solvent boil off (evaporate) and have your solid product left in the flask.

What is the boiling point of ether at room pressure? What happens to the boiling point of ether when the pressure drops?

If you do not see the solvent evaporate, warm the ether solution with your warm hands or by placing the flask in a warm water bath.

This solid is ______ (benzoic acid (acid), 4-tert-butylphenol (base), or dimethoxybenzene (neutral)?)

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d. Purify the crude dimethoxybenzene. 
Recrystallize the solid dimethoxybenzene from ethanol (this is a single solvent recrystallization). 
Measure the mass of crude product. 
Make a saturated solution of benzoic acid: Prepare a warm water bath. The temperature of the water bath is slightly below the boiling point of the recrystallization solvent. Place the crude solid in a test tube in the warm water bath. Place ethanol in a separate test tube in the warm water bath. Add the hot ethanol dropwise to the crude solid until all of the solid dissolves. Then, allow the solution to cool slowly to room temperature and then cool in an ice bath.

Separate the crystals from the liquid. 
What piece of equipment will you use to do this?

Wash the crystals with ice cold water. 
Dry the crystals. 
How will you dry your crystals?

g. (i) Determine the % recovery of dimethoxybenzene. 
(ii) Measure the melting point range.
Record your % recovery and m.p. in Table 1.

Table 1. Acid-Base-Neutral Separation data and results.
<table>
<thead>
<tr>
<th>Acid, base, or neutral?</th>
<th>Benzoid acid</th>
<th>4- tert-butyl phenol</th>
<th>dimethoxybenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Mass, g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube 1, 2, or 3?</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Which acid or base reacted with this compound?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass recovered, g</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>% recovery</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Experimental m.p., °C</td>
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<td></td>
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</tr>
<tr>
<td>True m.p., °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recrystallization solvent</td>
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</tbody>
</table>

4. Separation, isolation, and purification of 4-tert-butylphenol (base).
Tube 3 contains ____ ml of NaOH and should contain the conjugate base of 4-tert-butylphenol (base compound).
a. Backwash the liquid (this liquid is aqueous because ______) in Tube 3 with 0.3 ml of ether.
What substance are you removing in this step?

Discard the ether wash.
b. Calculate the volume of concentrated (12 M) HCl is needed to neutralize the NaOH (aq).
NOTE: you won’t see bubbles like you did with Tube 2.
Test the solution with litmus paper. Once you’ve neutralized the NaOH, add one extra drop of HCl. You should see solid form.

conjugate base of 4-tert-butylphenol ion + HCl -->
Is this solid the conjugate base of 4-tert-butylphenol or 4-tert-butylphenol?
c. Using a boiling stick, heat the contents of Tube 3 until most of the solid has dissolved. Remove the tube from the heat source and cool the tube slowly to room temperature and then in an ice bath.
You should see a solid form because ______.

Remove the solvent with a Pasteur pipet.
d. Purify the crude 4-tert-butylphenol.
Recrystallize the solid 4-tert-butylphenol from boiling water (this is a single solvent recrystallization).
Make a _____ solution of 4-tert-butylphenol: Prepare a hot water bath. The temperature of the warm water bath is slightly below the boiling point of the recrystallization solvent. Place the crude solid in a test tube in the hot water bath. Add the hot water dropwise to the crude solid until all of the solid dissolves. Then, allow the solution to cool slowly to room temperature and then cool in an ice bath.
Separate the crystals from the liquid. What piece of equipment will you use to do this?

Wash the crystals with ice cold water. Dry the crystals.
e. (i) Determine the % recovery of 4-tert-butylphenol.
(ii) Measure the melting point range.
Record your % recovery and m.p. in Table 1.

5. a. Analyze your procedure from your first run. Identify the specific procedural step(s) can you do better or change to improve your results.
b. If we have time, repeat the experiment.


Report
1. Discuss the % recovery and purity (based on melting point) of each component.

2. a. Show your Flow Chart of this separation of the benzoic acid, 4-tert-butyl phenol, and dimethoxybenzene. In your flow chart, identify the steps in which an acid-base reaction occurred.
b. For each reaction:
   (i) write a chemical equation. Use curved arrows to show how the acid reacts with the base and how each product forms.
   Example: HCl reacting with OH⁻ is shown below.
The arrow starts at the lone pair of the base and ends at the H on the acid. An O-H bond forms. But 2 bonds cannot form to H so the H-Cl bond breaks.

(ii) Explain why this reaction occurs based on pKₐ. Hint: compare the pKₐ of the acid to the pKₐ of the conjugate acid of the base. Include numbers.
(iii) What observation told you that a reaction occurred?
c. If you did a 2nd run, identify the specific procedural step(s) that you did better or changed to improve your results from Run 1 to Run 2.