

EXPERIMENT 6

EXTRACTION

A. PRELAB ASSIGNMENT

In your notebook, prepare a Table of Physical Constants for benzoic acid, 2-chlorobenzoic acid, salicylic acid (2-hydroxybenzoic acid), naphthalene, 1,4-dimethoxybenzene (hydroquinone dimethyl ether), 1,4-dichlorobenzene, ethyl acetate, and water.

B. THEORETICAL BACKGROUND

1. Theory of Extraction

The transfer of a solute from one phase to another is a very common technique in organic chemistry. It is called extraction, and it is also a common technique in everyday life. When you steep a tea bag in boiling water, add a bay leaf to a pot of soup, or wash a load of laundry, you are performing a solid/liquid extraction, in which a solution containing several components is mixed with a second, immiscible liquid, for the purpose of extracting one component of the solution into the second solvent.

We have seen that recrystallization is used to purify solids that are contaminated by relatively small amounts of impurities. By contrast, the technique of extraction is a more “coarse” or preliminary technique, in that it can be used to separate one compound from another or from large amounts of impurities.

Most uncharged organic molecules are more soluble in organic solvents than in water. If the organic solvent itself is not very soluble in water, then when the solvent or one of its solutions is mixed with water, two layers will form, and the solvents are said to be immiscible. The layers are called the organic layer and the aqueous layer. If the two layers are shaken together, small amounts of the components of the organic layer will dissolve in (or be extracted into) the aqueous layer, and small amounts of the aqueous layer components will dissolve (be extracted into) the organic layer, establishing

equilibrium between the two layers. Thus, if a neutral compound C is initially dissolved in one layer (phase), it will be distributed, or “partitioned,” between the two layers at equilibrium. The distribution is expressed quantitatively in terms of the coefficient, **K**. Ideally, the distribution coefficient of compound C is equal to the ratio of the individual solubilities of C in pure solvent, **S**, and in pure water, **W**.

$$K = \frac{\text{conc. of C in S}}{\text{conc. of C in W}} = \frac{\text{grams of C in S / mL of S}}{\text{grams of C in W / mL of W}}$$

For extraction of solute from solvent A into solvent B with a given volume of solvent B, several extractions each with small portions of solvent B are more efficient than a single extraction with the total volume of solvent B.

If several different solutes (P, Q, R) are dissolved in an organic solvent, then shaking the solution with water will extract small amounts of each into the aqueous layer, but not allow for a clean separation of any one compound.

However, if during the shaking we can run a reaction which converts one of the solutes, P, into a product which is more soluble in water than in the organic solvent (i.e., by converting it into a charged ionic species, such as a conjugate base or conjugate acid), the product will dissolve extensively in the aqueous layer and thus can be separated from the other organic solutes.

Now, if the reaction can be reversed in the separated aqueous layer, we can recover the original compound, P, separated from the other solutes, Q, and R. Such a procedure is possible when the mixture contains an organic acid (and/or base) that can be selectively converted to charged products (salts).

2. Acids and Bases in Organic Chemistry

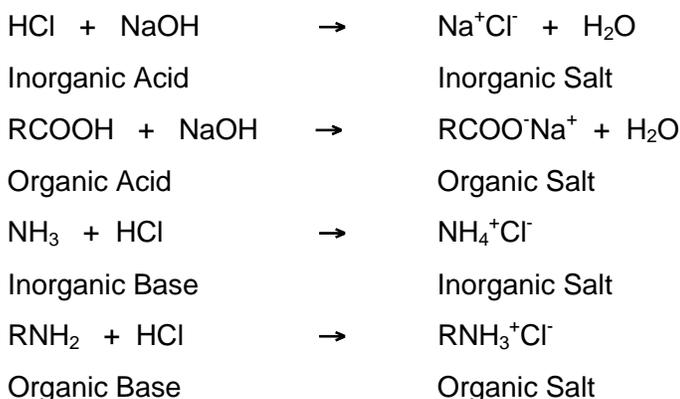
Acids RCOOH and ArCOOH (carboxylic acids)

ArOH (phenols), RSO₃H (sulfonic acids)

Bases RNH₂ (amines), ArNH₂ (anilines)

The symbol R represents any alkyl group, such as CH₃, C₂H₅, etc. For an aromatic compound, such as C₆H₆ (benzene), the symbol Ar is used. Organic acids and bases react in the same way as inorganic acids and bases, as can

be shown by the following reaction schemes. However, organic acids and bases are usually weaker.



Of the three organic acid groups listed above, the sulfonic acids are the strongest, followed by the carboxylic acids, and then the phenols. The sulfonic acids, R-SO₃H, where -SO₃H is the sulfonic acid group and R is the rest of the molecule, are strong acids, close in strength to sulfuric acid. The carboxylic acids, R-COOH, have the carboxyl group -COOH, with a pK_a of 4 to 7, depending on the rest of the molecule. The phenol group, in which -OH is attached to a benzene ring, is the weakest of the common organic acid groups, with a pK_a of around 10.

Because the hydroxide ion (OH⁻) is a strong base, it will deprotonate both type of acids, both the weak carboxylic acid and the very weak phenol.

Deprotonation produces the conjugate bases, the carboxylate ion (R-COO⁻) and the phenolate ion (Ar-O⁻). Bicarbonate ion (HCO₃⁻) is a weak base. It is strong enough to deprotonate the carboxyl group but not the phenol group.

Since most ions are soluble in water, deprotonation of these acids is a way of making them water-soluble. Extraction of an ether solution of benzoic acid and naphthalene with aqueous sodium hydroxide will separate these compounds by drawing the benzoic acid, as its conjugate base, into the aqueous phase. This is the principle behind this week's experiment.

3. Flow Diagrams

Procedures for the separation and purification of components of complex mixtures are commonly summarized by flow diagrams, in which each box represents a phase (solid, liquid, or vapor) or container, and connecting arrows represent operations (filter, extract, boil) or addition of reagents. The name of the phase or container is written above each box, and symbols, formulas, etc., for all of the components of the phase are written inside each box. Operations and/or reagents are written under or next to appropriate arrows. Separation of phases is shown by a split in the arrow, leading to two boxes. See the sample flow diagram on page 55.

C. GENERAL PROCEDURES

Separatory Funnels

In macroscale extractions, we use a separatory funnel to separate organic and aqueous layers.

To fill a separatory funnel, one supports it in an iron ring attached to a ring stand. Before adding any liquid, **close the stopcock**. (It is closed when it is perpendicular to the separatory funnel, and open when parallel to it.) Just in case the stopcock may not be completely closed, or it may leak a little, make it a habit to always have a container, such as a beaker, under a separatory funnel. The two liquids are added through the top of the separatory funnel. To allow for mixing of the liquids, one-third to one-half of the separatory funnel should be empty. The stopper is replaced. To mix the liquids, first secure the stopper and invert the separatory funnel. Slowly open the stopcock to vent any built-up pressure. Do not point it at your face or at any other person. Then close the stopcock, hold the stopper firmly in, and shake the funnel gently, a few times. Pause, invert, and vent again. Then close the stopcock and shake some more, this time more vigorously. Open the stopcock to vent again. Repeat this a few times, with longer shaking intervals and harder shakes. Then replace the separatory funnel on the iron ring to allow the solutions to separate. See the diagram of a separatory funnel on the

last page of this manual. The very narrow bottom is designed to allow a good separation of the two liquids. Precautions: In a closed separatory funnel, pressure can build up and blow out the stopper, unless the funnel is vented by inverting it and opening the stopcock while supporting the stopper firmly against the palm of your hand. Do this frequently.

Layer Identification

A common problem is determining which layer one wants. Since we almost always have an aqueous layer and an organic layer, you first need to know which is which. Then you have to know which layer contains the solute that you want to keep. The key to the first question is to know the densities of the two solutions. This is one of the reasons that we make a Table of Physical Constants for each experiment. This Table will tell you the densities of the two solutions. Assigned readings also come in handy here. Knowing in which layer a desired compound is found comes from understanding the experiment and thinking about what you are doing.

A good method to determine which layer is aqueous and which is organic is to withdraw a few drops of one layer with a dropper and add these drops to about 0.5 mL of water in a test tube. If the layer is organic, the drops will be visible as a second phase; if it is aqueous, a homogeneous solution will result.

Always label and save both layers from any extraction until the end of the experiment.

Drying the Extracts

After an aqueous extraction, organic solvents always contain some dissolved or suspended water, which should be removed before any dissolved compounds are isolated by solvent evaporation. This process is called “drying” the extracts. Drying requires two steps. As a first step, we perform one more extraction in each solution. We extract the water from the organic layer by shaking it with water that is saturated with sodium chloride, also called **brine**. This works because of an osmotic effect. In the second step, the last traces of water are removed from the organic layer with a drying agent,

such as calcium chloride, magnesium sulfate, sodium sulfate, or molecular sieves.

The amount of drying agent to use is determined empirically, since the amount of water present is variable. In general, enough drying agent is added to just cover the bottom of a flask, which is about 1/3 to 1/2 filled with the solution. The mixture is swirled and examined to be sure that some of the drying agent remains freely suspended in the liquid as it is swirled. If the entire drying agent sticks together, indicating saturation with water, more is added until swirling shows some loose material. Too large an excess of drying agent is to be avoided, since some dissolved material will be lost by adsorption on the surface of the drying agent.

Recovery of Compounds

After the organic solutions have been dried, the drying agent is removed by gravity filtration, and the solvent is evaporated, to leave the now pure compound.

D. EXPERIMENTAL PROCEDURE

In this week's experiment, you will be given an unknown that consists of a mixture of two components, an acid and a neutral compound, both solids. You will separate these compounds by an acid/base extraction and recrystallize each of them. You will identify these compounds by their melting points.

IMPORTANT! Save all layers in labeled containers until end of lab period!

1. Obtain a sample of an unknown mixture. Record the number of the vial.
2. Weigh the unknown mixture in the vial on an analytical balance. Transfer the contents of your vial to a 100 mL beaker. Weigh the empty vial.
3. Add 20 mL ethyl acetate to the beaker. Stir to dissolve the unknown mixture. Use a glass funnel to transfer the solution of unknown in ethyl acetate to a 125 mL separatory funnel on a ring. Rinse the beaker with two 10 mL portions of ethyl acetate, and add it to the separatory funnel.

4. Add 10 mL aqueous 1.5 M NaOH and shake the separatory funnel. Withdraw the aqueous layer. Repeat with a second 10 mL portion of NaOH.
5. Add 10 mL distilled water to the organic layer in the separatory funnel. Shake the separatory funnel well. Withdraw the aqueous layer. Aqueous layers from steps 4 and 5 may be combined in a beaker labeled "Aqueous Layer." Save this for later extraction of the acidic component.
6.
 - a. Dry the organic layer in the separatory funnel by shaking with 15 mL saturated NaCl solution.
 - b. Drain the lower aqueous layer and discard.
7.
 - a. Drain the organic layer from the separatory funnel into a 125 mL Erlenmeyer flask.
 - b. Add anhydrous Na_2SO_4 drying agent until no more clumping is observed. Set the flask aside for several minutes with occasional swirling.
 - c. Filter this through a fluted filter paper into a tared (pre-weighed) 100 mL round bottom flask. Rinse the Erlenmeyer flask with 3-5 mL of pure ethyl acetate and pour this rinse onto the same filter.
8. Remove the solvent using the RotoVap.
9. Weigh the round bottom flask containing the solid neutral component.
10. Determine the melting point of the compound.

Aqueous Layer

1. Add concentrated HCl dropwise to the beaker labeled "Aqueous Layer" until the solution is acidic to litmus. Then add a few drops of acid in excess. Check for complete precipitation.
2. Add 30 mL ethyl acetate and extract.
3. Drain the aqueous layer into a waste beaker.
4.
 - a. Dry the organic layer in the separatory funnel by shaking with 15 mL saturated NaCl solution.
 - b. Drain the lower aqueous layer and discard.

5.
 - a. Drain the organic layer from the separatory funnel into a 125 mL Erlenmeyer flask.
 - b. Add anhydrous Na_2SO_4 drying agent until no more clumping is observed. Set the flask aside for several minutes and swirl as before.
 - c. Filter this through a fluted filter paper into a tared (pre-weighed) 100 mL round bottom flask. Remember to rinse the Erlenmeyer flask as in step 7c above (p. 53).
6. Remove the solvent using the RotoVap.

Second Lab Period

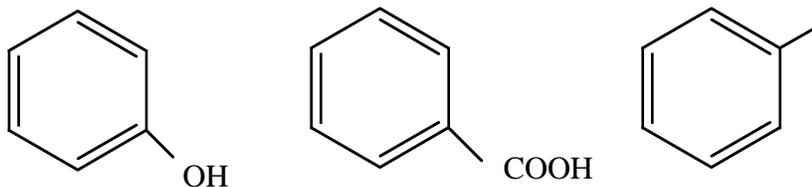
1. Weigh the round bottom flask containing the solid neutral component.
1. Determine the melting point of the compound.
2. Weigh the flask containing the solid acid component.
3. Determine the melting point of the compound.
4. Identify your components by comparing the melting points with the melting points of the known compounds in your Table of Physical Constants. If there is any ambiguity, do a mixed melting point.
5. Calculate total % recovery. (Total % recovery = % A + % B)

Sample calculation:

$$\% \text{ A} = \frac{\text{weight A}}{\text{starting weight of mixture}} \times 100$$

E. QUESTIONS

1. Give the names and structures of two functional groups in organic chemistry that are acidic.
2. A mixture contains the following three compounds:



An ether solution of this mixture is extracted with sodium bicarbonate solution to form aqueous layer A and organic layer B. The organic layer B is then extracted with sodium hydroxide solution to form aqueous layer C and organic layer D. Both solutions A and C are separately treated with hydrochloric acid to give solutions E and F respectively. Give the structure(s) of the organic solute(s) present in A, B, C, D, E and F.

Explain. Include a flow diagram.

3. Write an expression for the acidity constant, K_a , for benzoic acid, C_6H_5COOH , in terms of concentrations.
4. Suppose you do not know which layer in your separatory funnel is the aqueous layer, and you have no information about the density of the solvent, how could you determine which is the aqueous layer?

F. DISCUSSION AND CONCLUSIONS

In this section, also include a flow diagram for the extraction and separation you performed on your unknown mixture. (See the sample flow diagram below.)

NOTES