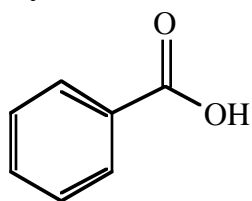


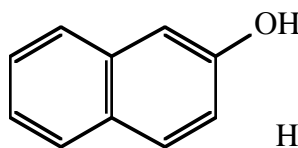
Chemically Active Extraction

Introduction

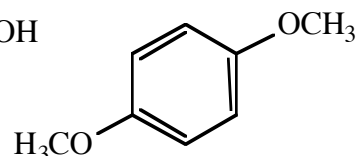
Today we are going to be performing another commonly used technique for the separation and isolation of organic compounds: acid/base extraction. Generally, most **neutral** organic compounds are more soluble in an organic solvent (such as ether) than they are in water. When ether is added to water, the two liquids will not mix because ether is fairly non-polar while water is very polar. Ether is less dense than water, so it will be the upper layer. Now if we add neutral organic compounds such as those shown below, they will preferentially dissolve in the ether layer and none will dissolve in the polar water. However, if an organic compound can be turned into a **charged** (ionic) compound, it will become more soluble in the polar water than the slightly polar ether. Today we will take a mixture of benzoic acid (**A**), 2-naphthol (**B**), and 1,4-dimethoxybenzene (**C**) and dissolve it in ether. They are all very soluble in ether, so we will not be able to separate them by recrystallization.



A
Benzoic Acid
MP = 123 °C
pKa = 4.2



B
2-naphthol
MP = 123 °C
pKa = 9.5



C
1,4-dimethoxybenzene
MP = 57 °C

However, they all have very different acidities, so we will be able to take advantage of this to separate them. If we use a base of an appropriate strength, we can turn **only** the most acidic compound (in today's lab it will be benzoic acid) into the anion. Now if there is water present, the charged species will prefer to be in the polar water, while the neutral compounds will stay in the ether. Then we can separate the aqueous layer from the organic layer (using the aptly named separatory funnel). This will remove the benzoic acid from the mixture. Now we can use a stronger base to turn the 2-naphthol into a charged compound. It will now dissolve into the water layer, and the neutral 1,4-dimethoxybenzene will remain in the ether layer. After once again separating the aqueous layer from the organic layer, we will have separated the anion of 2-naphthol from the neutral 1,4-dimethoxybenzene.

Experimental Procedure:

A: separation of benzoic acid. In a 125 mL erlenmeyer flask, dissolve approximately 1.5 g of a mixture of benzoic acid, 2-naphthol, and 1,4-dimethoxybenzene in 20 mL of ether (diethyl ether). Pour the solution into a separatory funnel (make sure the stopcock is closed!). Rinse the flask with 5 mL of ether and add the ether to the separatory funnel. Then add 10 mL of 5% NaHCO₃, and swirl the solutions gently in the separatory funnel while leaving the top open (CO₂ gas is formed in this acid/base reaction!). Then put in the stopper, invert the separatory funnel, and vent the mixture by quickly opening the stopcock. Gently invert the separatory funnel 2-3 more times, making sure to vent the solution each time. After there seems to be no more significant pressure building up, then begin to shake the mixture more thoroughly. Remember to vent it frequently. When there is no more gas escaping when you vent the solution, allow the layers to separate, and then draw off the lower aqueous layer into a clean erlenmeyer flask labeled "NaHCO₃ extract". Extract the ether again with 10 mL of 5% NaHCO₃,

draw off the aqueous layer, and combine it with the previous NaHCO_3 extract. The NaHCO_3 is a weak base and is only strong enough to turn the acidic benzoic acid (**A**) into the anion.

B: separation of 2-naphthol. Your ether solution containing **B** and **C** should still be in the separatory funnel. Now add 10 mL of 5% NaOH , and extract the solution. There should be only a small amount of pressure buildup now, so you do not have to be as careful when venting. After shaking the mixture thoroughly, you should still vent it frequently by opening the stopcock when the funnel is inverted. After shaking thoroughly, allow the layers to separate, and then draw off the lower aqueous layer into a clean erlenmeyer flask labeled “ NaOH extract”. Extract the ether again with 10 mL of 5% NaOH , draw off the aqueous layer, and combine it with the previous NaOH extract. The NaOH is a strong base and it will turn the weakly acidic 2-naphthol into the anion.

C: Isolation of 1,4-dimethoxybenzene. Pour the ether layer through the top of the separatory funnel into a 125 mL erlenmeyer flask and add approximately 1 g of anhydrous MgSO_4 . You should occasionally gently swirl the flask for 5-10 minutes. When you swirl the flask, the MgSO_4 should fly around like the snow in those decorative glass balls. (Think “rosebud” if you’ve seen the movie “Citizen Kane”). If all of the MgSO_4 is stuck on the bottom of the flask, you should add a little bit more until it “flies like snow”. While this solution is drying, you can begin part **D** of the procedure. After 5-10 minutes, place a **small** plug of cotton into the bottom of a conical funnel. Gravity filter the solution through the small plug of cotton in the bottom of a conical funnel and into a small tared beaker. Filter as much of the solution as possible through the funnel. Wash the remaining MgSO_4 with 1-2 mL of ether and filter this solution through the funnel. Add a couple of boiling chips or a boiling stick to the beaker and place the beaker in the fume hood on a hot plate and allow the ether to evaporate under low heating. Since **C** has a low melting point, the residue may be liquid even though all the ether has evaporated. When the residue no longer shows any bubbling, remove it from the hot plate and allow to cool. The residue will be the neutral 1,4-dimethoxybenzene. Weigh the compound and determine the melting point.

D: Neutralization and isolation of compounds A and B. Our two aqueous solutions contain the anions of compounds A and B, respectively. We will need to neutralize these anions by adding acid. Once the compounds are neutral, they will no longer be soluble in water and we can collect the precipitated solids by filtration. Cool the NaHCO_3 extract in an ice bath and acidify by adding 6M HCl . **WARNING:** This acid/base reaction will produce CO_2 , so it will bubble like crazy. You should add the HCl slowly and carefully. It should take about 5-10 mL of the HCl to completely acidify the solution. Use pH or Universal paper to make sure that the solution has a pH of 3 or less. The benzoic acid will precipitate out. Collect the product by suction filtration and wash the crystals with cold water. Allow the product to dry, weigh it, and determine the melting point.

Repeat this procedure with the NaOH extract. This solution will not produce CO_2 when acidified, so it will not bubble. The reaction between NaOH and HCl is exothermic however, so remember to keep it cool when adding the HCl . It should take about 10 mL of the HCl to completely neutralize this solution. Remember to make sure the solution is acidic before collecting the precipitated solid 2-naphthol by suction filtration. Allow the product to dry, weigh it, and determine the melting point.

Questions/Calculations

1. Determine the percent recovery of each of your solids, assuming that each compound makes up 1/3 of the mass of your original mixture.

2. Your melting points may not be very good. If we had more time, we could purify each compound by recrystallization (don't worry, you don't have to recrystallize!). Why are our solids from this lab less pure than when we recrystallize them?
3. Show the relevant acid/base equations (with K_{eq} 's) for all of the reactions (and non-reactions) in this lab. You should show the reactions of both **A** and **B** with NaHCO_3 , the reaction of **B** with NaOH , and the reactions of the anions of **A** and **B** with HCl . The pK_a of H_2CO_3 is 6.4, the pK_a of HCl is -2.2 , and the pK_a of H_2O is 15.7.
4. Yet another poorly prepared Stanford student made a mistake in this lab and he extracted first with NaOH , and then extracted with NaHCO_3 . What will be his results after he adds HCl to his NaOH extract and his NaHCO_3 extract?