

SEPARATION TECHNIQUES

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Chemistry

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Atul Singh Arora: *Separation Techniques*, Chemistry,

Every honest researcher I know admits he's just a professional amateur. He's doing whatever he's doing for the first time. That makes him an amateur. He has sense enough to know that he's going to have a lot of trouble, so that makes him a professional.

— Charles F. Kettering (1876-1958) (Holder of 186 patents)

ACKNOWLEDGEMENTS

I express my sincere gratitude to our instructors, Dr. R Vijaya Anand, for bringing the subject to life and helping us discover, in depth, the science behind the procedures.

I also thank Prashansa Gupta and Srijit Mukherjee for their contribution to this report as my lab-partners, who made the task of performing experiments immensely comfortable and productive at the same time.

CONTENTS

1	THIN LAYER CHROMATOGRAPHY (INTRODUCTORY)	1
1.1	Aim	1
1.2	Chemicals Required	1
1.3	Theory	1
1.4	Procedure	2
1.5	Observations and Results	3
1.6	Precaution	3
1.7	Acknowledgements	4
2	THIN LAYER CHROMATOGRAPHY (CONSTITUENT DETECTION)	5
2.1	Aim	5
2.2	Chemicals Required	5
2.3	Theory	5
2.4	Procedure	6
2.5	Observations and Results	7
2.6	Precaution	7
2.7	Acknowledgements	8
3	COLUMN CHROMATOGRAPHY (INTRODUCTION)	11
3.1	Aim	11
3.2	Chemicals Required	11
3.3	Theory	11
3.4	Procedure	12
3.5	Observations and Results	13
3.6	Precaution	14
3.7	Acknowledgements	15
4	COLUMN CHROMATOGRAPHY	17
4.1	Aim	17
4.2	Chemicals Required	17
4.3	Theory	18
4.4	Procedure	18
4.5	Observations and Results	19
4.6	Precaution	20
4.7	Acknowledgements	20
5	THE SOLVENT EXTRACTION TECHNIQUE	23
5.1	Aim	23
5.2	Chemicals Required	23
5.3	Theory	23
5.4	Procedure	24
5.5	Observations and Results	25
5.6	Precaution	25
5.7	Acknowledgements	26
6	DISTILLATION (INTRODUCTION)	29

6.1	Aim	29
6.2	Chemicals Required	29
6.3	Apparatus/Setup	29
6.4	Theory	30
6.5	Procedure	31
6.6	Observations and Results	31
6.7	Precaution	31
6.8	Acknowledgements	31
7	FRACTIONAL DISTILLATION	33
7.1	Aim	33
7.2	Chemicals Required	33
7.3	Apparatus/Setup	33
7.4	Theory	33
7.5	Procedure	34
7.6	Observations and Results	34
7.7	Precaution	35
7.8	Acknowledgements	35
8	THE DEAN STARK APPARATUS	37
8.1	Aim	37
8.2	Chemicals Required	37
8.3	Apparatus/Setup	37
8.4	Theory	37
8.5	Procedure	39
8.6	Observations and Results	39
8.7	Precaution	39
8.8	Acknowledgements	40
9	CRYSTALLIZATION	41
9.1	Aim	41
9.2	Chemicals Required	41
9.3	Theory	42
9.4	Procedure	42
9.5	Observations and Results	42
9.6	Precaution	42
9.7	Acknowledgements	42
10	PURIFICATION BY DERIVATISATION AND CRYSTALLIZATION	45
10.1	Aim	45
10.2	Chemicals Required	45
10.3	Theory	45
10.4	Procedure	45
10.5	Observations and Results	46
10.6	Causes of failure	46
10.7	Precaution	46
10.8	Acknowledgements	46
11	SELF-TEST	47
11.1	Aim	47

11.2 Chemicals Required	47
11.3 Theory	47
11.4 Procedure	47
11.5 Observations and Results	49
11.6 Precaution	50
11.7 Acknowledgements	51
12 PURIFICATION BY SUBLIMATION	53
12.1 Aim	53
12.2 Chemicals Required	53
12.3 Theory	53
12.4 Experimental Setup	54
12.5 Acknowledgements	54

LIST OF FIGURES

Figure 1	TLC plates after Iodine visibility treatment	3
Figure 2	Diagrammatic representation of the test setup	6
Figure 3	TLC plates for Mixture 1	8
Figure 4	TLC plates for Mixture 2	9
Figure 5	p-Nitroaniline	11
Figure 6	TLC plates for the Initial Run	13
Figure 7	TLC plates for various test tubes	14
Figure 8	TLC plates for the rest of the test tubes	15
Figure 9	Benzophenone	17
Figure 10	Bipyridine	17
Figure 11	TLCs Set 1	21
Figure 12	TLCs Set 2	22
Figure 13	Pyridine on the Left, Benzophenone on the Right	22
Figure 14	Aniline	23
Figure 15	2-Naphthol	24
Figure 16	TLCs Set 1	27
Figure 17	TLCs Set 2	28
Figure 18	Distillation Setup	29
Figure 19	Aniline	33
Figure 20	2-Naphthol	38
Figure 21	TLC for Naphthalene	41
Figure 22	TLC for Aniline	49
Figure 23	TLC for Phenol	49
Figure 24	TLC for Mixture 2	50
Figure 25	TLC for Benzoic Acid	50
Figure 26	TLC for Naphthalene	51

Figure 27 Phase Diagram 54

LIST OF TABLES

LISTINGS

ACRONYMS

THIN LAYER CHROMATOGRAPHY (INTRODUCTORY)

January 14, 2013

1.1 AIM

TO find the R_f values of the following compounds:

1. Naphthalene (least polar)
2. Benzophenone (partially polar)
3. Aniline (polar)

1.2 CHEMICALS REQUIRED

1. Naphthalene
2. Benzophenone
3. Analine
4. Hexane
5. Ethyl Acetate
6. Iodine
7. Silica

1.3 THEORY

Thin Layer Chromatography is a separation technique that involves the use a rigid porous structure (like that of a silica layer on a glass slide). The mixture is dissolved in a suitable solvent (the precise meaning of suitable will be made clear in a specific example) and a spot of this mixture is made near one end of the structure. This end is now dipped in a suitable solution (again suitable will be defined later), and due to capillary action, this solution begins to move up. When it comes in contact with the spot, the constituents of the spot, differentially move up the structure, allowing us to separate them.

For viewing the different components, some of the techniques used are as follows:

1. UV

2. Iodine Staining
3. KMnO₄ Staining

We now define an R_f value for a given concentration of the solution

$$R_f = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the solution}} \quad (1)$$

1.4 PROCEDURE

1. Preparing the TLC plates
 - a) Prepared a silica slurry, using silica and ethyl acetate
 - b) Dipped two glass slides, held together, into the solution, to coat about eighty percent of it with the slurry.
 - c) Allowed them to dry (could blow air on it to accelerate the process) and then separated them.
2. Visibility Chamber
 - a) Added a few granules of Iodine with silica granules dominant in number, in a beaker, covered with a watch glass.
3. 10% Ethyl Acetate Soln. in Hexane
 - a) Using a measuring cylinder, measured 1 mL Ethyl Acetate and made the volume 10 mL using Hexane. Transferred the contents in a suitable beaker and covered it with a watch glass.
4. Prepare a solution of the given compounds in Ethyl acetate and using a capillary tube, put a spot on the TLC plate, near the silica coated edge. Also, marked physically, by a method suitable, the position of the spot.
5. Placed the TLC plate, carefully (it's fragile) inside the the 10% Ethyl Acetate Soln., such that the spot is above the level of the solution initially and covered it again, with the watch glass.
6. Kept a watch on the TLC and removed it as soon as the solvent crossed about 90% of the height of the silica coating and placed it cautiously in the Visibility Chamber, until the spots became visible.
7. Now marked the lower portion of the visible spots (should ideally be only one, excluding the Ethyl Acetate Solution) and the Ethyl Acetate solution and measured their distances from the initial position of the spot marked earlier.



In our experiment, we scratched off some silica to mark, using the capillary tube



We actually had to repeat the experiment as we broke the silica coating!

1.5 OBSERVATIONS AND RESULTS

1. Naphthalene: $\frac{4.2}{4.4} = 0.954$
2. Benzophenone: $\frac{3.3}{4.2} = 0.785$
3. Aniline: $\frac{0.7}{4.4} = 0.159$

For details, please refer to

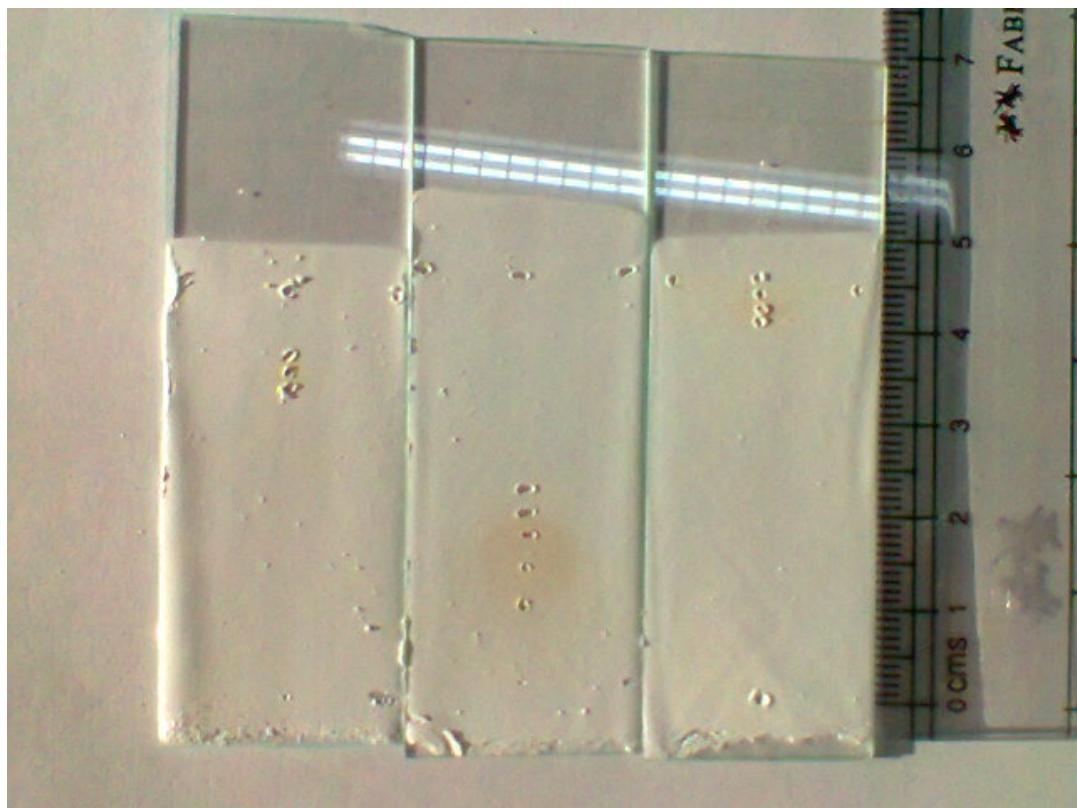


Figure 1

The R_f value decreases with increase in polarity of the compound being analysed.

1.6 PRECAUTION

1. The slurry shouldn't be very thick
2. Cover the beakers with a watch glass to ensure there's no loss of volatile substances (minimal that is)
3. The coating is very fragile, thus the TLC plates must be handled with caution

1.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Prashansa and Srijit for performance of the same.

2

THIN LAYER CHROMATOGRAPHY (CONSTITUENT DETECTION)

January 21, 2013

2.1 AIM

To find the constituents of the mixture samples given, which contain two of the following each:

- A) Resorcinol
- B) p-Hydroxybenzaldehyde
- C) 2,4 - Dinitrophenylhydrazine
- D) p-Nitro Aniline

and to find the corresponding R_f values, using suitable solvent systems.

2.2 CHEMICALS REQUIRED

- 1. Resorcinol
- 2. p-Hydroxybenzaldehyde
- 3. 2,4 - Dinitrophenylhydrazine
- 4. p-Nitro Aniline

2.3 THEORY

The theory here is rather straight forward. We already know that the sample contains two components. We, on a TLC, make three spots, the extreme right comprising of only, say A, the middle comprising of A and the mixture, and the extreme left spot, comprising of only the mixture. Now as shown in the diagram, we'll obtain three spots in the middle (called the co-spot), if A is not already present in the compound. If A is present, then only two spots will appear in the middle.

It is the same as saying that the extreme left should have fewer spots than the co-spot if A is not present, in general, and the 'extra spot' in the co-spot, must match with the spot of A on the extreme right.

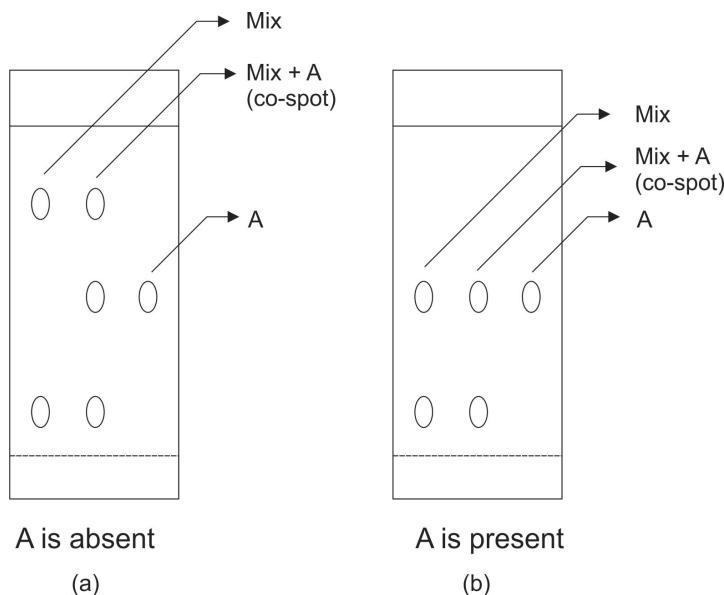


Figure 2

2.4 PROCEDURE

1. Preparing the TLC plates (same as the previous experiment, repeated here for convenience)
 - a) Prepared a silica slurry, using silica and ethyl acetate
 - b) Dipped two glass slides, held together, into the solution, to coat about eighty percent of it with the slurry.
 - c) Allowed them to dry (could blow air on it to accelerate the process) and then separated them.
2. Visibility Chamber (again, same)
 - a) Added a few granules of Iodine with silica granules dominant in number, in a beaker, covered with a watch glass.
3. Various concentrations (5%, 10% and 20%) Ethyl Acetate Soln. in Hexane
 - a) Using a measuring cylinder, measured the required volume of Ethyl Acetate and the made the volume 10 mL using Hexane. Transferred the contents in a suitable beaker and covered it with a watch glass.
4. Diluted the given solutions of A, B, C, D, Mixture 1 and Mixture 2 appropriately and using a capillary tube, put the spots as described in the theory, using compounds A, B, C and D, one after the other, on the TLC plate, near the silica coated edge. Also, marked physically, by a method suitable, the position of the spot.



Our
dilutions were not
sufficient the first
time we attempted
this and we had to
redo the entire
procedure

5. Placed the TLC plate, carefully (it's fragile) inside the Ethyl Acetate Soln. (its concentration was changed progressively in accordance with displacement of the spots), such that the spot is above the level of the solution initially and covered it again, with the watch glass.
6. Kept a watch on the TLC and removed it as soon as the solvent crossed about 90% of the height of the silica coating and placed it cautiously in the Visibility Chamber, until the spots became visible. This is the same as before, except that we setup two chambers simultaneously to speeden up the process.
7. Now marked the positions of all the spots, deduced presence of the substance taken and also calculated the R_f value for A, B, C and D.



We once ended up dipping the spots in the solution itself, which lead to trouble later

2.5 OBSERVATIONS AND RESULTS

Mixture 1 was found to be constituted of compounds A and B, viz. Resorcinol and p-Hydroxybenzaldehyde. In a 20% system, we observed:

1. Resorcinol : $R_f = 0.129$
2. p-Hydroxybenzaldehyde : $R_f = 0.477$
3. 2,4 - Dinitrophenylhydrazine : $R_f = 0.028$
4. p-Nitro Aniline : $R_f = 0.202$

Mixture 2 was found to be constituted of compounds C and D, viz. 2,4-Dinitrophenylhydrazine and p-Nitro Aniline. In a 20% system, we observed:

1. Resorcinol : $R_f = 0.129$
2. p-Hydroxybenzaldehyde : $R_f = 0.422$
3. 2,4 - Dinitrophenylhydrazine : $R_f = 0.085$
4. p-Nitro Aniline : $R_f = 0.259$

For details, please refer to [Figure 3](#) and [Figure 4](#)

2.6 PRECAUTION

Precautions are same as those in the previous experiment, viz.

1. The slurry shouldn't be very thick
2. Cover the beakers with a watch glass to ensure there's no loss of volatile substances (minimal that is)
3. The coating is very fragile, thus the TLC plates must be handled with caution

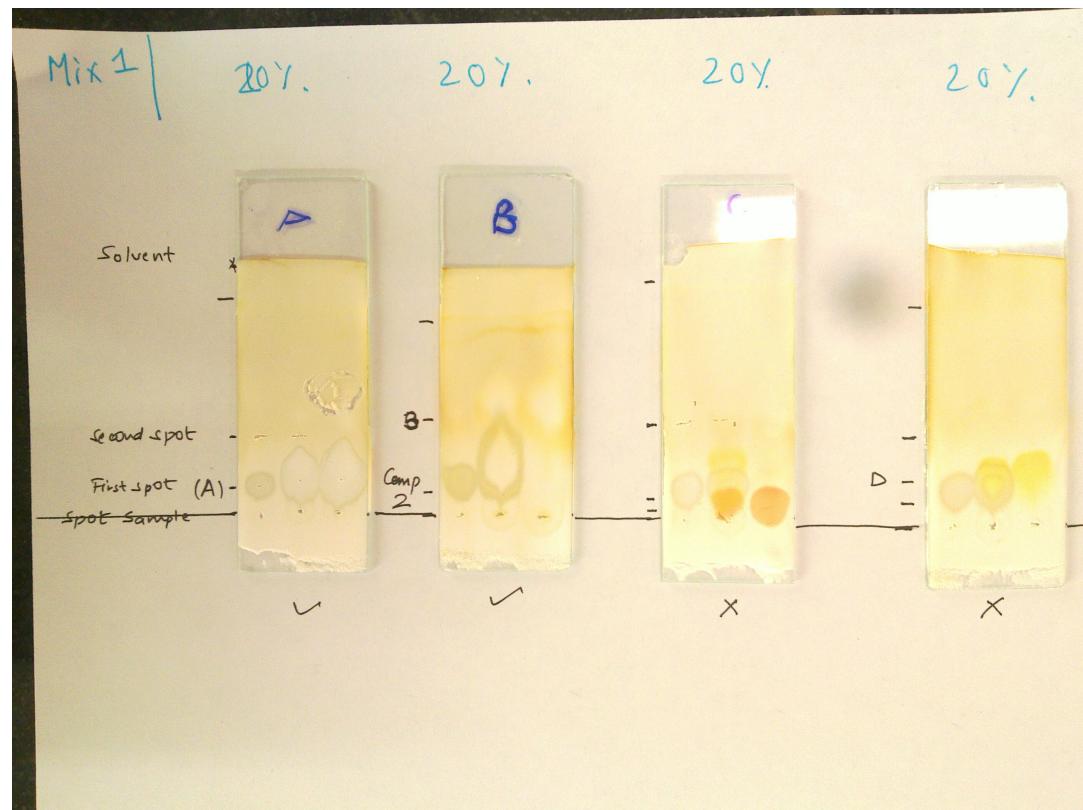


Figure 3

2.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Prashansa and Srijit for performance of the same. I especially thank them for maintaining their calm while we were forced to repeat the experiment numerous times.

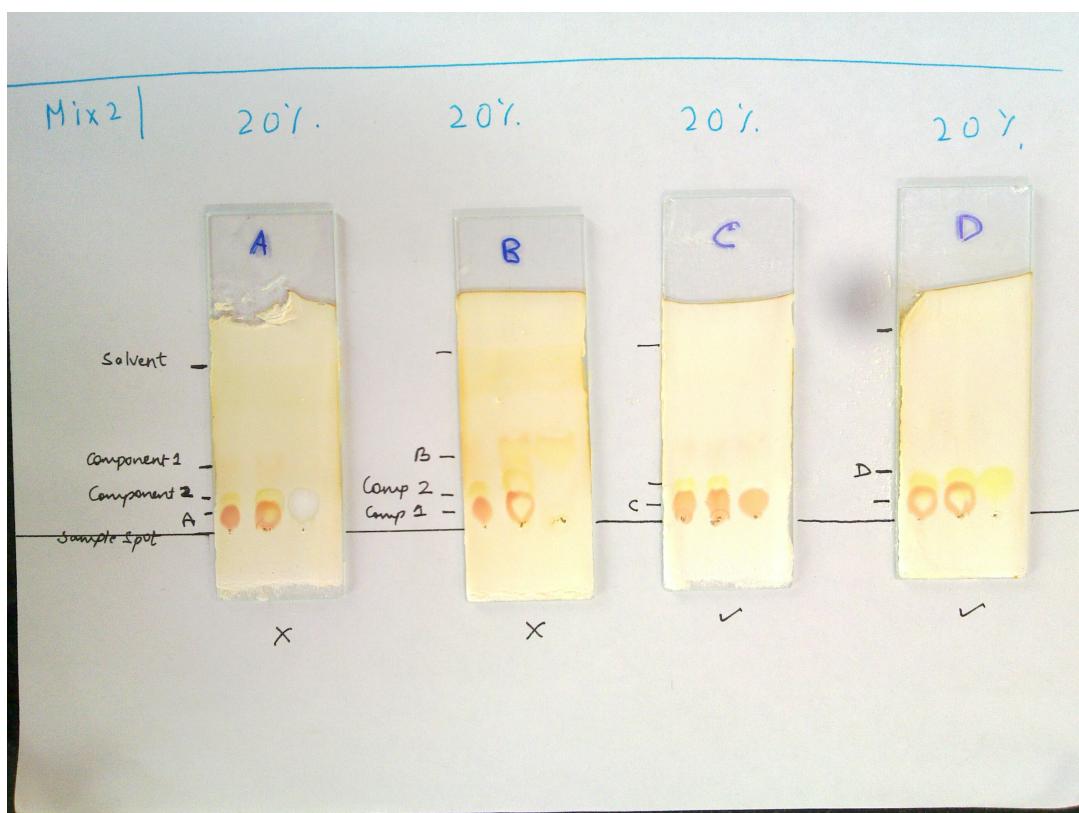


Figure 4

3

COLUMN CHROMATOGRAPHY (INTRODUCTION)

January 21, 2013

3.1 AIM

To get a hands on experience with the Column Chromatography technique, using a single compound, viz. p-Nitro Aniline.

3.2 CHEMICALS REQUIRED

1. Silica
2. Iodine
3. Ethyl Acetate
4. Benzene
5. p-Nitro Aniline (given compound, refer to [Figure 5](#))



Figure 5

3.3 THEORY

TLC is good for detecting what constitutes a mixture. However its yield is very little. To overcome this difficulty, we use a technique known as "Column Chromatography". The principle of differential binding of compounds with the solvent is still harnessed. However, instead of relying on the capillary action, we now rely on gravity. The setup consists of a vertical wet (hexane) silica column, contained in a suitable glass container with a flow control apparatus and a nozzle at the bottom. The compound (if solid, then first dissolved in an appropriate solvent) is added on top of the silica column and on top of it the eluent (a suitably polar solution) is added. This moves down through

the silica column, differentially moving the constituents of the mixture (which is just a compound in our case). Then if the compound is visible, we can easily use this property and collect the constituents in different test tubes. However, if the compounds are not visible, we may need to run a TLC for each small volume collected.

Wikipedia has a very concise and accurate description of the same, which can also be referred to.

3.4 PROCEDURE

1. Determining the concentration of Elluent to use
 - a) Prepared the TLC plates as in the previous experiments
 - b) Setup the Visibility Chamber, again as before
 - c) Various concentrations (50%, 30% and 20%) Ethyl Acetate Soln. in Hexane were created
 - d) The given compound was diluted in Ethyl Acetate.
 - e) TLC was run using the given compound for the various concentrations, till the R_f value was found to be less than $\frac{1}{2}$, just as described in the previous experiments.
 - f) Use the concentration value for which the TLC is roughly less than half, as the Elluent's concentration. This was found to be 20% for our case as is given in the next section.
2. Preparing the Wet Column
 - a) While the TLCs run, a slurry of silica was created in hexane (with about 20-30 spatula of silica) and it was poured in glass column, as described in the theory.
 - b) To this, hexane was added, and it was shaken until all air bubbles disappeared. Further the volume of hexane was reduced to about 1 cm above the silica gel alongside, by allowing hexane to flow through the nozzle.
 - c) The compound, along with silica, were mixed with ethyl acetate to form a thick slurry.
 - d) This mixture was transferred on top of the silica column.
 - e) After it settled reasonably, cotton was added to further level and to ensure that addition of elluent doesn't disturb the mixture (in this case the compound). This ensures that when the separation process proceeds, it doesn't happen out of plane (with respect to the cross section of the container)
3. Running the Column
 - a) Got a set of ordered test tubes in a suitable holder.



This step helps determine the kind of solution we use for the elluent as it determines the speed at which the separation process will take place.

- b) The Elluent was poured into the glass column cautiously and sealed from the top.
- c) The liquid was allowed to flow through the nozzle of the glass column, into the test tubes, progressively, as they filled.
- d) For various test tubes, TLC was run again to find its composition. However, since the compound was coloured, this process was initiated only when the test tubes were known to visibly contain the compound (as could be readily seen from the column as time progressed).

3.5 OBSERVATIONS AND RESULTS

To find the concentration of Elluent to use, please refer to [Figure 6](#). We obtained the following results

1. With 50% $R_f = 0.85$
2. With 30% $R_f = 0.62$
3. With 20% $R_f = 0.25$

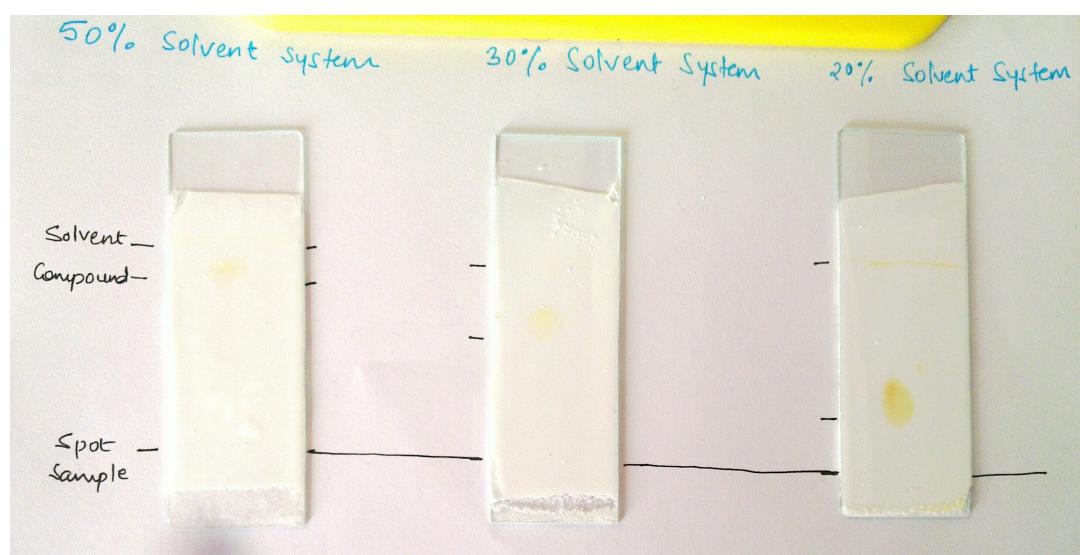


Figure 6

To find the constituents of the test tubes, we run TLC with a 20% system, on each of them and the results are as follows. Refer to [Figure 7](#) and [Figure 8](#) for details.

1. Plate 1, $R_f=0.17$
2. Plate 2, $R_f=0.18$

3. Plate 3, $R_f=0.21$
4. *Plate 4, $R_f=0.27$
5. Plate 5, $R_f=0.18$
6. *Plate 8, $R_f=0.10$
7. Plate 10, $R_f=0.17$
8. Plate 11, $R_f=0.15$

* appear to be outliers Since the mixture consists of only one compound, we expect to get the same R_f values for all coloured test tubes, which seems to hold good for the first place of decimal.

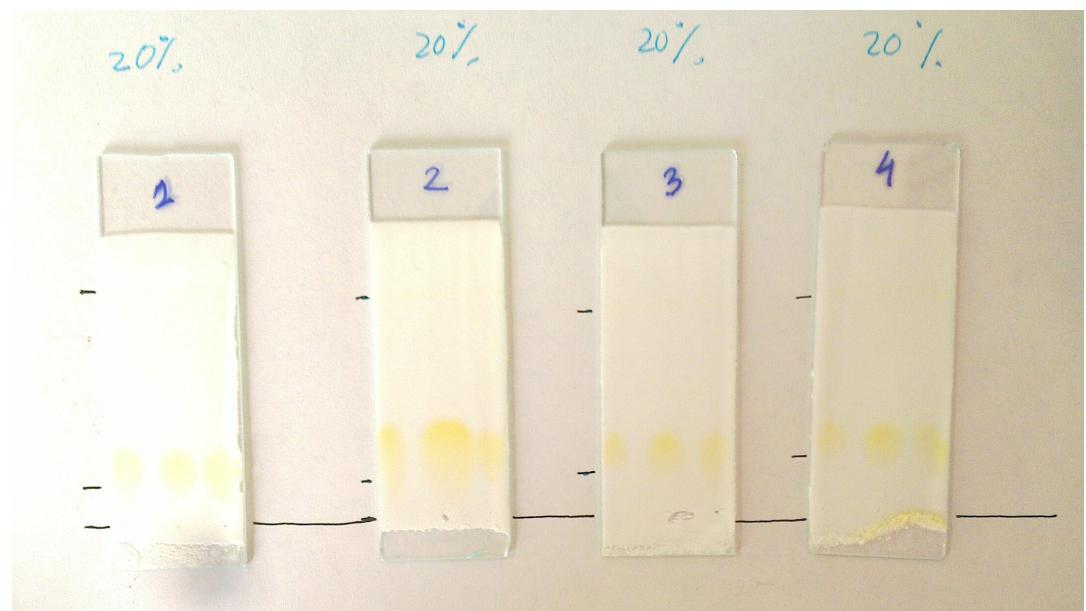


Figure 7

3.6 PRECAUTION

Precautions are same as those in the previous experiment, viz.

1. The slurry shouldn't be very thick
2. Cover the beakers with a watch glass to ensure there's no loss of volatile substances (minimal that is)
3. The coating is very fragile, thus the TLC plates must be handled with caution

Further,

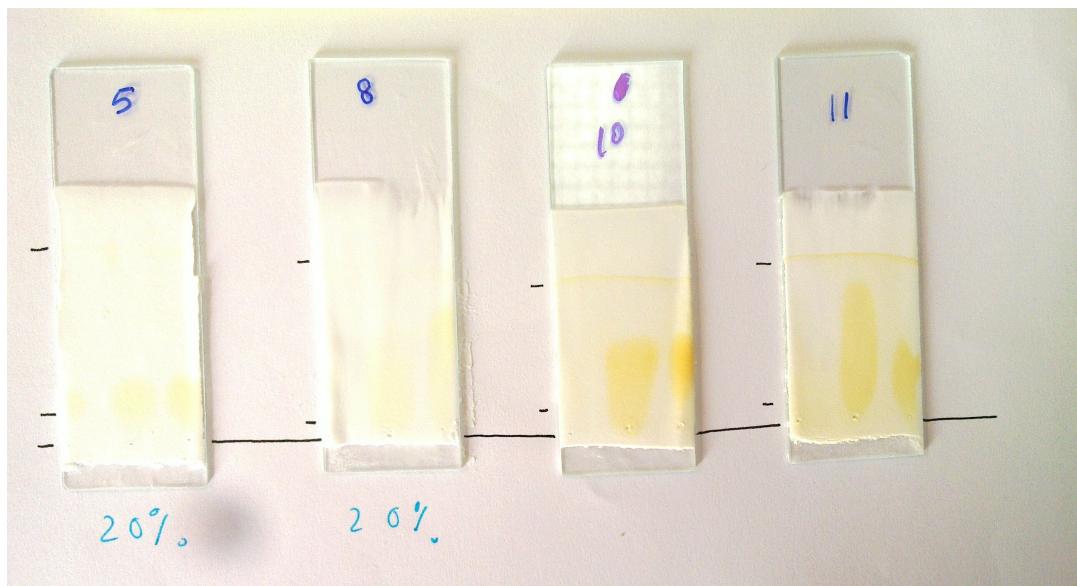


Figure 8

1. We've to ensure there aren't any air bubbles in the column created, by tapping it enough.
2. The hexane level shouldn't drop below the silica column's top, else cracks would begin to appear.
3. Ensure the test tubes aren't cracked.

3.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Saumya, Vivek, Prashansa and Srijit for performance of the same, especially for being able to work in harmony, despite being a large group of five. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.



One of our test tubes was in fact cracked from the bottom and we lost that volume of the recovered compound.

4

COLUMN CHROMATOGRAPHY

February 11, 2013

4.1 AIM

To separate a given mixture of 2 colourless compounds, using the Column Chromatography technique, viz. Benzophenone and Bipyridine.

4.2 CHEMICALS REQUIRED

1. Silica
2. Iodine
3. Ethyl Acetate
4. Benzene
5. Benzophenone (given compound, refer to [Figure 9](#))
6. Bipyridine (given compound, refer to [Figure 10](#))

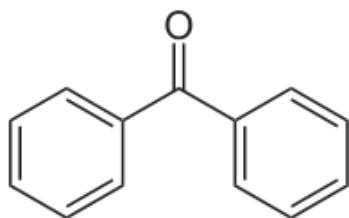


Figure 9

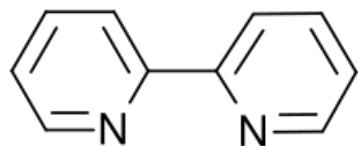


Figure 10

4.3 THEORY

The theory for this experiment is the same as that of the previous experiment, with specifically, the only difference being the use of colourless compounds in this experiment.

For easy reference, the theory of the previous experiment has been replicated here.

TLC is good for detecting what constitutes a mixture. However its yield is very little. To overcome this difficulty, we use a technique known as "Column Chromatography". The principle of differential binding of compounds with the solvent is still harnessed. However, instead of relying on the capillary action, we now rely on gravity. The setup consists of a vertical wet (hexane) silica column, contained in a suitable glass container with a flow control apparatus and a nozzle at the bottom. The compound (if solid, then first dissolved in an appropriate solvent) is added on top of the silica column and on top of it the eluent (a suitably polar solution) is added. This moves down through the silica column, differentially moving the constituents of the mixture (which is just a compound in our case). Then if the compound is visible, we can easily use this property and collect the constituents in different test tubes. However, if the compounds are not visible, we may need to run a TLC for each small volume collected.

Wikipedia has a very concise and accurate description of the same, which can also be referred to.

4.4 PROCEDURE

1. Determining the concentration of Elluent to use
 - a) Prepared the TLC plates as in the previous experiments
 - b) Setup the Visibility Chamber, again as before
 - c) Created a 10% Ethyl Acetate Soln. in Hexane
 - d) The given compounds were dissolved suitably in Ethyl Acetate.
 - e) TLC was run using the given compounds, with Benzophenone on the left, co-spot in the centre, and Bipyridine in the right.
 - f) Since the compounds' R_f values were satisfactory in this concentration, the experiment was carried out with an Elluent of 10% EtAc concentration. Refer to [Figure 11](#) for details.
2. Preparing the Wet Column (same as before, replicated here for convenience)

- a) While the TLCs run, a slurry of silica was created in hexane (with about 20-30 spatula of silica) and it was poured in glass column, as described in the theory.
 - b) To this, hexane was added, and it was shaken until all air bubbles disappeared. Further the volume of hexane was reduced to about 1 cm above the silica gel alongside, by allowing hexane to flow through the nozzle.
 - c) The compound, along with silica, were mixed with ethyl acetate to form a thick slurry.
 - d) This mixture was transferred on top of the silica column.
 - e) After it settled reasonably, cotton was added to further level and to ensure that addition of elluent doesn't disturb the mixture (in this case the compound). This ensures that when the separation process proceeds, it doesn't happen out of plane (with respect to the cross section of the container)
3. Running the Column (the first three points are the same as before)
- a) Got a set of ordered test tubes in a suitable holder.
 - b) The Elluent was poured into the glass column cautiously and sealed from the top.
 - c) The liquid was allowed to flow through the nozzle of the glass column, into the test tubes, progressively, as they filled.
 - d) After the first test tube, a sample from two test-tubes was run on a single TLC to determine the compounds present.
 - e) The concentration of the Elluent was increased once the first compound was recovered successfully.

4.5 OBSERVATIONS AND RESULTS

To find the concentration of Elluent to use, we ran the TLCs as required. For details, please refer to [Figure 11](#). We used a 10% EtAc solution, with the following R_f values from the first run:

1. Bipyridine $R_f = 0.202$
2. Benzophenone $R_f = 0.833$

and from the second run

1. Bipyridine $R_f = 0.289$
2. Benzophenone $R_f = 0.789$

We ran the column for about 38 test tubes, and ran TLC for 32 of them. R_f values for individual tubes were not calculated as they were clearly for the compounds in question. Following is a list of test tubes in which the compounds were found. Details for the same are given in [Figure 11](#) and [Figure 12](#).

NOTE: The starting point of the TLC is at the top for most slides shown in the image.

1. Benzophenone: Test tube 5 and 6
2. Bipyridine: Test Tube 19 to 28

The mixture was eventually separated into its constituents, as given shown in [Figure 13](#).

4.6 PRECAUTION

Precautions are same as those in the previous experiment (except the last), viz.

1. The slurry shouldn't be very thick
2. Cover the beakers with a watch glass to ensure there's no loss of volatile substances (minimal that is)
3. The coating is very fragile, thus the TLC plates must be handled with caution
4. We've to ensure there aren't any air bubbles in the column created, by tapping it enough.
5. The hexane level shouldn't drop below the silica column's top, else cracks would begin to appear.
6. Ensure the test tubes aren't cracked.
7. If the eluent level rises into the funnel, do not remove the funnel. The air-pressure causes oscillations to setup and the eluent doesn't overflow (assuming the funnel is in complete contact with the column).

4.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Vivek, Prashansa and Sriji for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

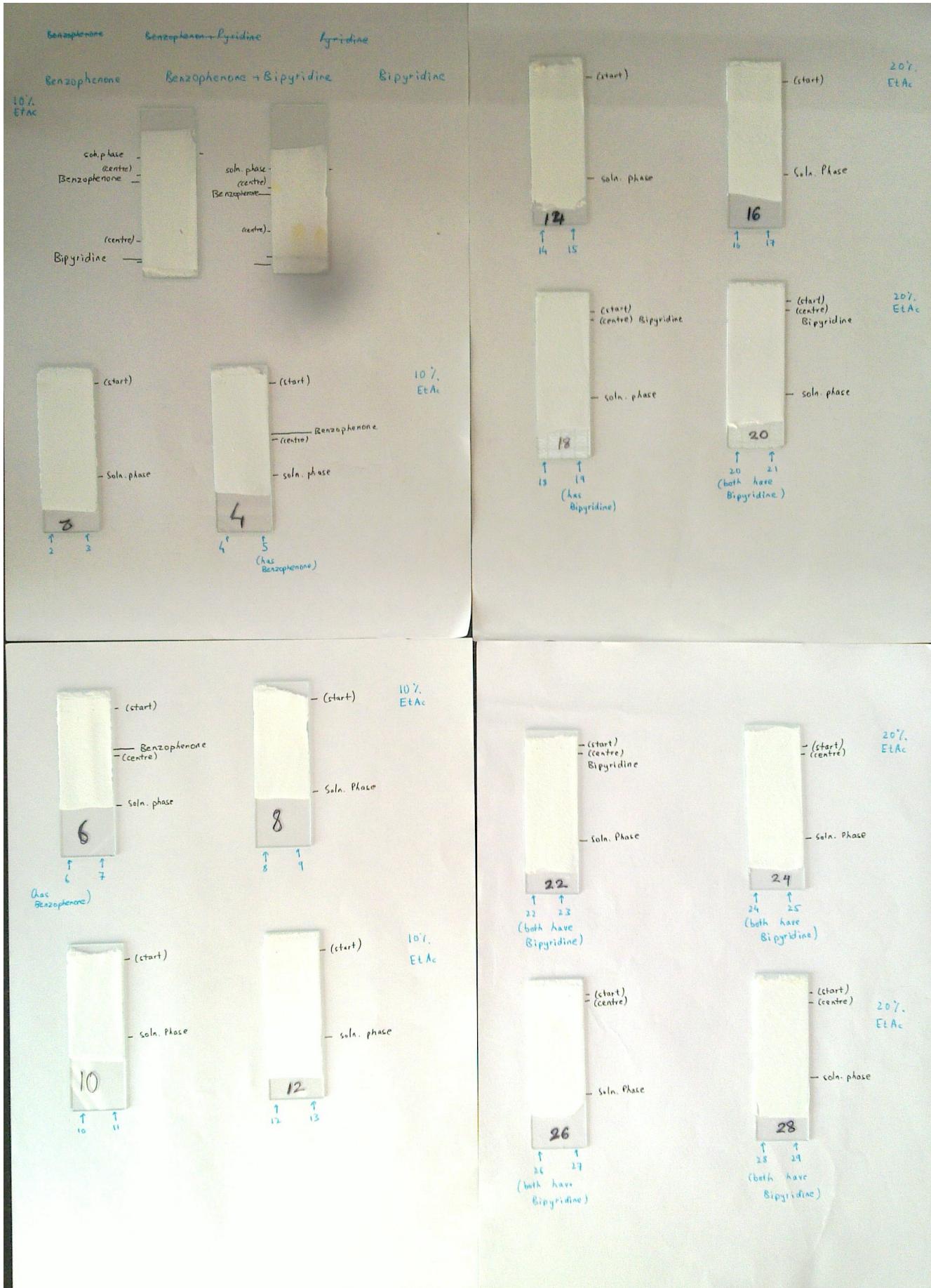


Figure 11

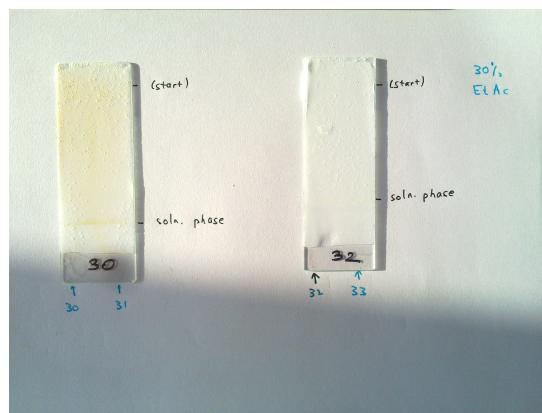


Figure 12



Figure 13

5

THE SOLVENT EXTRACTION TECHNIQUE

February 19, 2013

5.1 AIM

To separate a given mixture of 2 colourless compounds, using the Solvent Extraction Technique, viz. Naphthol and Aniline.

5.2 CHEMICALS REQUIRED

1. Silica
2. Iodine
3. Ethyl Acetate
4. Benzene
5. Naphthol (given compound, refer to [Figure 15](#))
6. Aniline (given compound, refer to [Figure 14](#))
7. NaHCO_3 saturated solution
8. HCl 1N

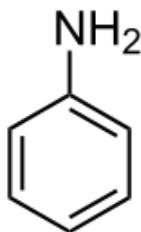


Figure 14

5.3 THEORY

The theory of this experiment is particularly elegant, as it's simple yet very powerful. Say if there are two compounds in a mixture, such that both have very close R_f values and both are soluble in an organic

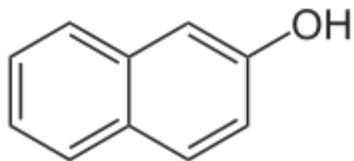


Figure 15

solvent. The methods we've learnt so far would fail to work in such a situation.

To solve this puzzle, we stop to realize that we can make one of these compounds soluble in an aqueous medium, how, well by ionizing it. So, to be more specific to our experiment here, we add NaHCO_3 , a base, to the given mixture, in a separating funnel and shake it. This results in formation of ionic Naphthol and it thus becomes soluble in the aqueous layer. On standing, the organic and aqueous layer separate, and the one with the higher density, occupies the bottom of the inter-phase. In this case, the aqueous layer is less dense in comparison to Ethyl Acetate, thus, using the stop cork, the aqueous layer is removed which now contains ionized Naphthol. This is now neutralized to bring Naphthol back to its form. This is added to the separating funnel and Ethyl Acetate is also added, and shaken well. This extracts the Naphthol back into the organic layer, which can be easily recovered.

Of course, in practice certain steps have to be repeated a few times, and TLCs used at various steps, but the principle idea remains the same. It is worth mentioning that the reverse of the process can also be attempted, that is, we can use an acid to start with, to ionize the base, Aniline. However, the efficiency can be predictably expected to be lower, since Aniline is a weak base.

5.4 PROCEDURE

1. Initial Setup

- TLC plates were prepared
- The visibility chamber was prepared
- TLC was run at a suitable concentration of Ethyl Acetate, with the mixture and both compounds as given in the figure.

2. Method 1: Using NaHCO_3 first

- The given mixture was taken in a separating funnel (after ensuring it's clean of course)
- To the mixture NaHCO_3 was added and the funnel shaken well

- c) The two layers were allowed to separate
 - d) The bottom layer was extracted in a beaker
 - e) Again NaHCO_3 was added and the procedure repeated
 - f) The organic layer should now contain only Aniline; This was confirmed by running a TLC
 - g) The contents of the beaker were neutralized using a pH paper and HCl
 - h) The content of the beaker was transferred into the separating funnel again and Ethyl Acetate was added, shaken
 - i) Both layers were collected in separate beakers and the aqueous layer was again put into the separating funnel, and the process repeated
 - j) The organic layer extracted should contain only Naphthol; This was confirmed by running a TLC
3. Method 2: Using HCl first
The process is identical to the previous case, except for the role of HCl and NaHCO_3 which were swapped systematically

5.5 OBSERVATIONS AND RESULTS

R_f values for the TLC run at 10% EtAc concentration are given below

1. Initial Test (refer to [Figure 16](#))
 - a) Aniline: 0.500
 - b) Naphthol: 0.364
2. Method 1 (after extraction) (refer to [Figure 16](#))
 - a) Aniline: 0.348
 - b) Naphthol: 0.326
3. Method 2 (after extraction) (refer to [Figure 16](#))
 - a) Aniline: 0.348
 - b) Naphthol: 0.489

Naphthol's R_f values don't seem to be consistent for the second method.
Aniline stains were brown, and Naphthol stains were white.

5.6 PRECAUTION

1. The slurry shouldn't be very thick
2. Cover the beakers with a watch glass to ensure there's no loss of volatile substances (minimal that is)

3. The coating is very fragile, thus the TLC plates must be handled with caution
4. Mixing should be done thoroughly to ensure proper extraction
5. The nozzle of the separating funnel was handled carefully to extract the desired solution only
6. A large volume of NaHCO_3 is required to neutralize HCl , so do not waste time with a dropper initially
7. Neutralize, do not overshoot, although in this case it doesn't matter, it might in some

5.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Vivek, Prashansa and Srijit for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

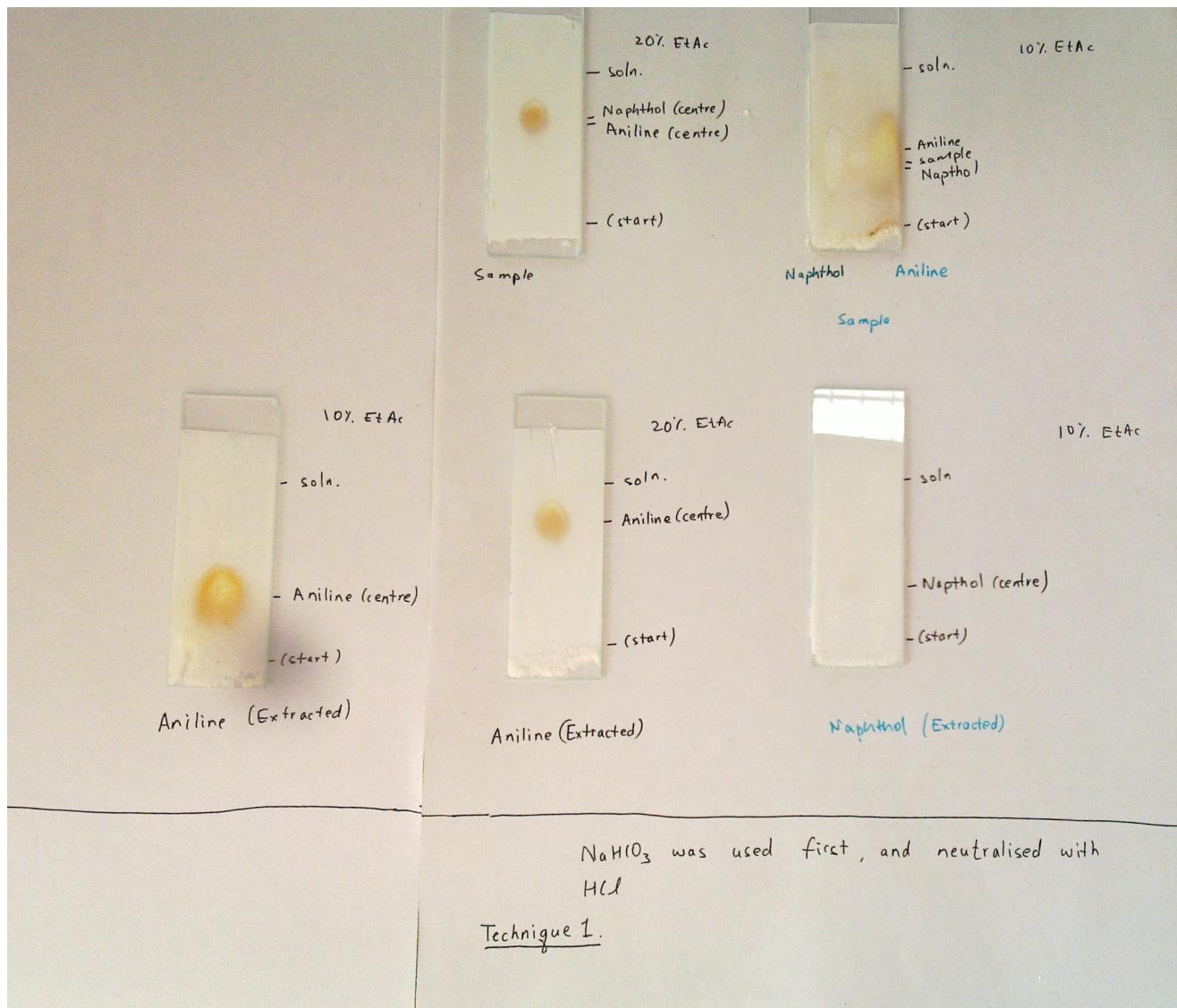


Figure 16

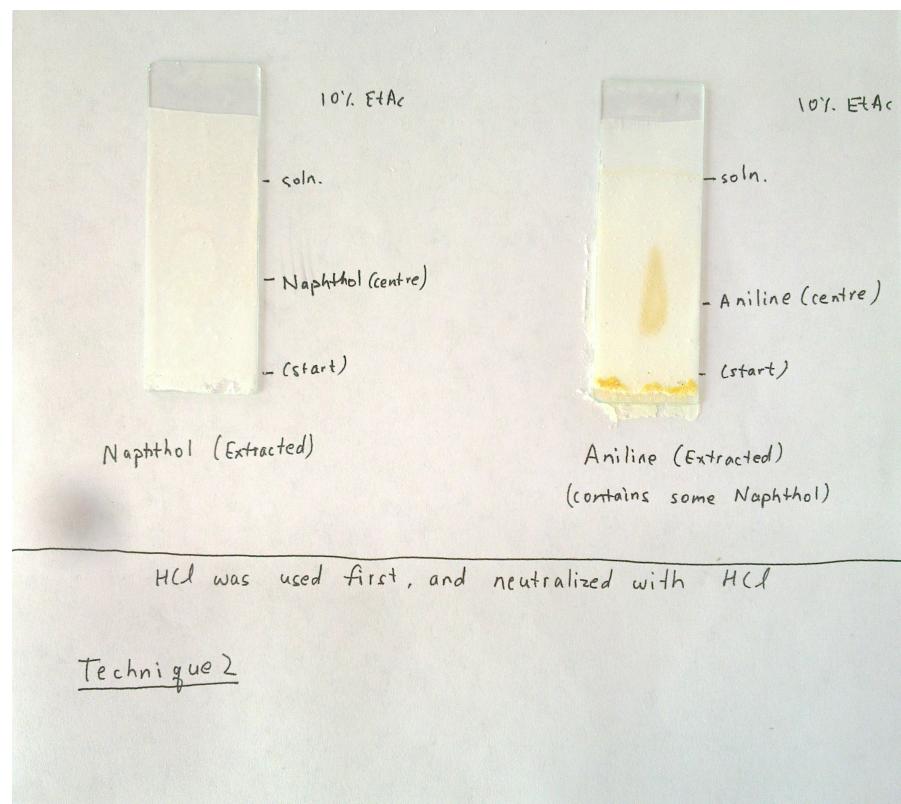


Figure 17

6

DISTILLATION (INTRODUCTION)

February 26, 2013

6.1 AIM

To purify Ethyl Acetate using the distillation technique.

6.2 CHEMICALS REQUIRED

1. Ethyl Acetate

6.3 APPARATUS / SETUP

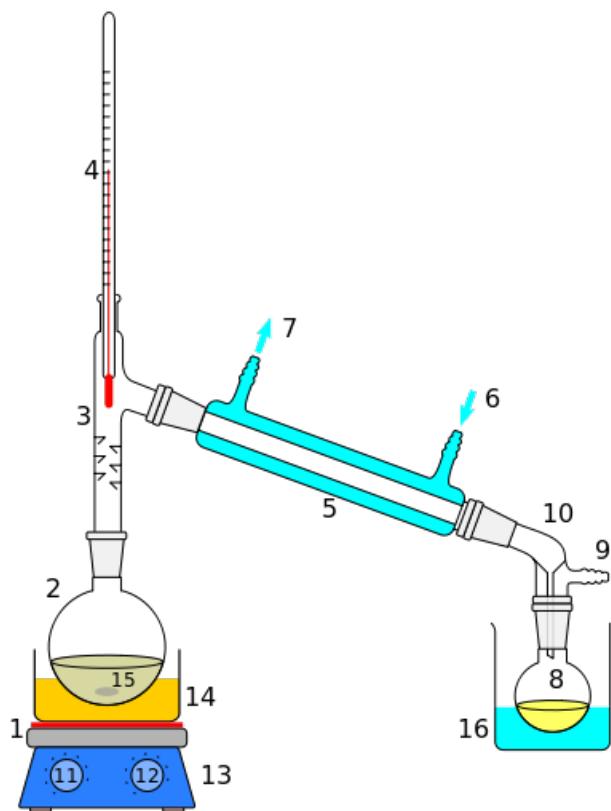


Figure 18

Refer to [Figure 18](#) for a schematic of the setup and the following for a description. The image was taken from Wikipedia.

1. Heating Device
2. Still Pot
3. Still Head
4. Thermometer
5. Condenser
6. Cooling water input
7. Cooling water output [if the nozzels are in opposite directions, this is the one which is higher, to ensure the water's completely filled in the condenser]
8. Distillate/receiving flask
9. Vacuum/gas inlet [we didn't use this]
10. Still receiver
11. Heat control
12. Stirrer speed control [we didn't use a stirrer]
13. Stirrer/heat plate [we didn't have this in our setup]
14. Heating (Oil/Sand) bath [we used an electric heater instead]
15. Stirring Mechanism (heating beads were used)
16. Cooling Bath (this wasn't used)

6.4 THEORY

Distillation as described in wikipedia is a method of separating mixtures based on the differences in the volatility of its constituents.

The idea is rather simple. To make it easy to follow, please refer to [Figure 18](#) and understand the labels. The mixture is heated. The constituent with a lower boiling point would initiate boiling at a lower temperature, which is maintained by adjusting the heater and using the thermometer. The vapours of this constituent pass through the condenser and condense. Then gravity pushes these vapours from the condenser to the receiving flask. Temperature of the vapour helps determine which constituent is being collected.

For this experiment however, we didn't use a mixture. Instead we used Ethyl Acetate and distilled that to purify it.

6.5 PROCEDURE

1. The system was setup as shown in [Figure 18](#)
2. The water circulator was turned on after submersing it in a large water bath
3. The heating was initiated and temperature monitored to keep it in the 75 - 80 °C range
4. When most of the content had been transferred, the process was stopped. (Some liquid was left in the flask to avoid adverse effects)

6.6 OBSERVATIONS AND RESULTS

The evaporation seemed to have started at 44 – 45°C, however the temperature was found to have stabilized at 77°C. Most of the Ethyl Acetate was evaporated and collected in the receiving flask successfully.

6.7 PRECAUTION

1. Do not forget to use boiling chips, else unequal heat spread may result in explosive circumstances
2. The water output should be facing upwards
3. The condenser tube should be sufficiently slanted in the right direction to ensure the condensed liquid flows to the receiving flask and not the other way.

6.8 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Vivek, Prashansa and Srijit for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

7

FRACTIONAL DISTILLATION

March 4, 2013

7.1 AIM

To separate Ethyl Acetate and Toluene using the fractional distillation technique.

7.2 CHEMICALS REQUIRED

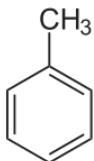


Figure 19

1. Ethyl Acetate
2. Toluene, refer to [Figure 19](#)

7.3 APPARATUS / SETUP

The setup is almost identical to that of the previous experiment. The only difference is that the still head in the previous experiment didn't have provision for providing extra surface area for condensation, whereas in this setup we have. It's called the fractionating column. Refer to [Figure 18](#) for details. The part labelled 3, is what's being referred to here.

7.4 THEORY

Fractional distillation is a method of separating constituents of a mixture which have a boiling point difference of less than 25°C. If the difference is greater than 25°C, then usual distillation suffices.

The idea is the same as that of a simple distillation setup. The only difference, as mentioned earlier, is addition of a fractionating column. This is given very clearly in wikipedia and has been scarcely modified and stated here.

The fractional distillation column is set up with the heat source at the bottom on the still pot. As the distance from the stillpot of the distillation column increases, a heat gradient is formed in the column where it is coolest at the top and hottest at the bottom. As the mixed vapour ascends through the temperature gradient, some of the vapour condenses and re-vaporizes. Each time the vapour condenses and vaporizes, the composition of the more volatile liquid in the vapour increases. This distills the vapour along the length of the column, and eventually the vapour is composed primarily of the more volatile liquid. The vapour condenses on the glass platforms, known as trays, inside the column, and runs back down into the liquid below, refluxing the distillate.

7.5 PROCEDURE

1. The system was setup as shown in [Figure 18](#) with the fractionating column as described earlier
2. The water circulator was turned on after submersing it in a large water bath
3. The heating was initiated and temperature monitored to keep it in the 80-85 °C range
4. The liquid took some time, but eventually started coming out in the collection flask
5. When the process stopped, the collection flask was changed and the heating was increased gradually. Note that the temperature of the thermometer is likely to drop during this time as there are no vapours in contact with the thermometer at this stage
6. This time the temperature was monitored to be in the 95-105 °C range
7. The heating was first reduced when the volume dropped and the process was halted when the decrease was substantial

7.6 OBSERVATIONS AND RESULTS

For Ethyl Acetate, the mantle was kept at 30 (there weren't any units on the mantle). The thermometer stabilized at 84°C. After the process completed, the mantle was kept at 50, and when the volume of the distillate dropped, it was dropped to 30 for Toluene. The thermometer stabilized at 100°C for the same.

7.7 PRECAUTION

1. The temperature of the thermometer would drop once one component has been separated. This doesn't mean the liquid is at that temperature, just that there isn't enough vapour in contact with the thermometer.
2. Clean the thermometer holder in the apparatus, else there would be latency in reflection of temperature on the meter.

Precautions given for the previous experiment must be taken here too.

1. Do not forget to use boiling chips, else unequal heat spread may result in explosive circumstances
2. The water output should be facing upwards
3. The condenser tube should be sufficiently slanted in the right direction to ensure the condensed liquid flows to the receiving flask and not the other way.

7.8 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Vivek, Prashansa and Srijit for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

8

THE DEAN STARK APPARATUS

March 11, 2013

8.1 AIM

To use the Dean Stark apparatus for separating water from a less dense reaction mixture.

8.2 CHEMICALS REQUIRED

1. Water
2. Toluene, refer to [Figure 19](#)

8.3 APPARATUS / SETUP

The setup of this experiment has been given in [Figure 20](#) (from wikipedia). The details are as follows:

1. Heating Beads
2. Reactants' RBF
3. Thermometer
4. Condenser
5. Cooling water in
6. Cooling water out
7. Burette
8. Tap
9. Collection RBF

8.4 THEORY

This is by far amongst the most simplistic and elegant solutions to a seemingly deal-breaking problem. So consider any reaction which is reversible and takes place at a high temperature. Also assume that at this temperature, the reactant mixture is azeotropic with a reactant and a by-product, but they're otherwise insoluble. Further assume

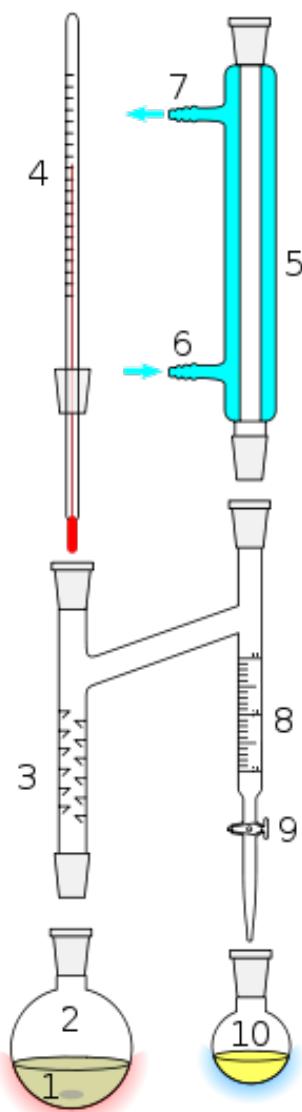


Figure 20

that the reactant is less dense than the by-product. So our objective is to separate the reactant and the by-product to ensure the reaction proceeds in the desired direction.

Ordinary techniques fail for achieving this. Dean-stark comes to the rescue here. The setup has already been shown. The reaction mixture is boiled and its vapours travel up. Now here's the trick. When they condense after the fractional distillation setup, they get collected in the burette which is connected to the reaction mixture as shown. After condensing, the components of the mixture separate out (as they're not miscible at room temperature). The heavier of the two components, viz. the by-product settles at the bottom. The reactant goes back into the reaction mixture to continue the forward reaction. If the by-product accumulates, it can be removed easily, using the tap.

8.5 PROCEDURE

1. The reaction mixture was emulated by using a Toluene and water mixture in the reactants' RBF (the boiling chips were added at this stage itself)
2. The system was setup as shown in [Figure 20](#). The glassware was thermally isolated using cotton and aluminium to avoid unnecessary cooling.
3. Toluene was added to the burette at a level where it just starts to flow into the reaction mixture.
4. The water circulator was turned on after submersing it in a large water bath.
5. The heating was initiated and temperature monitored to keep it in the 100-110 °C range
6. The liquid took some time, but eventually started coming out in the collection flask, while the temperature was maintained constant.
7. The process was halted after a suitable amount of time and allowed to cool.

8.6 OBSERVATIONS AND RESULTS

The stable thermometer read out for the boiling mixture of Toluene and water was approximately 104°C. Water was successfully removed from the 'reactant mixture'.

8.7 PRECAUTION

1. The setup was ensured to be properly insulated, else the procedure takes too long owing to excessive cooling.

Precautions given for the previous experiment must be taken here too.

1. The temperature of the thermometer would drop once one component has been separated. This doesn't mean the liquid is at that temperature, just that there isn't enough vapour in contact with the thermometer.
2. Clean the thermometer holder in the apparatus, else there would be latency in reflection of temperature on the meter.
3. Do not forget to use boiling chips, else unequal heat spread may result in explosive circumstances

4. The water output should be facing upwards
5. The condenser tube should be sufficiently slanted in the right direction to ensure the condensed liquid flows to the receiving flask and not the other way.

8.8 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Srijit, Prashansa, Vivek, Saumya, Manisha and Sandhya for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

9

CRYSTALLIZATION

March 18, 2013

9.1 AIM

To separate Naphthalene from a mixture of it with Aniline, using the crystallization technique

9.2 CHEMICALS REQUIRED

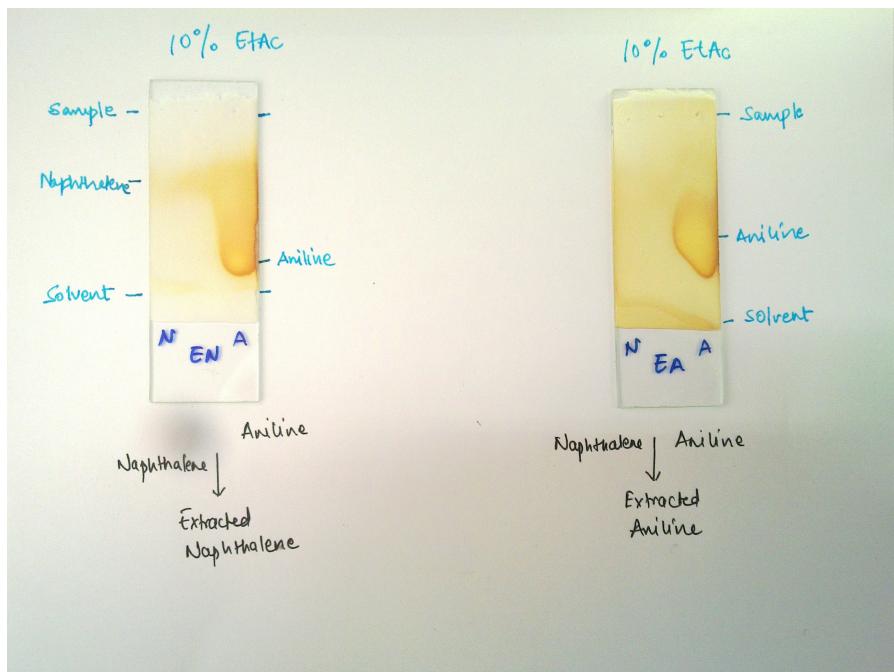


Figure 21

1. Naphthalene
2. Aniline
3. HCl (catalyst)
4. Ethanol
5. Ice
6. Filter paper

7. Silica Slurry
8. 10% Ethyl Acetate in Hexane (for TLC)

9.3 THEORY

Crystallisation is the process of formation of solid crystals precipitating from a solution.

It is an aspect of precipitation obtained through a variability of solubility conditions of the solute in the solvent, as compared to precipitation due to a chemical reaction.

Choice of a solvent is very important for crystallisation. For instance, if a compound is polar and the other is non-polar, and we use hexane as the solvent, then the non-polar will get dissolved completely. Upon cooling then, the polar compound will crystallise out while the solution would contain the non-polar solvent. This very phenomenon is used to purify in this experiment.

9.4 PROCEDURE

1. About 1g of a mixture of Napthalene and Aniline were added to 3-5 mL of rectified spirit.
2. This solution was boiled to dissolve both the substances. Napthalene however remains dissolved only at high temperatures (compared to that required for dissolution of aniline of a comparable concentration)
3. The solution was then cooled and filtered
4. The filtrate was washed with ice cold ethanol to remove any traces of soluble impurities sticking to the crystal.
5. The crystals were separated and the TLC checked.

9.5 OBSERVATIONS AND RESULTS

Naphthalene crystals were obtained and their purity confirmed by TLC as is given in [Figure 21](#).

9.6 PRECAUTION

1. The heating was done indirectly to avoid setting Ethanol to fire.

9.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Srijit, Prashansa

and Vivek for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

10

PURIFICATION BY DERIVATISATION AND CRYSTALLIZATION

March 25, 2013

10.1 AIM

To separate Benzaldehyde by forming its Hydrazone derivative and then crystallising it out to recover its pure form.

10.2 CHEMICALS REQUIRED

1. Benzaldehyde
2. 2,4 - DNP
3. Methanol
4. Ethanol
5. H_2SO_4 (catalyst)

10.3 THEORY

Derivitisation is a technique that's used in chemistry, for transforming a chemical compound into a derivative of itself, viz. a chemically similar product.

Formation of 2,4-Dinintrophenylhydrazones from carbonyls, though more commonly from Aldehydes and 2,4 - DNP, is a very common method of derivatisation.

The hydrazone forms orange crystals which may be purified by recrystallization.

The reaction is carried out in an acidic medium.

Recrystallisation is a technique often used to purify chemicals by dissolving them in an appropriate solvent, and as the name suggests, precipitating them to form crystals, while leaving out the impurities in the solution.

10.4 PROCEDURE

1. A solution of benzaldehyde and methanol was taken in a beaker. And the solution of 2, 4-Dinintrophenylhydrazine, sulphuric acid and methanol in another.

2. To the benzaldehyde solution, added was 2,4 - DNPH dropwise, while stirring was performed continuously.

An orange precipitate was observed alongside.

3. Filtered the solution. From the solute thereby obtained, taken was a small amount, and dissolved it was in ethanol.

4. Placed was this solution of hydrazone derivative, in ethanol on a water bath and heated it was, to approximately 80°C.

A priorly observed orange precipitate now was found to have just dissolved, creating a saturated solution

5. Filtered was the hot solution, with care.

6. Kept was the filtrate to allow cooling, in an ice bath.

An orange precipitate of hydrazone derivate of benzaldehyde was observed, however crystals were NOT observed

10.5 OBSERVATIONS AND RESULTS

The derivate of Benzaldehyde was created successfully, however its purification by recrystallization failed.

10.6 CAUSES OF FAILURE

Perhaps the immediate cooling is what resulted in the failure of the recrystallization process. Another possibility is that the dissolution wasn't complete, which may have interfered the process of forming crystals.

10.7 PRECAUTION

1. The heating was done indirectly again, since the substances are flammable
2. Special care was taken, especially while handling methanol

10.8 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Srijit, Prashansa and Vivek for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

SELF-TEST

April 8, 2013

11.1 AIM

To separate the following mixtures, using any suitable technique:

1. Mixture 1: Phenol and Aniline
2. Mixture 2: Benzoic Acid and Naphthalene

11.2 CHEMICALS REQUIRED

Aside from the mixtures provided, we required the chemicals used in [Chapter 5](#) viz.

1. Silica
2. Iodine
3. Ethyl Acetate
4. Benzene
5. NaHCO_3 saturated solution
6. HCl 6N

11.3 THEORY

The first set of compounds (mixture 1) could be separated directly using the method used in [Chapter 5](#) for Phenol and Napthol are chemically very similar. The idea is to selectively dissolve Napthol in a polar solvent by using a base (aqueous), leaving Aniline in the organic phase (in this case, Ethyl Acetate). Then the aqueous medium is neutralized and Napthol recovered in an organic phase which completes the separation.

For mixture 2, Benzoic Acid was selectively dissolved in the Sodium Bicarbonate solution. Naphthalene was filtered out and the solution neutralized. The Acid could then be recovered by crystallization.

11.4 PROCEDURE

Procedure for the first part is identical to that given in [Chapter 5](#). It has been reproduced here for clarity (with minor adaptations).

1. The volume of the given mixture was increased by adding Ethyl Acetate (the solvent).
2. The given mixture was taken in a separating funnel (after ensuring it's clean of course)
3. To the mixture NaHCO_3 was added and the funnel shaken well
4. The two layers were allowed to separate
5. The bottom layer was extracted in a beaker
6. Again NaHCO_3 was added and the procedure repeated
7. The organic layer should now contain only Aniline; This was confirmed by running a TLC
8. The contents of the beaker were neutralized using a pH paper and HCl
9. The content of the beaker was transferred into the separating funnel again and Ethyl Acetate was added, shaken
10. Both layers were collected in separate beakers and the aqueous layer was again put into the separating funnel, and the process repeated
11. The organic layer extracted should contain only Phenol; This was confirmed by running a TLC

For the second part,

1. The given mixture (which was a solid) was dissolved in Sodium Bicarbonate
only Benzoic Acid reacted and Naphthalene was left unreacted
2. The filtrate was removed using a filter paper and dried
3. It was then dissolved in hexane and was tested for purity using TLC.
4. The solution obtained after filtering was neutralized using pH paper and HCl
5. TLC for the same was tested
6. Crystallization/Extraction could be carried out to obtain Benzoic Acid (but couldn't be done successfully in the given constraints)

11.5 OBSERVATIONS AND RESULTS

Both the mixtures were separated into their corresponding components in accordance with the methods described. Benzoic Acid wasn't successfully purified however.

For Mixture 1, TLC for Aniline is given in [Figure 22](#), and the same for Phenol is given in [Figure 23](#).

For Mixture 2, TLC for the mixture is given in [Figure 24](#), for Benzoic Acid in [Figure 25](#) and for Naphthalene in [Figure 26](#).

(Calculation of R_f values has been omitted for there were only two known compounds and on the basis of polarity, the spots can be identified with the compounds.)

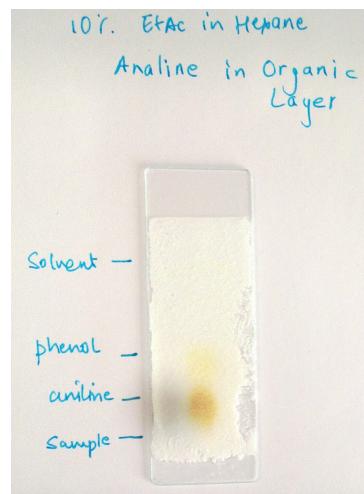


Figure 22: Aniline

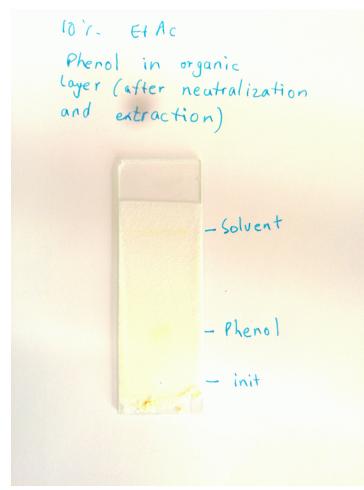


Figure 23: Phenol

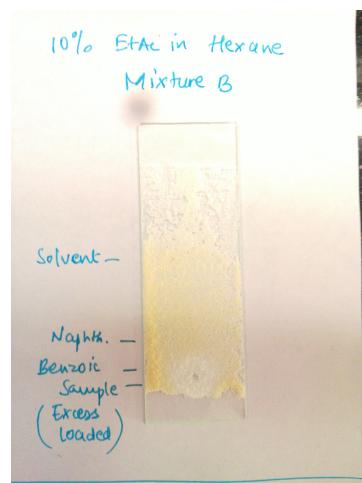


Figure 24: Mixture 2

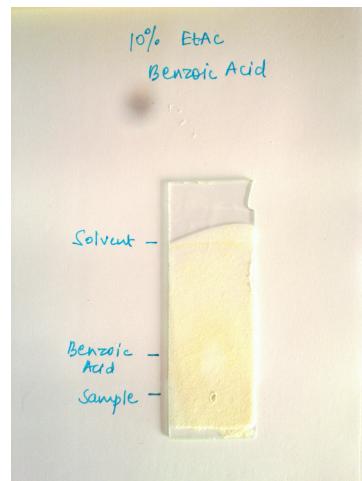


Figure 25: Benzoic Acid

11.6 PRECAUTION

Precautions are the similar to that given in [Chapter 5](#) viz.

1. The slurry shouldn't be very thick
2. Cover the beakers with a watch glass to ensure there's no loss of volatile substances (minimal that is)
3. The coating is very fragile, thus the TLC plates must be handled with caution
4. Mixing should be done thoroughly to ensure proper extraction
5. The nozzle of the separating funnel was handled carefully to extract the desired solution only

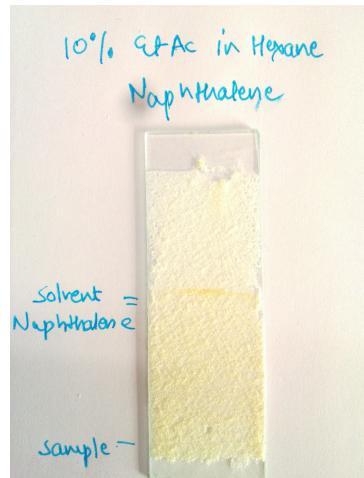


Figure 26: Naphthalene

6. A large volume of NaHCO_3 is required to neutralize HCl , so do not waste time with a dropper initially
7. Neutralize, do not overshoot, although in this case it doesn't matter, but it might in some

11.7 ACKNOWLEDGEMENTS

I thank Dr. R Vijaya Anand for his guidance during the experiment. I also acknowledge the contribution of my lab partners, Srijit, Prashansa and Vivek for performance of the same. I also thank our PhD guide for demonstrating the experiment and her assistance in general, with performance of the same.

 We mistakenly started with 0.1 N HCl , which resulted in a disproportionate increase of volume of the extract

12

PURIFICATION BY SUBLIMATION

April 15, 2013

12.1 AIM

To demonstrate the sublimation of Naphthalene as a viable method of purification

12.2 CHEMICALS REQUIRED

1. Naphthalene

12.3 THEORY

There are three typical states of matter, viz. Solid, Liquid and gas. There can be more states depending on the specific system in question.

Sublimation is the transition of a substance from the solid phase to its gaseous phase without transitioning through the liquid phase.

Sublimation is an *endothermic* phase transition that occurs at temperatures and pressures below the triple point of the material being studied.

For high triple points, the change in temperature and/or pressure results in the disturbance of the solid-vapour phase equilibrium. Refer to the phase diagram given in [Figure 27](#)

For Naphthalene, the atmospheric pressure is below its triple point¹. Thus when it is heated in an open vessel, the phase changes directly to the vapour phase, as expected.

Substances that do not sublime at atmospheric pressure may also be purified by this technique by lowering the pressure.

The idea is that the impurities would not sublime and the substance desired would.

¹ For Naphthalene we have,

$$\text{Molecular Formula} = \text{C}_{10}\text{H}_8$$

$$\text{Triple Point} = 0.99\text{kPa}$$

$$\text{Triple Point Temperature} = 353.3\text{K} = 80.15^\circ\text{C}$$

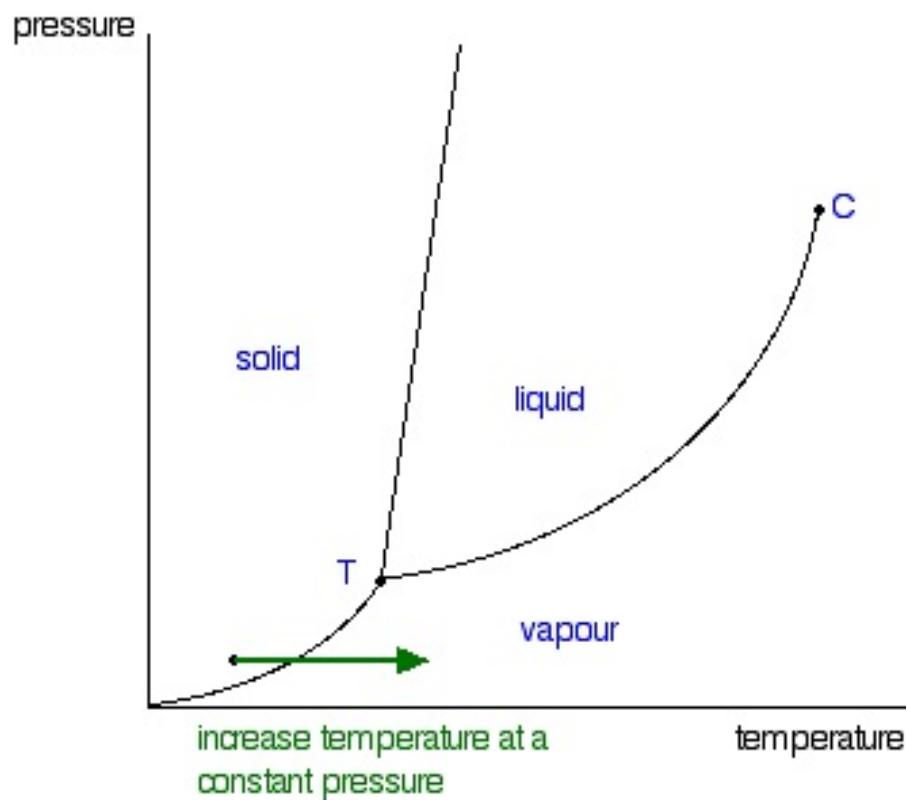


Figure 27: Phase Diagram

12.4 EXPERIMENTAL SETUP

Naphthalene was taken in a china dish. An inverted funnel was placed over it and cotton was used to block the opening. This was heated from the bottom and over a period of time, white spots could be observed on the inner surface of the funnel.

12.5 ACKNOWLEDGEMENTS

I thank our PhD guide for demonstrating the experiment, and also the lab assistants, including Mr. Mangat.

<http://www.chemeo.com/> was referred to for the data on Naphthalene.

The sublimation phase diagram was taken from <http://chemguide.co.uk>

COLOPHON

This document was typeset using the typographical look-and-feel `classicthesis` developed by André Miede, for L^AT_EX.
The style was inspired by Robert Bringhurst's seminal book on typography "*The Elements of Typographic Style*".

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