

Experiment #1, Two Base Extractions

Experimental Organic Chemistry: A Miniscale and Microscale
approach by Gilbert and Martin, Section 5.3

7-3-06

TA: Mike and Carolyn

INTRODUCTION:

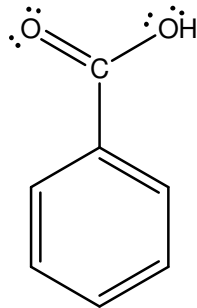
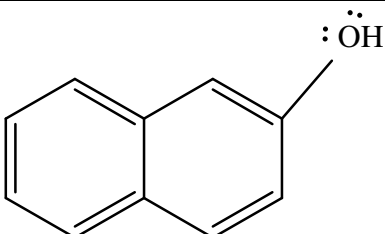
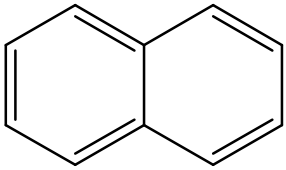
When two or more solutes are part of a mixture, one can separate the solute using a liquid-liquid extraction. If solutes contain differing polarities they can be partitioned between polar and non polar solvents. A polar solute dissolves in a polar solvent and a non-polar solute dissolves in a non-polar solvent. The solute will be dissolved in the preferred solvent. In this experiment, a water-insoluble molecule such as benzoic acid can be reacted with bicarbonate ion to produce a water soluble conjugate base. This enables a separation between the aqueous and organic phase (benzoic acid is with the mixture of organic compounds present). The same deprotonation can be used to separate the remaining mixture. The purpose of this experiment is to separate multi-component mixture as a function of the pH and solubility of solution. As various compounds have various solubility properties, they can be separated by extraction. Weak and strong bases will be used (as needed) for each extraction.

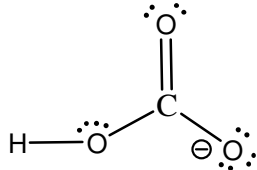
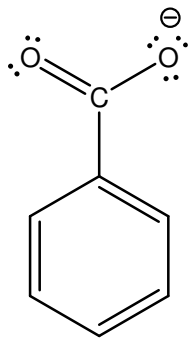
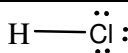
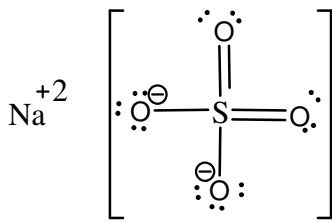
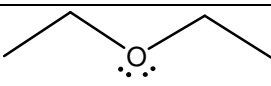
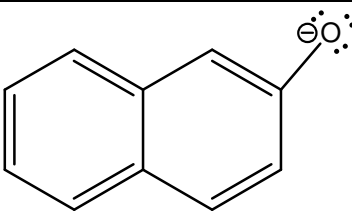
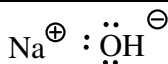
PROCEDURE

- Weigh your unknown mixture of benzoic acid, 2-naphthol, and naphthalene. Record the number of your unknown.
- Carry out the experiment in a fume hood.
- Dissolve the mixture in 30 mL of diethyl ether in a 125-mL Erlenmeyer flask.
- Transfer the ether solution to a 125 separatory funnel and add 20-mL of 10% aqueous sodium bicarbonate solution. (Caution: CO₂ gas is generated. Be sure to frequently release the gas by invert the funnel)
- Swirl the funnel until all foaming has subsided, then shake the funnel with frequent venting. Separate the layer transferring the aqueous layer to a clean, labeled 125-mL Erlenmeyer.
- Repeat the extraction of the organic layer with another 20-mL portion of 10% sodium bicarbonate solution. Separate the layers combining the aqueous layer with the first bicarbonate extract.
- Add 20-mL of cold 10% sodium hydroxide solution to the ether solution in the funnel. Shake the funnel with frequent venting. Separate the layers transferring the aqueous layer to a clean, labeled 125-mL Erlenmeyer flask.

- Transfer the ether solution to a clean 50-mL Erlenmeyer flask, and add about 0.7g of anhydrous sodium sulfate. Cork the flask and let it stand about 15 min.
- Cool the 2-naphthol and the bicarbonate solution before adding 3 M hydrochloric acid drop-wise to each of the aqueous extracts. A precipitate should form in each flask as the acid is added.
- Check to make sure both solutions are acidic to litmus. Cool the flasks in ice and collect the solids separately using vacuum filtration. Each precipitate can be washed using small portions of cold distilled water.
- Allow the two solids to dry over night and then obtain accurate weights and melting points of each.
- Filter the diethyl ether solution from the hydrous sodium sulfate into a tarred 100-mL round bottom flask. Remove the solvent using a rotary evaporator.
- Transfer the naphthalene into a labeled vial with no cap. Weigh a few days later and determine the accurate melting point.
- Calculate the percent recovery for the experiment and the percentage composition of your unknown from the weights obtained of the dry samples.

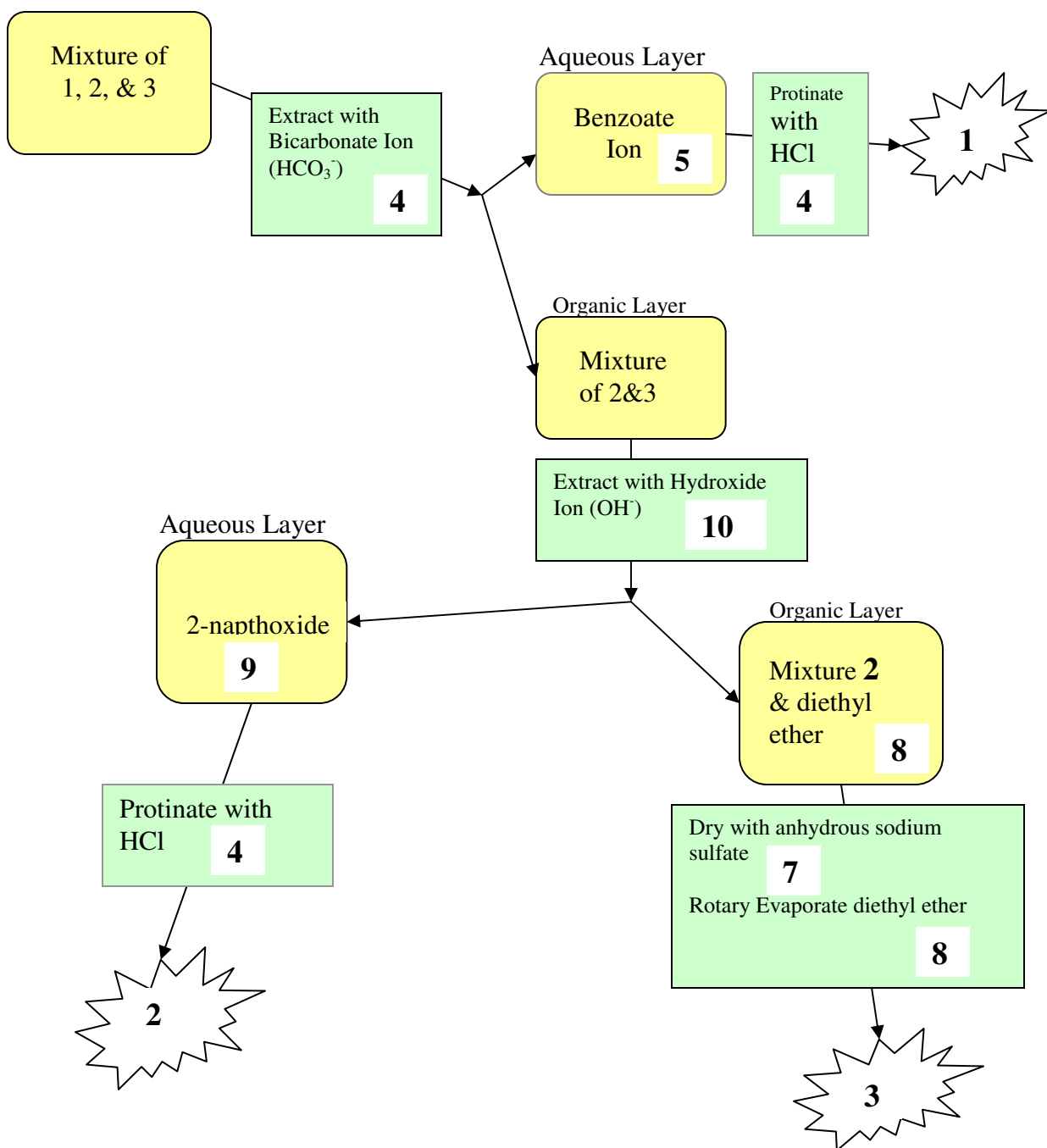
TABLE 1: REAGENTS

<u>Flow Chart</u> <u>Number</u>	<u>Compound</u>	<u>Melting</u> <u>Point (°C)</u>	<u>pKa</u>	<u>Solubility</u>
1	 Benzoic Acid	123	4.17	Soluble in alcohol and water
2	 2-naphthol	123	9.5	Soluble in alcohol but not in water
3	 Naphthalene	80	Neutral, >40	Soluble in alcohol but not in water

<u>Other Compounds Used</u>	
4	 <p>Bicarbonate Ion</p>
5	 <p>Benzoate Ion</p>
6	 <p>Hydrochloric Acid</p>
7	 <p>Sodium Sulfate</p>
8	 <p>Diethyl Ether</p>
9	 <p>2-Naphthoxide</p>
10	 <p>Sodium Hydroxide</p>

RESULTS AND OBSERVATIONS

Flow Chart of Reaction (The numbers in the following flow chart are derived from Table 1: Reagents)



RESULTS AND OBSERVATIONS (cont.)

1.98 g unknown sample of benzoic acid, 2-naphthol, naphthalene

19 # of unknown

0.70 g anhydrous sodium sulfate

TABLE 2: RESULTS
(using mel temp #16)

Compound	Empty Filter Paper (g)	Filter Paper & Compound (g)	Compound weight (g)	Standard Melting Point (°C)	Experimental Melting Point (°C)
Benzoic Acid	0.33	0.72	0.45	123	120.3-121.6
2-naphthol	0.35	0.77	0.42	123	119.0-119.9
Compound	Empty 100-mL flask	Flask & Compound	Compound weight (g)	Standard Melting Point (°C)	Experimental Melting Point (°C)
Naphthalene	69.98	70.79	0.7	80	80.5-81.5

During the first extraction using the sodium bicarbonate, the top layer was determined to be the organic layer after water was dropped into the top layer and the bottom layer was the aqueous layer. During the second extraction, the top layer was the organic layer while the bottom layer was the aqueous layer. After frequent venting, a white piece of paper was placed behind the second extraction to more easily distinguish the aqueous layer from the organic layer. After adding hydrochloric acid dropwise in the first extraction, white precipitate formed (benzoic acid). Continuous swirling is necessary in the first extraction as well as a litmus test to make sure that the solution is acidic. In the second extraction of the aqueous layer, I did cool down the aqueous solution beforehand but did not keep it cold during the addition of acid. As a result there was some oily precipitate formed in the 2-naphthol precipitate. After extracting the naphthalene organic layer in the second extraction, I added more than the 0.7 g of anhydrous sodium sulfate to eliminate any lingering water (about 0.7 g additional anhydrous sodium sulfate). This addition made the organic layer clearer.

After yielding three separate precipitates by vacuum filtration, each looked different. The bicarbonate was white granular, the 2-naphthol was white and flaky with some granules, and the naphthalene was shiny and flake like with an off white color. The percent recovered for each product is shown in Table 3 below. 79.3% was recovered from the original 1.98g sample. 22.7%, 21.2%, and 35.4% was recovered respectively for Benzoic Acid, 2-Naphthol, and Naphthalene. The percent composition for the original substance was 28.7%, 26.8%, and 44.6% respectively for Benzoic Acid, 2-Naphthol, and Naphthalene.

TABLE 3: RECOVERY AMOUNTS

Compound	Amount Recovered (g)	% Recovery (%)		% Composition (%)
Benzoic Acid	0.45	22.7		28.7
2-naphthol	0.42	21.2		26.8
Napthalene	0.70	35.4		44.6
TOTAL	1.57	1.57/1.98 = 79.3		

INTERPRETATION OF INSTRUMENTAL DATA

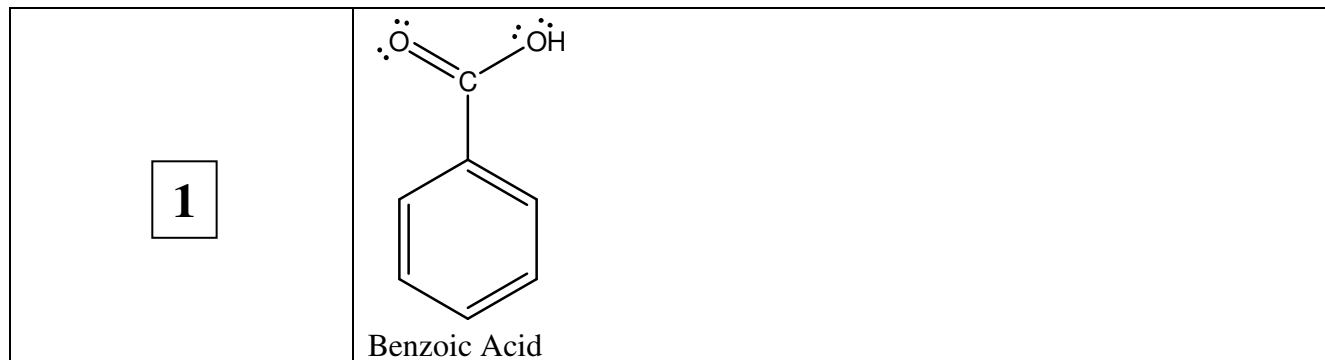
About 79.3% of the product was recovered in this experiment (Table 3). Error could have occurred in various places; during filtration or weighing. Each sample was relatively pure (compared with the known standard) with naphthalene being the purest based on its melting point of 80.5 to 81.5 °C. Bicarbonate and 2-Naphthalene each had a melting point with 2-3 °C different from the standard (As shown in Table 2). However, each melting point had a small range change, which indicates some impurities were present. Overall the experiment was a success, based on the % recovery and the melting points of each substance.

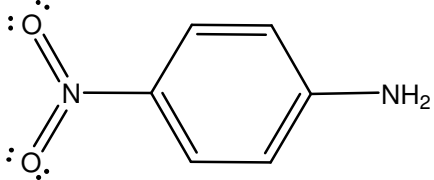
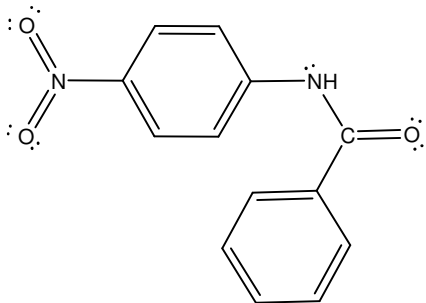
CONCLUSION

In this experiment, two solutes were separated using a liquid-liquid extraction. Based on the pH of the component, the solubility changed, thus allowing us to use pH and solubility of solution to separated by extraction. Benzoic acid, a relatively strong acid was extracted using a weak base (bicarbonate ion). Then a stronger base (hydroxide ion) was used to separate 2-Naphthol and Naphthalene. This technique of extraction was highly effective in extracting each component of the three-component mixture. The relative strength of the acid or base is an excellent way to separate a mixture of compounds.

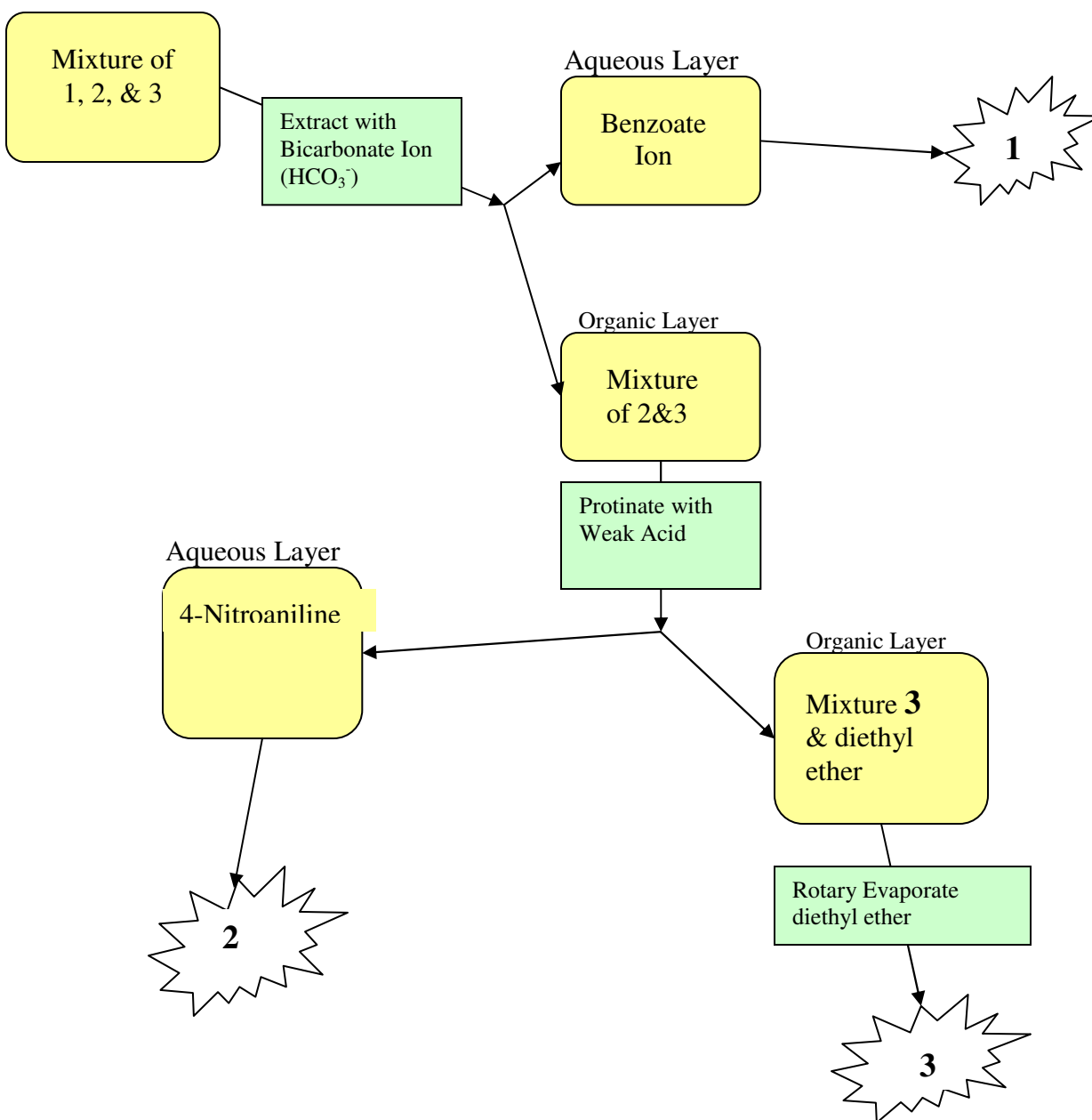
ANSWERS TO ASSIGNED QUESTIONS

8)



2	 <p>4-Nitroaniline</p>
3	 <p>N-(4-nitrophenyl)-benzamide</p>

Below is a flow chart of problem #8, which refers to the table above.



8) As seen above, the mixture can be extracted with bicarbonate ion, to yield an aqueous and organic layer. The aqueous layer can be protinated to yield product #1. The organic layer can then be reacted with a weak acid. This will allow the proton to attach to the strong base first, allowing the aqueous and organic layer to be separated. Once again the aqueous layer can be protinated with a weak acid and the organic layer can be rotary evaporated to yield the final product (#3) in the organic layer.

11) The sequence for extracting diethyl ether solution with aqueous bicarbonate first rather than the aqueous hydroxide involves the relative strength of the bases used. The pKa values of the reagents determine which base to use. Since aqueous bicarbonate is a weak

base, it will serve us much better to use it to attack the strong benzoic acid ($pK_a = 4.17$) to produce the benzoate ion in the aqueous layer. Because 2-naphthol is a weaker acid ($pK_a = 9.5$), we will need a much stronger base to extract the hydrogen in 2-naphthol to produce the 2-naphthoxide (which will be in the aqueous layer). Hence, we use the stronger base, the aqueous hydroxide ion. If we would have used the stronger hydroxide ion first, it would have produced the benzoate ion and 2-naphthoxide ion in the same aqueous layer. We would be unable to easily separate the two components then, which were both in the aqueous layer