LABORATORY MANUAL

CHEM F110 CHEMISTRY LABORATORY

DEPARTMENT OF CHEMISTRY

PILANI CAMPUS

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI

Semester – I, 2019-20

PREFACE

This manual is designed primarily to serve as an instructional book for students, technical staff and instructors to assist in performing and understanding the experiments in Chemistry. It is important that students do experiments in the laboratory to understand the theories that they have studied in lecture and in their textbook. An attempt has been made to identify concepts that are of particular interest or challenge to students and can be better understood through laboratory work. This will help the students to learn about chemistry, using laboratory equipment and data interpretation and presentation. The manual contains ten experiments. Questions are presented at the end of each experiment, and the students should answer each question as it will help in understanding the experiment.

In conclusion, we view this manual as one of continual modification and improvement. We encourage discussing ideas for improvements and suggestions for new experiments. For any new specific experiment HOD or instructor may be contacted. This manual is the culmination of the efforts of the faculty members of Department of Chemistry, BITS Pilani, Pilani Campus.

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GENERAL CHEMISTRY LABORATORY SAFETY

The chemistry laboratory is a place of discovery and learning. However, due to the nature of laboratory work, it can be a place of danger if proper common sense precautions are not taken. Do consult/inform your instructor when you have any doubts regarding safety.

Attire:

1. Always use protective eye wear (safety goggles). Contact lenses should not be worn.

2. COVERED SHOES and APRON must be worn in the Lab. Avoid very loose fitting clothes. Long hair must be tied.

Handling of Chemicals and Equipment:

1. Consider all chemicals to be hazardous. Know what chemicals you are using.

2. Avoid contact of chemicals with your skin or eyes. If such contact does occur, flush immediately with copious amounts of water, and inform the instructor.

3. Do not use flammable reagents near open flames.

4. Be careful while pipetting. Use a pipette bulb, or a burette for corrosive, toxic, or hazardous chemicals. Get advice from instructor.

5. Never point a test tube you are heating towards yourself or a neighbor, or vertically upwards.

6. Always pour acids into water, and not the other way around. Excess reagents should not be returned to stock bottles. Dispose off excess reagents properly.

7. Never taste or directly smell chemicals. To detect odor, by means of your cupped hand, waft a small sample of vapour towards your nose.

8. Dispose off chemical waste properly as directed by the instructor.

9. Follow directions carefully while using instruments.

10. Do not leave burners unattended. Turn them off when you leave. If the burner goes off, turn off the supply valve immediately. Open again only while relighting the burner. Never use paper torches for lighting burner.

11.   Beware, hot glass looks just the same as cold glass.

Conduct:

1. Read the experiment carefully before coming to the lab class.

2. Eating and drinking are strictly prohibited in the laboratory.

3. No unauthorized experiments are to be performed.

4. Keep your work area clean. Put paper trash and broken glass, if any, in the dustbins. Clean your work area before you leave.

5. Avoid spills. If you do spill something, clean up the area immediately taking adequate precautions. Inform the instructor.

6. Keep the area around instruments clean and free of used paper.

7. Always wash your hands thoroughly before you leave the laboratory

EXPERIMENT – 1

DETERMINATION OF THE pH CURVE OF ACID BASE TITRATION

Objective:

To carry out the titration of given acid solution using a base, obtain the pH curve and determine the concentration as well as the dissociation constant of the acid.

Principle:

(A) Acid- base titration:

Titration is one of the universal techniques, used to determine the concentration of a substance in solution (the analyte). Suppose, there is a solution of an acid in which the amount of acid is to be determined. This may be done by an acid–base titration, in which a sample of this solution, the analyte, is taken in a flask, and a solution of a base of known concentration (the titrant), is added in a controlled manner from burette. The stoichiometric equivalence point, at which an equivalent number of moles of base (OH^-) have been added to the number of moles of acid (H_3O^+) initially taken, may be determined by monitoring the pH ($- \log_{10}[H_3O^+]$) of the solution as the titration progresses. The pH curve for a titration in which a strong base is added to a strong acid is shown in figure 1(A). The pH, which is initially low, increases slightly as a titrant is added. However, in the immediate vicinity of the stoichiometric point, which occurs at pH 7.0, it increases sharply, and then levels off again as excess base is added.
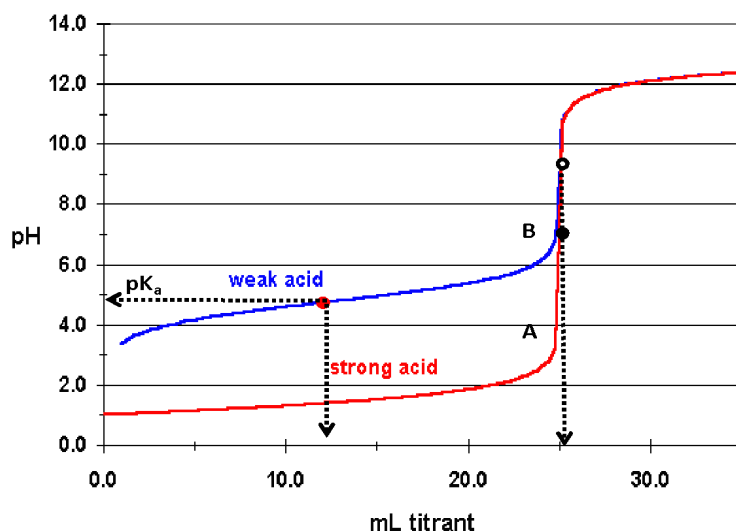
Fig1: pH curve for the titration of (A) strong acid using strong base. Note that pH is 7.00 at the stoichiometric equivalence point, (B) weak acid using strong base, pH > 7 at end point, at halfway point, pH = pK$_a$

The pH curve for the titration of a solution of weak acid HA, of dissociation constant K_a, using a strong base is shown in figure 1(B). Comparing figures 1A and 1B some points of distinction may be noted: (i) The pH at the stoichiometric point is greater than 7.00 for the latter case (weak acid vs strong base), (ii) For the same starting concentration, the change in pH near equivalence is not as sharp as in the earlier case.

Furthermore, from the definition of the dissociation constant

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{1}$$

And the resulting Henderson – Hasselbalch equation,

$$pH = pK_a + log_{10}\frac{[A^-]}{[HA]} \tag{2}$$

It follows that at the half equivalence point of the titration where $[A^-] = [HA]$, $pK_a = pH$, which yields the dissociation constant of the acid. Note further that in the vicinity of the half equivalenc point, the pH curve is very flat, indicative of buffer action. Hence, to understand the half equivalence point appropriately, first derivative of pH and volume ($\Delta pH/\Delta V$) versus volume of base added (V, in mL) needs to be plotted. The stoichiometric equivalence point will be the maximum as shown in figure 2. With the known sharp equivalence, the exact half equivalence point can be found out.
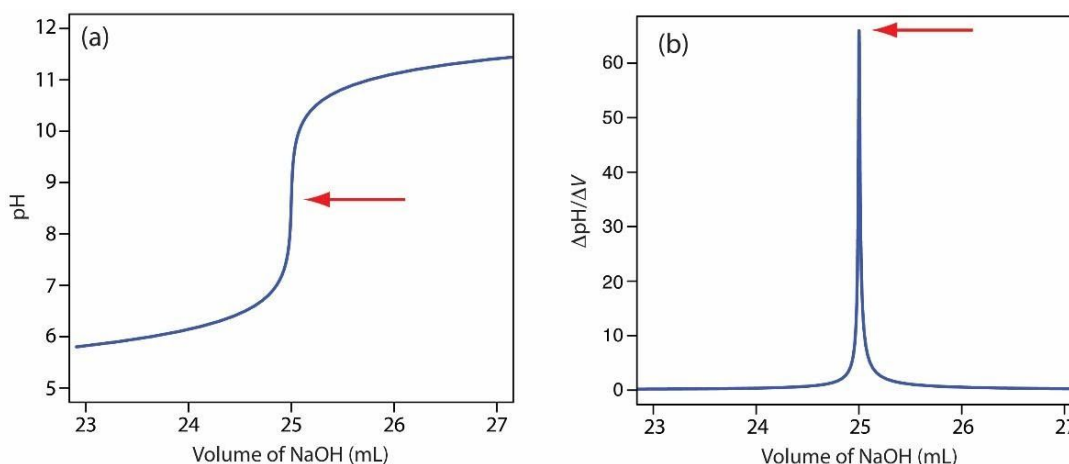

Figure 2: (a) Normal titration curve (b) First derivative plot of an acid-base titration

**(B) Measurement of pH using glass electrode**

The pH is most conveniently and accurately measured using a glass electrode. The electrode consists of a reversible internal reference with usually a Ag/AgCl electrode surrounded by a solution of constant pH and constant [Cl⁻] say 0.10 M HCl solution. This solution is contained in a bulb made of

very thin, soft glass membrane, situated at the end of hard glass tube or epoxy body. The physical mechanism of action of the glass electrode is attributed to the exchange of metal ions coordinated to oxygen atoms in the silicate framework of the glass membrane with H^+ ions in the immersed. The potential of this glass electrode varies with the pH of the solution in which it is immersed and is given by:

$$E = E^0 + 2.303 \, RT \, (pH) \qquad (3)$$

Where the pH refers to the pH of the solution of interest, R is the universal gas constant, T is absolute temperature and E^0 includes the standard electrode potential and various constant junction potentials present in the system. At 298 K, this becomes $E = (E^o + 0.059 \, pH)$ Volts, so that there is a 59 mV change in the potential for a change of 1 pH unit. The potential of the glass electrode is measured relative to the steady potential of an external reference electrode such as the calomel electrode. This external reference electrode is often built around the glass electrode thus yielding a so called combination electrode. The glass electrode and the external reference electrode together forms a cell of the following type:

Ag / AgCl /Cl⁻, H⁺/ glass membrane/test solution/calomel electrode   (reference)
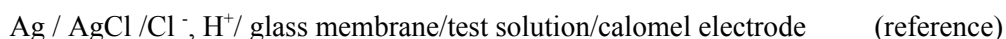
The voltage of the cell is measured using a pH meter, which is basically an electronic voltmeter with a very high internal resistance, so that it measures the voltage, drawing only a negligibly small current. As seen from the expression above (Eq. 3), the potential is dependent on the temperature. Most pH meters have an inbuilt provision to take into account this dependence, and so the temperature must be set correctly on the dial provided before the meter is calibrated and used for measurement. Calibration of the meter is done by using a buffer of accurately known pH.
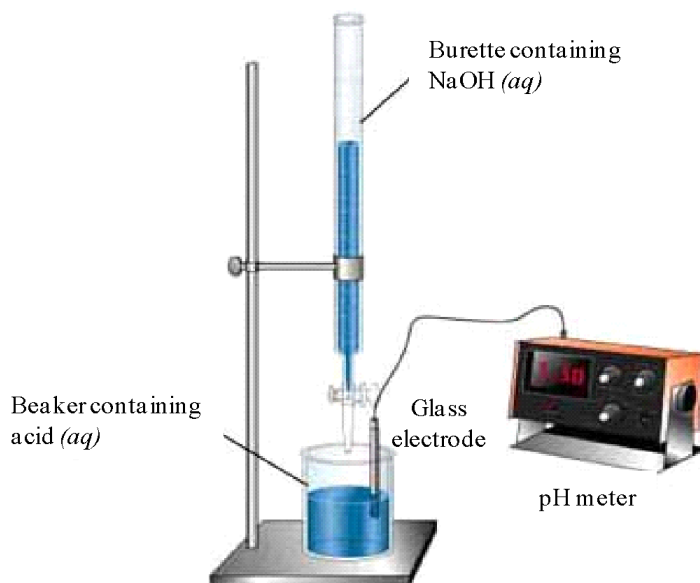
Setup for pH measurement during an acid-base titration

Experimental procedure:

In the experiment, given solutions of a weak monoprotic acid (say acetic acid) is to be titrated against a standardized NaOH solution (a secondary standard). The pH curve will be obtained, and the strength of the weak acid and its dissociation constant will be calculated.

(A) Standardization of NaOH solution:

The strength of the NaOH solution given is to be determined accurately as it is a secondary standard (meaning its strength changes with time and surrounding conditions). This can be done by titrating it against a primary standard (its strength is stable) solution of oxalic acid using an acid-base indicator such as phenolphthalein. Recall that an acid – base indicator is itself a dye with differently coloured acidic and basic forms, and so will undergo a sharp change in colour near the stoichiometric point of the titration, if properly chosen.

Take 10 mL of 0.25N solution of oxalic acid into a conical flask, add one drop of phenolphthalein indicator solution, and titrate using the given NaOH solution till a permanent but light pink (persistent for at least 30 s) colour is observed. Repeat to obtain at least two concordant readings. Record your observations carefully, and determine the strength of the provided NaOH solution.

(B) Titration of the weak acid (acetic acid) using the standardized NaOH solution

(i) Calibrate the pH meter using an acidic buffer of known pH (say 4.00) following the instructions given for the operation of the pH meter.

(ii) Accurately pipette out 25 mL of the weak acid solution into a clean 100 ml beaker and add a drop of phenolphthalein indicator. Immerse the glass electrode, making sure the bulb is completely immersed within the solution. If it is not, adding a little distilled water will not harm. Stir the solution very carefully and read the pH. Now add NaOH solution from the burette in small increments. First add in 1 mL steps and as endpoint approaches (indicated by the transient pink coloration appearnig before vanishing on stirring), deliver in steps of 0.1 mL till you observe a sharp rise in the pH suddenly. Continue additions in 1 mL steps for another 10-12 data points and record all the data till the pH appears to be getting to a constant value. Note the volume of NaOH added and the pH of the solution after each addition. The titration may be stopped when the pH curve levels off beyond the stoichiometric point.

(iii) Take the different of pH values for consecutive readings on addition of NaOH solution as required to obtain the derivative plot

(iv) Create TWO plots, one pH vs. volume of NaOH added and another for the derivative and determine the stoichiometric equivalence point as accurately as possible

(v) From the second plot, find out the exact volume needed for stoichiometric point.

(vi) From the first plot, find out the pH at half of the volume needed for stoichiometric point, this represents the pK_a of the weak acid in question. You may determine the dissociation constant K_a for the same from the pK_a value.

Notes:

Questions:

1. What factors govern the choice of a suitable indicator for an acid –base titration?

2. What can you say about the pH at the equivalence point of a weak base with a strong acid?

3. Calculate the pH at the equivalence point in the titration of 0.01 M NH_3 ($K_b = 1.8$ x 10^5) using 0.10 M HCl

(i) Schematically represent the pH curve you expect for the titration of A weak diprotic acid versus a strong base, say NaOH

4.   As suggested in the text above, convince yourself that given all relevant information such as the concentrations of the acid and base, and dissociation constants, you will be able to calculate the pH curve for a titration. Write equation for pH at different stages of titration

5.   How does an acid-base indicator work? Can there be an universal indicator for all pH range?

EXPERIMENT – 2

DETERMINATION OF TOTAL HARDNESS OF WATER WITH EDTA

Objective:

The purpose of this experiment is to determine the hardness of water by measuring the concentration of calcium in water samples by complexometric titration. The experiment also serves as an example of a method where complex ion formation can be used to do quantitative analysis of a cation.

Principle:

The total concentration of alkaline earth metal ions, such as calcium and magnesium, in water determine the hardness of water. The term hard water implies that these metal ions precipitate soap molecules from water making it "hard" to get things clean. Water hardness is usually determined by measuring the total amount of calcium and magnesium present, since the concentrations of these ions far exceed those of other alkaline earth metals. The accepted practice for reporting hardness is as amount of $CaCO_3$ in mg/L or ppm, as if all of the hardness is from calcium carbonate. An excellent way to determine water hardness is to perform a complexometric titration using a standard ethylenediaminetetraacetic acid (EDTA) solution. EDTA being a secondary standard needs to be standardized against a primary standard solution of Ca^{2+} ion of known strength. Quantitative analysis of an unknown water sample can thus be obtained.

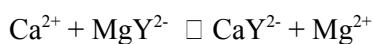In its ionized form, EDTA $(HOOC-CH_2)_2N-CH_2-CH_2-N(CH_2COOH)_2$ is able to form soluble complexes with cations such as calcium and magnesium by strong chelation. But the efficiency of binding will depend on the pH of the medium. The indicator used for this kind of complexometric methodology is Eriochrome Black T (EBT). Initially, when added to the analyte solution, the indicator will form wine red coloured complex with the cations present in the analyte (such as Ca[EBT] etc.). As the EDTA is added dropwise to the sample from the burette, it replaces the EBT indicator and forms more stable complexes with the ions (calcium and magnesium) in the analyte. As the titration proceeds, the added EDTA removes

Ca^{2+} from Ca(EBT), and when all the calcium has been chelated to EDTA at the end point, only the free EBT is present which thus shows its own uncomplexed blue colour. The colour change is progressive, with red giving way to bright blue via a purple intermediate hue. (so, the end point may not be too obvious in an initial run and needs repeating the experiment to obtain a clear endpoint). Sometimes, a small amount of Mg^{2+} ion is added to the standard EDTA solution to make this change sharper (since calcium does not form a strong chelate with the indicator to give a sharp end point). The aplication of metal complexe formation and its equilibria is used in this type of titration – hence the name complexometry.

EDTA is a powerful complexing agent for nearly all metal ions forming exclusively 1:1 complexes. Discrimination between different metal ions is achieved by careful control of the pH of the solution. Ca^{2+} and Mg^{2+} are bound in a tight complex only in strongly basic solution, optimally at pH 10. It is necessary to use an appropriate buffer solution to ensure the proper pH of the sample during the EDTA titration.

Reactions during titration

$$Ca^{2+} + H_2Y^{2-} \ \square \ CaY^{2-} + 2H^+$$
$$Ca^{2+} + MgY^{2-} \ \square \ CaY^{2-} + Mg^{2+}$$

Reaction at end point

$$Mg^{2+} + HIn^{2-} \quad \square \quad MgIn^- + H^+$$
$$MgIn^- + H_2Y_2 \quad \square \quad MgY^{2-} \quad + \quad HIn^{2-} + H^+$$
$$\text{(red)} \quad \text{(colourless)} \quad \text{(colourless)} \quad \text{(Blue)}$$

Here Y^{2-} is the anion of EDTA at pH = 10.

Experimental Procedure:

(A) Standardization of the given EDTA Solution (secondary standard)

Standardization of EDTA is done using a 100 mL primary standard solution of calcium containing 100.0 mg $CaCO_3$ solid.

1. Weigh around 100 mg of solid $CaCO_3$ and place it inside a 100 mL volumetric flask. Dissolve the solid COMPLETELY using some dilute HCl solution. Make up the volume till the mark. Calculate the exact strength IN MOLARITY based on the exact weight of $CaCO_3$ taken (MW_{CaCO3} =100 g/mol).

2. Pippet out exactly 25.0 mL of this $CaCO_3$ solution into a 250 mL flask and add 2.5 mL (use measuring cylinder only) of the buffer solution to maintain the pH to 10 (may check with pH paper).

3. Add TWO (2) drops of Eriochrome Black T solution (the indicator), the colour of the solution changes to wine red immediately.

4. Titrate this using the provided EDTA solution; at the end point the colour changes from wine red to bright blue.

5. Repeat this titration at least three times to ensure good reproducibility. Calculate the strength of the EDTA solution by using the data obtained and $V_1S_1 = V_2S_2$.

(B) Determination of hardness of water sample

Take 50 ml of tap water sample in a clean conical flask and perform the titration with EDTA solution three times in the same way as above for the standardization of EDTA. Take the concordant burette readings to calculate the amount of $CaCO_3$ present in this 50 mL water sample as follows [considering x mL of y(M) EDTA required to titrate 50 mL water sample],

1000 mL 1(M) EDTA ≡ 100 g of $CaCO_3$ (molar equivalence)

Hence, **x** mL of **y**(M) EDTA ≡ $(0.1 \times \mathbf{x} \times \mathbf{y})$ g of $CaCO_3$

Now, this $(0.1 \times \mathbf{x} \times \mathbf{y})$ g of $CaCO_3$ was present in 50 g water sample (considering the density of water, $\rho_{water} = 1$ g/mL)

Therefore, hardness in ppm can be obtained as $= \frac{0.1 \times x \times y}{50} \times 10^6$

Notes:

Questions:

1. Why it is important to estimate the hardness of the potable water?

2. What is the primary standard used?

3. What kind of reaction takes place between the magnesium and the EDTA?

4. At what pH condition is the titration performed? Why?

5. What indicator is used in the analysis? What is its colour change?

EXPERIMENT - 3

IDENTIFICATION OF SOME ORGANIC COMPOUNDS

Objective:

Illustrate organic qualitative analysis using some carboxylic acids, carbohydrates, and carbonyl compounds

Experimental Procedure:

(A) For compounds containing – COOH functional group

(a) Tartaric Acid

(i)   Dissolve a small quantity of the compound in distilled water (e.g. approx 5 mg of sample in 2 ml of water). Add to this $NaHCO_3$ solution; immediate effervescence indicates the presence of the acidic group in the compound.

Preparation of neutral solution of the given compound having–COOH group in it.

Dissolve a small quantity of the sample in distilled water. If not soluble, heat it. Add NH_3 solution in the solution of the compound drop by drop till you are able to get the smell of NH_3; add 3-5 ml of distilled water. Heat the solution in porcelain basin until vapours do not smell of NH_3. Prevent it from drying by adding more water, cool, and use this solution.

(ii)   Take a small amount of the neutral dilute solution (prepared above) and add a few drops of Tollen's reagent (Ammoniacal $AgNO_3$ solution) to it and warm it on a water bath. Appearance of silver mirror at the bottom of the test tube confirms tartaric acid. Ag_2O is formed from the mixture of aq. $AgNO_3$ and NaOH solution which is dissolved in NH_4OH solution.

$$Ag_2O + 4\ NH_4OH \rightarrow 2\ [Ag\ (NH_3)_2]OH + 3\ H_2O$$
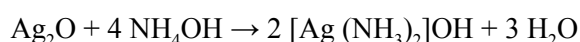
$[Ag\ (NH_3)_2]^+$ is then reduced to metallic Ag by tartaric acid.

(b) Succinic Acid

In a dry test tube, take small amount (5 mg) of the compound and 2 times of this amount of resorcinol. Add 2 drops of conc. H_2SO_4 [CAREFUL: CONC ACIDS SHOULD BE HANDLED CAUTIOUSLY] carefully along the test tube walls. Heat gently till the mixture becomes dark reddish brown. Cool it and add enough NaOH solution to make it alkaline. Transfer a few drops of this solution in a beaker and dilute it with ample amount of tap water. Appearance of yellowish green fluorescence confirms succinic acid.
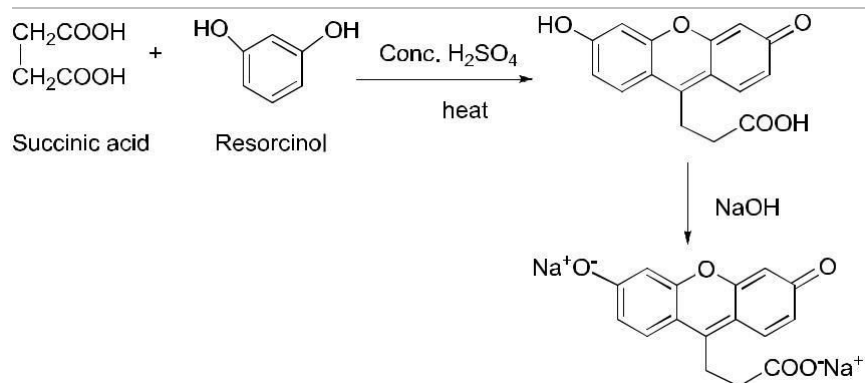
(B) For Carbohydrates

Molisch's reaction: Prepare the solution of the compound in water. Take a portion of this solution in a test tube and add 2 drops of 10% alcoholic solution of α-naphthol. Pour carefully, along the sides of the test tube, about 10-12 drops of conc. H_2SO_4 [CAUTION !!] such that it forms a separate layer at the bottom. A red ring changing to violet at the junction of two layers indicates carbohydrate.

i)   Perform the above test for Glucose or Fructose

Fehling's Solution: It is a mixture of two solutions: Solution 1 and Solution 2.

Solution 1: $CuSO_4$ crystals in water containing a few drops of dil. H_2SO_4 (to remove any hydroxide present). Solution 2: Prepared by dissolving sodium hydroxide and sodium potassium tartarate in water. The mixture of solutions 1 & 2 is called Fehling's solution and it is of blue color. Both glucose and fructose are reducible sugars. They reduce Fehling's solution to red Cu(I) oxide.

ii)   Perform the above test for Sucrose or Starch

Sucrose is a disaccharide which on hydrolysis produces glucose and fructose. Starch is a polysaccharide.

Distinction between Glucose and Fructose

Take few drops of a concentrated solution of the compound in a test tube and add 3 to 4 drops of conc. HCl [CAUTION !!] and a small amount of resorcinol. Stand the test tube in boiling water for 5 min. Deep red color, usually followed by a ppt., confirms fructose. In case of Glucose color appears after sometime and is light pink.

Distinction between Sucrose and Starch

To few drops of an aq soln of the original solid, add few drops of dil. I_2 solution and observe as follows:

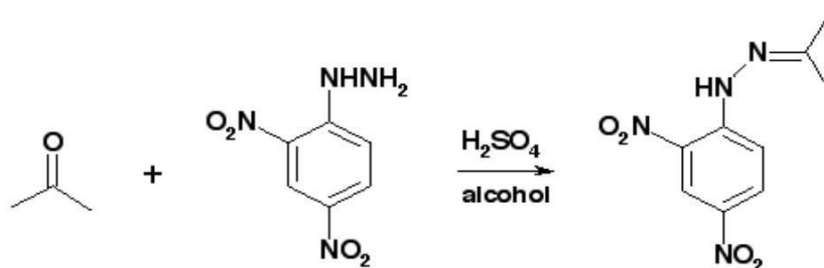Blue colour   -   Starch

No Blue colour   -   Sucrose

Starch forms a blue coloured complex with I_2, which is not formed by sucrose.

(C) For Aldehydes and Ketones:

2,4-DNP Test: Add a solution of (1 or 2 drops) the unknown compound to 3 mL of 2,4-dinitrophenylhydrazine (2,4-DNP) reagent. Shake vigorously. Formation of orange colored precipitate indicates carbonyl compound.

Notes:

Questions:

1. Write the structures of all the acids you have analyzed.

2. How do the structures of glucose and fructose differ?

3. You have performed Tollen's Reagent test for tartaric acid. If glucose is used instead of tartaric acid in the test, what will be the result?

4. What is the name of the functional group in the product of the DNP test?

5. Can the DNP test be given by allylic alcohols? If yes, why; if no why not?

6. Write the chemical structure of tartaric acid.

EXPERIMENT – 4

ESTIMATION OF COPPER BY IODOMETRY

Objective:

To estimate the amount of Cu in the given $CuSO_4$ solution by iodometric titration.

Principle:

In neutral or faintly acidic solutions, cupric salts react with iodide ion to liberate iodine. The reaction goes in two steps as follows :

$$2CuSO_4 + 4KI \rightleftharpoons 2CuI_2 + 2K_2SO_4 \qquad (1)$$

$$2CuI_2 \rightleftharpoons Cu_2I_2 + I_2 \qquad (2)$$
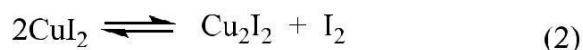
giving the overall reaction as

$$2Cu^{++} + 4I^- \rightleftharpoons Cu_2I_2 + I_2 \qquad (3)$$

The equilibrium of the redox reaction (3) is shifted towards right by continuous removal of Cu_2I_2 as insoluble complex.

The liberated I_2 is titrated against the sodium thiosulphate ($Na_2S_2O_3.5H_2O$, hypo) solution using starch as indicator as follows:

$$\underset{\text{(blue)}}{I_2} + 2S_2O_3^{2-} \longrightarrow \underset{\text{(colorless)}}{S_4O_6^{2-} + 2I^-} \qquad (4)$$
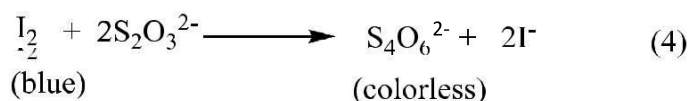
Two possible sources of error can influence the outcome of the iodometric titration. One is the aerial oxidation of acidic iodide solution i.e. iodide in acid medium is slowly oxidized by oxygen in air.

$$4I^- + 4H^+ + O_2 \rightleftharpoons 2I_2 + 2H_2O \qquad (5)$$

Furthermore, this reaction is accelerated by the presence of Cu^+ ions. [The cuprous ions formed in equation (3) catalyze the reaction and the cycle itself repeats indefinitely]. This error can be reduced by not allowing the solution to stand for a long time before titration. However, the most effective way

of retarding reaction (5) is to remove oxygen in the reaction vessel by carbon dioxide. This is done by adding sufficient Na_2CO_3 (or $NaHCO_3$) in the reaction vessel. The other source of error is the volatility of I_2 formed in equation (3). Practically, this problem is eliminated by using excess iodide solution which captures liberated iodine to form tri-iodide ions

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (6)$$

Experimental Procedure:

Because of its efflorescent nature, sodium thiosulphate is not suitable as a primary standard. So, to determine the strength of the given $CuSO_4$ solution, one has to follow a double titration method. The first one involves the standardization of thiosulphate solution with a standard $CuSO_4$ solution and then in the second step, the standardized thiosulphate is used to titrate the $CuSO_4$ solution of unknown strength.

(A) Preparation of standard (N/40) $CuSO_4. 5H_2O$ solution:

Accurately weigh between 0.5 to 0.7 g of copper sulfate on a watch glass. Transfer this weighed copper sulfate into a clean 100 mL standard flask carefully, by means of a funnel. If any copper sulfate crystals stick to the watch glass or funnel or the neck of the standard flask, then transfer them into the standard flask with minimum amount of distilled water. Remove the funnel and successively shake and dissolve the copper sulfate completely by adding small amount of water. See that the copper sulfate solution level in the standard flask is not more than $1/3^{rd}$. Add half a test tube of Na_2CO_3 solution into the flask. A bluish white ppt is formed. Add few drops of glacial acetic acid so as to dissolve the ppt. Add enough distilled water slowly into the standard flask and make up the volume up to the mark on the neck of the flask.

(B) Standardization of sodium thiosulfate:

Fill the burette (after rinsing) with the hypo solution to any mark and note the reading. Rinse the pipette with copper sulfate solution. Pipette out 25 mL of standard copper sulfate solution in a 250 ml conical flask. Add one small test tube full of KI (about 1 g KI dissolved in 10 mL water) solution to it. This addition of KI liberates I_2 which dissolves in excess of KI, thereby imparting brown color to the solution and a white precipitate of Cu_2I_2 is formed. Cover the flask with a watch glass and allow the solution to settle for a minute. Rinse down the sides of the flask and dilute the mixture to about 100 mL. Titrate by adding hypo solution from burette till the brown color fades. When the color is pale yellow, add one small test tube full of KSCN (potassium thiocyanate) and one small test tube full of starch solution. A dirty blue color is developed. Keep adding hypo drop by drop till this blue color disappears. Note the reading of the burette. Repeat the titration with standard copper sulfate solution till two concordant readings are obtained.

(C) Determination of the strength of unknown copper sulphate solution:

Do the titration with unknown copper sulphate solution till two concordant readings are obtained in the same way as above for the standard copper sulphate solution.

Notes:

Questions:

1.   Why is excess Na_2CO_3 added during iodine titration by hypo solution?

2.   What are the possible interfering ions for this experiment and how can they be eliminated?

3.   Standardization of hypo solution can also be done by standard $K_2Cr_2O_7$ solution. Write the redox reaction for that titration .

4.   What is the role of KSCN in the experiment?

5.   Why is excess iodide need to be added?

6.   Write the structure of starch-I_2 complex.

7.   Write the structure of I_3^- ion.

EXPERIMENT - 5

**SYNTHESIS AND RECRYSTALLIZATION OF DIBENZALACETONE**

Objective:

To provide experience in synthesis, vacuum filtration, recrystallization, measuring the reaction yield and melting point

Caution:

- Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

- Acetone and ethanol are flammable and irritating; keep them away from flames or other heat sources.

- Benzaldehyde is toxic and a suspected carcinogen.

- Aqueous sodium hydroxide (NaOH) is corrosive and toxic. Wear gloves when handling these compounds. Prevent eye, skin, and clothing contact. Do not inhale and ingest these compounds.

Principle:

Condensations are reactions that add together two or more molecules, often with the loss of a small molecule such as water or an alcohol. In its simplest form, the aldol condensation combines two carbonyl compounds to give a β-hydroxy aldehyde or ketone. The product is also called an aldol because it contains both an aldehyde group and an alcohol. The base-catalyzed condensation of two molecules of acetaldehyde to give 3-hydroxybutanal is shown in Scheme 1.
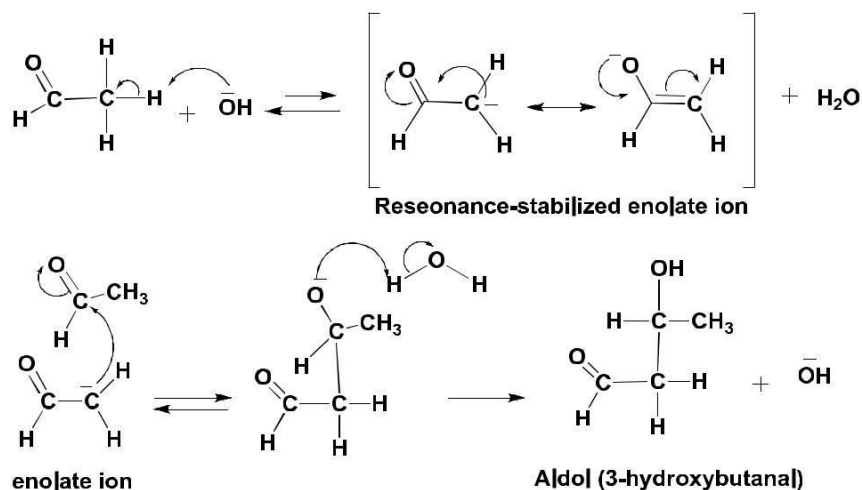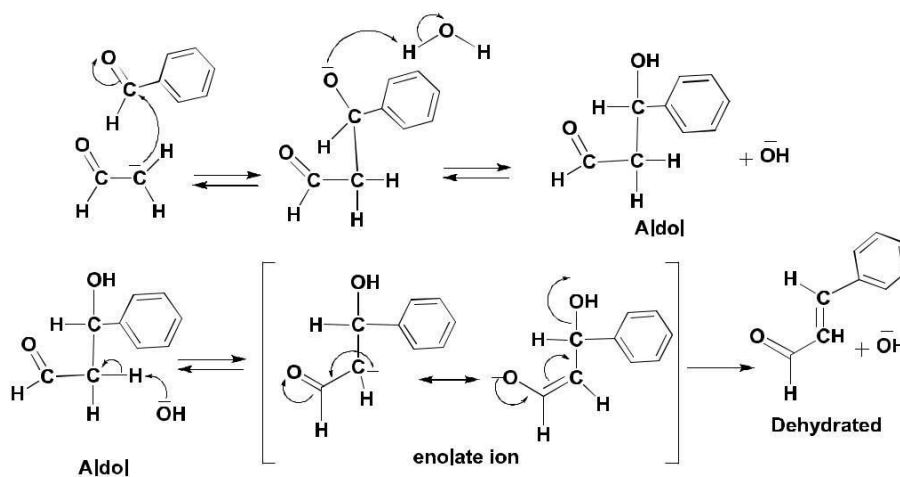

Scheme 1

Hydrogens adjacent to a carbonyl group are weakly acidic. Thus, loss of the acidic proton leads to a resonance-stabilized enolate ion. The enolate ion is a strong nucleophile that adds to another carbonyl group to form the aldol . Aldol products can dehydrate under either acidic or basic conditions to give, α, β -unsaturated aldehydes and ketones. Although aldol condensations are often evenly balanced equilibria, the dehydration is usually exothermic, driving the condensation to completion. The base-catalyzed dehydration of 3-hydroxybutanal is shown in Scheme 2.
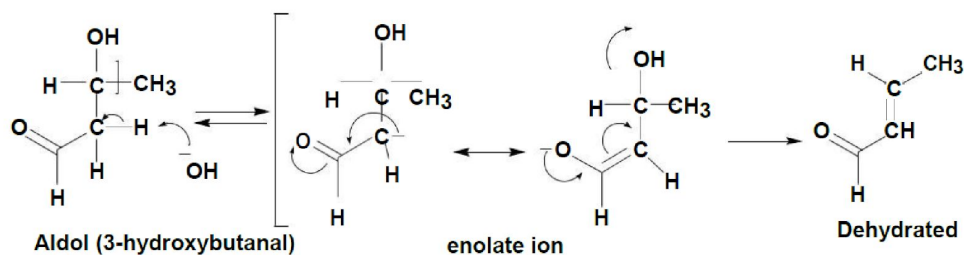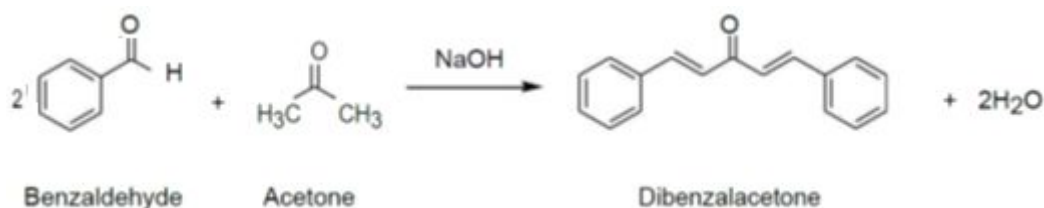

Scheme 2

A crossed aldol condensation is an aldol condensation in which one aldehyde or ketone adds to the carbonyl group of a different compound. The compounds used in a crossed aldol condensation must be carefully selected to avoid unwanted product mixtures. Crossed aldol condensations are most effective if only one of the reactants can form an enolate ion and the other reactant is particularly electrophilic toward enolates. Benzaldehyde is an excellent reagent for crossed aldols because it has no α -hydrogens, so it cannot form an enolate. The base-catalyzed condensation of acetaldehyde with benzaldehyde is shown in Scheme 3.

Scheme 3

The synthesis of dibenzalacetone is an example of Claisen-Schmidt condensation reaction. This reaction gives a solid product, which is impure when first isolated, but it can be purified by recrystalization. In this experiment, acetone is used as the enolate-forming compound, adding to benzaldehyde followed by dehydration to form a benzal group. Acetone has enolizable α-hydrogens on both sides of the carbonyl group, so acetone can add to two molecules of benzaldehyde. The condensation of acetone with two molecules of benzaldehyde to give dibenzalacetone is shown in Scheme 4. The systematic name for dibenzalacetone is 1,5-diphenyl-1,4-pentadien-3-one.

Benzaldehyde   Acetone   Dibenzalacetone

Scheme 4

Experimental Procedure:

(A) Synthesis of dibenzalacetone

Mix 2 mL of benzaldehyde (density 1.04 g/mL) with 0.7 mL of acetone (density = 0.790 g/mL) in a 25 or 50 mL Erlenmeyer flask. Set the flask (flask #1) aside. In a 125 or 250 mL Erlenmeyer flask (flask #2) dissolve 2 g of sodium hydroxide in 20 mL of water, add 15 mL of ethanol, and cool this solution to 20 ºC. Add benzaldehyde acetone solution (from flask #1) to the sodium hydroxide solution (flask #2) and swirl the mixture for 45 minutes. The mixture should turn cloudy within a couple of minutes of mixing and a yellow precipitate should form.

Collect the yellow precipitate by suction filtration in a Buchner funnel (The aqueous filtrate may be discarded in the sink). Transfer the yellow solid to a large beaker and add 300 mL of water. Stir this mixture to break up clumps of the product so the water can dissolve the remaining sodium hydroxide; the dibenzalacetone product being insoluble in water. Collect the crude product by suction filtration on a Buchner funnel using a fresh piece of filter paper. While the aspirator is on, press the filter cake with a cork to extract as much water as possible. (Again, the aqueous filtrate may be discarded in the sink.)

(B) Recrystallization:

For recrystallization place 1 g of crude product it in an Erlenmeyer flask of appropriate size and add enough ethanol to make thick slurry of the crystals: take ethanol in small quantities and **do not directly add from the reagent bottle**. Place a boiling chip in the flask (to prevent "bumping") and

warm the mixture on a hot plate (or water bath) and **do not spill ethanol on hot plate (do not directly heat on flame)**. While it is boiling gently, slowly add ethanol until the crystals just dissolve. Allow the solution to cool until crystals have formed and it is no longer hot. You may cool the mixture in ice at this point. After crystals have stopped forming, collect the recrystallized dibenzalacetone in a Buchner funnel and wash the crystals with a little cold ethanol. Transfer the crystals to a beaker, label the beaker "recrystallized dibenzalacetone," and allow the crystals to air dry. You can discard the filtrate in the beaker labeled "Filtrate from Recrystallization of Dibenzalacetone."

(C) Melting Point Measurement:

Measure the melting point of pure dibenzalacetone* using the melting point apparatus.
*Collect the pure sample from the lab attendants for melting point measurement.

Notes:

Questions:

1. Calculate the percent yield for your product.

2. Propose a mechanism for the base-catalyzed condensation of cyclohexanone with two molecules of benzaldehyde to give dibenzalcyclohexanone.

3. A student habitually adds excess reagents to try to maximize yields. In this procedure, he adds a two-fold excess of acetone. What product is he likely to isolate?

4. Dibenzalacetone is commonly used in sunscreens. Suggest what properties are valuable in a compound for use as a sunscreen. You may need to consult reference sources.

5. What is role of sodium hydroxide in this synthesis?

6. What are criteria for selecting a solvent for the recrystalization of the compound?

7. What products do you expect if 2-phenylethanal is used instead of benzaldehyde in this reaction?

EXPERIMENT – 6

Mechanochemical Synthesis of a Schiff's Base Ligand and its Copper(II) Complex:

A GREEN Chemistry Approach

Objective:

To gain experience in synthesis of ligand and subsequently its copper complex under neat conditions minimizing chemical hazard (GREEN CHEMISTRY approach)

Caution:

- Wear the safety goggles during the experiment.

- 2-Hydroxybenzaldehyde reacts with ethylenediamine vigorously; hence, they should be mixed dropwise while keeping the mixture covered.

- Organic solvents are flammable and irritating. Keep away from flames or other heat sources.

Principle:

Mechanochemical Reaction

Aldehydes react with amine under mild condition to afford Schiff's bases. Generally, reactants are stirred in alcohol either at room temperature or under reflux condition to obtain the desired product. From green chemistry point of view, it is always better to design a reaction, which should reduce the waste formation and can be achieved with low consumption of energy. Mechanochemical synthesis is one such reaction strategy, where starting materials are grinded together to synthesise the chemical products. In this process, use of solvents as reaction media is avoided and analytically pure products are obtained directly. This synthesis methodology follows some Green Chemistry principles focusing on minimization of solvent use and avoiding harsh reaction conditions such as high temperature, high pressure, etc.

Under this experiment, ethylenediamine will be reacted with 2-hydroxybenzaldehyde (Scheme 1) and the resultant ligand will be further grinded with cupric acetate to obtain the corresponding Cu(II) complex.
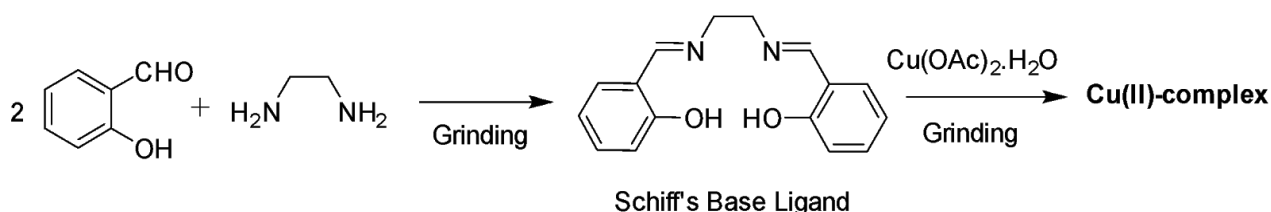
Scheme 1: Mechanochemical synthetic route of ligand and its Cu(II)-complex

Materials

2-Hydroxybenzaldehyde, Ethylenediamine, Ethanol, Ethylacetate, DCM, $Cu(OAc)_2.H_2O$, Micropipette, Mortar and Pestle, Watch glass, Spatula, Beaker (50 ml), Filtration setup.

Experimental Procedures

(A) Synthesis of Schiff's Base Ligand:

Take a clean mortar and transfer ethylenediamine (0.50 mL) into it. Add 2-hydroxybenzaldehyde (1.6 mL) into the mortar containing ethylenediamine drop by drop, while covering the mortar with watch glass (**Note: This addition has to be slow with proper covering of the mortar to avoid the spilling**). Grinding of reactants for about 15 min affords bright yellow coloured solid product. Transfer the product in a beaker, add 15 mL of cold ethanol, mix using glass rod/spatula and filter. Dry the solid product and proceed for metal complexation reaction.

(B) Synthesis of Copper(II) Complex of the Synthesized Schiff's Base Ligand:

Clean the mortar and transfer the above synthesized ligand (0.1 g) and copper(II) acetate monohydrate (0.074 g) into it. Add 4-5 drops of ethanol and grind the contents for about 15 min. to obtain the metal complex.

Notes:

Questions:

1. What is green chemistry?
2. What are the advantages of mechanochemical synthesis?
3. Write the mechanism of Schiff's base formation.
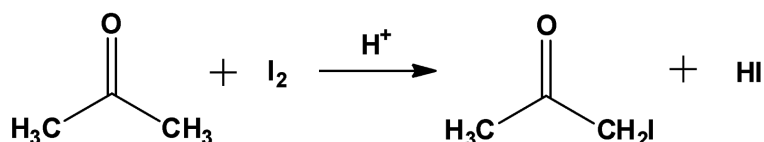4. How will you calculate the yield of this reaction?

5. What were potential sources for error in this experiment?

EXPERIMENT – 7

KINETICS OF THE IODINATION OF ACETONE

Objective:

To study the kinetics of the iodination of acetone in acidic medium using photometry, estimate the differential rate law, and calculate the rate constant.

The rate law may be written as

$$-\frac{d[I_2]}{dt} = k[I_2]^x[CH_3COCH_3]^y[H^+]^z$$

(1)

The aim is therefore to determine the orders of the reaction viz. x, y and z with respect to I_2, CH_3COCH_3, and H^+ respectively, and calculate k, the rate constant.

Principle:

(A) Determination of Order of Reaction:

A two pronged strategy is adopted in this procedure. For the determination of the order x with respect to I_2, the reaction rate is studied using a large excess of acetone, and a high concentration of H^+. Under these conditions, $[CH_3COCH_3]$ and $[H^+]$ remain virtually constant as the reaction proceeds, and the rate law reduces approximately to

$$-\frac{d[I_2]}{dt} = k'[I_2]^x \qquad (2)$$

where k' = k $[CH_3COCH_3]^y$ $[H^+]^z$ is a "pseudo rate constant", constant to the extent that the concentrations of CH_3COCH_3 and H^+ may be considered to be fixed. By measuring $[I_2]$ as a function of time as the reaction proceeds, and by comparing this to the integrated form of (2) for simple choices of x (say 0, 1 and 2), the order x with respect to I_2 may be found.

If x = 0, then, we can write $[I_2] = [I_2]_0 - k't$

If x = 1, then, $[I_2] = [I_2]_0 e^{-k't}$

If x = 2, then, $\dfrac{1}{[I_2]} = \dfrac{1}{[I_2]_0} + k't$

The orders of reaction with respect to CH_3COCH_3 and H^+ are found by the method of initial rates as follows. Holding the initial concentration of I_2 and H^+ fixed, and then varying the initial concentration of acetone, the change in initial reaction rate is used to determine y, the order with respect to CH_3COCH_3. Similarly by holding the initial concentration of I_2 and CH_3COCH_3 fixed and determining the initial rate for different concentrations of H^+, the order z with respect to H^+ is found.

(B) Photometry:

The kinetics of this reaction is monitored by exploiting the fact that of all the species involved, the only colored one is iodine, and that the concentration of such a light absorbing species in solution may be quantitatively determined by measuring the fraction of incident light that the solution absorbs. A block diagram of a simple photometer is shown below:
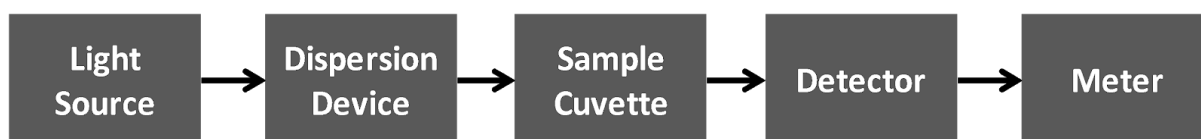
Light from the source falls on a dispersing element or monochromator. This may be a prism or grating, or a simple filter. While a grating or prism enables one to select radiation of a fairly narrow band of wavelengths for falling on the sample, this bandwidth is considerably greater in the case of a filter. Light transmitted by the sample then falls on a light detector which is a light sensitive device such as a photoconductor or a photocell that produces an electrical response proportional to the intensity of light reaching it. The construction of a traditional UV-visible spectrophotometer is shown in Figure 1. If at a particular wavelength, I_0 and I are the intensities respectively of the incident and transmitted light, then the transmittance T of the sample at that wavelength is defined as $T = I/I_0$ and the absorbance A as, $A = -\log_{10} T = \log (I_0/I)$. It is found that the absorbance of a solution varies with the (molar) concentration 'c' of the absorbing species according to the Beer –Lambert's law :

$$A = \varepsilon cl \qquad (4)$$

where 'ε' is the (molar) absorption coefficient, characteristic of the absorbing species and of the wavelength of light used, and 'l' is the length of sample through which the light passes. The product 'εc' is sometimes called the optical density (often imprecisely used as synonymous with absorbance) of the sample. The Beer-Lambert's law provides a means of accurately determining the amount of a

light-absorbing species in solution by photometry. Most commercial instruments are provided with meters which enable one to read both the transmittance and the absorbance (or optical density).
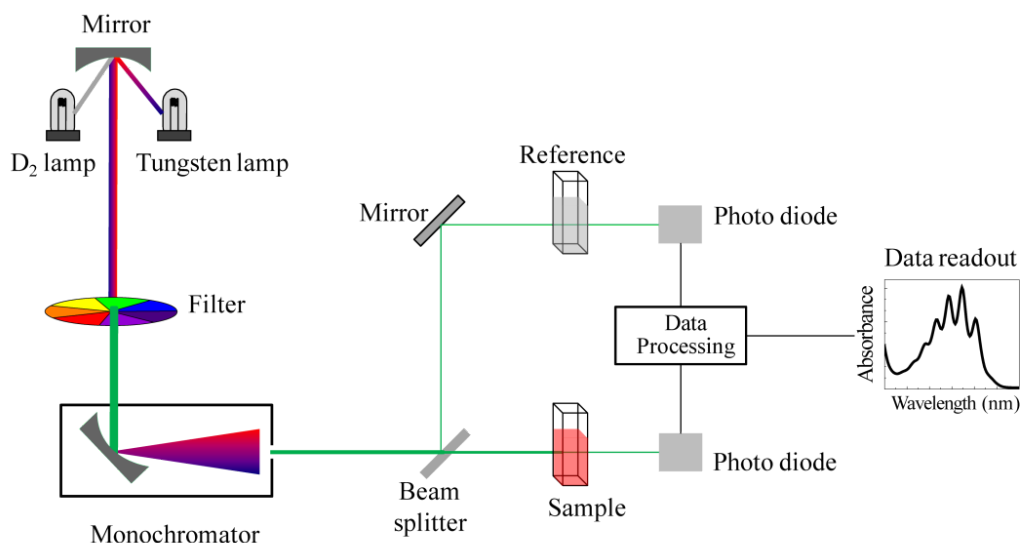

Figure 1. Schematic representation of a modern UV-vis spectrophotometer

(C) Kinetics of the Iodination Reaction by Photometry:

Iodine is a dark purple (almost black) solid, while a dilute aqueous solution of iodine is yellow. However it is only slightly soluble in water. If one uses a solution of KI (in excess) instead of pure water to dissolve the iodine, the solubility is enhanced due to the reaction:

$$I_2 \quad + \quad I^- \quad \rightarrow \quad I_3^-$$

The triodide ion I_3^- is a brown red species. Both I_2 and I_3^- act as iodinating agents. Further, both have nearly the same molar absorption coefficient at a wavelength of 565 nm so that absorbance measurements centered on this wavelength, which we will perform, enable a determination of the total concentration of iodine, I_2 and I_3^-.

Experimental Procedure:

(A) Calibration Curve:

In this portion the calibration curve to establish the connection between the total concentration of iodine in solution and the absorbance A is obtained. Turn on the photometer and let it warm up. Using a graduated pipette, measure out 1, 2, 3, and 4 mL respectively of the stock solution of iodine into 4 clean and dry test tubes. Dilute each of these with distilled water such that the total volume of solution in each tube is 10 mL. Mix the individual solutions properly. Measure the absorbance at 565 nm for each of these solutions in turn, following the instructions on the photometer.

Plot a graph of the absorbance versus $[I_2]$ and verify that you get a good straight line passing through the origin. Write down the equation of this line.

(B) Rate Measurements:

The kinetics must be followed for at least four runs with various starting concentrations (suggested in the table below). For each experiment, follow the sequence of steps given below:

Suggested trials:

Experiment	Acetone solution	HCl solution	H$_2$O	I$_2$ solution
1	2.0 mL	2.0 mL	4.0 mL	2.0 mL
2	4.0 mL	2.0 mL	2.0 mL	2.0 mL
3	2.0 mL	4.0 mL	2.0 mL	2.0 mL
4	2.0 mL	2.0 mL	2.0 mL	4.0 mL

1. Into a clean test tube, accurately measure out the indicated (or any other suitably chosen) volumes of CH_3COCH_3 solution, HCl solution and distilled water, and mix thoroughly. Use burettes for the acetone and hydrochloric acid solutions.

2. Into a second clean test tube, accurately measure out the desired volume of I_2 stock solution from a burette.

3. Add the contents of the first test tube to the second, mix rapidly and thoroughly, and start the stop watch.

4. Note down the absorbance as a function of time, taking reading at least every 30 seconds. Record readings till the absorbance reaches almost zero and remains constant.

5. For each experiment, plot the absorbance (or corresponding $[I_2]$) as a function of time. From the plot, the order with respect to iodine concentration can be calculated.

6. From each of the above mentioned four graphs find out the values of k' and then tabulate the initial rate data. From experiments 1 and 2, find the order with respect to CH_3COCH_3. Similarly from experiments 1 and 3, find the order with respect to H^+. For each experiment, calculate the rate constant (with the correct units) and check its constancy.

Notes:

Questions:

1. With concentrations in moles/L and time in sec, what will be the dimensions of the rate constant and overall order n of the reaction?

2. For each of the runs you carried out, verify the extent to which the approximation that the concentrations of CH_3COCH_3 and H^+ are constant is valid.

3. For a zero order (or a pseudo zero order) reaction, how does the half life depend on the initial concentration C_o?

4. Propose one or more mechanisms for the reaction which is consistent with the rate law you have found.

EXPERIMENT - 8

DETERMINATION OF THE CONCENTRATION EQUILIBRIUM CONSTANT (K_c) OF THE REACTION: $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

Objective:

To determine the concentration equilibrium constant (K_c) of the reaction: $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

Principle:

The concentration equilibrium constant (K_c) of the reaction:

$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$; is given by:

$$K_c = \frac{[CH_3COOC_2H_5]_{eq} \times [H_2O]_{eq}}{[CH_3COOH]_{eq} \times [C_2H_5OH]_{eq}}$$

Where $[\ldots]_{eq} \equiv$ Molar concentration at equilibrium.

To hasten the approach to equilibrium, hydrochloric acid is used as a catalyst.

Experimental Procedure:

1. Record the room temperature before and after the experiment and average it.

2. Prepare the following mixture in clean glass-stoppered bottles, shake and keep them for about one hour to reach equilibrium.

Bottle 1: 5 mL ~3N HCl solution + 4 mL pure ethanol + 1 mL glacial acetic acid.

3. Standardize ~1N NaOH solution (supplied) against 25 mL standard 0.3N oxalic acid solution (supplied), using phenolphthalein indicator and calculate the strength of NaOH.

4. Standardize ~3N HCl solution (supplied) against standard NaOH solution, taking 5 mL HCl solution each time. Use Phenolphthalein as indicator. Repeat titrations to obtain concordant readings.

5. Weigh the following liquids accurately, in well stoppered weighing bottle:

   (i) 5 mL ~3N HCl Solution   (ii) 4 mL pure ethanol

   (iii) 1 mL glacial acetic acid   (iv) 5 mL pure ethyl acetate

6. Titrate the whole contents of the bottles after reaching equilibrium, with standard NaOH solution using phenolphthalein indicator and the bottles should be placed in cold water (room temperature) taken in a wide container while titrating.

7. Calculate the K_c values for the reaction and report it as result.

Notes:

Questions:

1. What is the law of mass action?

2. What is equilibrium constant?

3. What is concentration equilibrium constant (K_c)?

4. What is Le-Chatelier's principle?

5. How is equilibrium constant dependent on temperature?

6. What is the role of hydrochloric acid in this experiment?

7. What is homogeneous catalysis?

8. How would you explain acid catalysis?

EXPERIMENT – 9

DISSOCIATION CONSTANT OF A WEAK ELECTROLYTE BY CONDUCTOMETRY

Objective:

To verify Ostwald's dilution law and to determine the dissociation constant of acetic acid.

Principle:

(A) Conductance of a solution:

The resistance of a solution containing an electrolyte can be determined by taking it in a conductivity

cell. The resistance, $R = \rho \dfrac{l}{a}$

where ρ = specific resistance, l = distance between two electrodes, a = cross section of electrode.

The conductance, $\Lambda = 1/R$. The specific conductance, $\kappa = \dfrac{1}{\rho} = \dfrac{1}{R} \cdot \dfrac{l}{a}$

The conductance of the solution is measured by dipping platinum electrode into the solution. This is called conductivity cell. This cell is connected with the conductometer. Alternating current should be used. If DC is used the solution undergoes electrolysis and the products of electrolysis set up a back emf which opposes the flow of current. There is also a change in the concentration of the electrolyte.

Now, we know that, specific conductance $\kappa = \dfrac{1}{R} \cdot \dfrac{l}{a}$ where $\dfrac{l}{a}$ is cell constant, which is equal to 1 for the electrode provided.

Therefore, specific conductance $\kappa = \dfrac{1}{R}$ = conductance.

Hence, we can say that the conductance shown by conductometer is equal to the specific conductance. It is known that the specific conductance of 0.1N KCl is 12.88×10^{-3} Ohm^{-1}cm^{-1} at 25 $^\circ$C. Therefore, before starting the experiment we will calibrate the conductometer by dipping the electrode into 0.1 N KCl solution and adjusting the conductivity value at 12.88×10^{-3} Ohm^{-1}cm^{-1}
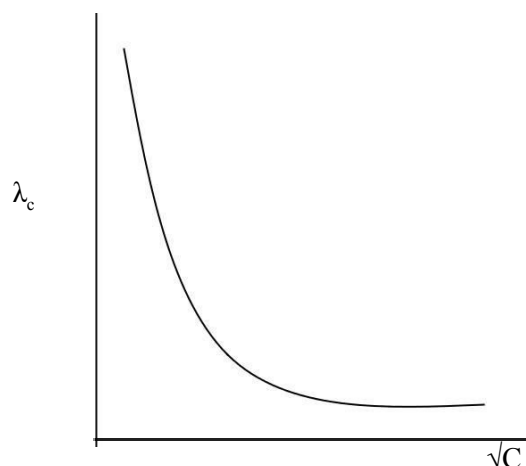
(B) Equivalent Conductance:

The equivalent conductance is defined as the conductance of a solution containing 1 gram-equivalent of the dissolved electrolyte such that the entire solution is placed between two electrodes 1 cm apart.

If the concentration of electrolyte is C gm-eqv. per litre, then 1 gm-eqv. is present in 1000/C cc. If this volume is placed between two electrodes 1 cm apart, then the cross section of the column of solution or electrodes would 1000/C sq.cm. Therefore, the equivalent conductance,

$$\lambda = \frac{a}{l} \cdot \frac{\kappa}{C} = 1000\kappa$$

The strong electrolytes (like KCl, HCl, H_2SO_4) have very high equivalent conductance even at ordinary concentrations. With dilution the conductance increases to some extent and ultimately tends to reach a limiting value. The equivalent conductance at infinite dilution (λ_∞) can be measured by extrapolating the linear curves to high dilution. But in case of weak electrolytes the equivalent conductance is low at ordinary concentrations (λ_c) say 0.1N. With dilution λ_c increases considerably as is shown by the plot of λ_c vs. $\sqrt{C}$ below:

It is seen that even when the concentration is made very small, the equivalent conductance rises steeply with dilution. It is not possible to reach a limiting value by extrapolation as in the case of strong electrolytes.

According to Kohlrausch's Law, the equivalent conductance at infinite dilution is the sum of ion conductance. This is known as law of independent migration of ions.

$\lambda_\alpha (CH_3COOH) = \lambda_\alpha (H^+) + \lambda_\alpha(CH_3COO^-)$
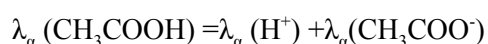
Here λ_α = ion conductance.

λ_α of acetic acid can be measured from the λ_α of strong electrolyte e.g..

$\lambda_\alpha(HCl) + \lambda_\alpha(CH_3COONa) - \lambda_\alpha(NaCl) = \lambda_\alpha(H^+) + \lambda_\alpha(Cl^-) + \lambda_\alpha(Na^+) + \lambda_\alpha(CH_3COO^-) - \lambda_\alpha(Na^+) - \lambda_\alpha(Cl^-)$

$$= \lambda_\alpha(H^+) + \lambda_\alpha(CH_3COO^-) = \lambda_\alpha(CH_3COOH)$$

For acetic acid this λ_α value is 390.8 Ohm^{-1}cm^2 at 25ºC.

(C) Ostwald's Dilution Law:

The ions produced on dissociation are in equilibrium with the undissociated molecules of weak electrolytes in solution. Thus a weak acid solution of HA will have the equilibrium,

$$HA \quad = \quad H^+ \quad + \quad A^-$$

$$C - \alpha C \qquad \alpha C \qquad \alpha C$$
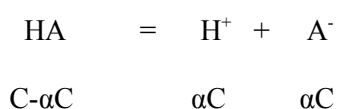
C is the concentration and α is the degree of dissociation. Applying the. Law of Mass action, the equilibrium constant, better known as dissociation constant, of the acid is given by

$$K_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} \quad = \frac{\alpha C \times \alpha C}{C(1-\alpha)} \quad = \frac{C\alpha^2}{1-\alpha}$$

The equilibrium representing the relationship between K_a, α, and C is known as **Ostwald's Dilution**

Law. The degree of dissociation $\alpha = \dfrac{\lambda_c}{\lambda_\infty}$ Therefore once the λ_∞ value is known ($\lambda_c = 1000\kappa / C$) from conductometer we can calculate α ($\alpha = \lambda_c / \lambda_\infty$), the degree of dissociation using the value λ_∞ as 390.8 Ohm^{-1}cm^2. From this value dissociation constant K_a can be calculated using equation

$K_a = C\alpha^2 / (1 - \alpha)$.

Experimental Procedure:

1. Wash a 100 mL beaker and the electrode of the cell thoroughly with distilled water.

2. Fill up the beaker with 50 mL of the given 0.1 N KCl solution.

3. Dip the conductivity electrode into the solution.

4. Make necessary connection.

5. Observe the value of conductance (which is equal to specific conductance) of the solution. Adjust the conductance value at 12.88×10^{-3} Ohm^{-1}cm^{-1}.

6. Throw out the KCl solution and again wash the beaker and electrode thoroughly with distilled water.

7. Pipette out 50 mL of 1N acetic acid in a standard flask and make up the volume upto 100 mL with conductivity water. The concentration of this solution is N/2.

8. Dilute the solution N/4, N/8, N/16, N/32, N/64 successively with conductivity water in the standard flask.

9. Measure the conductance of each of the above solutions.

Notes:

Questions:

1. Why in case of conductance measurement alternating current should be used?

2. The conductance of a solution of a given electrolyte depends upon ……… and ……..

3. What is equivalent conductance?

4. Although in case of strong electrolytes the ionization is complete at ordinary concentration, why then should the equivalent conductance in such solution vary with dilution?

5. Why in case of weak electrolytes the experimental determination of limiting value of equivalent conductance is difficult?

6. How can you find out the equivalent conductance of a weak electrolyte at infinite dilution from the value of equivalent conductance of strong electrolytes at infinite dilution?

7. What are Kohlrausch's law of independent migration of ions and Ostwald's dilution law?

8. Is it possible to titrate a weak acid by a strong base using conductometer?

9. At 18 ºC, the resistance of 0.1 N KCl in a conductivity cell is 86.8 Ohms and that of 0.05 N NaCl is 203 Ohms. What is the equivalent conductance of 0.05N NaCl? Given the specific conductance of 0.1 N KCl at 18 ºC is 0.011192 Ohm^{-1}cm^{-1}

EXPERIMENT - 10

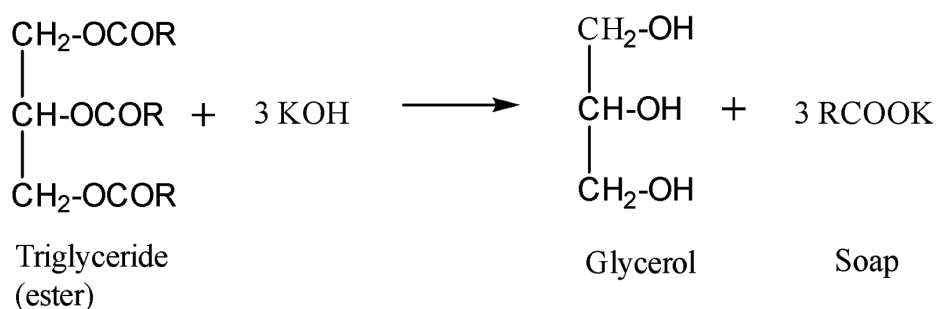## DETERMINATION OF SAPONIFICATION VALUE OF AN OIL

Objective:

To determine the saponification value of the given oil.

Principle:

Oil and fats are the triglycerides of higher fatty acids (carboxylic acids with hydrocarbon chains of 4 to 36 carbons), that can be saturated or unsaturated. Due to the presence of long hydrophobic hydrocarbon chains these are insoluble in water. These oil or fat samples undergo hydrolysis in basic conditions to afford glycerol and the salt of the corresponding fatty acid. This hydrolysis process is known as Saponification.

$$CH_2\text{-OCOR} \\ | \\ CH\text{-OCOR} \quad + \quad 3\ KOH \quad \longrightarrow \quad CH_2\text{-OH} \\ | \\ CH\text{-OH} \quad + \quad 3\ RCOOK \\ | \\ CH_2\text{-OCOR} \qquad\qquad CH_2\text{-OH}$$

Triglyceride (ester)   Glycerol   Soap

Saponification: It is the hydrolysis of fats or oils under basic conditions to afford glycerol and the salt of the corresponding fatty acid that literally means "soap making".

Saponification Value: It is the number of milligrams of KOH required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of fat. This value is useful for comparative study of the fatty acid chain length in oils. It is also considered as a measure of the average molecular weight (or chain length) of the fatty acids present.

The smaller the saponification number the larger the average molecular weight of the triacylglycerol present. The long chain fatty acids found in fats have low saponification value as they have a relatively fewer number of carboxylic functional groups per unit mass of the fat and therefore have high molecular weight.

Experimental Procedure:

(A) Reagents:

1. Oil sample
2. Fat Solvent (1:1 v/v, Ethanol: Diethyl ether)
3. Ethanolic KOH (95% ethanol, v/v): Dissolve KOH (40 g) in absolute alcohol (1 L), keeping the temperature below 15 ºC.

4. Standard solution of oxalic acid

5. NaOH solution

6. HCl solution

7. Phenolphthalein indicator

(B) Procedure:

1. Weigh oil sample (2.0 g) in a dry Erylenmayer flask.

2. Add 10 mL of fat solvent to the oil sample.

3. Also add alcoholic KOH (20 mL) slowly from the burette into the Erylenmayer flask (Label as No. 2).

4. Simultaneously prepare another Erylenmayer flask set up (blank, Label as No. 1) in the same way without adding the oil sample.

5. Connect air condensers to both the flasks and boil the contents gently on steam bath for about 45 minutes.

6. In the mean time, standardize (titrate) the given NaOH solution using a given standard solution of oxalic acid of known strength (*Phenolphthalein as indicator*).

7. Standardize (titrate) the given HCl solution with the above standardized NaOH solution. (*Phenolphthalein as indicator*).

8. After 45 minutes of heating, allow the contents to cool at the room temperature, and rinse the inside of the condensers with a little distilled water and then remove the condensers.

9. Titrate both the solutions (No. 1 & 2) separately against given HCl standard solution using phenolphthalein as indicator (end point is the disappearance of pink colour to colorless).

10. From the difference between the titration values of the blank flask (V_1) and the flask containing oil (V_2), the amount of KOH in mg (saponification value) that has been used for 1 g of the oil can be calculated.

A.   Calculations:

Weight of the oil taken = W g

Normality of HCl solution = N_1

Volume of HCl solution required to react with remaining KOH (in Flask No. 1) = V_1 mL

Volume of HCl solution required to react with remaining KOH (in Flask No. 2) = V_2 mL

Volume of HCl equivalent to KOH that reacted with the oil = (V_1-V_2) mL

As 1000 mL of x N HCl solution ≡ gram equivalent wt of KOH = 56 g of KOH

(V_1-V_2) mL of N_1 HCl solution $= \frac{56 \times (V_1 - V_2) \times N_1}{1000}$ g of KOH

The amount of KOH reacted with the oil

W g of the oil $= \frac{56 \times (V_1 - V_2) \times N_1}{1000}$ g of KOH

1 g of the oil $= \frac{56 \times (V_1 - V_2) \times N_1}{1000 \times W}$ g of KOH

1 g of the oil $= \frac{56 \times (V_1 - V_2) \times N_1}{W}$ mg of KOH

Saponification Value $= \frac{56 \times (V_1 - V_2) \times N_1}{W}$ mg of KOH

Notes:

Questions:

1. What is saponification?

2. What is the relationship between saponification value and molecular mass of oils ?

3. How many molecules of fatty acids are released from a triglyceride?

4. If a fat has low saponification value, what can be inferred about the chain length of the fatty acid?