M.Sc. CHEMISTRY LAB MANUAL

2nd Semester

Prepared By

Pure & Applied Science Dept.

Chemistrty

MIDNAPORE CITY COLLEGE

M.Sc. in Chemistry

Under Choice Based Credit System (CBCS)

(Semester Programme)

SEMESTER-II

CEM 295: Organic Practical

1. Thin-layer chromatography (TLC)

Thin-layer chromatography (TLC) is used for identifying compounds and determining their purity. The most common adsorbent used is silica gel. Alumina is gaining popularity, with good reason. Components of a mixture could be separated on an alumina / silica-gel plate as on an alumina / silica-gel column. Column chromatography using alumina is still very popular. It is easy to run test separations on TLC plates rather than carrying out tests on chromatographic columns. Nonetheless, both these adsorbents are powder and require a solid support. Microscope slides are extremely convenient. To keep the powder from just falling off the slides, manufacturers add a gypsum binder (plaster). Adsorbents with the binder usually have a "G" stuck on the name or say "For thin-layer use" on the container.

Sometimes a fluorescent powder is put into the adsorbent to help with visualization later. The powder usually glows a bright green when you expose it to 254 nm wavelength ultraviolet (UV) light. You can probably figure out that if a container of silica gel is labeled Silica Gel G-254, you've got a TLC adsorbent with all the bells and whistles.

Procedure

Briefly, mix the adsorbent with water to make slurry, spread the mix on the microscope slide in a thin layer, and let it dry (see *details of preparation below*). Then activate the coating by heating the coated slide on a hot plate / oven. Then you spot or place your unknown compound on the plate, let an eluent run through the adsorbent (development), and finally examine the plate (visualization).

a) Preparation of TLC plates

1. Clean and dry several microscope slides.

2. In an Erlenmeyer flask, weigh out some adsorbent, and add water.

a. For silica gel uses a ~ 1:2 ratio of gel to water. About 2.5 g gel and 5 g water will do for a start.

b. For alumina, use a ~ 1:1 ratio of alumina to water. About 2.5 g alumina and 2.5 g water is a good start.

3. Stopper the flask and shake it until all the powder is wet. This material MUST be used quickly because there is a gypsum (plaster) binder present.

4. Spread the mix by using a medicine dropper. Do not use disposable pipets! The disposable pipets have extremely narrow openings at the end and they clog up easily. There exists a "dipping method" for preparing TLC slides, but since the usual solvents, methanol and chloroform (Caution! Toxic!) do not activate the binder, the powder falls off the plate. Because the layers formed by this process are very thin, they are very fragile.

5. Run a bead of mix around the outside of the slide, then fill the remaining clear space. Leave 0.5 cm of the slide blank on one end, so you can hold onto the slide. Immediately tap the slide from the bottom to smooth the mix out (**Fig. 89**).[#] Repeat this with as many slides as you can. If the mix sets up and becomes unmanageable, add a little water and shake well.

6. Let the slides sit until the gloss of water on the surface has gone. Then place the slides on a hot plate / oven until they dry.

[[#]Alternately, take the slurry in a wide-mouthed bottle. Held a tlc plate at one end with two fingers and dip it into slurry in the inclined bottle of slurry. Take out the plate almost horizontally so that a uniform but thin layer of slurry remains on the top of the glass plate. Place it over paper (better waste newspaper) in air. The slurry will dry up to an immovable layer, and then activate the plate by heating on a hot plate / oven at ~ 150 ^{o}C for some time. After activation cool the same before use.]

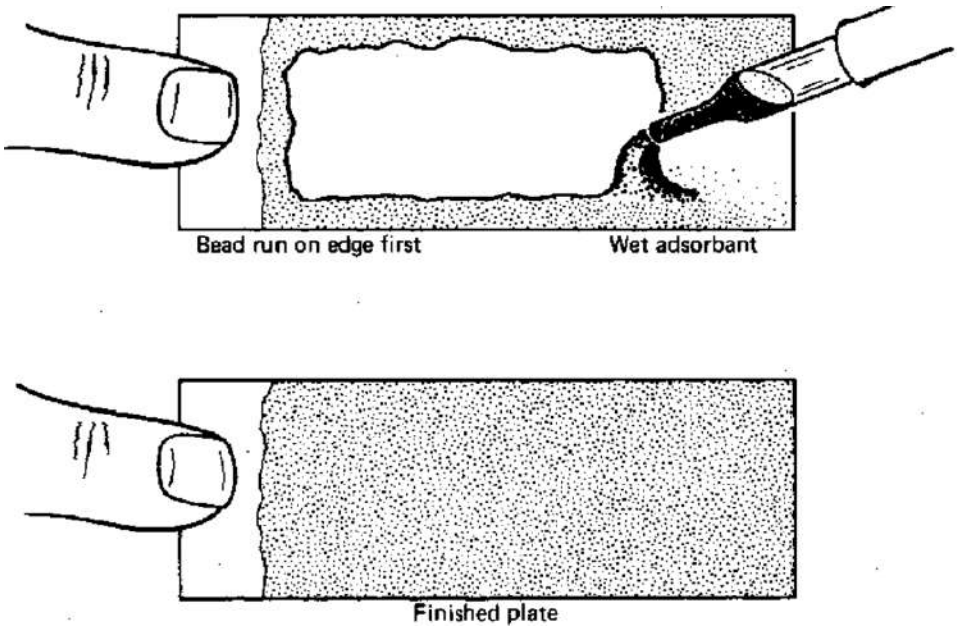
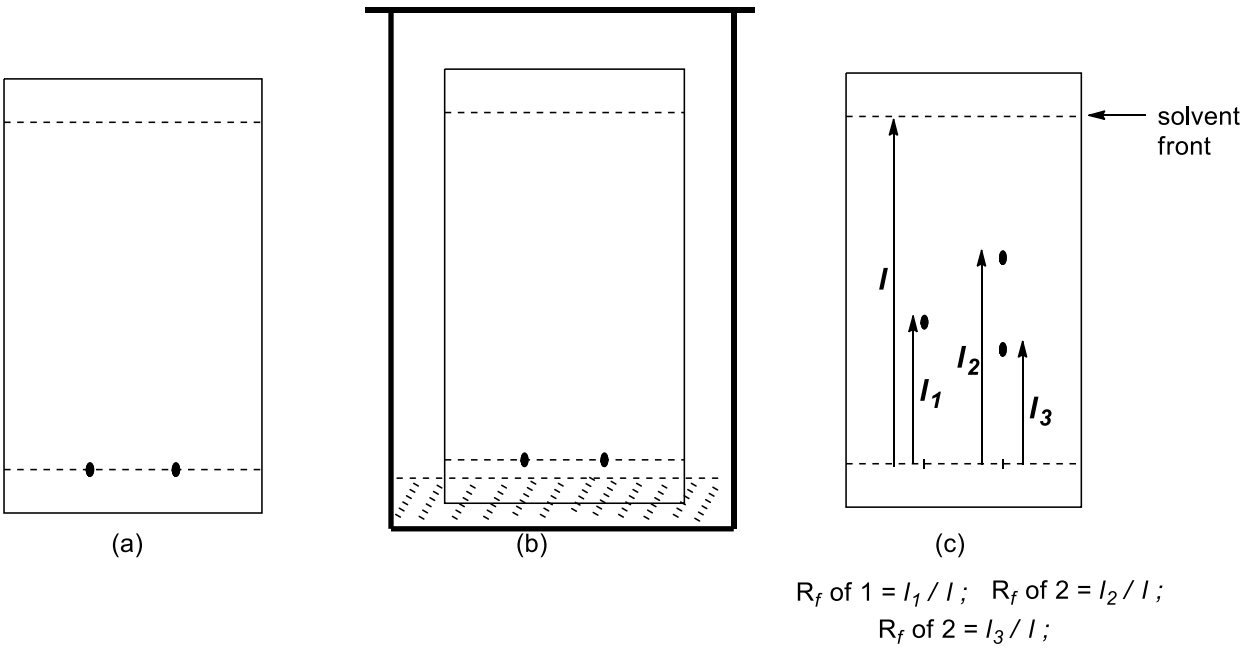


Fig. 1: Spreading adsorbent on a TLC plate.

b) The test compound / mixture of compounds is dissolved in an appropriate solvent on a watch glass. A small drop of the solution is applied by touching a capillary tube on the plate at one end (some 0.4 – 0.5 cm from the bottom) (Fig. 2a). The plate is then placed in a solvent (or solvent mixture) of appropriate polarity such that the spot at which the sample is placed remains marginally (~ 0.1 cm) above the solvent surface (Fig. 2b). The assembly should be kept within a closed glass vessel (a tea glass with a lid may be used). The solvent will rise along the plate (by capillarity action). As soon as the solvent moves to the top (or nearly so) of the plate should be brought out of the vessel and be dried in air (a blower may be used).

Now the plate need to be kept within an iodine chamber or viewed by an UV illuminator. The component(s) can be visible at different spots on the plate. The polarity of the developing solvent should be adjusted such that the R_f value* of the components remains within 0.4 – 0.6 range (Fig. 2c). The left hand side spot is due to single component while the one at the right hand side, as it appears, is mixture of two.



[*R_f (retention factor) value – It is the distance travelled by the component (l_1 / l_2 / l_3 for the respective components) divided by the distance traversed by the solvent i.e., from the base to the solvent front (l) (see Fig. 3). The less polar component moves larger and vice-versa. If the R_f is too low solvent polarity should be increased and if high solvent polarity is to be lowered.]

Sometimes identity of a component with a known sample is examined by **co-TLC**.

For this the test solution is applied at one side of the plate, the solution of the known compound at the other side and both solutions at the middle at the same spot (Fig. 3a). The middle spot will show a single spot having the same R_f value of the two components on either side if the two samples are identical (Fig. 3b). If not identical, two spots will be discernible at the middle – each one with same R_f on either side (Fig. 3c).

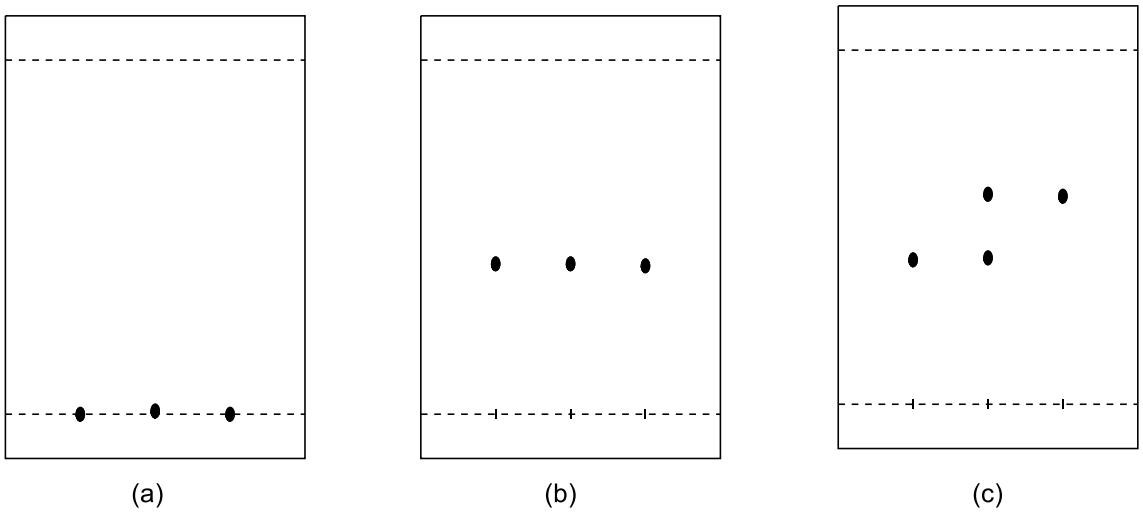


Fig. 3: Co-TLC

Determination of Boiling Point

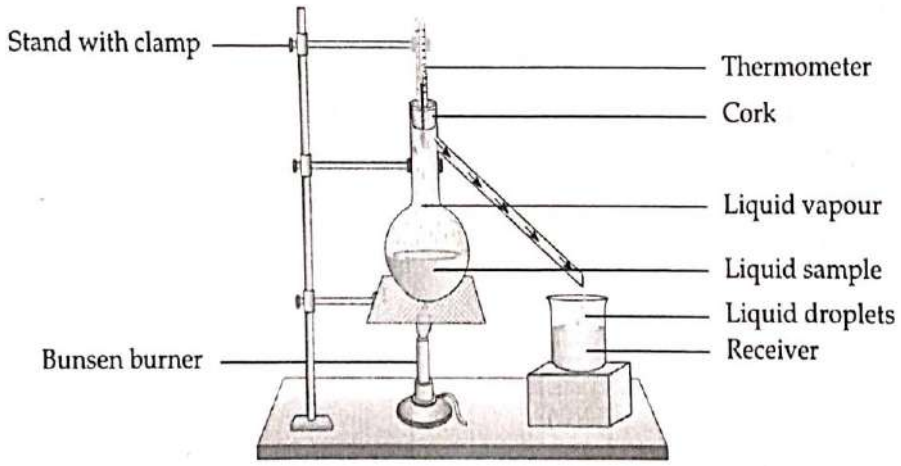
The boiling point of the liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure exerted upon the liquid surface. The boiling point of the liquid varies with the surrounding atmospheric pressure. The normal boiling point of a liquid is an indicator of the purity and volatility of that compound.

Equipments required:

1. Boiling point apparatus
2. Thermometer
3. Stand and Clamp
4. Small beaker (as receiver),
5. Burner

Materials required

Organic liquid



Boiling point apparatus

Procedure:

1. Place ~10 mL of liquid organic sample in a clean and dry boiling point apparatus, add a piece of porous bead (boiling stone) into the liquid.
2. Attach the thermometer in such a way that the bulb of the thermometer is held ~1 - 2 cm above the surface layer of the liquid sample.
3. Heat the liquid bath gently and uniformly; record the constant temperature at which continuous stream of liquid flows down into the receiver.

Basic Concepts of ^{1}H- NMR Spectra:

Hydrogen nucleus (proton) with a spin quantum number of (1/2) behaves as a tiny bar magnet. Under held free space the protons in an organic molecule are randomly oriented. However when exposed to an external magnetic field the protons adopt two orientations-aligned with the direction of external field(the low energy n state) and opposed to the direction of external field (the high energy state). Thus, an energy gap is created and matching of this energy gap with a suitable radio frequency causes transition (flipping) leading to a signal known as 'H-NMR or PMR signal.

Proton is associated with two types of motion. One is spinning motion about its own axis and the other is processional motion around the vertical axis of the earth's gravitational field. Spinning frequency of the nucleus is independent of

the strength of external magnetic field but the processional frequency (ν) is directly proportional to the strength of external field Be

$$\nu \propto B_0 \quad \text{or, } \nu = \gamma B_0/2\pi$$

where γ = magnetogyric or gyromagnetic ratio i.e., the ratio between nuclear magnetic moment p and the nuclear angular momentum I.

PMR signals are expressed in terms of **chemical shift** (δ) values.

$$\delta_x = (\nu_x - \nu_{TMS})/\nu_0$$

where δ_x, is the chemical shift in ppm, ν_x and ν_{TMS} are the frequencies (in Hz) of the signals for proton x and H of tetramethyl silane (internal standard) respectively and ν_0 is the operating frequency (in MHz) of the instrument.

All the protons in a molecule do not reside in identical environment. Some of the protons enjoy higher electron density around them than others. Circulation of this electron density under the influence of the external magnetic field generates a secondary magnetic field that shields the nucleus from the effect of the external field. Thus, increase in electron density around a proton shifts its signal to lower value of δ (upfield). Similarly, reduction in electron density shifts a signal to higher values of δ (downfield).

Besides, anisotropic effect plays a crucial role in determining the chemical shift of a H. Also, the electronegativity of the atom to which the proton is attached and the hybridization state of the C to which proton is linked are important in determining the chemical shift of a proton.

A proton or a group of Hs can appear as a single line signal (called singlet) or a multiplet (doublet, triplet, quartet, etc. called **multiplicity**, m, of a signal) depending on the number of protons (that are non-equivalent with the protons under consideration). In general, the signal consists of (n+1) lines where n is the number of non-equivalent Hs at the adjacent carbon(s). The intensity ratio of the lines within a signal (1:1 for a doublet, 1:3:1 for a triplet, etc.) as also the **relative intensity** of the different signals are informative regarding the structure determination. The latter provides an idea about the number different kinds of H in a molecule.

Further separation of the lines within a signal, called **coupling constants** (*J* value), is another set of data that gives vital information for the structure of a

compound. The spin-coupled sets e.g., AX, AX_2, AMX, etc. (1^{st} order spectra) can be analysed as also the *J*-values to gather several information. Complication can arise for higher order spectra. Anyway ^{1}H NMR provides an wealth of information which can be analysed to arrive at one (or alternative) structure for a compound.

For details about ^{1}H NMR the students are advised to consult a text book on spectroscopy.

^{13}C NMR Spectroscopy:

Carbon-13 (^{13}C) nuclear magnetic resonance (most commonly known as carbon-13 NMR spectroscopy or ^{13}C NMR spectroscopy or sometimes simply referred to as carbon NMR) is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is analogous to proton NMR (^{1}H NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. ^{13}C NMR detects only the ^{13}C isotope. The main carbon isotope, ^{12}C is not detected. Although much less sensitive than 1H NMR spectroscopy, ^{13}C NMR spectroscopy is widely used for characterizing organic and organometallic compounds.

The steps for interpreting the ^{13}C-NMR spectrum of a compound are almost the same as determining the ^{1}H-NMR spectrum and are described as follows:

Step 1: Identify the number of signals that appear on the ^{13}C-NMR spectrum (Noise decoupled). The number of carbon atoms (C) can be determined by looking at the number of peaks that appear and the chemical environment of the carbon in the compound. Just like ^{1}H-NMR, carbon atoms that are in a chemical environment appear as the same peak. For example, the pentane-2,4-dione compound shown in Figure 2 has five carbon atoms with two of them in the same chemical environment giving rise to three peaks of the ^{13}C-NMR spectrum.

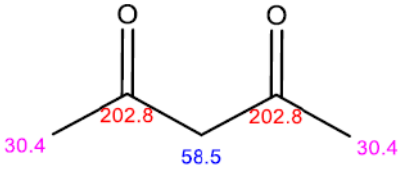
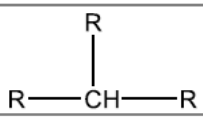
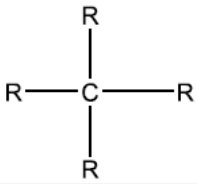
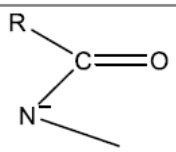
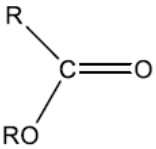
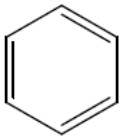
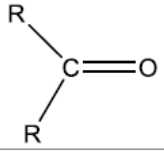


Figure 2. Structure of pentane-2,4-dione

Step 2: Identify the chemical shift value (δ) that appears in the ^{13}C-NMR spectrum. To predict the chemical shear value that appear in the ^{13}C-NMR spectrum, you can use the references in Table 1.

Table 1: Chemical shift ^{13}C-NMR

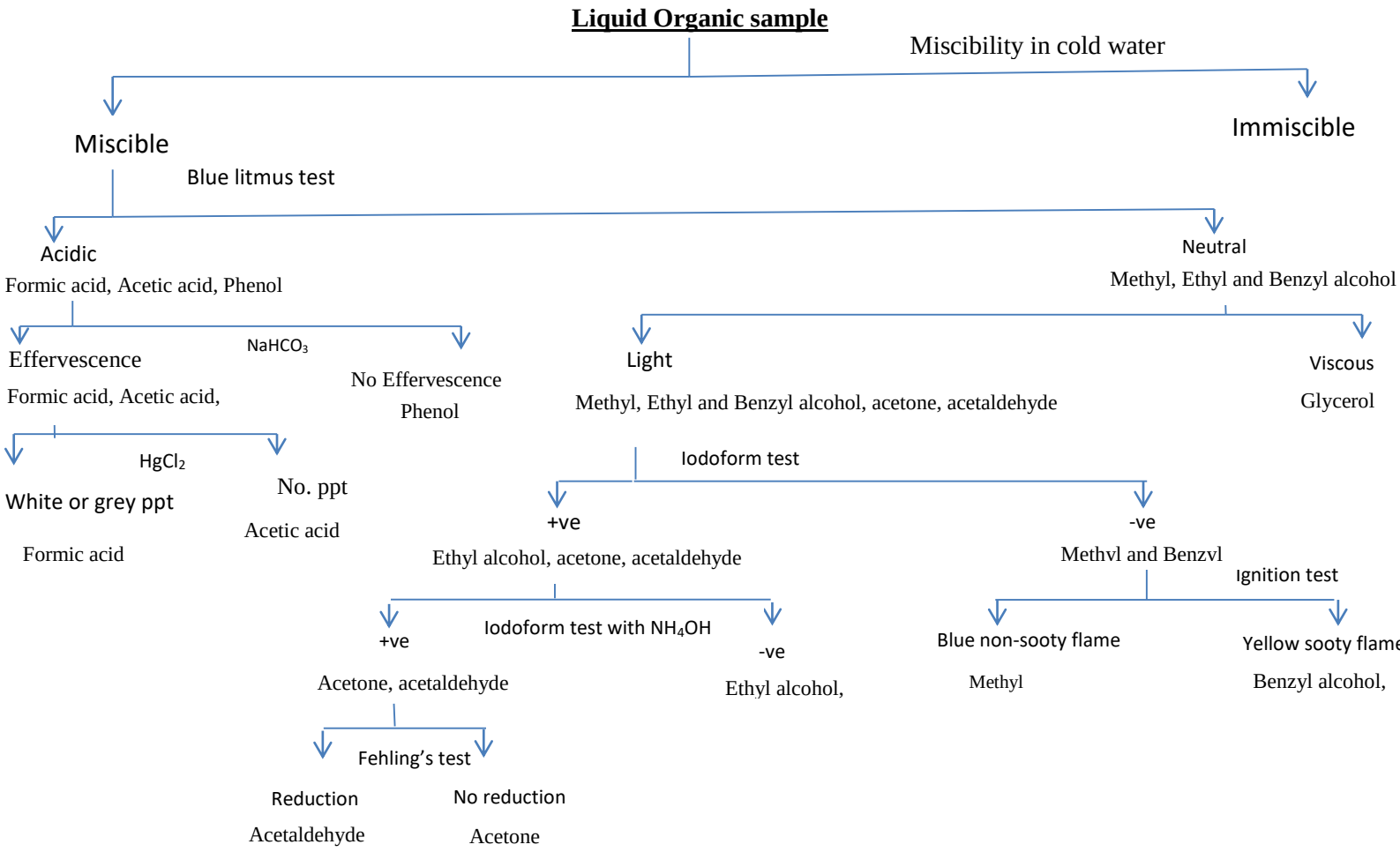
Type of Carbon	Approximate Chemical Shift (ppm)	Type of Carbon	Approximate Chemical Shift (ppm)
$(CH_3)_4Si$	0	C-I	0 – 40
R-CH_3	8 – 35	C-Br	25 – 65
R-CH_2-R	15 – 50	C-Cl	35 – 80
	20 – 60	C-N	40 – 60
	30 – 40	C-O	50 – 80
	65 – 85		165 – 175
	100 – 150		165 – 175
	110 – 170		205 – 220

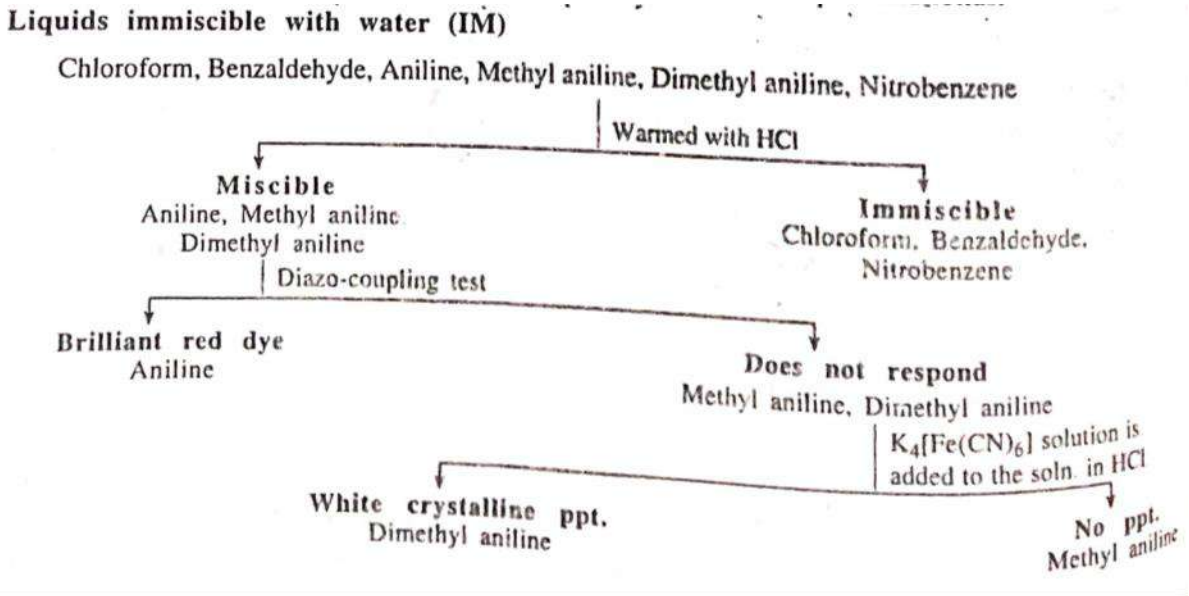
Step 3: The structure of an organic compound can be determined by combining the results of the analysis based on steps 1 and 2. First, after the amount of carbon and its chemical environment are known, the molecular formula of a compound can be determined. Then, the chemical shift values are compared with the chemical shift table values (Table 1) and the pieces of the molecules are combined to form a structural formula for the compound.

Besides there are DEPT spectra that gives the number of methyl C ($-CH_3$), methylene C ($-CH_2-$), methine (>CH-) and quaternary C (>C<) in the sample. Again there is 2D NMR which is developed to determine the structure of complex organic compounds.

Identification of liquid organic substance:

The following preliminary tests will be performed with the given sample;





2. Preparation of pure organic compound

I. Preparation of Iodoform from Ethanol:

Materials required:

Ethanol - 6.5ml

Sodium carbonate - 15g

Powdered iodine - 10g

Procedure: Ethanol (6.5ml) is added to sodium carbonate (prepared by dissolving 15g of sodium carbonate in 50ml of water) taken in a 100ml beaker. Powdered iodine (10g) is then added in small quantities at a time with constant stirring so that iodine dissolves in the mixture. The mixture is then warmed at 60-80℃ on water-bath and then cooled. The light yellow solid formed is filtered under suction, washed with ice water, recrystallized from 50% methanol or rectified spirit and dried.

II. Preparation of β-Naphthyl Benzoate:

Materials Required:

β –Napthol- 8g

Benzoyl chloride- 6ml

5% NaOH solution- 40ml

Procedure: β-Naphthol (8g) is dissolved in sodium hydroxide solution (40ml-5%) in a 100ml well-stoppered flask or bottle, cooled in ice-water, benzoyl chloride (6ml) is added to it and shaken well (vigorously) until the odour of benzoyl chloride disappears and white solid separates. It requires shaking of 15-20 minutes for the reaction to be completed. The separated solid is filtered under suction, washed with a little cold water, recrystallized from methylated spirit and dried.

III. Preparation of Dibenzalacetone:

Materials required:

Benzaldehyde - 8ml

Acetone - 4ml

Ethyl alcohol - 60ml

10% NaOH solution - 80ml

Procedure: Ethanol (60 ml), acetone (4 ml), Benzaldehyde (8 ml) and 10% aqueous NaOH solution (80 ml) are taken in a 250ml round-bottomed flask fitted with an air-condenser, boiled gently for 5 minutes with occasional shaking and the mixture is cooled in ice water. The solid separated is filtered under suction, washed thoroughly with cold water to make free from alkali, recrystallized from rectified spirit or ethyl acetate.

IV. Preparation of *m*-nitroaniline from *m*-Dinitrobenzene

Materials Required:

m-Dinitrobenzene — 10 g

Sodium sulphide — 16 g

Sulphur — 4 g

Procedure : Crystalline sodium sulphide (16 g) is dissolved in water (60 ml) taken in a 250 ml beaker; finely powdered sulphur (4 g) is added to it and the mixture is warmed until a clear solution is obtained. A mixture of *m*-dinitrobenzene (10 g) and water (400 ml) is heated in a 1,000 ml beaker until water boils gently. Sodium disulphide solution prepared previously is added drop wise from a dropping funnel to the suspension of *m*-dinitrobenzene in water, all the while vigorously stirring the mixture so that *m*-dinitrobenzene always remains in suspension and does not settle down at the bottom of the beaker. The addition must be completed within 30—40 minutes. The mixture is then boiled gently for 20 minutes and then cooled in ice. Then solid separated is filtered under suction, washed with cold water, boiled in dil. hydrochloric acid (prepared by mixing 4 ml of conc. HCl and 60 ml of water) in a 250 ml beaker, filtered to remove sulphur and remaining *m*-dinitrobenzene. The solution is heated with excess concentrated ammonia solution, filtered again, recrystallized from boiling water and the product is dried.

V. Condensation reactions

Materials Required:

Salicylaldehyde: 2.6 ml

Cyanoacetyl hydrazide: 2.5 g

Ethanol:

Procedure: 2.6 ml of salicylaldehyde is slowly added to 2.5 g of cyanoacetyl hydrazide in minimum volume of ethanol. The reaction mixture is magnetically stirred for 2 hours. The pale yellow product is filtered off, washed with water and ethanol, recrystallised from minimum volume of hot ethanol and dried in vacuum desiccator.

VI. Condensation reactions

Materials Required:

Benzaldehyde: 2.6 ml

Cyanoacetyl hydrazide: 2.5 g

Ethanol

Procedure: 2.6 ml of benzaldehyde is slowly added to 2.5 g of cyanoacetyl hydrazide in minimum volume of ethanol. The reaction mixture is magnetically stirred for 2 hours. The pale yellow product is filtered off, washed with water and ethanol, recrystallised from minimum volume of hot ethanol and dried in vacuum desiccator.

VII. Preparation of cyano acetyl hydrazide:

Materials:

Ethyl cyanoacetate - 10.63ml

Hydrazine hydrate - 4.85ml

Ethanol - 40ml

Procedure: 10.63ml (0.1mol) ethyl cyanoacetate and 4.8ml hydrazine hydrate (0.1mol) is mixed in a 250 ml beaker. To this 20 ml ethanol is added, and then the mixture is stirred at 0 - 10 ℃ for 10 mins. The white crystalline product formed is filtered, washed with ethanol and dried in a hot air oven at 60 ℃.

VIII. Knoevanagel condensation:

Materials required:

Acetyl acetone - 5.1ml

Salisaldehyde - 5.2ml

Ethanol - 25ml

Piperidine

Procedure: 5.1 ml (50 mmol) acetyl acetone and 5.2 ml (50 mmol) salisaldehyde are added to ~ 25 ml ethanol in a 250 ml beaker. One drop of piperidine is added to this mixture. The reaction mixture is then continuously stirred at room

temperature. The yellow precipitate is filtered with suction and recrystallized from ethanol.

CEM 296: Physical Chemistry Practical

1. Kinetics of Inversion of Cane-sugar by Polarimeter:

THEORY:

An optically active substance is one, which we can rotate the path of plane-polarised light. If it rotates the path towards right, it is called dextrorotatory and if rotation is towards left, the substance is levorotatory. In any case extent of rotation of a solution of an optically active substance depends on (1) its concentration,(2) temperature, (3) wavelength of the light used and (4) length through which light passes. At a given temperature and for a given wavelength it depends on (1) and (4).

APPARATUS AND CHEMICALS:

(a) Polarimeter with sodium lamp, (b) Volumetric flask, (c) Pipette,(d) Burette,(e) Cane sugar.

PROCEDURE:

An exactly 20% [20 g in 100 c.c.] cane-sugar solution is prepared. [During weighing you may weigh little more than 20 g, so that you get the scope of making exactly 20% by quantitative dilution.]

10%, 5% and 2.5% cane-sugar solutions are made by quantitative dilution from the 20% solution.

Vernier constant of polarimeter is determined.

Polarimeter tube is filled with water. Care should be taken, so that no air bubble remains. Now it is placed in the polarimeter and analyzer is adjusted both clockwise and anticlockwise to see subdued uniform illumination. The mean of these two readings should be zero. If it is other than zero, it is to be taken as

instrumental error and this reading is to be taken as zero-reading in all further works.

Now polarimeter tube is rinsed with 20% sugar solution; filled with it and reading is taken by above means.

The process is now repeated with 10%, 5%, and 2.5% solution.

A graph is drawn by plotting angles of rotation against percentage concentration of solution.

A suitable point on the graph paper is chosen and from concentration and angle of rotation corresponding to this point specific rotation is measured.

VERNIER CONSTANT DETERMINATION:

⋯division Vernier = ⋯division main scale

Vernier constant = (1^{-} ⋯) =

Zero-reading with water at ⋯^{o}

So instrumental error = ⋯^{o}

Length of tube = ⋯decimeter (1)

Solution	Clockwise reading			Anti-clockwise reading			Mean	Corrected
	Main	Vernier	Total	Main	Vernier	Total		
20%								
10%								
5%								
2.5%								

From graph rotation (α) at concentration ⋯is

So specific rotation = $\frac{100\alpha}{1C}$

CRITICAL COMMENTS:

For cane-sugar specific rotation in the temp. range 14°C to 30°C is 66.67°.

Above method can be utilized to determined concentration of unknown solution. In such case rotation (α) for the unknown solution is determined experimentally and then from (α) vs. (Cencn.) curve concn. of unknown solution can be known. Specific rotation of cane-sugar is independent of wavelength.

Polarimetric method can be used for kinetic study also. Thus inversion of cane-sugar catalysed by H^+, where optical rotation of solution changes with time can be studied polarimetrically.

2. Determination of concentration of Glucose-fructose in a mixture using polarimeter.

REQUIREMENTS:

1. APPARATUS:

(a) Polarimeter,(b) Measuring flasks, (c) Burette, (d) Pipette etc.

2. Chemicals:

(a) Glucose,(b) Fructose ,(c) Distilled water etc**.**

PROCEDURE

Prepare a 20% solution of given compound in distilled water. Prepare a series of different concentration – 20% to 2.5% from the stock solution. Determine zero reading of the polarimeter by filling the tube with distilled water. Then determine angle of rotation for each solution at least three times and record their average values. Plot observed angle of rotation [α] against C and determine the concentration of unknown solution from the calibration curve.

OBSERVATIONS:

1. Temperature of experiment T = …….^{o}C
2. Wave length of the light, λ = …..nm
3. Zero reading for water =….^{o}

OBSERVATION TABLE:

Choose angle rotation (α)

Concentration,(%)	1	2	3	4	Average
Mixture					

Calculation:

Graph:

Reaults:

The concentration of the mixture = ……

3. Conductometric determination of concentrations of KCl, HCl and NH_4Cl in a mixture.

THEORY:

In this method we determine the equivalence point where reaction is completed with the help of a conductometer that measures the change in conductance of solution produced by the ions in the solutions. At equivalence points, we measures the volume of base used to neutralize the acid ions completely in the solution. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

APPARATUS:

(a) Conductivity meter, (b) Conductivity Cell, (c) Burette, (d) Beaker Wash bottle etc.

CHEMICALS:

0.1 N NH_4Cl /KCl, 0.1N HCl, Distilled water, etc.

PROCEDURE:

Take 50 ml of given 0.1N NH_4Cl/KCl solution into a 150 ml beaker. Immerse conductivity cell into it. Titrate the solution with 0.1N HCl solution and measure the conductance at each stage of addition. The addition should be carried out at the rate of 0.5 ml. Plot Conductance against V. From the intersection of two linear lines and find out the volume of the titrant needed to neutralize the given solution.

OBSERVATION TABLE:

SL.	0.1N NH_4Cl /KCl (V,ml)	Conductance, mho
1.		
2.		

3.		
4.		
5.		
6.		
7.		
8.		
9.		

Graph: Plot conductance against V.

CALCULATION:

Normality of NaCl/KCl from graph

$$N_{NaCl} \times V_{NaCl} = N_{HCl} \times V_{HCl}$$

$$N_{NaCl} = \frac{0.1 \times V2(from\ graph)}{50}$$

Results:

1) Concentration of NaCl/KCl in a given solution = ……N

4.Verify the Onsagar equation using KCl, K_2SO_4 and $BaCl_2$ as electrolytes and determine their Λ_0 values.

THEORY:

The Debye-Huckel- Onsagar equation or simply onsagar equation for uni-univalent electrolytes is given by the expression

$$\Lambda = \lambda_0 - (A+B\lambda_0)\sqrt{C}$$

Where, λ = Equivalent conductance of conc^n 'c' gm-eqv litre

λ = Equivalent conductance at infinite dilution

$$A = \frac{82.4}{(DT)^{1}/_{2n}} \quad \text{and} \quad B = \frac{8.20\times10^{5}}{DT^{3}/_{2}}$$

D= Dielectric constant of the solvent

T= Abs temperature

Ƞ= Viscosity co-efficient of solvent

Thus for aqueous solution & at constant temperature (room temperature) A & B both are constant.

The above equation is mainly applicable for univalent electrolyte (e.g ; KCl) and nearly applicable for uni-bivalent & bi-univalent (e.g; $BaCl_2$) electrolyte.

So, If we get straight lines with positive intercept & negative slope by plotting 'λ' against '$\sqrt{c}$' for each KCl, K_2So_4 & $BaCl_2$, then we can say the onsagar equation is verified and applicable for KCl, K_2SO_4 & $BaCl_2$ type electrolytes, From the intercepts we will get then λ_0 values for KCl, K_2SO_4 and $BaCl_2$ easily.

$$\Lambda = \frac{1000K}{C}$$ where K=Specific Conductance

& $K = L\lambda$

$$\lambda = \frac{1}{R}$$ L= Cell constant, λ= Conductance, R=Resistance

APPARATUS REQUIRED:

a) Conductivity meter
b) Beaker- 100ml

c) Measuring cylinder-50 ml

CHEMICALS:

KCl, K_2SO_4, $BaCl_2$

PROCEDURE:

1) Prepare 100ml (N/10) KCl, K_2SO_4, $BaCl_2$ solution each.
2) From above (N/10) solution prepare 250ml exact (N/10) KCl, K_2SO_4 & $BaCl_2$ solution each.
3) From exact (N/10) solution prepare N/200,N/300,N/400,N/500, N/600 of 60ml each KCl, K_2SO_4 & $BaCl_2$ solution each.
4) Record the room temperature.
5) Standardized the 'Conductivity Meter' using 0.1(N) KCl solution at room temperature.
6) Take approx 60ml N/10 KCl solution in a clean & dry 100ml beaker & immerse in it dry clean cell & note that reading i.e, specific conductance same experiment perform using N/200, N/300, N/400, N/500 & N/600 solution.
7) Perform the procedure (6) for K_2SO_4 & $BaCl_2$.
8) Plot 'λ' against '√C' for each salt on separate graph paper.
9) Calculate λ_0 for each salt from graph.
10) Interpret the result.

5. Determination of CMC of a surfactant in aqueous solution by conductometric method.

THEORY:

Ionic surfactants like Sodium Decocyl Sulphate (SDS), in aqueous solution show difference conductometric behaviour below and above its CMC due to its different degree of ionization. Below CMC surfactant molecules behave like normal electrolyte in aqueous solution. If one assumes that aqueous SDS solution

obeys Kohlrausch's law then specific conductance (k) of the solution (Below CMC) can be represented as

$$K = (\lambda_{Na} + \lambda_{DS})[SDS] \quad \ldots\ldots(1)$$

Where, λ_{Na} is the ion conductance of sodium ion (Na^+) and λ_{DS} is the ion conductance of decodyl sulphate ion, [SDS] is the concentration of SDS solution (in moles/ml).

On the other hand specific conductance of the SDS solution above CMC have contribution (1) from the ions of free SDS molecules, (2) from the charged micelles and (3) from the from miceller counter ions then,

$$[S] = \alpha\{[SDS] - CMC\}$$

And $k = (\lambda_{Na} + \lambda_{DS})CMC + \lambda_M[micelles] + \alpha\lambda_{DS}\{[SDS]-CMC\}$ .....(2)

Let N_{agg} is the aggregation number of micelle and assume that the contribution of the micelle to the specific conductance is the same as that of the monomers with charge present in the aggregate. So, $\lambda_M = \alpha N_{agg}\lambda_{DS}$ and [micelles] = $\{[SDS]-CMC\}/N_{agg}$

Therefore, equation (2) becomes,

$$K = (\lambda_{Na} + \lambda_{DS})(1- \alpha)CMC + \alpha(\lambda_{Na} + \lambda_{DS})[SDS] \quad .....(3)$$

Plot of k vs [SDS] below CMC gives a straight line with slope $(\lambda_{Na} + \lambda_{DS})$ and plot of k vs [SDS] above CMC value can be obtained from the intersection of the two straight lines defined at equation (1) and (3). From the ratio of the slops of straight lines above CMC and below CMC, degree of miceller ionization (α) can be obtained. With the knowledge of the intercept of the straight line above CMC.

APPARATUS:

Conductivity meter, 250 mL volumetric flask- 1, 100 mL volumetric flask-3, 10 mL graduated pipette-1, 25mL pipette-1.

CHEMICALS:

SDS (Sodium Dodecyl Sulphate) , KCl.

PROCEDURE:

(1) Prepare 250mL nearly 0.1 (N) [slightly higher than 0.1(N)] KCl solution by accurate weighing and prepare 100 mL of an exact 0.1(N) KCl solution by proper dilution .Prepare 100 mL of an exact 0.01(N) KCl from the exact 0.1(N) KCl solution. Determine the cell constant of the conductivity cell using the exact 0.1 (N) KCl and the prepared exact 0.01 (N) KC solution. With the help of the literature value of specific conductance of these solutions at experimental temperature, calculate the mean value of the cell constant and use it subsequently. Measure the conductance of conductivity water also.

(2) Prepare 100 mL 50 mM SDS solution in conductivity water by accurate weighing in a volumetric flask.[Required weight of SDS= 1.442 g]

(3) With the help of 25mL pipette, take 50 mL of this solution in the clean and dry conductivity cell and measure its conductance.

(4) Use 10mL piette to take out 10 mL of the 50 mM SDS solution from the conductivity cell. Pipette out 10mL of the conductivity water into the conductivity cell to make the conductivity cell to make the solution exactly 40 mM in situ.

(5) Measure conductance and hence specific conductance of SDS solution of different concentration following step by step dilution-extraction as in step 4.

(6) Plot specific conductance vs. SDS concentration and find out the CMC of SDS corresponding to the intersection of two straight and their slopes. Determine of miceller ionization (α).

(4) EXPERIMENTAL RESULT:

(1) Experimental temperature:
(2) Preparation of 250 mL- 0.1(N) [slightly higher than 0.1(N)] KCl solution:
(3) Preparation of 100 mL exact 0.1(N) KCl solution:

Determination of cell constant:

Concentration of KCl solution	Conductance (mho)	Specific Conductance (mho cm^{-1})	Cell constant (cm^{-1})	Mean cell constant (cm^{-1})
0.01(N)				
0.1(N)				

(5) Determination of specific conductance of different SDS solutions:

Conductance of conductivity water:

Concentration of SDS solution (mM)	**Observed Conductance (mho)**	**Corrected specific conductance (mho cm^{-1})(k)[Observed conductance –Coductance of conductivity water×mean cell constant)**

Plot of 1 vs [SDS] will give two straight line intersections at a point corresponding to CMC of SDS. Determine degree of miceller ionization (α) from the ratio of the slope of the straight line after CMC and the slope of the straight line before CMC.

6. Potentiometric titration of halide mixture (Chloride, Bromide and Iodide).

THEORY:

According to the Nernst equation, the potential of the electrode depends upon the concentration of the ions reversible to the electrode and are in contact with it.

$$E_{cell} = E^0_{cell} - RT/nF \ln Q \ldots\ldots..(1)$$

The concentration of the ions can be changed by the neutralization, precipitation or a redox reaction and hence electrode potential varies accordingly. The end point coincides with a very rapid change in the potential of the indicator electrode. The potential change near equivalent point is a rapid as compared to other points

of the course of the titration. The end point can be determined accurately and precisely from the plot of E against V and plot of ΔE/ΔV against V show in the figure. The end point can be obtained precisely from the by extrapolation of two linear branches. The shape of the curve is depending on the type of transitions.

APPARATUS:

(a) Potentiometer, (b) SCE and silver electrode, (c) Burette, (d) Beaker wash bottles etc.

CHEMICALS:

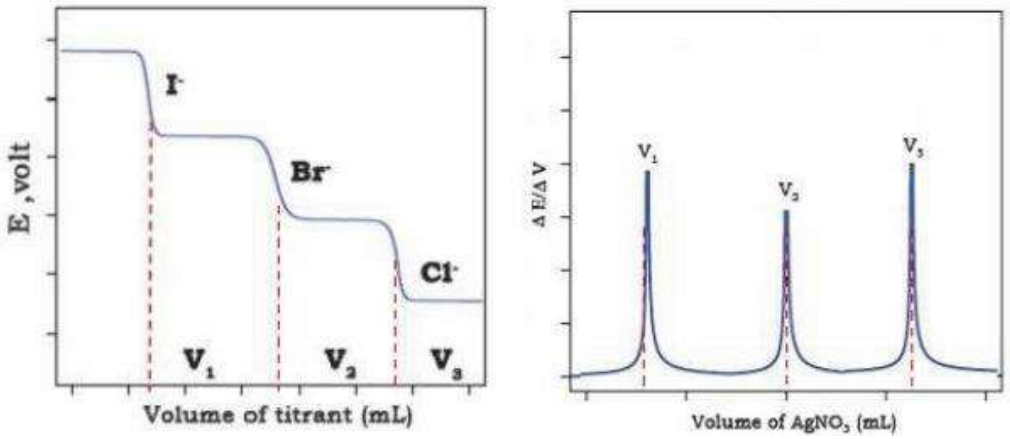
0.1 N $AgNO_3$, mixture of KCl, KBr, and KI, quinhydron powder, distilled water etc.

PROCEDURE:

Take 50 ml of a given mixture of halides into a 150 ml beaker. Add about 0.5 g quinhydron powder and mix well. Titrate the solution with 0.1 N $AgNO_3$ solution and measure the potential at each stage addition. The addition should be carried out at the rate of 0.5 ml. plot E against V and ΔE/ΔV against V. Determine the equivalence point by extrapolating the two linear lines and determine end point.

Sl.	0.1N $AgNO_3$ (V,ml)	E (volt)	ΔE (volt)	ΔV (ml)	ΔE/ΔV
1	0.0				
2	0.5				
3	1.0				
4	1.5				
5	2.0				
6	2.5				
7	3.0				
8	3.5				
9	4.0				

Graph: Plot E against V and ΔE/ΔV against V



Calculation

❖ **Normality of KI solution**

$$KI = AgNO_3$$

$$N_1V_1 = N_2V_2$$

$$N_{KI} = \frac{0.1 \times V_2 \text{ (from graph a)}}{50}$$

❖ **Normality of KBr solution**

$$KBr = AgNO_3$$

$$N_1V_1 = N_2V_2$$

$$N_{KBr} = \frac{0.1 \times V_2 \text{ (from graph a)}}{50}$$

❖ **Normality of KCl solution**

$$KCl = AgNO_3$$

$$N_1V_1 = N_2V_2$$

$$N_{KCl} = \frac{0.1 \times V_2 \text{ (from graph a)}}{50}$$

Result:

1) Normality of each halide in mixture KI, KCl and KBr .....N

7. Determine the E_0 value of Ag^+/Ag electrode and activity coefficients of different aqueous $AgNO_3$ solutions potentiometrically.

APPARATUS REQUIRED:

(a) Potentiometer with reference calomel electrode and agar-KNO_3 salt bridge
(b) Silver electrode
(c) 100 mL vol. flask- 1
(d) 100 mL beaker -1
(e) Burette-1
(f) Pipette 10 mL-1
(g) 250 mL glass bottle

CHEMICALS:

KCl, $AgNO_3$

PROCEDURE:

(1) Prepare 100 mL of (N/10) $AgNO_3$ solution in deionized water.
(2) Prepare 100 mL of (N/10) standard KCl solution by accurate weighing. Determine the volume of 50 drops from the burette and calculate the volume of one drop.
(3) Standardize the potentiometer with a standard cell.
(4) Take an aliquot of 10 mL of the prepared- (N/10) solution of $AgNO_3$ in a beaker. Add sufficient amount of deionized water and dip a clean silver electrode into the solution. Connect this half-cell with a saturated calomel electrode through an ager-KNO_3 salt bridge.
(5) Measure the EMF of the experimental cell.
(6) Add the (N/10) KCl solution from the burette dropwise into the $AgNO_3$ solution taken in the beaker, stir gently and measure the EMF each time. Take at least 4 readings after the end point.
(7) Plot the EMF versus the number of drops of KCl solution added.
(8) Find the Ksp of AgCl and the concentration of the prepared $AgNO_3$ solution from the graph.

EXPERIMENTAL RESULT:

(1) Room temperature:
(2) Preparation of 100 mL $AgNO_3$ solution (N/10):
(3) Preparation of 100 mL (N/10) KCl solution:
(4) 50 drops of KCl solution = …….. mL KCl.
(5) Potentiometric titration of (N/10) $AgNO_3$ solution vs (N/100 KCl solution:

Volume of (N/10) $AgNO_3$ solution	**No. of drops of KCl solution added**	**Total no. of KCl solution added**	**E_{cell} (volt)**
10 mL			

Graph plotting: Plot the EMF (**E_{cell}**) vs the total number of drops of KCl solution added. From the inflection point of the graph the number of drops of KCl solution and hence the volume corresponding to the equivalence point.

Calculation:

At equivalence point, …… drop KCl solution = …..mL KCl = V_{KCl}

Strength of AgNO3 solution (S_{AgNO3}) = ($V_{KCl} \times S_{KCl}$)/ V_{AgNO3})

Again, $E_{cell}(eqv.) = E^0_{Ag^+|Ag} + \frac{2.303RT}{2F} \log K_{sp} - E_{SCE}$

Or, K_{sp}= anti log[{$E_{cell}(eqv.) + E_{SCE} - E^0_{Ag^+|Ag}$} × $\frac{2F}{2.303RT}$

8. Determine the standard potential of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode by potentiometer.

THEORY:

The electrode potential of the following redox system

$$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$$

is given by

$$E = E^0 - \frac{RT}{F} \ln {}^{a}Fe(CN)_6^{4-} / {}^{a}Fe(CN)_6^{3-}$$

[where a= activity & E^0 = Standard potential(reduction) of $Fe(CN)_6^{4-}/ Fe(CN)_6^{3-}$ system.]

$$\text{Or, } E = E^0 + \frac{RT}{F} \ln [Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}] + \frac{RT}{F} \ln {}^{f}Fe(CN)_6^{3-}/ {}^{f}Fe(CN)_6^{4-} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Where, f= activity co-efficient

Now from Debye Hückel limiting law

$$\log f = -AZi^2\sqrt{u} \text{ (for dilute solution)}$$

where u= ionic strength = $1/2 \, \Sigma_i \, C_i Z_i^2$

where C_i= Molar concentration of i^{th} ionic species, Z_i= valency

A= constant for a particular temperature & solvent.

$$\ln {}^{f}Fe(CN)_6^{3-}/ {}^{f}Fe(CN)_6^{4-} = A[Z^2Fe(CN)_6^{4-} - Z^2Fe(CN)_6^{3-}]\sqrt{u} = K\sqrt{u} \quad \text{.....(2)}$$

Where K is another constant.

If an equimolar mixture of ferrocyanide and ferricyanide is taken,

Where , $Fe(CN)_6^{3-}/ Fe(CN)_6^{4-} = 1$ from equation (1) &(2)

We get, $E = E^0 + K\sqrt{u}$

To find out E^0, the cell used for the experiment is saturated

Calomel ‖ $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$| pt

The observed EMF of above cell is given by

$$E_{obs} = E - E_{cal}$$

$$= E^0 + K\sqrt{u} - E_{cal}$$

$$= E^0 - E_{cal} + K\sqrt{u}$$

Where, E_{cal} = reduction potential of saturated calomel electrode at lab temperature.

Plot of E_{obs} against $\sqrt{u}$ for different solutions will yield a straight line with intercept as $E^0 - E_{cal}$. Thus, knowing E_{cal} at lab temperature, E^0 can be found out at that temperature.

E_{cal} (at lab temperature, say t°c) = E_{cal}(at 25°C) – 0.00076(t-25)

= 0.2415 – 0.00076 (t-25) volt.

APPARATUS REQUIRED:

(a) Potentiometer
(b) 100 mL vol. flask- 1
(c) 100 mL beaker -1
(d) Burette-1

(e) Pipette 10 mL-1
(f) 250 mL glass bottle

CHEMICALS:

$K_4Fe(CN)_6$, $K_3Fe(CN)_6$,$K_2Cr_2O_7$, Starch indicator, Zn-salt, Thiosulphate solution.

PROCEDURE:

1) Prepare 100 mL (N/10) (slightly higher) $K_4Fe(CN)_6$ solution by accurate weighing. From this prepare 100 ml exact (N/10) $K_4Fe(CN)_6$ solution.
2) Prepare 100 ml (N/10) $K_2Cr_2O_7$ solution by accurate weighing.
3) Standardise~(N/10) thio solution by standard $K_2Cr_2O_7$ solution.
4) Standerdise~(N/10) (slightly higher) $K_3Fe(CN)_6$ solution by standard thio solution iodometrically in acid medium in presence of Zn^{++} salt using starch as an indicator. Then from this prepare 100 ml exact (N/10) $K_3Fe(CN)_6$ solution.
5) Prepare 250ml exact (N/100) mixture solution with respect to both ferrocyanide & ferricyanide. Then from this prepare (N/200), (N/300), (N/400), (N/500) & (N/1200) of 60ml each.
6) Measure the EMF's of the cells by potentiometer contained a saturated calomel electrode as one electrode & pt-electrode in prepared mixture solutions as another electrode.
7) Record the lab temperature.
8) Calculate the ionic strength of different mixture solutions.
9) Plot 'E_{obs}' against $\sqrt{u}$. From intercept calculate E^0 of $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ redox system.
10) Interpret the result.

9. Determine the dissociation constants (K_1, K_2, and K_3) of H_3PO_4 by pH meter.

THEORY:

H_3PO_4 is a tribasic acid, it dissociates in three steps-

$$H_3PO_4\,(K_1) \rightleftharpoons H_2PO_4^- + H^+$$

$$H_2PO_4^-(K_2) \rightleftharpoons HPO_4^{2-} + H^+$$

$$HPO_4^{2-}\,(K_3) \rightleftharpoons PO_4^{3-} + H^+$$

Where, K_1, K_2, K_3 are 1st, 2nd, 3rd dissociation constant respectively.

If we titrate H_3PO_4 by NaOH solution using P^H-meter after addition of small amount of NaOH solution the buffer system H_3PO_4/NaH_2PO_4 is formed and the P^H will be

$$P^H = P^k{}_1 - \log [NaH_2PO_4]/[H_3PO_4]$$

Where $P^k{}_1$of the first acidic hydrogen has been neutralized.

At that moment, $[NaH_2PO_4] = [H_3PO_4]$.

So, $P^H = P^k{}_1$ ….(1)

At the first equivalence point, the solution contains only NaH_2PO_4,which is an ampholyte, hence

$$P^H = ½\ P^k{}_1 + P^k{}_2 \qquad \ldots\ldots(2)$$

Similarly, after 1st equivalence point when more alkali is added, the solution contains the buffer mixture $NaH_2PO_4/\ Na_2HPO_4$, the P^H is given by.

$$P^H = P^k{}_2 + [\ NaH_2PO_4]/\ [Na_2HPO_4]$$

When total 1.5 equivalent of alkali has been added, then

$$[Na_2HPO_4] = [\ NaH_2PO_4]$$

So, $P^H = P^k_2$ .....(3)

Similarly, at the second equivalence point, the solution contains the ampholyte Na_2HPO_4 only, then $P^H = ½ P^k_1 + ½ P^k_2$ ……(4)

So, if we plot P^H against volume f alkali added we will get three inflextion point for complete neutralization of three hydrogens of H_3PO_4. By using equation (1), (2), (4) or (2), (3), (4),we will have P^k_1, P^k_2, P^k_3. From the volume of NaOH solution required for complete neutralization we will get strength of H_3PO_4 solution.

EXPERIMENTAL DATA:

(1) Temperature determination:

TABLE-1

Temp. before expt.(ºC)	Temp. after expt.(ºC)	Mean Temp.(ºC)

(2) Preparation of 250ml 0.3(M) NaOH solution:

TABLE-2

Weight taken (gm)	Weight to be taken (gm)	Strength

(3) Preparation of 100 ml 0.1(N) oxalic acid solution:

TABLE-3

Weight taken (gm)	Weight to be taken (gm)	Strength

(4) Preparation of 100 ml 0.1(M) H_3PO_4 solution from 15(N) H_3PO_4:

TABLE-4

Volume of H_3PO_4 (ml)	Water(ml)	Total Volume(ml)

(5) Standarisation of NaOH solution by oxalic acid solution:

Table-5

No. of obs.	Volume of oxalic acid(ml)	Burette reading(ml)			Mean volume(ml)	Strength (N/10)
		Initial	Final	Difference		

(6)P^H metric titration for tribasic acid (H_3PO_4):

No. of drops of alkali	P^H of the solution	No. of drop of alkali	P^H of the solution

Calculation:

When 50% of first acidic hydrogen has been neutralized then from the graph:

pk_{a1} =

k_{a1} =

pK_{a2} corresponding to that PH at which 1.5 equivalent of alkali has been added =

pk_{a2}=

k_{a2}=

From graph , equivalence point at

$pk_{a3}=1/2(pk_{a1}+pk_{a2})$

pk_{a3}=

k_{a3}=

For Table-2

1000ml 1(N) NaOH solution contain ……. gm NaOH.

250ml 0.3(N) NaOH solution contain ……..gm NaOH

Strength of NaOH solution=…….(N/10)

For Table -3

1000ml 1(N) oxalic acid solution contain ……gm oxalic acid.

100ml(N/10) oxalic acid solution contain ……gm oxalic acid.

Strength of oxalic acid=…… (N/10).

For Table -4

$V_1S_1=V_2S_2$

= ml

Volume of ….(N) H_3PO_4 needed=

For Table-5

$V_1S_1=V_2S_2$

S_2=……(N/10)

10. Study the kinetics of Iodination of acetone spectrophotometrically

THEORY:

The process of the reaction between acetone and iodine can conveniently be followed colorimetrically making use of the fact that the presence of iodine, mainly as trioxide ion [IO^{3-}] imparts reddish brown colour to the reaction mixture. The colour fades to pale yellow as the reaction proceeds due to the consumption of iodine. Isolation method can be used conveniently taking both

acetone and the acid in large excess. The order of the reaction is one each with respect to acetone & the acid and zero with respect to iodine.

APPARATUS REQUIRED:

a) Beaker
b) Pipette
c) Colorimeter
d) Stop watch

CHEMICALS:

Pure acetone, Iodine solution, sulphuric acid

PROCEDURE:

Diluted 10ml of pure acetone to 100ml and mixed each of acetone solution, 0.5M H2SO4 and water. Added 10ml of iodine solution started the stop watch. The wavelength is set at 530nm in colorimeter. Transferred the reaction mixture into the Erma tube and recorded the absorbance using water as the blank at suitable intervals of time. Repeated the experiments with the composition of reaction mixture listed below.

	I	II	III	IV
Acetone (ml)	5	10	5	5
0.01M I_2 solution (ml)	10	10	5	10
0.5M H_2SO_4 (ml)	5	5	5	10
Water (ml)	5	0	10	0

Plotted the absorbance Vs time for different reaction mixtures. The plots are linear with a constant slope showing the reaction to be zero order with respect to iodine.

Result:

Rate constant (1) = …….. $min^{-1}dm^3mol^{-1}$

Rate constant (2) = …….. $min^{-1}dm^3mol^{-1}$

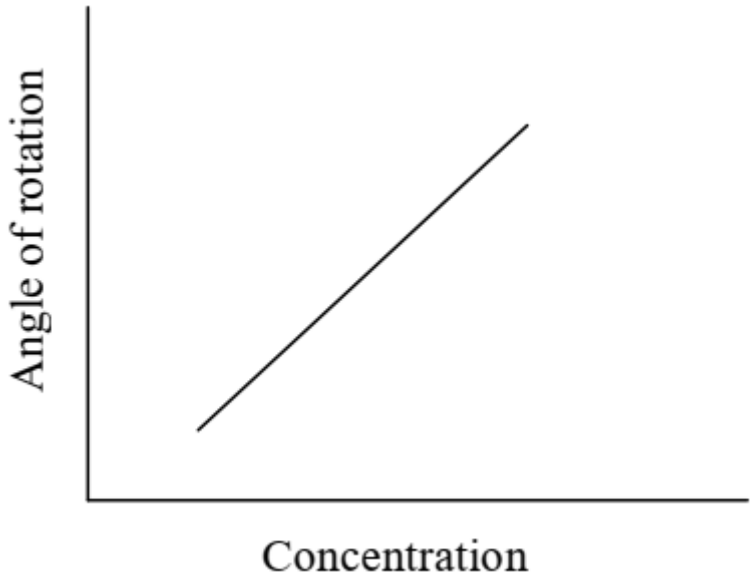
Rate constant (3) = …….. $min^{-1}dm^3mol^{-1}$

Rate constant (4) = …….. $min^{-1}dm^3mol^{-1}$

The rate constant (II) is twice that of rate constant (I), when acetone concentration is doubled. The rate constant (III) is approximately equal to the rate constant (I), when iodine concentration is doubled. The rate constant (IV) is twice as that of rate constant (I) when sulphuric acid concentration is doubled. Hence the reaction is first order each respect to acetone and sulphuric acid and zeroth order with respect to iodine.

Concentration	Angle of rotation	Specific rotation
5%		
10%		
15%		
20%		
25%		

Specific rotation $[\alpha] = \frac{a \times 100}{c \times 1}$



11.Determination of composition of complexes (Ferric-salicylate complex/Ferrous-orthophenanthroline complex) by Job's method.

THEORY:

Suppose, a metal ion(M) and a ligand(L) react in dil. Solution to form only one complex of appreciably high stability constant (β_{mn}) according to -

$$mM+nL=MmLn \quad \ldots\ldots\ldots\ldots(1)$$

$$\beta_{mn}=\frac{[MmLn]}{[M]^m[L]^n} \quad \ldots\ldots\ldots\ldots(1a)$$

Now if a series of solution of some volume are prepared by mixing varying volumes of equimolar solutions of the metal and the ligand in such a manner that the total volumes of equimolar solutions of the metal and the ligand remain fixed, then the mole fractions of the two reactants vary in a continuous manner and conc^n of the complex passes through maximum value. Any special property of the metal ligand mixtures such as color intensity which is directly proportional to the concentration of the complex formed. In the solution also varies in a continuous manner and passes through a max at a certain ratio of the

mole fractions of the metal to that of the ligand such ratio of the mole fractions of metal : ligand, corresponding to the maximum formation of the complex as indicated by the maximum value of the physical property corresponding to the metal:ligand ratio in the formula of the complex.

If vml of the ligand (L) of conc^n 'C' mole/lit (where V‹1ml) is mixed with (1-V) ml of the metal (M) also of conc^n 'c' mole/lit, so that the total volume after mixing is 1ml, then at equilibrium and if only one complex (M_mL_n) of appreciably high stability is formed, the mass balance equations for the ligand and the metal may be expressed according to (2) & (3) respectively,

$$Vc=[L]+n[M_m+L_n]\ldots\ldots\ldots(2)$$

$$(1-v)c=[M]+m[M_mL_n]\ldots\ldots\ldots\ldots(3)$$

When the terms within [ ] represents the equilibrium concentrations of the respective species. Here v & (1-v) represents the equilibrium concentrations of the mole fractions of the ligand and metal respectively.

Substituting for [L] and [M] from equation (2) & (3) in the expression (1a) for β_{mn}, obtains.

$$\beta_{mn}=\frac{[MmLn]}{\{(1-v)c-m[MmLn]\}^m\{vc-n[MmLn]\}^n} \ldots\ldots\ldots\ldots\ldots\ldots(1b)$$

Thus equations (1b),(2),and (3) shows that equilibrium concentration of the complex , [MmLn] is a linear function of the mole fraction (v) of the liquid, i.e, [MmLn]=f(v) ……(4)

Therefore the necessary condition for the concentration of the complex to pass through a maximum at a certain value of mole fraction (v_{max}) of the ligand, is that the first derivative of [MmLn] w.r.t v at $v=v_{max}$ is zero, i.e

$\frac{d}{dv}[MmLn]v=v_{max}=0\ldots\ldots\ldots(5)$

Now differentiating equations (2) and (3) w.r.t v and then subjecting to above condition (equation 5),one obtains, $(\frac{d[L]}{dv})v=v_{max}=c$ ……..(2a),

$$(\frac{d[M]}{dv})v=v_{max}=-c \ldots\ldots\ldots\ldots(3a)$$

Finally differentiating the logarithmic form of (1a) and using the equation (2a) and (3a), one obtains at $v=v_{max,}$ $m[L]=n[M]$……..(6)

Now multiplying equation (2) with m and equation (3) with n and replacing v with v_{max} and [MmLn] with $[MmLn]_{max}$ one may rewrite these two equations as-

$$mV_{max}.c=m[L]+mn[M_mL_n]_{max}\text{……(2b)}$$

$$n(1-V_{max})c=n[L]+mn[M_mL_n]_{max}\text{……(3b)}$$

Now applying the equation (6) and subtracting (3b) from (2b) and then rearranging, one obtains: $m/n = \frac{1-Vmax}{Vmax}$……(7)

Therefore, the metal:ligand ratio (m:n) in the complex, M_mL_n, may be determined by experimentally the mole fraction V_{max} of the ligand at which the corresponding concentration of complex passes through a max, V_{max} values for (1:1),(1:2) and (1:3) complexes as follows:

m:n	1:1	1:2	1:3
V_{max}			

If physical property (x) of the solution is a linear function of the concentration of the complex ,then at equilibrium

$$X=\{x_m[M]+x_L[L]+x_{mn}[M_mL_n]\}\text{……..(8)}$$

Where X_m, $X_{L,}$ and X_{mn} are the intensive factors for M,L and M_mL_n and l is a geometric factor of the measuring instrument .For colour intensity as the index property X_m, X_L and X_{mn} are the molar extinction co-efficient for M,L and M_mL_n for λ_{max} of the complex and l is the optical path length of the solution. If no complex is formed and the value of x under this condition be equal to'X^0' then

$$X^0=\{X_m[M]+X_L[L]\}l\text{ ……(9)}$$

Therefore, change in the physical property (X) due to complex formation will be, $\Delta X=(X-X^0)$ ……(10)

Now substituting for [L] and [M] in equations (8) and (9) using equations (2) and (3), the equation (10) is transferred to:

$$\Delta X = [MmLn](X_{mn} - mx_m - nx_L)l \ldots\ldots\ldots\ldots (10a)$$

Thus the change in the physical property (ΔX) of the solution is a linear function of the concentration of the complex, provided $(X_{mn}-m)(M-nx_L)\neq 0$, comparing equation (10a) with equation (4) one may conclude, ΔX=f(v)….10b, i.e, change in the physical property (ΔX)of the solution is a linear function of the mole fraction(V) of the ligand. Therefore, ΔX also passes through a maximum at $V=V_{max}$, at which [MmLn] is maximum plots of ΔX vs V show maximum at V=0.5,0.67 and 0.75 for (1:1), (1:2) and (1:3) metal: ligand complexes.

PROCEDURE:

1. Prepare 500ml 0.002(m) HCl solution.
2. Prepare 100ml 0.002(m) ferric ammonium solution in 0.002(m) HCl solution.
3. Prepare 100ml 0.002 (m) salicyclic acid in 0.002 (m) HCl solution.
4. Label 9 test tube 1-9 and prepared solution as the table(5).
5. Taken test tube no-2 and determine it's O.D using different filters from 420-470 nm.
6. Plotted O.D vs λ and found λ_{max}.
7. Set the colorimeter at the λ_{max} and taken O>D reading of all the solution.
8. Plotted O.D vs salicylic acid mole fraction and found the maximum absorbance. Find the ratio of vol. of Fe(III) and salicylic acid for this solution and determine the composition of the complex.

12.Determine the rate constant and the order of the reaction of $KBrO_3$ & KI in acid medium.

THEORY: The process of oxidation reduction between $KBrO_3$ and KI in acid medium is found to be second order one

$$KBrO_3+6KI+6HCl=KBr+KCl+3I_2+3H_2O$$

Let, the individual conc^n of the reactants are equal, say 'a' gm equiv/lit and if 'X' be the gm-equiv/litre of the reactant product in time 't' seconds, then the rate of the reactant →

$\frac{dx}{dt} = K(a-x)^2$ ……(1)K=Rate constant of the reaction

Integrating and applying condition, t=0,x=0, we get $K= \frac{1}{t}\frac{x}{a(a-x)}$

$$\text{Or, } \frac{V_t}{V_0-V_t} = kat$$

If we plot $(\frac{X}{a-X})$ against t and get a straight line passing through origin, then we can say that the order of reaction is two and from the slope of the straight line we will get the rate constant of the reaction. Again, if we plot 'x' against 't' for two reactions of different initial concentration say 'a_1' and 'a_2' and if 't_1' & 't_2' are the time required to reduce the individual concentration by a definite fraction then,

$$t_1/t_2= (a_2/a_1)^{n-1} \text{ because } t_{1/2} \propto \frac{1}{a^{n-1}}$$

Where, n=Order of the reaction

Or, (n-1) log (a_2/a_1)=log (t_1/t_2)

$$\text{Or, } n=1+\frac{\log\frac{t_1}{t_2}}{\log\frac{a_2}{a_1}} \quad \text{.....(II)}$$

From the above equation, we can easily calculate the order of the reaction, i.e, 'n'

PROCEDURE:

I. Prepare 100ml 0.1(N) $K_2Cr_2O_7$ solution by accurate weighing.
II. Prepare 100ml (N/20) (slightly higher) $KBrO_3$ solution by accurate weighing. Then prepare from it 100ml exact $KBrO_3$ solution.
III. Prepare 100ml (N/20) (slightly higher) KI solution by accurate weighing. Then prepared from it 100ml exact (N/20) KI solution.
IV. 250ml (N/20) $Na_2S_2O_3$ solution was prepared and standardize it against standard (N/10) $K_2Cr_2O_7$ solution using starch as a indicator. From above prepare 500ml exact N/100 thio solution.
V. 500ml (N/10) HCl solution was prepared.
VI. Perform two sets of experiments using composition of table 8. For each set the initial time should be noted (or stopwatch should be started) just at the half discharge of KI solution. Take aliquot from each of the sets after an interval. 3 minutes, nothing the time of half discharge of the aliquot, the 100ml (approx) ice cold water in a 250ml conical flask, then it was titrated quickly by exact (N/100) thio solution using starch as indicator.
VII. Room temperature was noted.

VIII. 'V_t' against 't' curve for each set on a single graph paper was plotted and find t_1 t_2 from the graph and the order of the reaction was calculated.

IX. $V_t/(V_0-V_t)$ against 't' was plotted for each set on a single graph and slope of the straight line was calculated followed by rate constant.

X. Interpret the result.

13. Determine the order and rate constant of the reaction between $K_2S_2O_8$ & KI and study the influence of ionic strength on the rate constant.

APPARATUS REQUIRED:

(a) 100 mL vol. flask-4
(b) 250 mL conical flask-2
(c) 100 mL beaker-1
(d) 500 mL conical flask-1
(e) Burette-1
(f) Pipette 10 mL-1
(g) Watch glass-2
(h) Glass bottle-2

CHEMICALS:

$K_2Cr_2O_7$, $K_2S_2O_8$, KI, $Na_2S_2O_3$, Starch, Glacial acetic acid.

PROCEDURE:

(1) Prepare 100 mL of standard (N/10) $K_2Cr_2O_7$ solution by accurate weighing.

(2) Prepare 250 mL (N/10) sodium thiosulphate solution.

(3) Standardize the (N/10) sodium thiosulphate solution idometrically sing starch solution as indicator. Take 10 mL of standard (N/10) $K_2Cr_2O_7$ solution solution in a 500 mL conical flask. Add about 15 mL (one test tube) of 105 KI solution and 20mL of 4(N) HCl solution. Cover the conical flask with watch glass and keep in dark for about 5 minutes.

Add 150 mL of deionized water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator.

(4) Prepare 250 mL $K_2S_2O_8$ solution [of strength> (N/10)].

(5) Standardize the prepared $K_2S_2O_8$ solution [of strength> (N/10)] using the following procedure:

Take 10 mL of the prepared $K_2S_2O_8$ solution in a 250 mL conical flask; add 20 mL of 10% KI solution and 2 mL of glacial acetic acid. Prepare two sets at the same time, cover the conical flask with watch glass and keep the mixture in dark for about 45 minutes. Add 50 mL of water and titrate the liberated iodine against the standard thiosulphate solution using starch solution as indicator.

(6) Prepare an exact (N/10) $K_2S_2O_8$ solution from the standardize $K_2S_2O_8$ solution by quantitative dilution (total volume 100 mL).

(7) Prepare 100 mL of a standard KI solution of strength greater than (N/10) by accurate weighing. From this prepare 100 mL of an exact (N/10) KI solution. Set up the colorimeter and adjust properly the SET 0 and SET 100 controls, using the filter at 525 nm.[peak wavelength].

(8) Pipette out 100mL of the exact (N/10) $K_2S_2O_8$ solution in a clean dry 100 mL beaker. Add 10 mL of the exact (N/10) KI solution to this solution by the same pipette and note the half discharge time as t= 0.Mix the solution carefully.

(9) Note the absorbance (A) of the reaction mixture at 525 nm (peak) wavelength at an interval of 1 minute for 15 readings.

(10) Plot $(1/A_t)$ versus (1/t) for the reaction mixture and calculate the rate constant from the graph.

Experimental Data:

1) Rom temperature,

2) Preparation of 100 mL (N/10) $K_2Cr_2O_7$ solution by accurate weighing:

3) Preparation of the prepared sodium thiosulphate solution:

4) Standardization of the prepared sodium thiosulphate solution:

Vol. of 0.1N $K_2Cr_2O_7$ (mL)	Burette reading		Vol. of $Na_2S_2O_3$ used (mL)	Average vol. of $Na_2S_2O_3$ (mL)
	Initial(mL)	Final(mL)		
10				
10				

Strength of $Na_2S_2O_3$ solution:

5) Preparation of 250 mL $K_2S_2O_8$ solution [of strength > (N/10)]:

6) Standardization of the prepared $K_2S_2O_8$ solution:

Vol. of $K_2S_2O_8$ solution(mL)	Burette reading		Vol. of $Na_2S_2O_3$ used (mL)	Average vol. of $Na_2S_2O_3$ (mL)
	Initial(mL)	Final(mL)		
10				
10				

Strength of $K_2S_2O_8$ solution:

7) Preparation of 100 mL exact (N/10) $K_2S_2O_8$ solution:

Required volume of prepared $K_2S_2O_8$ solution =

$$\frac{100\times 0.1}{strength\ of\ K2S2O8\ solution}\ \mathbf{mL}$$

…. mL prepared $K_2S_2O_8$ solution was taken (using burette) in a 100 mL volumetric flask and rest of the volume was made by adding deionized water up to the mark.

8) Preparation of 100 mL of a standard KI solution of strength slightly greater than (N/10) by accurate weighing:

9) Preparation of 100 mL of an exact (N/10) KI solution:

10) Measurement of absorbance (A_t) at different times:

Time	Time in Sec(t)	% Transmittance(T)	Absorbance(A_t)=2-logT

Conclusion:

A straight line is obtained on plotting (1/t) with

Intercept, $(1/A_\infty) = \ldots\ldots\ldots$ Slope = $(1/ak' A_\infty)$

So, $k' = \frac{\textbf{intercept}}{\textbf{a}\times\textbf{slope}}$, where a= initial concentration of $S_2O_8^-$ =N/20 or (M/40).

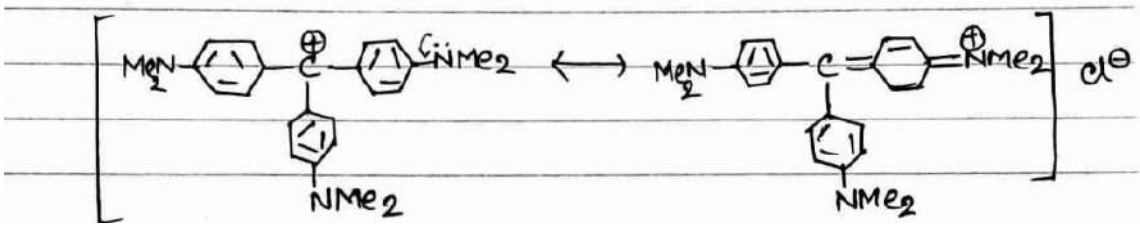
14. Study of the kinetic of alkaline hydrolysis of crystal violet. Determine the order with respect to alkali and salt effect on the system.

THEORY:

(a) Determination of order of the reaction with respect to HO^-

(b) Study of the salt effect of system

Colorimetrical technique can be employed to follow the reaction rate of alkaline hydrolysis of crystal violet dye because one of the reactant (dye) is highly coloured but its hydrolysis product is colourless. So the measure can be done by measure of the decrease of colorimetry of the dye in the reaction mixture. The hydrolysis of dye take place as follows



$+ Na^+ \quad OH^- \rightarrow$ pdt

Or, Simply $D^+Cl^- + Na^+OH^- \rightarrow$ products

(a) The rate of the reaction is rate of decrease of dye concentration which is $-d[D]/dt = k[D]^{\alpha} [OH^-]^{\beta}$

When order w.r.t dye i.e, $\alpha = 1$ & $[HO^-] >> [D]$ at that time,

$$-d[D]/dt = K_{obs}[D]$$

Integrating & applying proper limit,

Or, $- \int_{D0}^{Dt} d[D]/[D] = K_{obs} \int_0^t dt$

Or, $\ln [D]_0/[D]_t = K_{obs} .t$

$$\text{Or, } \log [D]_0/[D]_t = \frac{Kobs}{2.303}.t$$

Where, k = Specific reaction rate

D = Molar conc^n of dye

HO^- = Molar conc^n of alkali

Let, α & β are the order of the reaction w.r.t to dye & alkali respectively;

$K_{obs} = K [OH^-]^\beta$

$[D]_0$= Initial dye concentration

$[D]_t$= Dye concentration at time t.

Again we knew, Absorbance α Molar concentration, i.e, A α [ ]

$$\text{So, } \log A_0/A_t = \frac{Kobs}{2.303}.t \qquad [A_0=\text{Initial Absorbance}]$$

$$\log A_t = \log A_0 - \frac{Kobs}{2.303} \qquad [A_t=\text{Absorbance at time t}]$$

If we plot log A_t vs t we get a straight line with negative slope, (+ve) intercept from which we can easily calculate K_{obs}.

If we perform same experiment for sets of different compositions in which conc^n of alkali varied, we will get K_{obs} (different) values because,

$$K_{obs} = K [OH^-]^\beta$$

$$\text{Or, } \log K_{obs} = \log K + \beta \log [OH^-]$$

Again if we plot log K_{obs} vs log $[OH^-]$ we will get a straight line, from its slope we get β, i.e, order of the reaction w.r.t alkali.

(b) The reaction between dye & alkali takes place as follows –

$D^+ + OH^-(K) \rightleftharpoons X(K') \rightarrow$ Products [K= eqm const. ,K'= disproportionality const.]

The empirical rate equation, $Rate = K[D][OH^-]$ .....(1)

But from above scheme,

$$Rate = K'[X]$$

Again $K = a_x/a_D \times a_{HO^-}$

Or, $a_x = K\, a_D\, a_{HO^-}$

Or, $[X]f_x = K\,[D]\,[OH^-]\, f_D\, f_{OH^-}$

Or, $[X] = K'K[D][OH^-]\, f_D\, f_{OH^-}/f_x$ ……(2)

Comparing equation (1) & (2)

$$K = K'K\, f_D\, f_{OH^-}/f_x$$

$$= K_0\, f_D\, f_{OH^-}/f_x \quad \text{where } K_0 = KK'$$

Or, $\log K = \log K_0 + \log f_D + \log f_{OH^-} - \log f_x$

Applying Debye-Huckel limiting law for very dilute solution, i.e,

$$\log f_i = -0.51\, Z_i^2\sqrt{u} \quad \text{for aq sol}^n \text{ at } 25^oC,$$

We get, $\log K = \log k_0 - 0.51 Z_D^2\sqrt{u} - 0.51\, Z_{OH^-}\sqrt{u} + 0.51(Z_D + Z_{OH^-})^2\sqrt{u}$

$$\log k = \log K_0 + 1.02 Z_D Z_{OH^-}\sqrt{u}$$

Where, u= ionic strength of solution= $1/2\, \Sigma_i C_i Z_i^2$

X_i = Charge of ith species.

C_i = molar conc^n of species.

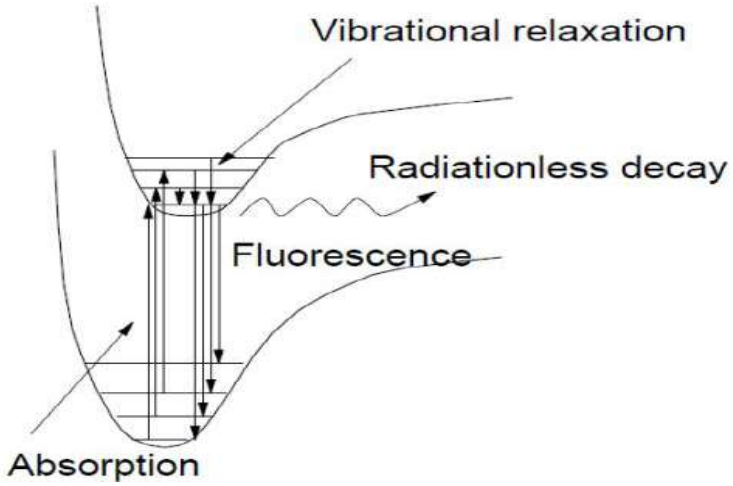
If we plot logK against $\sqrt{u}$ for sets of different composition with different ionic strength, we will get a straight line with (+ve) slope and positive intercept. From the slope we can realize the nature of reacting species.

15. Spectroscopic experiments relating to quenching of fluorescence.

THEORY: Electronically excited molecule dispose their excess energy in various ways: they may lose energy by emitting photon or pass energy to other molecules through collision, may undergo reaction, change oxidation state and so on. When a photon is emitted by an excited singlet state, the process, known as fluorescence, is generally rapid.

The molecular potential energy curve of the singlet ground state S0 and of an excited state S1 of a typical organic molecule in solution are shown in the diagram.
Since the excitation of an electron in a large molecule has little effect on the nuclear framework, the potential energy curves of the S0 and S1 states are usually similar, as are the spacing's of their vibrational levels.

The energy gaps between vibrational levels are quite large, so at room temperature most molecules are in the vibrational ground state, v = 0. The absorption spectrum thus arises from transitions from this state to different vibrational levels v_E of the S1 state. Collisions with solvent rapidly remove excess vibrational energy from the molecules, bringing them down to the lowest vibrational level, $v_E = 0$. Frequently, electronic energy is also lost through radiation less processes, but fluorescent molecules may emit a photon, and in this way return to one of the vibrational levels in the ground state. For most molecules in solution, the fluorescence spectrum is independent of the wavelength of the exciting light.



The excited molecule is denoted by A* and can now do one of several things.

1) It can emit a photon and in the process get converted back to the ground state. This process is a first-order rate process with a rate constant denoted by k_f.

$$A^* \rightarrow A + h\nu$$

2) A second possibility is for th excited molecule to lose its energy in the form of heat rather than light. This is known as nonradiative process with a rate constant denoted by k_{nr}.

$$A^* \rightarrow A + \text{heat}$$

The quantum yield of fluorescence, Φo, can be written as

$$\Phi o = \frac{k_f}{k_{f+k_{nr}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Now, let add some other molecule, Q, in the system, which interact with the excited molecule. Then there will be a additional decay rate of the excited molecule, with rate constant kq, which also depends on the concentration of the other molecule, Q.

$$A^* + Q \rightarrow A + Q'$$

For this system, we can write fluorescence quantum yield as

$$\Phi = \frac{k_f}{k_f + k_{nr} + k_q[Q]} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Thus,

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q}{k_f + k_{nr}}[Q] \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The relative quantum yield in this expression can be replaced by the relative fluorescence intensity $\frac{I_0}{I}$ which can be easily measured.

In order to determine the quenching rate constant kq, the *kf +knr* must be determine. The lifetime of the molecule in the absence of quencher, τ0, can be written as

$$T_0 = \frac{1}{k_f + k_{nr}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Thus we can rewrite the equation 3 as

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Thus by plotting $\frac{I_0}{I}$ vs [Q] one can determine the quenching rate constant, k_q , when τ_0 is known.

In this experiment we will first measure the absorption and fluorescence spectrum of anthracene molecule then we will measure the rate constant of fluorescence quenching of anthracene by CCl4 in ethanol.

Equipment and supplies

Spectrofluorimeter, Fluorescence cuvette, 7 x 25 ml volumetric flasks, 1 x 50 ml volumetric (for anthracene stock solution), 2 x 100 ml volumetric (for anthracene and CCl4 stock solutions), pipets: 2, 3, 5, 10, 15 ml, anthracene, CCl4, Ethanol

Procedure

Excitation and emission spectra of anthracene

Your first task is to record the absorption spectrum of anthracene in ethanol. Choose the wavelength corresponding to the maximum absorption. It is important that the absorbance of the solution is not more than about 0.2. The concentration anthracene should be 10 µM. Since the concentration of anthracene is so small, the stock solution should be made up in two steps. For example, first make a 5.0 x 10-4 M solution of anthracene by diluting about 9 mg of anthracene to the mark with ethanol in a 100 ml volumetric flask. Now dilute this by 5 by transferring 10 ml of this solution to a 50 ml volumetric and diluting to the mark, giving a 10 µM stock solution. Then measure the emission spectrum by exciting the anthracene molecule in that chosen wavelength. The emission spectrum shows the intensity of light emitted as a function of the emission wavelength, for a selected excitation wavelength.

Fluorescence quenching

Prepare 6 different solution of anthracene of the above mentioned concentration with 0.2 M, 0.4 M, 0.8 M, 1.2 M, 1.6 M, 2.0 M CCl_4 in ethanol. It is
important to keep these solutions out of bright light so that the fluorescence intensity measurements take place before any of the fluorescing molecule disappears through the photochemical reaction. Make sure to rinse the fluorescence cuvette several times with the new solution before taking its spectrum.

Determine the rate constant of fluorescence quenching using equation 5. Given, the
lifetime of of anthracene in ethanol is 5 ns.