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Polarographic Studies of Complexes Formed by Indole-3-Acetic Acid Hydrazide with Metal Ions Fe (III), Zn (II) and Ni (II)

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Abstract

The complexes formed by Indole-3-acetic acid hydrazide with metal ions Fe(III) , Zn(II) and Ni(II) were analysed through polarographic techniques.The polarographic techniques is successful in determination of composition and stability constant of complexes. The reversible waves are analysed and irreversible waves are also reported. The study of reversible and diffusion controlled nature of the cathodic waves produced by Fe^{+3},Zn^{+2},Ni^{+2} in Indole-3-acetic acid hydrazide on wave height was reported.Series of polarograms were drawn. Plots were drawn for reversible reactions slope was calculated by log C Vs $E_{1/2}$.For irreversible reaction the valve of 't' was measured at differential potential on the using portion of the waves .The reversible wave formation shows the formation of 1:1 complex between Fe^{+3} and Indole-3-acetic acid hydrazide. The irreversible polarograms is of zinc and nickle.

Keywords: Indole-3-Acetic Acid Hydrazide Polarograph, Cathodic Waves.

Introduction

The molecular interaction of quinone chlorimides with benzene and indoles have been reported [1-4]. The electron donor acceptor interactions of piperidine and methyl substitute piperidine as donors with p-Benzoquinone-4-chloramide, and 2:6 dichloro-p-benzoquinone-4-chlorimide as acceptors in chlorimide as acceptors in chloroform has been investigated spectrophotometrically. [5-6].Margerum et.al[7] studied the reduction of Cu (II) triglycine complex at pH~9.08. The reduction proceeds through two electron transfer process resulting in Cu(O) with no formation of copper (I) species. However zacharias et.al[8] observed the formation of Cu (I) dipeptide complexes during the reduction of Cu (II) dipeptide complexes. The Cu (I) complexes formed are observed to be unstable and undergo disproportionation forming Cu (II) complex and Cu (O) in aqueous medium[9-10]

Reversible Reduction Reactions

The polarographic technique can be successfully employed to determine the composition and stability constant of complexes usually the reversible waves are analyzed for this purpose although a few cases in irreversible waves have been reported recently. When the reduction or oxidation at the d.m.e is taking place reversibly, then the difference between the half wave potential of the simple and the complex ions at 25^0C is given as follows [11]

$$(E_{1/2})\,C - (E_{1/2})\,S = \frac{0.0591}{n}\log k_c \frac{-0.0591}{n}\log\frac{fs\ Kc}{fcKs}$$

$$\frac{-0.0591}{n}\quad p\log C_XF_X \_\_\_\_\_\_\_ (1)$$

Where, $(E_{1/2})$ C and $(E_{1/2})$ are the half wave potentials of complex and simple metal ion respectively at 25^0C. K_C is the dissociation constant for complex ion, C_X is the ligand concentration.

Neglecting K and activity coefficient the equation can be given as $(E_{1/2})$ C-

$$(E_{1/2})\,S = \frac{0.0591}{n}\log K_C - \frac{0.0591}{n}\ P\text{-}Log\ C_X \_\_\_\_\_\_ (2)$$

Equation (2) can be used to determine the value of P (No. of ligand). It gives the number of ligand molecules which combine with one atoms of the metal ion and hence the formula of the complex formed. The value of 'P' and the formula can be determined from the data of the half wave potentials of the complex at different concentrations of the complexing agents. On differentiating the equation (2) we get

$$(E_{1/2})C/\log C_X = -0.0591 \frac{P}{n} \quad (3)$$

Irreversible Reduction Reactions

The reversibility of the electrode reaction is pre-requisite of the methods due to lingane[12]. De Ford and Hume[13]. For the complexes which reduce irreversible at d.m.e other methods with certain limitations are available. Ringborm and Ericksson[14], Schqarzubach[15] and Matsuda[16] have developed method for the treatment of complexes which are reduced irreversible. A method due to subramanya[17] utilises a modification of the method by Tamanushi and Tanaka[18] for an irreversible process.

$$\frac{DS}{\log C_x} = J\times 2.303RT/\alpha nF \quad (4)$$

Where, DS is the shift in half wave potential of the complex metal ion, C_X is the concentration of ligand, J-the number of ligands bound in the complex and L-the fraction of the total applied potential that favours the forward reaction. By using the modified Hyrovsky Ilkovic equation for an irreversible reaction we get.

$$Ed_e = E_{1/2} - \frac{RT}{nF} \ln \frac{I}{id - 1} \quad (5)$$

We have

$$E_{3/4} - E_{1/4} = \frac{RT}{nF} \ln 3 \quad (6)$$

at 25^0C equation (6) becomes

$$E_{3/4} - E_{1/4} = \frac{2 \times 0.0591}{n} \log 3$$

$$\text{or } \alpha n = \frac{2 \times 0.0591 \times 0.4771}{E_{3/4} - E_{1/4}}$$

$$\text{or } \alpha n = \frac{0.05630}{E_{3/4} - E_{1/4}} \quad (7)$$

thus it knows from the values of $(E_{3/4}-E_{1/4})$. The values of 'J' were evaluated from equation (4), according to which

$$J = \Delta E/\log Cx \times \alpha n/0.059 \quad (8)$$

The discussion constant K_C can be evaluated from the expression $(E_{1/2})$ C-$(E_{1/2})$ S = -

$$\frac{RT}{nF} \ln K_C = \frac{-JRT}{mF} \ln CX \quad (9)$$

The reduction of the simple metal ion takes place reversibly simple metal ions Zn^{+2} and Ni^{+2} get reduced irreversibly at the d.m.e so the value of K_C cannot be calculated from the equation (9) meites and Israel have given the following equation to calculate different kinetics parameters for those cases where complete irreversibility prevails in the process.

$$Ede + 9.2412 = \frac{0.05915}{n} \log \frac{1.349\, k^O f, h, t_2^1}{Do^{\frac{1}{2}}} \frac{0.0542}{n} \log \frac{1}{id - 1} \quad (10)$$

which may be written as

$$Ed.e = E_{1/2} \frac{0.0542}{n} \log \frac{1}{id - 1} \quad (11)$$

with

$$E_{1/2} = -0.2412 + \frac{0.05915}{n} \log \frac{1.349\, K^o f, h, t_{1/2}}{D_{o1/2}} \quad (12)$$

The variation of 't' with potential sometimes poses a problem in the use of these questions. For waves occurring between 0 and -1.0V Vs S.C.E., the variation are not generally appreciable and may be ignored. But,for the wave in which 't' varies appreciably over the range of potentials covered by the rising part of the wave, the equation10 has been rewritten as:

$$Ed.e + 0.2412 = \frac{0.05915}{n} \log \frac{1.349\, K^O f\, h -}{D_O{}^{1/2}} \frac{0.0542}{n} \log \frac{i}{id - i} - 0.546 \log t \quad (13)$$

It is clear from the above equation that plot of Ed.e. Vs $\log \frac{1}{id - 1} - 0.546 \log t$ has a slope of $\frac{-0.0542}{n}$ and an intercept (where the quantity being plotted as abscissa is zero), which is equal to the parameters $E_{O1/2}$ defined by the equation.

$$E^O_{1/2} = -0.24121 + \frac{0.05915}{n} \log \frac{1.349\, k^O f, h,}{Do_{1/2}} \quad (14)$$

The kinetic parameters of the systems which showed irreversible behaviour at the d.m.e were thus evaluated from the equation(14) given above.

Since amongst the metals choosen iron complex gives reversible waves the composition and stability of it was polarographically determined. In other cases like nickel and zinc where irreversible waves are obtained, the various kinetics parameters were evaluated.

Experimental

Material and Method

Indole-3-Acetic acid hydrazide solution was prepared in ethanolacetone mixture. Ferric-chloride, Zinc chloride and nickel chloride metal salts of Analytical grade were used for the preparation of solutions. The solutions were prepared containing HCl, to avoid hydrolysis, and strength of stock solutions were determined gravimetrically, before diluting them to prepare solutions of required strengths.

Instruments

Heyrovsvy LP 55A- polaragraph operated manually in conjunction with pye scalamp galvanometer in external circuit was used. An external saturated calomel electrode connected to the cell by means of a low resistance salt bridge was used as reference electrodes. The capillary characteristics in different studies are as follows:

(1) Ferric chloride- Indole-3-Acetic acid Hydrazide

m = 1.743 mg/sec.

t = 3030 sec.

m 2/3 t 1/6= 1.759 mg 2/3 sec - ½

(2) Zinc chloride – Indole-3-Acetic Acid Hydrazide

m = 1.8401 mg/sec.

t = 3.4 sec.

$m^{2/3} t^{1/6} = 1.841\ mg^{2/3}\ Sec^{-1/2}$

(3) Nickel chloride-Indole-3-Acetic Acid Hydrazide

m= 1.8102 mg/sec.

t= 3.30 seconds

$m^{2/3} . t^{1/6} = 1.802\ mg^{2/3}\ Sec.^{-1/2}$

The polaographic cell and the reference electrode (SCE) were kept immersed in thermostatic water bath maintained at $28^0+1.^0C$. Purified hydrogen was used for detestation and maintaining inert atmosphere over the solutions.

Procedure

To investigate the reversibility and diffusion controlled nature of the cathode waves produced by Fe^{+3}, Zn^{+2} and Ni^{+2} in Indole-3-Acetic Acid Hydrazide on the wave heights were studied. For this purpose a series of polarograms according to the conditions mentioned below were drawn.

Effect of Mercury column

Set-I Solutions containing

1. 2.0 ml of 0.5 mM $FeCl_3$ and 10 ml of 5.0 mM – Indole-3-Acetic Acid Hydrazide.
2. 2 ml of 5.0 mM $NiCl_2$, 10 ml of 10.0 mm – Indole-3-Acetic Acid Hydrazide and 1 ml of 0.05% gelatin solution (maxima suppressor).
3. 2 ml of 5.0 mM $ZnCl_2$, 10 ml of 10.0 mM-Indole-3-Acetic Acid hydrazide and 1 ml of 0.05% gelatin solution (maxima suppressor) were prepared and total volume was made upto 20 ml with $KClO_4$ (saturated solution) and water. The amount of saturated solution of $KClO_4$ added was such that its strength in the diluted solution was always atleast 50 times more than the strength of the metal ion. The solution were transferred to the polargraphic cell and they were aerated with pure hydrogen before polarograms were recorded.

SET-II Effect of concentration of ligand

For complication studies, a series of polarograms were recorded of solution prepared as follows.

Solutions containing

1. 6.0 ml of 0.5 mM $FeCl_3$and 3.0 ml, 4.0 ml, 8.0 ml and 10.0 ml of 10.0 mM- Indole-3-Acetic Acid Hydrazide.
2. 6.0 ml of 0.5 mM ZnCl2 and 3.0 ml, 5.0 ml, 6.0 ml and 8.0 ml of 10 mM-Indole-3-Acetic Acid Hydrzide and 1 ml of 0.05% gelatin solution.
3. 8.0 ml of 0.5 mM $NiCl_2$ and 3.0 ml 4.0 ml, 5.0 ml and 6.0 ml of 10 mM^1- Indole-2-Acetic Acid Hydrazide and 1 ml of 0.05% gelatin solution. Were prepared and total volume was made to 20.20 ml in case of $FeCl_3$, $ZnCl_2$ and 25 ml for the polarographic studies of $NiCl_2$, with the addition of saturated solution of $KClO_4$ and water, alcohol. The strength of $KClO_4$ Solution in diluted state was always 50 times the strength of metal ion. The concentration of ligand was kept at least 10 times the strength of the metal ion concentration in the solution. The solutions were transferred to the polarographic cell and polarograms were recorded, after they were aerated with pure hydrogen.

Conventional log plots of log $\frac{i}{id - 1}$ Vs Ed.e in the case ofFerric chloride-Indole-3-Acetic Acid Hydrazide system and $\left[\log \frac{i}{id - i} - 0.546 \log t \right]$ Vs Ed.e for the other systems were plotted.

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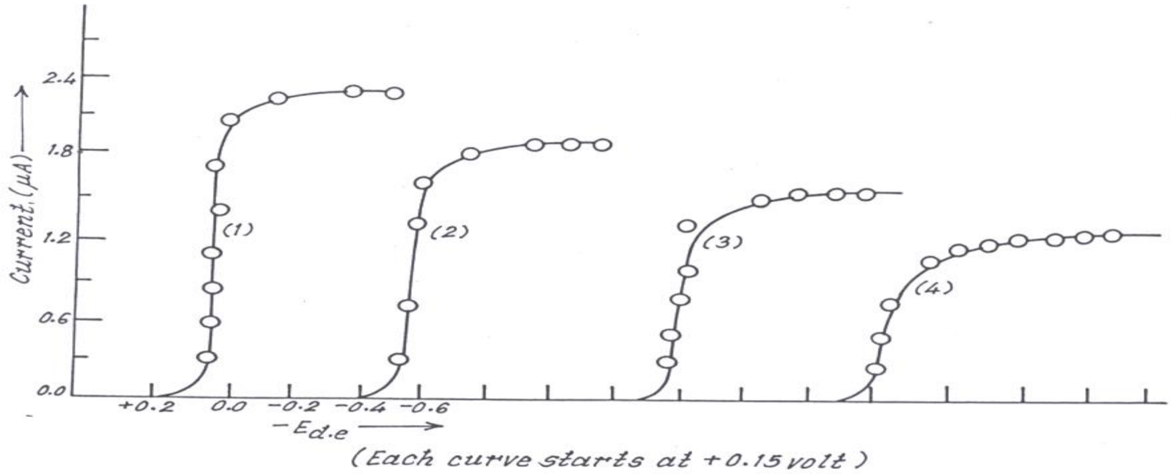

Fig. (4.1): Polarograms of solution containing 0.00015M $FeCl_3$ and varying concentrations of Indole-3-Acetic acid Hydrazide.

Table (1) ; Curve (1)

S.No.	Ed.e (Volts)	Log $\frac{1}{id-1}$	$E_{1/2}$ Volts	Slope
1	0.0	-0.4796	-0.015	0.060
2	-0.02 +	0.21228		
3	-0.04 +	0.5320		
4	+ 0.04 -	1.8770		

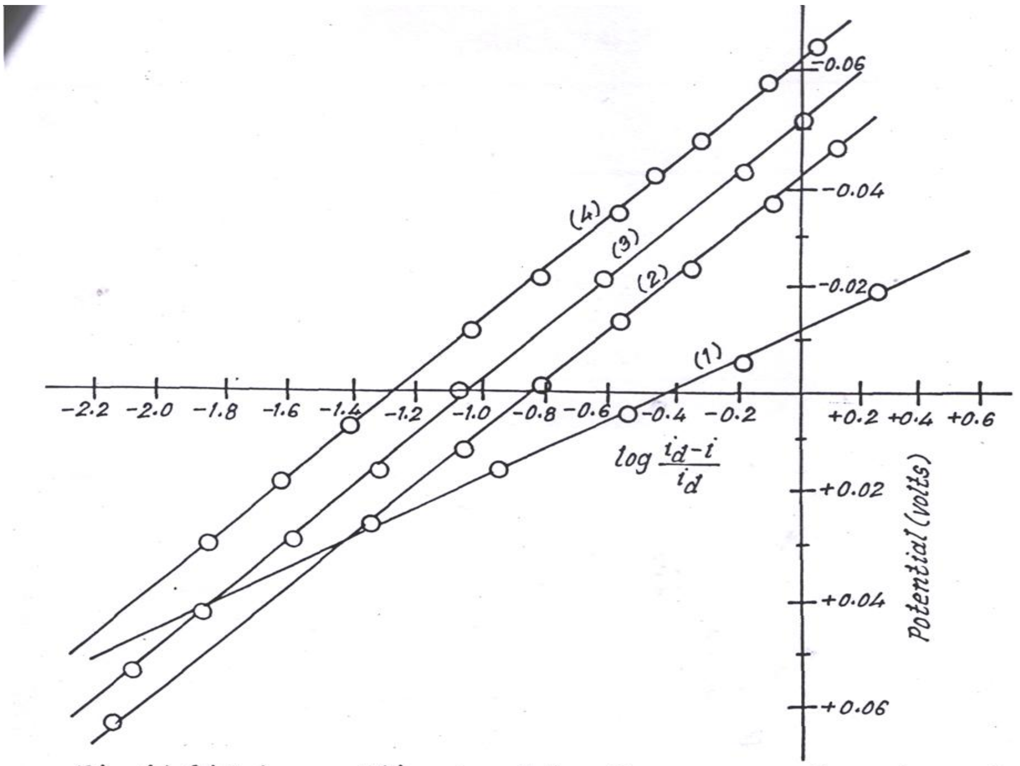

Fig.(4.2): Logarithmic plots of $-E_{de}$ as a function of $\log \frac{i_d}{i_d - i}$ corresponding to curves 1–4 of Fig.(4.1).

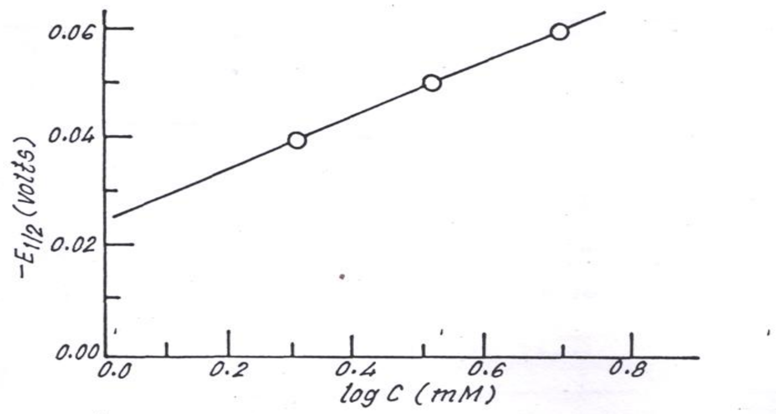

Fig. (4.3): Plot of $-E_{1/2}$ as a function of log C.

Curve (2)

S.No.	E.d.e (Volts)	log $\frac{1}{1d-1}$	$E_{1/2}$ Volts	Slope (Volts)
1	0.0	-0.8873		
2	-0.02	-0.4845	-0.04	0.053
3	-0.04	+0.1001		
4	+0.06	-2.1402		

Curve (3)

S.No.	E.d.e (Volts)	Log $\frac{1}{id-1}$	$E_{1/2}$ Volts	Slope (Volts)
1	0.0	-1.0985		0.052
2	-0.02	-06168	-0.05	
3	-0.04	-0.1833		
4	+0.04	-1.8682		

Curve (4)

S.No.	E.d.e (Volts)	Log $\frac{1}{1d-1}$	$E_{1/2}$ Volts	Slope (Volts)
1	-0.0	-1.65990		
2	-0.02	-0.8493	-0.06	0.054
3	-0.04	-0.4610		
4	+0.04	-2.0604		

Effect on concentration of ligand on the complex formed between Ferric chloride and Indole-3-Acetic Acid Hydrazide.

Table 2

S.No.	Curve	$E_{1/2}$ (Volts)	Conc. mM	log	Remarks
1	2	-0.04	2.000	0.3010	log C Vs-$E_{1/2}$, is a straight line showing formation of one complex
2	3	-0.05	3.500	0.5441	
3	4	-0.06	5.000	0.6990	

Logarithmic Analysis of Polarograms Corresponding to curves (1-5)

Table (3) Curve (1)

S.No.	E.d.e	log $\frac{1}{1d-1}$	$E_{1/2}$ (Volts)
1	-0.00	-0.4102	-0.03 volt
2	-0.02	-02026	
3	-0.04	+0.1172	
4	+0.05	-1.1026	
5	+0.06	-1.1956	

Curve (2)

S.No.	E.d.e	$\log \frac{1}{1d - 1}$	$E_{1/2}$ (Volts)
1	0.00	-0.4852	-0.038
2	-0.02	-0.2126	
3	-0.04	-0.0845	
4	+0.06	-1.3002	

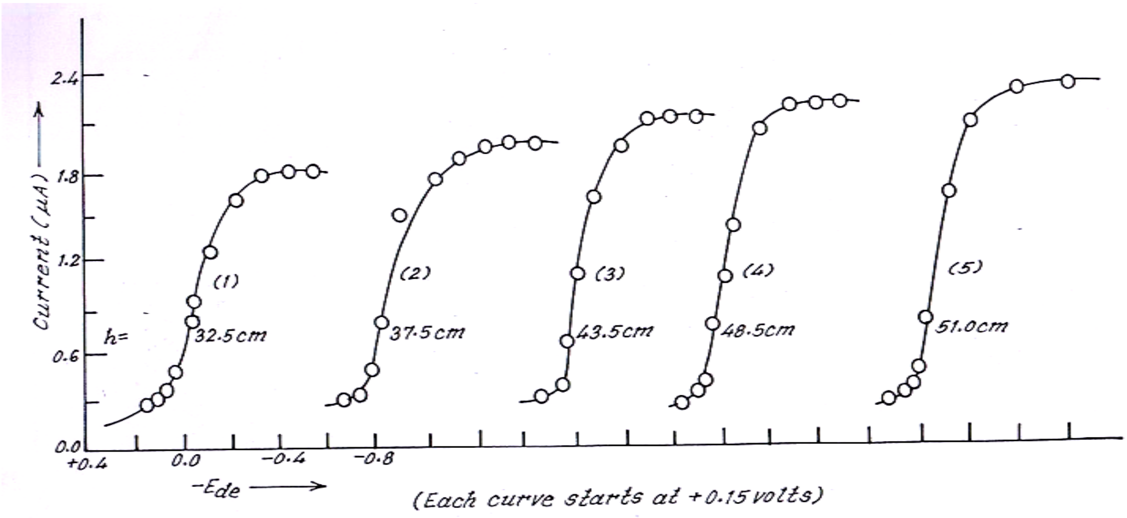

Fig.(4.4): Polarograms of 0.005M ligand and 0.0005M $FeCl_3$ at different heights of Hg column.

Curve (3)

S.No.	E.d.e (Volts)	$\text{Log} \frac{i}{id - i}$	E1/2 (Volts)
1	0.00	-0.7673	
2	-0.02	-04929	-0.05
3	-0.04	-.1958	
4	+0.06	-1.6021	

Curve (4)

S.No.	E.d.e (Volts)	$\text{Log} \frac{i}{id - i}$	E1/2 (Volts)
1	0.00	-0.8212	
2	-0.02	-0.5402	-0.054
3	-0.04	-0.3201	
4	+0.05	-1.5462	
		log (4.5	

Curve (5)

S.No.	E.d.e (Volts)	$\text{Log} \frac{i}{id - i}$	E1/2 (Volts)
1	0.00	-08402	
2	-0.02	-05604	-0.056
3	-0.04	-.2420	
4	+0.06	-1.8120	

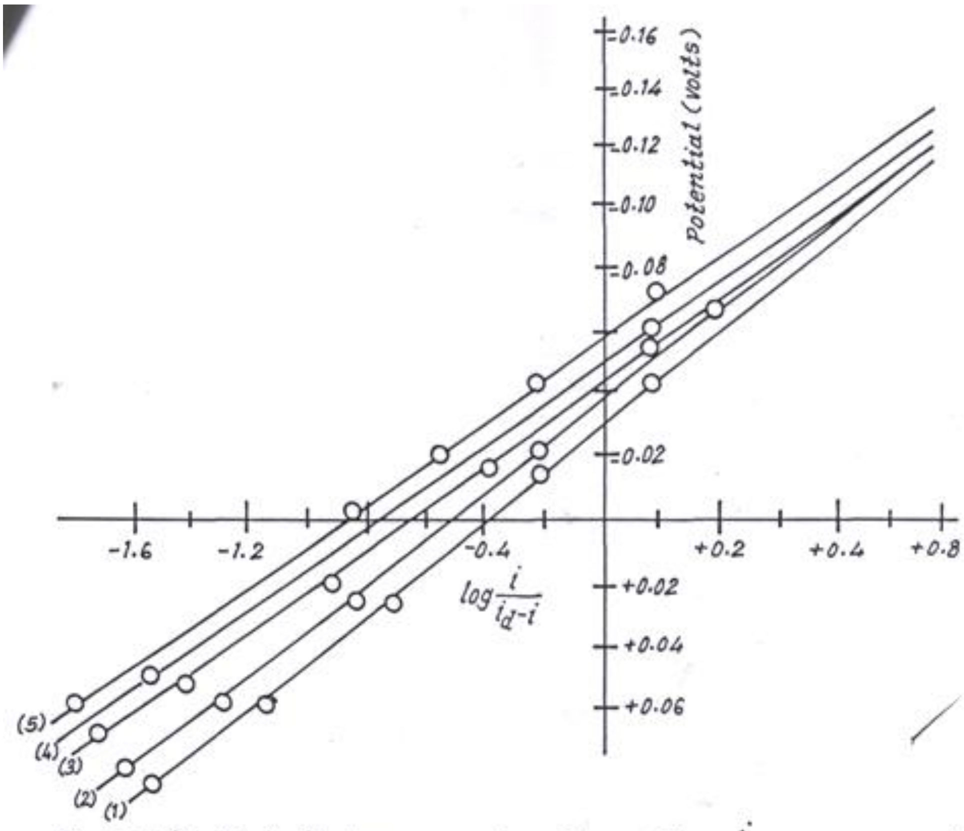

Fig.(4.5): Plot of $-E_{de}$ as a function of $\log \frac{i}{i_d - i}$ corresponding to curves 1-5 of fig.(4.4).

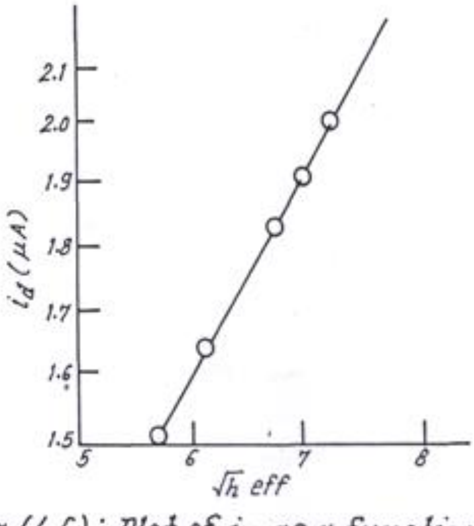

Fig.(4.6): Plot of i_d as a function of $\sqrt{h}$ eff.

Effect of height of Hg-column on the complex formed between Ferric-Chloride and Indole-3-Aceted Acid Hydrazide.

S.No.	Curve No.	Height cm	Height (eff) cm	$h_{1/2}$ (eff)	id (UA)	$E_{1/2}$ (volts)
1	1	33.0	32.5	5.09	1.50	-0.03
2	2	38.0	37.5	6.12	1.64	-0.038
3	3	44.0	43.5	6.59	1.85	-0.65
4	4	49.0	48.5	6.96	1.92	-0.054
5	5	51.5	51.0	7.14	2.00	-0.056

Logarithmic Analysis of Polargrams of 0.0015 M ZnCl2 and varying concentration of Indole--3Acetic Acid Hydrazide.

Corresponding to curves (1, 2, 3, 4, 5)

S.No.	-Ed.e (volts)	log $\frac{1}{1d-1}$	0.546 log t	log $\frac{1}{1d-1}$	-0.546×$E_{1/2}$ logt)
1	0.86	+0.1761	0.2881	-0.1120	
2	0.90	+0.3087	0.2867	+0.0220	-0.8954V
3	0.94	+0.4051	0.2850	+0.1201	
4	1.00	+0.6690	0.2840	+0.3850	
5	1.10	+1.1195	0.2820	+0.8375	

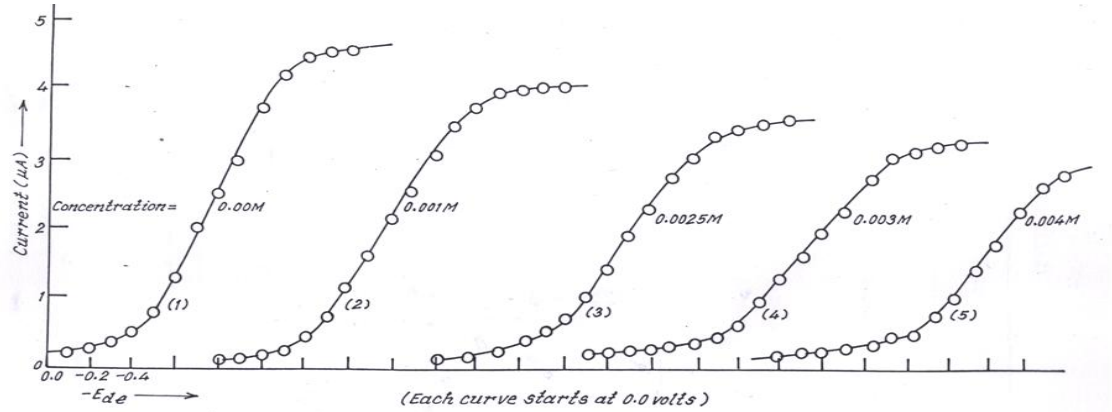

Fig.(4.7): Polarograms of solution containing 0.0005M $ZnCl_2$ and varying concentration of Indole-3-Acetic acid Hydrazide.

Curve (2)

S.No.	**-Ed.e**	**log** $\frac{1}{1d-1}$	**0.546 log t**	**log** $\frac{1}{1d-1}$	**-0.546** χ **E/1/2 logt)**
1	0.86	+0.0688	0.2897	-0.2209	
2	0.90	+0.2341	0.2887	-0.0545	-0.925 V
3	0.96	+0.3900	0.2872	+0.1028	
4	1.00	+0.5082	0.2850	+0.2232	
5	1.10	+0.7269	0.2840	+0.4429	

Curve (2)

S.No.	**-Ed.e**	**log** $\frac{1}{1d-1}$	**0.546 log t**	**log** $\frac{1}{1d-1}$	**-0.546** χ **E/1/2 logt)**
1	0.86	+0.0688	0.287	-0.2209	
2	0.90	+0.2341	0.2887	-0.0546	
3	0.96	+0.3900	0.2872	+0.1028	-0.925 V
4	1.00	+0.5082	0.2850	+0.2232	
5	1.10	+0.7269	0.2840	+0.4429	

Curve (3)

S.No.	**-Ed.e**	**log** $\frac{1}{1d-1}$	**0.546 log t**	**log** $\frac{1}{1d-1}$	**-0.546** χ **E/1/2 logt)**
1	0.86	-0.1327	0.2910	-0.4237	
2	0.96	0-0.263	0.2899	-0.3160	
3	0.94	+0.0792	0.2885	-0.2093	-1.025v
4	1.00	+0.2149	0.2872	-030723	
5	1.10	+0.4948	0.2860	+0.2088	

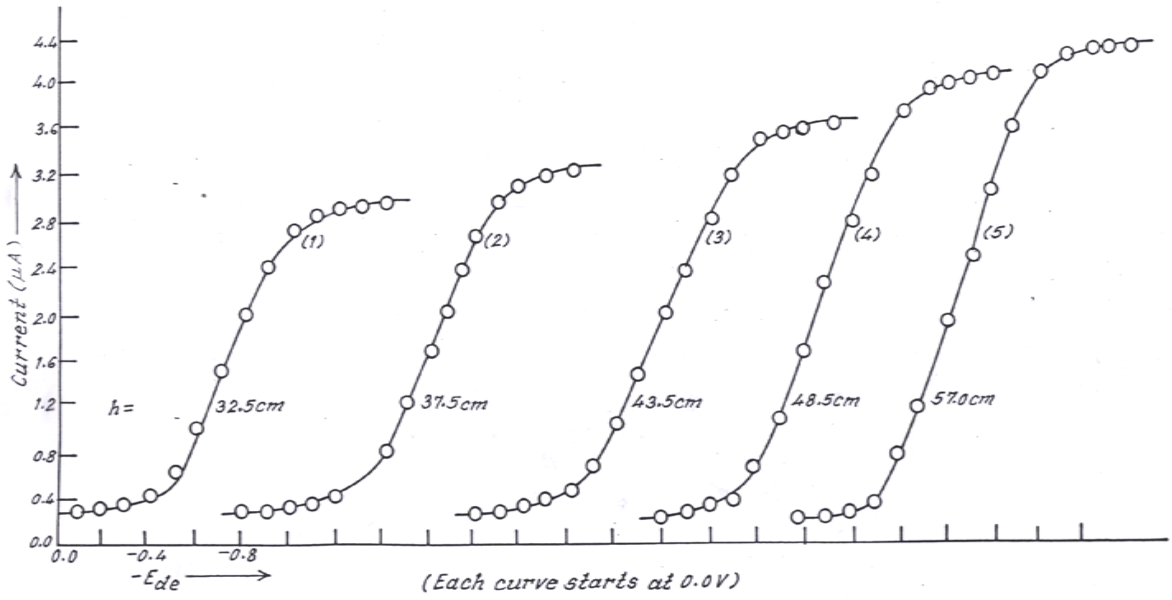

Fig.(4.8): Polarograms of 0.005M Indole-3-Acetic acid Hydrazide and 0.005M $ZnCl_2$ at different height of Hg-column.

Curve (4)

S.No.	-E d.e (Volts)	$\log \frac{1}{1d-1}$	0.546 log t	$\log \frac{1}{1d-1}$	-0.546 χ E/1/2 logt)
1	0.86	-0.1461	0.2940	-0.4401	
2	0.90	-0.0872	0.2916	-0.3788	
3	0.94	0.000	0.2892	-0.2892	-1.06v
4	1.00	+0.1461	0.2878	-0.1417	
5	1.10	+0.3341	0.2854	+0.0487	

Curve (5)

S.No.	-E d.e (Volts)	$\log \frac{1}{1d-1}$	0.546 log t	$\log \frac{1}{1d-1}$	-0.546 χ E/1/2 logt)
1	0.86	-0.1963	0.2956	-0.4919	
2	0.90	-0.1296	0.2939	-04235	-1.07V
3	0.94	0.000	0.2914	-0.2914	
4	1.00	+0.1296	0.2890	-0.1594	
5	1.10	+0.4559	0.2860	+0.1699	

Effect of varying concentration of ligand Indole-3-Acetic Acid Hydrazide on the complex formed between Zn^{+2} and Indole-3-Acetic Acid Hydrazide.

Table (6)

S.No.	**Curve No.**	**Concn of ligand (mM)**	**log C**	**$E_{1/2}$(Volts)**
1	1	0.00	0.00	-0.895
2	2	1.5	0.1761	-0.925
3	3	2.5	0.3979	-1.025
4	4	3.0	0.4771	-1.06
5	5	4.0	0.6021	-1.07

Table (7)

Effect of height of fig-column on the complex formed between Indole-3-Acetic Acid Hydrazide and ZnCl2

S.No.	**Curve No.**	**h cm**	**heff cm**	**$h^{1/2}$ eff**	**id (A)**	**Remarks**
1	1	33.0	32.5	5.64	2.64	Straight line obtained between id Vs $h^{1/2}$ eff. which shows diffusion controlled nature of the process
2	2	38.0	37.5	6.12	2.96	
3	3	44.0	43.5	6.59	3.46	
4	4	49.0	48.5	6.96	3.80	
5	5	51.5	51.0	7.14	4.04	

Values of n and K^0f, h, corresponding to curves (2-5) Fig (7)

Table (8)

S.No.	Conc of Indole-3-Acetic acid Hydrazide (nM)	id (μA)	$Dc^{1/2}$	Slope from log plots (Volts)	Intercept $E_{1/2}$ (Volts)	αn	Rf, h
1	1.5	3.80	1.133×10^{-3}	0.2076	-0.8950	0.1762	9.47×10^{-4}
2	2.5	3.30	5.961×10^{-4}	0.3653	-1.025	0.1483	4.78×10^{-5}
3	3.0	3.00	4.47×10^{-4}	0.4000	-1.066	0.1355	4.444×10^{-5}
4	4.0	2.70	3.132×10^{-4}	0.3750	-1.07	0.1445	2.189×10^{-6}

Logarithmic Analysis of polarograms of 0.000166 M-$NiCl_2$ and Varying Concentration of Indole-3-Acetic Acid Hydrazide corresponding to curves (1-5) Fig (11)

Table (9) Curve(1)

S.No.	-E d.e	$\log \frac{1}{1d - 1}$	0.546 log t	$\log \frac{1}{1d - 1}$	-0.546 log t ${}^{\chi}_{\chi}E_{1/2}$
1	0.86	-0.0580	0.2880	-0.3460	
2	0.90	+0.0580	0.2870	-0.2290	
3	0.96	+0.1761	0.2852	-0.1091	-0.98V
4	1.00	+0.3273	0.2838	+0.0435	
5	1.10	+0.6985	0.2812	+0.3273	

Fig (13)

Curve 2

S.No.	-E d.e (Volts)	$\log \frac{V}{1d - 1}$	0.546 log t	$\log \frac{1}{1d - 1}$	-0.546 log t ${}^{\chi}_{\chi}E_{1/2}$
1	0.86	-0.1439	0.2896	-0.4335	
2	0.90	+0.0129	0.2885	-0.2756	
3	0.96	+0.1707	0.2866	-0.1159	-1.02V
4	1.00	+0.2253	0.2850	-0.0597	
5	1.10	+0.5034	0.28526	+0.2208	

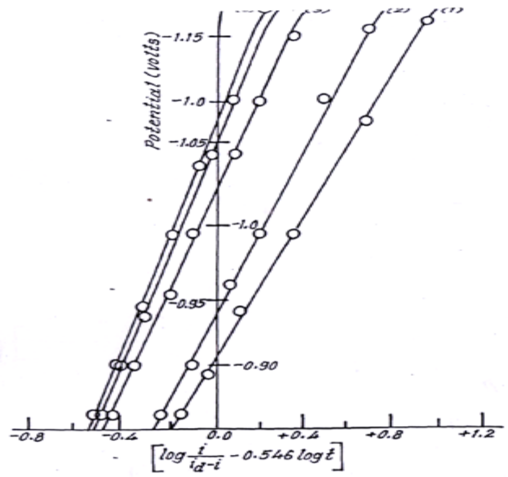

Fig.(4.9): Logarithmic plots of $-E_{de}$ as a function of $\left[\log \frac{i}{i_d - i} - 0.546 \log t\right]$ corresponding to curves 1-5 of fig.(4.7).

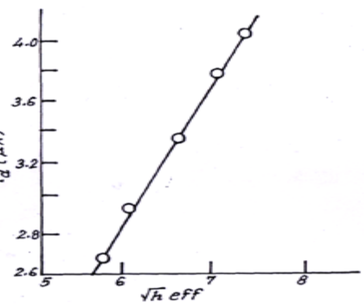

Fig.(4.10): Plot of i_d as a function of $\sqrt{h}$ eff.

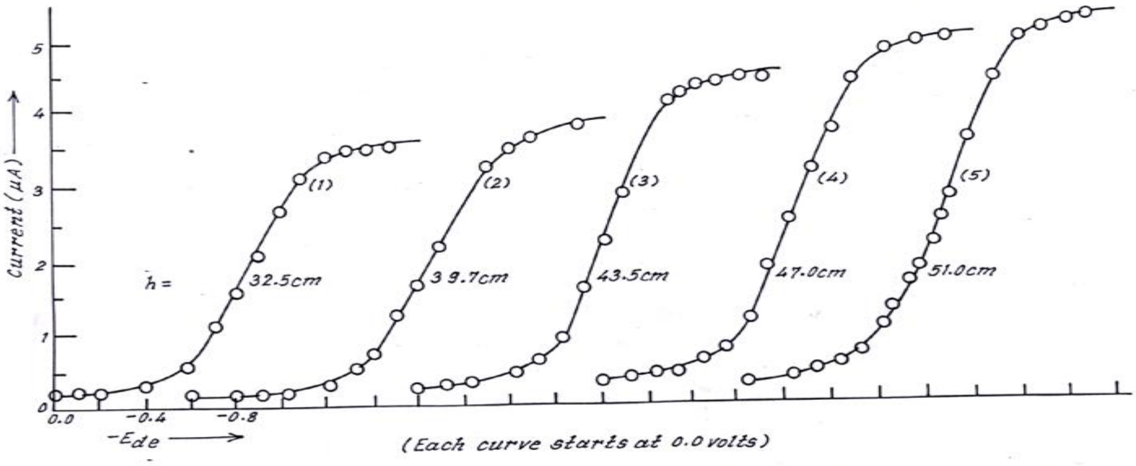

Fig.(4.12): Polarograms of 0.0025M Indole-3-Acetic acid Hydrazide and 0.0005M $NiCl_2$ at different heights of Hg-column.

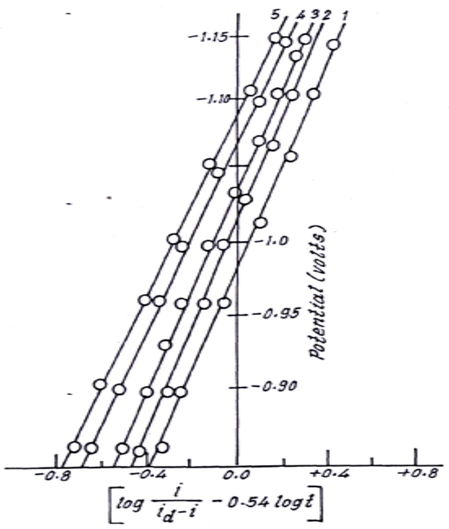

Fig.(4.13): Logarithmic plots of $-E_{de}$ as a function of $\left[\log \frac{i}{i_d-i} - 0.54 \log t\right]$ corresponding to curves 1-5 of fig.(4.11).

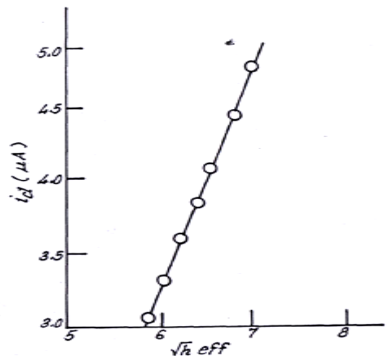

Fig.(4.14): Plot of i_d as a function of $\sqrt{h}$ eff.

Curve 3

S.No.	**-E d.e (Volts)**	**log** $\frac{i}{id - 1}$	**0.546 log t**	**log** $\frac{i}{id - i}$	**-0.546 log t** χ χ $E_{1/2}$
1	0.86	-0.2326	-0.2898	-0.5224	
2	0.90	-0.0939	-0.2886	-0.3825	
3	0.96	+0.0134	-0.2870	-0.2736	-1.044V
4	1.00	+0.1761	-0.2852	-0.1091	
5	1.10	+0.4508	-0.2827	+0.1681	

Fig.13

Curve (4)

S.No.	**-E d.e (Volts)**	**log** $\frac{i}{id - 1}$	**0.546 log t**	**log** $\frac{i}{id - i}$	**-0.546 log t** χ χ $E_{1/2}$
1	0.90	-0.2586	0.2890	-0.5476	
2	0.96	-0.0714	0.2880	-0.3594	-1.07V
3	1.00	+0.0427	0.2868	-0.2441	
4	1.10	+0.4130	0.2842	+0.1288	

Fig.13
Curve (3)

S.No.	-E d.e (Volts)	log $\frac{i}{id - 1}$	0.546 log t	log $\frac{i}{id - i}$	-0.546 log t $^{\chi}_{\chi}$ $E_{1/2}$
1	0.90	-0.2258	0.2902	-0.5160	-1.08V
2	0.96	-0.0738	0.2890	-0.2628	
3	1.00	+0.0147	0.2880	-0.2733	
4	1.10	+0.2258	0.2860	+0.602	

Fig (13)

Effect of Varying Concentration of Ligand-Indole-3-Acetic Acid Hydrazide on the Complex Formed Between and Indole-3-Acetic Acid Hydrazide

Table 10

S.No.	Curve No.	Conc.of Ligand mM	$E_{1/2}$ (Volts)	Remarks
1	1	0.00	-0.98	-$E_{1/2}$ Shifts to more negative value on addition of ligand
2	2	1.25	-1.02	
3	3	1.60	-1.04	
4	4	2.08	-1.07	
5	5	2.50	-1.08	

Table 11

Effect of Height of Hg-Column on the Complex Formed Between -Indole-3-Acetic Acid Hydrazide and $NiCl_2$

S.No.	Curve No.	h cm	h^{eff}cm	$h_{1/2}^{eff}$	id (μA)	Remarks
1	1	33.0	32.5	5.64	3.25	Straight line obtained between id Vs $h_{1/2}$ eff. which shows diffusion controlled nature of the process
2	2	38.0	37.5	6.12	3.60	
3	3	44.0	43.5	6.59	4.10	
4	4	49.0	48.5	6.96	4.45	
5	5	51.5	51.0	7.14	4.75	

Fig 14

Values of αn And K^0f, h

Corresponding to curves (2-5) Fig (11) Table (12)

S.No.	Conc. of Indole - Acetic Acid Hydrazide mM	$D_C^{1/2}$: id : (μA)	-$E_{1/2}$ (From intercept of log plot) volts	Slope from log plots (Volts)	αn	K^0fh
1	1.25	1.172×10^{-3} 3.20	1.02	0.3750	0.1445	1.083×10^{-5}
2	1.66	8.3608×10^{-4} 3.05	1.045	0.3125	0.1734	2.715×10^{-6}
3	2.08	6.453×10^{-4} 2.95	1.080	0.3120	0.1731	1.654×10^{-6}
4	2.50	5.197×10^{-4} 2.85	1.085	0.3325	0.1626	1.8358×10^{-6}

Result & Discussion

Polarograms of Fe^{+3} in varying concentration of ligand Indole-3-Acetic Acid Hydrazide, have been shown graphically in Fig (1) (Curves 1-4).

A single well defined cathode wave appeared in each case. All plots of log $\frac{1}{1d - 1}$ Vs E d.e (Fig .2) yield straight lines with slopes which agreed with theoretical value. The mean slope for the series was 0.053 V, showing reversibility of the reduction and one electron transfer process. The half wave potentials evaluated from these log plots are given in table (2) which indicates that half wave potential shift to more negative values with the increasing concentration of the ligand.

Current-voltage curves of Fe^{+3} in a constant concentration of ligand but at different heights of Hg-Column (Fig 4) curves (1-5) were recorded in order to test the diffusion controlled nature of the reduction. A linear plot of id Vs $h_{1/2}$ show that the reduction is diffusion controlled.

A plot of $E_{1/2}$ as a function of log C(conc. of ligand) showed a straight line Fig.3 which indicate the formation of single complex. Hence the classical method of ligand was applied to determine the stability constant of the complex formed between Fe^{+3} and Indole-3-Acetic Acid hydrazide.

The value of 'P' was obtained from the slops after extraplotting the $E_{1/2}$ VS log C curve to C_X=0

$$\text{Slope} = 0.059\,\frac{P}{N}$$

The value of 'P' obtained forms the above relation which shows formation of 1:1 complex between Fe^{+3} and Indole-3-Acetic Acid Hydrazide. The ($E_{1/2}$) C was evaluated from the log plot $E_{1/2}$ Vs ($E_{1/2}$) log C. The intercept at log C=0 gives value of ($E_{1/2}$) C Fig 30. The value of stability constant is 5.021×10^5.

Interversible Systems

The polarograms of zinc and nickel as well as those of complexed metal ions gives cathodic waves (Fig. 7, 11). The half wave potential values of the metal ions viz Ni^{+2} and Zn^{+2} shift to more negative values with the increasing concentration of ligand (Tables 6, 9) indicating thereby that complexes are formed in both the cases. The shift in half wave potentials to more negative values is apperciable in the beginning but it is almost negligible at higher concentration of the ligand.

It was found that the plots of log $\frac{i}{id - 1}$ Vs. E. d.e. are linear but the slopes do not agree with the theoretical values of slope indicating that both the simple as well as the complex ions reduce irreversibly at the d.m.e.

The electrode reactions were found in all the systems to be diffusion controlled as id was found to be proportional to $h^{1/2}$(Fig 10-14) which has been tested by recording polarograms of $ZnCl_2$ and $NiCl_2$ at constant ligand concentrations, but at different height of mercury column (Fig 8,12).

The values of αn and K^0 f,h were calculated from the following equation.

$$E\ d.e. = E^0{}_{1/2} - \frac{0.0542}{\alpha n} \log \left[\frac{i}{id - i} - 0.546 \log t \right] \quad (15)$$

Where

$$E\ d.e = E^0_{1/2} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.349K^0 f, h}{D^{1/2}} \quad (16)$$

In these equations both Ed.e and $E^0{}_{1/2}$ are referred to S.C.E. The values of αn were obtained from the slopes of the plots of Ed.e vs. log $\frac{i}{id - 1}$ - 0.546 log t which yielded straight lines (Fig 4.9, 4.13). The slope being equal to $\frac{-0.0542}{\alpha n}$. The intercept of the same plot gave the value of $E^0{}_{1/2}$ which was used to calculate K^0f,h while having as estimate of $D_0{}^{1/2}$from the Ilkovic equation. The values of αn and K^0f, h calculated at different concentrations of ligand are recorded in tables (8-12).

From the data presented in tables (8-12) it is evident that the values of K^0 f, h and αn are affected by the concentration of the ligand in both the cases. Since these kinetics parameters are directly evaluated from $E_{1/2}$. Variation in their values on the addition of the ligand is a direct evidence of complex ion formation between these metal ions and Indole-3-acetic acid hydrazide.

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