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RESEARCH ARTICLE

POLAROGRAPHIC BEHAVIOUR OF SOME DIVALENT METAL COMPLEXES OF 4-METHOXYBENZALDEHYDE THIOSEMICARBAZONE

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Abstract

Analysis of the complexes formed by 4-methoxybenzaldehyde thiosemicarbazone with Manganese (II), Iron (II),Cobalt (II) ,Nickel (II) and Zinc(II) metal ions was made through the polarographic technique. 4-methoxybenzaldehyde thiosemicarbazone was obtained by the reaction of hydrazinecarbothioamide with para-methoxybenzaldehyde in ethyl alcohol. Polarographic technique is best suited for the study of coordination complexes and their substitution reactions and more significantly the technique is especially useful in calculating stability constant of complexes that are formed by direct combination of metal ion and the ligands. A sharp change is observed in the $E_{1/2}$ values of the transition metal ions in presence of the ligand indicating complexation .Irreversible polarographic behaviour has been shown in all the compounds studied and kinetic parameter α_n and $k^{o}_{f,h}$ have been calculated .All the complexes prepared were found to have 1:2 stoichiometry.

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Introduction:-

The ligands Thiosemicarbazone are found to be of significant interest due to their structural diverseness , biological applications ,bonding modes and ability of ion sensing (1) . Thiosemicarbazones are basically obtained by combining a thiosemicarbazide either with an aldehyde or with a ketone and represent an important class of useful ligand type for obtaining coordination spheres with mixed N and S donors. Thiosemicarbazones are widely studied in coordination chemistry , analytical applications (2) and pharmacology (3). Derivatives of thiosemicarbazones having general formulae $R^1 R^2 C{=}N{-}NH{-}C({=}S){-}NR^3 R^4$ have presented a broad spectrum of properties against a number of diseases due to their antifungal (4) , antibacterial , antidiabetic (5), anticancer (6) and antiinflammatory (5) activities . Introduction of metal ions like Cu(II), Co(II) and Ni(II) into the thiosemicarbazone ligands dramatically increases or decreases their biological activities like antibacterial, anti HIV, antifungal and anti-inflammatory (7-10). A wide range of survey on the importance and utility in various fields of the transition metal complexes of substituted thiosemicarbazone have revealed the pharmacological importance of both ligand as well as complex (11). In the Present work attempt has been made to establish the stoichiometry by polarographic studies of substituted thiosemicarbazone complexes with the number of transition metal ions such as Mn(II), Fe (II) ,Cobalt(II) ,Nickel(II), and Zinc(II) metal complexes.

Polarography is the technique based on current voltage curve obtained on electrolysis of solution of electro-oxidisable or reducible substance at d.m.e (i.e dropping mercury electrode) . The technique of polarography was

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developed for the first time in 1922 by Heyrovsky (12). Polarography is a voltammetric technique (Voltammetry comprises a group of electrochemical methods in which information about the analyte is derived from the measurement of current as per a function of applied potential). Usually this method is successfully employed with reversible waves to study the complex formation and also to calculate the stability constant etc. Half wave potential or ($E_{1/2}$) may be defined as the potential on a polarographic curve at which the current reaches half of its limiting value. $E_{1/2}$ value is dependent on the nature of electrolyzed substance and therefore on the constitution of the solution .It is a quantity that may be used to reflect chemical effects, such as complexation of the electro active substance(13)

The reduction wave of polarograph of a simple aqua metal ion is shifted in the direction of more negative potential on addition of a complex forming agent .Direct computation of the shifting in half wave potential can serve for the determination of stability constants of complexes in solutions , provided that the reaction occurring at the dropping mercury electrode is reversible. With suitable modifications , however the irreversible cases can be studied within many instances(14).

Only in a few cases direct application of simple theory serves for the determination of stability constants. In a number of cases the reduction waves have been found to be both kinetically controlled as well as diffusion controlled and the rates of dissociation of complex species control to a greater or lesser extent , the shapes of waves .Systems that consists of several complexes are encountered in which both reducible and non reducible species occur , in which equilibria between some species are less mobile than others .The overall kinetics of many of such systems have been elucidated and the nature , structure and behaviour of each species identified in addition to the calculation of their stability constant . From such applications it has been established that polarographic technique may be employed as a useful tool for the determination of the structure of the complexes .

In the present work all the complexes reduce irreversibly at d.m.e and hence their kinetic parameters α_n and $k^{o}{}_{f,h}$ have been calculated using the equation as given below : limiting diffusion current (Id)

$$E_{d.e} = E_{1/2} - \frac{0.0542}{\alpha_n} \,.\, \log \frac{i}{i_d - i}$$

with $E_{1/2} = -0.2412 + \frac{0.05915}{\alpha_n} .\log \frac{1.349}{D_0^{1/2}} \; k^{o}{}_{f,h}{}^{t1/2}$

in case of wave occurring above -1.0 volt the equations employed are

$$E^0_{1/2} = -0.2412 + \frac{0.05915}{\alpha_n} .\log \frac{1.349}{D_0^{1/2}} \; k^{o}{}_{f,h}$$

and $E_{d..e} = E^0_{1/2} - \frac{0.0542}{\alpha_n} \,.\, (\log \frac{i}{id - i} - 0.546 \log t)$

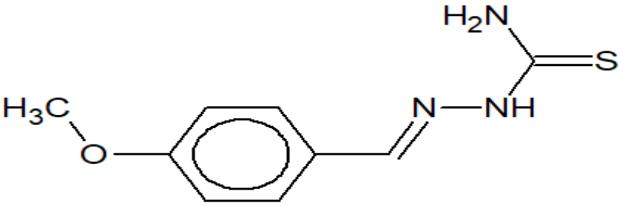
The value of $E_{1/2}$ and αn are obtained from plot of $\log \frac{i}{id - i} - 0.546 \log t$ vs $E_{d.e.}$

Literature survey:-

Complex forming agents are widely used as reagents in various titrimetric , spectrophotometric , polarographic and electrophoretic methods. Substituted thiosemicarbazones represent an imperative class of Nitrogen and sulphur donor ligands over past few decades of time on account of their varying donor properties, structural divergence and biological utility (15) . For their biological and medicinal importance chemistry of thiosemicarbazones have been widely studied in the field of coordination chemistry(16) . Thiosemicarbazones may act as flexible poly-dentate chelating ligands that may coordinate with various transition metal ions by coordinating through the sulphur (S) as well as hydrazinic nitrogen (N) atoms(17,18) .A number of workers have investigated thiosemicarbazones polarographically at d.m.e (19,20). Polarographic behaviour of Thiosemicarbazones of Fe (II)and Zn (II) was studied by Sugam Shivhare (21).Polarographic studies of cobalt (II) in different supporting electrolytes reveals the existence of reversible and irreversible cathodic waves .Positive shift in $E_{1/2}$ value has been reported by many workers (22).Well defined cathodic waves are observed in the reduction of nickel (II) at d.m.e in presence of supporting electrolytes. The important feature of electrochemical reduction of Nickel (II) at d.m.e is + shift in the half wave potential on complexation. For simultaneous determination of copper and cobalt differential pulse polarography has been employed and Well-defined diffusion-controlled waves were obtained for both systems. Both Reversible as well as irreversible waves have been observed for copper (Cu) and cobalt (Co) systems, respectively(23)

Experimental :

Ligand (structure.1) was synthesized by the reaction of hydrazinecarbothioamide with para - methoxybenzaldehyde in ethanol . Purity of ligand was checked before use.



Structure.1

All the chemicals used such as Potassium nitrate ,Potassium chloride, Manganese Sulphate , Ferrous ammonium sulphate ,Nickel sulphate, Cobalt sulphate and Zinc sulphate etc. were of AnalaR B.D.H grade .standard solutions of metal ions were prepared in doubly distilled air free conductivity water . Freshly prepared 0.1% solution of gelatin was used as maximum suppressor to avoid ageing and hydrolysis.

Apparatus:

A Toshniwal manual Polarograph associated with pye galvanometer was used .The polarograph contained saturated calomel electrode connected to a cell through a salt bridge .Triply distilled mercury was used as d.m.e. Alkali accumulators were used to give a voltage of 4 volts.

Procedure:

Various known volumes of standard solutions of metal ions and ligands were mixed in pyrex tubes fitted with stoppers. The deaeration of these solutions was done by passing purified nitrogen for ten minutes. The currents were measured as usual at the end of the drop. Capillary characterstics were measured in several supporting electrolytes at different concentration of ligand. Half wave potentials are measured by plotting $E_{d.e}$ Vs log $\frac{i}{id-i}$. In all the cases under investigation straight lines were obtained. The slope values predicts the nature of the wave . Diffusion controlled nature of the wave is determined by recording the polarograms at different mercury heights.

Preparation of solutions :

Following solutions were prepared for recording the polarograms:

1.1.0 ml of 5m M manganese sulphate and 0.0 ml, 2.0 ml, 4.0 ml and 6.0 ml of 5m 4-methoxybenzaldehyde thiosemicarbazone diluted to 20 ml supporting electrolyte potassium chloride.

2. 0.25ml of ferrous ammonium sulphate and 0.0 ml, 0.50 ml, 1.0 ml and 1.50 ml of 5m M of 4-methoxybenzaldehyde thiosemicarbazone diluted to 10 ml supporting electrolyte potassium chloride.

3. 1.0 ml of 5m M cobalt sulphate and 0.0 ml, 2.0 ml and 5.0 ml of 5m M of 4-methoxybenzaldehyde thiosemicarbazone diluted to 10 ml supporting electrolyte potassium chloride.

4. 2.0 ml of 5m M nickel sulphate and 0.0 ml, 2.0 ml, 3.0 ml and 5.0 ml of 5m M of 4-methoxybenzaldehyde thiosemicarbazone diluted to 20 ml supporting electrolyte potassium chloride.

5. 1.0 ml of 5m M zinc sulphate and 0.0 ml, 2.0 ml, 4.0 ml and 8.0 ml of 5m M of 4-methoxybenzaldehyde thiosemicarbazone diluted to 25 ml supporting electrolyte potassium chloride.

The percentage of alcohol was fixed in every case by adding required quantity of alcohol.The gelatin solution of 1% was used as maximum suppressor .Total volume was made up by adding the supporting electrolyte .

For studying the effect of mercury pressure various sets were prepared.

Logarithmic analysis of the polarograms of manganese sulphate and varying concentrations of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-4 (Fig.1)

Table 1:- **Curve 1**

S.No	- $E_{d.e}$ (Volts)	log $\frac{i}{id-i}$	0.546 log t	log $\frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.25	-0.0196	0.2455	-0.2651	
2	1.27	+0.0413	0.2423	-0.2010	
3	1.29	+0.0738	0.2390	-0.1651	
4	1.31	+0.1157	0.2372	-0.1215	-1.36

5	1.33	+0.1698	0.2351	-0.0653	
6	1.35	+0.2026	0.2338	-0.0312	
7	1.37	+0.2575	0.2325	-0.0250	

Table 1:- **Curve 2**

S.No	- $E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.33	+0.0966	0.3278	-0.2312	
2	1.39	+0.2479	0.3230	-0.0751	
3	1.43	+0.2651	0.3155	-0.0505	
4	1.49	+0.5183	0.3057	-0.2125	-1.41
5	1.53	+0.6029	0.2917	-0.3114	

Table 1:- **Curve 3**

S.No	- $E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.33	-0.0007	0.3218	-0.3225	
2	1.39	+0.1959	0.3210	-0.1251	
3	1.43	+0.3240	0.3088	-0.0152	
4	1.49	+0.4725	0.3010	-0.1715	-1.43
5	1.53	+0.5834	0.2923	-0.2911	

Table 1:- **Curve 4**

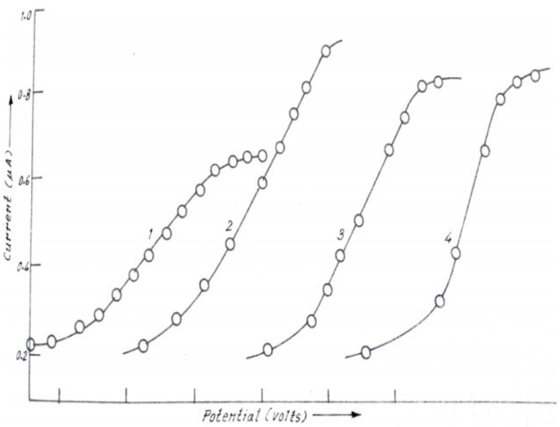
S.No	- $E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.33	-0.2445	0.3278	-0.5723	
2	1.39	-0.0122	0.3230	-0.3352	
3	1.43	+0.1310	0.3155	-0.1845	
4	1.49	+0.3735	0.3126	0.0609	-1.48
5	1.53	+0.5188	0.3035	0.2153	

Table 2:- Effect of height of mercury column

S.No	$h_{effective}$	$h^{1/2}_{effective}$	I_d (μA)
1.	40	6.32	0.50
2.	45	6.70	0.60
3.	50	7.07	0.71
4.	55	7.41	0.83

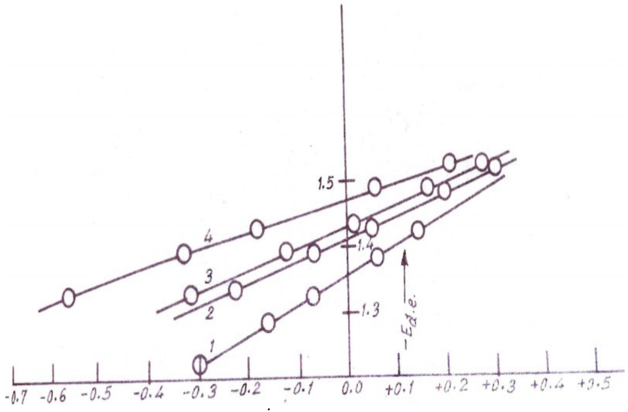
Table 3:- Values of α_n *and* $k^o_{f,h}$

S.No	Con.of ligand (mM)	Intercept	Slope	$D_0^{1/2}$	α_n	$k^o_{f,h}$
1	0.5	1.41	0.40	4.612×10^{-4}	0.1355	7.358×10^{-7}
2	1.0	1.43	0.38	2.035×10^{-4}	0.1426	2.046×10^{-7}
3	1.5	1.47	0.27	1.485×10^{-4}	0.2007	6.739×10^{-7}



(each curve starts at -0.7 volts ,1div=0.2 volts)

Fig.1:- Polarograms of solutions of MnSO4 and varying concentration of 4-methoxybenzaldehyde thiosemicarbazone .



← $\log\frac{i}{id-i}$ -0.546 log t →

Fig. 2:- Logarithmic plot of $-E_{d.e}$ as a function of $\log\frac{i}{id-i}$ to curves 1-4 ,Fig 1

Logarithmic analysis of the polarograms of Iron (II) and varying concentrations of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-3 (Fig.3)

Table 4:- **Curve 1**

S.No	$-E_{d.e}$ (Volts)	$\log\frac{i}{id-i}$	0.546 log t	$\log\frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.22	-0.0020	0.2995	-0.3015	
2	1.28	+0.1332	0.2982	-0.1650	
3	1.32	+0.2105	0.2910	-0.0850	
4	1.38	+0.3486	0.2935	+0.0551	-1.340
5	1.42	+0.4392	0.2880	+0.1512	

Table 4:- **Curve 2**

S.No	$-E_{d.e}$ (Volts)	$\log\frac{i}{id-i}$	0.546 log t	$\log\frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.23	-0.1256	0.3154	-0.4410	
2	1.27	-0.0400	0.3126	-0.3526	
3	1.33	+0.0520	0.2870	-0.2350	
4	1.37	+0.1255	0.2835	-0.1580	-1.45
5	1.43	+0.2290	0.2741	-0.0451	

6	1.49	+0.2757	0.2715	+0.0582	

Table 4:- **Curve 3**

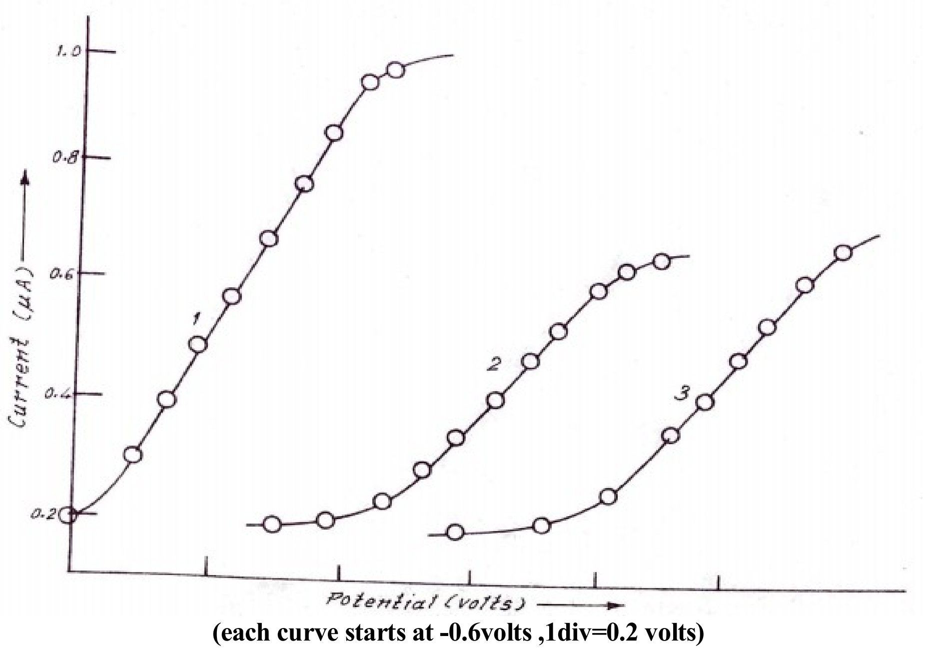
S.No	- $E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.23	-0.2496	0.3015	-0.5511	-1.50
2	1.27	-0.1547	0.2978	-0.4525	
3	1.33	-0.0518	0.2936	-0.3454	
4	1.37	-0.0327	0.2849	-0.2522	
5	1.43	-0.1560	0.2810	-0.1250	
6	1.49	-0.3001	0.2786	+0.0215	

Table 5:- Effect of height of mercury column

S.No	$h_{effective}$	$h^{1/2}_{effective}$	I_d (μA)
1.	32	5.65	0.59
2.	36	6.00	0.60
3.	40	6.32	0.71

Table 6 : Values of α_n and $k^o_{f,h}$

S.No	Con.of ligand (mM)	Intercept $E^0_{1/2}$	Slope	$D_0^{1/2}$	α_n	$k^o_{f,h}$
1	0.5	1.45	0.4666	9.58 $\times 10^{-4}$	0.1161	3.009 $\times 10^{-6}$
2	1.0	1.50	0.4175	2.37 $\times 10^{-5}$	0.1298	3.037 $\times 10^{-8}$



(each curve starts at -0.6volts ,1div=0.2 volts)

Fig 3:- Polarograms of solutions of Ferrous ammonium sulphate and varying concentration of 4-methoxybenzaldehyde thiosemicarbazone.

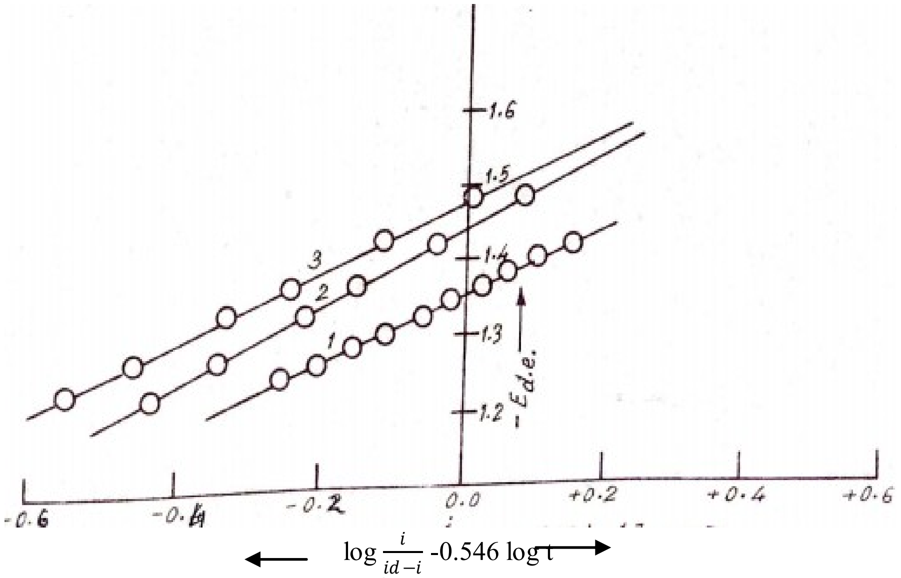


Fig .4:- Logarithmic plot of $-E_{d.e}$ vs [$\log \frac{i}{id-i} - 0.546\ log\ t$] $corresponding$ to curves 1-3 ,Fig 3

Logarithmic analysis of curves of cobalt (II) and varying concentration of of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-4 (Fig .5)

Table 7:- **curve 1**

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.11	-0.1940	0.2410	-0.4350	-1.215
2	1.13	-0.1020	0.2395	-0.3415	
3	1.15	-0.0230	0.2382	-0.2612	
4	1.17	+0.0686	0.2366	-0.1680	
5	1.19	+0.1232	0.2352	-0.1120	
6	1.21	+0.2028	0.2338	-0.0310	

Table 7:- **Curve 2**

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	0.91	-0.1915	0.2505	-0.4420	-0.940
2	0.93	+0.1524	0.2474	-0.0950	
3	0.95	+0.4468	0.2458	+0.2010	
4	0.97	+0.7549	0.2439	+0.5110	
5	0.94	+0.2927	0.2426	+0.0501	

Table 7:- **Curve 3**

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.01	-0.1412	0.2477	-0.0985	-1.05
2	1.03	+0.4468	0.2448	+0.2020	
3	1.05	+0.6908	0.2428	+0.4480	
4	1.07	+0.9735	0.2410	+0.7325	

Table 7:- **Curve 4**

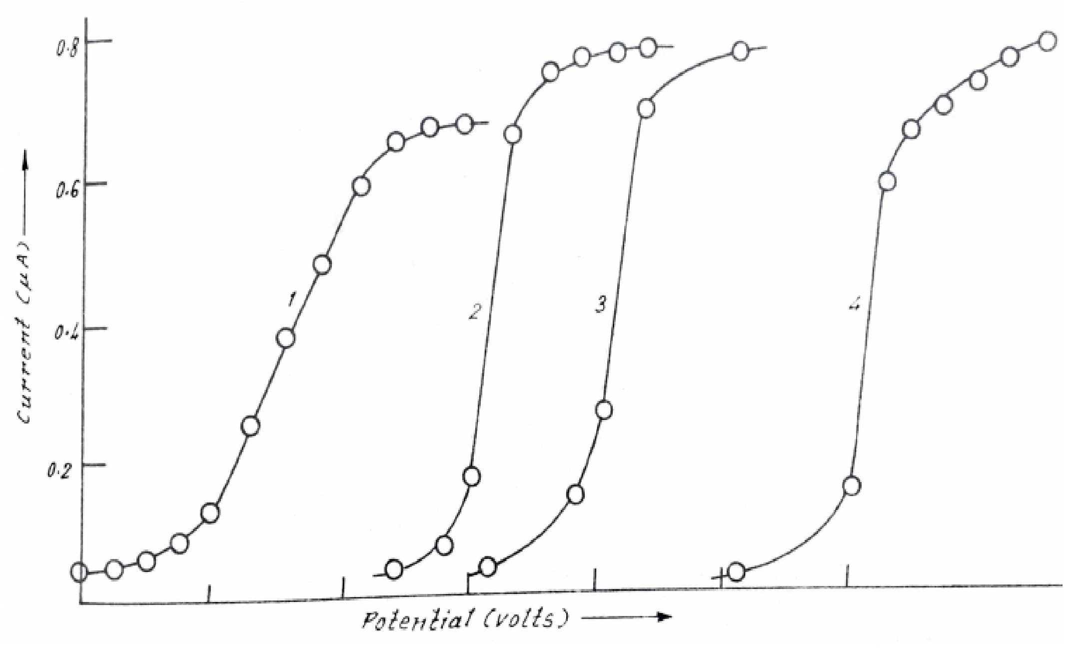
S.No	- $E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.01	+0.0067	0.2584	-0.2517	
2	1.03	+0.2784	0.2534	+0.0250	
3	1.05	+0.5725	0.2477	+0.3248	
4	1.00	-0.1697	0.2428	-0.4125	-1.06

Table 8 :- Effect of height of mercury column

S.No	$h_{effective}$	$h^{1/2}{}_{effective}$	I_d (µA)
1.	25.5	5.049	0.40
2.	31.2	5.58	0.45
3.	35.5	5.97	0.49
4.	38.3	6.18	0.51

Table 9 :- Values of α_n and $k^o{}_{f,h}$

S.No	Con.of ligand (mM)	Intercept $E^0_{1/2}$	Slope	$D_0^{1/2}$	α_n	$k^o{}_{f,h}$
1	0.5	0.940	0.1785	4.821×10^{-4}	0.3036	9.245×10^{-8}
2	1.0	1.05	0.1666	2.575×10^{-4}	0.3253	6.790×10^{-9}
3	1.5	1.06	0.1764	1.560×10^{-4}	0.3072	6.452×10^{-9}



(each curve starts at - 0.6volts ,1div=0.2 volts)

Fig. 5:- Polarogram of solutions of cobalt sulphate and varying concentration of 4- methoxybenzaldehyde thiosemicarbazone.

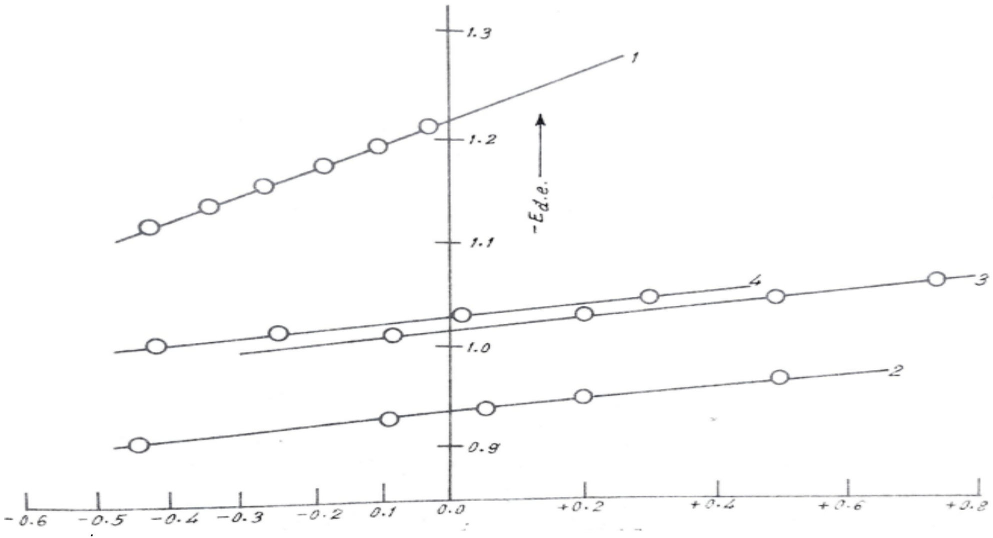


Fig. 6:- Logarithmic plot of $-E_{d.e}$ vs [$\log \frac{i}{id-i} - 0.546\, log\, t$] $corresponding$ to curves 1-4 ,Fig 5.

Logarithmic analysis of curves of nickel sulphate and varying concentration of of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-4 Fig .7

Table 10:- Curve 1

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	$-E_{1/2}$ (Volts)
1	0.68	-0.7645	0.835
2	0.71	-0.6194	
3	0.73	-0.5150	
4	0.76	-0.3825	
5	0.78	-0.2795	
6	0.80	-0.1950	
7	0.90	+0.3010	

Table 10 :- Curve 2

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	$-E_{1/2}$ (Volts)
1	0.48	-0.1875	0.505
2	0.53	+0.1435	
3	0.58	+0.4420	
4	0.63	+0.7225	

Table 10:- Curve 3

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	$-E_{1/2}$ (Volts)
1	0.48	-0.2650	0.540
2	0.53	-0.0418	
3	0.58	+0.2065	
4	0.63	+0.4250	
5	0.68	+0.6310	

Table 10:- **Curve 4**

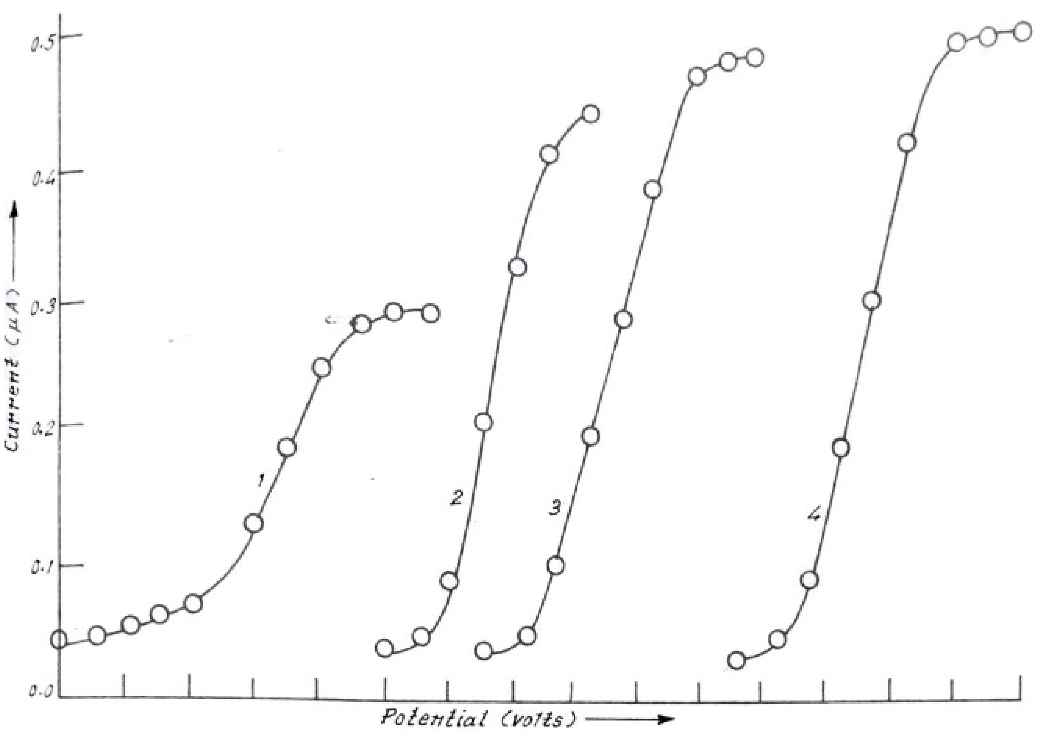
S.No	- $E_{d.e}$ (Volts)	$\log \frac{i}{id - i}$	$-E_{1/2}$ (Volts)
1	0.48	-0.4065	
2	0.53	-0.1825	
3	0.58	+0.1125	0.560
4	0.63	+0.3402	
5	0.68	+0.5895	

Table 11 :- Effect of height of mercury column

S.No	$h_{effective}$	$h^{1/2}_{effective}$	I_d (μA)
1.	33.5	5.80	0.225
2.	38.5	6.20	0.260
3.	42.0	6.50	0.285

Table 12 :- Values of α_n and $k^o_{f,h}$

S.No	Con.of ligand (mM)	Intercept $E^0_{1/2}$	Slope	$D_0^{1/2}$	α_n	$k^o_{f,h}$
1	0.5	0.505	0.5500	2.821×10^{-3}	0.0985	7.605×10^{-3}
2	0.75	0.540	0.4857	2.352×10^{-4}	0.1115	4.700×10^{-4}
3	1.25	0.560	0.6470	1.106×10^{-4}	0.0837	2.901×10^{-4}



(each curve starts at - 0.2 volts ,1div=0.2 volts)

Fig .7:- Polarogram of solutions of cobalt sulphate and varying concentration of 4- methoxybenzaldehyde thiosemicarbazone

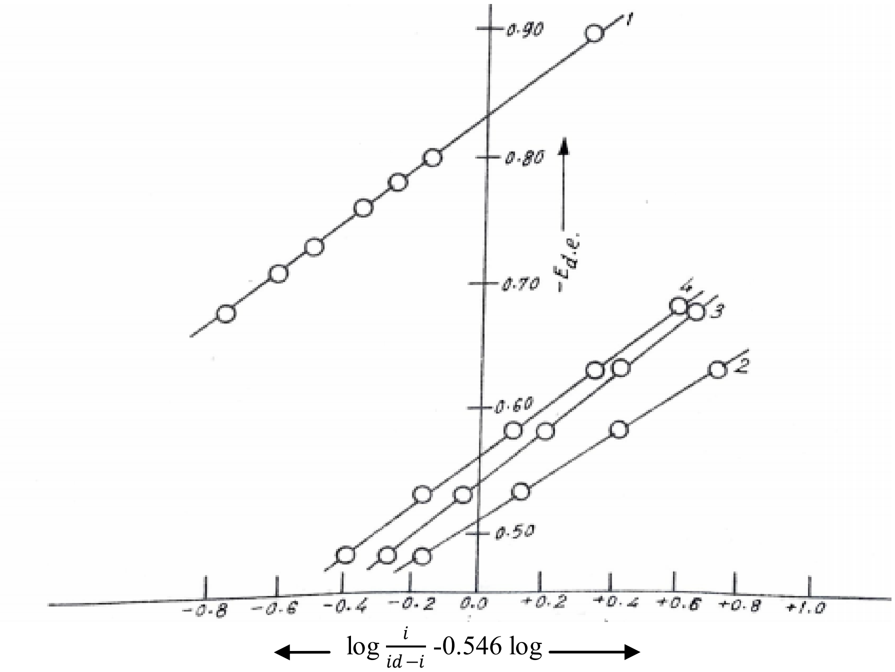


Fig. 8:- Logarithmic plot of $-E_{d.e}$ as a function of $\log \frac{i}{id-i}$ *corresponding* to curves 1-4 , Fig 7.

Logarithmic analyses of curves of Zinc sulphate and varying concentration of of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-4 (Fig .9)

Table 13:- curve 1

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.01	-0.3574	0.2327	-0.5901	
2	1.03	-0.2702	0.2315	-0.5017	
3	1.05	-0.1816	0.2302	-0.4118	
4	1.07	-0.0724	0.2291	-0.3015	-1.14
5	1.09	+0.0073	0.2274	-0.2201	
6	1.11	+0.1023	0.2258	-0.1235	
7	1.13	+0.1987	0.2242	-0.0255	
8	1.15	+0.2882	0.2231	+0.0651	
9	1.17	+0.3893	0.2218	+0.1675	
10	1.19	+0.4615	0.2205	+0.2410	

Table 13:- curve 2

S.No	$-E_{d.e}$ (Volts)	$\log \frac{i}{id-i}$	0.546 log t	$\log \frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.01	-0.5906	0.2344	-0.8250	
2	1.05	-0.3887	0.2326	-0.6213	
3	1.09	-0.1753	0.2298	-0.4051	
4	1.13	+0.0456	0.2281	-0.1825	
5	1.15	+0.1616	0.2273	-0.0657	-1.16
6	1.19	+0.4070	0.2245	+0.1825	

Table 13:- **curve 3**

S.No	- $E_{d.e}$ (Volts)	log $\frac{i}{id-i}$	0.546 log t	log $\frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.08	-0.1630	0.2385	-0.4015	
2	1.12	+0.0106	0.2360	-0.2254	
3	1.16	+0.1718	0.2329	-0.0611	-1.18
4	1.20	+0.3456	0.2315	+0.1150	

Table 13 **curve 4**

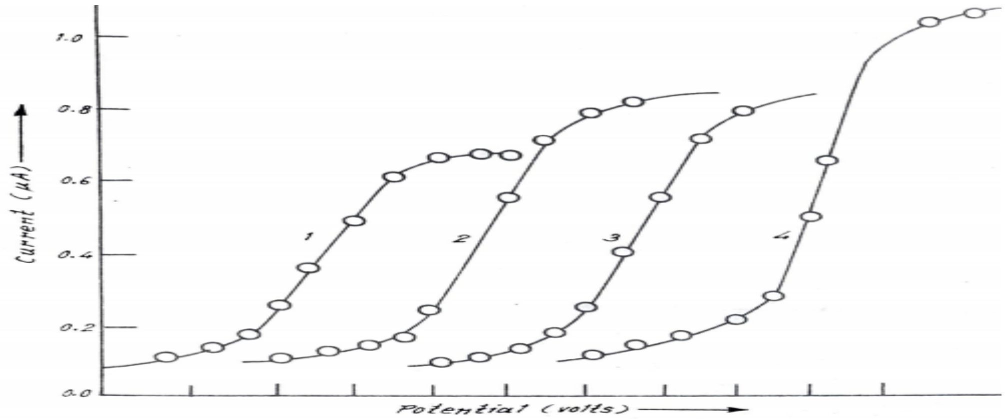
S.No	- $E_{d.e}$ (Volts)	log $\frac{i}{id-i}$	0.546 log t	log $\frac{i}{id-i}$ -0.546 log t	$E_{1/2}$ (Volts)
1	1.15	-0.4100	0.2315	-0.6415	
2	1.17	-0.2220	0.2302	-0.4522	
3	1.19	+0.0479	0.2274	-0.2753	
4	1.21	+0.1283	0.2235	-0.0952	
5	1.23	+0.3166	0.2215	+0.0951	-1.22
6	1.25	+0.5050	0.2200	+0.2850	

Table 14 :- Effect of height of mercury column

S.No	$h_{effective}$	$h^{1/2}{}_{effective}$	I_d (μA)
1.	27.0	5.19	0.35
2.	31.5	5.60	0.38
3.	36.0	6.00	0.42
4.	41.0	6.40	0.45

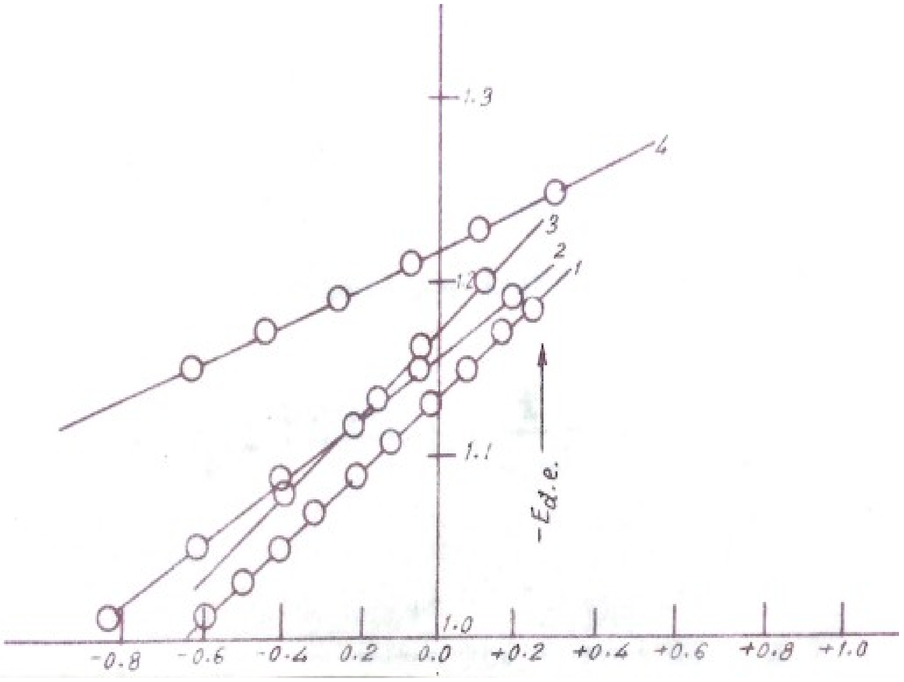
Table 15 :- Values of α_n and $k^o{}_{f,h}$

S.No	Con.of ligand (mM)	Intercept $E^0_{1/2}$	Slope	$D_0^{1/2}$	α_n	$k^o{}_{f,h}$
1	0.4	1.22	0.7000	$5.18x10^{-4}$	0.0774	$2.011 x10^{-5}$
2	0.8	1.18	0.6481	$2.45 x10^{-4}$	0.0836	$8.555 x10^{-6}$
3	1.2	1.16	0.4150	$2.12x10^{-4}$	0.1306	$1.471x10^{-5}$



(each curve starts at - 0.6 volts ,1div=0.2 volts)

Fig .9:- Polarogram of Zinc sulphate and varying concentration of 4-methoxybenzaldehyde thiosemicarbazone.



$\log \frac{i}{id-i}$ -0.546 log ⟵ ⟶

Fig.10:- Logarithmic plot of $-E_{d.e}$ as a function of $\log \frac{i}{id-i}$ *corresponding* to curves 1-4 , Fig 9.

Result and Discussion:-

Well defined cathodic waves are obtained for Manganese(II), Iron(II),Cobalt (II) , Nickel (II) and Zinc(II) metal ions . $E_{1/2}$ values of metal ions change on complexation .Appreciable change in $E_{1/2}$ value to the negative side has been observed in case of Mn (II) ,Fe (II) and Zn (II) while in case of Co(II) and Ni (II) a positive shift has been observed .On analysis of the waves it has been found that plot of $\log \frac{i}{id-i}$ vs $E_{d.e}$ are linear (Fig. 2,4,6,8 and 10). All the metals as well as their complexes with 4-methoxybenzaldehyde thiosemicarbazone reduce irreversibly at d.m.e .The polarograms reveal the reduction to be diffusion controlled as i_d on plotting against $\sqrt{h_{effective}}$ gives straight line (Tables 2,5,8,11,14

Because of the irreversible character of the reduction of the complex at d.m.e only kinetic parameters α_n and $k^o{}_{f,h}$ have been calculated (tables 3,6,9,12,15).The calculation of kinetic parameters have been made by Koutecky's theoretical treatment as extended by Meits and Israel.The general equations are

$$E_{d.e} = E_{1/2} - \frac{0.0542}{\alpha_n} .\log \frac{i}{i_d - i}$$

with $E_{1/2} = -0.2412 + \frac{0.05915}{\alpha_n} .\log \frac{1.349}{D_0^{1/2}} \; k^o{}_{f,h}{}^{t1/2}$

In these equations $E_{d.e}$ and $E_{1/2}$ are referred to S.C.E. but in case of Mn (II) , Zn (II) and Fe (II) (for the waves occurring above -1.0 volts vs S.C.E) the equations employed to calculate α_n and $k^o{}_{f,h}$ are

$$E^0_{1/2} = -0.2412 + \frac{0.05915}{\alpha_n} .\log \frac{1.349}{D_0^{1/2}} \; k^o{}_{f,h}$$

and $E_{d..e} = E^0_{1/2} - \frac{0.0542}{\alpha_n} . (\log \frac{i}{id-i} - 0.546 \log t)$

The values of α_n and $E^0_{1/2}$ are obtained from the plot of $E_{d..e}$ vs $\log \frac{i}{id-i}$ .The slope being equal to $0.0542/\alpha_n$. The value of $D_0^{1/2}$ has been estimated from Ilkovic equation.

Conclusion:-

In the current work we have discussed the polarographic behaviour of thiosemicarbazones of Manganese(II), Iron(II),Cobalt (II) , Nickel (II) and Zinc(II) metal ions . Polarographic measurements have proved the complex formation of thiosemicarbazones with these metal ions. Keeping in view the biological as well as therapeutical importance of the transition metal complexes of substituted thiosemicarbazone much work is needed to be done in the future on these complexes.

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