LAB 3:

EXTRACTION

Submitted by:

[redacted]

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Submission Due: February 13th, 2019

CHM1321 - Z05

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Procedure

See lab manual Experiment 3: Extraction(pg 1-6)

Qualitative Observations

Part A

- ➢ Methyl red was a bright red dye in colour, however, after adding the dye to the water and ether the solution turned a pale yellow.
    - After shaking the test tube, two distinct layers were formed, one translucent yellow/white on the top and a transparent yellow on the bottom
- ➢ Methylene blue was a bright cobalt dye in colour and remained being that colour after in contact with water and ether
    - After shaking the test tube, two distinct layers were formed, one clear on the top and a transparent cobalt blue on the bottom
- ➢ Initially after mixing the tubes containing methyl red and methylene blue and waiting a minute a new colour was formed with a few layers to it. The first later was clear and small, the next layer was a gradient going from translucent to transparent tinted by a greenish blue.
    - After leaving the mixed solutions alone for a minute the clear layer on the top got thicker and the layer of green/blue became fully transparent.
- ➢ Aqueous crystal violet was a very dark purple dye, however, after adding the dye to the water and 1-butanol the solution turned a consistent transparent violet
    - The addition of NaCl solid changed the initially fully violet solution to having two layers. The first layer was the translucent purple being quite thin and the second was a nearly clear and transparent layer.

Part B

- ➢ Unknown sample #110 was used for the extraction. The sample was a powder of white crystals. This sample was dissolved in dichloromethane which was a clear solution with a strong odour.
- ➢ A 2M solution of NaOH was also added to the separatory funnel with the sample solution. This was also a clear solution
- ➢ The separatory funnel with the 2 solutions was then inverted and shaken for the extraction.
    - When the stop cock was opened there was a “hissing” sound due to the release of gas. This occurred every time stop cock was opened after shaking the mixture.
- ➢ After the shaking process the separatory funnel was placed in a rack to allow the mixtures to separate undisturbed.
    - The mixtures separated into 2 layers. The layers both contained clear solutions, but the separation was fairly visible to see as there was a dark line indicating so.
- ➢ The organic layer (bottom layer) was collected first.
    - When opening the stop cock too fast there was a rush of air bubbles into the funnel. This was corrected by more slowly opening the stopcock.
- ➢ The aqueous layer (top layer) was collected last.

- ➢ The collected aqueous layer was acidified with 12 M Hydrochloric acid which was a clear solution.
    - The aqueous layer had to be strongly acidic. The acidity of the solution was determined using litmus paper. When the litmus paper turned red, the solution was acidified.
    - While adding the hydrochloric acid to the solution mixture a white precipitate formed and dissolved until all of the solution was acidified. At this point all of the precipitate came out of the solution.
- ➢ The precipitate was extracted from the aqueous solution using gravity filtration and suction filtration.
    - The precipitate was composed of flaky white crystals.

Part C

- ➢ The solid formed at the end of part B was easily diluted with the transparent dichloromethane forming an equally transparent solution
- ➢ When the samples were dotted on the TLC, a dot spread onto the plate and then disappeared.
- ➢ TLCs were removed from the eluant when the solvent line was about 1 cm from the top of the TLC plate.
- ➢ When the TLC plate was removed elution, the solvent on the TLC plate disappeared very quickly.
- ➢ TLCs were clear and developed successfully

Quantitative Observations and Results

Part A

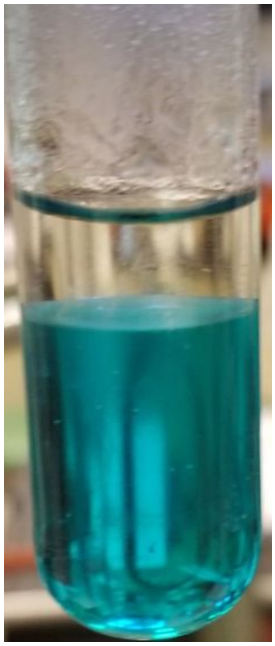
Figure 1.1. 1 ml ether, 2 ml H_2O, 1 drop 0.006 M methyl red after shaking for 10 seconds	**Figure 1.2**. 1 ml ether, 1 ml H_2O, 1 drop 0.006 M methylene blue after shaking for 10 seconds	**Figure 1.3**. Test tube depicted in figure 1.1 mixed with test tube depicted in figure 1.2. Immediately after shaking for 10 seconds	**Figure 1.4.** Test tube depicted in figure 1.1 mixed with test tube depicted in figure 1.2. after 5 minutes
			

	**Figure 1.5**. 5 ml H_2O, 0.5 ml 1-butanol, 1 drop 0.003 M aqueous crystal violet after shaking for 10 seconds		**Figure 1.6**. 5 ml H_2O, 0.5 ml 1-butanol, 1 drop crystal violet, NaCl solid after shaking for 10 seconds and waiting a minute

Part B

Figure 2.0. Flow chart depicting the steps of separation and precipitation of benzoic acid

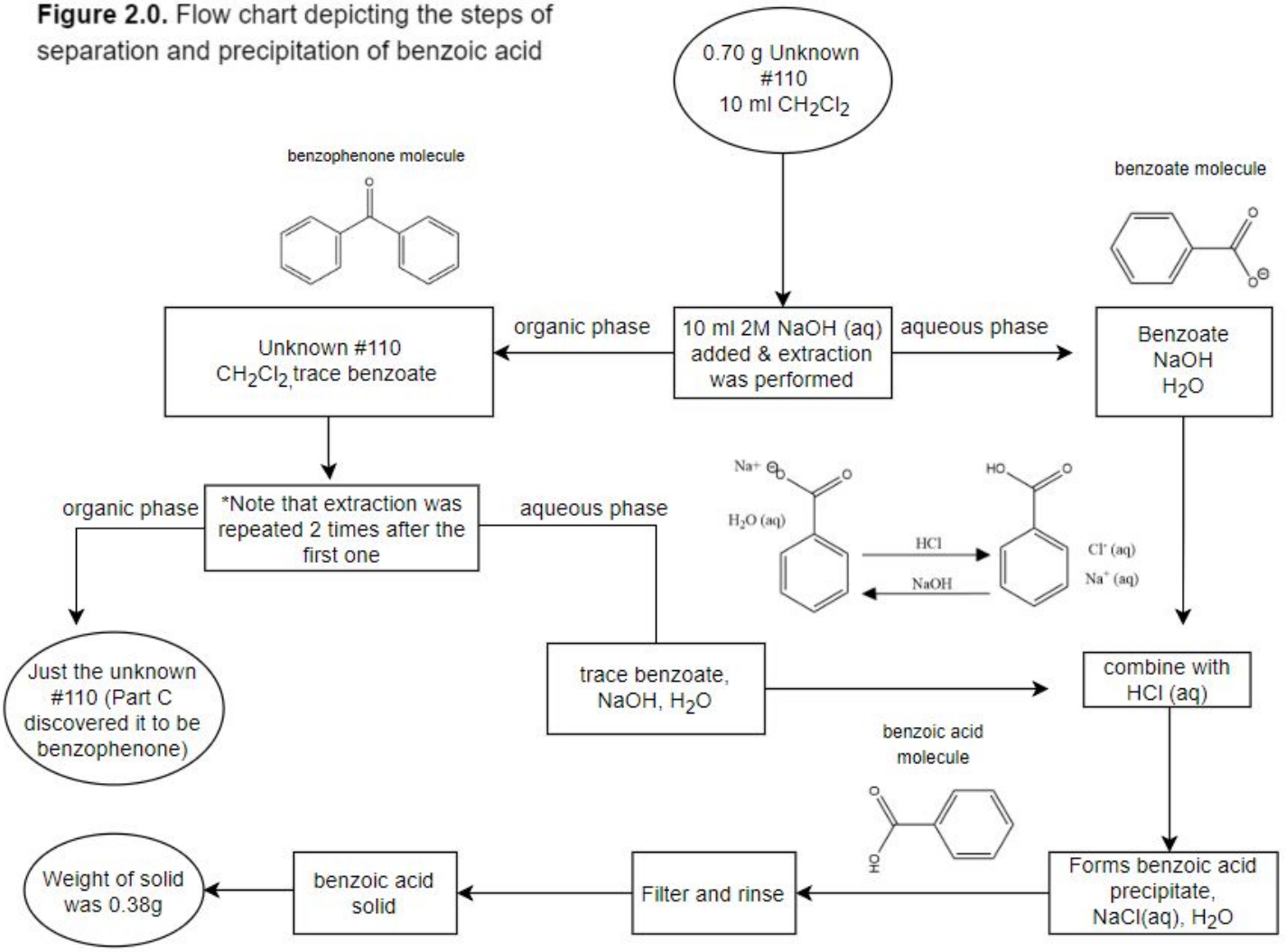


Table 1.0: Summary of results from Part B

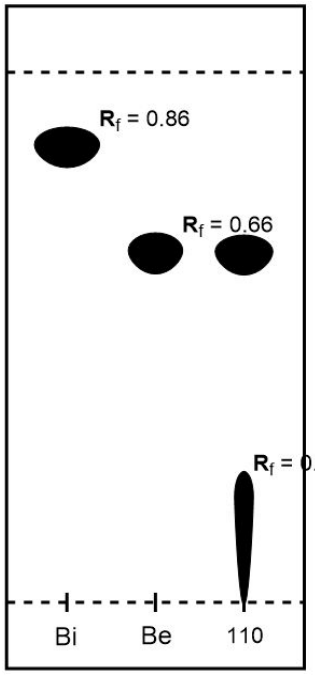
Unknown:#110	Contained: ● Benzophenone ● Benzoic acid
	Initial weight: 0.70g (Benzophenone + Benzoic acid) solid
	Final weight: 0.38g (Benzoic acid) solid
Percent Composition	● Benzophenone 46% ● Benzoic acid = 54 %

Part C

Figure 3.1. TLC of Biphenyl, Benzophenone and the unknown sample 110

Legend:

L = lowest Spot (Vertically)
H = Highest Spot (Vertically)
d_s = displacement between former and new solvent line
d_X= displacement between starting solvent line and molecule
● = 1 Spot visible under UV light

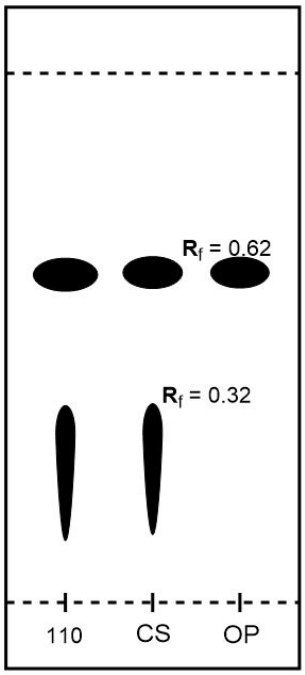


Solvent System:
EtOAc:hex
1:9

displacements:
d_s= 5.0 cm
d_{Bi}= 4.2 cm
d_{Be} = 3.3 cm
$d_{110(L)}$= 1.5 cm
$d_{110(H)}$= 3.3 cm

Bi = Biphenyl
Be = Benzophenone
110 = Unknown Sample 110

Figure 3.2. TLC of the separated organic layer using sample 110 as reference

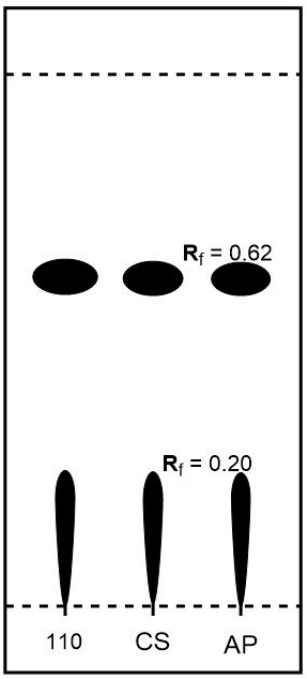


Solvent System:
EtOAc:hex
2:8

displacements:
d_s= 5.0 cm
$d_{110(L)}$= 1.6 cm
$d_{110(H)}$= 3.1 cm
$d_{CS(L)}$= 1.6 cm
$d_{CS(H)}$= 3.1 cm
d_{OP}= 3.1 cm

110 = Unknown Sample 110
Co = Co-Spot
OP = Organic Phase from extraction

Figure 3.3. TLC of the separated organic layer using sample 110 as reference



Solvent System:
EtOAc:hex
1:9

displacements:
d_s= 5.0 cm
$d_{110(L)}$= 1.0 cm
$d_{110(H)}$= 3.1 cm
$d_{CS(L)}$= 1.0 cm
$d_{CS(H)}$= 3.1 cm
$d_{OP(L)}$= 1.0 cm
$d_{OP(H)}$= 3.1 cm

110 = Unknown Sample 110
Co = Co-Spot
AP = Aqueous Phase from extraction

Calculations

Sample Rf Calculation from Part C, Figure 3.2.

Given:	*Calculation:*
d_s= 5.0 cm $d_{110(L)}$= 1.6 cm $d_{110(H)}$= 3.1 cm $d_{CS(L)}$= 1.6 cm $d_{CS(H)}$= 3.1 cm d_{OP}= 3.1 cm	**$Rf = d_x/d_s$** $Rf_{110(L),\ CS(L)}$ = 1.6 cm /5.0 cm = 0.32 $Rf_{110(H),\ CS(H),\ OP}$ = 3.1 cm /5.0 cm = 0.62

Percent Composition

Known:	*Calculation:*
Initial mass of 110 (benzophenone) = 0.70g Mass of benzoic acid = 0.38g Percent composition = $\frac{\text{Mass benzoic acid}}{\text{mass of sample}} \times 100$	Percent composition = $\frac{0.38\text{ g benzoic acid (s)}}{0.70\text{ g \#110(s)}} \times 100 = 54\%$ ∴ percent composition is 54% benzoic acid

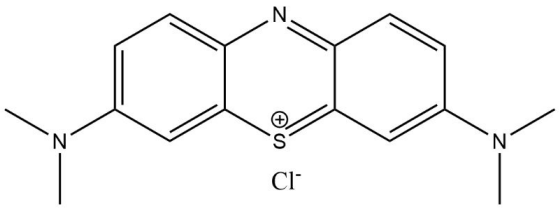
Discussion

Part A

Extraction of Water soluble dyes

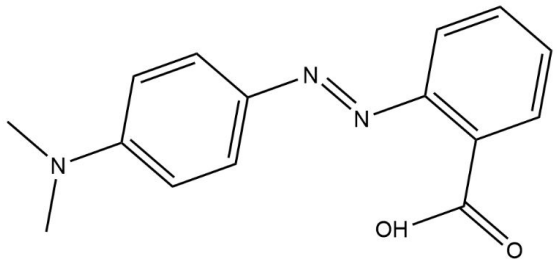
The two organic and aqueous solutions used for this separation were ether and water, respectively. Ether is non-polar organic compound and water is a polar compound, therefore these two substances are immiscible and should separate when mixed. When mixed in a test tube the ether would separate into the top layer and the water into the bottom layer because ether, like most organics, is less dense than water.

Figure 1.7. Line structure of methylene blue molecule



Methylene Blue is a polar compound because of the chlorine atom associated with it (Fig 1.7.). Thus, it is miscible with water and not with other organic compounds (ether) ("Experiment 3 : Extraction," 2014). When methylene blue was mixed with water and ether in the test tube, the blue colour of methylene blue was only seen in the bottom layer and not in the top organic layer. This was as expected because water is more dense than ether is and since both water and methylene blue are polar they are miscible and both appear separate from the organic layer on the bottom of the test tube.

Figure 1.8. Line structure of methyl red molecule



Methyl Red, on the other hand, is a nonpolar compound and thus, is not miscible with polar compounds (Fig 1.8.). Methyl red is an indicator and turns yellow when in a pH range between 4.8 and 6.0 (National Center for Biotechnology Information. PubChem Compound Database; CID=10303). When methyl red was mixed with water and ether in the test tube, an almost opaque clouded yellow layer formed on top and a clear yellow layer formed on the bottom (Fig 1.1). This showed that the methyl red, while nonpolar did mix with the water. This was unexpected; however, it can be explained by the carboxyl group which makes up part of methyl red. The carboxyl group means that methyl red is a carboxylic acid, so it is able to give up a proton in water. This gives a resulting anion and anions have a negative charge which enables it to mix with the polar water layer. In theory it would be expected that just a yellow layer in the organic phase will be seen on top, this is not so practical in experimentation though.

When the two solutions (methylene blue, water, ether and methyl red, water ether) were mixed there was a separation. The bottom layer was a clear blue-green solution and the top layer was a slightly yellow tinged clear solution (Fig 1.4). This meant that the bottom layer must have consisted of methyl blue, water and a bit of methyl red whose yellow colour contributes to the slight green colour of the bottom layer. The top layer must consist of ether and methyl red which gave the layer a slightly yellow tinge. Since the two layers are shown to separate out in the mixed test tube (Fig 1.4), methyl red and methylene blue are immiscible, thus an extraction would be a good way to separate the two substances.

Salting Out Effect

For this part of the experiment, two test tubes were prepared each of which contained water, crystal violet and 1-butanol. Solid NaCl was added to one of the test tubes. In the test tube without NaCl, there was a solid purple colour throughout the solution (Fig 1.5). This was to be expected because while 1-butanol and water should separate into layers due to their difference in polarity crystal violet is both nonpolar and polar, therefore it mixes well with both water and 1-butanol and appears throughout the entire test tube without any layering effects. In the test tube with the NaCl crystals, the crystal violet was restricted to a small section at the top of the solution (Fig 1.6). This was because the NaCl saturates the water as it is only soluble in water, it also makes the water even more polar than it was. The NaCl ended up pushing the crystal violet out of the water (aqueous layer) and into the 1-butanol (organic layer) (“Experiment 3 : Extraction,” 2014). 1-butanol is less dense than water therefore it was observed to be the top layer which is why the crystal violet band on top of the solutions was seen.

Part B

For this lab, there was a choice of two unknowns one of which was composed of biphenyl and benzoic acid and the other was composed of benzophenone and benzoic acid. The unknown compound obtained was sample #110 for the extraction of benzoic acid. Dichloromethane was used to dissolve the unknown solid. Dichloromethane is an organic compound and is also moderately polar (due to the Chlorine). This solution went into the separatory funnel together with 2 M NaOH solution which is very polar. Due to the difference in their polarities these solutions are immiscible ("Experiment 3 : Extraction," 2014). Since benzoic acid is also a polar compound, during the shaking of the mixture the benzoic acid would be almost completely removed from the dichloromethane and benzophenone and will dissolve in the NaOH. Furthermore, benzoic acid can become polar by getting deprotonated. This allows it to be dissolved in the NaOH solution rather than in the more nonpolar organic solution. Thus, the benzoic acid is able to remain in solution in its deprotonated form (benzoate) in the aqueous phase as seen on the left side of Fig 2.4. The bottom layer in the separatory funnel should be that of the dichloromethane and benzophenone. It is also the organic layer because it is less polar than the NaOH solution and it is the bottom layer because of the heavy atom chlorine and thus is more dense. Thus, the aqueous layer comprised of NaOH and the benzoic acid. Although traces, of benzoic acid would have been left in the organic layer, thus two more separations were dome to separate out all of the benzoic acid from the organic layer. Once all of the aqueous layer has been collected, the aqueous solution was acidified with the addition of HCl slowly. This was done very carefully, so as not to precipitate out NaCl. The HCl was added bit by bit and the solution was checked with litmus paper to determine the pH. When HCl was added to the aqueous layer the HCl ionized into H+ and Cl-. The H+ binds to the negatively charged oxygen on the benzoate molecules (when dissolved benzoic acid is just benzoate which is the ionic counterpart). This neutralizes the oxygen and forms benzoic acid which precipitates out of the solution as it is no longer a deprotonated ion (This reaction is summarized in Fig. 2.4).

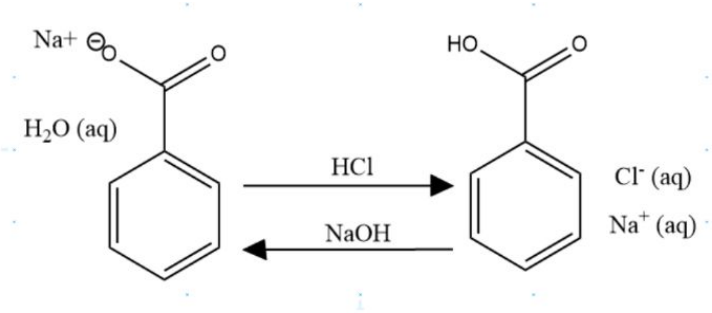


Figure 2.4. The addition of HCl or NaOH to benzoic acid and benzoate

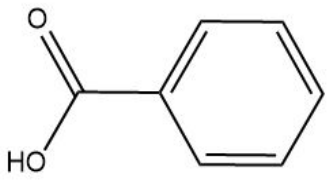
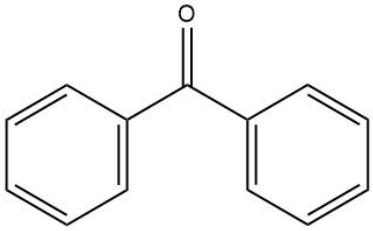
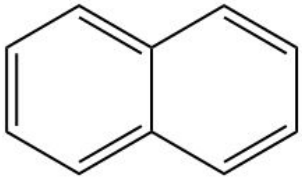
The Cl- ion remains aqueous along with the Na+ ion. If too much HCl was added, the solution could become much too saturated with Cl- ions and cause the precipitation of NaCl. Once acidified, the dry benzoic acid crystals formed in the flask. This was collected via gravitational and suction filtration. Gravity filtration was performed by pouring the aqueous phase into a buchner funnel with filter paper ("Experiment 3 : Extraction," 2014). The solution was allowed to drain into another flask, while the solid precipitate remained in the funnel. Unfortunately, a lot of the precipitate remained in the flask and could not be obtained. This issue is further discussed

in sources of error. Once all of the aqueous solution was drained from the funnel, the funnel was inserted into the suction filtration apparatus and filtered once more. Once dry the extracted precipitate was weighed and the percent composition was calculated to be 54% that of the original sample which was composed of benzoic acid.

Part C

TLC plates were developed in order to determine the composition of the various compounds that were being handled during the lab. Fig 3.1. was a TLC prepared in order to determine the components of the unknown mixture #110. The R_f values for the spot made by benzophenone and for one of the spots made by the unknown mixture are the same, therefore one of the components of the unknown sample must be benzophenone. Since the R_f value (0.66) of the spot made by biphenyl does not match that of any of the spots created by the unknown sample, there must be no biphenyl present in the unknown sample #110. Additionally, this makes sense because the biphenyl is a nonpolar molecule and so has a higher R_f value than benzophenone and benzoic acid (see Table 1.1.). Benzoic acid is able to deprotonate and become highly polar and benzophenone while not polar is slightly more so than biphenyl which is very symmetrical. Fig. 3.2. was a TLC prepared in order to determine the composition of the organic layer that was obtained during the separation process. The R_f value of the spot created by the organic layer is the same as one of the spots created by the reference which is the unknown sample 110. This R_f value was determined to be 0.62. This is not very different from the R_f value (0.66) for the benzophenone from the previous figure. Therefore, the organic phase contains one of the components of the unknown sample, specifically the organic component which was benzophenone. Fig. 3.3. was a TLC prepared in order to determine the composition of the aqueous layer. Due to the separation, the aqueous layer must only be composed of the aqueous component of the unknown sample. This part was the benzoic acid. On the TLC; however, the lane for the aqueous layer shows 2 spots instead of one. The R_f value of the lower spot matches that of the R_f value of the lower spot for the reference (sample 110) and the upper spot also matches that of 110's upper spot. This meant that the sample placed on the aqueous lane was not completely pure and must have contained a bit of the organic layer (the benzophenone). Some contamination must have occurred on this lane or the extraction was not performed properly. This is further discussed in the sources of error.

The TLC plates all had elongated oval blots which were made by the benzoic acid. This is because benzoic acid is in equilibrium between its protonated and deprotonated version. This means that benzoic acid keeps shifting between two phases, one of which is nonpolar (protonated) and the other is polar (deprotonated). The polar end would be towards the bottom and the nonpolar would be towards the top (the solvent line).

Table 1.1. Comparing the polarities of substances		
Most Polar → Least Polar Lowest Rf → Highest Rf		
benzoic acid	benzophenone	biphenyl
		

Sources of Error

A few sources of error may have hindered the success of this experiment.

When collecting the precipitate, there was a lot that was left out in the erlenmeyer flask and did not go through the extraction process of gravity and suction filtration. Some of the precipitate was also lost when removing the precipitate from the filter paper after the filtration and during the drying process as a few gusts of wind might have carried off the precipitate crystals. This would mean that the percent composition calculated would be much higher than the current calculation suggests. Additionally, tiny solid particles were able to get through the filter paper and as a result was not obtained to be weighed.

Some human error might have occurred when performing the extraction with the separatory funnel. A major error could have occured when releasing the organic contents of the funnel into a beaker. If one were not fast enough to close the stop cock, there is risk of releasing some of the aqueous layer into the organic layer. This would have most effect if the error was made during the final extraction. If the stopcock was shut off too early as well there would be some organic phase in the aqueous phase and the aqueous phase collected would be contaminated.

Cross contamination could have occurred while performing the TLC plates. Since small capillary tubes were used it is possible that by human error a tube could have been misplaced and used on another sample with some sample still inside of the tube. This leads to cross contamination and incorrect TLC blotting.

Conclusion

Part A - The observations of the test tube with the mixed solutions proved that using water and ether for the extraction of methylene blue and methyl red would be successful.

Part B - Benzoic acid was successfully extracted from the unknown sample (110). The composition was determined to be 54% benzoic acid and the rest would have been solid benzophenone.

Part C - The unknown sample was benzophenone because the R_f value of the circular blot in Fig 3.1. matched that of the R_f value of benzophenone.

Questions

1.

For an extraction to be performed successfully the compounds must be completely immiscible and differ in polarities ("Experiment 3 : Extraction," 2014). This is not the case for water and acetone, they are both polar and will form a homogenous mixture making extraction impossible. Acetone and water would also both be in aqueous. Therefore it would be extremely difficult to perform extraction with water and acetone. Two distinct layers would not form and so there would not be an organic and aqueous phase for the components of a mixture to separate into.

2.

Putting a salt into the solution of ether, water, and methylene blue would push out the methylene blue from the aqueous water layer to the organic ether. This would be a textbook example of the salting effect ("Experiment 3 : Extraction," 2014). The salt would make the water too polar and saturate it, and the methylene blue will be forced/pushed up into the organic layer. This effect was observed in Part A of this experiment with crystal violet, 1-butanol, water and NaCl salt. (Figures 1.5 and 1.6).

3.

K_D (diffusion coefficient) = $\frac{\text{solubility of ether}}{\text{solubility of water}}$

$K_D = \frac{20\text{g}/100\text{ml in ether}}{2\text{g}/100\text{ml in water}} = 10$

How much extracted?

$K_D = \frac{x}{1.4\text{ g} - x} = 10$

$x = 10(1.4\text{g} - x)$

$11x = 14$

$x = 11/14$

$x = 1.3\text{ g}$

⁂ 1.3 grams of compound Y will be removed from a solution of 1.4g Y/100 ml water by a single extraction with 100 ml of ether

4 .

K_D=10 (from question 3)
$K_D = M_{ether}/V_{ether} \div M_{water}/V_{water}$

1st extraction:

$$10 = \frac{x/50ml}{(1.4\ g - x)/100ml}$$

X = 1.2 g extracted

2nd extraction:

$$10 = \frac{x/50ml}{(1.2\ g - x)/100ml}$$

x = 0.17g extracted

Total extracted = 1.2g +0.17g = 1.37 g

- 1.37 grams of compound Y will be removed from a solution of 1.4g Y/100 ml water by using two extractions with 50 ml of ether each time. This proves that the doing more extractions will increase the yield of the product.

5.

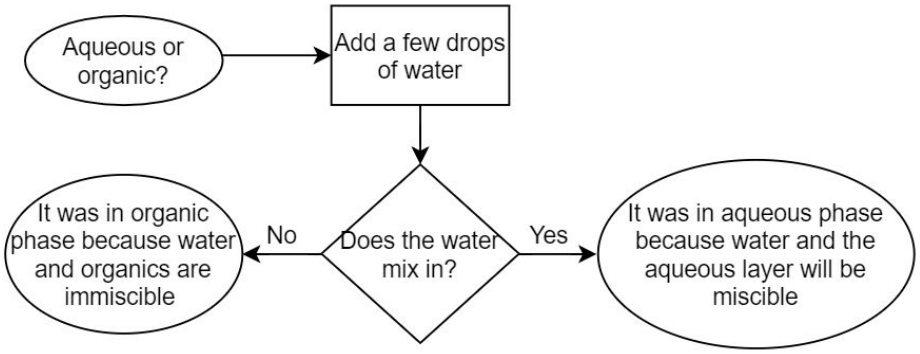


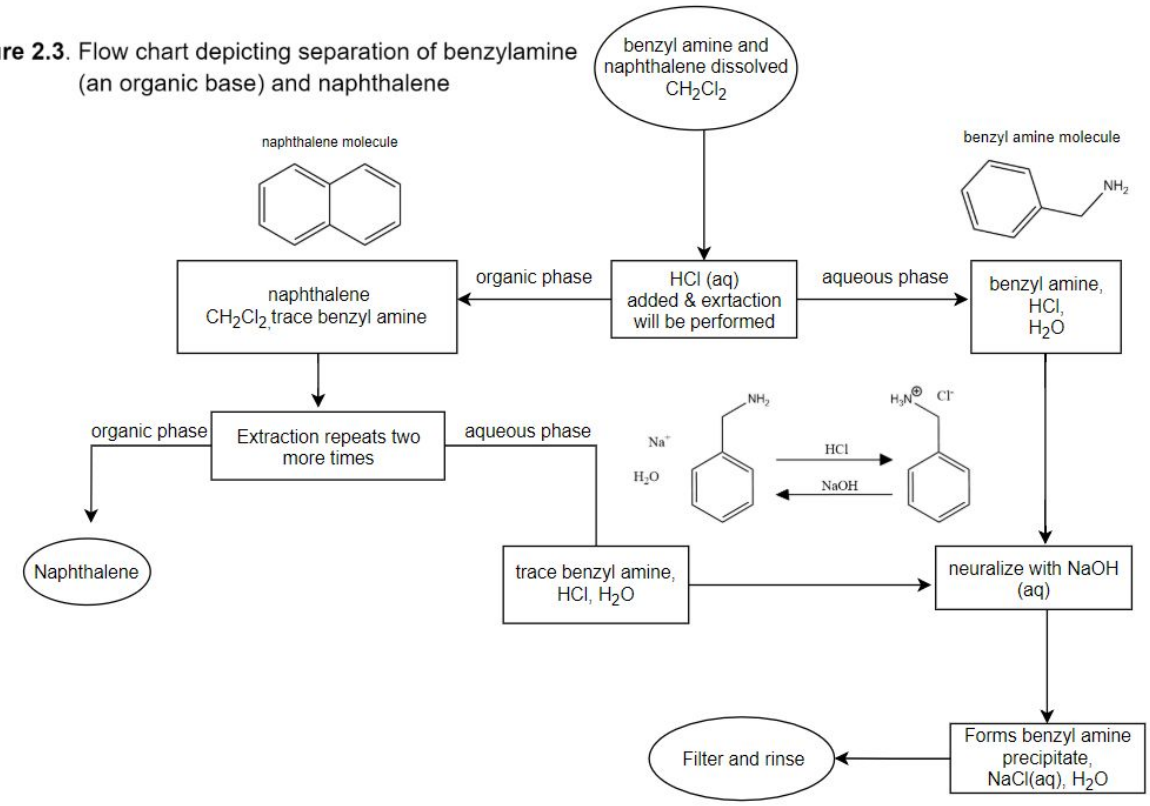
Figure 2.2. Flow chart depicting process of testing which phase a substance is in

6.

(Refer to figure 2.3. bellow)

- ➢ Benzyl amine is strong so an acid is needed to help interact with the organic base and not with the naphthalene.
- ➢ HCl will give it's proton to benzyl amide as seen in figure 2.3 and the spectator ions will remain soluble in the aqueous phase
- ➢ Meanwhile the naphthalene will be solely in the organic phase on the top
- ➢ The aqueous phase will require a base to deprotonate and neutralize the benzylamine and force it to solidify into a precipitate.
- ➢ Then the precipitate will be filtered out through a filter paper and then suction filtered until dry

Figure 2.3. Flow chart depicting separation of benzylamine (an organic base) and naphthalene



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National Center for Biotechnology Information. PubChem Compound Database; CID=10303, https://pubchem.ncbi.nlm.nih.gov/compound/10303 (accessed Feb. 12, 2019).

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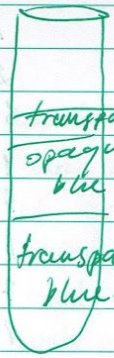
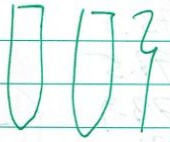
PART A – EXTRACTION of water soluble dyes

TEST TUBE 1	TEST TUBE 2	TEST TUBE 1+2
		
1 mL ether ✓ 1 mL H_2O ✓ 1 drop 0.006 M methylene blue	1 ml ether 2 mL H_2O ✓ 1 drop 0.006 M methyl red	
aq? org? both?	aq? org? both?	

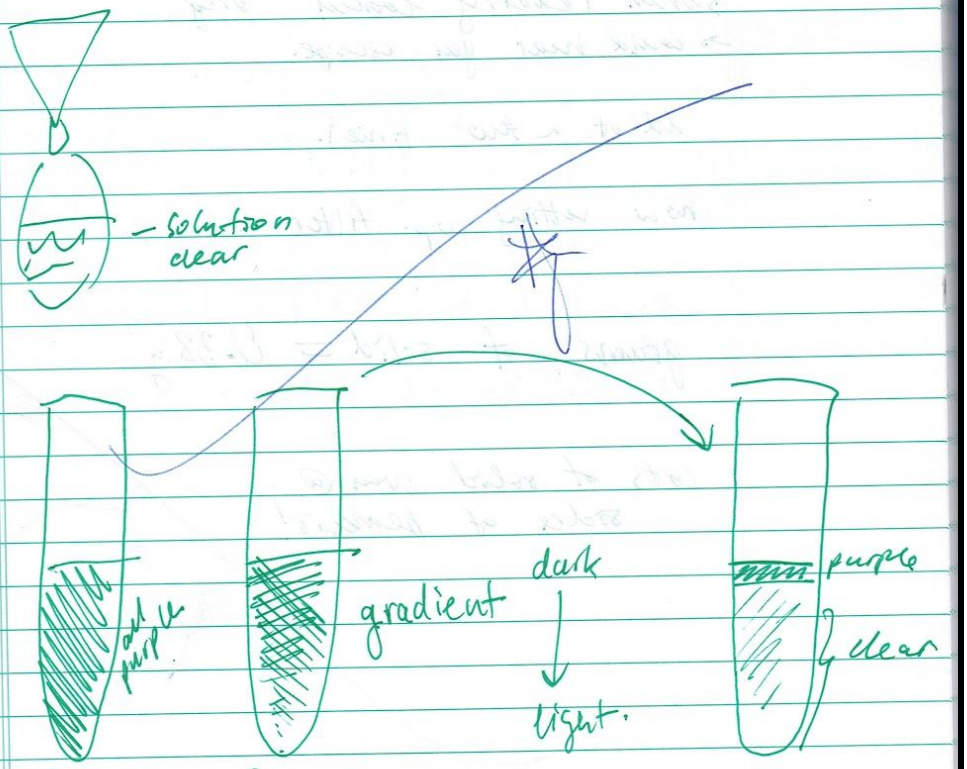
The salting out effect



5 ml H_2O
1 drop 0.003 M aq crystal violet
0.5 mL of 1 butanol
+Shake

PART B.

UNKNOWN #110 = 0.70 grams.
- white small crystals.



- 5ml H_2O
- 1 drop crystal violet

0.5 ml
1 butanol

5ml H_2O
- 4 drop crystal viole.

PART B.

unknown = 110 ⟹ 0.70 grams.

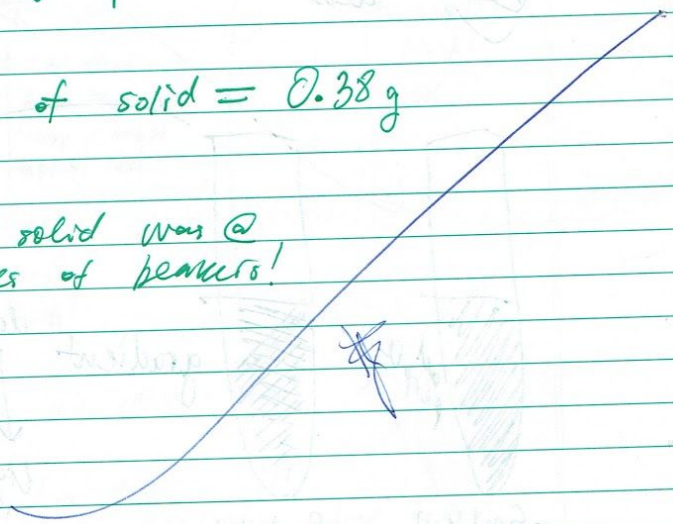
→ when reacting looked "oily"
→ could hear gas escape.

did it a few times.

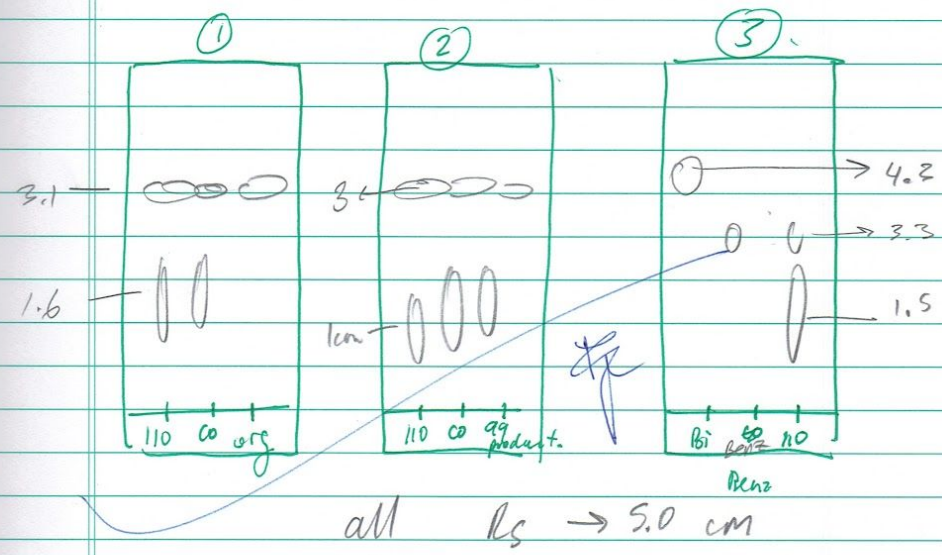
now setting up. filter...

grams of solid = 0.38 g

lots of solid was @ sides of beakers!

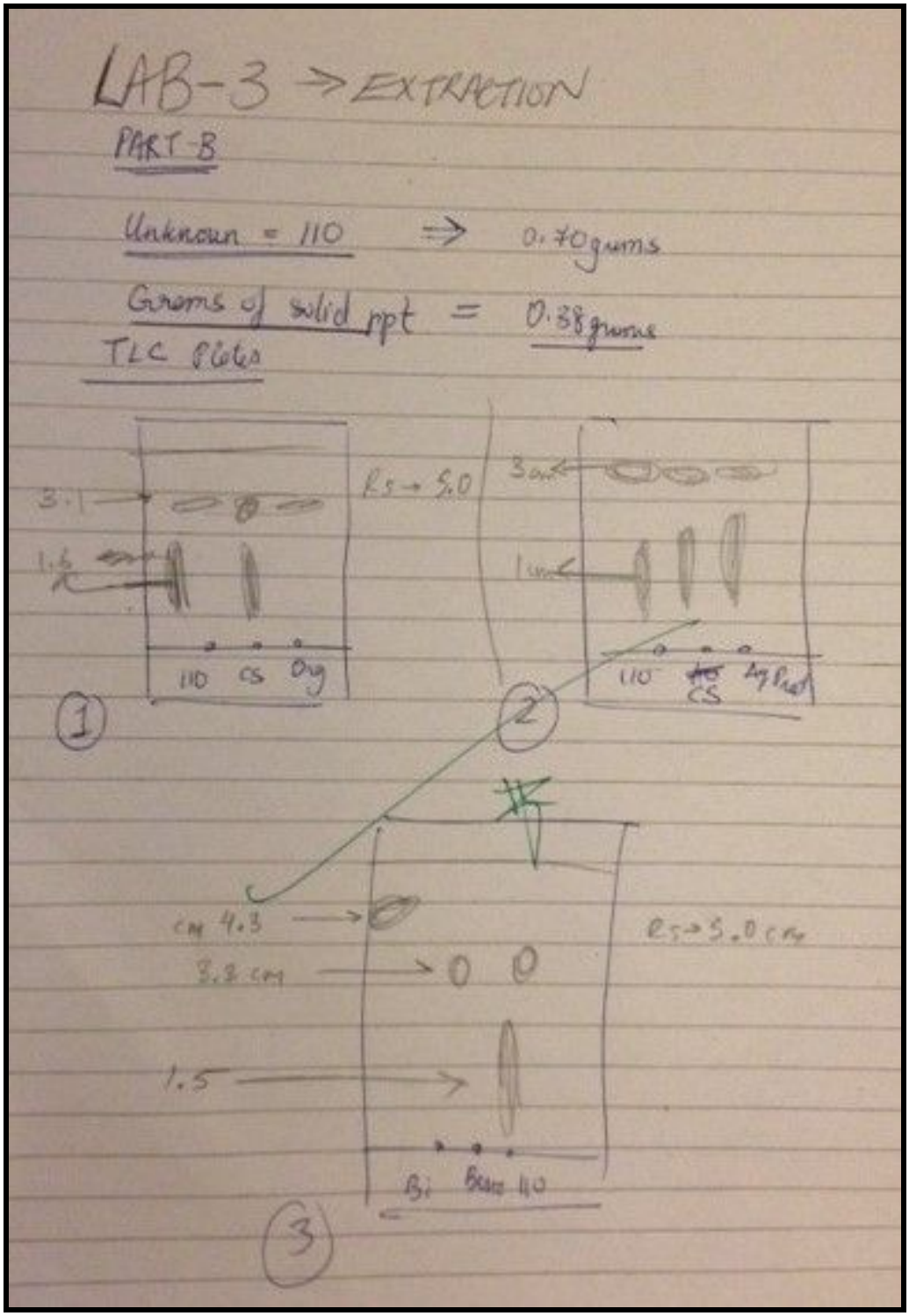


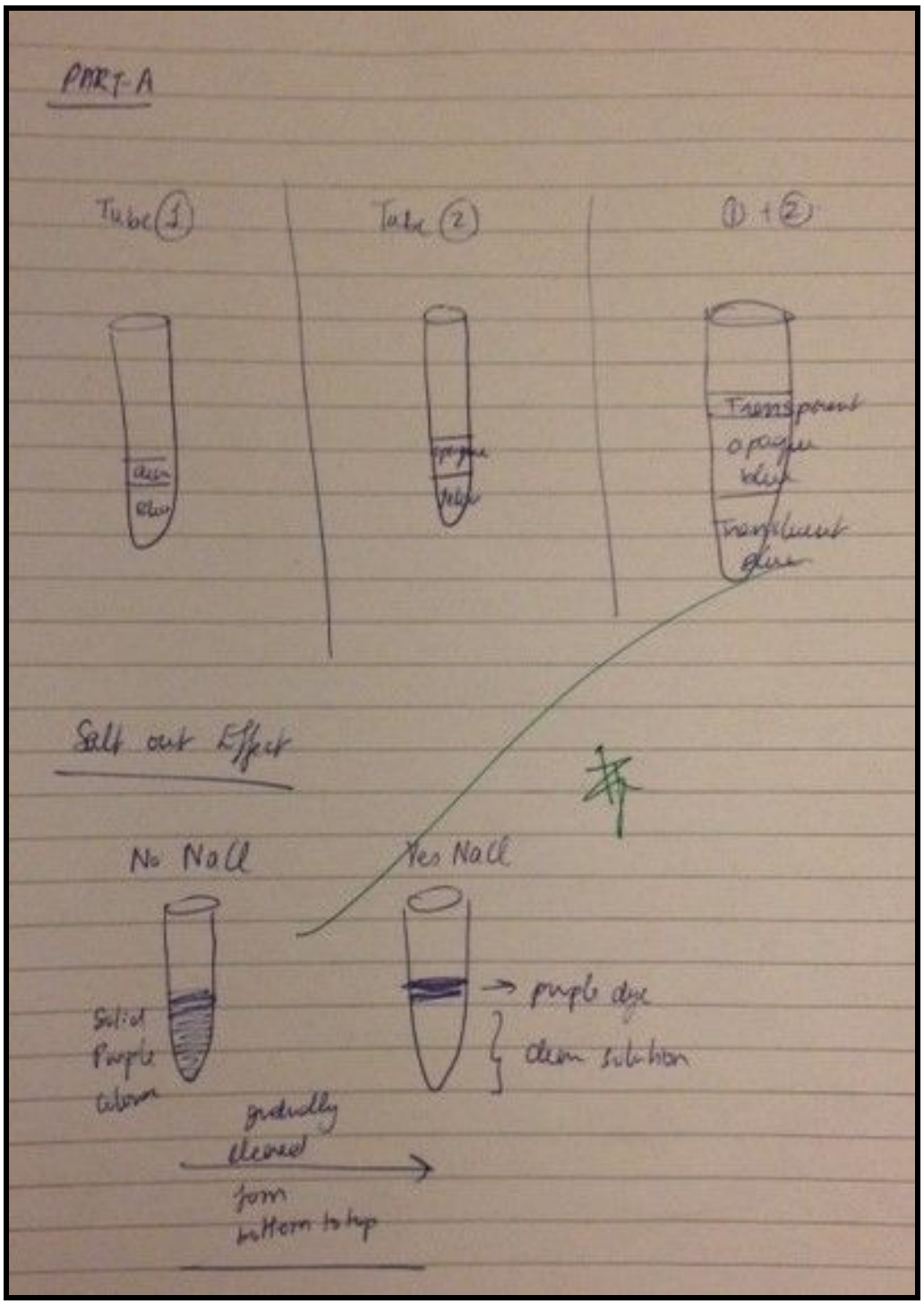
PART C → TLC PLATES



all R_f → 5.0 cm

[redacted]


LAB-3 → EXTRACTION
PART-B
Unknown = 110 ⇒ 0.70 grams
Grams of solid ppt = 0.38 grams
TLC Plates
3:1
Rf → 5.0
110 CS Dg
1
3.3 cm
1 cm
110 CS
2
cm 4.3
3.3 cm
1.5
Rf → 5.0 cm
Bi
3


PART-A
Tube (1)
Tube (2)
(1) + (2)
Transparent
opaque
blue
Translucent
blue
Salt out Effect
No NaCl
Yes NaCl
Solid
Purple
colour
purple dye
clear solution
gradually
cleared
from
bottom to top