EXTRACTION

OVERVIEW: You will be given an unknown mixture to separate by the technique of extraction. If needed, you will purify these compounds by recrystallization. You will identify the compounds that made up the mixture by determining their melting points.

BACKGROUND: Extraction is one of the most useful separation techniques in organic chemistry. The concept of extraction is that of separating the components of a mixture based on differences in solubilities in two immiscible solvents. Often one of the solvents is an organic compound and the other is water. In extraction one compound dissolves in one solvent while other compounds, by-products, or starting materials dissolve in the other. Since the two liquids are immiscible, they form two layers and can be separated using a separatory funnel. The name extraction refers to the fact that one component is extracted from a mixture and leaves other components of the mixture in another solution.

The unknown mixture you will be using contains two compounds. Both are soluble in methyl t-butyl ether (MTBE, an organic solvent) but insoluble in water. One is a neutral compound. The other is either an acidic compound (a carboxylic acid, RCOOH) or a basic compound (an amine, RNH₂).

If it is an organic acid, it will react with aqueous base (NaOH) to form a water-soluble salt.

\[
\text{RCOOH} + \text{NaOH} \rightarrow \text{RCOONa} + \text{H₂O}
\]

If it is an organic base, it will react with aqueous acid (HCl) to form a water soluble salt.

\[
\text{RNH}_2 + \text{HCl} \rightarrow \text{RNH}_3^+\text{Cl}^-
\]

In either case, the mixture is separated by producing a salt, which is extracted into the water layer, leaving the neutral compound in the ether layer.

SAFETY: Methyl t-butyl ether is very volatile. It is also very flammable. Do not allow flames, sparks, or hot plates during this lab. The procedure must be done under the hood at all times. The separatory funnel and any flasks containing ether must not be removed from the hood.
PROCEDURE: *Determination of acid or base*: To test whether your unknown mixture contains either an acidic or basic component, mix a small portion of the solid, about the size of a green pea, with the same amount of solid sodium bicarbonate on a watch glass. Add a few drops of water and stir. Effervescence of carbon dioxide gas indicates that the mixture contains an organic acid component (carboxylic acid).

\[ RCOOH + HCO_3^- \rightarrow RCOO^- + CO_2 \]

No effervescence indicates the mixture contains an organic base (amine).

\[ RNH_2 + HCO_3^- \rightarrow \text{No Reaction} \]

Use the above test to decide whether the mixture contains an acid or a base. Confirm your decision with your instructor before proceeding. Discard the test mixture in the sink with running water.

*Separating the components*: Get the separatory funnel from your glassware kit and place it in a ring on a ring stand in the hood. Do not support it with a clamp. Be sure the stopcock is secure and closed (normally horizontal is closed and vertical is open, but confirm this with your separatory funnel).

In the hood, dissolve approximately 2 g of the unknown in approximately 30 mL of methyl t-butyl ether (MTBE) in an Erlenmeyer flask. Be sure as much as possible of the solid completely dissolves. Carefully pour the ether solution into the separatory funnel. (If the solid is not completely dissolved, carefully decant the solution.)

If the unknown contains an organic acid (as indicated by the bicarbonate test above), you will extract it with aqueous base (NaOH). If the unknown contains an organic base, you will extract it with aqueous acid (HCl). Now add to the separatory funnel 15 mL of 3M NaOH or 3M HCl, whichever is appropriate. Stopper the funnel. (Keep the funnel in the hood throughout this experiment.)

Holding the separatory funnel as demonstrated by the instructor, turn it upside down and open the stopcock to release the pressure. Be sure the stopcock is not pointing toward anyone – it must be pointed into the hood! Close the stopcock and
shake. Vent again. Repeat the shaking and venting processes several more times.

With the stopper in place, allow the layers to separate. Remove the stopper and drain off the lower layer into an Erlenmeyer flask. *(Is this the water solution or the ether solution?)* This layer contains the salt of the acid or base component. Label the flask and set it aside.

The neutral component is in the ether layer. Still working under the hood, wash the ether layer with 15 mL of saturated NaCl solution, using the same procedure as before. This step is to remove (extract) most of the water that has dissolved in the ether layer. Again drain off the lower aqueous layer and discard it in the sink with running water.

Pour the ether layer (which still contains the neutral component) out through the top of the separatory funnel into an Erlenmeyer flask. Add several scoops of anhydrous magnesium sulfate (MgSO₄) and swirl the solution. This will absorb the last traces of water from (that is, completely dry) the ether solution. You will know your solution is dry when it is crystal clear and some of the solid magnesium sulfate floats easily in the liquid when it is swirled (the “snow test”). If the solution is cloudy or contains droplets of water, it is not dry. Add more magnesium sulfate and swirl until the solution is perfectly clear.

Decant the solution from the solid into a 50 or 100 mL round bottom flask from your glassware kit. Remove the ether using the rotary evaporator as directed by your instructor. Discard the used MgSO₄ solid in the solid waste containers (not the sink).

The solid that remains when the ether is evaporated is the neutral component. Scrape the solid out of the round bottom flask, using a spatula (bend the spatula necessary). Allow the solid to dry thoroughly on a piece of filter paper while you continue to work.

The aqueous solution that was set aside earlier contains the salt of the acid or base component. Pour the solution into a 100 mL beaker and cool it in an ice bath.

**Recovering the original acid or base compound from the solution:** If your original mixture had an acid component, add 3M HCl in small amounts, with stirring. Continue adding acid until pH paper indicates that the solution is acid. The solid carboxylic acid component will precipitate.
RCOONa + HCl → RCOOH(s) + NaCl

If the original mixture had a base component, add 3M NaOH in small amounts, with stirring. Continue adding base until pH paper indicates the solution is basic. In this case, the solid amine component will precipitate.

RNH₃Cl + NaOH → RNH₂(s) + H₂O + NaCl

Cool the resulting suspension, and collect the solid by suction filtration, as you have done previously. (Recall that for suction filtration, you need a Büchner funnel and a filter flask.) Scrape the solid onto a piece of dry filter paper and dry the solid completely. Discard the filtrate in the sink with running water. The solid is the acid or base component.

Using the procedure you learned last week, determine the melting point range for each component of mixture (the neutral compound and the acid or base compound).

**DISPOSAL:** When you have finished, place the solids in the appropriate waste jars in the side hood.

**IDENTIFICATION OF THE COMPOUNDS:** Consult the *CRC Handbook of Chemistry and Physics* (or any other reliable reference) to find the melting points of each of the compounds in the following list. This melting point is called the literature value since it has been reported as a part of the chemical literature, the published results of working chemists. Then, using the melting points of you have determined for the two compounds, identify them.

<table>
<thead>
<tr>
<th>acid</th>
<th>neutral</th>
<th>base</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzoic acid</td>
<td>acetanilide</td>
<td>3-nitroaniline</td>
</tr>
<tr>
<td>4-nitrobenzoic acid</td>
<td>anthracene</td>
<td>4-nitroaniline</td>
</tr>
<tr>
<td>phenyl acetic acid</td>
<td>naphthalene</td>
<td>4-toluidine</td>
</tr>
</tbody>
</table>

**LAB NOTEBOOK:** Your lab notebook should include a table containing each of the above compounds and their literature melting points. In your lab report draw a table to summarize your results. Include in your table for each compound 1) whether it is the acid or base or neutral component of the mixture; 2) name of the compound; 3) literature melting point; 4) observed melting point range, and 5) the appearance of the crystals of each compound.