Organic Chemistry Experiment 3: Extraction

Morgan Lynds, 8654967

Lab Partner: Dylan Singh, 8605832

Demonstrator: Yixin Zhang
Lab Section: Tuesday Mornings (10:00-13:00), Odd Weeks

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University of Ottawa

Procedure

The procedure was followed as described in the lab manual (CHM 1321 Introductory Organic Chemistry Laboratory Manual 2017, Dr. William Ogilvie and Dr. Tony Durst, 2017, Exp.1, p. 28 to 33).

However, a few modifications were made to the procedure:

- A modification was made to **Step 4** in **Part A** of the procedure and it is as follows:
    1. 1.0 ml of ether, 1.0 ml of distilled water and 1 drop of 0.006 M methylene blue solution were placed in a test tube labelled #1. To mix the contents, a stopper was placed on the test tube and the test tube was shaken vigorously for 10 seconds. It was then placed in the test tube rack and separation into two layers was qualitatively observed. The observations were written in the raw data, along with whether the dye was in the aqueous layer, organic layer, or both layers.

- Another modification was made to **Step 2** in **Part A** of the procedure and it is as follows:
    1. 1.0 ml of ether, 1.0 ml of distilled water and 1 drop of 0.006 M methyl red solution were placed in a test tube labelled #1. To mix the contents, a stopper was placed on the test tube and the test tube was shaken vigorously for 10 seconds. It was then placed in the test tube rack and separation into two layers was qualitatively observed. The observations were written in the raw data, along with whether the dye was in the aqueous layer, organic layer, or both layers.

- Another modification was made to **Step 6** in **Part B** of the procedure and it is as follows:
    6. Unknown Sample #2 was acquired from the jar.

- A last modification was made to **Step 7** in **Part B** of the procedure and it is as follows:
    7. A mass of 1.0 g of Unknown Sample #2 was measured out on an electronic scale. This mass was recorded in the raw data. It was then dissolved in 10 mL dichloromethane in a 50 mL Erlenmeyer flask. A small amount of this solution was set aside in a test tube to be a TLC reference later in the experiment.

Observations

<u>Part A. Extraction of Water Soluble Dyes</u>

- Methylene blue was a translucent royal blue liquid and was odourless.
- The ether was a transparent, colourless liquid with a strong pungent smell.
- Methyl red was a translucent dark red liquid and was odourless.
- When the 1 mL of ether, 1 mL of distilled water and 1 drop of methylene blue were mixed, separation occurred and wo distinct layers were formed right away.
- There was dye in the bottom layer (aqueous layer), and there was no dye in the top layer (organic layer).
- The bottom layer was a royal blue translucent substance and the top layer was a clear, colourless, transparent substance.
- When the 1 mL of ether, 1 mL of distilled water and 1 drop of methyl red were mixed, separation occurred and two distinct layers were formed. However, both layers were a clear, colourless, transparent substance. There was no dye in either layer.
- Methylene blue solvated in the distilled water (it is a salt) and the methyl red was forced to solvate in the ether.

- The Salting Effect caused vibrant purple colour to be through the whole test tube at first. However, after awhile, a distinct purple layer formed at the rim of the NaCl solution, and separation occurred.
- There was a small top layer (organic layer) that was a translucent, vibrant purple substance, and a large bottom layer (aqueous layer) that was a clear, colourless, transparent substance.

Part B. Separating a Mixture with Reactive Extraction

- Unknown Sample #2 was a white, crystalline power, with no odour.
- Dichloromethane was a clear, colourless, transparent liquid with a strong pungent odour.
- The 2:8 EtAOC : Hexane mixture solution was a clear, colourless, transparent liquid, with a strong odour.
- NaCl was a transparent, colourless liquid, with a strong odour.
- When the HCl was added to the aqueous phase, a precipitate was eventually formed and it was white and grainy.
- A small amount of solute was left in the filtrate.
- Refiltration resulted in a better, clearer separation of solute from solvent (liquid)

Results

Table 1. The Rf Values of the TLC Plate with the Organic Layer as the Sample Spot

TLC Plate Number	Reference Spot	Co-Spot	Sample Spot	Rf Value of Reference Spot		Rf Value of Sample Spot
#1	Original Solution of Unknown Sample and Benzoic Acid	Original Solution and Organic Layer	Organic Layer	0.85	0.53	0.85

Table 2. The Rf Values of the TLC Plate with the Aqueous Layer as the Sample Spot

TLC Plate Number	Reference Spot	Co-Spot	Sample Spot	Rf Value of Reference Spot		Rf Value of Sample Spot
#2	Original Solution of Unknown Sample and Benzoic Acid	Original Solution and Aqueous Layer	Aqueous Layer	0.40	0.83	0.00

Table 3. The Rf Values of the Organic Layer and Aqueous Layer TLC Plate

TLC Plate Number	Reference Spot	Co-Spot	Sample Spot	Rf Value of Reference Spot	Rf Value of Co-Spot	Rf Value of Sample Spot	
#3	Biphenyl	Benzophenone	Unknown Mixture of Unknown Sample and Benzoic Acid	0.82	0.64	0.82	0.42

Figure 1. Drawing of the TLC Plate with the Organic Layer as the Sample Spot

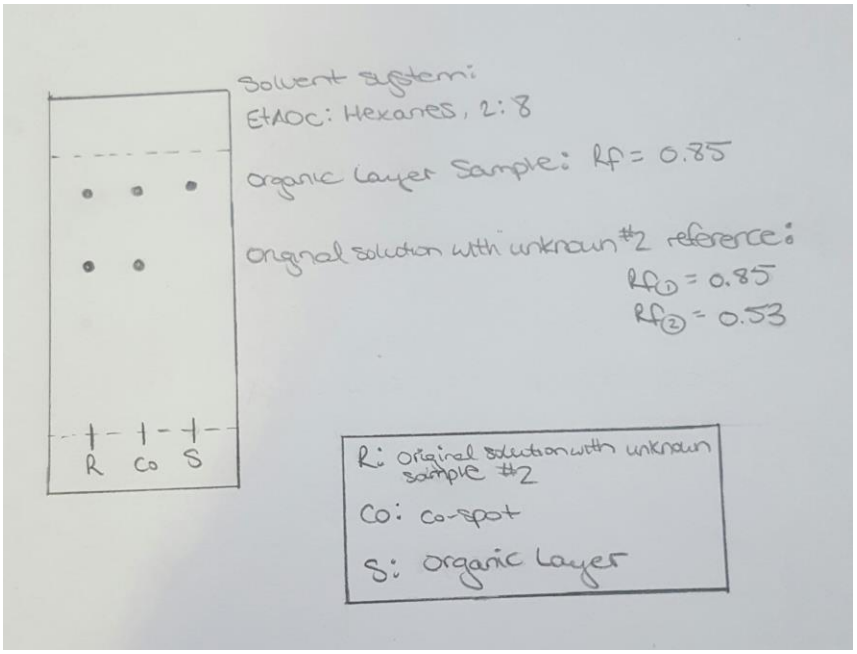


Figure 2. Drawing of the TLC Plate with the Aqueous Layer as the Sample Spot

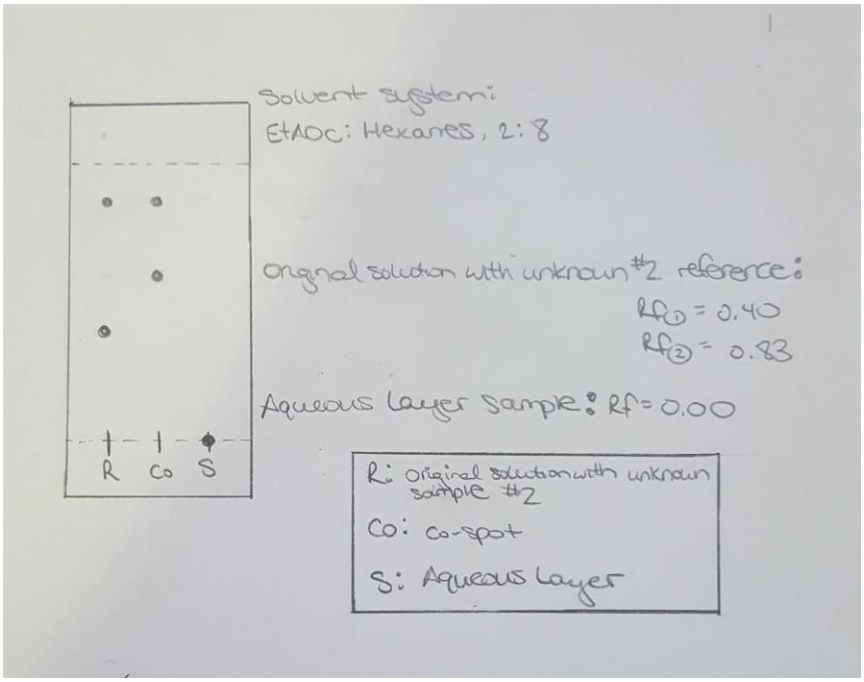
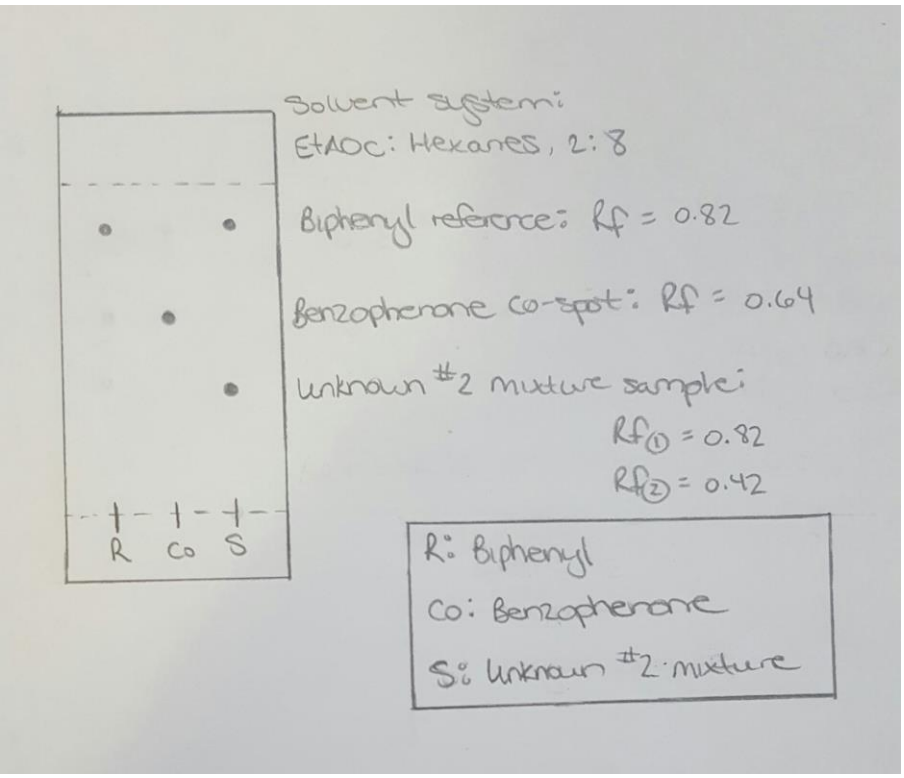


Figure 3. Drawing of the TLC Plate with Biphenyl as the Reference Spot and Benzophenone as the Co-Spot



Calculations

Percent Yield of Benzoic Acid

Mass of precipitate product formed: m = 0.25 g
Mass of unknown sample #2 used: m = 1.0 g

Percent Yield of Benzoic Acid = (mass of product / mass of unknown sample #2) · 100%
= (0.25 g / 1.0 g) · 100%
= 25%

Therefore, the percent yield of benzoic acid is 25%.

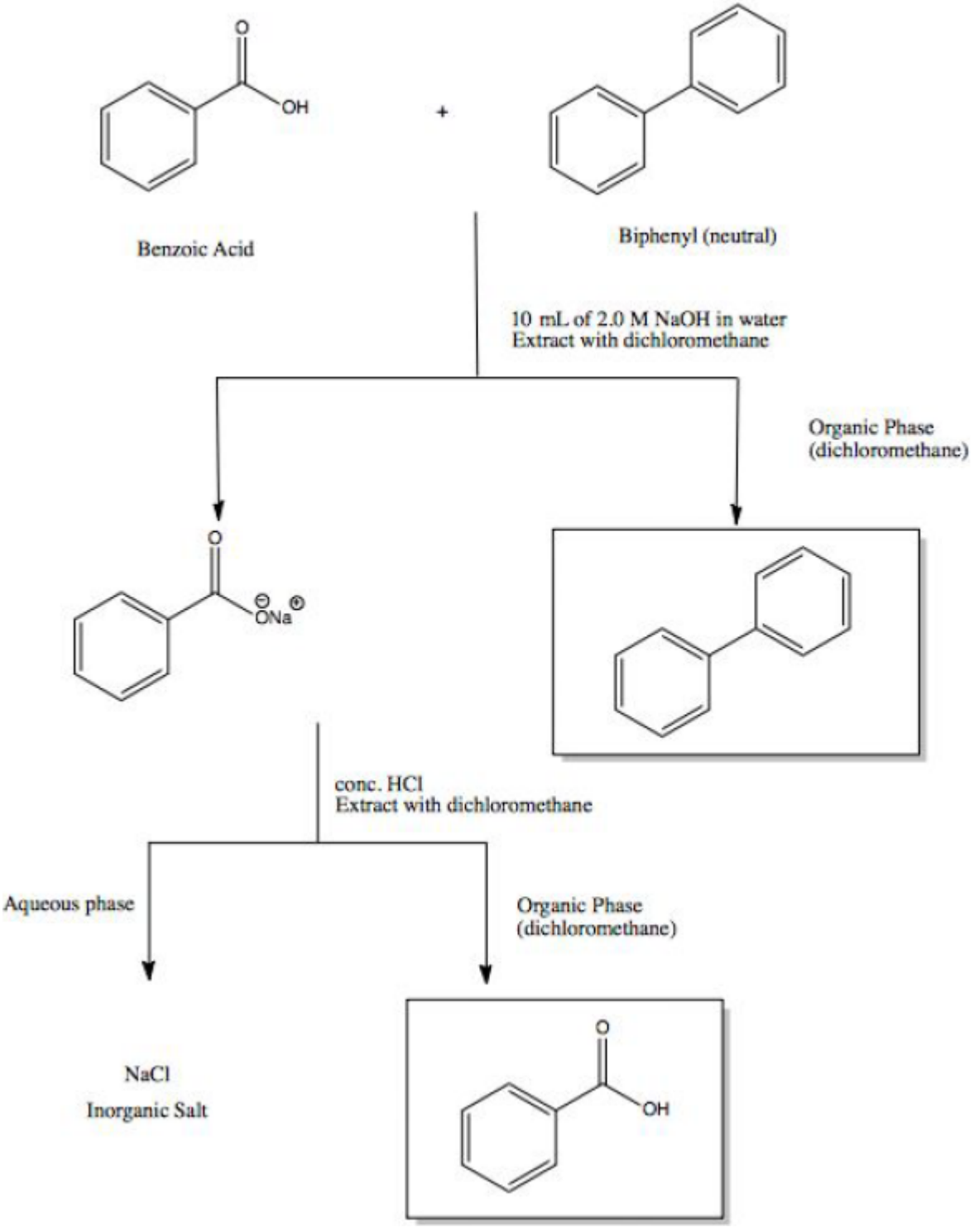
Sample Rf Value Calculation

Rf value = distance travelled by the compound / distance travelled by the solvent

Rf value for one of the reference spots on TLC plate #1:
Rf value = distance travelled by compound / distance travelled by solvent
= 2.9 / 5.5
= 0.53

Therefore, the Rf value for one of the reference spots on TLC plate #1 is 0.53.

Mechanism Describing the Reactive Separation of a Mixture Containing Benzoic Acid and Biphenyl



The addition of NaOH to the mixture caused a reaction to occur between NaOH and benzoic acid, which produced the conjugate basic salt of the acid. Separation of the mixture ensued as the salt dissolved in the aqueous phase while biphenyl was left unreacted in the organic phase. Acidification of the benzoate salt with concentrated HCl reverted this basic, ionic salt back to benzoic acid while producing the inorganic salt NaCl in the process.

Note: The images for biphenyl and benzoic acid were replicated from Wikipedia.com.

Discussion

The technique of extraction involves the separation of the components of a mixture by the tendency of the individual components to dissolve a particular solvent. The compounds are differentiated by preferential solubility in a medium consisting of two immiscible solvents. In most extractions, the two solvents involved compose either the organic phase or the aqueous phase, with water being usually the aqueous phase. The organic phase consists of an organic, carbon containing solvent that does not mix with water (immiscible).

The first part of the experiment demonstrated the separation of compounds based on their affinity to dissolve in either the organic or aqueous layer. This portion of the experiment employed the use of dyes, which made the separation more clearly visible. Methylene blue exists as a charged species with a chloride cation and a sulfur anion and thus, interacts favorably and readily dissolves in water. So, methylene blue, a polar compound was greatly attracted to the polar water molecules, caused the blue dye to appear in the aqueous layer. Methyl red, an organic, nonpolar substance interacted favorably with the nonpolar solvent of ether. Organic, uncharged substances are not soluble in aqueous phase, thus methyl red appeared in the organic phase. The mixture of methylene blue and methyl red was effectively separated in the immiscible solvents of ether and water. Methyl blue strictly dissolved in water while methyl red readily dissolved in ether causing the aqueous phase to appear blue while the organic phase exhibited a very slight tinge of red. In the portion of the experiment on the salting out effect, the input of NaCl into one of the test tubes containing aqueous crystal violet, 1-butanol, and water caused the dye to be slightly displaced from the bottom of the test tube. The presence of NaCl in the solution, which is an ionic salt, it interacted strongly with water and forced the crystal violet out of the aqueous layer and into the organic layer. NaCl saturated the aqueous water phase and caused the water molecules to be fully occupied in dispersing the sodium cation and chloride anions in solution. Thus, the crystal violet compound was forced to rise to the organic phase. Thus, a slight discoloration was observed at the bottom of the test tube as ionic salt was heavily present and the crystal violet was relatively absent from that portion of the solution. The bottom of the test tube was relatively colourless and clear, while the top of the test tube displayed a small dark violet layer, which was the crystal violet occupying the organic phase. The presence of NaCl had forced the portion of the crystal violet compound as far as possible from the bottom of the test tube.

The organic and aqueous TLC plates indicate that effective separation had occurred between the benzoic acid and the organic compound. The isolated organic phase exhibited only one spot the TLC plate, indicating only the organic compound was present in that phase. The spot in the sample organic phase lane corresponded with the upper unknown spot with matching a Rf value of 0.85. It was expected that the isolated aqueous phase spot on the aqueous TLC plate would correspond with the lower spot of the unknown compound in the reference and co-spot lanes. However, the acidic spot remained stationary which may have resulted due to its high concentration and resulting high polarity that prevented the spot from traveling across the plate. Through the TLC plates, it was confirmed that effective separation had occurred as the spotted organic phase contained a single, nonpolar compound and the spotted aqueous phase contained a single, highly polar compound.

The streaking of the lower unknown on the third TLC plate indicated the high polarity of that particular component. The streaking of the spots as indicated by the elongated ovals on the TLC plate photos are due to affinity of the acid to the silica gel coating of the plate. The correspondence of the higher unknown sample spot with the biphenyl spot indicated that the other component of the unknown mixture was biphenyl. The matching Rf value of 0.82 confirmed this correspondence. Benzophenone was not in the unknown compound as the benzophenone spot did not correspond with either of the unknown sample spots, as seen in the differing Rf values of 0.64, and 0.42 and 0.82, respectively. Thus, it was concluded that the unknown compound #2 consisted of biphenyl and benzoic acid.

Reactive separation of the biphenyl and benzoic acid mixture was achieved by applying properties of acids and bases. The results of the extraction were as expected as acid-base extraction relies on the tendency of an acid or base to react, which is a clear distinction between compounds such as an acid and an organic

compound. Because acid base reactions produce salts that are able to dissolve in water, separation between an organic acid and an uncharged organic substance can occur. In the case of the experiment, NaOH, a strong base, was added to the mixture and reacted with benzoic acid. Benzoic acid donated a proton to the base, a reaction which produced water and sodium benzoate, the conjugate base. Sodium benzoate exhibits ionic properties as a salt and displays a slight positive charge on the sodium cation and a partial negative charge on the oxygen anion as oxygen disperses the charge due to its higher electronegativity. The slight negative charge on the oxygen atoms in water attract the sodium cations while the negatively charged hydrogen atoms from water interact with the oxygen anions causing sodium benzoate to dissociate in the aqueous phase. Extraction is complete as the conjugate base of the acid rests in the aqueous phase while the organic compound remains in the organic, dichloromethane solvent. Because dichloromethane exhibits a higher density than water, the organic phase stabilizes at the bottom of the separatory funnel while the aqueous phase rests directly above the organic phase. To ensure that no acid was left in the organic phase either because the added NaOH did not completely react with the acid or there was residual acid interacting with the organic compound, extraction was performed twice more by running the organic phase through the separatory funnel with an additional 10 mL of NaOH each time.

To convert the conjugate basic salt back to the original acid, a strong acid, HCl, was added to the aqueous flask. The addition of HCl caused reprotonation of the salt which transformed the salt back into the acid with an inorganic salt produced in the process. The method of deprotonation and protonation effectively draws the acid out of the organic solution, since the tendency of the acid to react differentiates it from the nonpolar, more stable organic compound. Deprotonation of an acid or protonation of a base causes the acid or base to exhibit ionic properties which results in a better ability of these substances to dissolve in a non-organic solvent, such as water. This in turn causes a separation between the organic compound and the acid or base.

There were possible sources of error in this experiment that could have influenced the results. When performing the extraction, it is very difficult and improbably that a 100% pure sample of the organic compounds or aqueous solution was obtained, even though the solution was purified in the separatory flask three times. A full pure separation is very difficult to do; therefore, there was probably contamination in each separated solution. In other words, a small percentage of each compound was in each solution and therefore, the results such as the percent composition and TLC plate Rf values were influenced. Meaning the correct values could be a bit less or a bit more than the results we obtained. Another source of error could have occurred when the TLC plates were spotted. The same capillary was used to spot the organic layer and the aqueous layer, and this means that cross contamination could have occurred in each TLC spot, even though the capillary was thoroughly cleaned out between spots. A final source of error could have occurred when measuring the mass of the precipitate. Some of the precipitate stuck to the inside of the top of the washing apparatus and to the filter paper. Also, some of the precipitate fell onto the counter when taking out the filter paper from the washing apparatus. This means that the actual mass of precipitate formed is higher than the mass noted in the raw data and then used in the calculations.

Questions

1. Extraction distinguishes the separate compounds in solution by their polarity, and thus, miscibility in a certain solvent. Ethanol and water are both polar substances and therefore they are miscible. If the solvents are able to mix together, as in the case of ethanol and water, the compounds from the inputted solution may separate but will still occupy the same vicinity as ethanol and water interact with each other. Thus, since ethanol is miscible in water, a successful extraction would prove to be very difficult.

2. As NaCl dissolves well in water, its free-floating ions more readily interact with the molecules of water than does methylene blue, a slightly charged organic compound. NaCl saturates the water which forces the methylene blue to the organic phase and subsequently causes the amount of dye in the aqueous layer to decrease in a process known as “salting out.”. The amount of dye in the aqueous layer would decrease in the aqueous layer.

3. KD = (W1 / V1) / (W2 / V2)
= (2.0 g / 100 mL) / (20.0 g / 100 mL)
= 0.1
Let w represent the mass of compound Y in the aqueous (distilled water) phase.
Let m represent the mass of compound Y in the organic (ether) phase.
m + w = 1.8 g
m = 1.8 g - w
0.1 = (w / 100 mL) / (1.8 g - w / 100 mL)
w = 0.08 g
m = 1.8 g - w
= 1.8 g - 0.08 g
= 1.72 g
Therefore, 1.72 grams of compound Y will be removed from the solution of 1.8 g of Y in 100 mL of water by the single extraction with 100 mL of ether.

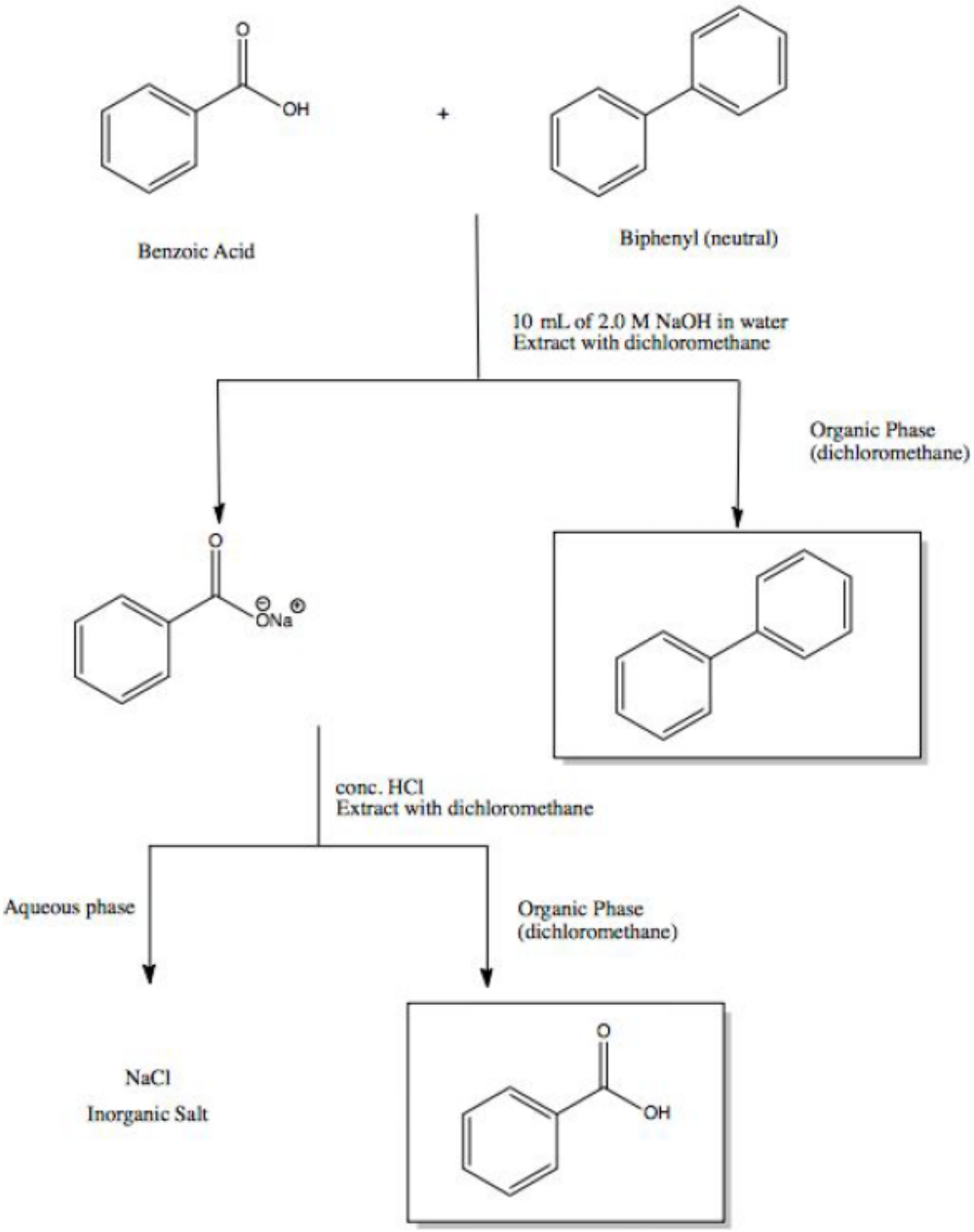
4. Extraction One, using 50 ml of ether:
Let w represent the mass of compound Y in the aqueous (distilled water) phase.
Let m represent the mass of compound Y in the organic (ether) phase.
m + w = 1.8 g
m = 1.8 g - w
KD = (W1 / V1)/(W2 / V2)
0.1 = (w / 100 mL) / (1.8 g - w / 50 mL)
w = 0.30 g
m = 1.8 g - w
= 1.8 g - 0.30 g
= 1.50 g
Therefore, in the first extraction, 1.50 grams of compound Y will be removed from the solution of 1.8 g of Y in 100 mL of water by the extraction with 50 mL of ether.

Extraction Two, also using 50 ml of ether:
m + w = 0.30 g
m = 0.30 - w
KD = (W1 / V1) / (W2 / V2)
0.1 = (w / 100 mL) / (0.3 – w / 50 ml)
w = 0.05 g
m = 0.30 g - 0.05 g
= 0.25 g
Therefore, in the second extraction, 0.25 grams of compound Y will be further removed from the solution of 1.8 g of Y in 100 mL of water by the extraction with 50 mL of ether.

Total extracted amount of compound Y:
Total mass of Y removed = 1.50 g + 0.25 g
= 1.75 g
Therefore, in total after the two extractions, 1.75 grams of compound Y were removed from the solution.

5. The student could add some water, possibly dyed water (for visibility), to the solution to determine which layer is aqueous and which is organic. Water resides in the aqueous phase so the student could note to which phase water travels and determine which layer is the aqueous phase.

6. The mixture of benzyl amine and naphthalene can be separated by adding HCl, a strong acid, to the solution. HCl will react with the base, benzyl amine, to produce its conjugate acid in salt form, which dissolves in water. The organic and aqueous phases will be divided in through the use of the separatory funnel and the organic phase can be poured back into the funnel to undergo further extraction of benzyl amine. More HCl can be added to draw out the benzyl amine from the organic phase. After several extractions, the organic phase is transferred to a beaker as now only the organic compound, naphthalene is present in the organic phase. Once the aqueous phases are extracted and transferred to a single flask, NaOH can be added to this solution containing the salt. Enough NaOH must be added to convert the salt back into the base, benzyl amine. The beaker can then be immersed in an ice water bath and the solution can be filtered suctioned to obtain the pure precipitate of benzyl amine. The following flowchart describes the reactive separation:



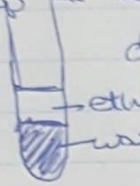
Raw Data

exp 3 - extractions — Morgan Lynds

Methylene blue → translucent royal blue
ether → strong smell, clear

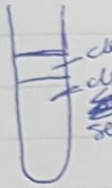
Part A — 1 drop methylene blue

Step 1 → 1mL ether, 1 mL distilled water
separation between ether and water
dye in aqueous layer, clear top layer
bottom (organic)

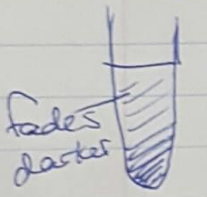


2 distinct layers (1 blue, 1 clear)

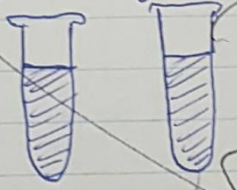
Step 2 → 1 mL ether, 2 mL water, 1 drop methylene blue
separation, but the layers are the same clear
Clear, transparent colourless all the colours
way through
2 distinct layers, but they're both clear liquid



Step 3 → Yes, it is.
(It is all a cloudy medium aqua blue, translucent. No separation into layers
very strong smell similar to nail polish remover

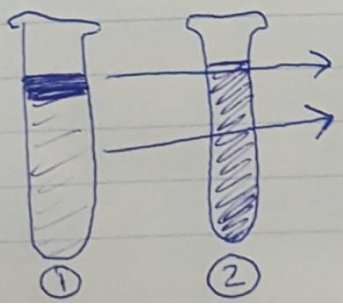


Step 4 →



Bright violet colour distributed evenly in both

Step 5 →
① Test tube 1: violet solution + NaCl solid until saturated
② Test tube 2: Just the violet solution



Part B — Identification #: unknown sample #2

Step 6 → Mass unknown #2 = 1.00 g

Step 7 → Volume dichloromethane = 18.0 mL

Separatory funnel

1.0 g unknown

10.0 mL dichloromethane

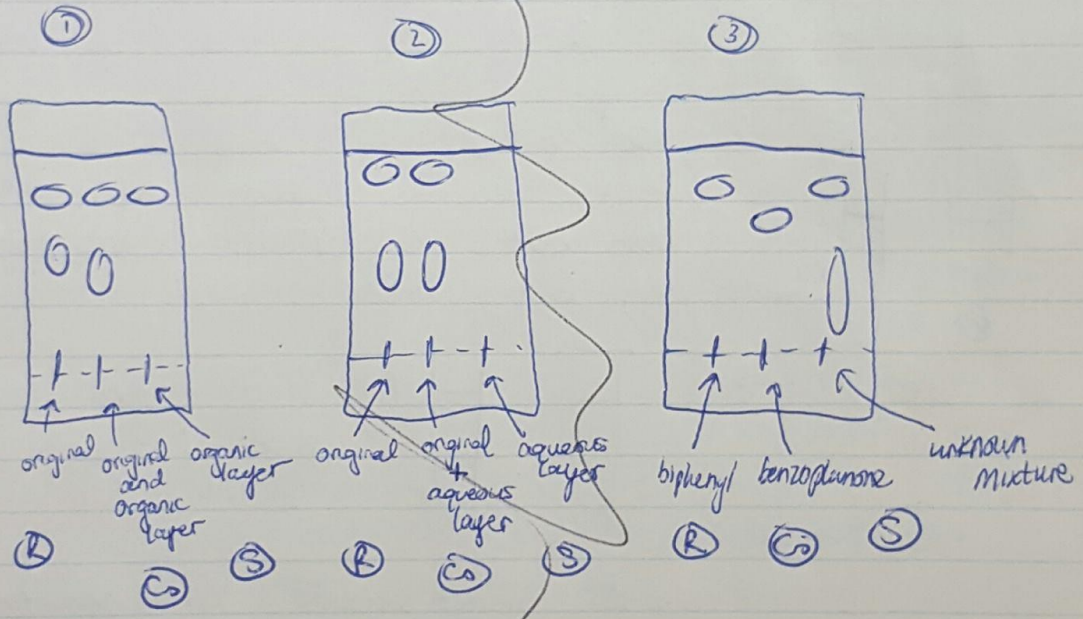
5.0 mL more of dichloromethane

10.0 mL 2M NaOH (aq)

Step 12 → Repeat twice

Step 13 → 40 drops ~~HCl~~ added to aqueous (bottom) layer (in the small erlenmyer flask)

Step 17 → TLC plates:



Step 16 → Mass of solid created (salt product) = 0.55 g.

Step 18 → Developed using 2:8 mixture of EtOAc : Hexanes