

Experiment 1: Thin Layer Chromatography



**CHM 1321
Organic Chemistry Lab
University of Ottawa**

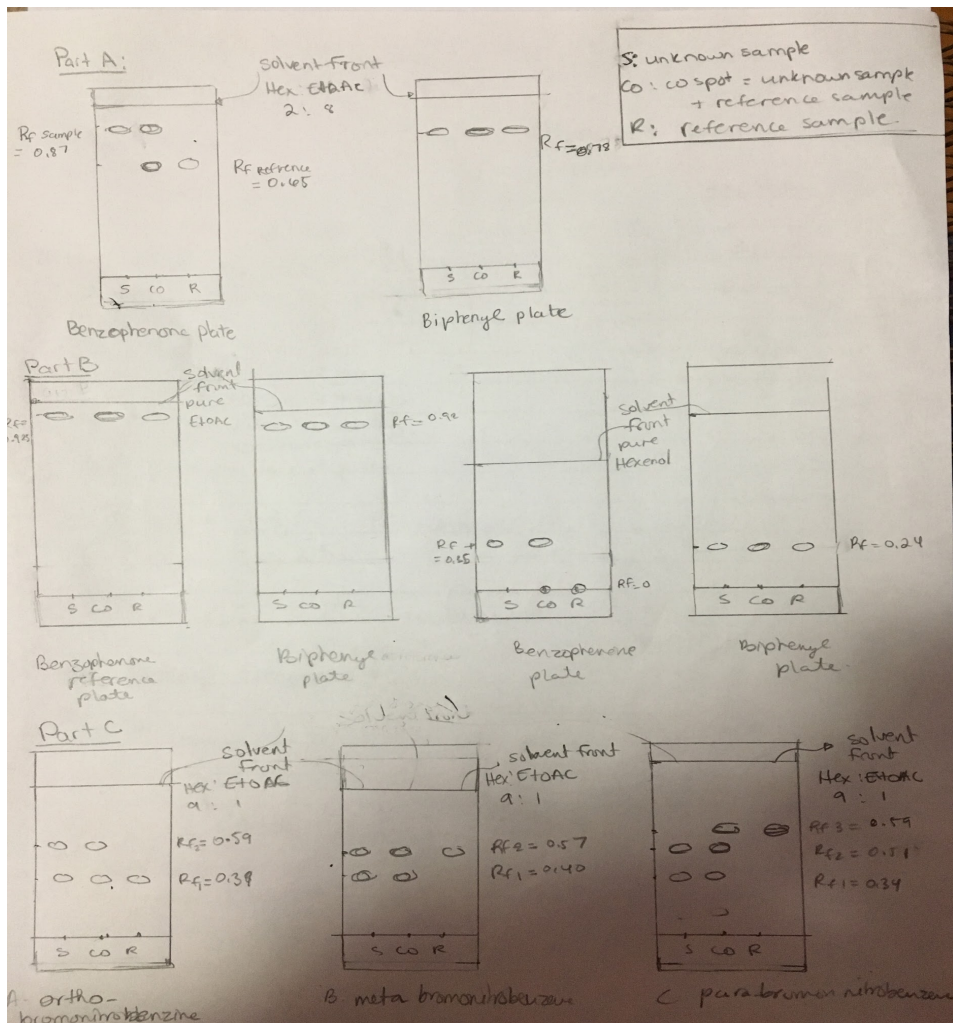
Procedure:

Refer to the lab Manual for the procedure for the Lab 1 Thin Layer Chromatography (P. 17-19)

Observations:

- When adding the reference and the unknown drops on the TLC paper, it was observed that it forms a small drop, and quickly evaporates off of it.
- The solvent was able to climb on the TLC paper as soon as it was placed inside the jar, and create a solvent line.
- As soon as the TLC paper was out of the solvent jar, the solvent line evaporates in a short time of period.
- When presenting the TLC paper under a UV light, it displayed a dark colored dots, representing the reference and unknown drops that were added. This applies to all parts of the experiment (A, B and C)
- Part B of the experiment, it was observed that both Biphenyl TLC paper and the Benzophenone TLC paper, had approximately similar Rf values when using pure Ethyl Acetate as a solvent.

TLC Analysis



Calculations:

Part A:

TLC plate 1: Benzophenyl plate

$$\begin{aligned} R_f(\text{unknown}) &= d_1/d_s \\ &= 4/4.6 \\ &= 0.87 \end{aligned}$$

$$R_f(\text{reference}) = 0.65$$

d_1 = distance of dot from starting line

d_s = distance from starting line to solvent line

Plate 2: Benzoylphenyl plate

$$R_f(\text{unknown}): 0.78$$

$$R_f(\text{reference}): 0.78$$

Part B:

Pure Acetyl solvent

Benzophenone TLC plate :

$$R_f(\text{unknown}) = 0.92$$

$$R_f(\text{reference}) = 0.92$$

Biphenyl TLC Plate:

$$R_f(\text{unknown}): 0.92$$

$$R_f(\text{reference}) = 0.92$$

Hexanol Solvent:

TLC Benzophenone plate:

$$R_f(\text{unknown}): 0.35$$

$$R_f(\text{reference}): 0$$

TLC Biphenyl Plate

$$R_f(\text{unknown}): 0.24$$

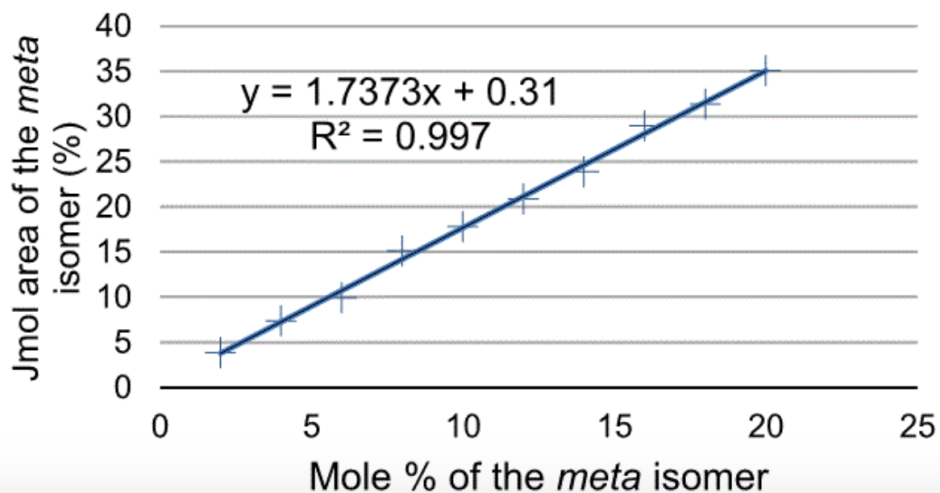
$$R_f(\text{reference}) = 0.24$$

Part C:

- Percentage of Absorbance:
 - Absorbance of Ortho = 16395.702
 - Absorbance of Meta = 8686.296
 - % of Absorbance (Ortho) = $\frac{16395.702}{16395.702+8686.296} \times 100$
 - % of Absorbance (Ortho) = 65.36 %
 - % of Absorbance (Meta) = $100 \% - 65.36 \%$
 - % of Absorbance (Meta) = 34.63 %
- Mole Percentage
 - $y = 1.7373x + 0.31$
 - $y = \% \text{ of Absorbance (Meta)} = 34.63\%$
 - $34.63 = 1.7373x + 0.31$
 - $x = 19.75$
 - % mole (Meta) = 19.75 %
 - % mole (Ortho) = $100 \% - 19.75 \%$
 - % mole (Ortho) = 80.245 %

Calibration Curve:

Amount of the *meta* isomer in a *meta-ortho* mixture of bromonitrobenzene



Discussion :

During part A of the experiment, the purpose was to find the contents of the unknown sample that was dissolved with dichloromethane using the TLC method. After preparing and applying the samples on the TLC paper, dipping it in the 2:8 ethyl acetate (EtOAc) and finally visualizing it under a UV light, black dots were visible, and it was possible to figure out whether the unknown was a Biphenyl or Benzophenone. Comparing the R_f values of the Unknown and the reference samples applied on the TLC papers, the Biphenyl TLC paper showed the same R_f value for both, the unknown and the reference. On the other hand, the unknown and reference samples showed different R_f values on the Benzophenone TLC paper, which concludes that the unknown sample contains Biphenyl. Comparing the R_f values of the samples applied, the Biphenyl or the Unknown sample had a large R_f value, but Benzophenone on the other hand had small R_f value. This is due to the polarity of the molecule. Since Benzophenone is a polar molecule, and Biphenyl is non-polar, this explains how Benzophenone was able to attract itself to the polar silicon on the TLC paper via hydrogen bonding, and not travel a longer distance. However, the Biphenyl molecule was not attracted to the polar silica on the TLC paper, and it was able to travel a longer distance, providing a larger R_f value.

In part B of the experiment, the purpose was to observe the effect on the R_f values of the compounds added to the TLC paper by changing the polarity of the solvent. On one hand, pure ethyl acetate was used a solvent, and the result of the TLC paper shows that both compounds, Benzophenone and Biphenyl have traveled a long distance on the TLC papers, expressing a large R_f value approximately of 0.92. The explanation to the results obtained is due to the fact that pure ethyl acetate is a strong polar molecule that was able to become attracted to the polar silica on the TLC paper, leaving no room for Benzophenone or Biphenyl to become attracted to the silica, other than being pushed to the top of the TLC paper close to the Solvent line (1).

On the other hand, pure hexane was also used as the other solvent, and the results were different from the pure ethyl acetate. The TLC papers that were dipped in pure hexane were observed under UV light, and displayed different R_f values for both compounds Benzophenone, and Biphenyl. The Benzophenone drop did not travel at all from the starting line on TLC paper, but Biphenyl drop had an R_f value of 0.24. Pure hexane is a strong non-polar compound, and adding drops of Benzophenone which is a polar compound on the polar TLC paper, increases the chances of attracting the Benzophenone on the silica via hydrogen bonding, which is why Benzophenone did not move from the starting point. However, Biphenyl was able to travel a little far from the starting line, and that's because Biphenyl is a nonpolar molecule, which was able to have an attraction with the pure non-polar molecule hexane via London dispersion forces.

Finally, part C of the experiment had the purpose of finding the components of an unknown ZZ compound using TLC paper whether it contains o-bromonitrobenzene, m-bromonitrobenzene and p-bromonitrobenzene, and the percentage of how much do those isomers contain in the unknown ZZ compound. After simply adding drops on the TLC paper, dipping them in a 9:1 Hexane ethyl acetate, and visualizing them through a UV light, the TLC paper indicated only two dots. This concludes that the ZZ compound only contains two isomers out of the 3. Comparing the 3 TLC papers, the dots of Co side of the Ortho TLC and Meta TLC papers were matched to the ZZ compound, but the Co side of the Para TLC paper did not match the ZZ compound side of the TLC paper. Furthermore, this indicates that the unknown ZZ compound contains the isomers o-bromonitrobenzene, and m-bromonitrobenzene only. In addition, using ImageJ to analyze and calculate the percentage absorbance of each isomer in the ZZ compound was found to be 65.36% for the Ortho isomer, and 34.63% for Meta isomer approximately. Lastly, using the calibration curve equation to find the mole percentage of the isomers to be approximately 80.245% Ortho, and 19.75% Meta.

This experiment was not perfect, and it was possible that couple errors might have come across it, which can result in an inaccurate calculations and outcomes. This could have been because of adding too much drops of the reference compound or the unknown compound on the TLC paper, which can result in an inexact measurement of the dots under the UV light. Also, trying to place and take out the TLC paper out of the jar that contains the solvent might have affected the results. This is due to the fact that it was not an easy process and the solvent might have evaporated which can change the solvent line visually to the naked eye, and result in an different Rf value.

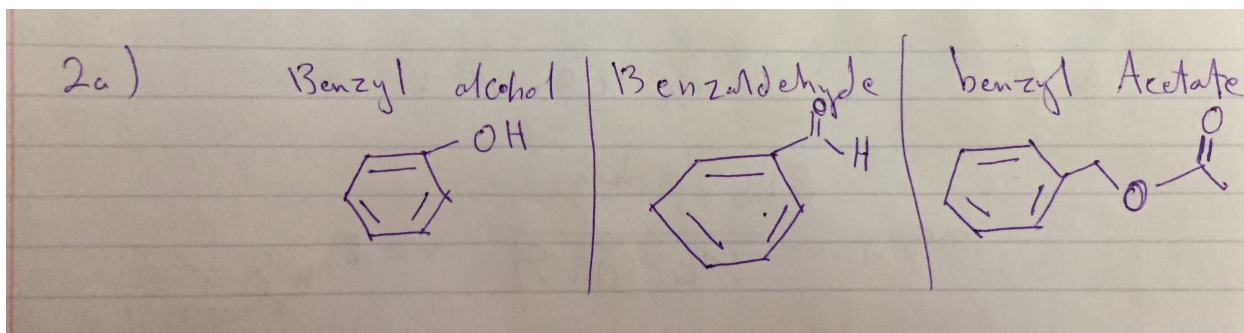
Questions:

1. How does increasing the polarity of the solvent system affect the results of a TLC? (3 points)

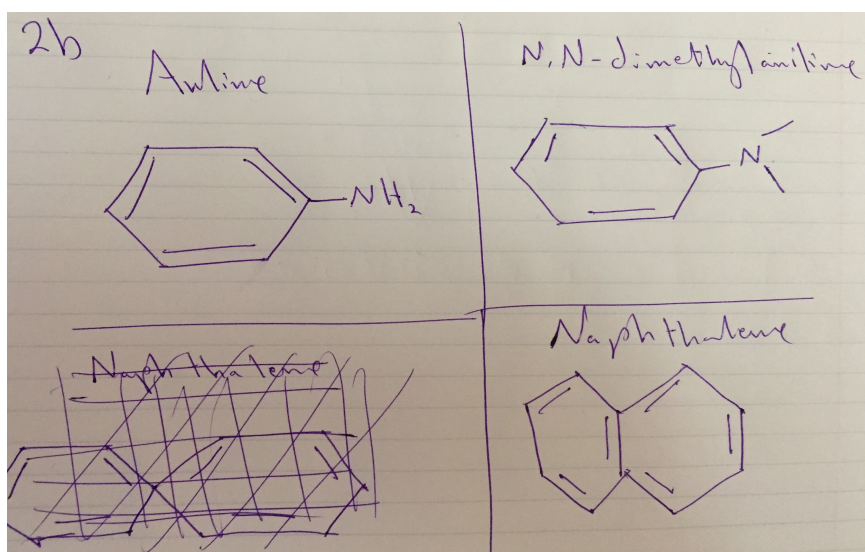
- Increasing the polarity of a the solvent can have an effect on the dots that are visualized under the UV light. Having a strong polar solvent will cause the silica on the TLC paper to strongly become attracted to the solvent since they are both polar. Which leaves no room or attraction to the applied compounds on the TLC paper to become attracted to the silica and thus be pushed to the top of the TLC, close to the solvent line (1). This can result in a confusion and misleading conclusion regarding the polarity of the compounds applied since they are close dots and cannot determine which is more polar and which is less.

2. In the following sets of compounds, which would have the smallest R_F on silica gel? Use a sentence to explain your reasoning. Draw line structures of each compound

- Benzyl alcohol, benzaldehyde, benzyl acetate

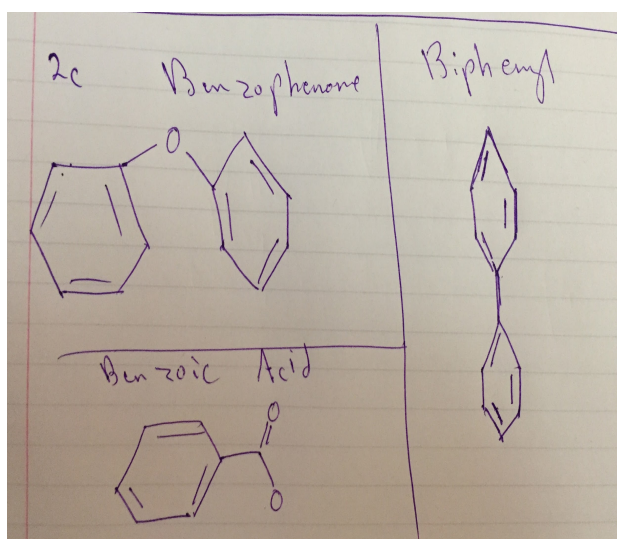


- For this set of compounds, all of the three are polar. However, the polarity degree is different, which provides different R_f rates. The most polar molecules will have the smallest R_f value on the silica gel. This is due to the fact that the attraction or the intermolecular forces will be present between those molecules and the polar silica gel. The most polar molecule between these three would be benzyl acetate. This is because it has two polar functional groups that contains two electronegative oxygen atoms. This raises its polarity against benzaldehyde and Benzyl alcohol because those two only got one electronegative oxygen atom. Benzyl Acetate will be able to attract to the silica gel and travel shorter distance comparing to the other two molecules.



b. Aniline, N,N-dimethylaniline, naphthalene

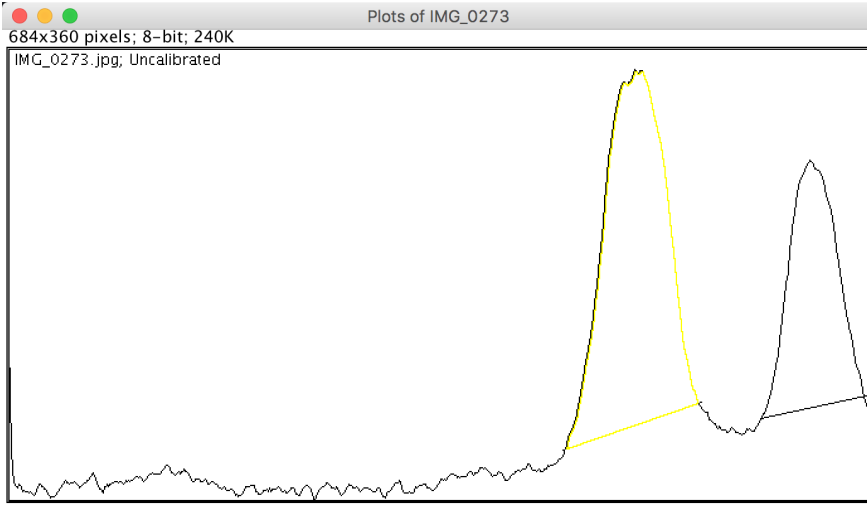
- These set of compounds also have different polarity degree. However, Naphthalene is a symmetrical molecule with non-polar functional group that makes it a nonpolar molecule. Aniline and N,N-dimethylaniline are both polar, but what makes Aniline have a higher polarity degree is that it has two hydrogen atoms bonded to the nitrogen atom making an amino functional group. On the other hand, N,N-dimethylaniline has a nitrogen atom connected to two non-polar functional group which are nonpolar. Therefore, Aniline is the strongest polar molecule between these three molecules, resulting of having a low Rf value on a TLC paper.



c. Benzophenone, Biphenyl, Benzoic acid

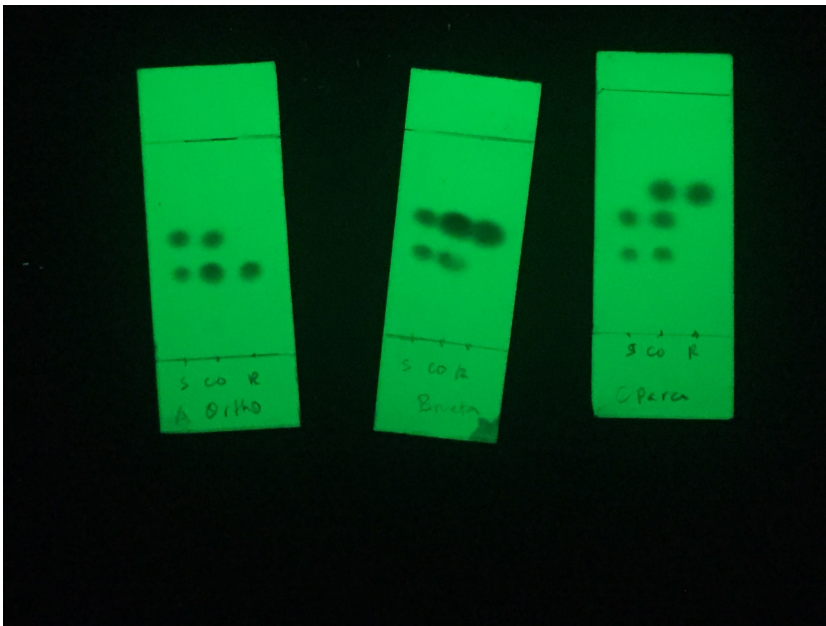
- For those last three molecules, Biphenyl is a nonpolar molecule since it is a symmetrical which causes the net dipole moment to cancel in both directions which results in a nonpolar molecule. However, Benzophenone is a polar molecule, but not as polar as Benzoic acid. This is because Benzoic acid has two electronegative oxygen atoms, which one of them makes the carboxyl functional group that increases the polarity of the compound, comparing it to Benzophenone, which has only one electronegative oxygen atom. Thus, Benzoic acid got the highest polarity, which indicates small Rf value.

Raw Data:



Results

	Area
1	16395.702
2	8686.296

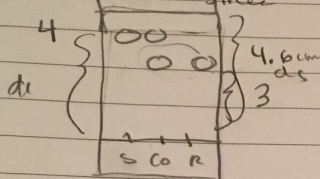


Experiment 1: TLC

Procedure: refer to manual

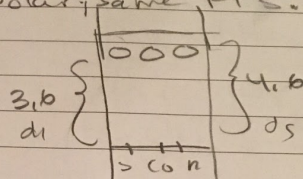
Part 1 } white jar part 1 (8:2) Hex: ethyl acetate
 1 } benzophenone in middle test tube more polar
 biphenyl in right test tube less polar
 Sample is unknown, CO = both sample and Ref. benz/bi.

How we know Part 1 is biphenyl, went further same less polar, same Rf's.



$$\begin{aligned} \text{benz} \\ R_f &= \frac{d_i}{d_s} \\ \text{Sample} &= \frac{4}{4.6} \\ &= 0.869 \\ &= 0.87 \end{aligned}$$

$$\begin{aligned} R_f \text{ ref} &= \frac{3}{4.6} \\ &= 0.652 \end{aligned}$$



$$\begin{aligned} \text{biph.} \\ R_f &= \frac{d_i}{d_s} \\ &= \frac{3.6}{4.6} \\ R_f &= 0.78 \end{aligned}$$

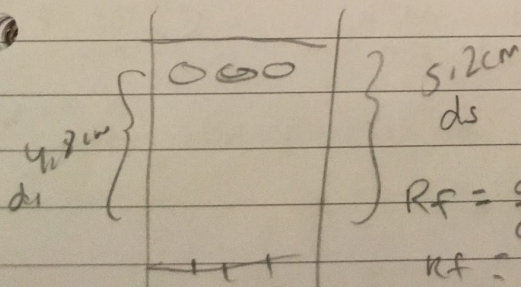
$$\begin{aligned} R_f \text{ ref} &= \frac{3.4}{4.6} \\ &= 0.74 \end{aligned}$$

Part 2: white jar → pure acetyl.
 black jar → pure Hexane

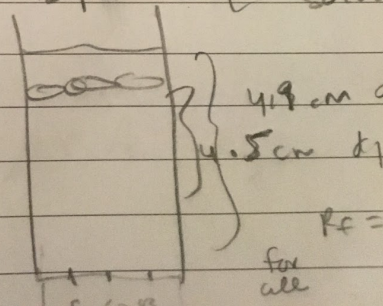
white Jar
 Benz

Biph.

Silica cubes are so polar that attract H₂O. So all samples have no spots but still solve.



$$\begin{aligned} R_f &= \frac{d_i}{d_s} \\ R_f &= 0.923 \end{aligned}$$



$$R_f = \text{for all}$$

References:

1. CHEM 344 Thin Layer Chromatography . (n.d.). Retrieved January 23, 2018, from <https://www.chem.wisc.edu/deptfiles/OrgLab/handouts/CHEM%20344%20TLC%20info.pdf>