B.Sc. CHEMISTRY LAB MANUAL

3rd Semester

Prepared By

Pure & Applied Science Dept.

Chemistry

MIDNAPORE CITY COLLEGE

CHEMISREY HONOURS

[Choice Based Credit System]

SEMESTER-III

C07P: LAB (Organic Chemistry)

Background

Organic chemists often must identify unknown compounds. In some cases, such as a reaction, you may have a good idea of what the compound in question is. However in other cases, such as when you isolate a compound from a natural source, you may have no idea what the compound might be. In this experiment you will determine the identity of an unknown compound. First,you will need to purify your compound, then you will need to identify its functional group (it will contain only one), and finally you will need to make a derivative of the compound. You will confirm your results with boiling or melting point, IR, and NMR.

Impurities in your compound will make it extremely difficult to identify. Thus, before you do anything else, you will need to make sure your unknown compound is pure. Consider each of the following purification techniques you have learned over the courseof the year.

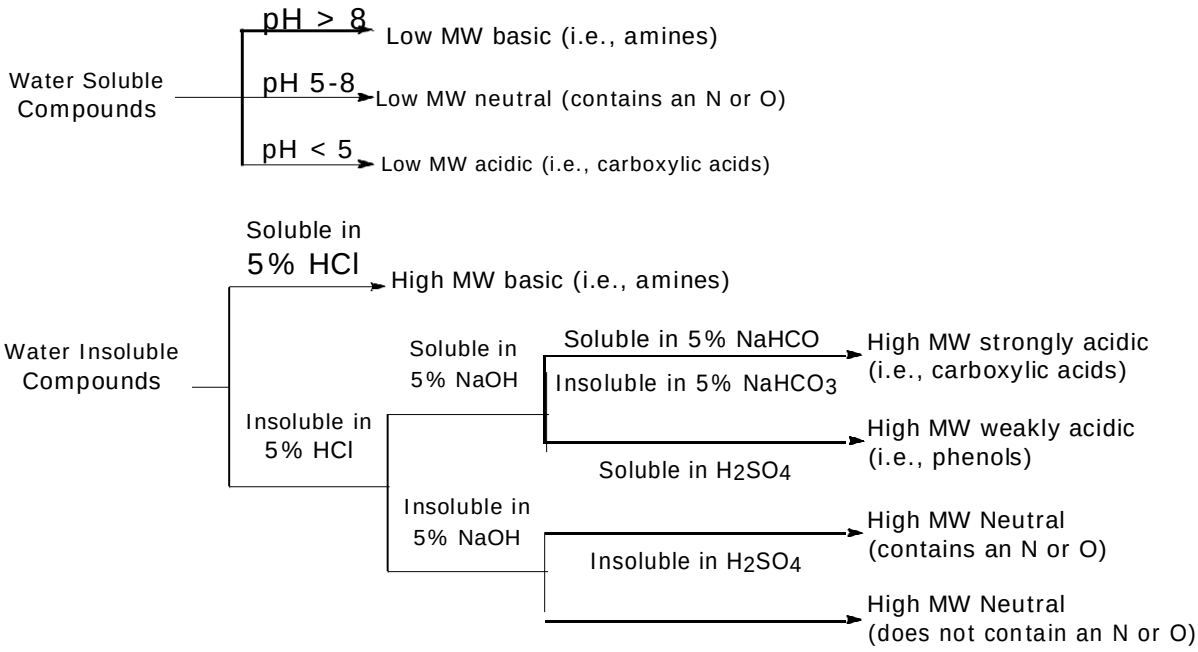
1. *Recrystallization:* Works well for solid compounds. You will need to find an appropriate recrystallization solvent. Consider a variety of solvents and mixed solvent systems.
2. *Distillation:* Works well for liquids that have a boiling point of <250 ◦C. (Note: Fractional distillation may be required if you suspect impurities close to the boiling point of your unknown.)

3. *Column Chromatography:* Works well for UV active compounds. You will need to use TLC to identify a solvent system that will separate your unknown from any impurities.

After you have purified your unknown, verify that it is pure enough to proceed by measuring the boiling or melting point. Note that while you will not know what the melting point or boiling point of your unknown should be, the narrowness is an excellent indicator of whether or not your product is pure. Also pay attention to the appearance of your unknown and see if it has changed (hopefully for the better) during the course of the purification process.

Once your unknown is pure, you will need to identify its functional group. Your unknown will have one major functional group (alcohol, ketone, aldehyde, amide, amine, carboxylic acid, or ester). Additionally, your unknown compound may or may not contain an aromatic ring. To determine the functional group, it is recomanded that you start with solubility tests, and then conduct functional group classification tests. IR spectroscopy may also be useful at this point. Solubility can sometimes provide a surprisingly useful amount of information. First, you will test your unknown's solubility in water. Compounds with 4 carbons or less will easily dissolve in water, whereas compounds with 8 carbons or

more will be insoluble. Compounds containing 5----7 carbons may or may not dissolve (often they will display "partial" solubility). If your compound dissolves in water, you will also want to check the pH of the solution. Amines will typically be basic, and carboxylic acids will typically be acidic. Most other compounds will be neutral. Compounds that are insoluble in water should then be subjected to a solubility test in 5% HCl. Typically, only amines will be soluble in HCl because they form water-soluble hydrochloride salts when they react with HCl. Compounds that are not soluble in HCl, should be subjected to testing in basic solutions (5% NaOH and 5% $NaHCO_3$). Both strong and weak acids (Carboxylic acids and phenols) will be deprotonated by NaOH to form water-soluble alkoxides. Only strong acids like carboxylic acids will react with $NaHCO_3$. Compounds that are not soluble in base should then be reacted with a very strong acid, sulfuric acid (note that in the case of sulfuric acid, "solubility" is also indicated by any type of reaction such as heat, gas generation, or a color change). Compounds that cannot become protonated by sulfuric acid at all (i.e., alkanes, alkyl halides, and aromatic carbons) will still remain insoluble. These solubility tests are summarized in the flow charts below.



The results from the solubility tests can significantly help in determining which classification tests should then be performed, or at least narrow down the list. By no means do you need to conduct all classification tests. In fact, you should do your best to select only tests that will provide you with additional information about your unknown and/or confirm results. Also, make sure that your glassware is clean and dry so you do not get any false positive or false negative results. Keep in mind that a negative result for a classification test provides useful information, so be sure to keep track of negative results as well as positive results. Also, for each classification test that you

perform, be sure to run a blank, and one or more controls. These will help you to determine if a reaction actually occurred. A blank includes everything but the unknown, and a control includes a compound for which the outcome is known in place of the unknown. Controls can be positive (a compound you know will react) or negative (a compound that you know will not react). The classification tests are summarized in the table below.

Functional group	Test	Test no	Notes
Elemental analysis	Lassaigne test	C-1	Test for nitrogen, sulphur, halogens
Amine	Basicity test Bleaching powder test Dye test	C-2 C-3 C-4	Test for aromatic amine
Nitro	Reduction test Muliken and barker test	C-5 C-6	Test for aromatic nitro group
Amido	Nitrous acid test Hydrolysis test	C-7 C-8	Test for amido group
Phenolic –OH	Ferric chloride test Back dye test	C-9 C-10	Test for phenolic-OH
Carboxylic acid	Bicarbonate test Esterification test	C-11 C-12	Test for carboxylic acid
Aldehyde	Benedict test Tollens test	C-13 C-14	Test for aldehyde
Ketone	2,4-Dinitrophenoyl Hydrazine test	C -15	Test for ketone

At this point, you should be able to use your boiling or melting point data combined with the results of your functional group data to develop a hypothesis as to what your unknown might be or at least narrow down the list to only a few candidates. Note tha due to the accuracy (or lack thereof) of our thermometers, your boiling or melting points may be up to 15◦C lower than the literature values.

Once your functional group has been determined, you will prepare a derivative of your unknown. To prepare a derivative, you will select a suitable reaction that converts your unknown into a different functional group for which the boiling or melting point is known. This is particularly useful because compounds that have similar boiling or melting points will oftenhave derivatives that differ significantly in terms of boiling or melting point. You should then be able to identify your unknown using this information.

Finally, you can confirm the identity of your product using IR and NMR. Note that these measurements can be taken at any time during the course of the lab after you purified your product. In fact, it is recommended that you conduct them sooner rather than later as they may provide valuable information as to the identity of your unknown (e.g., IR may reveal your functional group).

Lab Notebook Preparation A

Before coming to lab on the first day of this experiment, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. Outline of your plan for determining the identity of your unknown
4. Hazards of and appropriate precautions for the safe handling of unknown organic compounds
5. References

Lab Notebook Preparation B

Before coming to lab on the day you plan to prepare a derivative, the following items must be in your lab notebook:

1. Title of experiment
2. Date the experiment is to be performed
3. List of possible unknowns
4. The chemical reaction(s) you are attempting (with skeletal structures…R groups are okay if you do not know the identity of your unknown yet)
5. For each reaction you are attempting, include a table with information about your starting materials. Include molecular weight, molar equivalents, and mmoles to be used. For solids include grams. For liquids, include grams, density, and volume. For solutions, include the concentration and volume. (Note: You will not be able to completely fill in the table if you do not know the identity of your unknown yet. If that is the case, list whatever data you can.)
6. Any relevant physical properties (i.e., melting points or boilingpoints of possible unknowns and their derivatives)
7. Hazards of and appropriate precautions for the specific reaction(s) you are conducting
8. References

Safety Notes

- Assume that all unknowns are flammable and harmful by inhalation, ingestion, and skin absorption. Do not inhale their vapors and avoid contact with eyes, skin and clothing.

Directions

1. Purify your unknown using distillation, recrystallization, or column chromatography. It is recommended that purify the entire unknown provided so that you have enough pure material for all of the tests.
2. Measure the boiling or melting point of your unknown to confirm its purity.
3. Confirm with your instructor that the boiling or melting point you obtained for your unknown is within 15 °C of the reported literature value before proceeding.
4. Test the solubility of your unknown in water. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or smallvial.
    b. Add 1 mL of water and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, test the pH of the solution and then skip to step 9.
5. Test the solubility of your unknown in 5% HCl. (If your unknown is a solid, crush it intoa fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of 5% HCl and shake vigorously for approximately 30 seconds. If the unknown appears to be soluble, skip to step 9.
6. Test the solubility of your unknown in 5% NaOH. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of 5% NaOH and shake vigorously for approximately 30 seconds. If the unknown appears to be insoluble, skip to step8.
7. Test the solubility of your unknown in 5% $NaHCO_3$. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of 5% $NaHCO_3$ and shake vigorously for approximately 30 seconds.
    c. Note whether your unknown is soluble or insoluble and then skip to step 9.

8. Test the solubility of your unknown in concentrated H_2SO_4. (If your unknown is a solid, crush it into a fine powder.)
    a. Add approximately 30 mg of your unknown to a test tube or small vial.
    b. Add 1 mL of concentrated H_2SO_4 and shake vigorously for approximately 30 seconds.
    c. Note whether your unknown is soluble or insoluble. (Any indication of a reaction such as heat, gas generation, or a color change also indicates solubility.)
9. Conduct classification tests as needed. See directions for specific tests below.
10. Confirm the identity of your functional group with your instructor before proceeding.
11. Prepare one or more derivatives of your unknown. See directions for specific derivatives below.
12. Measure the melting point of any derivatives.
13. Confirm with your instructor that the melting point you obtained for your derivative is within 15 °C of the reported literature value.

Classification Tests

C-1 Elemental Analysis

This reaction tests for the presence of nitrogens, sulphur and halogens.

Safety Notes: Sodium can cause serious burns and the sodium-lead alloy may react violently with some substances. Wear gloves, avoid contact, and keep the sodium-lead alloy away from other chemicals.

Recommended Controls: butylamine, acetamide, bromobenzene

Procedure:

1. In the fume hood or under a snorkel, place 0.25 g of 10% sodium-lead alloy in a small, dry test tube held vertically by a clamp.
2. Melt the alloy with a Bunsen burner flame and continue heating until the sodium vapor rises about 1 cm up the tube.
3. Using a Pasteur pipet, add 2 drops of the unknown (or 10 mg of a solid) directly onto the molten alloy so that it does not touch the sides of the tube.
4. Heat gently to start the reaction, remove the flame until the reaction subsides, then heat the tube strongly for a minute or two, keeping the bottom a dull red color.
5. Let the tube cool to room temperature.
6. Dropwise add 1.5 mL of water and heat gently for a minute or so until the excess sodium has decomposed and gas evolution ceases.

7. Filter the solution through a Pasteur pipet with a small plug of cotton, wash the cotton with 1 mL of water, and combine the wash water with the filtrate. (Use a rubber bulb to expel any liquid that adheres to the cotton.) The filtrate should be colorless or just slightly yellow. If it is darker, repeat the fusion with stronger heating or more of the alloy.

To test for nitrogen:

1. Put 5 drops of the sodium fusion solution into a small test tube.

2. While stirring, add enough solid sodium bicarbonate, to saturate it (a little excess solid should be present).

3. Add 1 drop of this solution to a test tube containing 10 drops of PNB reagent (*p*-nitrobenzaldehyde in dimethyl sulfoxide) and note any color change.

To test for halogens:

1. Acidify 10 drops of the sodium fusion solution with dilute nitric acid.

2. Boil it gently under the hood for a few minutes.

3. Add a drop or two of 0.3 M aqueous silver nitrate, and note the color and volume of any precipitate that forms. (If a voluminous precipitate forms, let the precipitate settle and then remove the solvent using a pipet.)

4. Add 2 mL of 3 M aqueous ammonia to the solid, shake vigorously, and note your observations.

5. To test further for bromine and iodine, acidify 1 mL of the original sodium fusion solution with 1 M sulfuric acid, boil for a few minutes, and add 0.5 mL of dichloromethane and a then a drop of freshly prepared chlorine water. Shake and look for a color in the dichloromethane layer.

To test for sulphur:

1. Put 1ml of sodium-extract into a test tube.
2. Add 1 ml dil.NaOH solution followed by 2-3 drops of sodium nitroprusside.

Interpretation*:* In the PNB test, a purple color indicates the presence of nitrogen (green indicates sulfur). In the halogen tests, formation of a voluminous precipitate on addition of silver nitrate indicates that a halogen is present, and the color of the precipitate (a silver halide) may suggest which halogen: white for chlorine, pale yellow for bromine, and yellow for iodine. If only a faint turbidity is produced, it may be caused by traces of impurities or by incomplete sodium fusion. If the precipitate is silver chloride, it will dissolve in aqueous ammonia; silver bromide is only slightly soluble and silver iodide is insoluble. In the chlorine water test, a red-brown color is produced by elemental bromine and a violet color by elemental iodine. In the sulphur test, a violet or purple color indicates the presence of sulphur.

C-2 Basicity Test

This test is useful if you have already determined that you have an amine. It is used to distinguish alkyl amines from aromatic amines.

Recommended Controls: p-toluidine, dibutylamine

Procedure for water-soluble compounds:

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of water.

2. Measure the pH of the solution using pH paper.

Procedure for water-insoluble compounds:

1. Dissolve 4 drops of your unknown (0.10 g of a solid) in 3 mL of a pH 5.5 acetate-acetic acid buffer.

2. Mix thoroughly.

Interpretation: Water-soluble alkyl amines give pH values above 11, whereas water-soluble aromatic amines have pH values below 10. Water-insoluble alkyl amines should dissolve in the buffer, but water-insoluble aromatic amines will not dissolve.

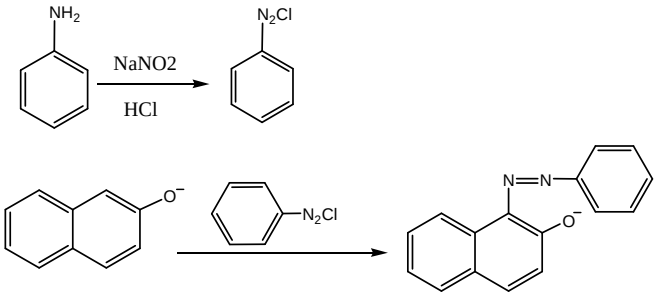
C-3 Bleaching powder test

Procedure:

1. Dissolve 0.05 g of your unknown in 5 mL of water.
2. Add 3-4 drops of bleaching powder solution.
3. Shake vigorously.

Interpretation: Transient purple color which soon turns brown or light purple color.

C-4 Dye test:

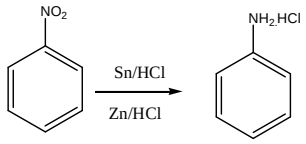


Procedure:

1. 0.1 g of organic sample is dissolved in 5ml of dil.HCl.
2. The mixture is cooled at 0º-5ºC in an ice-bath.
3. Then add 1ml of ice cold solution of dil. $NaNO_2$.
4. The mixture is added to ice-cold alkaline solution of β-Napthol.

Interpretation: Red or orange red dye (brown or raddish purple or violet dye indicates the presence of two amino groups; soluble dye indicates the presence of SO3H or Ar-OH along with Ar-NH_2 group).

C-5 Reduction test



1. A mixture of 0.1 g of organic sample, few pieces of granulated tin or zinc and 3ml of Conc. HCl is warmed gently with occasional shaking till the reaction is complete.
2. The mixture is cooled.
3. Filtered, if required, diluted and diazo-coupling reaction is performed.

Interpretation: Brilliant red or scarlet dye obtained.

C-6 Muliken and Barker Test

Procedure:

1. 0.1 g of organic sample is dissolved in 5 ml of 50% alcohol.
2. A little solid NH_4Cl or 10% $CaCl_2$ solution and a pinch of Zn-dust is added to it.
3. The mixture is boiled for a few minutes.
4. Then the mixture is cooled and allowed to stand for 5 minutes and then filtered.
5. With the filtrate following three tests are performed:

a) A portion of the solution is added to Tollen's reagent and then warmed in a water bath.

b) Two drops of benzoyl chloride and 2 drops of conc. HCl are added to another portion of the filtrate followed by 12 drops of $FeCl_3$ solution.

c) The last portion of the filtrate is warmed with a little Fehling's solution.

Interpretation: From the part (a), a silver mirror or black or grey precipitation is obtained. From part (b), a wine-red color of ferric hydroxamate is present, from last part (c), a red precipitation is obtained.

C-7 Nitrous Acid Test

Procedure:

1. A little of the aqueous solution of organic sample is treated with with a few drops of HNO_2 (NaNO2 and HCl).

Interpretation: Effervescence due to evolution of N_2 gas.

C-8 Hydrolysis Test

Procedure:
0.2 g of organic sample is heated with 2ml of 50% NaOH solution.

Interpretation: Characteristics smell of NH_3 which turns mercurous nitrate paper black or copper sulphate paper deep blue.

C-9 Ferric Chloride

This reaction tests for the presence of phenols.

Recommended Control: phenol

Procedure:

1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of water. If(you know based on the results of your solubility tests that the unknown is insoluble in water, use 0.5 mL of water and 0.5 mL of methanol instead of 1 mL of water.)
2. Add two drops of 2.5% ferric chloride solution.

Interpretation: Formation of an intense red, green, blue, or purple color suggests a phenol or an easily enolizable compound (such as an aldehyde or ketone). Some phenols do not react under these conditions.

C-10 Back Dye Test

This reaction tests for the presence of phenols.

Procedure:

1. A few drops of aniline dissolved in dil. HCl.
2. Few drops of cold dil. $NaNO_2$ solution is added.
3. Then the clear solution is added to the cold solution of organic sample in NaOH.

Interpretation: A brilliant red dye is obtained. Phenolic OH group present and confirmed.

C-11 Bicarbonate Test

This reaction tests for the presence of carboxylic acid.

Procedure:

1. A small amount of organic sample is sprinkled over aqueous solution of sodium bicarbonate.

Interpretation: Effervescence due to the evolution of CO_2.

C-12 Esterification Test

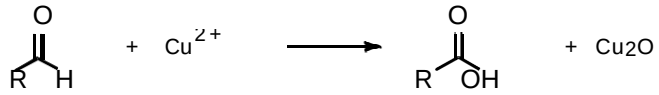
This reaction tests for the presence of carboxylic acid.

1. 0.5 g of organic sample is taken in a dry test tube.
2. To this, add 1 ml of dehydrated ethanol.
3. Then 2-3 drops of conc. H_2SO_4 is added and heated for 5 minutes in a water bath.
4. The mixture is then poured into a beaker containing large volume of Na_2CO_3 solution.

Interpretation: Characteristics sweet fruity smell of ester.

C-13 Benedict's Test

This reaction tests for the presence of aldehydes. Note that most ketones and aromatic aldehydes will not react.



Recommended Controls: butanal

Procedure:

1. Add 2 drops of the unknown (80 mg if it is a solid) to 2 mL of water.
2. Add 2 mL of Benedict's reagent.
3. Heat the mixture to a boil.
4. Observe if a precipitate forms, and note its color.

Interpretation: Benedict's reagent contains copper(II) sulfate,sodium citrate, and sodium carbonate. Aldehydes will react with the Cu_{2+} from the copper(II) sulfate to form copper(I) oxide which appears as a yellow or orange precipitate (it may look a little green in the blue reaction solution). Note that most ketones and aromatic aldehydes will not react.

C-14 Tollen's Test

This reaction tests for the presence of aldehydes.

Recommended Controls: benzaldehyde

Procedure:

1. Measure 2 mL of 0.3 M aqueous silver nitrate into a test tube and add 1 drop of 3 M sodium hydroxide.
2. Add 2 M aqueous ammonia drop by drop, with shaking, until the precipitate of silver oxide just dissolves (avoid an excess of ammonia).
3. Add 1 drop of the unknown (40 mg of a solid) to this solution, shake the mixture, and let it stand for 10 minutes. (If a silver mirror is observed at this point, this is considered a positive result.)
4. Heat the mixture in a 35 ℃ water bath for 5 minutes.
5. Immediately after the test has been completed, dissolve any solid residue in 1M nitric acid and then dispose of the solution in the designated waste container.
6. *Interpretation:* Formation of a silver mirror on the inside of the test tube is a positive test for an aldehyde. (Note that if the tube is not sufficiently clean, a black precipitate or a suspension of metallic silver may form instead.)

C-15 2,4-Dinitrophenylhydrazine

This reaction tests for the presence of aldehydes and ketones.

Safety Notes: 2,4-Dinitrophenylhydrazine (DNPH) is harmful if absorbed through the skin. Wear gloves and avoid contact.

Recommended Controls: cyclohexanone, benzaldehyde

Procedure:

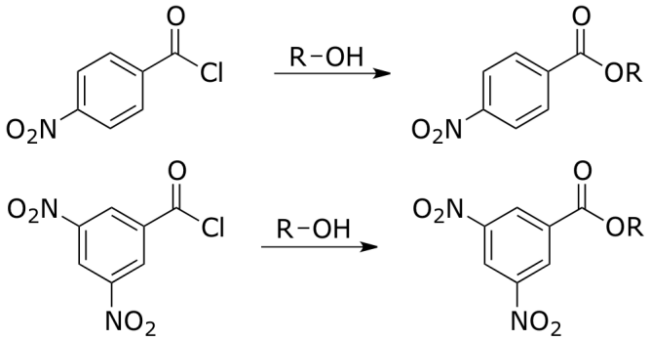
1. Dissolve 1 drop of the unknown (40 mg of a solid) in 1 mL of 95% ethanol (use more ethanol if necessary to completely dissolve the unknown).
2. Add this solution to 2 mL of the DNPH reagent.
3. Shake and let the mixture stand for 15 minutes or until a precipitate forms. (If a precipitate is observed at this point, this is considered a positive result.)
4. Scratch the inside of the test tube and observe if a precipitate forms, and note its color.

Interpretation: Formation of a crystalline yellow or orange-red precipitate indicates an aldehyde or ketone. The color of the precipitate may give a clue to the structure of the carbonyl compound (unconjugated aliphatic aldehydes and ketones usually yield a yellow precipitate, while aromatic and α,β-unsaturated aldehydes and ketones yield a orange-red precipitate).

Derivatives of Alcohols

D-1* p-*Nitrobenzoates and 3,5-Dinitrobenzoates

For these derivatives, it is extremely important to ensure that your glassware and your alcohol are dry (i.e., free of water). Water can easily react with the acid chlorides to form carboxylic acids to form the respective carboxylic acids rather than the desired esters. (Note: The *p*----nitrobenzoic acid has a melting point of 237 °C. and the 3,5----dinitrobenzoic acid has a melting point of 205----207 °C.) If necessary, dry your glassware in an oven before proceeding.



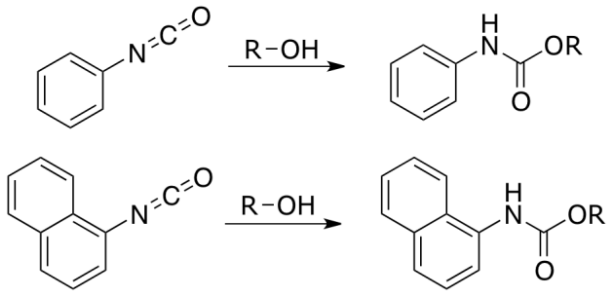
Procedure:

1. Dry your unknown alcohol with magnesium sulfate or sodium sulfate.
2. Filter to remove the drying agent.
3. If you are making the *p*-nitrobenzoate derivative, add 0.20 g of *p*-nitrobenzoyl chloride to a small round bottom flask. If you are making the 3,5-dinitrobenzoate derivative, add 0.20 g of 3,5-dinitrobenzoyl chloride to a small round bottom flask.
4. In the fume hood or under a snorkel, dropwise add 0.10 g of your unknown alcohol to the acid chloride while stirring.
5. Heat the mixture in a 60-70 °C water bath. If your alcohol has boiling point of < 160 °C, heat the mixture for 5 minutes. If your alcohol has boiling point of > 160 °C, heat the mixture for 15 minutes.
6. Stir in 4 mL of 0.2 M sodium carbonate.
7. Heat the mixture to 50-60 °C for 30 seconds.
8. Cool to room temperature and then in an ice bath.
9. Collect the precipitate by small-scale vacuum filtration. Wash with cold water.

10. Recrystallize the precipitate from ethanol or an ethanol-water mixture.

D-2 Phenylurethanes and 1-Naphthylurethanes

For these derivatives, it is extremely important to ensure that your glassware and your alcohol are dry (i.e., free of water). Water can easily react with the isocyanates to form the respective ureas rather than the desired carbamates. (Note: The dipheylurea has a melting point of 241 °C, and the di-1-naphthylurea has a melting point of 297 °C.) If necessary, dry your glassware in an oven before proceeding.



Safety Notes: Isocyanates are irritants and lachrymators. Avoid contact with these reagents and use in a fume hood or under a snorkel.

Procedure:

1. Dry your unknown alcohol with magnesium sulfate or sodium sulfate.

2. Filter to remove the drying agent.

3. If you are making the phenylurethane derivative, add 5 drops of phenyl isocyanate to a small round bottom flask. If you are making the 1-naphthylurethane derivative, add 5 drops of 1-naphthyl isocyanate to small round bottom flask.

4. In the fume hood or under a snorkel, dropwise add 5 drops of the dry alcohol to the isocyanate. If no reaction is apparent, heat the mixture in a 60-70 °C water bath for 15 minutes.

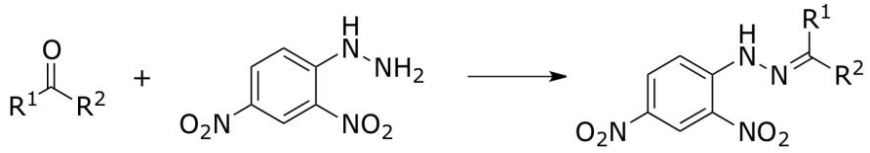
5. Cool to room temperature and then in an ice bath.

6. Collect the precipitate by small-scale vacuum filtration.

7. Recrystallize the precipitate from petroleum ether or heptane. (If necessary, perform a hot gravity filtration.)

Derivatives of Aldehydes and Ketones

D-3 2,4-Dinitrophenylhydrazones

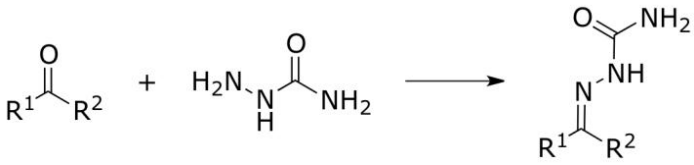


Safety Notes: 2,4-Dinitrophenylhydrazine is toxic and sulfuric acid is corrosive. Avoid contact with these reagents and use in a fume hood or under a snorkel.

Procedure:

1. In a small round bottom flask, dissolve 0.10 g of the unknown aldehyde or ketone in 1 mL of ethanol. (If your unknown is not completely dissolved, add ethanol drop bydrop until it goes into solution).
2. In the fume hood or under a snorkel, dropwise add 3 mL of the 2,4-dinitrophenylhydrazine-sulfuric acid reagent.
3. Allow the solution to stand at room temperature until crystallization is complete. If no crystals form, heat the mixture in a 60-70 °C water bath for 15 minutes, and then it cool again. If there is still no precipitate, add cold water drop by drop to the solution until precipitate is observed.
4. Collect the precipitate by small-scale vacuum filtration. Wash once with 5 mL of cold 5% $NaHCO_3$ and once with cold water.
5. Recrystallize the precipitate from ethanol or an ethanol-water mixture. (Note: If more than 6 mL of ethanol is needed for recrystallization, add ethyl acetate drop by drop to the hot solution until everything is dissolved.)

D-4 Semicarbazones



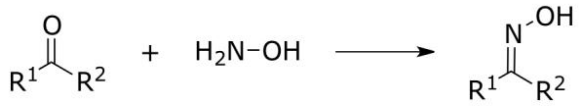
Safety Notes: Semicarbazide hydrochloride is a suspected carcinogen. Avoid contact with the reagent.

Procedure:

1. Mix together 0.20 g of semicarbazide hydrochloride, 0.30 g of sodium acetate, and 2 mL of water in a small round bottom flask.
2. If your unknown aldehyde or ketone is water soluble, add 0.20 g of it directly to the flask and stir to dissolve. If your unknown aldehyde or ketone is not water soluble, add a minimum amount of ethanol to the mixture until your unknown goes into solution.

3. Stir the mixture for two minutes.
4. Cool the mixture in an ice bath. If no crystals form, heat the mixture in a 60-70 °C water bath for 5 minutes, and then it cool again.
5. Collect the precipitate by small-scale vacuum filtration. Wash with cold water.
6. Recrystallize the precipitate from ethanol or an ethanol-water mixture.

D-5 Oximes



Safety Notes: Hydroxylamine hydrochloride is toxic and mutagenic. Avoid contact with the reagent.

Procedure:

1. Mix together 0.125 g of hydroxylaminehydrochloride, 0.30 g of sodium acetate, and 2 mL of water to a small round bottom flask.
2. If your unknown aldehyde or ketone is water soluble, add 0.20 g of it directly to the flask and stir to dissolve. If your unknown aldehyde or ketone is not water soluble, add a minimum amount of ethanol to the mixture until your unknown goes into solution.
3. Stir the mixture for two minutes.
4. Cool the mixture in an ice bath. If no crystals form, heat the mixture in a 60-70 °C water bath for 15 minutes, and then it cool again. If there is still no precipitate, add cold water drop by drop to the solution until precipitate is observed.
5. Collect the precipitate by small-scale vacuum filtration. Wash with cold water.
6. Recrystallize the precipitate from ethanol or an ethanol-water mixture.

Reporting Your Results

Write your report according to the guidelines described in “Topic 4: Writing an Organic Chemistry Lab Report”. Work by yourself on this report.

References & Additional Resources

1. Lehman, J. W. *Operational Organic Chemistry: A Problem----Solving Approach to the Laboratory Course*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 1999; pp 529----572.

Table 1. Possible Alcohol Unknowns

Alcohol	BP (°C)	3,5-Dinitro benzoate MP (°C)	4-Nitro benzoate MP (°C)	1-Naphthyl urethane MP (°C)	Phenyl urethane MP (°C)
methanol	65	108	96	124	47
ethanol	78	93	57	79	52
2-propanol	83	123	110	106	88
2-methyl-2-propanol	83	142	-	-	136
2-propen-1-ol	97	49	28	108	70
1-propanol	97	74	35	105	57
2-butanol	99	76	26	97	65
2-methyl-2-butanol	101	116	85	72	42
2-methyl-1-propanol	108	87	69	104	86
3-pentanol	116	101	17	95	48
1-butanol	118	64	36	71	61
2-pentanol	119	62	24	74	-
3-methyl-3-pentanol	123	94 (62)	69	104	43
3-methyl-1-butanol	132	61	21	68	57
4-methyl-2-pentanol	132	65	26	88	143
1-pentanol	137	46	11	68	46
cyclopentanol	141	115	62	118	132
2-ethyl-1-butanol	148	51	-	60	-
1-hexanol	157	58	5	59	42
cyclohexanol	161	113	50	129	82
furfuryl alcohol	172	80	76	130	45
1-heptanol	177	47	10	62	60
2-octanol	174	32	28	63	114
1-octanol	195	61	12	67	74
1-phenylethanol	202	95	43	106	92
benzyl alcohol	204	113	85	134	77
2-phenylethanol	219	108	62	119	78
1-decanol	231	57	30	73	60
3-phenyl-1-propanol	236	45	47	-	92
1-dodecanol	259	60	45 (42)	80	74

*A dash indicates that no information is reported in the literature

**Melting points in parenthesis represent conflicting literature values

Table 2. Possible Aldehyde Unknowns

Alcohol	BP (°C)	MP (°C)	2,4-Dinitro phenylhydrazone MP (°C)	Semicarbazone MP (°C)	Oxime MP (°C)
ethanal	21		168 (157)	162	47
propanal	48		148 (155)	154	40
propenal	52		165	171	-
2-methylpropanal	64		187 (183)	125 (119)	-
butanal	75		123	106	-
3-methylbutanal	92		123	107	48
pentanal	103		106 (98)	-	52
2-butenal	104		190	199	119
2-ethylbutanal	117		95 (30)	99	-
hexanal	130		104	106	51
heptanal	153		106	109	57
2-furaldehyde	162		212 (230)	202	91
2-ethylhexanal	163		114 (120)	254d	-
octanal	171		106	101	60
benzaldehyde	178		239	222	35
phenylethanal	195	33	121 (110)	153 (156)	99
4-methylbenzaldehyde	204		234	234 (215)	80
3,7-dimethyl-6-octenal	207		77	84 (91)	-
2-chlorobenzaldehyde	209		213 (209)	229 (146)	76 (101)
4-methoxybenzaldehyde	248		253d	210	133
2-methoxybenzaldehyde		38	254	215	92
4-chlorobenzaldehyde		48	265	230	110 (146)
3-nitrobenzaldehyde		58	290	246	120
4-nitrobenzaldehyde		106	320	221 (211)	133 (182)

*A dash indicates that no information is reported in the literature
**Melting points in parenthesis represent conflicting literature values

***If the substance changes color and smokes, this is considered decomposition (d = decomposes)

Table 3. Possible Ketone Unknowns

Ketone	BP (°C)	MP (°C)	2,4-Dinitro phenylhydrazone MP (°C)	Semicarbazone MP (°C)	Oxime MP (°C)
acetone	56		126	187	59
2-butanone	80		118	146	-
3-methyl-2-butanone	94		124	113	-
2-pentanone	101		143	112 (106)	58
3-pentanone	102		156	138	69
3,3-dimethyl-2-butanone	106		125	157	75 (79)
4-methyl-2-pentanone	117		95 (81)	132	58
2,4-dimethyl-3-pentanone	124		95 (88)	160	34
2-hexanone	128		110	125	49
4-methyl-3-penten-2-one	130		205	164 (133)	48
cyclopentanone	131		146	210 (203)	56
4-heptanone	144		75	132	-
2-heptanone	151		89	123	-
cyclohexanone	156		162	166	91
2,6-dimethyl-4-heptanone	168		92	122	210
2-octanone	173		58	124	-
cycloheptanone	181		148	163	23
acetophenone	202		238	198 (203)	60
2-methylacetophenone	214		159	205	61
propiophenone	218	21	191	182 (174)	54
3-methylacetophenone	220		207	203	57
4-methylacetophenone	226	28	258	205	88
2-undecanone	228		63	122	44
4-phenyl-2-butanone	235		127	142	87
3-methoxyacetophenone	240		-	196	-
2-methoxyacetophenone	245		-	183	83 (96)
4-methoxyacetophenone		38	228	198	87
4-phenyl-3-buten-2-one		42	227 (223)	187	117
benzophenone		48	238	167	144
2-acetonaphthone		54	262d	235	145
3-nitroacetophenone		80	228	257	132
9-fluorenone		83	283	234	195

*A dash indicates that no information is reported in the literature

**Melting points in parenthesis represent conflicting literature values

***If the substance changes color and smokes, this is considered decomposition (d = decomposes)

CHEMISREY HONOURS

[Choice Based Credit System]

SEMESTER-III

C5P: LAB (Physical Chemistry)

Experiment 1: Study of viscosity of unknown liquid (glycerol, sugar) with respect to water

Theory:

The viscosity of liquid is a resistance to flow of a liquid. All liquids appear resistance to flow change from liquid to another, the water faster flow than glycerin, subsequently the viscosity of water less than glycerin at same temperature. Viscosity occurs as a result of contact liquid layers with each other. The viscosity is measuring by Ostwald viscometer.
Relative Viscosity is the ratio of the absolute viscosity of the fluid on the viscosity of water at a certain temperature.

The viscosity coefficient is force (dyne) necessary to move the layer of liquid 1 cm^2 in speed 1 cm/sec on another layer of liquid and the distance between them is 1cm.

Equation the Poisellieh:

$\eta = t (\pi r^4 f/8vl)$

For two liquids:

$\eta_1/\eta_2 = f_1t_1/f_2t_2$

Where:

$\pi r^4/8vl$ is constant.

When:

$f = gdh$

$\therefore \eta_1/\eta_2 = t_1d_1/t_2d_2$

η_1 is viscosity of liquid 1.

η_2 is viscosity of liquid 2.

t_1 flow time of liquid 1.

t_2 *flow time of liquid* 2.

d_1 density of liquid 1.

d_2 *density of liquid* 2.

Experiment:

Apparatus required:

Ostwald viscometer, pipette

Reagents:

Ethanol, Glycerin, Di water

Procedure:

1. Clean the viscometer by the water and ethanol and dry it.
2. Put a certain amount of liquid in the large bulge viscometer and pull it by pipette until the small bulge is full.
3. Put viscometer vertically in the water bath at the desired temperature.
4. Let the liquid to flow through the capillary tube with run time when the liquid reaches the mark shown on the viscometer and then stopped time when the liquid reaches the bottom mark.
5. Repeat the experiment and record the results (take average of results).
6. Repeat the experiment to other liquids.
7. Change the temperature and calculate the viscosity.

Calculation:

Calculate the viscosity by the relationships:

$\eta_1/\eta_2=t_1d_1/t_2d_2$

η_1 is viscosity of liquid 1.

η_2 is viscosity of water 0.891 poise.

t_1 flow time of liquid 1.

t_2 flow time of water.

d_1 density of liquid 1.

d_2 density of water 0.997 g/cm3

.

Can be calculate the Relative Viscosity by the relationships:

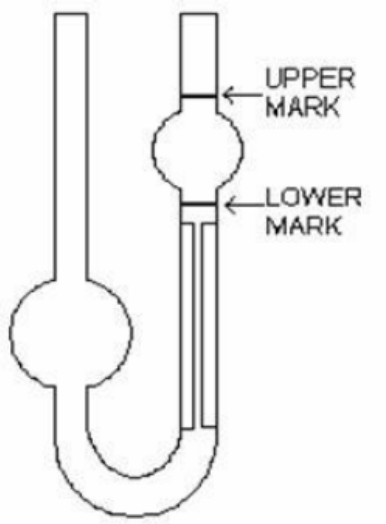
$$\eta_{relative} = \frac{\eta_l}{\eta_{H_2O}}$$

Liquid 1: ethanol (density of ethanol = 0.789 g/cm3)

Temperature(C^O)	Time (Sec.)			Average time	Viscosity (poise)	Relative Viscosity
25						
30						
35						

Liquid 2: glycerin (density of glycerin = 1.261 g/cm3)

Temperature(C^O)	Time (Sec.)			Average time	Viscosity (poise)	Relative Viscosity
25						
30						
35						



Ostwald viscometer

Experiment 2: Determination of partition coefficient for the distribution of I_2 between water and CCl_4

Theory:

When a common solute is added to a system of two immiscible liquids, solute distributes itself in a definite concentration ratio such way that its concentration ratio is constant at constant temperature irrespective of the amount of solute is added.

The Distribution coefficient is given by

$K_D = C_{aq}/C_{org}$

$\log C_{aq} = \log K_D + \log C_{org}$

Where C_{org} & C_{aq} are concentrations of solute in organic & aqueous layers respectively.

Experiment:

Apparatus required:

Reagent bottle, Burette, Pipettes, Conical flasks & measuring jar

Reagents:

Saturated I2/CCl4, M/20 Hypo, M/600 Hypo Starch indicator

Procedure:

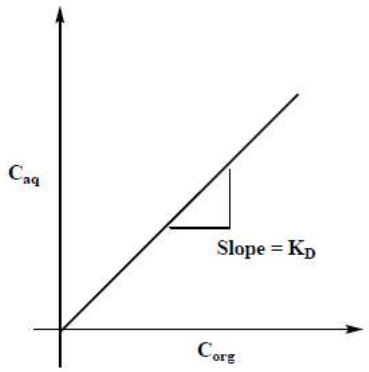
1. Take 25mL of I2/CCl4 and add 25mL of distilled water in a clean reagent bottle. Shake vigorously about 15 minutes for proper distribution.
2. Allow the reagent bottle for the layers to separate. Meanwhile fill the burettes with M/20 Hypo M/600 Hypo.
3. Now pipette out 10mL of organic (lower) & 10mL of aqueous (upper) layers into two conical flasks separately. Titrate organic layer with M/20 Hypo solution and titrate aqueous layer with M/600 Hypo solution by adding 2-3 drops of Starch indicator. Note down the readings as Vorg & Vaq respectively.
4. Now add 10mL of CCl4& 10mL of distilled water to the reagent bottle. Shake vigorously about 10-15 minutes for proper distribution of solute between two layers.
5. Do the titrations as described above. Repeat the same experimental procedure for both the layers (4-6 times) and then calculate concentrations of Iodine as Corg & Caq respectively.

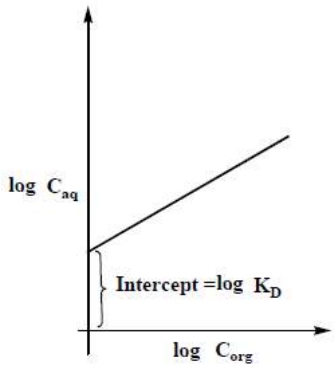
Note: Density of Water = 1.028 gm/ml; Density of CCl4 = 1.59 gm/m

Calculation:

S.No	V_{org}	V_{aq}	C_{org}	C_{aq}	log C_{aq}	log C_{org}	$K_D = C_{aq}/C_{org}$
1							
2							
3							
4							
5							

Model graph: Plot a graph between C_{aq} and C_{org}, straight line passing through origin is obtained. From the slope distribution constant (K_D) can be calculated.





K_D (From calculations) = ……

K_D value from Graph -1 = ……

K_D value from Graph - 2 = ……..

Experiment 3: Determination of Keq for KI + I_2 = KI_3, using partition coefficient between water and CCl_4

Theory:

I_2 distributes itself between CCl4 and aq KI. The solubility of I2 is due to formation of KI3 complex, the solubility of I2 increases with increase in concentration of KI. The partition study experiment can be used to get the equilibrium constant.

$$KI + I_2 \underset{}{\overset{K}{\rightleftharpoons}} KI_3$$

According to law of mass action equilibrium constant,

$$K = \frac{[KI_3]}{[KI]\,[I_2]}$$

Where, [KI_3], [KI] and [I_2] represent the equilibrium concentrations. From previous experiment, we have,

$$K_D = \frac{C_{aq}}{C_{org}}$$

Where Corg and Caq are concentrations of I2 in organic and aqueous layers respectively

Caq = Corg/ K_D, Total concentration of I_2 in aqueous layer represented as C_1 Since KI combines with equivalent amount of I_2 to form KI_3 complex Concentration of free I_2 in aqueous layer = C2

Concentration of KI_3 = C_1- C_2 (Combined concentration of I_2)

Initial concentration of KI = C_3

By knowing the values of [KI_3], [KI] and [I_2] equilibrium constant can be evaluated as follows:

$$K = \frac{(C_1-C_2)}{C_3 * C_1}$$

Experiment:

Apparatus required:

Five Reagent bottles, Burette, Pipettes, Conical flasks & measuring jar

Chemicals:

Saturated I2/CCl_4, aq KI (0.25M), M/20 Hypo, Starch indicator

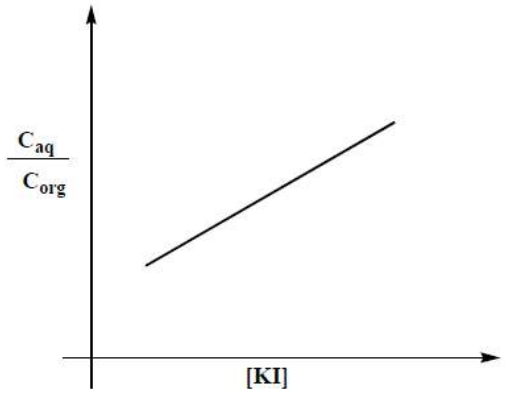
Procedure:

1. Take five reagent bottles and prepare following solution mixtures.

S. No	I2 in CCl_4 (mL)	Aq KI (mL)	H_2O (mL)
1	25	25	0
2	25	20	5
3	25	15	10
4	25	10	15
5	25	5	20

2. Now stopper the bottles and shake each bottle for 15 min. Then keep aside.Allow the reagent bottle for the layers to separate. Meanwhile fill the burette with M/20 Hypo.
3. Now pipette out 10mlof Organic (lower) & Aqueous (upper) layers into two conical flasks separately.
4. Titrate both the layers against M/20 Hypo solution by adding 2-3 drops of Starch indicator. Note down the readings as Vorg & Vaq respectively. Same experimental procedure is repeated for other reagent bottles.

Model graph: Plot a graph between Caq/ Corg and concentration of KI, straight line with positive slope is obtained.



Model tabular form:

Reagent bottle	V_{org}	V_{aq}	C_{org}	C_{aq}	C_{aq}/C_{org}	[KI]
1						0.25
2						0.20
3						0.15
4						0.10
5						0.05
Unknown						

Result: Concentration of given KI (Unknown) solution =.....

Experiment 4: Conductometric titration of an acid (strong, weak/ monobasic, dibasic) against base strong

4.1: Titration between a strong acid and strong base:Titration between HCl and NaOH

Theory:

The reaction between HCl and NaOH can be represented as:

$$HCl + NaOH \rightarrow NaCl + H2O$$

HCl undergoes reaction with sodium hydroxide resulting in the formation of sodium chloride and unionized water. At the beginning of the titration the acid solution has a high conductivity due to highly mobile hydrogen ions. When NaOH is added to HCl solution the highly mobile H+ ions are replaced by less mobile sodium ions. This will result in the decrease of conductivity rapidly. At the end point the solution will contain only sodium and chloride ions. Hence there will be minimum conductivity. After the end point the conductivity rises due to the presence of fast moving OH– ions. Thus the graph which is plotted between the conductance and the volume

of sodium hydroxide added include two straight lines. The point of intersection of these two sharp lines gives the end point of the titration.

Experiment:

Apparatus required:

Conductivity bridge, conductivity cell, 100 ml beaker, pipette, stand, etc.

Chemicals:

HCl solution (≈ 0.1M), 0.5 M NaOH solutions.

Procedure:

1. Pipette out 40 ml of the given HCl solution into a clean 100 ml beaker and dip the conductivity cell in it.
2. Connect the conductivity cell to a conductivity bridge and measure the initial conductance of the given HCl solution.
3. Fill the burette with the given sodium hydroxide solution. Then add 0.5 ml of the given NaOH solution to the HCl solution present in the beaker and stir the contents well.
4. Measure the conductance of the solution. Continue the addition of the sodium hydroxide solution in equal volumes (0.5 ml) until you get a minimum of 25-30 conductance readings.
5. The end point of the titration can be detected by plotting a graph in between the measured conductance and the volume of sodium hydroxide that is added during the titration.

Result: The concentration of the given acetic acid solution is _____M.

Observations:

S. NO.	Volume of NaOH added (ml)	Conductance (mS)

Calculation: HCl vs NaOH

$M_1V_1 = M_2V_2$

M_1 = Molarity of the given HCl solution

V_1 = Volume of the HCl taken in the beaker

= 40 ml

M_2 = Molarity of the given NaOH solution

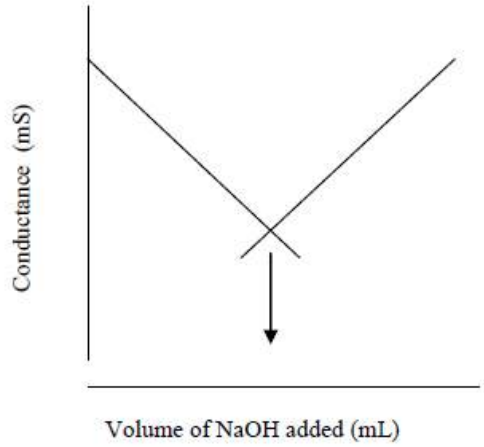
= 0.5M

V_2 = Volume of the NaOH required to neutralize the given acid

= end point volume

$M_1 = M_2V_2 / V_1$

M1 = 0.5 × E.P.V / 40



4.2: Titration between a weak acid and strong base:Titration between

CH_3COOH and NaOH

Theory: The reaction between acetic acid and sodium hydroxide can be represented as:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

At the beginning of the titration the conductance of the solution is found to be less because of poor dissociation of the acetic acid, which is a weak acid. Thus the number of ions produced by the dissociation of the acid is found to be less. When small amount of NaOH is added to the acetic acid solution the conductance increases due to the formation of sodium acetate which is a strong electrolyte than the acetic acid, hence dissociates rapidly producing more number of ions than acetic acid. At the end point of the titration both the sodium and acetate ions are present in the solution. The conductance of the solution increases when further sodium hydroxide is added to the solution at the end point. This increase is due to the presence of fast moving OH– ions.

Experiment:

Apparatus required:

Conductivity Bridge, conductivity cell, 100 ml beaker, pipette, stand, etc.

Chemicals:

CH3COOH solution (≈ 0.1M), 0. 5M NaOH solution.

Procedure:

1. Pipette out 40 ml of the given CH_3COOH solution into a clean 100 ml beaker and dip the conductivity cell in it.
2. Connect the conductivity cell to a conductivity bridge and measure the initial conductance of the given CH_3COOH solution.
3. Fill the burette with the given sodium hydroxide solution. Then add 0.5 ml of the given NaOH solution to the CH_3COOH solution present in the beaker and stir the contents well.
4. Measure the conductance of the solution. Continue the addition of the sodium hydroxide solution in equal volumes (0.5 ml) until you get a minimum of 25-30 conductance readings.
5. The end point of the titration can be detected by plotting a graph in between the measured conductance and the volume of sodium hydroxide that is added during the titration.

Result: The concentration of the given acetic acid solution is _____M.

Observations:

S. NO.	Volume of NaOH added (ml)	Conductance (mS)

Calculation: CH_3COOH vs NaOH

$M1V1 = M2V2$

M1 = Molarity of the given CH_3COOH solution

V1 = Volume of the CH_3COOH taken in the beaker

= 40 ml

M2 = Molarity of the given NaOH solution

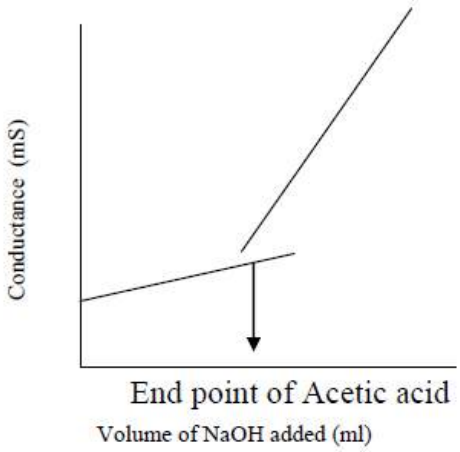
= 0.5M

V2 = Volume of the NaOH required to neutralize the given acid

= end point volume

$M1 = M2V2/ V1$

$M1 = 0.5 \times E.P.V / 40$



Experiment 5: Verification of Ostwald's dilution law and determination of K_a of weak acid

Theory:

The equivalent conductance of any electrolytes is defined as the conducting power of all the ions produced by 1 gm equivalent of the electrolyte. The equivalent conductance of the solution depends upon the number and rate of migration of anions and cations. The experiment indicates that equivalent conductance increases with dilution. This would arise either from an increase in the number of individual ions (or) from the speed of ions. The ionic mobilities are independent of concentration so that λ is proportional to the number of ions present at different concentrations. Arrhenius theory is applicable only for weak electrolytes. For such solutions conductivity measurements are used to obtain the degree of dissociation and hence the dissociation constant.

Thus for acid of different normality the specific conductance and hence the value of dissociation constant at different concentrations are calculated λc is plotted vs $\sqrt{c}$. According to Ostwald's dilution law $\alpha^2 c/(1-\alpha) = ka$, where ka is dissociation constant, α is the degree of dissociation and c is the concentration.

Experiment:

Apparatus required:

Conductivity sensor, Beaker, 100 ml, volumetric flasks, 100 ml, Bulb pipette, 10 ml, Bulb pipette, 25 ml

Chemicals:

Acetic acid, Distilled water

Procedure:

1. Acetic acid of the following normalities 0.1N, 0.08N, 0.06N, 0.04N, 0.02N and 0.01N are pipetted out in a dry conductivity cell one by one.
2. The conductivity cell is immersed in the solution. The respective value for the conductance is obtained.
3. The specific conductance and equivalent conductance of each of these solutions are calculated from these values of λc and λ∞ can be calculated.

A = λc / λ∞ and a plot of λc vs $\sqrt{c}$ are noted.

Result:

Dissociation constant of Acetic acid is ---------- mol dm-3

S. No.	Concentration of CH_3COOH (N)	Conductance (m.mho)	λc(mho.m^2)	$\sqrt{C}$	$k_a = \frac{\alpha^2 C}{1-\alpha} x10^3$

Average =