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Homi Bhabha Centre for Science Education
Tata Institute of Fundamental Research

In collaboration with

Gogate Joglekar College, Ratnagiri

Inorganic Chemistry Task

This workshop is organized by Centre for Excellence in Science and Mathematics Education (CESME-HBCSE) and set up under the Pandit Madan Mohan Malaviya National Mission for Teachers and Teaching Programme

Synthesis of iron-oxalate complex and determine its molecular formula using redox titrations

Introduction

In this present experiment,we will be synthesizing a coordination complex of iron with oxalate ligand. The formula of the same can be represented as $K_p[Fe_q(C_2O_4)_r].sH_2O]$ (green coloured complex see the image) Using redox titrations and calculation, we will determine the values of p,q,r and s. We will also calculate the % yield of the product.

This experiment is divided into 4 parts.
In **part A**, you will be synthesizing the iron complex, whereas **part B** deals with estimation of oxalate and iron content in the complex that will help to derive the molecular formula of the complex.
In **part C**, you will be performing few qualitative tests to compare the relative binding strengths of different ligands. The photochemical reaction of iron-oxalate complex with potassium ferricyanide will be explored in **part D**.

You have 10 members in your group. You are expected to read the given experimental module together as a group, discuss and understand what exactly needs to be done in the laboratory. After discussion, you will split as pairs and conduct the laboratory work as pairs. After completion of the entire work, all of you will again form a group, collate your data and reflect.

Safety Considerations for the experiment:

Permanganate (MnO_4^-) is toxic and an environmental pollutant. All solutions containing permanganate, including the initial washes of glassware, should be disposed of in labeled containers 'liquid waste'.

Care should be taken to avoid contact with permanganate solutions. Wash your hands and clean up immediately with tissue paper (provided) if any solution is spilled.

Be careful while using strong acids and while heating solutions in the lab. Do not bend on the flask while heating the solution and kindly wear safety gloves/goggles.

Part A. Synthesis of complex of Fe and oxalate ion

List of Glassware

Beakers 50 mL, 100 mL and 250 mL	2 each
Measuring cylinder 10 mL	1
Glass rod	1
Pasteur pipettes	2
Ice bath	1
Buchner Funnel, 3” diameter	1
Metal spatula	1

List of Chemicals

Anhydrous Ferric chloride	1.60 g, 1 vial
Hydrochloric acid, concentrated	1 mL, 1 tube
potassium oxalate monohydrate	5.80 g, 1 vial

Part B. Estimation of the prepared complex

List of Glassware

Burette	25 mL	1
Conical flasks	100 mL	2
Measuring cylinder	10 mL	1
Volumetric flask	100 mL	1
Pipette, graduated	10 mL	1
Glass rod		1
Dropper		2
Rubber bulb		1
Wash Bottle 500 mL		1
Watch glass		1

List of Chemicals

$KMnO_4$ 0.2M, H_2SO_4 3M, Zn dust (0.15 g/vial)

Part C and Part D. Qualitative tests for determination of spectrochemical series and photochemical activity

List of Glassware

Glass vials	1
Droppers	6
Wash Bottle 500 mL	1
Watch glass	1

List of Chemicals

8 mL of 0.1 M solutions each of HCl, NH_3, NaOH, H_2SO_4, Na_2EDTA, Na_2S, $Na_2C_2O_4$, Acetylacetone, KSCN 0.1 M, Ethylene diamine (0.2 M), 0.1 M $K_3Fe(CN)_6$ solution, Ammonia (1:1 aq. solution) Solution 1 ($FeCl_3$), Solution 2 (this is the solution of complex prepared by you)

On the tables for the common use
Filter paper, Balances, Büchner funnel, Filtration flask, Water-jet pump, Scissors, Liquid waste container, Solid waste container

Chemicals

For anhydrous iron (III) chloride, potassium oxalate and oxalic acid - note the formula, the grade and other relevant information from the bottle. You are not expected to prepare any other solution required for the experiment.

H_2SO_4 	3 M	250 mL
$KMnO_4$ 	About 0.2 M	250 mL
Oxalic acid 		
NaOH 		
$K_3Fe(CN)_6$ 		

Exact molarity of $KMnO_4$ solution will be provided to you in laboratory.

Hazard symbols

It is helpful if you are familiar with chemical hazard symbols. Such awareness gives a better understanding regarding handling

Procedure:

Part A: Synthesis of the complex

1. Dissolve anhydrous iron chloride (1.60 g) in about 5mL of water in a beaker. Add 4-5 drops of concentrated hydrochloric acid to this solution.

2. Similarly, in another beaker, dissolve potassium oxalate monohydrate (5.80 g) in about 20 mL of water (warm if necessary).

3. To the beaker containing solution of oxalate, slowly add iron chloride solution with stirring.

4. Cool the solution to room temperature and keep the beaker in ice bath for 10 min.

5. Filter the product obtained on suction and dry the product in dark (it takes about 20 mins.)

6.Weigh the product after drying and find its practical yield.

While the product is getting dried, proceed with **part C** of the experiment.

Answer Sheet (for synthesis)

Calculate the amount of mmols of anhydrous iron chloride used

Calculate the amount of mmols of potassium oxalate used

Using the above answers, calculate the ratio of mmols of anhydrous iron chloride: potassium oxalate

Based on above calculations, write which reagent is acting as limiting reagent?

Mass and colour of the product obtained

Calculate the theoretical yield and after you weigh the product calculate the practical yield.

In your opinion, on the basis of the given procedure, state two factors that can lower the final percentage yield of the complex.

Part B: Analysis of the complex for estimating the oxalate and iron from the complex:

Making of Sample solution

Weigh accurately about 0.100 to 0.150 g of the crude product, dissolve in small amount of water (add 1-2 drops of conc. sulphuric acid carefully) and dilute to 100 mL. You need to record the exact mass of the complex weighed by you for preparation of sample solution.

Analysis of oxalate content

1. Pipette 10 mL of the diluted sample solution in a conical flask.
2. Add about 10 mL of 3M H_2SO_4. Heat the solution to about 60-70 ºC.
3. Titrate this hot solution with supplied $KMnO_4$ till you get stable light pink colour.
4. Note the titration reading at appropriate place in the answer sheet.

Do not discard the solution. Continue with the above solution for estimation of iron as discussed below.

Analysis of Iron content

1. After oxalate titration, add 0.15 g of zinc dust to the same solution and heat the solution to about 60-70ºC covering the flask with a watch glass.
2. Shake the mixture gently while heating.
3. After about 5 min, remove the flask carefully and allow the solution to cool.
4. Filter the solution if any excess zinc dust remains in the flask, otherwise proceed to step 5.
5. Rinse the watch glass, draining the washings into the flask.
6. Titrate this solution with same potassium permanganate till you get stable light pink color.
7. Note the reading and record it in the answer sheet.

Repeat both the titrations one more time and enter your readings in the answer sheet.

Answer Sheet (for estimation of oxalate and iron)

Molarity of $KMnO_4$:_____ Amount of complex weighed: _____

	Trial I		Trial II		Trial III	
	Titration 1	Titration 2	Titration 1	Titration 2	Titration 1	Titration 2
Initial Reading (mL)						
Final Reading (mL)						
Difference (mL)						

1. Write balanced chemical equations for the reaction that takes place during estimation of oxalate by permanganate.

2. Why we have to do this titration in acidic medium?

3. Write balanced equations for the chemical reaction/s that is/are taking place after addition of Zn powder.

4. Write balanced equation for the reaction that takes place in estimation of iron by permanganate.

5. Using the titration readings for any one trial, calculate (a) the oxalate and iron content in the amount of the complex weighed by you for analysis and (b) the molar ratio of oxalate to iron.
You are expected to show the main steps for calculations.

6. Using your answer in question 5, calculate the values of p and s in the product formula $K_pFe_q(C_2O_4)_r.sH_2O$? (Express the values of p, q, r and s as whole integer)

p = q = r = s =

7. Write balance equation for formation of complex.

Part C: Comparing binding strength of different ligands

In this part you will take solutions of complex synthesized by you and that of original salt for performing some qualitative tests. You will be adding different solutions of ligand to the solution of complex and then observe the changes in colour of the resultant solutions or formation of any precipitates or any other changes. Through these observations, you will try to develop a feel for the ligand displacement reactions occurring which is an important area of study for transition metals.

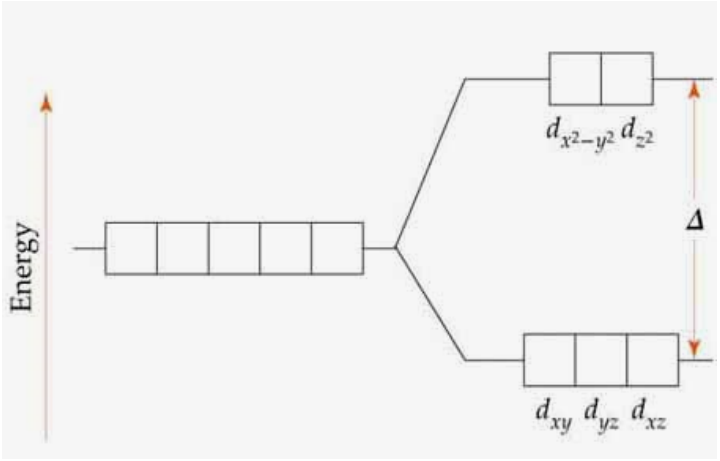
You are supplied with 0.1 M solution of $FeCl_3$ (**solution 1**) and the complex (**solution 2**). In solution 1, iron exists as $[Fe(H_2O)_6]^{3+}$.

Carry out the following tests and report your observations.

Reagents	**Observations**	
	Solution 1	Solution 2
NaOH		
HCl		
KSCN		
1:1 ammonia solution		
Ethylene diamine (en)		
H_2SO_4		
Na_2EDTA		
Na_2S		
Acetylacetone (acac)		
$Na_2C_2O_4$		

*en=ethylene diamine

The following figure indicates qualitatively the d orbital splitting of a metal ion in presence of ligands or complexing agents.



Splitting energy, Δ

Spliting of d orbitals

For a given metal ion, one of the factors of the magnitude of the splitting of d orbitals is the type of the ligands. This energy of splitting of d orbitals is designated as Δ. When several ligands are compared for a particular metal ion, it is possible to arrange the ligands in the order of their increasing splitting energy, Δ. Such an arrangement is known as the *spectrochemical series*.

1. Based on your observations, arrange the ligands H_2O, NH_3, Cl^-, OH^-, en, SCN^-, EDTA, S^{2-}, aq. NH_3, acac and $C_2O_4^{2-}$ on the basis of their binding strength with iron. Justify your answer in brief.

2. From your observation, which ligand will have
   a) maximum splitting energy, Δ
   b) minimum splitting energy, Δ

The following table gives the list of the complementary color and the corresponding wavelengths of absorption.

Absorbed Wavelength (nm)	**Absorbed Color**	**Transmitted Color**
400	violet green	yellow
450	indigo	yellow
480	blue	orange
490	blue-green	red
530	green	purple
570	yellow-green	dark blue
600	orange	blue
650	red	green

3. From your observations, write the approximate wavelength region of the spectrum that is absorbed by the species present in the solution after the reaction.

Reagents added	Absorbed Wavelength (nm)	
	Solution 1	Solution 2
NaOH		
HCl		
KSCN		
1:1 ammonia solution		
Ethylene diammine (en)		
H_2SO_4		
Na_2EDTA		
Na_2S		
acetylacetone		
$Na_2C_2O_4$		

Part D: Photochemical reaction of the synthesized complex

1. Dissolve 0.05 g of your complex in 30 mL distilled water in a beaker. Add 4 drops of 2M H_2SO_4 and swirl the mixture.

2. Take 5 mL of this solution in two test tubes.

3. Keep one test tube (**TT1) away from the light source** as the control and another test tube (**TT2)** in the sunlight for 5 min.

4. Add about 1 mL of 0.1 M potassium ferricyanide solution $K_3Fe(CN)_6$ to each test tube.

1. What colour change do you observe in both the test tubes?

TT1
TT2

2. Explain your observations with the help of balanced chemical equations for both the reactions.
