**EXPERIMENT 2: Covalent Bonding - Benzoic Acid from Ethyl Benzoate by Base Hydrolysis**

**Introduction**

Ethyl benzoate (boiling point 211-213°C, melting point -34°C) belongs to a class of compounds called esters. It is a sweet smelling, colourless, liquid used in perfumery under the name *Essence de Niobe*; in the manufacture of *Peau d’Espagne*; and as an artificial fruit essence. It is soluble in organic solvents but insoluble in water.

When ethyl benzoate is shaken with water two liquid layers form. The upper layer is ethyl benzoate (less dense) and the lower layer is water. There is no clear indication of any reaction taking place. A more careful study shows that ethyl benzoate reacts very slowly with water and is hydrolyzed\(^1\) to give benzoic acid and ethanol but the reaction does not go to completion. However, ethyl benzoate is found to react much faster with aqueous sodium hydroxide, the reaction going to completion, to give sodium benzoate (water soluble) and ethanol (miscible with water).

\[
\text{Reaction 1} \quad \begin{align*}
\text{ethyl benzoate} & \quad \text{aqueous sodium hydroxide} \\
(C_9H_10O_2) & \quad (\text{aq})
\end{align*} \quad \rightarrow \quad \begin{align*}
\text{sodium benzoate} & \quad \text{ethanol} \\
(C_7H_5O_2Na) & \quad (\text{C}_3\text{H}_7\text{OH})
\end{align*}
\]

This process is called base hydrolysis (or saponification) of an ester and is used in this experiment to first obtain sodium benzoate solution, and then benzoic acid from ethyl benzoate. The ethanol may be recovered by simple downward distillation from the reaction mixture and collected as a solution in water. But this step is omitted in this experiment to allow it to be completed in the available time. The sodium benzoate is non-volatile and remains in solution. Treatment of this solution with hydrochloric acid (Reaction 2) releases the free benzoic acid as a white crystalline solid that is washed with ice cold water and then recrystallized from hot water.

\[
\text{Reaction 2} \quad \begin{align*}
\text{sodium benzoate(aq)} & \quad \text{HCl(aq)} \\
(C_7H_5O_2Na) & \quad (\text{aq})
\end{align*} \quad \rightarrow \quad \begin{align*}
\text{benzoic acid} & \quad \text{NaCl(aq)} \\
(C_7H_6O_2) & \quad (\text{s})
\end{align*}
\]

**Laboratory Techniques**

Three important new techniques are covered in this experiment:

The reflux distillation of a liquid.

Hot gravity filtration.

The recrystallization of a solid.

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\(^1\)Hydrolysis = Hydro - “water”, lysis - “to split apart”
In addition, the use of laboratory glassware with ground glass joints is introduced.
Procedure 1 - Base Hydrolysis of Ethyl Benzoate Using Reflux Distillation

Ethyl benzoate is heated with aqueous sodium hydroxide. At the start of the reaction the flask contains two immiscible layers, a liquid layer of the water insoluble ethyl benzoate floating on the aqueous sodium hydroxide layer. As the ethyl benzoate reacts, water soluble products are formed and the upper layer decreases in size until a homogeneous solution is obtained and the reaction is complete.

Fig. 1: Reflux Distillation

1. Clean the glassware and lightly grease the ground glass joints. Use only a small amount of the lubricant supplied (on the upper bench top) to grease the joints, then rotate them together to form a smooth seal. Excess grease may be wiped off with a towel.

2. Set up the apparatus as shown in Figure 1 with the condenser attached to the flask in the reflux position.
   **NOTE**: When assembling apparatus, use care in clamping to prevent joints from being pulled apart allowing vapours to escape. **Do not clamp too tightly or the glass may break.** Never store glassware with the joints connected as they may “freeze” together.

3. Carefully detach the 100 mL round-bottomed flask from the apparatus and dispense 5.0 mL of ethyl benzoate (density = 1.047 g·mL⁻¹) into it. Add 30 mL (graduated cylinder) of 2.0 mol·L⁻¹ sodium hydroxide followed by 3 or 4 boiling granules to the ethyl benzoate in the flask and reattach it to the apparatus. **Have the apparatus checked by an instructor before starting step 4.**

4. Heat the flask gently over a low flame so that the liquid refluxes². The mixture in the flask should be shaken almost continuously to speed up the hydrolysis reaction.

5. When all of the oily drops of ester have disappeared (about 15 minutes) and the solution is almost clear when shaken, stop heating and cool the reaction mixture to room temperature by holding an ice bath up around the flask.

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²hydrolysis = hydro - “water”, lysis - “split apart”
Procedure 2 - Formation of Crude Benzoic Acid

1. Using the clamp as a handle, pour the contents of the 100 mL round bottom flask into a 400 mL beaker and place the beaker in an ice bath. In the fume hood, use a graduated cylinder to measure 10 mL of concentrated (12.0 mol·L⁻¹) hydrochloric acid and add it cautiously to the contents of the 400 mL beaker while stirring the solution with a glass rod. (Rinse the graduated cylinder with cold water as soon as you have transferred the hydrochloric acid.)

2. Allow the mixture to cool to room temperature and collect the precipitated solid using a Buchner flask and funnel (vacuum filtration -- remember to put filter paper in the funnel!).

Procedure 3 - Recrystallization of Benzoic Acid

1. Wash the solid in the Buchner funnel with a little ice-cold deionized water and then (using the rubber policeman on your glass rod) carefully transfer it to a 250 mL Erlenmeyer flask. Set up a stand with a ring clamp and wire gauze. Clamp the flask to the stand and add 150 mL of hot tap water and a few boiling granules to the solid. Heat the mixture until all of the solid dissolves, stirring the mixture frequently to prevent bumping.

2. Filter the solution while it is still very hot (use the clamp as a handle) through a fluted filter paper into another clean 250 mL Erlenmeyer flask. The funnel holding the filter paper must be hot to prevent premature crystallization of the product (hold it in a beaker of hot tap water until needed). Since the solution must be completely filtered before any product crystals form you must work quickly to prevent product loss during filtration.

3. Allow the solution to cool at room temperature for 5 minutes and then cool it in an ice bath.

4. Dry the crystals by pressing them between filter papers. Finally, transfer the crystals to a pre-weighed, labelled (see sample below) sample vial and reweigh to determine the mass of product obtained.

Collect the crystals by vacuum filtration using a Buchner flask and funnel. Rinse the crystals with a little ice cold water and allow them to dry under suction in the Buchner funnel for a few minutes.

[Name and formula of substance]

Yield: _______ g ______%
### Laboratory Report

<table>
<thead>
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<th>Name</th>
<th>Bench Number</th>
<th>Date</th>
<th>Lab. Slot</th>
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#### Summary Table (Reactants)

<table>
<thead>
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<th>Compound</th>
<th>Formula</th>
<th>Amount used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mass or volume</td>
</tr>
<tr>
<td>ethyl benzoate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrochloric acid</td>
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#### Benzoic acid product

<table>
<thead>
<tr>
<th></th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of vial + lid + benzoic acid</td>
<td></td>
</tr>
<tr>
<td>mass of empty vial + lid</td>
<td></td>
</tr>
<tr>
<td>mass of benzoic acid</td>
<td></td>
</tr>
</tbody>
</table>

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#### Calculations - show all details

1. Calculate the mass of ethyl benzoate and hence the number of moles used in procedure 1.

2. Calculate the number of moles of sodium hydroxide used in procedure 1.

3. Calculate the number of moles of concentrated hydrochloric acid added in procedure 2 to precipitate the benzoic acid.
Calculations continued -- show all details

4. Write the equations leading to formation of benzoic acid from ethyl benzoate.


6. Calculate the theoretical yield of benzoic acid.

7. Calculate the percentage yield of benzoic acid.
Questions

1. Why does shaking the reaction mixture speed up the reaction?

2. Explain, in terms of the relevant interparticle forces, why the initial mixture of ethyl benzoate and aqueous sodium hydroxide forms two layers.

3. Explain, in terms of the relevant interparticle forces, why the product mixture of the first step is homogeneous (i.e. one layer).
Questions

1. Methyl benzoate reacts with base according to the following equation:

\[
\text{C}_8\text{H}_8\text{O}_2 + \text{NaOH} \rightarrow \text{C}_7\text{H}_5\text{O}_2\text{Na} + \text{CH}_3\text{OH}
\]

When the reaction is complete the methanol is distilled off and collected. The remaining solution is acidified with \(\text{HCl(aq)}\) to yield a precipitate of benzoic acid, \(\text{C}_6\text{H}_5\text{COOH}\).

(a) Write an equation to represent the formation of benzoic acid from the acidification of the solution remaining after the distillation of methanol.

(b) What is the limiting reagent when 5.0 mL of methyl benzoate (density = 1.089 g·mL\(^{-1}\)) is hydrolyzed with 30 mL of 2.0 mol·L\(^{-1}\) \(\text{NaOH(aq)}\)?

(c) Calculate the percentage yield of benzoic acid from the reaction if 4.18 g of benzoic acid is recovered after acidification with excess hydrochloric acid and recrystallization of the benzoic acid formed.