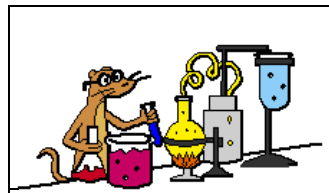


EXPERIMENT 6 - Extraction

Determination of Distribution Coefficient



Purpose:

- To purify samples of organic compounds that are solids at room temperature
- To dissociate the impure sample in the minimum amount of an appropriate hot solvent

Equipment / Materials:

Benzoic acid solution	ring & ring stand	burette	burette clamp
spatula	0.1 M NaOH (or 0.02 M) solution		
separatory funnel	methylene dichloride	125 ml Erlenmeyer flask	
10 and 50 mL graduated cylinders	50 and 100 mL beakers	funnel	

Discussion: Crystallization, purification, and isolation (may only be restricted to a solid) are insufficient ways to separate mixtures of compounds. Extraction is the recovery of a substance from a mixture by bringing it into contact with a solvent, which dissolves the desired material. Partitioning is the separation between two distinct phases (immiscible liquids) and also called fractional separation.

Like recrystallization and distillation, **extraction** is a separation technique frequently employed in the laboratory to isolate one or more components from a mixture. Unlike recrystallization and distillation, it does not yield a pure product; thus, the former techniques may be required to purify a product isolated by extraction. In the technical sense extraction is based on the principle of the **equilibrium distribution** of a substance (solute) between two immiscible phases, one of which is usually a solvent. The solvent need not be a pure liquid but may be a mixture of several solvents or a solution of some chemical reagent that will react with one or more components of the mixture being extracted to form a new substance soluble in the solution. The material being extracted may be a liquid, a solid, or a mixture of these. Extraction is a very general, highly versatile technique that is of great value not only in the laboratory but also in everyday life.

Extraction is a convenient method for separating an organic substance from a mixture, such as an aqueous reaction mixture or a steam distillate. The extraction solvent is usually a volatile organic liquid that can be removed by evaporation after the desired component has been extracted.

The extraction technique is based on the fact that if a substance is insoluble to some extent in two immiscible liquids, it can be transferred from one liquid to the other by shaking it together with the two liquids. For example, acetanilide is partly soluble in both water and ethyl ether. If a solution of acetanilide in water is shaken with a portion of ethyl ether (which is immiscible with water), some of the acetanilide will be transferred to the ether layer. The ether layer, being less dense than water, separates out above the water layer and can be removed and replaced with another portion of ether. When this in turn is shaken with the aqueous solution, more acetanilide passes into the new ether layer. This new layer can be removed and combined with

the first. By repeating this process enough times, virtually all of the acetanilide can be transferred from the water to the ether.

As we stated above, the substance being extracted may be a solid. Extractions of this type will not be conducted here, but they are probably already a part of your own experience. The brewing of tea from tea leaves (or the tea bag that combines extraction and filtration) and of coffee from the ground bean are excellent examples of the extraction of a solid mixture with a hot solvent (water).

In the laboratory one of the more important applications of the extraction process has been its use to remove an organic compound from a solution when distillation is not feasible. Extraction is accomplished by shaking the solution in a **separatory funnel** with a second solvent that is immiscible with the one in which the compound is dissolved, but dissolves the compound more readily. Two liquid layers are formed, and the layer that has most of the desired product in it can be separated from the other. Sometimes not the entire product is extracted in a single operation and the process must be repeated once or twice more to assure a clean separation. It has been found that when two immiscible solvents are shaken together, the solute distributes itself between them in a ratio roughly proportional to its solubility in each. The ratio of the concentration of the solute in each solvent at equilibrium is a constant called the **distribution ratio(d) or partition coefficient (K_d)**.

The larger the value of K_d, the more solute will be transferred to the ether with each extraction, and the fewer portions of ether will be required for essentially complete removal of the solute.

$$K_d = \frac{[\text{solute}]_o}{[\text{solute}]_{aq}} = \frac{C_o}{C_{aq}} = \frac{W_o/V_o}{W_{aq}/V_{aq}}$$

where o and aq refer to the organic (ether) and aqueous layers, respectively, and W_o and W_{aq} are the weights in grams of material dissolved in each respective layer.

C_o = concentration of organic solution and C_{aq} = concentration of aqueous solution

Example (1) - Give at 20° C only 0.24 g of an organic acid “A” dissolves in 100 ml of water, but 2.70 g of the same acid dissolves in 100 ml of ether.

a) calculate the value of partition coefficient.

$$K_d = \frac{[\text{solute}]_o}{[\text{solute}]_{aq}} = \frac{C_o}{C_{aq}} = \frac{W_o/V_o}{W_{aq}/V_{aq}}$$

$$K_d = (2.70 \text{ g} / 100\text{ml}) / (0.24 \text{ g}/100\text{ml}) = 11.25$$

b) calculate the percentage of extraction if 0.12 g of acid extracted in 100 ml of aqueous solution.

$$K_d = (X_o / 100) / (0.12 / 100) \rightarrow 11.25 = (X_o / 0.12)$$

$$X_o = 11.25 \times 0.12 = 1.35 \text{ g, acid extracted in organic phase}$$

$$X_{\text{total}} = X_o + X_{\text{aq}} = 1.35\text{g} + 0.12 \text{ g} = 1.47 \text{ g}$$

$$\% \text{ Ex} = (X_o / X_{\text{total}}) \times 100 = (1.35 / 1.47) \times 100 \approx \mathbf{92 \%}$$

c) calculate the volume of ether required to extract 85% of a 3.00 g of acid “A” in 100 ml solution.

$$X_o = (85\%) \times 3.00 \text{ g} = 2.55 \text{ g} , X_{\text{aq}} = 3.00\text{g} - 2.55\text{g} = 0.45 \text{ g remained in aqueous solution}$$

$$11.25 = (2.55/V_o) / (0.45/100) \rightarrow V_o \approx 51 \text{ ml}$$

- d) calculate the total amount of acid extracted by a double extraction of 50 ml ether in each extraction in part (c).

First extraction (first 50 ml ether)

$$11.25 = (X_{o1}/50) / (X_{w1}/100) \rightarrow 11.25 = (X_{o1}/50) / (3.00 - X_{o1}/100), \text{ solve for } X_{o1}$$

$X_{o1} = 2.57 \text{ g}$ acid extracted in first extraction

$X_{w1} = 3.00 \text{ g} - 2.57 \text{ g} = 0.43 \text{ g}$ acid remained in aqueous solution after first extraction

Second extraction (second 50 ml ether)

$$11.25 = (X_{o2}/50) / (X_{w2}/100) \rightarrow 11.25 = (X_{o2}/50) / (0.43 - X_{o2}/100), \text{ solve for } X_{o2}$$

$X_{o2} = 0.38 \text{ g}$ acid extracted in second extraction

$X_{o(\text{total})} = X_{o1} + X_{o2} = 2.57 \text{ g} + 0.38 \text{ g} = 2.93 \text{ g}$

$$\%E = (2.93/3.00) \times 100 = 97.7 \%$$

Or use the following formula;

$\%E = [1 - (V_{aq} / (V_{aq} + K_d V_o))^n] \times 100$, where n is the number of extraction.

$$\%E = [1 - (100 / (100 + 11.25 \times 50))^2] \times 100 = 97.7 \%$$

Example (2) – Isobutyric acid has a solubility in water (at 25 °C) about one-third of its solubility in diethyl ether; thus $K_d = 3.0$. Imagine 4.0 g of isobutyric acid dissolved in a mixture of 35.0 ml of diethyl ether and 100.0 ml of water.

- What weight of acid is in each layer at equilibrium after first extraction and second extraction?
- Calculate the percentage extraction after second extraction.

Solubility of butyric acid in water = $X \text{ g/ml}$

Solubility of butyric acid in diethyl ether = $3X \text{ g/ml}$

First Extraction

$$X_w = V_w \cdot X = (100.0 \text{ ml})(X \text{ g/ml}) = (100.0) X$$

$$X_o = V_o \cdot 3X = (35.0 \text{ ml})(3X \text{ g/ml}) = (105.0) X$$

$$X_w + X_o = 4.0 \text{ g} \rightarrow 4.0 = (100.0) X + 105 X \rightarrow 4.0 = 205.0 X \rightarrow X = 0.0195 \text{ g}$$

$$X_{w(1)} = (100.0) X = (100.0)(0.0195) = 1.95 \text{ g (remained in water after first extraction)}$$

$$X_{o(1)} = (105.0) X = (105.0)(0.0195) = 2.05 \text{ g (extracted by diethyl ether after first extraction)}$$

Second Extraction

$$1.95 = 205.0 X \rightarrow X = 0.00951$$

$$X_{w(2)} = (100.0) X = (100.0)(0.00951) = 0.951 \text{ g (remained in water after second extraction)}$$

$$X_{o(2)} = (105.0) X = (105.0)(0.00951) = 0.999 \text{ g (extracted by diethyl ether after second extraction)}$$

$$\%E = [(X_{o(1)} + X_{o(2)}) / X_{\text{total}}] \times 100 = [(2.05 + 0.95) / 4.0] \times 100 = \mathbf{76 \%}$$

Extraction solvents

If a solvent is to be used to extract an organic compound from aqueous mixture or solution, it must be virtually insoluble in water, and it should have a low boiling point so that the solvent can be more soluble in the extraction solvent than in water, since otherwise too many extraction steps will be required to remove all of the solute.

Ethyl ether is the most common extraction solvent. It has a very low boiling point (34.5°C) and can dissolve a large number of organic compounds, both polar and nonpolar. However, ethyl ether must be used with great care, since it is extremely flammable and tends to form explosive peroxides on standings.

Methylene Chloride (dichloromethane) has most of the advantage of ethyl ether; in addition, it is nonflammable and denser than water. However, it has a tendency to form emulsions, which can make it difficult to separate the layers cleanly. Other useful solvents and their properties are listed in the following table. Various grades of petroleum ether (a mixture of low boiling hydrocarbons) can be used in place of pentane.

From the foregoing discussions some of the desirable properties of an organic extraction solvent become apparent. (1) It must readily dissolve the substance being extracted but must not dissolve to any appreciable extent in the solvent from which desired substance is being extracted. (2) It should extract neither the impurities nor other substances present in the original mixture. (3) It should not react with the substance being extracted. (4) It should be readily separated from the desired solute after extraction. Few solvents will meet all of these criteria, and in some cases a completely satisfactory solvent cannot be found. Therefore, the scientist must select a solvent system that most nearly approaches the ideal.

Some of the solvents commonly used for extracting aqueous solutions or mixtures include diethyl ether, methylene chloride, chloroform, carbon tetrachloride, benzene, n-pentane, n-hexane, and various mixtures of saturated hydrocarbons from petroleum (petroleum ether, ligroin, etc.). Each of these has a relatively low boiling point so that it may be fairly easily separated from the solute by evaporation or distillation. Methanol and ethanol are not good solvents for extracting aqueous solutions or mixtures because of their solubility in water; however, if an aqueous solution can be saturated with potassium carbonate without affecting the solute, ethanol can be used to extract polar solutes from the solution.

Properties of commonly used extraction solvents

<u>Solvent</u>	<u>b.p. (°C)</u>	<u>D (g/ml)</u>	<u>Comments</u>
Ethyl acetate	77	0.90	Absorbs much of water good
Ethyl ether	34.5	0.90	general solvent; absorb some water, easy to remove; very flammable; vapor should not be inhaled
Methylene dichloride	40	1.34	Good general solvent; easy to dry and remove; suspected carcinogen
Chloroform	62	1.48	Can form emulsion easy to dry and remove; health hazard; suspected Carcinogen
1,1,2-trichloro-Fluoroethane (Freon TF)	48	1.58	Maybe substituted for carbon tetrachloride
Pentane	36	0.63	Easy to dry & remove; very Flammable
Hexane	69	0.66	Easily dried

Extract Solvents

<u>Solvent</u>	<u>Solubility in Water (g/100 ml)</u>	<u>Fire hazard</u>	<u>Toxicity</u>
Petroleum ether	Low	High	Low
Ligroin	Low	High	Low
Hexane	0.02	High	Low
Ethyl ether	6	High	Low
Toluene	0.06	Medium	Medium
Water	Infinite	None	None
Saturated NaCl (aqueous)	Infinite	None	None
Methylene chloride	2	Low	Medium

Criteria for selecting an extracting solvent

- 1) It should be insoluble or slightly soluble with the solvent of the solution being extracted.
- 2) It should have a favorable distribution coefficient for the substance being extracted and an unfavorable distribution.
- 3) It should be able to be easily removed from the extracted substance after the extraction. Since the removal is often by distillation, the solvent should therefore have a reasonably low boiling point.
- 4) It should be chemically inert to the extracted substance, other components in the mixture, and the solvent to the solution being extracted.
- 5) It should be reasonably safe to work with and relatively inexpensive.

The procedure in this experiment involves the use of the separatory funnel. It is important that you learn how to use this piece of equipment properly, for an efficient separation and for safety. It is made of thin glass and is easily broken unless handled carefully. Unfortunately, in various student manuals you will find descriptions of about as many ways of holding the separatory funnel as for holding a pair of chopsticks. Probably for you there is some best method, depending on the size of your hands, the strength of your fingers, your manual dexterity, and the size and shape of the funnel. The following are important rules to observe.

1. Hold the funnel firmly but gently in both hands so that it can be turned from the vertical to horizontal direction and back again easily and can be shaken vigorously while observing (2) and (3).
2. Keep the stopper tightly seated with one hand at all times, using the forefinger of that hand, the base of the forefinger, or the palm of the hand.
3. Keep the stopcock tightly seated with the fingers of the other hand in such a way that the fingers can open and close the stopcock quickly to release the pressure that may be built up from solvent vapor or evolved gases.

The use of the separatory funnel is a skill and is best learned by practice with an empty funnel while watching your instructor demonstrate the technique. In the figure below are shown two slightly different methods of handling the separatory funnel. In the first method the stem of the funnel projects between the thumb and first finger of the left hand (for a right-handed person). The stopcock is held in place and operated with the thumb and first finger. The stopper is kept in place by pressure against the base of the first finger of the right hand.

In the second method the stem of the funnel projects between the first and second fingers of the left hand. The stopcock is held in place by the pressure from these fingers and is operated by them in conjunction with the thumb. The stopper is held in place by pressure against the middle of the palm of the right hand. (Fig 1)

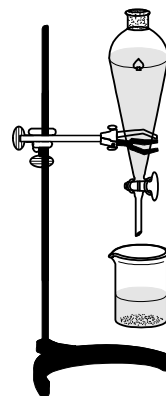
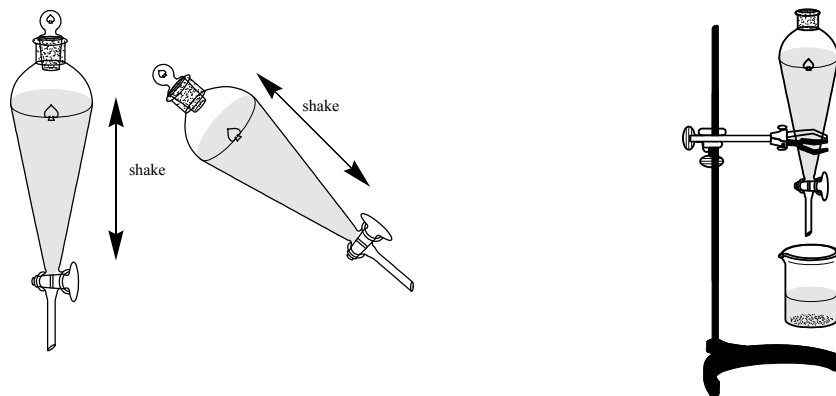


Fig. 1- methods for holding and shaking the separatory funnel. Fig. 2- support and use of the separatory funnel.

Support the separatory funnel in a ring on ring stand. Close the stopcock and add the liquids to the funnel to be separated. Insert the stopper, and immediately invert the funnel. **Point the barrel away from your face and that of your neighbors.** *Open the stopcock to release the pressure*, which may have accumulated inside the funnel (volatile solvents such as ether develop considerable pressure).

Close the stopcock and, holding the funnel horizontally, shake the funnel two or three times. Invert the funnel and release the pressure as before. Repeat this process until opening the stopcock causes no further pressure release. Close the stopcock and shake the funnel 15-20 times. Replace the funnel in the holder (ring on ring stand) and **remove the stopper** (Fig. 2). Allow the liquids to stand until the layers have completely separated. Draw the lower layer into a flask or beaker of proper size (see figure below).

CHEM 2423 Extraction of Benzoic Acid

Dr. Pahlavan

Do not draw the liquid through the stopcock too rapidly. Slow the flow carefully as the boundary between the two layers approaches the stopcock. Stop the flow of liquid completely just as the upper layer enters the hole in the stopcock. Pour the upper layer *through the neck* of the funnel into a second flask. *Never discard either layer until you are absolutely certain which is the proper layer to keep.* Usually one layer will be an aqueous layer or solution, and the other will be an organic liquid. The one of greater density will be on the bottom.

To check the identity of a layer, should you be in doubt, withdraw a few milliliters of the lower layer into a test tube containing an equal volume of water. If the lower layer in the separatory funnel is water or an aqueous solution it will be homogeneous (only one layer). If the layer being tested is the organic layer, the sample withdrawn will fall to the bottom of your test tube and also form two liquid layers. In either event, return the test mixture to the separatory funnel.

Experimental Procedures

Part 1 – Standardization of NaOH solution

Use a 10 mL graduated cylinder measure 10.0 ml of the acid solution and transfer the solution to a 125 mL Erlenmeyer flask. Add 2-3 drops of phenolphthalein and titrate to the end point (light pink) with a standardized ($\approx 0.1\text{M}$ or 0.02 M) sodium hydroxide solution. Record in report form the number of milliliters of base required to neutralize this volume of acid solution. Calculate the molarity of the NaOH.

Discard the neutralized acid solution and rinse your flasks. REPEAT.(TWO TRIALS)

Part 2 – Single extraction

Use a 50 mL graduated cylinder to measure out a second 50.0 ml volume of acid solution and transfer it to your separatory funnel. Add 10 ml of methylene dichloride, CH_2Cl_2 , to the funnel and extract according to the procedure outlined in the part 1 of this experiment. Separate the *bottom* layer (organic phase) in a 100 mL beaker and collect the *top* layer (aqueous) into a 125 mL Erlenmeyer flask and add 2-3 drops of indicator. Record the volume of the sodium hydroxide solution in the burette and titrate to the phenolphthalein end point (light pink). Again record the number of milliliters of base required and calculate a-g. Discard the neutralized acid solution and the methylene dichloride layer into the large bottle marked "Organic Waste".

NOTE: This lab has been modified in that methylene dichloride is now used in place of ether as the organic phase. This avoids the problem of ether fumes and explosions. However, the extraction with methylene dichloride is not as clean because methylene dichloride is more miscible in water than ether. As a result, you will find that your aqueous layer is cloudy after extraction. You can still titrate the aqueous layer to a light pink endpoint.

Part 3 - Multiextraction

Repeat the procedure from Step 2, but this time extract 50 ml of fresh acid solution with two 5 ml portions of methylene dichloride. Separate the aqueous layer into a flask and dispose of the organic layer. Transfer the aqueous layer back into the empty, cleaned, separatory funnel and extract it with a second 5 ml portion of fresh methylene dichloride. Separate the extracted aqueous layer, add indicator as before and titrate to the end point. Record the volume of standard base required and calculate a-f. Dispose of the organic layer extracts as directed and clean your separatory funnel.

Laboratory –EXP 6**Name:****Data and Results (Extraction of Benzoic Acid)****Date:** _____**Lab Report:** _____**Part 1: Standardization of NaOH Solution**

- a. Volume of base required to neutralize 10.0 ml of the benzoic acid solution:

Trial 1: _____ ml

Trial 2: _____ ml

Average: _____ ml

- b. Molarity of the NaOH solution:

 $(\text{ml of base}) (\text{M of base}) = (\text{ml of acid}) (\text{M of acid})$ _____ M

Calculation:

Part 2: Distribution Coefficient

- a. Volume of base required to neutralize 50 ml of benzoic acid solution after a single extraction with 10.0 ml of
- CH_2Cl_2
- _____ ml

- b. Moles of benzoic acid neutralized: (2a in L) (1b) _____ mole

Calculation:

- c. Grams of benzoic acid neutralized: (2b) (MW of benzoic acid) _____ g

Calculation:

- d. Grams of benzoic acid originally present in 50 ml before extracting with
- CH_2Cl_2
- :
- 0.122
- g
-
- $0.61 \text{ g}/250 \text{ ml} = x/50 \text{ ml}$
- ,
- $x = 0.122 \text{ g}$

- e. Grams of benzoic acid extracted in
- CH_2Cl_2
- : (2d – 2c) _____ g

Calculation:

- f. Percent of benzoic acid in extracted in
- CH_2Cl_2
- : (2e/2d) x 100 _____ %

Calculation:

- g. Distribution coefficient
- $K_d = C_{\text{CH}_2\text{Cl}_2}/C_{\text{H}_2\text{O}}$
- : (2e/10 ml)/ (2c/50ml) _____

Calculation:

Part 3: Multiple Extraction

- a. Volume of base required to neutralize 50 ml of benzoic acid solution after two extraction with 5.0 ml of CH_2Cl_2 each: _____ ml
- b. Moles of benzoic acid neutralized: (3a in L) (1b) _____ mole
Calculation:
- c. Grams of benzoic acid neutralized: (3b) (MW of benzoic acid) _____ g
Calculation:
- d. Grams of benzoic acid originally present in 50 ml before extracting with CH_2Cl_2 _____ 0.122 _____ g
Calculation:
- e. Grams of benzoic acid extracted in CH_2Cl_2 : (3d – 3c) _____ g
Calculation:
- f. Percent of benzoic acid in extracted in CH_2Cl_2 : (3e/3d) x 100 _____ %
Calculation:

Calculate amount of benzoic acid which would be extracted in two 5.0 ml extractions with CH_2Cl_2 based on your K_d obtained in part 2:

Show calculation:

Pre-Laboratory Questions–EXP 6 Name:

Due before lab begins. Answer in space provided.

1. The distribution coefficient, K , is 10 for compound Y. What weight of compound Y would be removed from a solution of 4.0 g of Y in 100 ml water by a single extraction with 100 ml of ether?
2. Reconsider question 1 above; what weight of compound Y would be removed by two (double) extractions using 50 ml of ether each time?
3. Student during an extraction experiment lost track of which layer is the aqueous layer. How could student determine which layer is which by a simple test?
4. Why must the stopper be removed from the separatory funnel before the lower layer is removed.
5. An aqueous solution containing 5.0 g of solute in 100 ml is extracted with three 25 ml portions of diethyl ether. What is the total amount of solute that will be extracted by the ether, $K = 1.0$?

Post-Laboratory Questions–EXP 6 Name:

Due after completing the lab.

1. What are the advantages and disadvantages of using ether as a solvent for the extraction of organic compounds?
2. What volume of an organic solvent must be used to effect 90% separation in one extraction when only 2.7 g of a certain compound dissolves in 100 ml of water? ($K = 15$)
3. What percentage of the organic compound could be recovered if two extractions were made, each time using half of the volume calculated 2?
4. An organic compound can be extracted from a water layer by an organic solvent more efficiently if the water layer is saturated with an inorganic salt such as sodium chloride. This effect, called “salting out”, increase the participation coefficient in favor of the organic compound. (explain)
5. The pain reliever phenacetin is soluble in cold water to an extent of 1.0 g /1310 ml and soluble in diethyl ether to an extent of 1.0 g /90ml.
 - a) Determine the approximate distribution coefficient for phenacetin in those two solvents.
 - b) If 150 g of phenacetin were dissolved in 100 ml of water, how much ether would be required to extract 90% of phenacetin in a single extraction?
 - c) What percent of the phenacetin would be extracted the aqueous solution in part (b) by two 25ml portions of ether?