Experiment 3: Extraction

Written by:
Tabatha Dovan, 300058293

TA: Paul Richardson
Section Z04

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Procedure: As described in lab manual *Experiment 3: Extraction*, p. 1-6

Modifications:

- Dichloromethane was added to the unknown mixture after it dried.

Observations:

Part A: Extraction of water soluble dyes

- 1 mL of ether and 1 mL of distilled water were placed in a test tube with one drop of 0.006 M methylene blue solution. After the test tube was shaken and the contents were effectively mixed together, the methylene blue solution settled on the bottom of the test tube to form the aqueous layer, while the top "organic" layer remained clear and colourless.
- 1 mL of ether and 2 mL of distilled water were placed in a test tube with one drop of 0.006 M methyl red solution. After the test tube was shaken and the contents were effectively mixed together, the methyl red solution settled in the top "organic" layer, while the bottom "aqueous" layer remained clear and colourless.
- When both mixtures were placed in the same test tube and mixed together, the methyl red solution settled in the top "organic" layer, while the methylene blue solution settled in the bottom "aqueous" layer.

The salting out effect

- 5 mL of distilled water, 0.5 mL of 1-butanol, and one drop of 0.003 M aqueous crystal violet were placed in two separate test tubes. After the test tubes were shaken and the contents were effectively mixed together, the aqueous crystal violet distributed evenly throughout both the organic layer and the aqueous layer.
- Solid NaCl was added to one of the test tubes. After the NaCl was dissolved, the aqueous crystal violet settled in the top "aqueous" layer, while the bottom "organic" layer remained clear and colourless.

Part B: Separating a mixture with reactive extraction

- Unknown substance #49 is solid, white and opaque.
- Unknown substance is dissolved into dichloromethane (clear, colourless liquid); the resulting solution is a clear, colourless liquid.
- NaOH solution is a clear, colourless liquid.
- NaOH is added to the dichloromethane + unknown substance mixture; the resulting solution is a clear, colourless liquid that has been clearly divided into two distinct layers.
- HCl is a clear, colourless liquid.

- HCl is added dropwise to the isolated sample of the aqueous layer of the above solution until the aqueous solution is strongly acidic (blue litmus turns red); once the mixture has been cooled in an ice bath, a white powder precipitate forms on the surface.

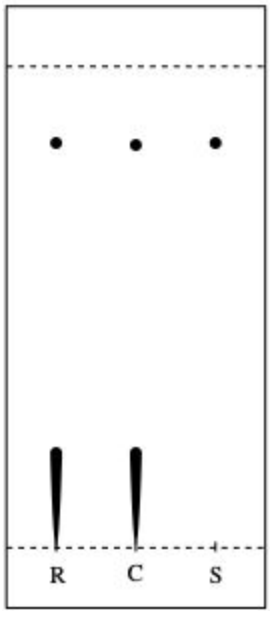
TLC:

Legend:

R: reference
C: co-spot
S: sample spot
Higher: spot closest to solvent front
Lower: spot closest to baseline
Middle (1): middle spot with greater R_f
Middle (2): middle spot with smaller R_f
Bi: biphenyl
Be: benzophenone
Un: unknown #49

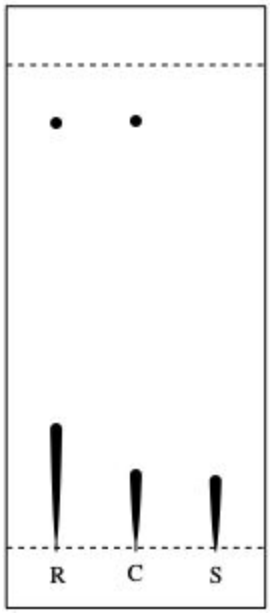
- Top dashed line represents solvent front

Figure 1: TLC using unknown mixture #49 as the reference compound, the organic layer as the sample compound, and 2:8 Ethyl acetate:Hexanes as the solvent system



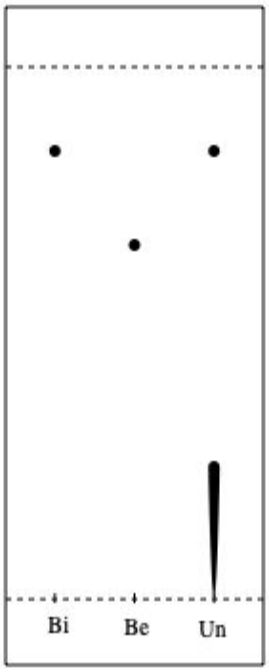
d_1 higher = 4.2 cm
d_1 lower = 1.0 cm
R_f higher = 0.84
R_f lower = 0.20

Figure 2: TLC using unknown mixture #49 as the reference compound, the precipitate from the aqueous layer dissolved in dichloromethane as the sample compound, and 2:8 Ethyl acetate:Hexanes as the solvent system



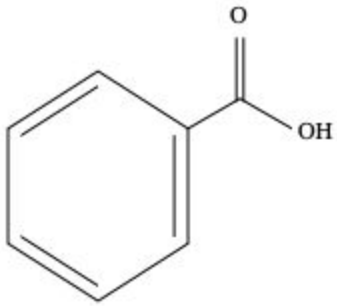
d_1 higher = 4.5 cm
d_1 middle (1) = 1.3 cm
d_1 middle (2) = 0.8 cm
d_1 lower = 0.7 cm
R_f higher = 0.88
R_f middle (1) = 0.25
R_f middle (2) = 0.16
R_f lower = 0.14

Figure 3: TLC using biphenyl in one lane, benzophenone in the second lane, unknown mixture #49 in the third lane, and 2:8 Ethyl acetate:Hexanes as the solvent system

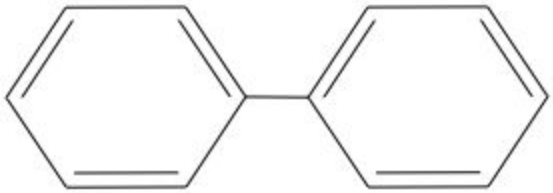


d_1 Bi = 4.6 cm
d_1 Be = 3.7 cm
d_1 Un (1) = 4.6 cm
d_1 Un (2) = 1.4 cm
R_f Bi = 0.84
R_f Be = 0.67
R_f Un (1) = 0.84
R_f Un (2) = 0.25

Flowchart:



Benzoic acid

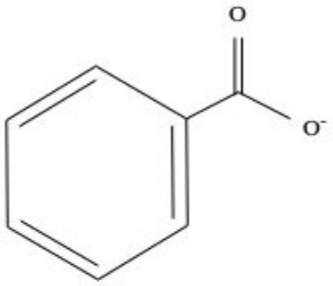


Biphenyl

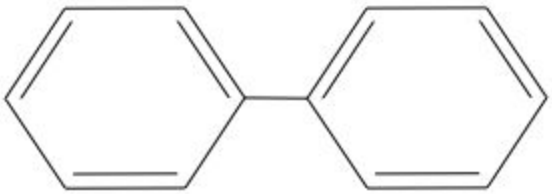
Dilution with DCM
Extraction with NaOH (aq) 3x

Aqueous Phase

Organic Phase



+ NaOH + H2O



Biphenyl + DCM

Addition of concentrated HCl
Precipitation
Filtration and drying

Benzoic acid

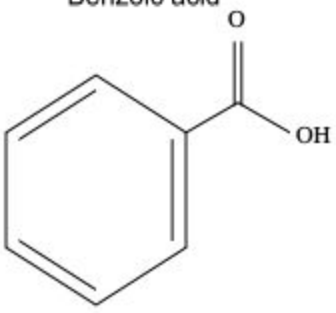


Table of Results

Unknown sample #	49
Initial Mass	0.71 g
Mass Obtained	0.22 g
Composition	Benzoic acid and biphenyl
Percent Yield	31%

Calculations:

R_f - Figure 1

d_1 higher = 4.2 cm

d_1 lower = 1.0 cm

d_s = 5.0 cm

R_f = ?

R_f higher = d_1 higher / d_s
= 4.2 cm / 5.0 cm
= 0.84

R_f lower = d_1 lower / d_s
= 1.0 cm / 5.0 cm
= 0.20

Percent Yield

% yield = (final mass / initial mass) x 100%
= (0.22 g / 0.71 g) x 100%
= (0.31) x 100%
= 31%

Discussion:

Explanation for observations made during the extractions performed in Part A:

Extraction of water soluble dyes

- For the reaction involving 1 mL of ether, 1 mL of distilled water, and a drop of 0.006 M methylene blue, the organic layer settled on top of the aqueous layer as ether has a greater density than water. The methylene blue solution settled in the aqueous layer, which indicates that it is a polar solution.
- For the reaction involving 1 mL of ether, 2 mL of distilled water, and a drop of 0.006 M methyl red, the organic layer settled on top of the aqueous layer as ether has a greater density than water. The methyl red solution settled in the organic layer, which indicates that it is non-polar.

- An extraction between ether and water is a good way to separate a mixture of methyl red and methylene blue, as methyl red will always mix with the ether and methylene blue will always mix with the water, and because ether is not soluble in water the two will always settle into separate layers.

The salting out effect

- 5 mL of distilled water, 0.5 mL of 1-butanol, and a drop of 0.003 M aqueous crystal violet were placed in two separate test tubes.
- When solid NaCl was added to one of the test tubes, the aqueous crystal violet accumulated in the organic layer of that test tube. This is because when the aqueous layer became saturated with NaCl, the ionic strength of water increased and pushed the aqueous crystal violet into the organic phase which resulted in the formation of two distinct layers.

<u>Justification of the procedure:</u>

The salting out effect

Salting out is a purification method that occurs in aqueous solutions with high ionic strength that reduce the molecule's solubility, which causes some proteins to precipitate. The type of salt being used is specifically chosen in order to precipitate a particular molecule. In this lab procedure, we used NaCl for the salting out effect because;

- It is a strong ionic compound, and therefore dissolves completely in water, which results in a saturated solution.
- The saturated solution it produces when dissolved in water provides the high ionic strength that is needed to reduce the solubility of the aqueous crystal violet and push it up into the organic phase.

It is also important to note that 1-butanol was used as the organic solvent during this procedure because it is a non-polar solvent and therefore will not dissolve NaCl, which is a polar molecule. It is essential that the salt dissolves only in the water in order to obtain an effective extraction, which is why the use of 1-butanol as the organic solvent is a good choice as NaCl is insoluble in alcohol.

Reactive extraction

Reactive extraction is a method of extracting a particular compound from a mixture based on differences in polarity between the desired molecule and the other components of the mixture. In this lab procedure, we converted the water insoluble benzoic acid into its water soluble salt by added a strong base (NaOH). In this procedure, we used NaOH because;

- It is a strong base, therefore it deprotonates the benzoic acid, thus transforming the acid into an ionic (polar) compound which is soluble in the aqueous phase.

- It will not react with the biphenyl, thus allowing the biphenyl to remain in the organic phase (any neutral organic compound is soluble in the organic phase), which results in the formation of the two distinct layers.

Now that we have separated the benzoic acid + NaOH + H_2O solution (aqueous layer) from the biphenyl + DCM solution (organic layer), we want to extract the benzoic acid from its salt solution. In order to do this we need to make it insoluble in the aqueous phase by re-protonating the compound, which is achieved by the addition of a strong acid (HCl). In this lab procedure we used HCl because;

- It is a strong acid capable of re-protonating the benzoic acid back into a neutral species which does not want to be soluble in the aqueous phase (non-polar), thus causing the acid to precipitate, and therefore isolating it from the other components of the salt solution.

Analysis of TLC plates;

Figure 1:

- On this TLC, the unknown mixture #49 was used as the reference compound and the organic layer as the sample compound.
- Two rows of spots were produced; one row containing a spot in each lane and the other only containing a spot in the reference and the co-spot lanes.
- In the reference lane, the bottom spot represents the benzoic acid component of the unknown solution, as it is the more polar compound. The top spot represents the biphenyl/benzophenone component of the unknown solution, as it is a non-polar compound.
- In the sample lane, the top spot represents the biphenyl/benzophenone component of the organic phase, however no bottom spot is present as the benzoic acid has been effectively extracted from the organic phase.
- In the co-spot lane, there is a top spot and a bottom spot, as both the organic layer and the unknown solution were spotted in this lane and therefore both benzoic acid and biphenyl/benzophenone are present.
- The R_f of the top row of spots is 0.84 (they all represent biphenyl/benzophenone) and the R_f of the bottom row of spots is 0.20 (they both represent benzoic acid).

Figure 2:

- On this TLC, the unknown mixture #49 was used as the reference compound and the precipitate from the aqueous layer dissolved in dichloromethane as the sample compound.
- Once again, two rows of spots were produced; one row containing a spot in each lane and the other only containing a spot in the reference and the co-spot lanes.

- As mentioned above, the bottom spot in the reference lane represents the benzoic acid component of the unknown solution and the top spot represents the biphenyl/benzophenone component.
- In the sample lane, the bottom spot represents the benzoic acid component of the aqueous phase, however no top spot is present as the organic compounds in this solution (biphenyl/benzophenone) have been effectively separated from the aqueous phase.
- Once again, the co-spot lane contains both biphenyl/benzophenone and benzoic acid.
- The R_f of the top rows of spots is 0.88 (they both represent biphenyl/benzophenone). The bottom spot in the reference column has an R_f of 0.25, the bottom spot in the co-spot column has an R_f of 0.16, and the bottom spot in the sample column has an R_f of 0.14 (they all represent benzoic acid).

Figure 3:

- To determine the nature of the unknown substance (whether it contains biphenyl or benzophenone), a third TLC is created using biphenyl in one lane, benzophenone in the second lane, and the unknown mixture #49 in the third lane.
- Three rows of spots were produced; the top row contains a spot in both the unknown and the biphenyl lanes (represents biphenyl), the second row only contains a spot in the benzophenone lane (represents benzophenone), and the final row only contains a spot in the unknown lane (represents benzoic acid).
- The R_f of the bottom spot in the unknown column is 0.25 and the R_f of the spot in the benzophenone column is 0.67. The R_f of the top spot in the unknown lane is equal to the R_f of the spot in the biphenyl lane ($R_f = 0.84$) which indicates that the unknown mixture is composed of biphenyl.

Some possible sources of error that could have occurred throughout the lab include;

- Not allowing the product obtained from suction filtration to dry completely before weighing it. This would lead to an inaccurate (increased) value for the mass obtained and thus distort our calculations for percent yield, resulting in an increased value for percent composition.
- Extracting some of the organic layer into the aqueous layer. This may lead to inaccurate results on our TLC plates (ie. an extra spot may appear in the aqueous lane of the TLC plate as some organic layer was extracted into the aqueous layer and therefore some biphenyl is present in the aqueous layer).
- The presence of residual salt from a previous lab in the test tubes. If residual NaCl from previous labs remains inside the test tubes, it may cause the aqueous crystal violet to settle in the organic layer of the solution before the addition of NaCl in the current lab. This may cause students to come to the false conclusion that NaCl dissolves in 1-butanol.

- Sources of error could be avoided and the results of the experiment can be improved by ensuring that the product obtained from suction filtration is completely dry before weighing it, closing the stopcock early when draining the aqueous phase from the organic phase (it is better to have residual aqueous phase left in the organic phase than vice versa), and thoroughly cleaning each test tube before using it to ensure that no residual salt is left.

Questions:

1. It would be difficult to perform an extraction using acetone and water because acetone is completely miscible with water (they mix together in all proportions to form a homogeneous solution, as they are both polar compounds and "like dissolves like"). The mixture of these two substances would result in a homogeneous mixture, and therefore the formation of two distinct layers would not occur. Furthermore, any molecule that is added to this mixture would either be soluble or insoluble in both components. If the molecule were polar, it would dissolve into both components, therefore making extraction nearly impossible.

2. Adding NaCl to a test tube containing water, ether, and methylene blue would decrease the amount of dye in the aqueous layer. The addition of a strong ionic compound such as NaCl to the mixture would result in the saturation of the aqueous layer, which would therefore reduce the solubility of the dye and push it up into the organic layer. This process is known as the salting out effect.

3. Calculate the K_d;
Solubility of compound Y in water = 2.0 g/100 mL
Solubility of compound Y in ether = 20.0 g/100 mL

K_d = Solubility in water / Solubility in ether
= (2.0 g/100 mL) / (20.0 /100 mL)
= 0.10

Calculate the mass of compound Y that would be removed from a solution of 1.4 g of Y in 100 mL of water by a single extraction with 100 mL of ether;
0.10 = [(1.4 g - Y) / (100 mL)] / (Y / 100 mL)
(0.001)(Y) = (1.4 g - Y) / (100 mL)
(0.1)(Y) = (1.4 g - Y)
(1.1)(Y) = 1.4 g
Y = 1.3 g

∴ 1.3 g of compound Y would be removed from the solution.

4. Mass of compound Y removed from the original water solution in question 3 - first extraction;
Volume of ether = 50 mL

K_d = Solubility of Water / Solubility of Ether
0.10 = [(1.4 g - Y) / (100 mL)] / (Y / 50 mL)
Y_1 = 1.2 g

∴ After the first extraction, 1.2 g of compound Y would be removed from the solution.

Second extraction;
Volume of ether = 50 mL
Mass remaining = 1.4 g - 1.2 g
= 0.20 g

0.10 = [(0.20 g - Y) / (100 mL)] / (Y / 50 mL)
Y_2 = 0.17 g

∴ After the second extraction, 0.17 g of compound Y would be removed from the solution.
∴ After two extractions, 1.37 g of compound Y would be removed from the solution.

5. Should a student lose track of which layer is the organic layer during an extraction, she could determine which layer is the aqueous phase by placing a drop of methylene blue in the solution. The dye will dissolve into the aqueous phase, therefore causing the aqueous layer to turn blue.

6. In order to separate a mixture of benzylamine and naphthalene, I would add concentrated HCl (or any strong acid) to the solution. The addition of HCl will cause benzyl amine to become protonated as it is a base, thus transforming benzyl amine into a cationic salt and making it soluble in the aqueous phase. The naphthalene is not a base, and therefore is unaffected by the addition of HCl; it will remain in the organic phase, thus creating two distinct layers.

References:

"Salting Out." *Chemistry Libretexts*, CC BY-NC-SA 3.0, 23 January 2018, https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/Real_(Non-Ideal)_Systems/Salting_Out

"The Extraction of Benzoic Acid from a Mixture." *University of Pittsburgh*, March 2019, http://www.pitt.edu/~ceder/lab2/exp2text.html

Rashmi Venkateswaran, "Experiment 3: Extraction", 2014

Organic Chem Lab #3 Part B UN#99

Part A

Water settles @ bottom (more dense than ether)

Blue dye - aqueous layer (water)

Red dye - organic layer (ether)

Red dye + Blue dye

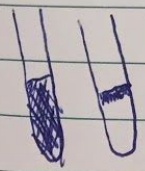
∴ Yes, this is a good mix to separate methylene blue and methyl red

*but and less dense than water

Violet dye

↳ Without salt equally distributed between two layers

↳ + salt - dye accumulates in the organic layer (top) - charge ion aqueous layer pushes salt to organic layer



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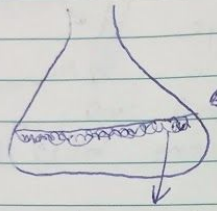
Part B

Unknown #49 → 0.71 g

← water / aqueous layer

← unknown + dichloromethane + NaOH
organic layer

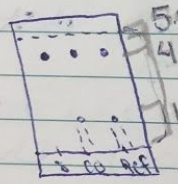


← aqueous layer + HCl
after ice bath

Solid product : 0.22 g

TLC Plates

①



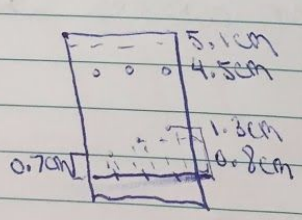
d_1 =

d_2 =

d_3 =

05/03/19

②



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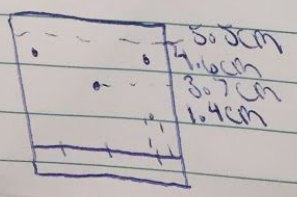

∴ unknown 49 = biphenyl