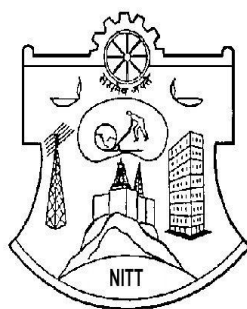


NATIONAL INSTITUTE OF TECHNOLOGY

TIRUCHIRAPPALLI – 15

Department of Chemistry



II Year B.Tech

IV SEMMESTER

LAB MANUAL



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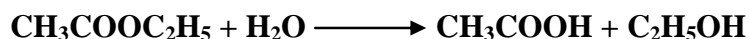
1. KINETICS OF ACID HYDROLYSIS OF AN ESTER

AIM:

To determine the rate constant of the hydrolysis of Ethyl acetate using an acid as a catalyst.

PRINCIPLE:

The hydrolysis of an ester occurs according to the equation



This reaction follows pseudo first order kinetics.

PROCEDURE:

100 ml of 0.5 N HCl is taken in a clean dry conical flask. 5 ml of ester is pipetted out into the conical flask and the mixture is immediately withdrawn into another dry conical flask. A stop watch is started simultaneously. The reaction is then arrested by the addition of ice cubes and the mixture is titrated against 0.2 N NaOH using phenolphthalein as indicator. End point is the appearance of permanent pink colour. The volume of NaOH consumed in this titration is taken as V_0 .

5 ml of acid – ester mixture is similarly withdrawn after 10, 20, 30, ..., 60 minutes respectively and titrated against NaOH using phenolphthalein as indicator. The volume of NaOH consumed for each of the above time intervals (t), is taken as V_t .

The contents are transferred into boiling tube with a cap and heated in a water bath for about 15 minutes. 5 ml of this mixture is withdrawn and titrated against NaOH to get V_∞ .

CALCULATION:

The rate constant K is determined using the equation,

$$K = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

Rate constant is also determined graphically by plotting $\log (V_\infty - V_t)$ Vs **time**.

TABULATION:

S.No.	Time Min	Volume of NaOH ml	$(V_{\infty} - V_t)$ ml	$\log (V_{\infty} - V_t)$ ml	$K = \frac{2.303}{t} \log \frac{(V_{\infty} - V_0)}{(V_{\infty} - V_t)}$ min^{-1}
1	0				
2	10				
3	20				
4	30				
5	40				
6	50				
7	60				
8	∞				

RESULT:

The Rate Constant for the hydrolysis of an ester from

1. Calculated value =
2. Graphical value =

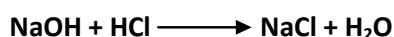
2. ESTIMATION OF MIXTURE OF ACIDS CONDUCTOMETRICALLY

AIM:

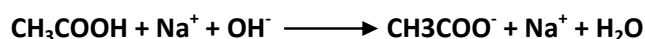
To estimate the amount of acids present in a given mixture conductometrically.

PRINCIPLE:

The conductivity of the solution is related to the mobility of ions which in turn related with the size of the ions. When a mixture of acids like a strong acid (HCl) and weak acid (acetic acid) are titrated against a strong base (NaOH), strong acid reacts first followed by a weak acid. When the titration of strong acid and strong base are carried out, there is a decrease in conductivity as highly mobilized hydrogen ions are replaced by sodium ions.



When the whole strong acid is consumed, base reacts with weak acid and conductivity increases as unionised weak acid becomes the ionised salt.



After both the acids are consumed, there is a steep increase in conductivity which gives the end point and this increase in conductivity is due to the fast moving hydroxyl ions from the base. From this, amount of base consumed for acid and in turn, the amount of acids present is calculated.

PROCEDURE:

The given mixture of acids is made up to 100 ml using distilled water. 10 ml of this made up solution is pipette out into clean beaker and 100 ml of distilled water is added. The conductivity cell is dipped into the test solution and the base NaOH is added in an interval of 0.5 ml with uniform stirring. The conductance is measured after each addition of NaOH at various stages of neutralization. After complete neutralization, the amount of acid present in the given mixture is determined based on the volume of base consumed. Volume of base consumed for strong acid and weak acid are determined by plotting a graph between corrected conductance and volume of base added, where first end point corresponds to strong acid and second end point corresponds to weak acid.

3. ESTIMATION OF COPPER (II) BY SPECTROCOLORIMETRY

AIM:

To verify the Beer-Lamberts law and estimation of copper (II) in the given solution by spectrophotometry.

PRINCIPLE:

According to Beer-Lamberts law, the optical density of absorbance of a solution of concentration ' c ' mol dm⁻³ placed in a cell of ' b ' cm width is given by

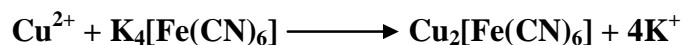
$$A = \epsilon bc$$

where ϵ is called the molar absorption coefficient or molar extinction coefficient. The absorbance A is defined as

$$A = \log (I_0/I)$$

where I_0 and I represents the intensities of incident and transmitted radiations, since the optical density is linearly proportional to the concentration of the solution, a linear plot is expected for absorbance Vs concentration.

Copper (II) forms a coloured complex with $K_4[Fe(CN)_6]$ by the reaction,



This complex absorbs bluish green light of wavelength maximum 480 nm and therefore exhibits its complementary colour. The absorbance of this complex can be measured by using a spectrophotometer fixing max at 480 nm. A calibration line is plotted by measuring the optical density of the standard solution of various concentrations. The concentration of the unknown is determined by matching its optical density in the calibration curve.

PROCEDURE:

0.2 g of $CuSO_4$ is weighed accurately in a chemical balance transferred into a 100 ml SMF and made upto the mark using distilled water. A drop of concentrated H_2SO_4 is added to prevent precipitation of $Cu(OH)_2$. This solution is approximately diluted to 10 times in a 100 ml SMF. 1 ml of this solution is taken in a test tube. 5 ml of 10% NH_4NO_3 and 1 ml of 4% $K_4[Fe(CN)_6]$ are added and made up to 15 ml. The optical density of this solution is measured using a spectrophotometer after fixing maximum wavelength at 480 nm. Similar measurements are made with 2, 3, 4, 5, 6 and 7 ml of standard $CuSO_4$ solution and the

calibration line is obtained. From the calibration line, the amount of copper (II) present in the unknown is determined using its optical density.

TABULATION:

S.No	Volume of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution (ml)	Optical density	Concentration g
1	1		
2	2		
3	3		
4	4		
5	5		
6	6		
7	7		

RESULT:

The amount of copper (II) present in the whole of the given solution is _____ g.

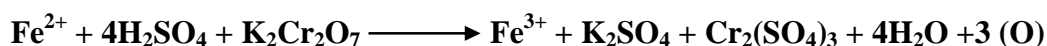
4. ESTIMATION OF Fe(II) USING POTENTIOMETER

AIM:

To estimate the amount of Fe(II) present in the whole of the given solution potentiometrically.

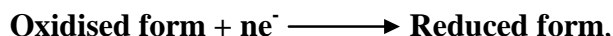
PRINCIPLE:

Potentiometric titration is the titration in which potentiometric measurements are carried out in order to fix the end point. In this method, the interest is with the change in electrode potential, rather than with an accurate value for the electrode potential in a given solution. In a potentiometric titration, the change in cell e.m.f. occurs most rapidly in the neighbourhood of the end point. The Fe(II) –K₂Cr₂O₇ redox system is represented as



The determining factor is the ratio of the concentrations of the oxidised and the reduced forms of the iron species.

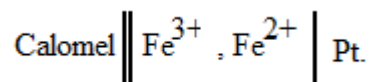
For the reaction,



The potential E acquired by the indicator electrode at 25°C is given by,

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}$$

where E° is the standard Reduction Potential of the system. Thus the potential of the immersed electrode is controlled by the ration of these concentrations. During redox reactions, the potential changes more rapidly at the vicinity of the end point. The indicator electrode is usually a bright platinum wire or foil, the oxidising agent is taken in the burette. The cell can be represented as,



Here Pt is the indicator electrode and calomel is the reference electrode.

PROCEDURE:

PREPARATION OF 0.1 N K₂Cr₂O₇:

0.1 N K₂Cr₂O₇ is prepared by dissolving 0.49 g of analar crystals in distilled water in a 100 ml SMF. The solution is made up to the mark.

CALIBRATION OF THE POTENTIOMETER:

A standard cell of known emf is connected to the instrument and its emf is set in the voltage scale. The galvanometer key is pressed to complete the circuit and the deflection of the galvanometer needle is noted. If there is any deflection, the current passing through the rheostat is adjusted for null deflection. This procedure makes sure that the value of emf which is read on the scale is the true potential of the cell considered. The potentiometer is calibrated using the Weston standard cell of potential 1.018 V.

ESTIMATION OF Fe(II):

The given Fe(II) solution is made upto 100 ml in SMF. 20 ml of the solution is pipetted out into a clean beaker. To this, 25 ml of 2.5 M H₂SO₄ and 50 ml of distilled water are added. A platinum electrode is dipped into this solution, and it is coupled with a calomel electrode through a salt bridge. The resulting cell is connected to the potentiometer. Standard K₂Cr₂O₇ solution is added from the burette, to this solution, insteps of 1 ml and the emf is recorded after each addition. At the end point, there is a jump in emf due to the absence of Fe²⁺. The approximate range of the end point is determined. The experiment is repeated by adding the titrant in steps of 0.1 ml near the end point. A graph is plotted between emf, E and the volume of dichromate added. The inflexion point gives the volume of titrant at the end point.

The first derivative ($\Delta E/\Delta V$ vs. Volume of titrant) and the second derivative ($\Delta E^2/\Delta^2 V$ vs. Volume of titrant) curves give the exact volume of dichromate required for the reaction. From the plot of E vs. Volume of titrant, potential at the equivalent point is obtained.

Atomic weight of Fe is 55.85

TABULATION:

S. No.	Volume of K ₂ Cr ₂ O ₇ ml	EMF	ΔE	$\Delta E/\Delta V$	V _{mean}

RESULT:

The amount of iron present in the whole of the given solution is _____ g.

5. DETERMINATION OF pKa VALUES OF ORTHO PHOSPHORIC ACID USING pH METER

AIM:

To determine the pKa values of Ortho phosphoric acid using pH meter.

PRINCIPLE:

Phosphoric acid is a tribasic acid and neutralised in three stages as follows.



The successive ionization constants, neglecting the activity coefficient terms are,

$$pK_{a_1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]}$$

$$pK_{a_2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$$

$$pK_{a_3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]}$$

The pH's of the solution at half neutralization points of the first second and third ionization stages are equal to pKa₁, pKa₂, pKa₃ respectively.

PROCEDURE:

0.2 N phosphoric acid and 0.2 N NaOH are prepared respectively. 20 ml of the 0.2 N phosphoric acid is pipetted out into a clean SMF and made upto 100 ml. 20 ml of the made up solution is pipetted out into a clean beaker and 100 ml of water is added for dilution. The glass pH electrode is immersed in the solution after the calibration with buffer solutions of pH 4.7 and 9.3. The pH of the phosphoric acid is measured and then NaOH is added in drops, stirred and the pH value is measured. The addition of NaOH is continued till the end points are reached. A graph is plotted between pH vs. Volume of NaOH added.

TABULATION:

S. No	Volume of NaOH (ml)	pH	Δ pH	Δ V	Δ pH/ Δ V	V_{mean} ml
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						

RESULT:

From the graph,

- $\text{pK}_{\text{a}1} = \text{_____}$ (first acid dissociation constant)
- $\text{pK}_{\text{a}2} = \text{_____}$ (second acid dissociation constant)
- $\text{pK}_{\text{a}3} = \text{_____}$ (Third acid dissociation constant)

6. ADSORPTION BY SOLIDS FROM SOLUTION

AIM:

To study the adsorption of a solute (Oxalic acid) by activated charcoal from an aqueous solution.

PRINCIPLE:

Adsorption is accumulation of a substance at an interface. The adsorption of a solute from a solution, generally follows the Freundlich empirical adsorption isotherm given by

$$\frac{x}{m} = KC^n$$

where x = weight of adsorbent,

m = mass of adsorbent,

K = constant representing the capacity of the adsorbent, and

C = equilibrium concentration of the solution.

PROCEDURE:

From the 1N stock solution of oxalic acid, prepare 100 ml of the required dilution. Standardize the NaOH solution using 0.2 N oxalic acid. Make up the given solution of oxalic acid to 100 ml. Weigh out accurately 1g of activated charcoal. Transfer this into a 250 ml well cleaned dry stoppered bottle. Then add 50 ml of 0.5 N oxalic acid to the bottle. Shake the mixture intermittently for about one hour. After equilibrium is reached, filter the solution. Pipette out 10 ml of the filtrate and titrate it against NaOH using phenolphthalein as indicator. Repeat the above procedure for different concentrations of oxalic acid.

TREATMENT OF RESULTS:

From the concentration (C), the volume of each original solution and concentration of each solution after equilibrium (C_e), the weight of oxalic acid per gram of the adsorbent (x/m) is calculated as follows.

$$\frac{x}{m} = \frac{(C - C_e) \times 60}{10}$$

Draw a graph of $\log \frac{x}{m}$ vs. $\log C_e$ and calculate the constant n and K using the equation.

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e$$

TABULATION:

Bottle	Volume of Oxalic acid (ml)	Burette Reading		Volume of NaOH (ml)	Concordant Value (ml)
		Initial	Final		
I	10.0				
	10.0				
II	10.0				
	10.0				
III	10.0				
	10.0				
IV	10.0				
	10.0				
V	10.0				
	10.0				
VI	10.0				
	10.0				

Weight of Charcoal (g)	Volume of oxalic acid (ml)	Concentration of oxalic acid	Volume of NaOH	Normality of oxalic acid	$\frac{x}{m}$	$\log \frac{x}{m}$	$\log C_e$
1	50						
1	40						
1	30						
1	20						
1	10						
1	unknown						

RESULT:

1. Concentration of the unknown sample is _____ g.
2. Adsorption capacity of charcoal (K) =
3. The intensity of adsorption is (1/n) =

7. DISTRIBUTION COEFFICIENT

AIM:

- (i) To determine the distribution coefficient of iodine between CCl₄ and water at room temperature.
- (ii) To find the equilibrium constant of above distribution.
- (iii) To find the concentration of given KI solution.

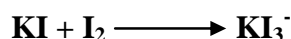
PRINCIPLE:

According to Nernst distribution law, when a solute distributes between two immiscible solvents in contact with each other, there exists, for similar molecular species, at a given temperature, a constant ratio of distribution between the two solvents irrespective of the total amount of the solute and irrespective of any other molecular species which may be present. In other words,

$$\frac{C_1}{C_2} = K_D$$

where K_D is termed as the distribution coefficient, and, the terms C_1 and C_2 refer to the concentrations of similar molecular species in the two liquids at a constant temperature.

Now we are considering a system of distribution of iodine between aqueous and CCl₄ layer in the presence of KI in aqueous layer. Equilibrium between KI and I₂ will be attained in the aqueous layer. The equilibrium attained is



The equilibrium constant

$$K_{equ} = \frac{[\text{KI}_3^-]}{[\text{KI}][\text{I}_2]}$$

PROCEDURE:

Serially labelled three bottles are taken and mixtures are made in each bottle as follows:

Bottle No.	Contents
I	20 ml of I ₂ in CCl ₄ + 40 ml of water
II	20 ml of I ₂ in CCl ₄ + 40 ml of known KI
III	20 ml of I ₂ in CCl ₄ + 40 ml of unknown KI

These bottles are stoppered well and shaken in a mechanical shaker for about an hour. After shaking, they are set aside for about 20 minutes in a water trough so that it will attain

equilibrium. Exactly 2 ml of the CCl₄ layer from bottle I is pipetted out into a conical flask and approximately 20 ml of distilled water is added this biphasic solution is titrated against previously standardised thio solution using starch as indicator. The end point is the disappearance of blue colour. The experiments are repeated to get concordant values. From bottle I, about 10 ml of the aqueous layer is pipetted out and the amount of I₂ is estimated as done with CCl₄ layer. The above procedure is repeated for bottles II and III.

TABULATION:

Bottle	Volume of CCl ₄ layer(ml)	Burette Reading		Volume of Thio (ml)	Concordant Value (ml)
		Initial	Final		
I	2.0				
	2.0				
II	2.0				
	2.0				
III	2.0				
	2.0				
Bottle	Volume of aqueous layer(ml)	Burette Reading		Volume of Thio (ml)	Concordant Value (ml)
		Initial	Final		
I	10.0				
	10.0				
II	10.0				
	10.0				
III	10.0				
	10.0				

Bottle No	Layer	Volume of Thio (ml)	Strength of Iodine	$K_D = \frac{C_1}{C_2}$
I	CCl ₄			
	Aqueous			
II	CCl ₄			
	Aqueous			
III	CCl ₄			
	Aqueous			

RESULT:

- (i) The distribution coefficient of iodine between CCl₄ and water is found to be _____.
- (ii) The equilibrium constant, K_{equ} , for above equilibrium is found to be _____ M⁻¹.
- (iii) The concentration of given KI solution is found to be _____ M.

8. DETERMINATION OF MOLECULAR WEIGHT OF POLYMER BY VISCOSITY MEASUREMENT

AIM:

To determine the molecular weight of a given polymer using Ostwald's Viscometer.

PRINCIPLE:

Molecular weight of a polymer is nothing but the average molecular weight. This can be determined by measuring the intrinsic viscosity (η_i) of a dilute polymer solution. This intrinsic viscosity is related to the molecular weight by following relationship

$$\eta_i = KM^a \text{ (Mark-Howink equation)}$$

where η_i = Intrinsic viscosity

K & a = constants for a given polymer-solvent combination at a given temperature.

M = average molecular weight.

PROCEDURE:

PREPARATION OF POLYMER SOLUTIONS OF DIFFERENT CONCENTRATIONS:

Polymer solution of different concentration say 0.5%, 1.0%, 1.5%, 2.0%, 2.5% are prepared from the given polymer stock solution as shown in the table.

DETERMINATION OF MOLECULAR WEIGHT OF POLYMER:

20 ml of the solvent is taken into the viscometer and is sucked through the capillary tube up to the upper mark without any air bubbles. Now note the flow time of the solvent to flow from the upper mark (m_1) to lower mark (m_2).

Now fill the viscometer with 20 ml of the polymer solution (say I) into the viscometer and determine the flow time of the polymer solution to flow from the upper mark (m_1) to lower mark (m_2). Using the same procedure, determine the flow time of the various concentrations of polymer solution.

From the flow times, reduced viscosity (η_{sp}/C) can be calculated. Graph is plotted between η_{red} vs. concentration, a straight line is obtained with an intercept called intrinsic viscosity (η_i).

TABULATION:Flow time of the solvent $t_0 =$ _____ sec.

Concentration C (g/100ml)	Flow time ' t ' sec	$\eta_o/\eta = t/t_o = \eta_{rel}$	$\frac{t}{t_o} - 1 = \eta_{sp}$	$\eta_{red} = \frac{\eta_{sp}}{C}$
0.5				
1.0				
1.5				
2.0				
2.5				

RESULT:

The molecular weight of the given polymer is _____.

CL204 PHYSICAL CHEMISTRY

OBJECTIVE : This paper makes the students learn the nature of chemical reactions taking place in solid, liquid and gaseous phases.

1. GASEOUS STATE:

Vander wall's equation. Law of equipartition principle, Translational, Rotational and vibrational energies of molecules, Joule-Thomson effect, liquefaction of gases. Critical constants.

2. REACTION KINETICS:

Rate order and molecularity of chemical reactions. Methods of their evaluation. Calculation of rate constants. Consecutive - Parallel and opposing reactions. Chain reactions. Energy of activation - Theories on reaction rates. Heterogeneous reactions - zero order reactions.

3. PHASE EQUILIBRIA:

Phase rule: Application - to one components system (water, sulphur and carbon dioxide), Two component systems (Eutetic, Intermediate compound formation and solid solutions) and simple three component systems. Solutions: Ideal and non-ideal solutions solubility of gases in liquids. Henry's law. Completely miscible liquids - Raoult's law - vapour pressure and boiling point diagrams. Partially miscible liquids - Critical solution temperature -completely immiscible liquids - Nernst: distribution law - Dilute solution and their colligative properties. Molecular weight determination using these properties.

4. ELECTRICAL CONDUCTANCE:

Debye - Huckel Onsager theory; Ostwald's dilution law - solubility of electrolytes and solubility product - Applications, common ion action - acids, bases - definitions a) based on proton transference, dissociation constant, amphoteric electrolyte - pH -Buffer solutions. hydrolysis of salts.

Decomposition potential, over voltage, definitions of current density, current efficiency, energy consumption; oxidation - reduction redox couple; e.m.f. and energy relations. Conductometry, Potentiometry, Voltammetry, their applications. Fuel cells.

5. SURFACE CHEMISTRY:

Derivation of Langmuir adsorption isotherm, B.E.T adsorption isotherm, Determination of surface area of solids by B.E.T. method. Catalysis- Homogeneous catalysis, heterogeneous catalysis, Langmuir - Hinshelwood mechanism of a bimolecular surface reaction, Elay - Rideal mechanism of a surface reaction, Enzyme catalysis, Industrial applications of catalysis, zeolites as catalysts, Self-assembled monolayers and Langmuir-Blodgett films, adsorption chromatography.

TEXTBOOKS:

1. B. R. Puri and SL. R. Sharma, "Principles of Physical Chemistry", Shoban Lal Nagin Chand & Co.
2. P.L. Soni, "Text Book of Physical Chemistry ", S. Chand & Co., New Delhi.

REFERENCES:

1. K. J. Laidler, "Chemical Kinetics", 3rd Edn., Harper & Row Publishers, 1987.
2. Atkins, P.W. 'Physical Chemistry', 6th Edn., Oxford University Press, 1998.