Experiment 4

EXTRACTION

Separation of aspirin, β-naphthol, and naphthalene by extraction

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Principle: Extraction relies on the **solubility of substances** into solvents and the **insolubility of the solvents** into each other.

It also means the selective **transfer of any solute or impurity** from one solvent to another. One of the solvents is usually **water** and the other is a **water-insoluble solvent** such as ether or chloroform. Removal of the solvent yields the substance to be isolated.

Frequently, the **solute is not completely transferred** from one solvent to another.
In these cases, **repeated extractions** would be required to transfer the solute from one solvent to the other.

When an organic solution (ether) of a substance “A” is shaken with water, substance “A” will distribute itself between water and ether. The concentration of ”A” in each solvent is proportional to its solubility.

The ratio of concentrations in each solvent is the Distribution Coefficient: K_D.

$$K_D = \frac{\text{Concentration of “A” in Water}}{\text{Concentration of “A” in Organic Solvent}} \quad \text{or} \quad K_D = \frac{[A] \text{ in } S_x}{[A] \text{ in } S_o}$$

$$= \frac{\text{Solubility of “A” in water (g/mL)}}{\text{Solubility of “A” in Org. Solvent (g/mL)}}$$

- if $K_D > 1$, solute *A* will be mainly in the *extracting* solvent
- *increasing the volume of extracting solvent (Sx) will result in a net increase in the amount of solute A in Sx*

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Example 1 (**single extraction**):

a) Given the solubility of solute “A” is 0.56 g/100 ml of ether and 0.14 g/100 ml of water, find K_D.

$$K_D = \frac{\text{Solubility in water}}{\text{Solubility in Org. Solvent}} = \frac{0.14 \text{ g/100 ml}}{0.56 \text{ g/100 ml}} = 0.25$$

b) If a 40 mg of “A” were present in 50 ml of ether and extracted with 50 ml of water, then the amount of ”A” removed [extracted] by water can be calculated:

Assume the amount of ”A” removed by water = Y mg

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$$K_D = \frac{\text{Concentration of "A" in Water}}{\text{Concentration of "A" in Organic Solvent}} =$$

$$\frac{\text{Y mg/ 50 ml of water}}{\text{(40 mg -Y)/ 50 ml of ether}} = 0.25$$

Y = 8 mg of solute extracted by water.
Remaining amount in ether = 40-8= 32mg

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Example 2 (**multiple extraction**):

$$FA = \frac{C_f}{C_i} = \left(\frac{V_o}{K_D V_x + V_o}\right)^n$$

FA: fraction of solute *A* remaining in the original solvent
Vo and Vx= volume (mL) of original and extracting solvents

Single extraction
KD= 5, Vo = 10 mL, Vx= *30 mL*

$$FA = \left(\frac{10}{5x30 + 10}\right)^1 = 1/16$$ *Mass= 1/16x 40mg= 2.5mg remains in So*

Multiple extraction
KD= 5, Vo = 10 mL, Vx= *10 mL, Vx= 10 mL and 10 mL*

$$FA = \left(\frac{10}{5x10 + 10}\right)^3 = 1/216$$ *Mass= 1/216x 40= 0.18mg remains in So*

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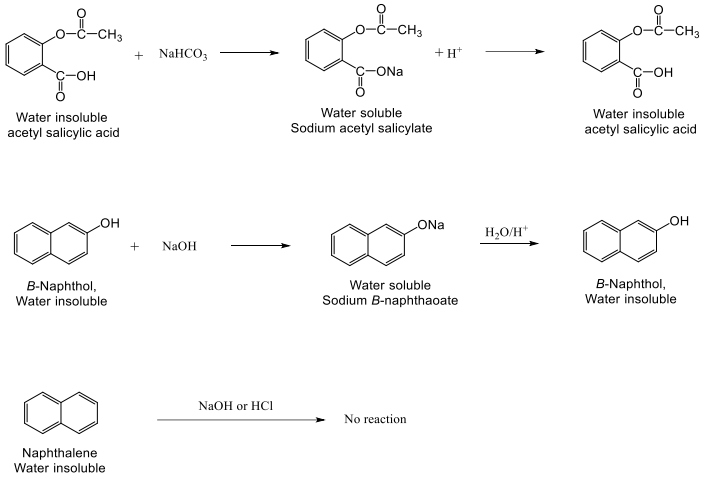
Separation of mixture of Aspirin, *ß*-naphthol, and naphthalene.

Aspirin, *ß*-naphthol, and naphthalene: soluble in diethyl ether and insoluble in water



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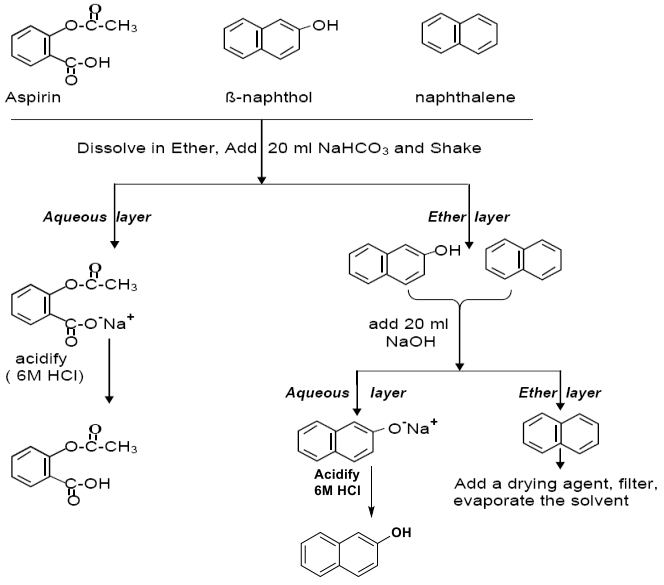
Separation Scheme



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Using the Separatory Funnel

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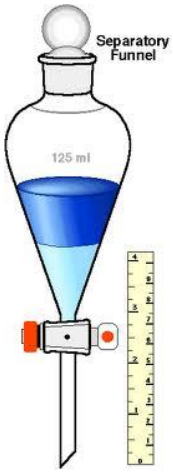

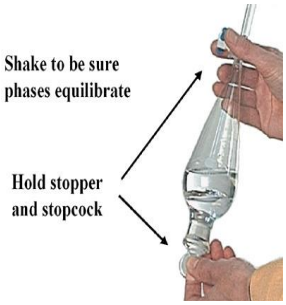

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PROCEDURE

1. Obtain a 6 gram sample of an aspirin/β-naphthol/naphthalene mixture .
2. Weigh and transfer to a 125 ml Erlenmeyer flask.
3. Add 50 ml of diethyl ether and dissolve the sample by gently swirling.
4. Pour the solution into a 250 ml separatory funnel. Make sure the stopcock is in the closed position.
5. Rinse the flask into the separating funnel with several small portions of ethyl ether.
6. Add 20 ml of 5% sodium bicarbonate ($NaHCO_3$) to the separatory funnel. This will react with the aspirin to form a water soluble salt.
7. Stopper the separating funnel. While holding the stopper in place with your fingers, invert the funnel and shake several times.
8. Slowly open the stopcock to relieve any pressure in the funnel.
9. Close the stopcock and repeat the shaking - pressure release procedure until no further pressure build up is noticed. This will indicate the aspirin/NaHCO3 reaction is completed.

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Extraction of Aspirin

1. Place the separatory funnel into the ring stand to hold the funnel upright.
2. Remove the stopper from the funnel.
3. Open the stopcock on the separatory funnel and draw off the lower aqueous portion of the liquid into a 125 ml Erlenmeyer flask.
4. Since some of the aqueous solution is still dissolved in the ethyl ether, add an additional 20 ml portion of 5% $NaHCO_3$ and repeat the extraction procedure. Combine this second aqueous portion with the first.
5. Place the 125 ml flask into a warm water bath (60^0C) and gently heat. This will evaporate any ether still present in the aqueous portion. (No overheat)
6. Cool the aqueous solution to room temperature.
7. Carefully and slowly, with constant stirring, add 6M HCl with stirring until a pH of 1-2 is indicated by pH paper. The HCl will convert the water soluble salt into the insoluble aspirin. The aspirin will start to precipitate out as the pH is reduced.
8. Collect the crystals by suction filtration on a Buchner funnel and use ice cold water to rinse.
9. Allow to air dry. Weigh, determine melting point, and calculate the percent composition of aspirin in the mixture.

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Extraction of β-naphthol

1. Add 20 ml of 10% NaOH to the separatory funnel containing the ethyl ether portion.
2. Using the extraction technique learned previously, invert, shake, and relieve pressure until no further pressure build up is noted. The NaOH is forming a sodium salt with the β-naphthol which is soluble in the aqueous phase.
3. Draw off the lower aqueous portion into a 125 ml Erlenmeyer flask.
4. Add a second 20ml portion of 10% NaOH to the funnel and extract.
5. Combine this second aqueous portion with the first one.
6. Carefully add 6M HCl to a pH of 1-2. The HCl will convert the β-naphthol salt back into β-naphthol which is insoluble in water at the reduced pH. The β-naphthol will precipitate out.
7. Collect the crystals by suction filtration on a Buchner funnel and use ice cold water to rinse.
8. Allow to air dry. Weigh, determine melting point, and calculate the percent composition of β-naphthol in the mixture.

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Collection of Naphthalene

1. Transfer the ether remaining in the funnel to a 125 ml Erlenmeyer flask.
2. Rinse the funnel with an additional 10 ml of ethyl and combine.

3. Add anhydrous calcium chloride ($CaCl_2$), about 1/10 the volume of the ethyl ether solution, to the 125 ml flask containing the ether. Since there is about 1.5% water still dissolved in the ether, the anhydrous $CaCl_2$ will absorb the remaining water.

4. Allow the ethyl ether solution to stand over the anhydrous $CaCl_2$ for 15-20 minutes with occasional swirling.

5. Decant the ethyl ether solution off the $CaCl_2$ into a dried 125 ml Erlenmeyer flask. Use a cotton plug in an ordinary funnel if necessary.

6. Evaporate the liquid on a hot water bath in the hood. After the ether has evaporated, naphthalene should remain behind.

7. Weigh, determine melting point, and calculate the percent composition of naphthalene in the mixture.

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Drying agents

The capacity of the drying agent refers to the amount of water absorbed by the drying agent(per unit weight).

A good drying agent should have a high efficiency and a rapid rate of drying.

Examples of commonly used drying agents include
magnesium sulfate, $MgSO_4$
sodium sulfate and, Na_2SO_4
calcium chloride. $CaCl_2$

Saturated salt solution (NaCl): when large amount of water is present in the organic solvent

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Advantages of using ethyl ether as an extracting solvent :

high solvent power,
relative inertness,
low boiling point.

Ether has some **disadvantages** such as its high flammability.

Another minor problem is that ether dissolves some water.

One needs to treat the ether solution with a **drying agent** to remove traces of water.

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