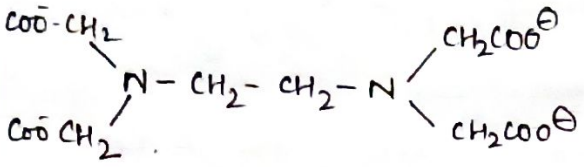
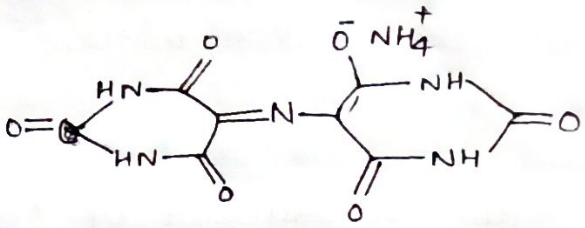
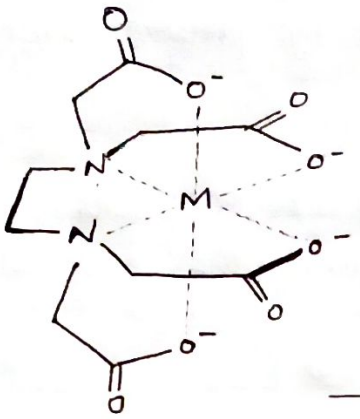


Structure of EDTA



structure of Murexide



M = Ni^{+2}

Structure of Ni-EDTA complex.

Chemical Reactions:

$$Ni^{+2} + 2Cl^- + 6H_2O \longrightarrow [Ni(H_2O)_6]Cl_2$$

$$Ni^{+2} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{+2}$$

$$[Ni(NH_3)_6]^{+2} + EDTA^{4-} \longrightarrow [Ni(EDTA)]^{-2} + 6NH_3$$

$$[Ni(H_2O)_6]Cl_2 + 6NH_3 \longrightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

blue/violet

$$[Ni(NH_3)_6]Cl_2 + EDTA^{-4} \longrightarrow [Ni(EDTA)]^{-2} + 6NH_3 + 2Cl^-$$

Date 02.03.2022

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Aim: Preparation of Nickel-hexammine complex and its estimation by complexometry and spectrophotometry.

Materials Required: Ice bath, UV vis-spectrophotometer, beaker, measuring cylinder, hand pipette, volumetric flask, burette, watch glass.

Chemicals Required: $NiCl_2 \cdot 6H_2O$, NH_3 solution, 0.05M EDTA, murexide indicator, 1N H_2SO_4, 0.5M NH_4Cl solution, distilled water.

Principle: An arrangement of ligands according to their increasing ability to split the d-orbitals is termed as the spectrochemical series. This splitting is quantified using the crystal field splitting parameter (Δ). Ligands arranged according to increasing strength: $I^{\ominus} < Br^{\ominus} < S^{2-} < SCN^{\ominus} < Cl^{\ominus} < NO_3^{\ominus} < F^{\ominus} < C_2O_4^{-2} < H_2O < NCS^- < CH_3CN < NH_3 <$ en $<$ bipy $<$ phen $< NO_2^{\ominus} < PPh_3 < CN^{\ominus} < CO$.

Splitting parameter (Δ) is related to colour of complex. A stronger ligand can remove a weaker ligand from a complex. So, NH_3 replaces H_2O from metal centre and en (ethylene diamine) replaces NH_3. The additional stability due to chelation also drives the reaction forward. The ΔH, ΔS of complex formation, starting with $[Ni(NH_3)_6]^{+2}$, indicates that contribution from entropy is the deciding factor for chelate effect.

Procedure:

(A) Preparation of Hexamminonickel(II) chloride.

(1) Take 10 ml solution of nickel chloride hexahydrate (contains 6g $NiCl_2$) in 250 ml beaker.

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Observations and calculations

Conc. of EDTA solution = 0.05 M

S.No.	Volume of EDTA used from burette
1.	9.6 ml
2.	9.7 ml
3.	9.7 ml

1 mole Ni reacts with 1 mole of EDTA to form Ni-EDTA complex

Moles of Ni = Moles of EDTA

Molarity x Volume (Ni) = Molarity x Volume (EDTA)

$\Rightarrow$ Molarity of Ni x 10 = 0.05 x 9.7

Molarity of Ni = 0.0485 mol/l

Grams per liter of Ni = 0.0485 x 58.69 (Atomic weight of Ni)

= 2.846 g/L.

Hence, in 100 ml, 0.284 g of Ni is present.

We started with 1.15 g of $[Ni(NH_3)_6]Cl_2$; 0.246 g of Ni is present per gram of $(Ni(NH_3)_6)Cl_2$.

S.No.	Conc. of solution (M)	conc. in mg/ml = conc. in M x 58.69	Absorbance
1.	0.01	0.5869	0.039
2.	0.04	2.3476	0.177
3.	0.05	2.9345	0.213
4.	0.06	3.5214	0.269
5.	unknown	unknown	0.082

(2) Take 12 ml solution of aqueous ammonia in measuring cylinder.
(3) Add the ammonia solution drop wise to the solution of nickel chloride with constant stirring till the colour of solution has changed from pale green to intense violet.
(4) Allow the solution to stand at room temperature for 5 minutes; cover with watch glass. Then cool it in ice bath for about 15 minutes.
(5) Filter the solution and wash the crystals with 3-5 ml ammonia solution.
(6) Dry the crystals using filter paper.
(7) Report the weight of dried complex.

(B) Estimation of Nickel by EDTA.
(1) Take 80 ml 0.05 M EDTA in 250/500 ml plastic beaker and fill it in clean burette upto the mark.
(2) Weigh accurately 1.15 g of $[Ni(NH_3)_6]Cl_2$ complex and transfer to a 100 ml volumetric flask. Now add 50 ml of 1N H_2SO_4 to dissolve it and make up the solution to the mark with distilled water.
(3) Pipette out 10 ml complex solution in 250ml conical flask and dilute with 15 ml distilled water.
(4) Add 2-3 drops murexide indicator and 5 ml NH_4Cl solution to conical flask. Now add 7-10 drops NH_3 solution to maintain a pH 7 (light green color).
(5) Titrate it with EDTA solution till the endpoint is near, add 3 ml NH_3 solution and continue titration till the endpoint.
(6) Repeat the titration and get concordant values.
(7) Calculate the amount of Ni present in complex.

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using Beer Lambert's law,

$A = \varepsilon \cdot c \cdot I$. where ε and I are constants and c is concentration.

$\therefore A = mc$ where m is the slope of the graph.

Now, from graph,

$A = 0.082$

So, unknown c = 1.15 g/dl on the X axis

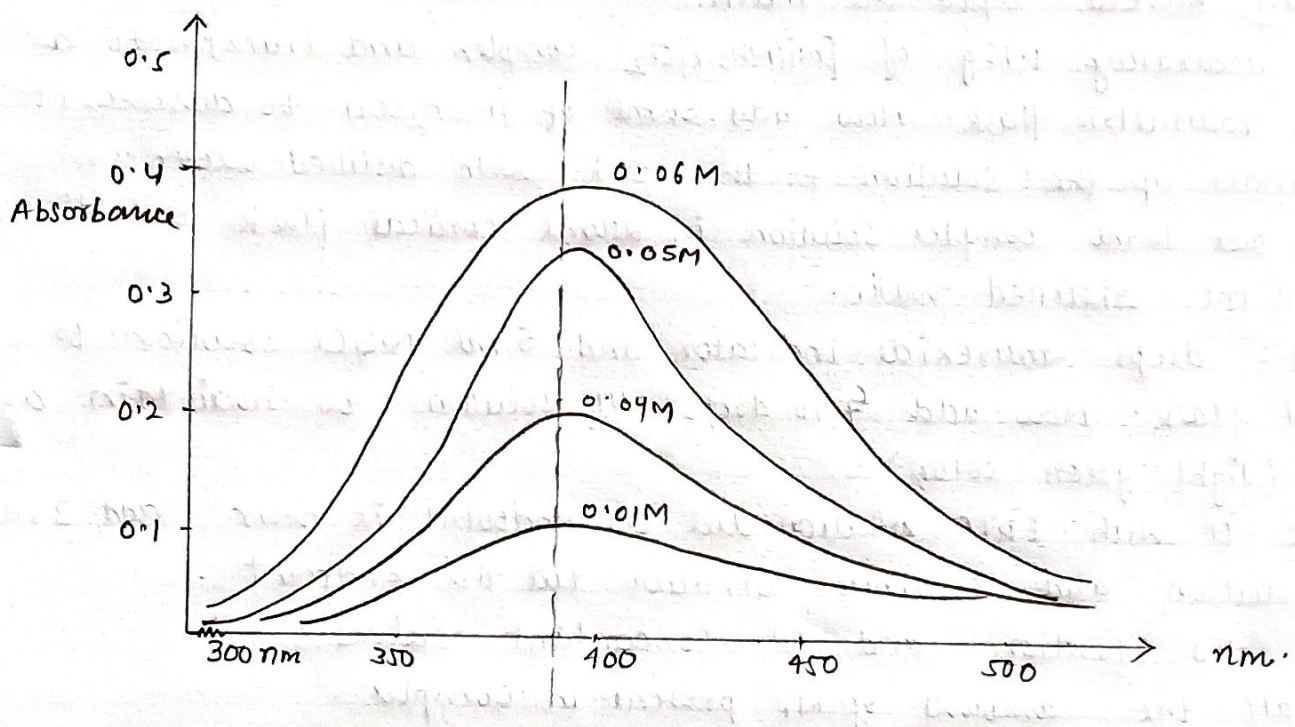
Also verified from graph; 0.082 corresponds to 1.15 g/dl.

concentration of unknown solution in Mol/l = $\frac{c}{58.69} = \underline{0.019\ M}$.

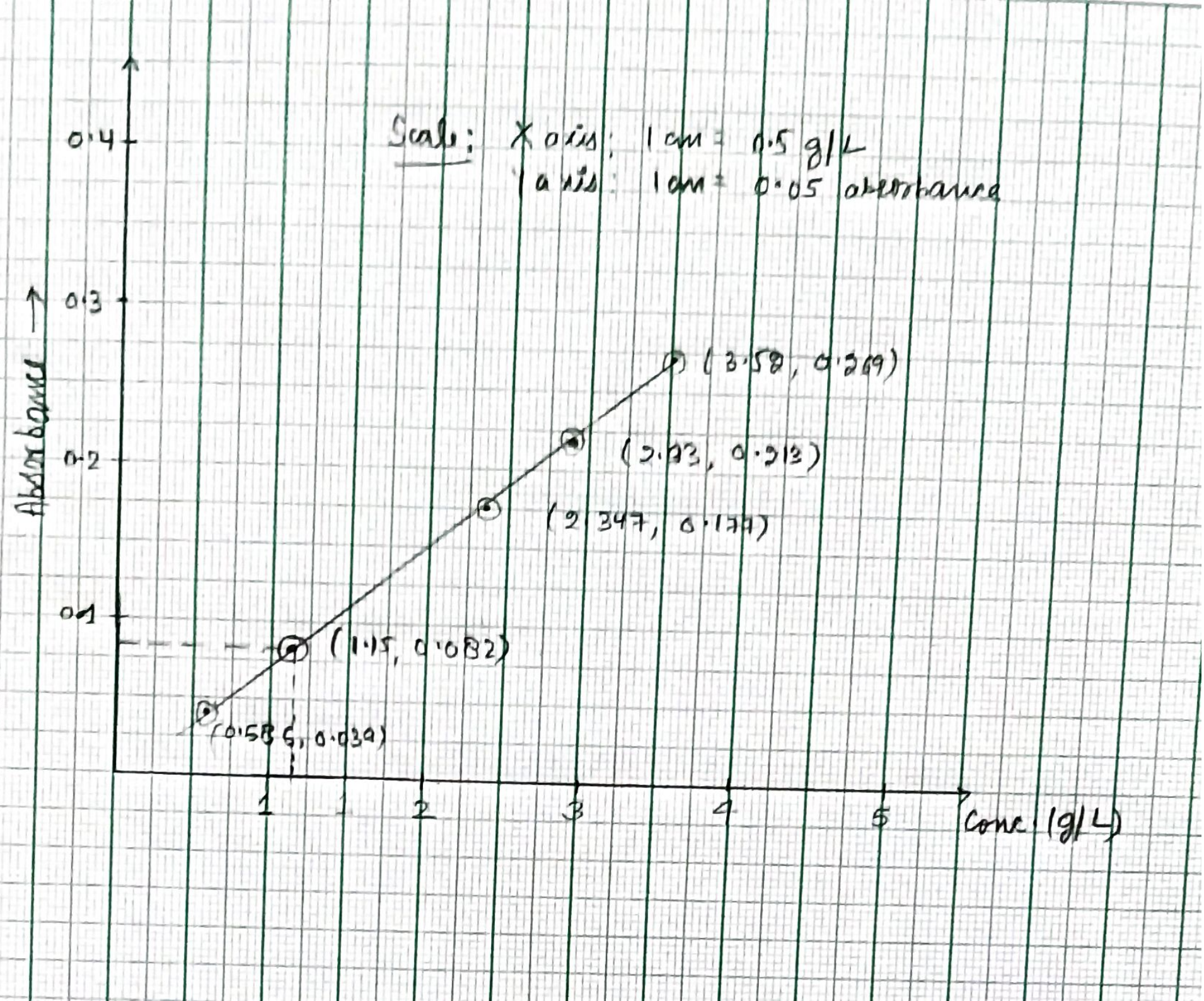
Weight of Ni in 100 ml = 0.115 g.

Weight of Ni used = $\frac{1.15}{237.5} \times 58.69 = \underline{0.284\ g}$

So, % yield = $\frac{0.115}{0.284} \times 100 \approx \underline{41\%}$.



Rough-overlay of Absorbance vs. wavelength curve.


Scale: X axis: 1 cm = 0.5 g/L
Y axis: 1 cm = 0.05 absorbance
Absorbance →
0.4
0.3
0.2
0.1
(3.58, 0.269)
(2.93, 0.213)
(2.347, 0.171)
(1.15, 0.082)
(0.585, 0.039)
1
2
3
4
5
Conc. (g/L)

Date

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(5) Estimation of Nickel by Spectrophotometry.

(1) Several solutions of known conc. and one of unknown conc. will be provided.

(2) Measure absorbance of all the solutions at 395 nm using UV-visible spectrophotometer.

(3) Plot absorbance vs mg/mL of nickel. Determine conc. of nickel present in unknown solution in g/L.

Results

(1) $[Ni(NH_3)_6]Cl_2$ was synthesised from $[Ni(H_2O)_6]Cl_2$.

(2) obtained amount was then used to estimate the amount of nickel present.

(3) Amount of Nickel present; 0.216 g of Nickel present per gram of $[Ni(NH_3)_6]Cl_2$

(4) Concentration of given solution was determined using solutions of known concentration with help of UV-Visible spectroscopy.

(5) Concentration of unknown solution = 0.019 M.

(6) Percentage yield = 41%.

Precautions.

(1) Acids must be handled carefully.

(2) Read lower meniscus while taking readings.

(3) solution of $[Ni(NH_3)_6]Cl_2$ must be frozen for long time.

(4) Use Ammonia with care.

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