Experiment 2
Separation of Unknown Mixture Using Acid-Base Reactions

In this experiment you will be given an unknown mixture of three compounds, consisting of one of the two carboxylic acids, one of the two possible phenols and one of the two possible amines pictured in Figure 1. Your task will be to separate the three unknown compounds in the mixture and then identify them using the mixed melting point technique. We will use acid-base chemistry, taking advantage of the different pKa's. We will use a separatory funnel to separate the immiscible organic and aqueous phases, which contain the ionized unknowns, and we will collect the neutralized solids from the aqueous solutions using vacuum filtration. The physical constants for these compounds, including the pKa's are given in Table 1. Note that the pKa values given for the bases are those of the conjugate acids of these compounds.

Figure 2.1

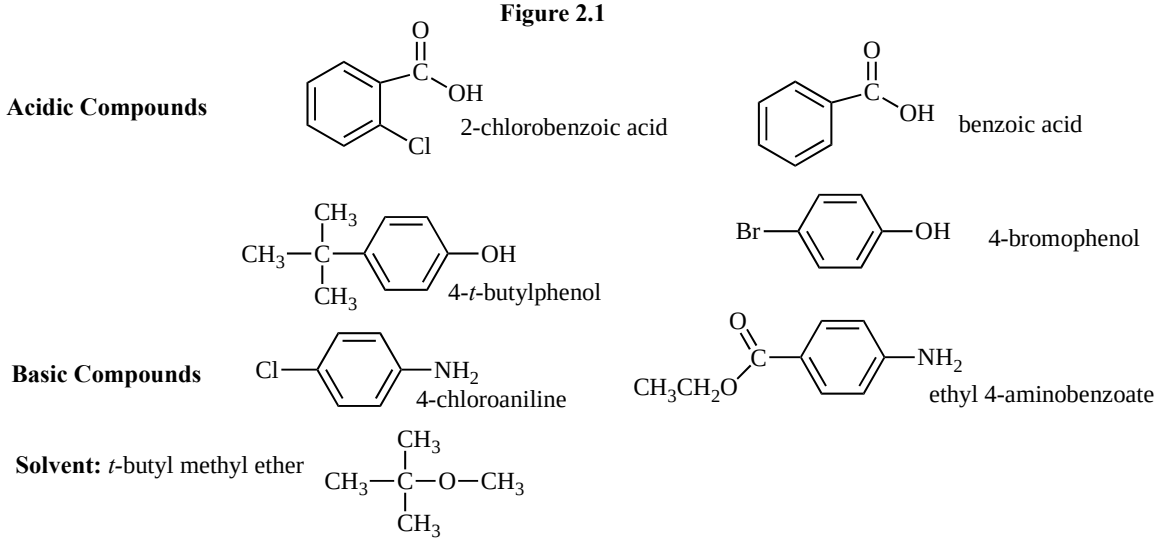


Table 1

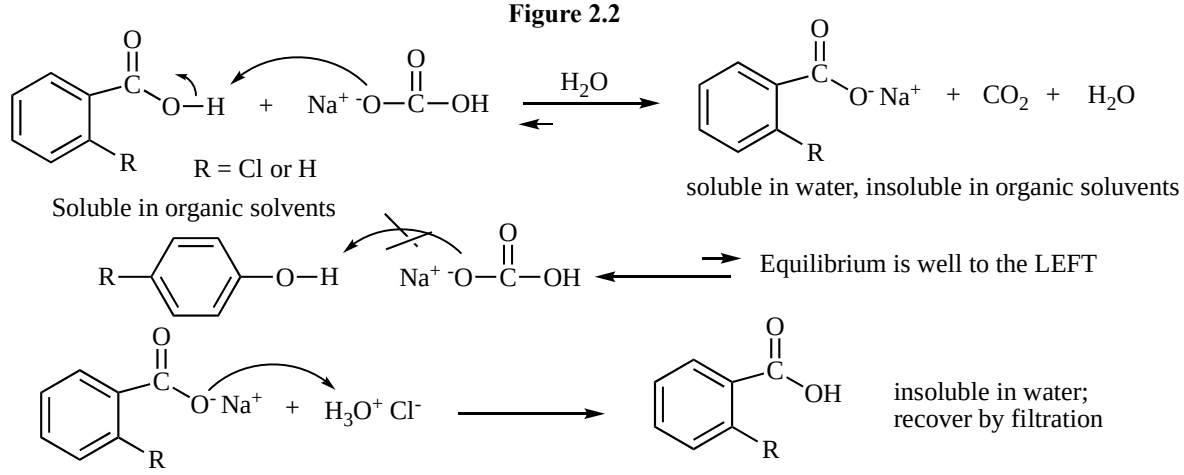
Compound	Formula	Mol. Wt (g/mol)	pKa	m.p. (°C)
2-chlorobenzoic acid	$C_7H_5O_2Cl$	156.57	2.92	141
Benzoic acid	$C_7H_6O_2$	122.12	4.17	123
4-*t*-butylphenol	$C_{10}H_{14}O$	150.22	10.17	101
4-bromophenol	C_6H_5OBr	173.01	10.2	66
4-choloraniline	C_6H_6NCl	127.57	4.15*	68-71
Ethyl 4-aminobenzoate	$C_9H_{11}NO_2$	165.19	4.92*	88-90
Sodium bicarbonate	$NaHCO_3$	84.01	6.35*	
Sodium hydroxide	NaOH	40	15.7*	
Tert-butyl methyl ether	$C_5H_{12}O$	88.15		b.p. 75

* These values are pKa's for the corresponding conjugate acids of these bases (i.e. RNH_3^+, H_2CO_3, and H_2O).

All three solid compounds are soluble in *tert*-butyl methyl ether, a common organic solvent. We will extract the more acidic unknown, benzoic acid or 2-chlorobenzoic acid, from the organic layer into the aqueous layer by reacting it with dilute sodium bicarbonate (pKa of carbonic acid 6.35). This will deprotonate the carboxylic acid to form the anion, which is soluble in the aqueous

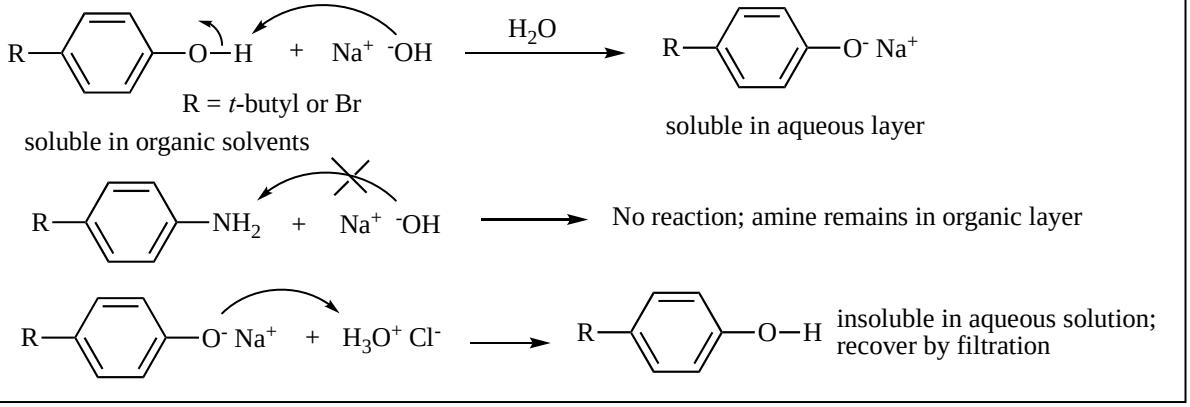
layer (see Figure 2.2). Note also that the weakly basic bicarbonate anion is not strong enough to deprotonate (and ionize) the less acidic phenols. The phenols, along with the basic amines, will remain dissolved in the organic layer. We will separate the aqueous layer containing the unknown carboxylic acid from the organic layer using the separatory funnel. We can recover the carboxylic acid from the aqueous layer by treating it with hydrochloric acid. This will cause the anion to become re-protonated and insoluble in water. We can then recover the pure carboxylic acid by vacuum filtration and identify it on the basis of its melting point, using the mixed melting technique we learned in Experiment 1.

Figure 2.2



We will separate the unknown phenol from the basic amine by treating the organic layer with dilute sodium hydroxide. This base will deprotonate the phenol, making the anion soluble in the aqueous layer and leaving the basic amine still dissolved in the organic layer (Figure 2.3). As

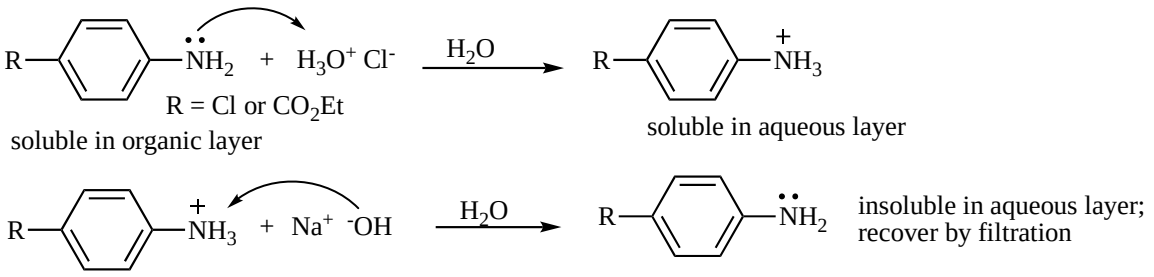
Figure 2.3



before, we separate the aqueous layer from the organic layer and neutralize the aqueous layer with hydrochloric acid to re-protonate and precipitate the phenol so that it can also be collected by vacuum filtration.

The final step is then to separate the basic amine from the organic solvent. One way to do this would be to remove the volatile solvent by distillation, a technique we will learn in Experiment 3, leaving the solid amine behind in our distilling flask. A more convenient method in this case is to simply extract the amine into the aqueous layer using dilute hydrochloric acid. The acid will react with the basic amine lone pair to form the water soluble cation. This can then be recovered from the aqueous layer by neutralization with sodium hydroxide and filtration as shown in Figure 2.4.

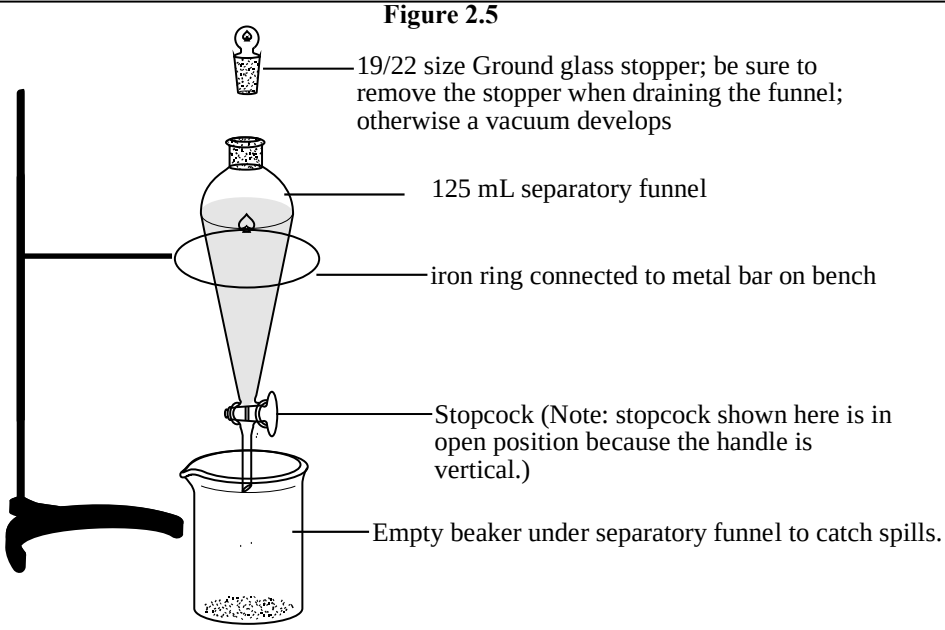
Figure 2.4



General Directions for Separatory Funnel Use

Set up the separatory funnel as shown in Figure 2.5. Use a small iron ring to hold the funnel. You can also use a metal clamp attached to the top neck of the separatory funnel but

Figure 2.5



the iron ring is more convenient. **ALWAYS KEEP A BEAKER UNDERNEATH THE SEPARATORY FUNNEL TO CATCH ANY SPILLS.** When the handle of the stopcock is parallel to the separatory funnel, the stopcock is in the open position. When the handle is perpendicular to the length of the funnel it is closed.

With the stopcock in the closed position, pour in your solution into the top of the funnel. Place a very small amount of stop cock grease on the ground glass stopper to prevent "freezing" of the stopper. Insert the glass stopper into the funnel. Hold the funnel in one hand by grasping the top around the glass stopper. Lift it from the iron ring and **SLOWLY** invert the funnel, holding it with your other hand. When it is now upside down, the glass stopper should be in the palm of one hand, holding it securely. **IMMEDIATELY VENT** the funnel by opening the stopcock and pointing the end of the funnel **AWAY** from your lab neighbor. **CAUTION**: always vent the separatory funnel immediately when you invert it. Pressure can build up and the contents of the funnel can shoot out uncontrollably. Once you have vented the separatory funnel, close the stopcock and shake it **GENTLY AT FIRST** 2-3 times. Then VENT the funnel again. Now you can shake it more vigorously several times. Then vent it again. You may hear the sound of escaping gases when you open the stopcock to vent. Once this subsides then it is safe to shake the

separatory funnel vigorously for 2-3 minutes. It is very important to shake the funnel very thoroughly to ensure intimate mixing of the two layers.

When you have finished shaking, replace the separatory funnel back in the iron ring and **REMOVE THE GLASS STOPPER** before draining off the bottom layer. Otherwise you will create a vacuum inside the separatory funnel and it will not drain.

Note that if there are two layers in a separatory funnel it is because the two liquids contained in the funnel are not soluble in each other. In most of our experiments, including the one today, we have a relatively non-polar organic layer – usually containing the product that we want to isolate – and a polar aqueous layer. The more dense layer is on the bottom. In many cases, this is the water layer (recall that oil floats on the surface of water), but not always!! Be careful. It is generally advisable when using the separatory funnel to **SAVE BOTH LAYERS** until you are sure that you have isolated the correct layer. Never throw anything away until you are finished with your experiment. To test which layer is which – organic or aqueous – simply add a little water to the layer that you think is the aqueous layer. If you see only one layer then you were correct in thinking that this was the aqueous layer.

Procedure

Obtain an unknown mixture from the Teaching Assistant and write down the unknown number in your notebook. Dissolve the 3.0 g of the mixture in 30 ml *t*-butyl methyl ether in a small beaker and transfer this solution to your separatory funnel. Add 5 ml of water and note which layer is organic and which is aqueous. Then add 10 mL of a 3 M aqueous solution of sodium bicarbonate to the funnel. Stopper the funnel and **CAUTIOUSLY** invert the funnel. **PRESSURE WILL BUILD UP.** Vent the liberated carbon dioxide immediately. Then re-stopper the funnel and shake it a once or twice. Vent the funnel again. Then shake again more vigorously, venting frequently.

NOTE: In order for this experiment to work you must shake vigorously for <u>several minutes</u>. You are doing an extraction of the organic compound from the organic layer into the aqueous layer.

Allow the layers to separate completely and drain the lower layer into a 50-mL beaker or Erlenmeyer flask. Label this as **Flask 1**. (What does this layer contain?)

Add 10 mL of 1.5 M aqueous sodium hydroxide to the separatory funnel, shake the mixture thoroughly, allow the layers to separate, and drain the lower aqueous layer into a small (25 or 50 mL) beaker or Erlenmeyer flask. Label this as **Flask 2**. Add an additional 5 mL of water to the organic layer in the separatory funnel, shake the mixture as before and add the bottom aqueous layer to Flask 2. (What does this layer contain?)

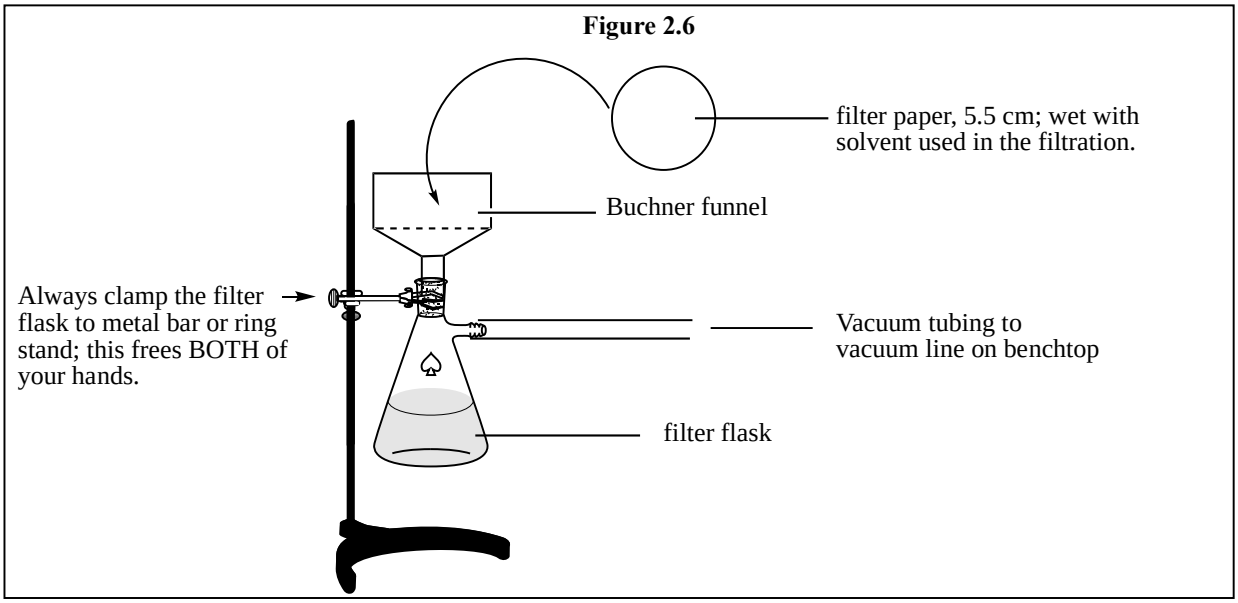
Add 10 mL 1.5 M hydrochloric acid to the separatory funnel and shake as described above. Be sure to vent. Allow the layers to settle and drain the bottom aqueous layer into a small beaker or Erlenmeyer flask. Label this as **Flask 3.** (What does this layer contain?)

Isolation of Products

Cautiously add concentrated hydrochloric acid to Flask 1 using a pipette. Add only a few drops at a time since there will be foaming caused by the carbon dioxide that is released. Add the HCl until the solution is acidic (red to neutral litmus). Cool the beaker in an ice bath and filter the solid using the Buchner funnel. The proper set-up for this is shown in Figure 2.6. You will use the vacuum line that that is at your bench. First clamp your filter flask to one of the steel bars ("monkey bars') on your bench near the vacuum line. Connect the side arm of the filter flask to the

vacuum line using the thick, black vacuum tubing that is available at the front of the lab. **Please return this when you are done using it.**

Figure 2.6



Before you filter, wet the filter paper with the solvent used in the reaction (in this case it is water). This causes the paper to adhere to the surface of the Buchner funnel, preventing solid material from going under the filter paper and into the filter flask. After no more water is dripping from the end of the funnel, disconnect from the vacuum by removing the rubber tube from the filter flask. Pour 5 mL of ice cold water onto the crystals, wait one minute and connect to the vacuum again.

Remove the crystals from the Buchner funnel, spread them out on a watch glass and leave them to dry in your locker until the next laboratory period when you will weigh them. Tare a piece of weighing paper and then scrape your product onto the weighing paper using your spatula. Identify your unknown by taking a mixed melting point as described in Experiment 1 and calculate the % recovery based on 1.0 gram of starting material. Note that you must compare moles of starting unknown versus moles of recovered compound.

Repeat the above process for Flask 2. Acidify the contents of Flask 2 using concentrated hydrochloric acid, cool in an ice bath, filter the solid, dry it and identify the unknown phenol on the basis of its melting point using the mixed melting point technique as described above and calculate the % recovery based on moles of starting unknown compared to recovered compound.

Neutralize the contents of Flask 3 using 3 M sodium hydroxide. You will need approximately 5 mL of solution. Add the sodium hydroxide until the solution is basic (blue to neutral litmus). Cool the beaker in an ice bath, filter and identify the unknown amine as above, calculating the % recovery as described above.

Hand in the Unknown Report Sheet, identifying the three unknowns and reporting the actual melting points that you obtain.