Experiment 4

EXTRACTION

Separation of:

aspirin, β-naphthol, and naphthalene

Theory of Extraction

- **Liquid-liquid extraction** is one of the most common methods for removing an organic compound from a mixture.

- **Extraction** is used in isolation of natural products and in purification of products from most chemical reactions.

- **Extraction** involves distributing a solute, **A**, between two immiscible liquids, **Sx**, the **extracting phase,** and **So**, the **original phase.**

- The immiscible liquids are mainly water and some organic solvent, such as diethyl ether, $(C_2H_5)_2O$, or dichloromethane, CH_2Cl_2

- At a given temperature, the amount of **A, in g/mL**, in each phase is expressed *quantitatively* in terms of a constant ,**K** , commonly called the **partition coefficient (or distribution coefficient)**.

Theory of Extraction

- The partition coefficient **K** is simply dividing the solubility of **A** in the extracting solvent **Sx** by the solubility of **A** in the original solvent **So**.

$$K = \frac{[A] \text{ in } S_x}{[A] \text{ in } S_o}$$

- The mathematical expression in the equation shows that *at equilibrium*, the ratio of concentrations of **A** in the two phases will always be constant.
- Increasing the volume of extracting solvent **Sx** will result in a net *increase* in the amount of solute **A** in **Sx**.

$$K = \frac{\text{grams of } A \text{ in } S_x}{\text{grams of } A \text{ in } S_o} \times \frac{\text{mL of } S_o}{\text{mL of } S_x} = \frac{A_x}{A_o} \times \frac{V_o}{V_x}$$

Theory of Extraction

Examples

a) Given the solubility of solute "x" is 0.56 g/100 ml of ether and 0.14 g/100 ml of water, find K.

$$K = \frac{\text{Solubility in organic solvent}}{\text{Solubility in water}} = \frac{0.56 \text{ g/100 ml}}{0.14 \text{ g/100 ml}} = 4$$

b) If a 40 mg of "x" were present in 50 ml of water and extracted with 50 ml of ether, calculate the amount of "x" removed [extracted] by ether .

Assume the amount of "x" removed by ether = Y mg

$$\frac{\text{Y mg/ 50 ml of ether}}{\text{(40 mg -Y)/ 50 ml of water}} = 4$$

Y = 32 mg of solute extracted by ether.

Remaining amount in water = 40-32= 8mg

Theory of Extraction

Is it better to perform a single extraction with all of the solvent, or to perform several extractions with smaller volumes? Will *three* extractions with 10-mL portions of ether provide better recovery of solute than a *single* one with 30 mL?

The fraction, **FA**, of **A** still in the original solvent is obtained through the generalized equation below, in which **Ci** and **Cf** are the *initial* and *final* concentrations, respectively when *n* extractions are performed.

$$F_A = \frac{C_f}{C_i} = \left(\frac{V_o}{KV_x + V_o}\right)^n$$

$C_i = A_o/S_o$ and $C_f = A_1/S_o$, respectively

where A_o = amount (grams) of solute in S_o before extraction

$A_1 = (A_o - A_x)$ = amount (grams) of solute in S_o after extraction

V_o and V_x = volume (mL) of original and extracting solvents, respectively

Theory of Extraction

According to the previous equation if **K = 5**, we obtain **FA** = 1/16 for a single extraction with 30 mL of diethyl ether, and 1/216 for three extractions with 10-mL portions. This means that 6.3% of **A** remains in the aqueous phase when one extraction, whereas 0.5% in the case of three successive extractions with the same total volume of solvent.

Requirements for the best recrystallization solvent:

1. The extracting solvent *must not react* chemically with the components of the mixture.
2. The extracting solvent *must be immiscible,* or nearly so, with the original solution.
3. The extracting solvent *must selectively remove* the desired component from the solution being extracted. (The partition coefficient **K** of the component being removed must be high).
4. The extracting solvent *should be readily* separable from the solute. (Use of a volatile solvent).

Theory of Extraction

- **Advantages of using ethyl ether** $(C_2H_5)_2O$,as an extracting solvent :
  - high solvent power
  - relative inertness
  - low boiling point

- **Disadvantages of using ethyl ether :**
  - its high flammability.
  - ether dissolves some water.

- One needs to treat the ether solution with a **drying agent** to remove traces of water. 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 :$MgSO_4$,Na_2SO_4 ,$CaCl_2$

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

Using the Separatory Funnel

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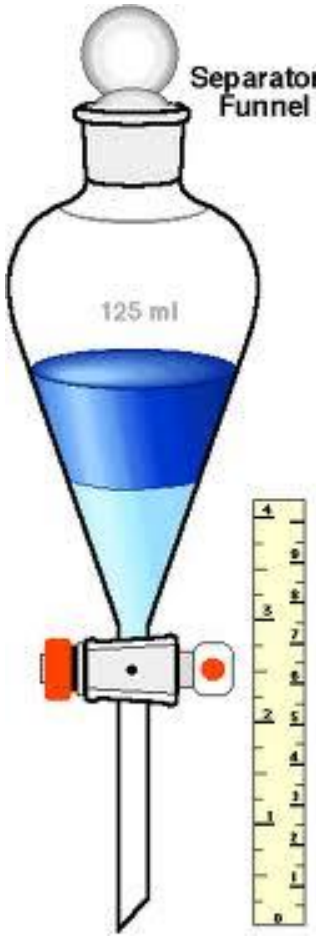


Shake to be sure phases equilibrate

Hold stopper and stopcock

Separatory funnel positioned on iron ring with beaker located to catch liquid if funnel leaks.

Using the Separatory Funnel

There are a number of general guidelines for using separatory funnels:

1. Filling Separatory Funnels.

The stopcock should be closed and a clean beaker placed under the funnel before any liquids are added to the funnel in case the stopcock leaks or is not completely closed. A separatory funnel should never be more than three-quarters full

2. Holding and Using Separatory Funnels.

If the user is right-handed, the stopper should be placed against the base of the index finger of the left hand and the funnel grasped with the first two fingers and the thumb. The thumb and the first two fingers of the right hand can then be curled around the stopcock. Holding the funnel in this manner permits the stopper and the stopcock to be held tightly in place during shaking.

Using the Separatory Funnel

3. Shaking Separatory Funnels.

The shaking process increases the surface area of contact between the immiscible liquids so that the equilibrium distribution of the solute between the two layers will be attained quickly; however, overly vigorous or lengthy shaking may produce **emulsions**

- The funnel must be vented every few seconds to avoid the buildup of pressure within the funnel.
- Venting is accomplished by inverting the funnel with the stopcock pointing upward and away from you and your neighbors and slowly opening it to release any pressure .
- If the funnel is not vented frequently, the stopper may be blown out accidentally; under extreme circumstances the funnel might blow up.
- After shaking and venting the layers are allowed to separate.

Using the Separatory Funnel

4. Layer Identification.

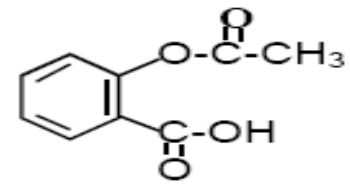
a. Add a few drops of water to the layer you believe to be the aqueous one. Watch closely as you add the water drops, to the top layer in the funnel, to see whether they dissolve. If the drops form a new layer on either the top or bottom of the layer you are testing, then the test layer is organic.

b. Withdraw a few drops of the upper layer with a pipet and add these drops to about 1 mL of water in a test tube. If the upper layer is aqueous, these drops will be miscible with the water in the test tube and will dissolve.

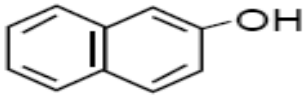
5. Emulsions.

- The two immiscible liquids will not separate cleanly into two distinct layers after shaking, because an **emulsion** may form that results from a colloidal mixture of the two layers.
- An emulsion left unattended for an extended period of time sometimes separates.
- Add a few milliliters of a *saturated* solution of aqueous sodium chloride, commonly called brine, to the funnel and gently reshake the contents. This increases the ionic strength of the water layer, which helps force the organic material into the organic layer.

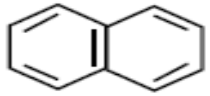
Separation Scheme



Aspirin



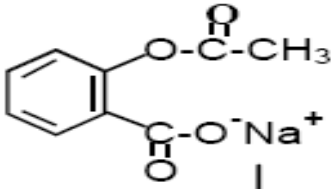
ß-naphthol



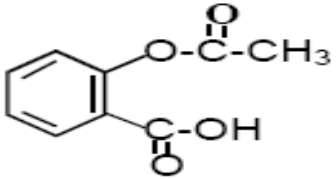
naphthalene

Dissolve in Ether, Add 20 ml $NaHCO_3$ and Shake

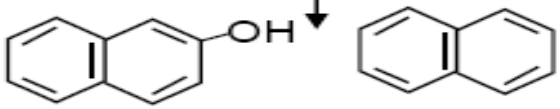
Aqueous layer



acidify
(6M HCl)

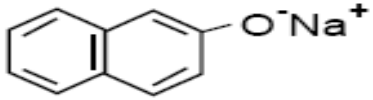


Ether layer

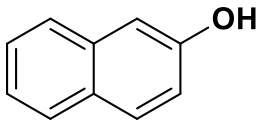


add 20 ml
NaOH

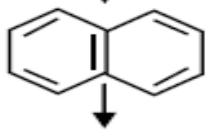
Aqueous layer



Acidify
6M HCl



Ether layer



Add a drying agent, filter,
evaporate the solvent

Procedure

1. Weigh the plastic bag containing your unknown sample (aspirin+βnaphthol + naphthalene mixture) .

2 Transfer to a 125 ml Erlenmeyer flask.

3. Weigh the empty plastic bag (record the number of the unknown first).

4. Add 50 ml of diethyl ether and dissolve the sample by gently swirling ***(Caution: no flame in the lab is on)*** .

5. Transfer the solution into a 250 ml separatory funnel supported on a ring stand with beaker located to catch liquid if the funnel leaks. Make sure the stopcock is in the closed position.

6. Rinse the Erlenmeyer flask with about 5 ml more of ether to ensure complete transfer of the solution.

7. 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.

8. Stopper the separating funnel. While holding the stopper in place with your fingers, invert the funnel and shake several times.

Procedure

9. Slowly open the stopcock to relieve any pressure in the funnel.

10. Close the stopcock and repeat the shaking - pressure release procedure until no further pressure build up is noticed. This will indicate the aspirin/ $NaHCO_3$ reaction is completed.

11. Place the separatory funnel into the ring stand to hold the funnel upright.

12. Remove the stopper from the funnel.

13. Open the stopcock on the separatory funnel and draw off the lower aqueous portion of the liquid into a 125 ml Erlenmeyer flask.

14. Since some of the aqueous solution is still dissolved in the ethyl ether, add an additional 10 ml portion of 5% $NaHCO_3$ and repeat the extraction procedure. Combine this second aqueous portion with the first.

Procedure

15. With the ether still in the separatory funnel add 20 ml of 5% NaOH to the separatory funnel

16. 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.

17. Draw off the lower aqueous portion into a 125 ml Erlenmeyer flask.

18. Add a second 10ml portion of 5% NaOH to the funnel and extract.

19. Combine this second aqueous portion with the first one.

Procedure

20. Transfer the ether remaining in the funnel to a clean dry 100 mL beaker

21. Add about 1 gram of anhydrous drying agent ($CaCl_2$), to the 100 mL beaker containing the ether.(There is about 1.5% water still dissolved in the ether, the anhydrous $CaCl_2$ will absorb the remaining water).

22. Allow the ethyl ether solution to stand over the anhydrous $CaCl_2$ for 5 minutes with occasional swirling.

23. Decant the ether solution into another 100 mL **dry weighed beaker** to remove the drying agent .

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

25. Weigh directly after cooling the beaker, and calculate the percent composition of naphthalene in the mixture.

Procedure

26. Acidify the aqueous sodium bicarbonate solution using diluted acid(10% sulfuric acid or 6M HCl) till the solution is acidic to the blue litmus.

27. Cool the solution in an ice bath for few minutes and **collect aspirin by suction filtration.**

28. Transfer the solid to a piece of paper, let it dry overnight.

29. Weigh your aspirin and calculate and calculate the percent composition of aspirin in the mixture.

Procedure

30. Acidify the aqueous sodium hydroxide solution using diluted acid(10% sulfuric acid or 6M HCl) till the solution is acidic to the blue litmus.

31. Cool the solution in an ice bath for few minutes and **collect** B-naphthol **by suction filtration.**

32. Transfer the solid to a piece of paper, let it dry overnight.

33. Weigh your B-naphthol and calculate and calculate the percent composition of B-naphthol in the mixture.

(Important notice; do not keep your samples in your locker, ask your instructor to assign you a safe locker for that purpose so nobody will tamper with your samples.)