Thin Layer Chromatography

Experiment 1

Written by:

Hannah Prazak, 300062850

Hope Boyle, 300053465

TA: Daliane Regis

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Introduction

Thin layer chromatography (TLC) is used for analyzing and studying organic and inorganic reactions by separating the components of a reaction , and is a great method for determining what compounds are comprised of.

Chromatography is performed by using solvent with a certain polarity to in turn determine how polar the components of a reaction are. The phases are one stationary phase and one mobile phase. In this lab, the stationary phase is an aluminum plate with silica gel on one side (TLC plate), and the mobile phase is a liquid substance. The stationary phase is placed in a developing jar and remains still in the jar as the mobile phase moves up through it. As the mobile phase moves through the stationary phase, the differences in the affinities of the components in the substance will cause the components to move at different speeds through the TLC plate so that they are physically separated from each other.

After the separation has been completed, the compounds will have separated into a couple dots in a vertical line, which can be seen by developing the plates using a UV light. After the compounds have separated, the retention factor (R_f) can be calculated by dividing the distance travelled by a compound by the distance travelled by the solvent front. When comparing the retention factors of compounds, the compound with the larger R_f is less polar because it moved a larger percent of the distance the solvent travelled, meaning it was less attracted to the silica which is very polar. Polar molecules are attracted to polar molecules, likewise how non-polar molecules are attracted to non-polar molecules.

Procedure

As described in the lab manual. (Durst et al., *Organic Chemistry Laboratory Manual,* exp. 1, 2019)

Data

Salt # 21

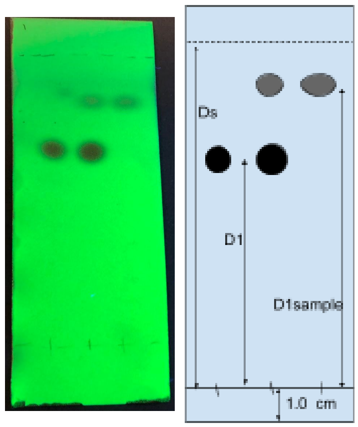
Part 1: (2:8) Ethyl Acetate and Hexane as Solvent

TLC #1.1: Dichloromethane and benzophenone

$D_1 = 3.4$ cm

$D_{1\ Sample} = 4.3$ cm

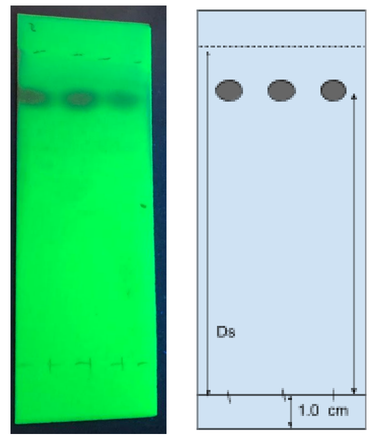
$D_s = 5.0$ cm



TLC #1.2: Dichloromethane and biphenyl

$D_1 = 4.4$ cm

$D_s = 5.2$ cm



Part 2: Ethyl Acetate/ Hexane as Solvent

TLC #2.1: Dichloromethane and benzophenone (Ethyl Acetate)

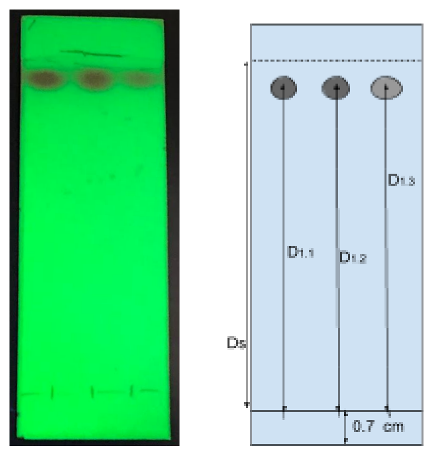
$D_{1.1} = 4.9$ cm

$D_{1.2} = 4.9$ cm

$D_{1.3} = 4.9$ cm

$D_s = 5.3$ cm

$D_{1\ avg} = 4.9$ cm



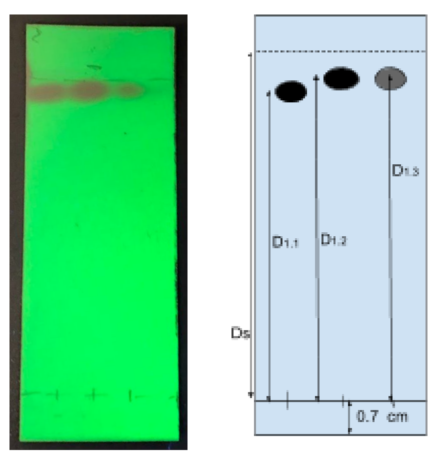
TLC #2.2: Dichloromethane and biphenyl (Ethyl Acetate)

$D_{1.1} = 4.8$ cm

$D_{1.2} = 4.9$ cm

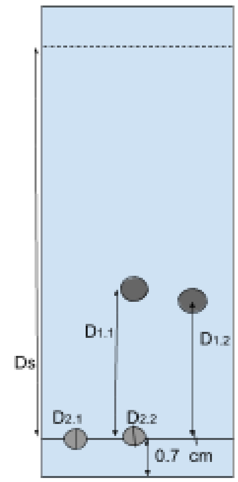
$D_{1.3} = 4.9$ cm

$D_s = 5.3$ cm



$D_{1\ avg}$ = (4.8+4.9+4.9)/3 = 4.8666667 cm

TLC #2.3: Dichloromethane and benzophenone (Hexane)



$D_{1.1}$ = 2.4 cm

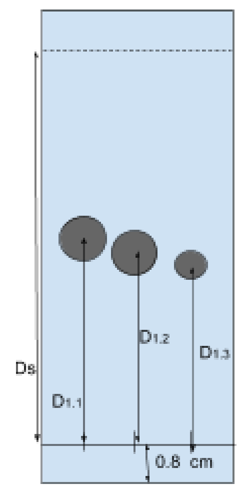
$D_{1.2}$ = 2.2 cm

$D_{2.1}$ = $D_{2.2}$ = 0 cm

D_s = 5.3 cm

D_{1avg} = (2.4 +2.2)/2= 2.3 cm

TLC #2.4: Dichloromethane and biphenyl (Hexane)



$D_{1.1}$ = 2.7 cm

$D_{1.2}$ = 2.5 cm

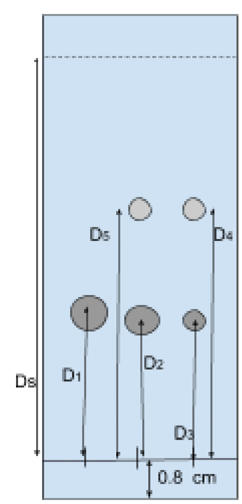
$D_{1.3}$ = 2.4 cm

D_s = 5.3 cm

$D_{1\ avg}$ =2.5333333 cm

<u>Part 3: Unknown Sample D</u>

TLC #3.1: O and Unknown Sample D



D_1 = 1.8 cm

D_2 = 1.7 cm

D_3 = 1.7 cm

$D_4 = 2.9$ cm

$D_5 = 2.9$ cm

$D_s = 5.0$ cm

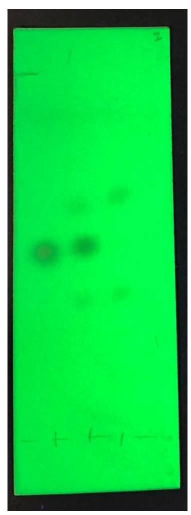
$D_{1\,avg} = (D_1 + D_2 + D_3)/3$

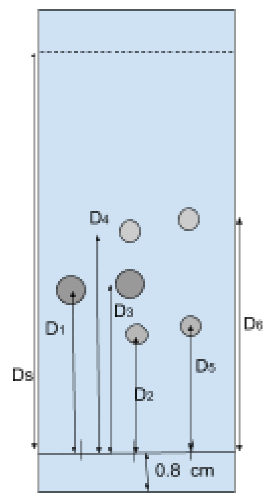
$= 1.733333$ cm

$D_{2\,avg} = (D_4 + D_5)/2$

$= 2.9$ cm

TLC #3.2: M and Unknown Sample D





$D_1 = 2.6$ cm

$D_2 = 1.9$ cm

$D_3 = 2.7$ cm

$D_4 = 3.3$ cm

$D_5 = 2.0$ cm

$D_6 = 3.5$ cm

$D_s = 5.3$ cm

$D_{1avg} = (D_2 + D_5)/2$

$= 1.95$ cm

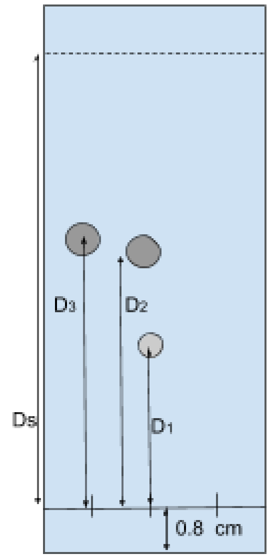
$D_{2\,avg} = (D_1 + D_3)/2$

$= 2.65$ cm

$D_{3\,avg} = (D_4 + D_6)/2$

$= 3.4$ cm

TLC #3.3: P and Unknown Sample D



$D_1 = 3.1$ cm

$D_2 = 3.0$ cm

$D_3 = 1.9$ cm

$D_s = 5.0$ cm

$D_{2\,avg} = (D_3 + D_2)/2$

$= 3.05$ cm

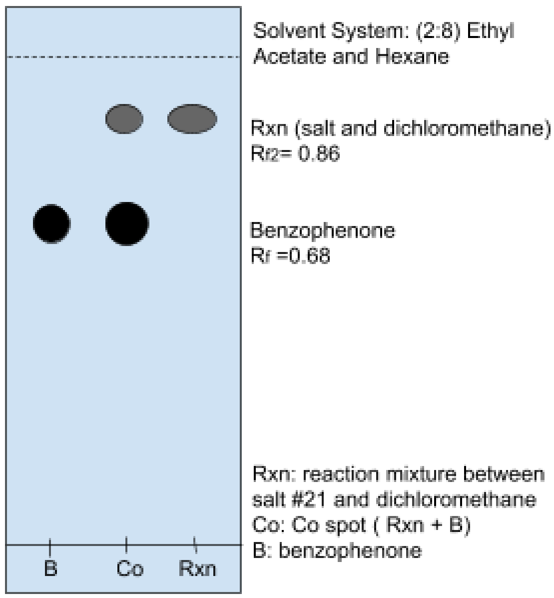
Calculations

Part 1

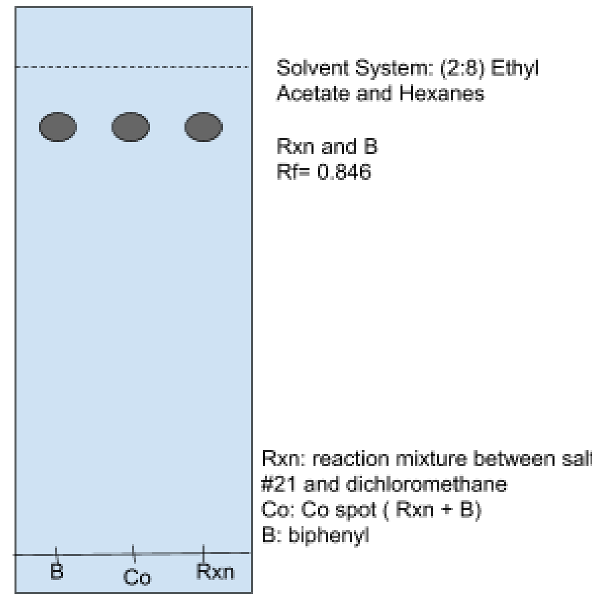
	TLC #1.1	TLC #1.2
D_1	3.4 cm	4.4 cm
$D_{1\,Sample}$	4.3 cm	___________
D_s	5.0 cm	5.2 cm
R_f	*0.68	0.846
$R_{f\,2}$	*0.86	__________

*TLC #1.1: $R_f = \frac{d_1}{d_s} = \frac{3.4}{5.0} = 0.68$ $R_{f\,2} = \frac{d_{1sample}}{d_s} = \frac{4.3}{5.0} = 0.86$

TLC #1.1



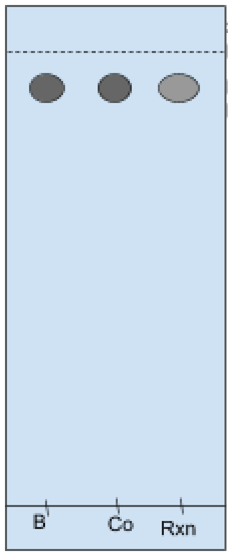
TLC #1.2



Part 2

	TLC #2.1	TLC #2.2	TLC #2.3	TLC #2.4
D_1	4.9 cm	4.86666667 cm	2.3 cm	2.53333 cm
D_2	__________	__________	0 cm	__________
D_s	5.3 cm	5.3 cm	5.3 cm	5.3 cm
R_f	0.9245	0.918239	0.43396	0.477987
R_{f2}	__________	__________	0	__________

TLC #2.1

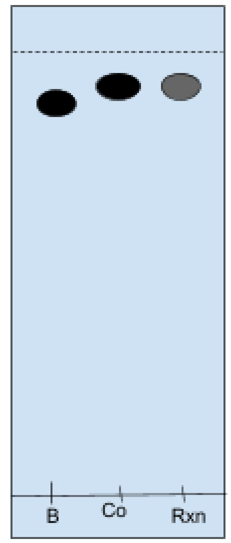


Solvent System:
Ethyl Acetate

Rxn and B
Rf=0.9425

Rxn: Reaction mixture between dichloromethane and salt #21
Co: Rxn and B
B: benzophenone

TLC #2.2

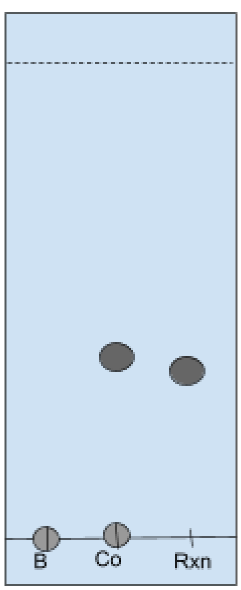


Solvent System: Ethyl Acetate

Rxn and B
Rf= 0.918

Rxn: Reaction mixture between dichloromethane and salt #21
Co: Rxn and B
B: biphenyl

TLC #2.3



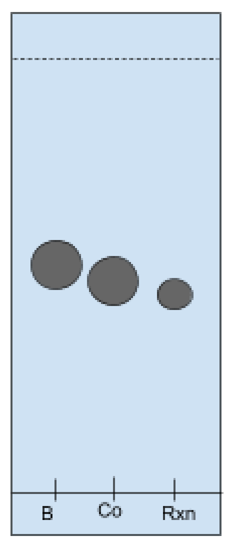
Solvent Systems: Hexane

Rxn: Reaction mixture between dichloromethane and salt #21
Co: Rxn and B
B: benzophenone

Dichloromethane
Rf= 0.43396

Benzophenone
Rf2=0

TLC #2.4



Solvent Systems: Hexane

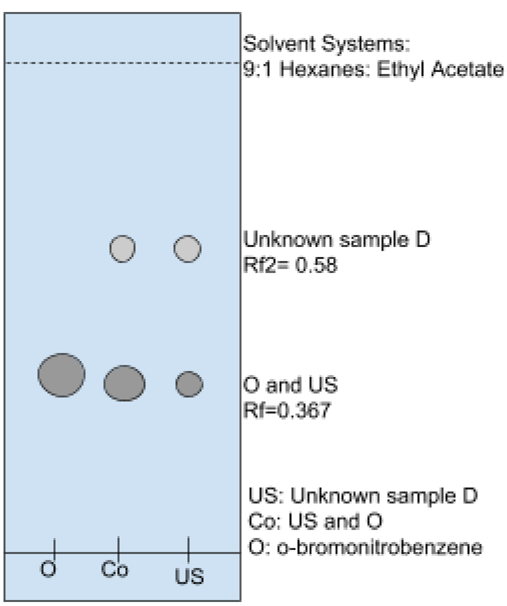
B and Rxn
Rf=0.478

Rxn: Reaction mixture between dichloromethane and salt #21
Co: Rxn and B
B: biphenyl

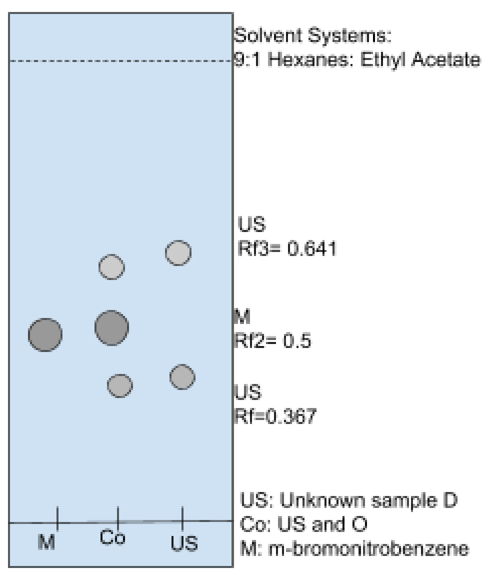
Part 3

	TLC #3.1	TLC #3.2	TLC #3.3
D_1	1.73 cm	1.95 cm	1.9 cm
D_2	2.9 cm	2.65 cm	3.05 cm
D_3	---	3.4 cm	---
D_s	5.0 cm	5.3 cm	5.0 cm
R_f	0.346666667	0.3679245	0.38
R_{f2}	0.58	0.5	0.61
R_{f3}	---	0.6415094	---

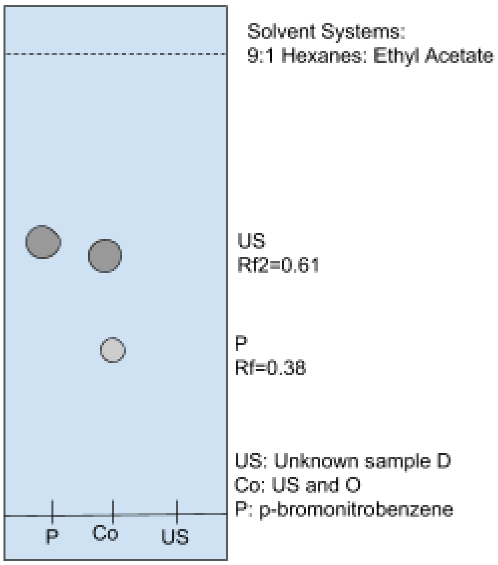
<u>TLC #3.1</u>



<u>TLC #3.2</u>



TLC #3.3



Discussion and Observations

Observations:

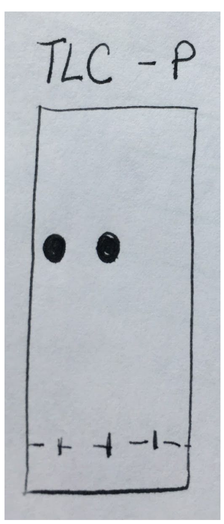
- The unknown compound #21 is a white salt
- All liquid aqueous solutions were a colourless transparent solution

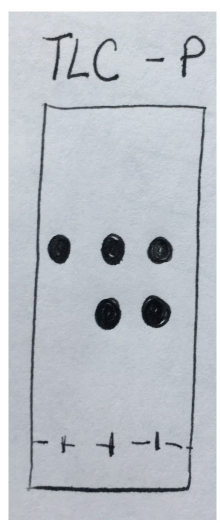
Discussion:

The goal of part A of the experiment is to determine what the unknown salt assigned was. Looking at the two TLC plates that were developed, it is clear that since the plate that has the biphenyl as the reference has a spot in both the reference and the sample lane, with the same R_f value, that the unknown salt #21 was biphenyl. To prove the conclusion correct, looking at the TLC plate with the benzophenone, it is clear that the salt is not benzophenone as the sample spot has a higher R_f value than the reference spot, meaning that the salt was not benzophenone.

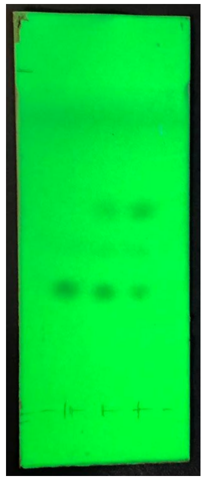
The intention of part B in the experiment is to determine which solvent is a better choice regarding the TLC's performed. The most appropriate solvent will have the perfect polarity in regard to the sample and reference compounds being used. If the polarity of the solvent is too high, both compounds will travel farther up the TLC plate, and possibly overlap, making it more difficult to determine R_f values, and could falsely conclude that there is only one compound instead of two, because the overlapping spots might look like one spot. This would be due to the compounds hydrogen bonding with the solvent, and not with the silica, making the compounds travel more quickly up the TLC plate. Similarly, if the solvent is not polar enough, again the two compounds will appear so close together that it might be mistaken for only one compound, again leading to the wrong conclusion. However, in this case, the compounds would do more hydrogen bonding with the silica and not enough with the solvent in order to move at a moderate speed, and would appear lower on the TLC plate. By looking at the TLC plates that were developed and using the above argument, it is clear that between ethyl acetate and hexanes, hexanes are the better option. The hexanes are the better option because it is easy to differentiate between the visible spots when the plate was developed, the R_f values are not close together, and are easily identifiable.

In part C of the experiment, the goal is to determine what the unknown sample D is comprised of. It is in this portion of the experiment where a problem occurred. The third TLC plate had p-bromonitrobenzene as the reference and the unknown sample D. It is thought that when the unknown sample D was applied to the TLC plate via capillary, that the sample spot was too small to clearly see any reaction process because when the plate was developed there were no visible spots in the sample column whatsoever. The plate looked like the below image on the left. It is believed that the plate was actually supposed to look something like the image on the right.





That being said, it is impossible to say what the actual TLC would have looked like without redoing this part of the procedure using a new TLC plate, providing there was enough time to do so (there was not). As a result of this complication, the definite answer cannot be provided regarding what compound D contained, because it may or may not have contained p-bromonitrobenzene. However, looking at the 1st TLC for part C, using o-bromonitrobenzene, it is clear from the TLC below, that since there is a sample, reference, and co-spot with the



same R_f value, that compound D does contain o-bromonitrobenzene.

Questions

1. Why is it important to make co-spots last?

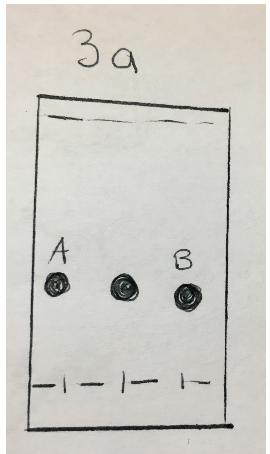
   It is important to make co-spots last to avoid cross contaminating the sample and the reference. For example, if you started with the sample, and put it on the middle and right side spots, and then applied the reference substance to first the middle and then the left side spots, both the co-spot and the left side spot would contain both the reference and the sample solutions, therefore the TLC would be inaccurate.

2. How does increasing the polarity of the solvent system affect the results of the TLC?

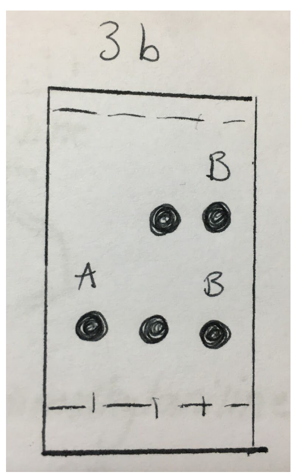
   If the solvent is too polar, the compound may not be able to separate and instead will be pushed to the top of the plate.

3. A student is monitoring a reaction using a TLC. The chemical reaction converts compound A into compound B, and she uses molecule A as her reference. Compound A has an R_f value of 0.45; while compound B has an R_f value of 0.68 in the solvent system being used.

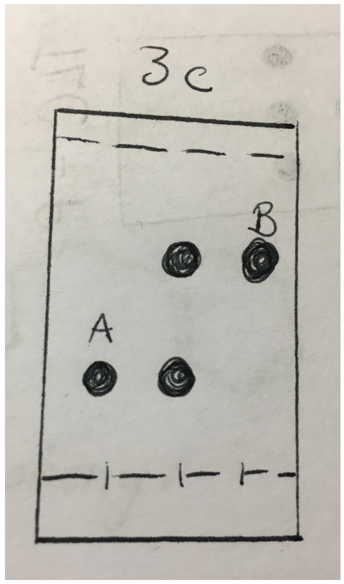
a. Draw a picture of her TLC plate at the beginning of the reaction.



b. Draw a picture of her TLC plate after 50% completion (50% of the A molecules have been converted into B molecules)



c. Draw a picture of her TLC plate at the end of the reaction (all A molecules have been converted to B molecules

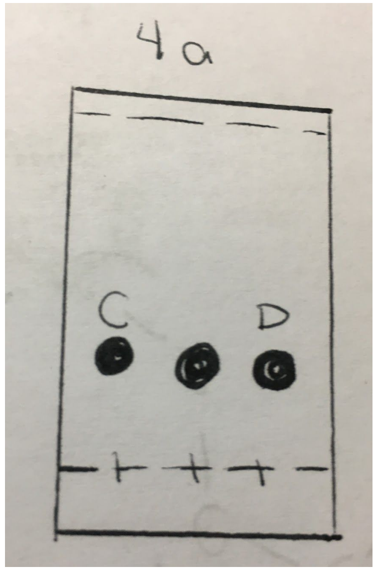


d. Why is it better to have a sample molecule A rather than molecule B to follow the reaction.

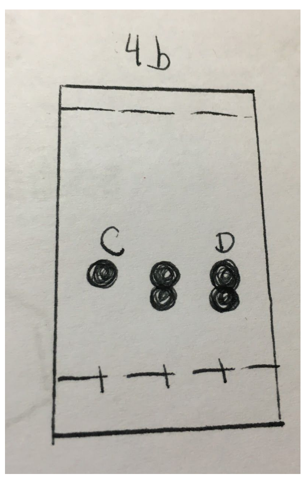
To follow a reaction the initial and final components need to be visible in order to compare the change from initial compound to final compound. Additionally, to be able to see if a reaction is complete, the initial reaction material needs to be completely gone.

4. A student is monitoring a reaction involving compounds C and D using TLC. Compound C has an R_f value of 0.43; compound D has an R_f value of 0.40.

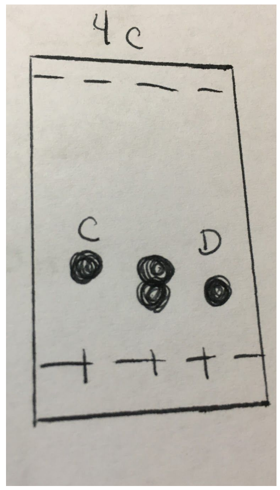
a. Draw a picture of her TLC plate at the beginning of the reaction.



b. Draw a picture of her TLC plate after 50% completion (50% of the C molecules have been converted into D molecules)



c. Draw a picture of her TLC plate at the end of the reaction (all C molecules have been converted to D molecules)



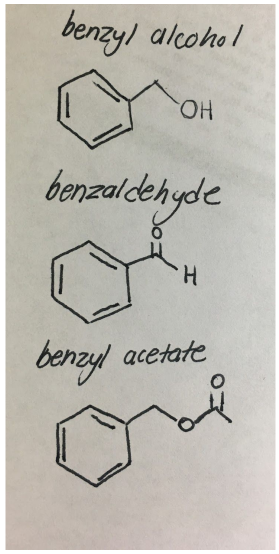
d. Why is it important to use a co-spot?

It is important to use a co-spot in case things go wry and it is fairly difficult to distinguish between the R_f values of the sample and reference lanes. So, by having a lane with both compounds in it, it is easier to see where each compound elutes in a single lane.

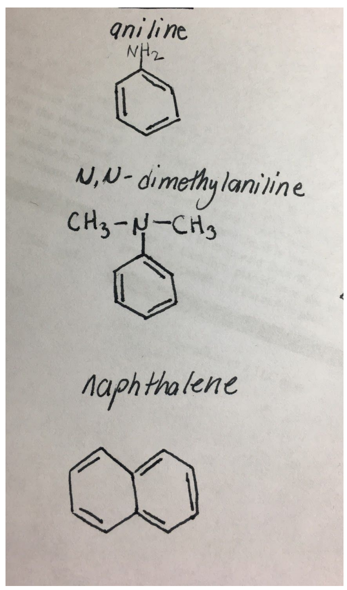
5. For each of the following sets of compounds
    i. Benzyl alcohol, benzaldehyde, benzyl acetate
    ii. aniline , N,N-dimethylaniline, naphthalene
    iii. Benzophenone, biphenyl, benzoic acid

perform the following:

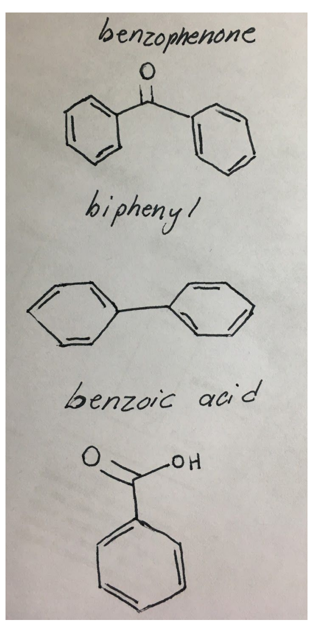
a. Draw the line structure of each molecule.


benzyl alcohol
OH
benzaldehyde
O
H
benzyl acetate
O
O

i.


aniline
NH2
N,N-dimethylaniline
CH3-N-CH3
naphthalene

ii.


benzophenone
O
biphenyl
benzoic acid
O
OH

iii.

b. Arrange them in order of increasing polarity.
    i. benzaldehyde → Benzyl acetate→ benzyl alcohol
    ii. Naphthalene→N,N-dimethylaniline→Aniline
    iii. Biphenyl→Benzophenone→Benzoic acid
c. Explain your reasoning in part b.
    i. Benzyl alcohol is the most polar because the hydroxyl functional group is the most polar functional group. Aldehydes and esters are similar in terms of their functional groups and their ability to hydrogen bond to the silica. However, benzyl acetate has more opportunities to hydrogen bond with the silica making it more polar.
    ii. Naphthalene is the least polar because it is a hydrocarbon, and hydrocarbons are not polar. N,N-dimethylaniline is less polar than aniline because the dipoles in the two methyl groups are effectively acting against the dipole in the phenyl group, minimizing the final dipole moment.
    iii. Benzophenone had a lower R_f value than biphenyl did, making it more polar. Benzoic acid is more polar than both because of the hydroxyl group, which is more polar than the benzophenone carbonyl group. Biphenyl has no polar functional group which makes it the least polar of the three.

Conclusion

Part A: Unknown salt #21 is biphenyl.

Part b: Hexanes are the superior option for the solvent system as the R_f values are easily distinguishable.

Part c: Unknown sample D contains some o-bromonitrobenzene and does not contain m-bromonitrobenzene. May contain some p-bromonitrobenzene, but due to an error in the experiment it remains indefinite.

Raw Data

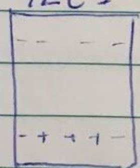
Hope's Raw Data

Exp. 1
Part a)
Salt # 21

Jan 9

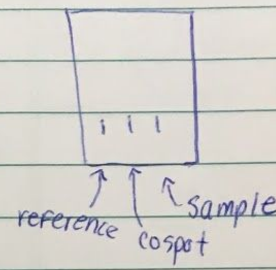
2 ml dichloromethane
1ml benzophenone

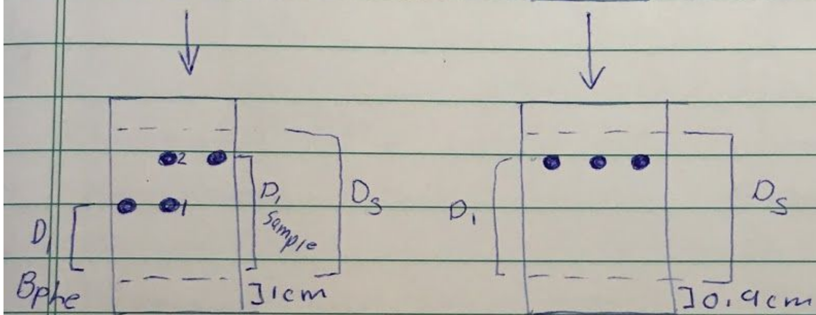
TLC 1



TLC 2

1ml biphenyl





measured D1 from bottom of plate so subtract 1cm for TLC 1 and 0.4 cm for TLC 2

TLC 1:

$D_1 = 4.4cm$ $D1 = 5.3cm$ (sample) $D_1 =$ ~~0.4~~ $5.3cm$

$D_s = 6.0cm$ $D_s = 6.1$

~~Part B)~~
TLC

Rf Benzophenone: $\frac{D_1}{D_s} = \frac{4.4-1}{6-1} =$

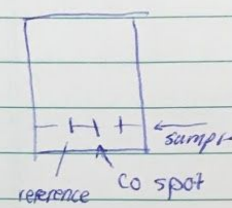
Rf co spot? $Rf_1 = \frac{D_1}{D_s} = \frac{4.4-1}{6-1}$

$Rf_2 = \frac{D1}{Ds} = \frac{5.3-1}{6-1}$

Rf Biphenyl: $Rf = \frac{D_1}{D_s} = \frac{5.3-1}{6-1}$

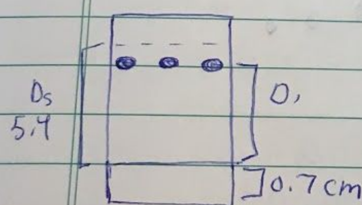
~~Part B)~~

Part B) 5ml ethyl acetate



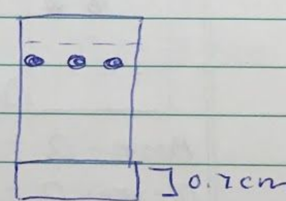
TLC 1

benzophenone



TLC 2

biphenyl



Benzophenone

D_1 = 4.9 cm

CO spot = 4.9 cm

Sample = 4.9cm

D_s = 5.~~4~~3 cm

Biphenyl

D_1 = 4.8 cm

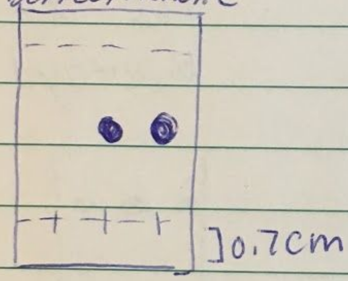
cospot = 4.9cm

Sample = 4.9cm

D_s = 5.3 cm

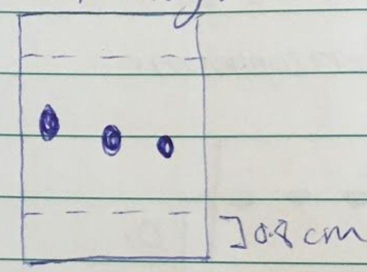
5ml Hexanes

TLC 1
benzophenone



Benzo - D_1 = /
CO-spot - D_1 = 2.4cm
Sample - D_1 = 2.2 cm
D_s = 5.3cm

TLC 2
biphenyl

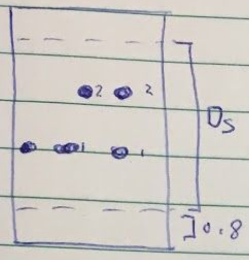


Bi - D_1 = 2.7cm
co-spot D_1 = 2.5cm
Sample D_1 = 2.4cm
D_s = 5.3 cm

Part C

Unknown: D sample

TLC 1: O



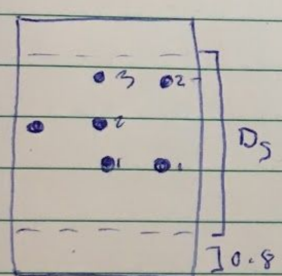
O D1 = 1.8cm

Co-spot D1 = 1.7cm D1 2 = 2.9 cm

? Sample D1 1 = 1.7cm D1 2 = 2.9cm

Ds = 5cm

TLC 2: M



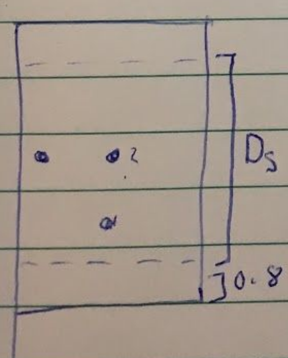
M D1 = 2.6

Co-spot D1 = 1.9 D.2 = ~~1.~~ 2.7 D.3 = 3.3

? Sample D1 = 2.0 D.2 = ~~2.0~~ 3.5

Ds = 5.3

TLC 3: P



P D1 = 3.1

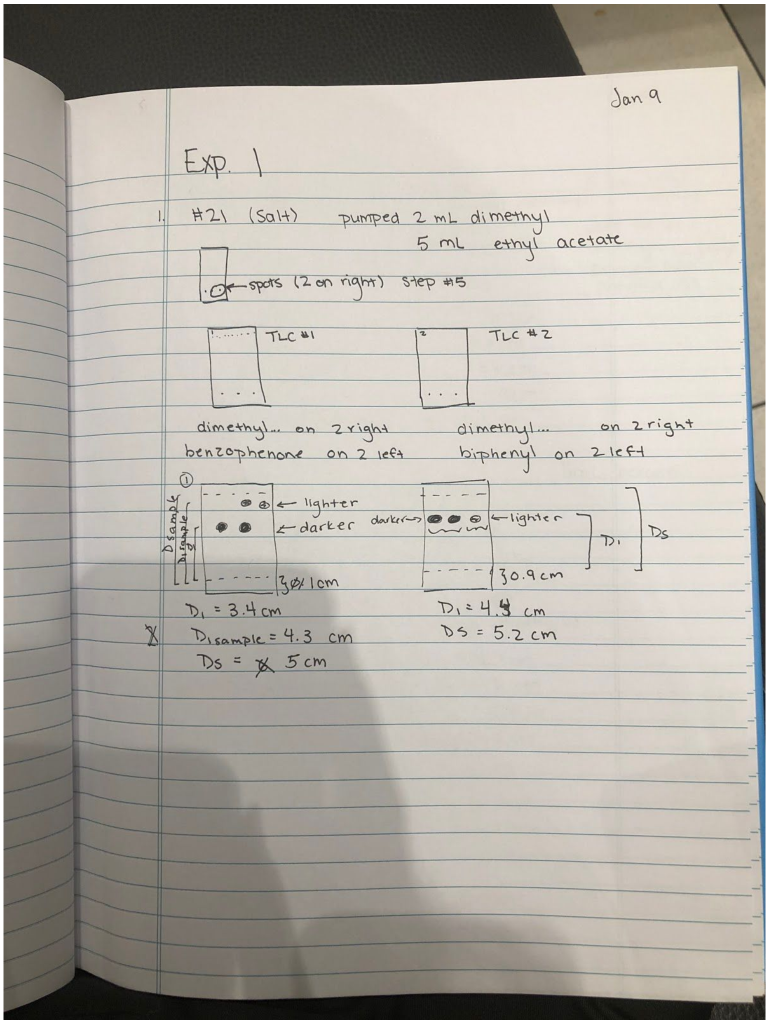
Co-spot D1 = 1.9cm D1 2 = 3.0

? sample ~~D1 = 1.9cm D1 2 = 3.0~~

Ds = 5.cm

DACS

Hannah's Raw Data:



Jan 9

Exp. 1

1. #21 (Salt) pumped 2 mL dimethyl
5 mL ethyl acetate

spots (2 on right) step #5

TLC #1

TLC #2

dimethyl... on 2 right
benzophenone on 2 left

dimethyl... on 2 right
biphenyl on 2 left

① lighter
darker
3.0 1cm

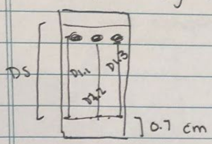
darker lighter
D1
Ds
0.9 cm

D1 = 3.4 cm
D1 sample = 4.3 cm
Ds = 5 cm

D1 = 4.3 cm
DS = 5.2 cm

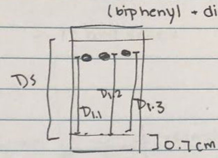
Jan 9

2. 1. Same as ①
(benzo.. + dimethyl..)



$D_{1.1}$ = 4.9 cm
$D_{1.2}$ = 4.9 cm
$D_{1.3}$ = 4.9 cm
D_s = ~~5.4 cm~~ 5.3 cm

2. Same as ①
(biphenyl + dimethyl)



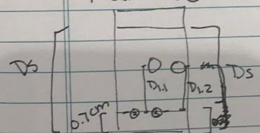
$D_{1.1}$ = 4.8 cm
$D_{1.2}$ = 4.9 cm
$D_{1.3}$ = 4.9 cm
D_s = 5.3 cm

5 mL ethyl acetate

used benzo..., dimethyl..., biphenyl solutions from previous (①)

5mL hexane

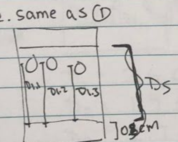
1. Same as ①



(benzo.. + dimethyl..)

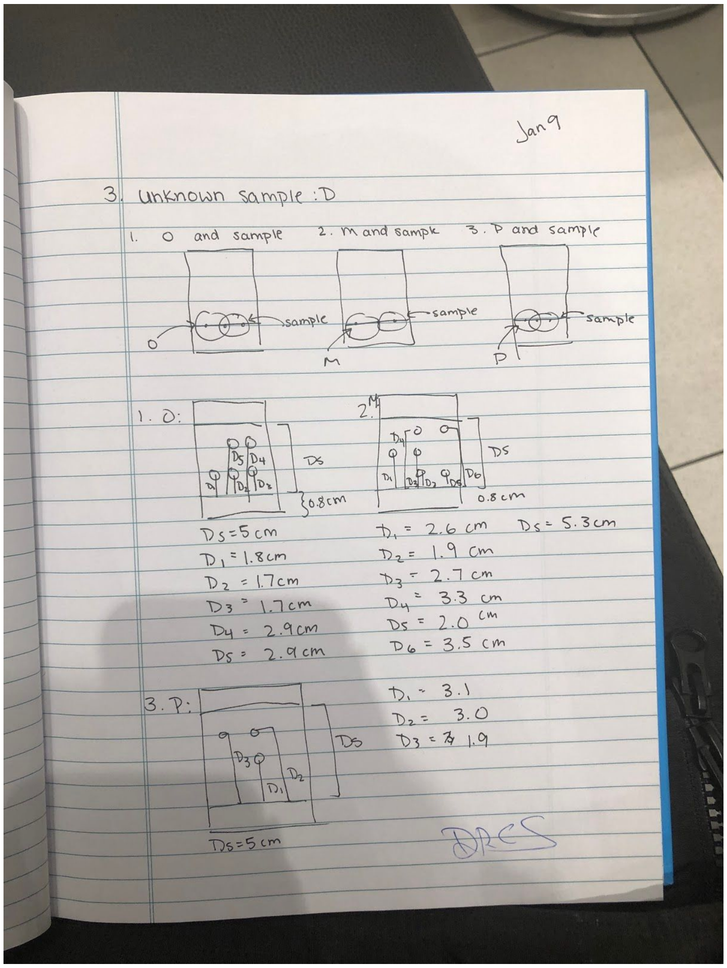
②.③ at 0 cm
$D_{1.1}$ = 2.4 cm
$D_{1.2}$ = 2.2 cm
D_s = 5.3 cm

2. Same as ①



(biphenyl + dimethyl..)

$D_{1.1}$ = 2.7 cm
$D_{1.2}$ = 2.5 cm
$D_{1.3}$ = 2.4 cm
D_s = 5.3 cm



References

Bernard Fried, Joseph Sherma, "Thin-Layer Chromatography", Ch. 1, CRC Press, pg. 1, 1999

COURSE: CHM 1321 **TA Name:** Daliane Regis
YOUR NAME (PRINT): Hope Boyle **SIGNATURE:** Hope Boyle

CONFIDENTIAL PEER EVALUATION FORM FOR EXPERIMENT 7

Each team member must submit one assessment form evaluating each other member of the team.
Teams will consist of 2 (max 3) members for reports.
You may edit this form.
Do not share or discuss the contents or possible contents of this assessment with others.

In assessing the work of your fellow team members, consider the following aspects:

- Quality of work
- Contribution to the work as a whole
- Ability to get along with others
- Improvements when asked to correct

Team member name	Comments	Grade (/5)
Hannah Prazak	Great partner	5

A – Excellent (5) B: Great (4) C: Good (3) D: Fair(2) F: Poor (1)

Note: Do not evaluate yourself on this form