

**Manual for Advanced Physical
Chemistry Laboratory-II**
(BS 8th Semester & MSc 4th Semester)

CODE No: 3564

UNITS: 1-9



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Message from Chairperson

Chemistry laboratories are essential part of our chemistry department. These are source of providing students with the knowledge of laboratory procedures and experimental techniques. These 'hands-on' activities are practical training which can help the students to understand of scientific concepts and phenomena. Demonstrations in chemistry laboratories can depict the phenomenon discussed in class room. Designing and planning the investigations can flare the sense of research in the student. That is why the chemistry lab is affirmed essential part of MSc level program. The qualified and dedicated faculty members of chemistry department are engaged in developing laboratory courses and their manual for smooth running of chemistry laboratory course.

We, in chemistry laboratories, are engaged in dealing with chemicals, equipment and instruments which can be dangerous if mishandled. Our activities at work sites involve working with many hazardous chemicals; sophisticated gadgets and equipment which can be injurious unless we adopt safety measures and work with safe practices. Following standard operating procedures, the risk of accident reduces drastically. The detailed manual of standard operating procedures in chemistry laboratory is available in each chemistry laboratory. Students should go through it and student should follow the instructions/precautions mentioned in SOPs manual before working into chemistry laboratories.

Prof. Dr. Naghmana Rashid
Chairperson

Message from Course Coordinator

Physical chemistry is one of the important branches of chemistry. Due to keen interest shown by the students and keeping in view the present need; department of Chemistry at AIOU has launched specialization in “Physical Chemistry” from spring 2017. The course “Advanced Physical Chemistry Laboratory IV” is a practical based 3 credit course with course code “3564”. This course consists of advance practicals that are designed according to the approved course outlines and laboratory facilities available in the department. This course is offered in the last semester (i.e., BS 8th and M.Sc 4th semester) in a 20 days practical workshop as a continuity after completing 20 days laboratory course “Advanced Physical Chemistry Laboratory III; code: 3563”. Hope students will find this practical course more informative and comprehensive from learning point of view. I am assured that these trainings in the advanced level practicals could help students in future research at post graduate levels.

Feel free to give your feedback, which will help us for the further improvement of this manual.

Dr. Nasima Arshad
Course Coordinator

Introduction

This Physical Chemistry practical manual is designed for BS 8th Semester and MSc 3rd semester students under 3 credit course with course code 3564. It consists of various physical chemistry practical. These practicals are divided into 09 units. The whole practical course (3563 & 3564) will be conducted in a 40 days' workshop in the Department of Chemistry, Allama Iqbal Open University, Islamabad. Participation in the practical workshop is mandatory for students doing specialization in Physical Chemistry with at least 70% attendance and minimum 50% marks are required to pass this course.

His manual offers a range of experiments which will help to provide conceptual understanding to different aspects of chemical kinetics and equilibrium, electrochemistry, spectroscopy, solution chemistry and computational chemistry. The background of the experiment is written in a clear and conceptual way. After getting through these experiments students will be able to implement the concepts of above mentioned subjects in practical format.

Feel free to give your feedback, which will help us for the further improvement of this manual.

Dr. Erum Jabeen
Course Development Coordinator

COURSE OUTLINE

- Unit 1.** Determination of the strength of the base 2-nitro-4-methylaniline by spectrophotometric method. **07**
- Unit 2.** Study of mutual solubility of tri-methylamine and water and finding the critical solution temperature. **11**
- Unit 3.** Determination of mutual solubility curve of phenol and water and hence the consolute point. Determination of the critical solution temperature of phenol and water in the presence of (a) 1.0% NaCl, (b) 0.50% naphthalene and (c) 1.0% succinic acid. **15**
- Unit 4.** Determination of specific rate of the alkaline hydrolysis of ethyl acetate by volumetric method. **21**
- Unit 5.** Study of kinetics of the acid catalyzed hydrolysis of methyl acetate and evaluation of activation energy for the reaction. **26**
- Unit 6.** Determination of critical micelle concentration of a surface active material by surface tension and conductivity method. **32**
- Unit 7** Precipitation, titration and determination of solubility of a sparingly soluble salt. **39**
- Unit 8.** Determination of redox activity of $K_4Fe(CN)_6$ and estimation of redox parameters i.e. **43**
- Anodic and cathodic currents and potentials.
 - Number of electrons involved in the electrochemical reaction
 - Linear dependency of current with square root of scan rate.
- Unit 9.** Using Hyperchem program, perform semi-empirical AM1 calculations for the following compounds **49**
- CO_2
 - NH_3
 - BF_3

Recommended Books

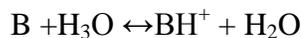
1. J.P. Erikson, Partially Miscible Water-Triethylamine Solutions and Their Temperature Dependence, **Journal of Chemical Education**, 94, 2017, 75-78.
2. A. Findlay, **Practical Physical Chemistry**, Forgotten Books (Amazon. com), 2015.
3. P.R. Bonomo, G. Tabbì, L.I. Vagliasindi, Solubility and Solubility Product Determination of a Sparingly Soluble Salt: A First-Level Laboratory Experiment, **Journal of Chemical Education**, 2012,89, 545-547.
4. F. Daniel, **Experimental Physical Chemistry**, 5th ed., McGraw Hill, 1956.
5. V.K. Ahluwalia, S.D.A. Gulati, **College Practical Chemistry**. Universities press (India) private Limited. 2005.
6. A. Sing, **Advanced Experimental Physical Chemistry**, New Delhi Campus Books International, 2002,ISBN: 9788180300059.
7. B. Viswanathan, P.S. Raghavan, **Practical Physical Chemistry**. Viva Book private Limited. 2005.
8. A.M. James, F.E. Prichard, **Practical Physical Chemistry**, 3rd ed., Longman Group Limited, New York, 1974.
9. D. Shoemaker, **Experiments in Physical Chemistry**, 8th ed., McGraw Hill Publishing Company Limited, 2003.
10. M.K. Zia, **Laboratory Manual Physical Chemistry**, BS (H) & BSc., Al-Farabi Publishers, 2012.
11. B.J. Yadav, **Advance Practical Physical Chemistry**, 29th ed., Karishna Prakashan Media (P) Ltd., Meerut, India, 2010.
12. S.A. Iqbal, Y. Mindo, **Physical Chemistry**, Discovery publishing house, New Delhi, 2005.
13. E.A. Moelwyn-Hughes, **Physical Chemistry**, 2nd Ed., Pergamon, New York,1961.
14. https://www.chem.uni-potsdam.de/groups/kolloid/3_lehre/mops/e06_con.pdf

Unit-1

Determination of the Strength of the Base 2-Nitro-4-Methylaniline by Spectrophotometric Method

Theory:

The strength of a base is its ability to accept the proton. Thus, the equilibrium constant K of the reaction



Is the measurement of the strength of the base B . The equilibrium constant K_a for the reverse reaction i.e. the ionization constant of the conjugate acid BH^+ is given by;

$$K_a = 1/K = \frac{([B] \times [H_3O^+])}{([BH^+] + [H_2O])} \quad (3)$$

The larger the value of K_a , the weaker is the base B . if the water is present in excess then its concentration can be regarded as unity. Then,

$$K_a = 1/K = \frac{([B] \times [H_3O^+])}{[BH^+]} \quad (4)$$

The ratio $[B]/[BH^+]$ can be obtained from uv-vis spectrophotometry making use of the fact that the neutral base is orange and the protonated form is colorless.

If the A_{BH^+} , A_B and A are the absorbances of completely protonated base BH^+ in strongly acidic medium, neutral base in alkaline medium and a solution at intermediate pH (all measured at same wavelength) and α is the degree of ionization of the conjugate acid i.e. protonated base (BH^+) then

$$\frac{[B]}{[BH^+]} = \frac{\alpha}{(1-\alpha)} \quad (5)$$

And according to Beer Lambert law,

$$A_x = \epsilon b [X] \quad (6)$$

Therefore,

$$A_{BH^+} = \epsilon b [BH^+] \quad (7)$$

and

$$A_B = \epsilon b [B] \quad (8)$$

Combining equation 7 and equation 8;

$$\frac{[B]}{[BH]} = \frac{A_B}{A_{BH+}} \quad (9)$$

Thus,

$$\frac{A_B}{A_{BH+}} = \frac{\alpha}{(1-\alpha)} \quad (10)$$

and

$$A = (1 - \alpha)A_{BH+} + \alpha A_B \quad (11)$$

Rearranging;

$$\alpha = \frac{A_{BH+} - A}{A_{BH+} - A_B} \quad (12)$$

and

$$(1 - \alpha) = \frac{A - A_B}{A_{BH+} - A_B} \quad (13)$$

Putting the values of α and $1 - \alpha$.

$$\frac{A_B}{A_{BH+}} = \frac{\alpha}{(1-\alpha)} = \frac{A_{BH+} - A}{A - A_B} \quad (14)$$

Combining equation (14) and equation (4)

$$K_a = \frac{A_{BH+} - A}{A - A_B} \times [H_3O^+] \quad (15)$$

Apparatus

Spectrophotometer, glass cuvette, beakers, volumetric flasks (25 mL), volumetric flask (50 mL) etc.

Materials

2-nitromethylaniline, 3 M HCl, 5 M NaOH, distilled water

Procedures

Prepare aqueous stock solution of 2nitro-3-methyl aniline (mol.wt. 152.1 gmol^{-1}) of concentration of about 1×10^{-4} M. then prepare the following solutions:

$I = 10 \text{ cm}^3$ stock solutions + distilled water to make 25 cm^3

II = 10cm³ stock solutions + 10 cm³ of concentration HCl + distilled water to make 25 cm³

III = 10cm³ stock solutions + 10 cm³ of concentration NaOH + distilled water to make 25 cm³.

In solution II, the base is almost in the protonated form BH⁺ and in the solution III it is in neutral state (B).

Measure the absorbance of each solution against water as blank, at different wavelengths at 20 nm interval (5 nm interval near wavelength of maximum absorbance) in the range of 360-560 nm. From the absorption curve find the wavelength of maximum absorption.

Now prepare a series of solutions in 25 cm³ measuring flasks, each containing 10 cm³ of stock solution of the base 0.5, 1, 2, 3, 4, 6, 8 cm³ of 3 M HCl and rest water to make up 25 cm³. Determine the absorbance of each of the solution at the selected wavelength.

Calculations

In the equation 15, A_{BH^+} and A_B are the absorbances of solution II and Solution III and A is the absorbance in the presence of different concentration of hydrochloric acid. Since A_{BH^+} cannot be measured experimentally, so rearranging the equation 15 we get;

$$A = A_{BH^+} + K_a \frac{A - A_B}{[H_3O^+]} \quad (16)$$

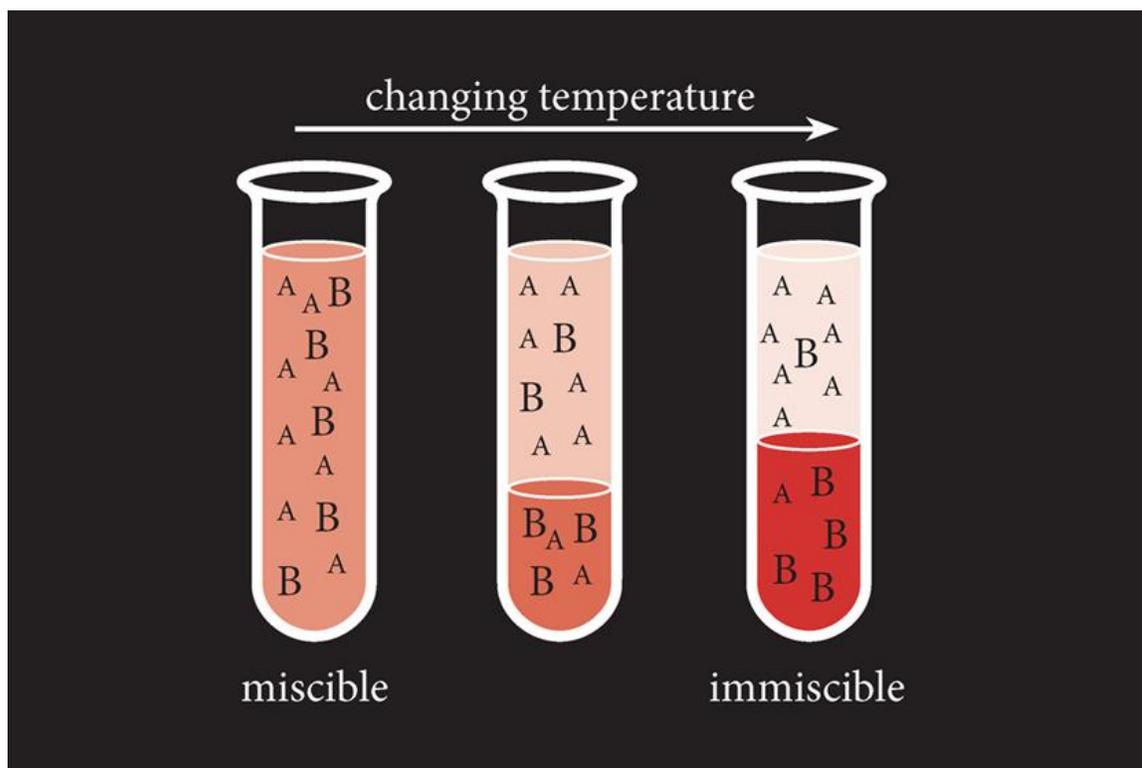
Plot $A - A_B$ values along y-axis vs. $A - A_B / [H_3O^+]$ along x-axis and extrapolate the graph to $A - A_B / [H_3O^+] = 0$. The slope would be the value of K_a at each acid concentration and intercept would correspond to A_{BH^+} .

Precautions

- Handle glass cuvettes very carefully.
- No stain or liquid should be left over transparent side of cuvette before recording each reading.
- Flap of spectrophotometer should be closed during recording each spectrum.

Unit 2

Study of Mutual Solubility of Tri-methylamine and Water and Find the Critical Solution Temperature.



Theory

The Gibbs phase rule aids interpretation of partial miscibility. Under appropriate conditions, the chemical components are miscible and thus form one phase; temperature and composition are independently variable. In the immiscible, two-liquid phase situation, temperature and composition of the two phases is not independent, meaning that, at a particular temperature, each of the two phases has a fixed composition. Graphical presentation of binary partially miscible systems is the norm (Fig.2.1). In a T–X (temperature–composition) diagram, regions of one homogeneous solution are separated from regions of two immiscible liquids by a phase boundary. At a temperature and bulk composition within the immiscible region, coexisting liquids, LiqA and LiqB, are connected by tie lines at their compositions (X_1 and X_2 , respectively). The lever rule is used to determine their relative amounts (because the Gibbs phase rule says nothing about quantities) and the Temperature–Composition Diagram Fig.2.1 is representative of many partially miscible liquids, in that it shows increasing miscibility with increasing temperature. Examples include phenol/water and hexane/nitrobenzene.

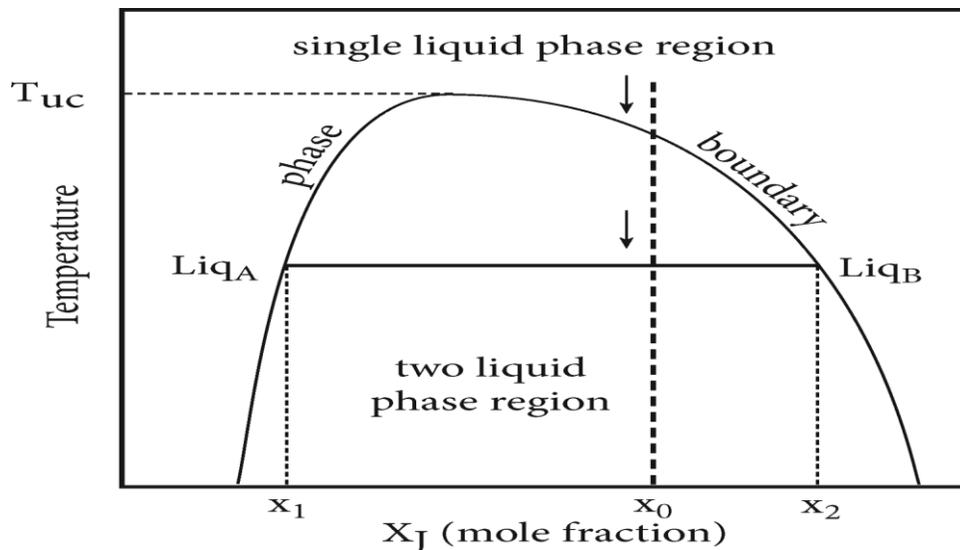


Fig.2.1. Temperature–composition (T–X) diagram for a hypothetical mixture of two partially miscible liquids. Composition is indicated as mole fraction of compound “J” increasing to the right. T_{uc} is the upper consolute temperature. A mixture of composition X_0 will form a single miscible phase at all temperatures above the phase boundary. As temperature drops, the monotectic phase boundary will be intersected, and two immiscible liquids will form. Compositions of the separated liquids (Liq.A and Liq.B) are indicated at the phase boundary (X_1 and X_2 , respectively). Amount (in moles) of each liquid is determined through the lever rule.

Apparatus

- Six 6–10 mL test tubes
- Two water baths: 1000 mL beakers work well
- Hot plate and magnetic stirrer
- Glass rod
- Test tube stoppers or aluminum foil
- Thermometer
- Ice
- 10 mL graduated cylinder and/or pipettes

Materials

- TEA (tri-ethyl amine)
- Deionized water
- Hydrophilic dye solution (synthetic food coloring FD&C).

Procedure

1. A linear arrangement of six test tubes is recommended in test tube stand. Solutions (5 mL) are prepared by sequential addition of appropriate volumes of one drop of dye, and then DI (de-ionized) water, and finally TEA (tri-ethylamine) into the test tubes (Table 2.1).

Table 2.1 Mixing proportions for experiments

Component	Test tube Number					
	1	2	3	4	5	6
Water (mL)	4.5	4	3	2	1	0.5
TEA (mL)	0.5	1	2	3	4	4.5
X _{TEA}	0.14	0.031	0.079	0.162	0.341	0.538

2. The TEA-rich liquid will float above the water-rich liquid due to the lower density of TEA (0.73 g/mL) as compared to that of water.
3. Place the liquid in the cold bath ($T < 10^\circ \text{C}$) and stir the mixtures individually so that a homogeneous phase is formed at low temperature.
4. Then place one test tube warm bath, set the temperature of hot plate at 100 C and allow gradual rise in temperature.
5. Observe the temperature at which a phase separation starts to be visible.
6. Repeat the gradual heating steps with all the test tubes and note the temperature for phase separation.
7. Then plot a graph between temperatures for phase separation vs. compositions.

Precautions

- Tri-ethylamine (TEA) is a hazardous liquid with potentially harmful effects for humans and the environment. TEA is an irritant for the eyes, skin, and lungs with acute exposure. Therefore, follow labs safety measures.
- TEA has a high vapor pressure and thus readily evaporates and is flammable. Therefore, heating can not only ignite the TEA but can also alter the composition. Therefore, test tubes should be covered with Al foil with a hole in it to exhaust inbuilt pressure.

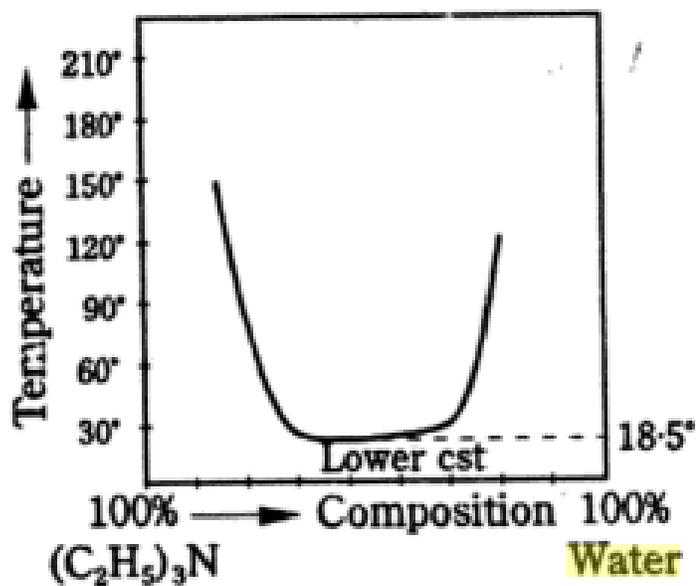


Fig.2.2 Plot of composition Vs. Temperature.

Unit 3

Determination of Mutual Solubility Curve of Phenol and Water And Hence the Consolute Point.

Determination of the Critical Solution Temperature of Phenol and Water in the Presence of (A) 1.0% NaCl, (B) 0.50% Naphthalene and (C) 1.0% Succinic Acid

Theory

Phenol is partial miscible with water. When phenol is added to water, the liquid structure of water gets distorted. At very low concentration of phenol this distortion would be less and water would retain its phase. As the concentration of phenol increases in water, the distortion of water molecules increases. This would result in rise in energy of the system and system would try to retrieve its lower energy state by getting rid of this randomness. In order to get lower energy state, water will push the molecules of phenol outside it. On the other hand, phenol molecules at higher concentration, would organize in the form of separate layer. This would result in separation phenol from water as two layer would be visible. When the temperature of this system would be raised to comparatively much higher value, the rapid Brownian motion of the molecules of water and phenol would result in their intermingling. This will lead to single phase formation at higher temperatures.

When the impurity (e.g. salt (NaCl), Succinic acid or naphthalene) is present in the system then this third component would keep exchanging itself between two layers. These molecules would act as cementing force that would bring the molecules of two phases together mixing them as single phase. Thus the presence of impurity would result in decrease in upper consolute temperature (UCT). The ionic compounds, which get hydrated with water, are expected to show lesser increase in CST as they decrease the miscibility to a lesser extent as compared with non-ionic compound such as naphthalene.

Apparatus

- Seven 10 mL volumetric flasks with stopper
- Two water baths: 1000 mL beakers work well
- Hot plate and magnetic stirrer
- Glass rod
- Thermometer
- Ice
- 10 mL graduated cylinder and/or pipettes

Materials

- Phenol
- Deionized water

- NaCl
- Naphthalene
- Succinic Acid

Procedure

Part I: Phenol-Water phase solubility curve

1. Take six or seven 10mL measuring flasks. Place sequential weight of phenol then DI (de-ionized) water up to the mark into the test tubes (Table 3.1).

Table 3.1 *Mixing proportions for experiments*

Component	Test tube Number						
	1	2	3	4	5	6	7
Percentage of phenol (%) (label of flasks)	0.0	8.0	11.0	25.0	37.0	63	80
Weight of phenol (g)	0.0	0.8	1.1	2.5	3.7	6.3	8.0

2. At room temperature, phenol act as solid phase while it melts at 40.5°C. above 40.5°C, it would be a liquid phase. We shall take its w/V percentage for making solution.
3. Place the liquid in the cold bath ($T < 10^{\circ}\text{C}$) and stir the mixtures individually so that a homogeneous phase is formed at low temperature.
4. Then place one test tube warm bath, set the temperature of hot plate at 100°C and allow gradual rise in temperature.
5. Observe the temperature at which a phase separation starts to be visible.
6. Repeat the gradual heating steps with all the test tubes and note the temperature for phase separation.
7. Then plot a graph between temperatures for phase separation vs. compositions.

Part II: Phenol-Water phase solubility curve in 1%NaCl

1. Take seven 10mL measuring flasks. Place sequential weight of phenol and NaCl then DI (de-ionized) water up to the mark into the test tubes (Table 3.2).

Table 3.2 *Mixing proportions for Part II*

Component	Test tube Number						
	1	2	3	4	5	6	7
Percentage of phenol (%) (label of flasks)	0.0	8.0	11.0	25.0	37.0	63	80
Weight of phenol	0.0	0.8	1.1	2.5	3.7	6.3	8.0

(g)							
Weight of NaCl (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1

- Repeat the step 2-7 of part I and plot Phenol-Water phase solubility curve in 1% NaCl.

Part III: Phenol-Water phase solubility curve in 0.5% Naphthalene

- Take seven 10mL measuring flasks. Place sequential weight of phenol and Naphthalene then DI (de-ionized) water up to the mark into the test tubes (Table 3.3).

Table 3.3 Mixing proportions for Part III

Component	Test tube Number						
	1	2	3	4	5	6	7
Percentage of phenol (%) (label of flasks)	0.0	8.0	11.0	25.0	37.0	63	80
Weight of phenol (g)	0.0	0.8	1.1	2.5	3.7	6.3	8.0
Weight of Naphthalene (g)	0.05	0.05	0.05	0.05	0.05	0.05	0.05

- Repeat the step 2-7 of part I and plot Phenol-Water phase solubility curve in 0.5 % Naphthalene.

Part IV: Phenol-Water phase solubility curve in 1% Succinic acid

- Take seven 10mL measuring flasks. Place sequential weight of phenol and Succinic acid then DI (de-ionized) water up to the mark into the test tubes (Table 3.4).

Table 3.4 Mixing proportions for Part IV

Component	Test tube Number						
	1	2	3	4	5	6	7
Percentage of phenol (%) (label of flasks)	0.0	8.0	11.0	25.0	37.0	63	80
Weight of phenol (g)	0.0	0.8	1.1	2.5	3.7	6.3	8.0
Weight of Succinic acid (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1

- Repeat the step 2-7 of part I and plot Phenol-Water phase solubility curve in 0.5 % Succinic acid.

Results

For each part, results would be reported as Table 3.5.

Table 3.5 Experimental data record

Test tube No.	Percentage of phenol (%)	Temperature (°C)			Average temperature (°C)
		1	2	3	
1	0.0				
2	8.0				
3	11.0				
4	25.0				
5	37.0				
6	63.0				
7	80.0				

Average Temperature would then be plotted against each percentage of phenol for each part as given in Fig. 3.1.

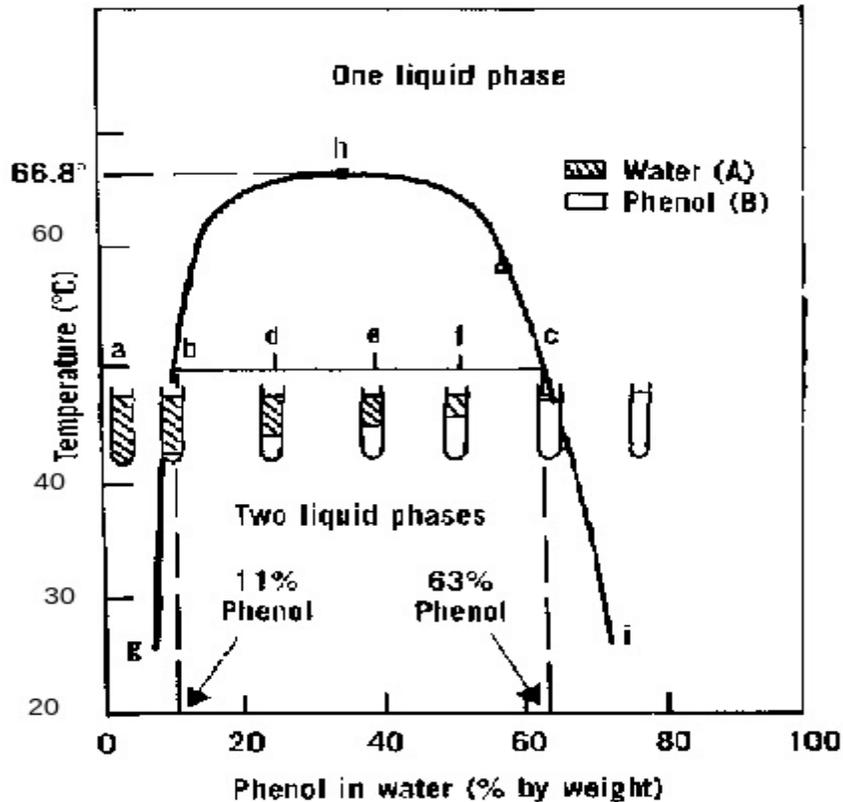


Fig. 3.1. Temperature composition plot for phenol-water system.

Precautions

- After the addition of phenol into the conical flask, the top of conical flask should be wrapping with the film with thermometer in the middle to avoid evaporation of phenol.
- As phenol is acidic and carcinogenic compound, extra care should be taken.

Reference

Effect on the upper consolute temperature (uct) of a partially miscible phenol-water solution with addition of ionic compounds like NaCl, KCl, and organic compounds like $C_{10}H_8$ (naphthalene), and $C_{10}H_{16}O$ (camphor) producing a ternary system, IJRES. 4 (3), 2017, 344-353.

Unit 4

Determination of Specific Rate of the Alkaline Hydrolysis of Ethyl Acetate by Volumetric Method

Theory

Chemical reaction takes place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and by a change in structure or configuration of these atoms. In this classical approach to chemical change, it is assumed that the total mass is neither created nor destroyed when a chemical reaction occurs. The reaction rate or rate of reaction for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place. For example, the oxidation of iron under the atmosphere is a slow reaction which can take many years, but the combustion of butane in a fire is a reaction that takes place in fractions of a second. The rate of reaction is defined as the change in the number of molecules of reacting species per unit volume per unit time.

Consider a typical chemical reaction:



The lowercase letters (a, b, p and q) represent stoichiometric coefficients, while the capital letters represent the reactants (A and B) and the products (P and Q). The reaction rate (v) for a chemical reaction occurring in a closed system under constant-volume conditions, without a build-up of reaction intermediates, is defined as:

$$v = -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = -\frac{1}{c} \frac{dC_C}{dt} = -\frac{1}{d} \frac{dC_D}{dt}$$

Factors which determine rate of reaction

- Availability of reactants and its surface area. The greater the surface area of a solid, the greater the rate of reaction.
- Concentration: increase in concentration increase the rate of reaction
- Pressure: increase in pressure results in an increase in the rate of reaction, if the reactants and products are gaseous
- Catalyst: The presences of a catalyst generally increase the rate of reaction. There are however, negative catalysts that lower the rate of reactions.
- Temperature: increase in temperature increase rate of reaction

Rate constant: Rate constant, K quantifies the speed of a chemical reaction for unit concentration terms. For a chemical reaction where substance A and B are reacting to produce C, the reaction rate has the form:



$$v = K[A]^m[B]^n$$

Where K is the rate constant that depends on temperature

A is the concentration of substance A in moles per volume of solution assuming the reaction is taking place throughout the volume of the solution. Rate constant is the rate of reaction when the concentration of each reactant is taken as unity.

Hydrolysis of an ester such as acetate in presence of a NaOH:

The hydrolysis of ethyl acetate illustrates a bimolecular reaction that gives sodium acetate and ethanol as the product from which second order rate constant can be calculated:



Ethyl acetate sodium hydroxide sodium acetate ethanol

As the reaction proceeds, each hydroxide ion removed in the formation of ethanol removes one molecule of ethyl acetate, being the number of moles of either OH or ethyl acetate so removed, the concentration of the reactants decreases. If we start with equal concentrations of the reactants, the concentration of NaOH can be conveniently followed at different time intervals by withdrawing an aliquot from the reaction mixture and determining the NaOH present in it direct or indirect titration with a standard solution of an acid.

The fact that it is a second order reaction can be established by the consistency of the values of K determined by substituting the titration results at different time intervals in the second order rate equation as follows:

$$K = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{V_t \cdot V_0} \quad (2)$$

Where V_0 is the volume of the acid equivalent to the alkali present at the beginning of the experiment and V_t is the volume of the acid equivalent to the alkali present at any selected time interval.

Apparatus

Flasks, Pipette, Burette, Burette stand, dropper

Materials

HCl, NaOH, Ethyl acetate, deionized water

Procedure

- Measure 25mL of 0.05N HCl with a pipette into each of eight (6) numbered 250mL conical flasks.
- Place 400mL of 0.05N NaOH solution in the reactor (500 mL conical flask immersed in a thermostatic water bath set at 28°C).
- At time zero, measure 1mL of ethyl acetate with a syringe into the reaction vessel and the mixture thoroughly shaken for ten seconds. withdraw 25mL of the sample and at time 10, 20, 30, 40 and 90 minutes after the reaction has gone to completion and discharge it as rapidly as possible into the respective 250mL conical flask containing the 25mL 0.05N HCl already and titrated against 0.05N of NaOH solution using two drops phenolphthalein as indicator.
- Repeat the experiment with the volume of ethyl acetate increased to 2mL at the same temperature.

Record the data as;

Table 4.1 Temperature = 28°C and volume of ethyl acetate = 1ml

Time (min)	Titre (mL)	$(V_\infty - V_0)$ (mL)	$\frac{V_\infty - V_0}{V_t \cdot V_0}$	$\text{Log} \frac{V_\infty - V_0}{V_t \cdot V_0}$
0	$X = V_0$			
5				
10				
15				
.....				
90	$X = V_\infty$			

Table 4.2 Temperature = 28°C and volume of ethyl acetate = 2ml

Time (min)	Titer (mL)	$(V_{\infty} - V_0)$ (mL)	$\frac{V_{\infty} - V_0}{V_t \cdot V_0}$	$\text{Log} \frac{V_{\infty} - V_0}{V_t \cdot V_0}$
0	$X = V_0$			
5				
10				
15				
.....				
90	$X = V_{\infty}$			

Plot a graph of $\text{Log} \frac{V_{\infty} - V_0}{V_t \cdot V_0}$ against time.

Precautions

- Chill the solution as rapidly as possible.

Unit 5

Study of Kinetics of the Acid Catalyzed Hydrolysis of Methyl Acetate and Evaluation of Activation Energy for the Reaction

Theory

Chemical reaction takes place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and by a change in structure or configuration of these atoms. In this classical approach to chemical change, it is assumed that the total mass is neither created nor destroyed when a chemical reaction occurs. The reaction rate or rate of reaction for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place. For example, the oxidation of iron under the atmosphere is a slow reaction which can take many years, but the combustion of butane in a fire is a reaction that takes place in fractions of a second. The rate of reaction is defined as the change in the number of molecules of reacting species per unit volume per unit time.

Consider a typical chemical reaction:



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$$v = -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = -\frac{1}{c} \frac{dC_C}{dt} = -\frac{1}{d} \frac{dC_D}{dt}$$

Factors which determine rate of reaction

- Surface area: Availability of reactants and its surface area. The greater the surface area of a solid, the greater the rate of reaction.
- Concentration: Increase in concentration increase the rate of reaction
- Pressure: Increase in pressure results in an increase in the rate of reaction, if thereactants and products are gaseous
- Catalyst: The presences of a catalyst generally increase the rate of reaction. Thereare however, negative catalysts that lower the rate of reactions.
- Temperature: Increase in temperature increase rate of reaction

Rate constant: Rate constant, K quantifies the speed of a chemical reaction for unit concentration terms. For a chemical reaction where substance A and B are reacting to produce C, the reaction rate has the form:



$$v = K[A]^m[B]^n$$

Where K is the rate constant that depends on temperature

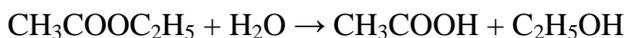
A is the concentration of substance A in moles per volume of solution assuming the reaction is taking place throughout the volume of the solution.

Rate constant is the rate of reaction when the concentration of each reactant is taken as unity.

Hydrolysis of an ester such as acetate in presence of a mineral acid:

Hydrolysis is a chemical decomposition involving breaking of a bond and the addition of elements of water. The use of an acid catalyst accelerates the hydrolysis. The reaction rate is expressed in terms of chemical composition of the reacting species.

The hydrolysis of an ester such as ethyl acetate in the presence of a mineral acid gives acetic acid and ethyl alcohol.



The kinetics of the reaction can be studied by taking a known quantity of ethyl acetate and mixing it with a relatively large quantity of HCl. An aliquot of the reaction mixture is withdrawn at different intervals of time and titrated against a standard alkali. Obviously, as the reaction proceeds, the value of alkali required to neutralize the acid (HCl present as catalyst + CH₃COOH produced by hydrolysis of the ester) progressively increases.

The fact that this is a first order reaction is established by substituting the results in the first order rate expression;

$$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

And verifying the constancy of the value of rate constant, K or in this case,

$$(a - x) = (V_{\infty} - V_0)$$

and

$$a = (V_t - V_0)$$

$$K = \frac{2.303}{t} \log \frac{(V_{\infty} - V_0)}{V_t - V_0} \quad (2)$$

Where,

V_0 = Initial titre value

V_{∞} = Final titre value at the end of the experiment

V_t = Titre value at the various time intervals chosen

As the hydrolysis proceeds, there will be proportional increase in the concentration of acetic acid formed.

Apparatus

Flasks, Pipette, Burette, Burette stand, dropper

Materials

HCl, NaOH, Ethyl acetate, deionized water

Procedure

1. Measure 25 mL of 0.05N NaOH with a pipette into each of eight (6) numbered 250 mL conical flasks.
2. Place 400 mL of 0.05N HCl solution in the reactor (500mL conical flask immersed in a thermostatic water bath set at 28°C).
3. At time zero, measure 1 mL of ethyl acetate with a syringe into the reaction vessel and the mixture thoroughly shaken for ten seconds. Withdraw 25 mL of the sample and at time 10, 20, 30, 40 and 90 minutes after the reaction has gone to completion and discharge it as rapidly as possible into the respective 250 mL conical flask containing the 25 mL 0.05N NaOH already and titrated against 0.05N of HCl solution using two drops phenolphthalein as indicator.
4. Repeat the experiment with the volume of ethyl acetate increased to 2 mL at the same temperature.

5. Record the data as;

Table 5.1 Temperature = 28°C and volume of ethyl acetate = 1mL

Time (min)	Titre (mL)	(V _t - V _o) (mL)	$\frac{V_0 - V_\infty}{V_t - V_\infty}$	$\text{Log} \frac{V_0 - V_\infty}{V_t - V_\infty}$
0	X = V ₀			
5				
10				
15				
.....				
90	X = V _∞			

Table 5.2 Temperature = 28°C and volume of ethyl acetate = 2mL

Time (min)	Titre (mL)	(V _t - V _o) (mL)	$\frac{V_0 - V_\infty}{V_t - V_\infty}$	$\text{Log} \frac{V_0 - V_\infty}{V_t - V_\infty}$
0	X = V ₀			
5				
10				
15				
.....				
90	X = V _∞			

- Plot a graph of $\text{Log} \frac{V_0 - V_\infty}{V_t - V_\infty}$ against time.
- Perform above mention experiments at 5 different temperatures (28°C, 33°C, 38°C, 43°C and 48°C) and plot $\text{Log} \frac{V_0 - V_\infty}{V_t - V_\infty}$ against time at each temperature. Calculate rate constant from each plot. Plot k (rate constant) against $\frac{1}{T}$ and calculate activation energy from slope;

$$\text{Slope} = E_a / R$$

Where;

E_a = Activation energy

R = General gas constant

Precautions

- Chill the solution as rapidly as possible.

Unit 6

Determination of Critical Micelle Concentration of a Surface Active Material by Surface Tension and Conductivity Method

Theory

Surfactants (micelle forming agents)

The surfactants have a characteristic molecular structure consisting of a structural group that has little/no attraction for solvent, known as lyophobic group, together with a group which has strong attraction for solvent, called lyophilic group. Thus, surfactants have amphiphilic structure with a polar head and non polar tail. Whenever these are dissolved in water or hydrophilic solvent, the presence of lyophobic group in the solvent distort the solvent molecules, the solvent pushes the surfactant towards the surface in order for the system to attain the lower free energy but lyophilic group prevents the surfactant from being expelled completely from the solvent as a separate phase. The surfactant can also adsorb on the surface of hydrophobic liquid but with opposite orientation. The amphiphilic structure of surfactant causes orientation of the molecule at the surface with their lyophilic end in the liquid and lyophobic end oriented away from the liquid or vice versa (depending upon nature of solvent).

Micellization

The distortion of solvent structure can also be decreased by the aggregation of surfactant molecules into clusters with their lyophobic groups directed towards the interior of the cluster and lyophilic groups directed towards solvent. This is an entropy driven process. The structures thus formed are called micelle and the process is termed as micellization. However, the surfactant molecules transferred from the solution to the micelle may experience some loss of freedom from being confined to the micelle. In addition, they may experience an electrostatic repulsion from other similarly charged surfactant molecules in the case of ionic surfactants. These forces increase the free energy of the system and oppose micellization. Hence, micelle formation depends on the force balance between the factors favoring micellization (van der Waals and hydrophobic forces) and those opposing it (kinetic energy of the molecules and electrostatic repulsion).

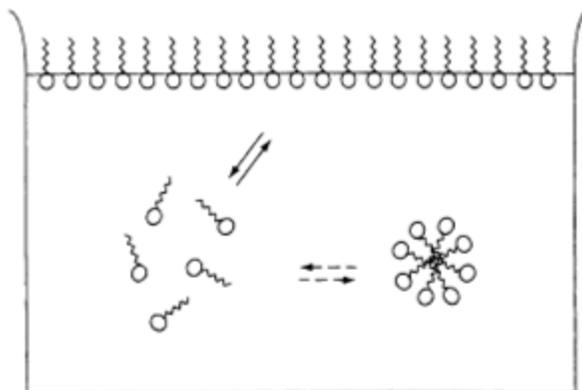


Fig.6.1. Orientation of surfactant over the liquid-gas interface and within the bulk liquid.

The concentration of surfactant at which micelles first appear in solution is called the **critical micelle concentration or CMC**. Representing the surfactant by S , the micellization process can be described by the following reaction:



In which S_n is the micelle with a degree of aggregation n . The formation of micelles from the constituent monomers involves a rapid, dynamic, association-dissociation equilibrium.

Micelles are undetectable in dilute solutions of monomers, but become detectable over a narrow range of concentrations as the total concentration of surfactant is increased, above which nearly all additional surfactant species form micelles. The concentration of free surfactant at which micelles start to form is termed as critical micelle concentration (CMC). Above the CMC, the concentration of free surfactant is essentially constant and the concentration micellar surfactant increases approximately linearly. This phenomenon results in abrupt shift in any measurable property such as surface tension or conductivity (in case of ionic surfactant). Below and above CMC the measurable property varies gradually with concentration of surfactant as depicted in Fig. 6.2.

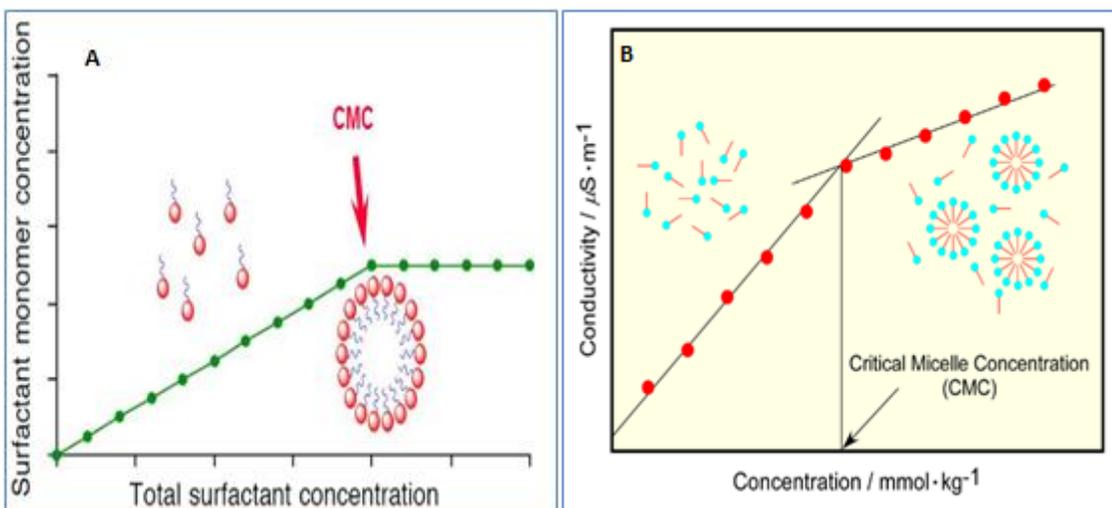
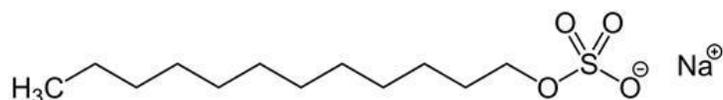


Fig. 6.2. Calculation of CMC from (a) surface tension (b) Conductivity.

Anionic surfactant sodium dodecyl sulfate (SDS) would be used in this experiment.



Sodium dodecyl sulfate (SDS)

Fig. 6.3. Structure of anionic surfactant sodium dodecyl sulfate (SDS).

Apparatus

Tensiometer, conductivity meter, micropipette (2-2000 μl), 50 mL beakers

Materials

Sodium dodecyl sulfate (SDS), Distilled water

Procedures

Part A : Determination of CMC through surface tension measurements

1. Prepare 120 mM Solution of sodium dodecyl sulfate (SDS) in 10 mL of water.
2. Clean the tensiometer and its vessel properly.
3. First place 30 mL distilled water in the vessel
4. Tie a clean ring with the cable of tensiometer, hang it in air and set the scale of tensiometer to zero value by rotating its knob.

5. Dip the ring in the water and rotate the knob until ring gets detach from the surface of the water. Note the reading of surface tension directly from the scale.
6. Add slight amount of 50 μL of 120 mM SDS in the water, stir well and then note surface tension.
7. Repeat the steps by successive addition 50 μL of 120 mM SDS in each solution and noting the surface tension in the Table 6.1.

Table 6.1 SDS concentration vs. Surface tension data.

Volume of 120 mM SDS solution added to the vessel (μL)	SDS concentration in the 30 mL vessel (mM)	Surface tension ($\mu\text{S/m}$)
0	0	
50	0.2	
100	0.4	
150	0.6	
200	0.8	
250	1.0	
300	1.2	
350	1.4	
400	1.6	
450	1.8	
500	2.0	
550	2.2	
600	2.4	
750	3.0	
1000	4.0	
1300	5.2	
2500	10.0	

8. Plot a graph of surface tension in mN/m vs. concentration of surfactant in mM .
9. Mark CMC from point of intersection of two straight lines.

Part A : Determination of CMC through conductivity measurements

1. Prepare 120 mM Solution of sodium dodecyle sulfate (SDS) in 10mL water.
2. Clean the conductivity meters electrode and beaker properly.
3. First place 30 mL distilled water in the beaker.

4. Dip the electrodes of conductivity meter in the water and note the reading of conductivity directly from the scale.
5. Add slight amount of 50 μL of 120 mM SDS in the water, stir well and then note conductivity.
6. Repeat the steps by successive addition 50 μL of 120 mM SDS in each solution and noting the surface tension in the Table 6.2.

Table 6.2 SDS concentration vs. Conductivity data.

Volume of 120 mM SDS solution added to the vessel (μL)	SDS concentration in the 30 mL vessel (mM)	Conductivity (mN/m)
0	0	
50	0.2	
100	0.4	
150	0.6	
200	0.8	
250	1.0	
300	1.2	
350	1.4	
400	1.6	
450	1.8	
500	2.0	
550	2.2	
600	2.4	
750	3.0	
1000	4.0	
1300	5.2	
2500	10.0	

7. Plot a graph of surface tension in mN/m vs. concentration of surfactant in mM.
8. Mark CMC from point of intersection of two straight lines.

Precautions

- Turn the knob of tensiometer carefully otherwise abrupt pulling can damage the connections.
- Turn the knob very slowly when the ring is near the surface of liquid so that the surface tension can be recorded correctly.
- Make sure that the electrodes of conductivity meters are neat and clean before recording each reading.

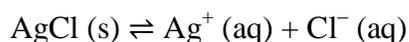
Unit 7

Precipitation, Titration and Determination of Solubility of a Sparingly Soluble Salt

Theory

There are many compounds such as lead chloride (PbCl_2), silver chloride (AgCl) etc. which are very slightly soluble in water. These substances are called sparingly soluble salts. When these sparingly soluble salts are dissolved in water, equilibrium is established between the undissolved solid salt and ions of the dissolved salt. For example:

For a sparingly soluble compound like AgCl , the following equilibrium occurs between the undissolved solid salts and the silver and chloride ions in the saturated solution:



Applying the law of chemical equilibrium, we will get:

$$K = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{AgCl}]}$$

Rearranging;

$$K \times [\text{AgCl}] = [\text{Ag}^+] [\text{Cl}^-]$$

The concentration of the pure solid substance remains constant. Therefore, the concentration of solid AgCl in the solid state i.e. $[\text{AgCl}]$ is constant at a particular temperature, no matter how much solid is present in contact with the solution. It follows:

$$K \times \text{constant} = K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$$

Where K_{sp} is known as solubility product constant or solubility product. Since the solubility of a salt usually varies widely with temperature, the numerical value of K_{sp} for a salt changes with temperature.

Apparatus

Filter paper, Funnels, beakers (50 mL), measuring cylinder, iron stands with clamps

Materials

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 , sodium oxalate, Distilled water

Procedure

1. Prepare 20 mL of 0.1M solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 20 mL of 0.1M solution of Na_2SO_4 .
2. Mix 10 mL of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ with 10 mL of Na_2SO_4 .
3. In order to speed up the precipitation process, heat the mixture at 50°C and allow it to cool to room temperature.
4. After the solution is sufficiently cooled down, filter the solution through to separate supernatant from precipitates.
5. Wash the precipitates thoroughly with known volume of cold water to remove dissolved $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Washing water temperature should be around 4°C so that extra $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ does not remove from the precipitates only already dissolved $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is removed from solution. The volume of water added to wash the precipitates should be known as it would be added to 20 mL initial volume in order to calculate Ca^{2+} ions concentration.
6. Place the beaker carrying the filtrate over the hot plate and fix a thermometer in it to monitor the temperature. Heat the filtrate up to 80°C .
7. Add 10 mL of 0.1M sodium oxalate to precipitate Ca^{2+} as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, the solubility product of which is very small $K_{\text{sp}} = 2.6 \times 10^{-9} \text{ mol}^2/\text{dm}^6$.
8. Filter the precipitates of calcium oxalate through pre-weighed filter paper. Dry the crystal properly and weigh them.
9. Place the crystal for further drying and re-weigh the precipitates until the weigh becomes constant.
10. From the weight of calcium oxalate calculate the molar concentration of calcium oxalate which will be equivalent to the molar concentration of Ca^{2+} ions.
11. From the molarity of Ca^{2+} ions (in moles/ L), calculate the solubility of S of Ca^{2+} ions and calculate solubility product of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as;

$$K = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = S^2$$

Precautions

- Do not use high molarity of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2SO_4 for forming precipitates of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.
- Carefully note the volume of washing liquid in step 5 which would be added to filtrate.
- Wash the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sample in the filtrate solution nowhere else.
- Carefully note the weight of final precipitate after complete drying. For this purpose repeat weight 3 to 4 times after one hour successive drying following the first reading.

Unit 8

Determination of Redox Activity of $K_4Fe(CN)_6$ and Estimation of Redox Parameters

- a. Anodic and Cathodic Currents and Potentials.
- b. Number of Electrons Involved in the Electrochemical Reaction
- c. Linear Dependency of Current with Square Root of Scan Rate.

Background

Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is a versatile electro-analytical technique for the study of electroactive species. CV monitors redox behavior of chemical species within a wide potential range. The current at the working electrode is monitored as a function of potential is applied to the electrode. A cyclic voltammogram is the plot of the response current at the working electrode to the applied excitation potential which can be analyzed for fundamental information regarding the redox reaction.

The potential at the working electrode (WE) is controlled vs a reference electrode (RE), Ag/AgCl(s)/(satd. KCl) electrode. The controlling potential is applied across the WE which varies in cyclic manner with time.

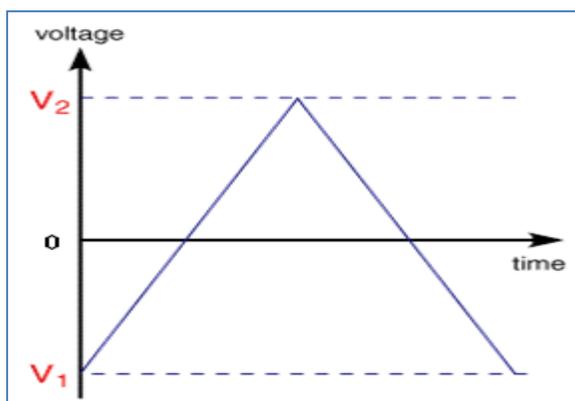


Fig. 8.1. Variation of potential in cyclic voltammetry.

The current response obtained in response to above mentioned potential variation is called cyclic voltammograms.

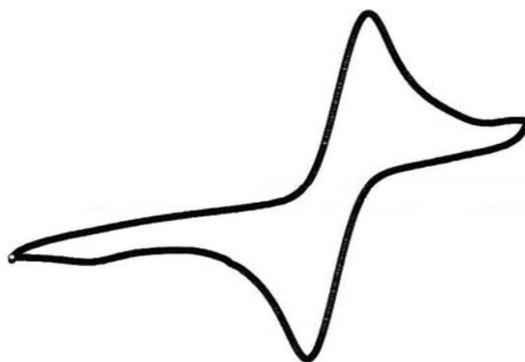


Fig. 8.2. Variation of potential in cyclic voltammetry.

Shape of cyclic voltammograms

As the potential is scanned positively (forward scan, here) and is sufficiently positive to oxidize the analyte or negative to reduce analyte, the rapid rise in current takes place (Fig. 8.3.a).

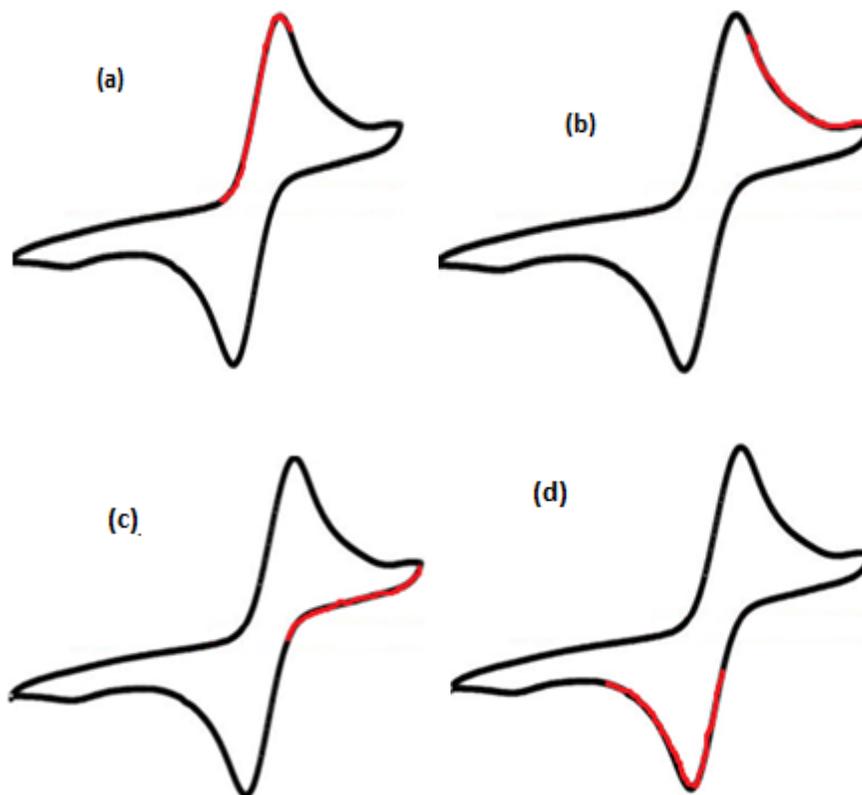


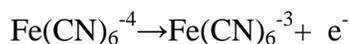
Fig. 8.3.(a) Current rise near E_p , (b) current fall due to decreasing analyte concentration, (c) Slow rise in current and (d) rapid current rise near E_p .

A maximum current is reached at E_p the value the anodic current (Fig. 8.3a) is due to the oxidation process and cathodic current is due to reduction process (Fig. 8.3d). The concentration of $\text{Fe}(\text{CN})_6^{-4}$ at the electrode surface depletes and the current then decays till the end of the forward scan (Fig. 8.3.b). Then, the scan changes its direction and the reverse process starts (Fig.8.3. c & d) (reduction would take place now if oxidation happened in forward scan and vice versa).

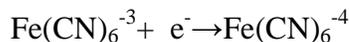
The current varies slowly with potential then abruptly decreases near E_p for the reverse process. E_p can be labeled as E_{pa} for anodic peak potential and E_{pc} for cathodic peak potential.

Electrochemical investigations of Ferrocyanide/Ferricyanide Redox Couple:

As the potential is scanned positively (forward scan, here) and is sufficiently positive to oxidize $\text{Fe}(\text{CN})_6^{-4}$, the rapid rise in current takes place;



The concentration of $\text{Fe}(\text{CN})_6^{-4}$ at the electrode surface depletes and the current then decays. As the scan direction is switched to negative for the reverse scan the potential resulting in a cathodic current which peaks and then decays as $\text{Fe}(\text{CN})_6^{-3}$ in the solution adjacent to the electrode is consumed.



The quantities to be noted are the anodic peak current i_{pa} , cathodic peak current i_{pc} , anodic peak potential E_{pa} , and cathodic peak potential E_{pc} .

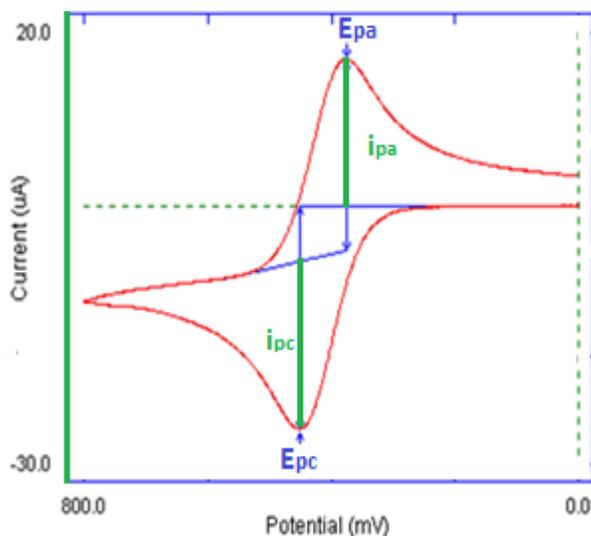


Fig. 8.4.Characteristic parameters of a voltammogram.

Measuring ip does involve the extrapolation of the base-line current. A redox couple in which half reactions rapidly exchange electrons at the working electrode are said to be electrochemically reversible couples.

Apparatus

Potentiostat, glassy carbon working electrode (diameter 1mm), platinum auxiliary electrode, Ag/AgCl reference electrode, nitrogen cylinder, polishing material, electrochemical cell, if cell is not available then upper edge of 25mL beaker can be cut and fire round it and take a cork that fits into the beaker drill three holes in a cork according to the size/thickness of electrodes. Then fix the cork into the beaker and use it as electrochemical cell.

Chemicals $K_4Fe(CN)_6$, Potassium nitrate or KCl, Distilled water

Procedure

1. Prepare 100mL of 1.0 M KCl by dissolving calculated amount of KCl in distilled water.
2. Prepare 50 mL of 1mM $K_4Fe(CN)_6$ solution in 1.0 M KCl by dissolving calculated amount of $K_4Fe(CN)_6$ in 1.0 M KCl.
3. Fill the cell with 10 mL 10 mM $K_4Fe(CN)_6$ in 1.0 M KNO_3 using a pipette.
4. First polish the working electrode and polish counter electrode if needed.
5. Connect working, reference and counter electrodes with their respective (marked) jaws and place the electrodes in the solutions. Their tips should be dipped in the solution.
6. Degas/Purge the solution prior to each scan by passing N_2 or Ar gas through the solution for 1-2 minutes. For this purpose dip the gas cylinder's needle in the solution and open the knob such that gas flows through the solution at moderate rate.

- Turn on the computer, and the electrochemical unit. Open the CV software. Set the scan rate (start with lower scan rate), potential window, label the voltammograms and run the scan.
- Record/note Peak potential, scan rate and peak current.
- Remove the working electrode; polish it and reassemble and using the same solution repeat the scan with higher scan rate. Record the data in the form of table as;

Table 8.1 Experimental data record.

Sr. No.	Scan rate ν (mV/s)	$\sqrt{\text{Scan rate}}$ $\nu^{1/2}$ (mV/s) ^{1/2}	Peak potential E_p (V)	Anodic Peak Current i_p (A)	Anodic Peak Current I_c (A)
1	10				
2	100				
3	200				
4	300				
5	And so on				

From the variation between peak potentials at different scan rates, the reversibility of process can be defined. If the peak potential does not changes with scan rate the process would be reversible otherwise it would be irreversible.

Treatment of Results

- The number of electrons involved in the redox reaction for a reversible couple is related to the difference of peak potentials by:

$$E_{pa} - E_{pc} = \frac{59 \text{ mV}}{n}$$

- Plot a graph of i_{pa} Vs. $\nu^{1/2}$. From the slope of the plot calculate diffusion coefficient using the following equations;

$$\text{Slope} = 2.69 \times 10^9 n^{2/3} A D^{1/2} C$$

where,

i_{pc} = peak current (A)

$n = \#$ electrons involved

$A =$ electrode area(cm^2)

$D =$ diffusion coefficient (cm^2/s)

$C =$ concentration (mol/L)

3. Determine the concentration of the unknown solution. Record another table of the CV data for the solution of unknown concentration. Plot i_{pa} Vs. $v^{1/2}$ and calculate the concentration from its slope.

Precautions

- Electrode surface should be dip in the solution before recording signal.
- Clean the surface of electrode carefully before each experiment.
- Solution should be stirred throughly before recording each reading.
- Solutions should be done degased properly.

Unit-9

Using hyperchem program, perform semi-empirical AM1 calculations for the following compounds

- **CO₂**
- **NH₃**
- **BF₃**

Background

Computational chemistry allows us to calculate different parameters which can reveal about their properties. Among the above mentioned molecules, CO₂ is a linear molecule therefore its dipole moment would be zero and out of theoretically calculated vibration mode one mode (symmetric stretch) would be vibrationally inactive due to no change in dipole moment. Similarly BF₃ due to its trigonal structure is expected to be non-polar with zero dipole moment. Charge densities would reveal the charge distribution over the atoms within the molecules. In order to remove electron from a molecule, electron can be removed from occupied molecular orbital and ionization process removes electron from highest filled molecular orbital. Therefore, ionization potential would be dependent upon HOMO orbital energy. Similarly, as incoming electron would find its place in LUMO orbital, electron affinity would be proportional to LUMO. Although the electrons can jump from any filled energy level to any empty energy level but only those transitions would take place for which symmetry of the orbital would be retained. Therefore a number of possible transitions would be forbidden. So using hyperchem calculations allowed transitions can be compared with predicted UV-Vis spectra.

Activity

Draw molecule:

- Open hyperchem release 8.0 software → Select “Display” → Go to “Labels” → Select Symbols → Click ‘O.K.’
- Go to main toolbar click on “” → Click on “” then Click on main screen. Repeat the step with “O” selection and connect it with C to draw CO₂ molecule.
- Go to “Build” → “Add hydrogens and model build” → CO₂ molecule would be built up.
- Go to “Setup” → “Semi-empirical” → “AM1” → “OK”.
- Go to “File” → “Startlog” → Select file location → “Save”.
- Go to “Compute” → “Geometry Optimization” → Select “Polak method 150 cycles and 0.5 gradient” → “OK” → Let it optimize the geometry
- Go to “Compute” → “Single Point” → Let it calculate
- Go to “File” → “Stoptlog”

- Now go to the file location where the Hyperchem file was saved previously at the time of start log. A notepad file of the same name as that of hyperchem file would be there.
- Click Notepad File → Click ok in error window → Click “Yes” on file loading window. You can close Gaussian window.
- Find out the required parameters from notepad file.

Q. 1 Find and compare following parameters;

- **Dipole moments**
- **Charge densities**
- **Energies**

Q. 2. From the spectrum read Number of active vibrational modes and compare them with those calculated from $3N-5$ formula for linear and $3N-6$ formula for non-linear molecules.

Then Compute “vibrational rotational analysis” followed by clicking on vibrational spectrum.

Q. 3. Compare UV-Vis spectra with selected transition from molecular orbital levels.

Click “Startlog” save file and Compute “single point CI” and then click “Stoplog”.

Then click on “orbitals” Click on “label” in small window the identify HOMO (“highest occupied Molecular orbital” and LUMO “lowest unoccupied molecular orbitals”).

- Calculate frequency of transition from HOMO → LUMO.
- Selecting 3 higher occupied molecular orbitals and 3 lower unoccupied molecular orbitals. Predict possible transition in accordance with symmetry selection rule.
- I.P. and Electron affinities.
- Tendency of NH_3 interaction with BF_3 .

Then Compute “Single point CI” followed by clicking on Electronic Spectrum.