EXTRACTION

**Required Readings:** McMurry, Chapter 2.7 - 2.11, Padias, pp. 130 – 142

**Previously learned techniques you must understand and be able to perform:** Identification by melting point, vacuum filtration and collection of a solid.

In this experiment, you will receive approximately 1.5 g of a 1:1 mixture of two of the compounds below and you will use extractions to separate the compounds from one another. One of the compounds will be either benzoic acid or 4-bromoanaline and the other will be either biphenyl or napthalene.



This experiment is intended to simulate the type of problem often encountered by a practicing organic chemist. A just-completed chemical reaction may have a mixture of products to identify. The separation and identification process is called a “work-up” of the product. If organic acids or bases are present in the mixture, extraction procedures effect the separation of a mixture with such ease that it would be foolish to spend time on a lengthy chromatography or distillation. An experienced chemist can go through the operations necessary to isolate and identify the components of an acid-base-neutral mixture in one or two hours. To discuss this process it is first necessary to understand the solubility properties of organic acids, bases, and their conjugates.

**Organic Acids**

Of course, all substances containing hydrogen atoms may be considered acidic to some degree. However, only those substances whose conjugate base is relatively stabilized will form salts with common bases such as NaOH or NaHCO3. In general, the most acidic organic compounds are the carboxylic acids, RCO2H or ArCO2H. The vast majority of carboxylic acids are soluble in organic solvents and insoluble in water. In contrast, the conjugate bases of carboxylic acids (carboxylate ions) are usually water-soluble. Thus, by reacting a water-insoluble carboxylic acid with an appropriate base, it can be converted into a water-soluble salt, as suggested by the equation below. The process can be reversed by treating a carboxylate ion with an acid, converting a water-soluble compound into one soluble in organic solvents.



**Organic Bases**

All organic substances containing non-bonding electrons may be considered bases. However, only the amino group is basic enough to form stable salts in dilute aqueous acid. The amines, themselves, are insoluble in water, whereas their salts are freely soluble (see the equation below). By treating an amine with dilute acid one can convert an insoluble base into its soluble conjugate acid. As with carboxylic acids, the process may be reversed. Treating an ammonium salt with base will convert the compound to an organic soluble (water insoluble) species.



Note: Low molecular weight carboxylic acids or amines may be soluble in water (*e.g.*, formic and acetic acids, methylamine).

**Neutral Compounds**

For this experiment, neutral compounds can be considered as those which cannot ionize in the presence of acid (5 % HCl) or base (5 % NaOH). Since these compounds cannot accept or donate a hydrogen they are insoluble in water, and soluble in organic solvents.

The take home message is:

***If a compound is ionized (has a charge, exists as a salt) it will be soluble in water.***

***If a compound is neutral, (does not have a charge, is not a salt), it will be soluble in organic solvents.***

**Separation Flowchart:**

***Prior to coming to lab, you must draw out a separation flowchart.*** You must have this completed before you are given your unknown mixture. It should contain a method for adequately separating your unknown compounds assuming that you have a mixture of organic neutral, acidic and basic compounds. ***Use the structures of the compounds in this experiment*** to create a flow chart to show how a mixture of these compounds can be separated into acid, base and neutral fractions by extraction. Draw **STRUCTURES** of the results of each extraction procedure; in other words, do not write names (*i.e.*,“the conjugate acid of the base”). Predict what you will see (*i.e.*, "a precipitate will form"). A partial flowchart and the chemicals you will have available to you are below. You should also come to lab with an idea the volume and number of extractions you will need at each step.



**PROCEDURE**

Since you will not know which of the unknowns you will have, you will need to go through the entire extraction process. In some cases where you are asked to collect a precipitate (*p*‑bromoaniline and benzoic acid), you may not have any solid, **not** because you have performed the experiment incorrectly but rather because you may not have been given any of that compound in your unknown mixture. So, BE CAREFUL!! And remember: DON'T THROW OUT ANY LAYERS UNTIL YOU HAVE ISOLATED YOUR UNKNOWN(S).

Record your unknown number!!

In an Erlenmeyer flask, dissolve your unknown in 50 mL of ether. Pour this into your separatory funnel mounted in a ring.

Pour 15 mL of 5% HCl solution into the funnel, stopper, and swirl the funnel. Invert and open the stopcock to vent the mixture. Shake a few seconds and repeat the venting. Once you no longer hear gases vent, shake the mixture vigorously for several seconds, then place the separatory funnel back in the ring, remove the stopper, and let the layers separate. Drain the acid/water layer into a 100 mL Erlenmeyer flask. Repeat this procedure once more with a second 15 mL portion of HCl, combining the extracts. Generally, "multiple extractions" are performed. Calculations show that multiple extractions are more efficient than one 45 mL extraction of equal volume. The equations are found in Mohrig, pp. 115-117.

If you had any amine in your unknown, it will now be in the water solution as the amine hydrochloride. The amine can be liberated by treating the solution with base. The process of neutralizing a strong acid with a strong base (or *vise*-*versa*) should always be done in an ice-water bath. Add 3 M NaOH until pH paper indicates that a pH of 11 or higher. If you have amine in your unknown, you will now have a precipitate, which you can collect by vacuum filtration, wash with water, and allow to air dry.

The ether layer, which is still in your separatory funnel, now contains a neutral compound (biphenyl or naphthalene) and possibly a carboxylic acid. Extract with two 15 mL portions of 5% NaOH, combining the extracts as before. The base/water layer may now contain the sodium salt of benzoic acid. Acidify (ice-water bath) with 6 M HCl to approximately pH 3 (you should already know approximately how much 6 M HCl will be required to do this). A precipitate should be benzoic acid, which you need to collect, wash with water, and dry.

Now the ether layer contains only neutral product, so you can proceed to isolate either biphenyl or naphthalene. The ether will be “wet”, so add anhydrous sodium sulfate in increments until a fresh addition remains granular (*i.e.* does not clump). (Padias, p. 139-141). Carefully decant the liquid into a preweighed round-bottom flask, rinsing the drying agent with a little more solvent and adding it to the round-bottom flask, if desired. The solvent can then be evaporated on the rotary evaporator. Identify the recovered solid by simultaneously taking its melting point along side of mixed melting points with pure samples of the two unknowns.

Run a TLC of your neutral compound vs. the two standards using hexane as the eluant. You can spot the TLC plate from the ether solution while it is drying and you can develop the plate while you are rotary evaporating the solvent.

**Avoiding Unnecessary Grief**

1) ***Which layer is the water layer??*** Look at both layers in the separatory funnel and get an idea of how big they are in relation to one another. Now, *add water to the funnel*. Watch where the water goes. Watch which layer grows. Water to water. That's how to find the water (aqueous) layer.

2) ***How come there are three layers??*** Sometimes, when you pour fresh water or some other solvent into your separatory funnel, you get a small amount hanging at the top, and it looks as if there are three layers. Yes, it looks as if there are three different layers but actually there are only two layers, and one which has lost its way. Gently swirl the funnel and your third layer should disappear.

3) ***What's the density of sodium hydroxide??*** You've just done a wash with a 5-10% sodium hydroxide solution, you've just read something about finding various layers in the funnel by their densities, and, by this question you've just missed the point. Most wash solutions are 5-10% active ingredient dissolved in water. This means they are 90-95% water. Looking up the density of solid reagents then is a waste of time since the density of these solutions is very close to water.

4) When shaking your mixture of organic and aqueous solvents in your separatory funnel, don't be afraid to shake the funnel vigorously! Just sloshing the solutions back and forth isn't very effective. The effectiveness of your extraction depends upon a thorough mixing of these two layers.

5) If only the top layer is being extracted or washed, it does not have to be removed from the funnel. Just drain off the bottom layer and then add more fresh extraction or washing solvent.

6) If you get an emulsion you will not have two distinct layers but rather a fog of particles. Sometimes you can break up the charge on the particles by adding a little salt. Or stir the solution slowly with a glass rod. If you decide to add salt to the separatory funnel, don't add so much that it clogs up the stopcock!! For the same reason, keep drying agents out of the separatory funnel.

7) Never, never, never, never, ever throw away any layer until you are absolutely sure you will never need it again. Not very much of your product can be recovered from the sink trap!

**EXTRACTION**

**DATA SHEET**

|  |  |  |  |
| --- | --- | --- | --- |
| **NAME:** |  | **Section:** |  |

**Unknown Number:**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Initial unknown mass: | |  | |  |  |  |  |  |
|  | |  |  |  |  |  |  |  |
| Recovered mass | |  |  |  |  |  |  |  |
|  | |  |  |  |  |  |  |  |
| Acid / base: |  | |  | a% recovery: |  |  | melting point: |  |
| (circle one) |  | |  |  |  |  |  | (experimental) |
|  |  | |  |  |  |  |  |  |
| neutral: |  | |  | a% recovery: |  |  | Rf value: |  |
|  |  | |  |  |  |  |  |  |
|  |  | |  | TLC solvent: | |  | | |
|  |  | |  |  | |  | | |
|  |  | |  | Identity of neutral : | |  | | |

a % recovery based on total initial mass

Calculations: (you may include these on a separate attached sheet)

Post lab questions:

Use the principle of “like dissolves like” to explain the solubility properties of benzoic acid and its sodium salt. Do the same for 4-bromoaniline and its hydrochloride salt.

A crude non-acidic product mixture dissolved in ethyl ether contains a carboxylic acid side product as an impurity. Describe an extraction procedure to remove the acid impurity from the product mixture.

You have been given 75 mL of a solution of an acid in water, estimated to contain about 1.25 g of the acid. The distribution coefficient of the acid for ether and water is approximately 20. Calculate the amount of acid that would be left in the water solution after two 25 mL extractions with ether. Do the same with one 50 mL extraction to determine which method is more efficient. Show your work and clearly indicate which method is more efficient.

Why is it important to neutralize the basic solution (the one that contains the acid unknown) to pH 3 instead of just pH 7? Why is the acidic solution (containing the basic unknown) neutralized to pH 11 or greater? To answer this question you will need to discuss pKa’s.

Write equations for the reactions of all the unknowns used in this experiment, and use curved arrows to show electron movement. Clearly identify those reactions involving your unknown(s).