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

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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 thiosemicarbamide 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 R¹ R² C=N–NH–C(=S)–NR³ R⁴ have presented a broad spectrum of properties against a number of diseases due to their antifungal (4), antibacterial, antidiabetic (5), anticancer (6) and anti-inflammatory (5) activities. Introduction of metal ions like Cu(II), Co(II) and Ni(II) into the thiosemicarbazide 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
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.

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.

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 \( a_n \) and \( k^0_{f,h} \) have been calculated using the equation as given below: limiting diffusion current (Id)

\[
E_{de} = E_{1/2} - 0.0542 \frac{a_n}{a_n} \log \frac{i}{i_{id}}
\]

with \( E_{1/2} = -0.2412 + \frac{0.05915}{a_n} \log \frac{1349}{k^0_{f,h}} \)

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

\[
E_{1/2} = -0.2412 + \frac{0.05915}{a_n} \log \frac{1349}{k^0_{f,h}}
\]

and \( E_{de} = E_{1/2} + 0.0542 \frac{a_n}{a_n} \cdot (\log \frac{i}{i_{id}} - 0.546 \log t) \)

The value of \( E_{1/2} \) and an are obtained from plot of \( \frac{i}{i_{id}} - 0.546 \log t \) vs \( E_{de} \).

**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 polydentate 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 polargraphically at d.m.e (19,20). Polargraphic behaviour of Thiosemicarbazones of Fe (II) and Zn (II) was studied by Sugam Shivhare (21). Polargraphic 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 polargraphy 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.

\[
\begin{align*}
\text{Structure.1}
\end{align*}
\]

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 characteristics were measured in several supporting electrolytes at different concentration of ligand. Half wave potentials are measured by plotting \( E_{de} \) Vs log \( i_{id}/i_{0} \). 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 M 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:
| S.No | \(- E_{de} \) (Volts) | log \( i_{id}/i_{0} \) | 0.546 log t | log \( i_{id}/i_{0} \) -0.546 log t | \( E_{1/2} \) (Volts) |
|------|----------------------|------------------------|--------------|---------------------------------|-------------------|
| 1    | 1.25                 | -0.0196                | 0.2455       | -0.2651                         | -1.36             |
| 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                         |
### Table 1:

| Curve 2 |     |     |     |     |
|---------|-----|-----|-----|-----|
| S.No    |  E<sub>de</sub> (Volts) | log<i><sub>i</sub></i> <sub>id−i</sub> | 0.546 log t | log<i><sub>i</sub></i> <sub>id−i</sub>-0.546 log t |
| 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 |
| 5       | 1.53 |  +0.6029 | 0.2917 | -0.3114 |
|         |     |     |     | -1.41  |

### Table 1:

| Curve 3 |     |     |     |     |
|---------|-----|-----|-----|-----|
| S.No    |  E<sub>de</sub> (Volts) | log<i><sub>i</sub></i> <sub>id−i</sub> | 0.546 log t | log<i><sub>i</sub></i> <sub>id−i</sub>-0.546 log t |
| 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 |
| 5       | 1.53 |  +0.5834 | 0.2923 | -0.2911 |
|         |     |     |     | -1.43  |

### Table 1:

| Curve 4 |     |     |     |     |
|---------|-----|-----|-----|-----|
| S.No    |  E<sub>de</sub> (Volts) | log<i><sub>i</sub></i> <sub>id−i</sub> | 0.546 log t | log<i><sub>i</sub></i> <sub>id−i</sub>-0.546 log t |
| 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 |
| 5       | 1.53 |  +0.5188 | 0.3035 |  0.2153 |
|         |     |     |     | -1.48  |

### Table 2:

| Effect of height of mercury column |
|-----------------------------------|
| S.No    | h<sub>effective</sub> (mm) | h<sub>1/2 effective</sub> (mm) | I<sub>l</sub>(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<sub>n</sub> and k<sub>α f,h</sub> |
|-----------------------------------------------|
| S.No    | Con.of ligand (mM) | Intercept | Slope  | D<sub>0</sub><sup>1/2</sup> | α<sub>n</sub> | k<sub>α f,h</sub> |
|---------|-------------------|-----------|--------|----------------|-----------|-----------------|
| 1       | 0.5               | 1.41      | 0.40   | 4.612x10<sup>4</sup> | 0.1355   | 7.358 x10<sup>-7</sup> |
| 2       | 1.0               | 1.43      | 0.38   | 2.035x10<sup>4</sup> | 0.1426   | 2.046 x10<sup>-7</sup> |
| 3       | 1.5               | 1.47      | 0.27   | 1.485x10<sup>4</sup> | 0.2007   | 6.739 x10<sup>-7</sup> |
(each curve starts at -0.7 volts, 1 div = 0.2 volts)

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

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

| Curve 1 |                                                                 |
|---------|------------------------------------------------------------------|
| S.No    | - E<sub>de</sub> (Volts)                                        |
|         | \( \log \frac{i_{id-i}}{i_{id-t}} \)                           |
|         | \( 0.546 \log t \)                                             |
|         | \( \log \frac{i_{id-i}}{i_{id-t}} - 0.546 \log t \)           |
|         | \( E_{1/2} \) (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                                                          |
| 5       | 1.42                                                             |
|         | +0.4392                                                          |
|         | 0.2880                                                           |
|         | +0.1512                                                          |
|         | -1.340                                                          |

| Curve 2 |                                                                 |
|---------|------------------------------------------------------------------|
| S.No    | - E<sub>de</sub> (Volts)                                        |
|         | \( \log \frac{i_{id-i}}{i_{id-t}} \)                           |
|         | \( 0.546 \log t \)                                             |
|         | \( \log \frac{i_{id-i}}{i_{id-t}} - 0.546 \log t \)           |
|         | \( E_{1/2} \) (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                                                          |
| 5       | 1.43                                                             |
|         | +0.2290                                                          |
|         | 0.2741                                                           |
|         | -0.0451                                                          |
Table 4:-

| S.No | -E<sub>dc</sub> (Volts) | log (i<sub>id</sub>/i<sub>0</sub>) | 0.546 log t | log (i<sub>id</sub>/i<sub>0</sub>) - 0.546 log t | E<sub>1/2</sub> (Volts) |
|------|-----------------|-----------------|-------------|---------------------------------|-----------------|
| 1    | 1.23            | -0.2496         | 0.3015      | -0.5511                         |                 |
| 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                         | -1.50           |
| 6    | 1.49            | -0.3001         | 0.2786      | +0.0215                         |                 |

Table 5:- Effect of height of mercury column

| S.No | h<sub>effective</sub> | h<sup>1/2</sup><sub>effective</sub> | I<sub>d</sub> (µA) |
|------|-----------------------|-------------------------------------|-----------------|
| 1    | 32                    | 5.65                                | 0.59            |
| 2    | 36                    | 6.00                                | 0.60            |
| 3    | 40                    | 6.32                                | 0.71            |

Table 6: Values of α<sub>n</sub> and k<sup>n</sup><sub>f,h</sub>

| S.No | Con.of ligand (mM) | Intercept | Slope | D<sub>0</sub><sup>1/2</sup> | α<sub>n</sub> | k<sup>n</sup><sub>f,h</sub> |
|------|--------------------|-----------|-------|-----------------|----------|-----------------|
| 1    | 0.5                | 1.45      | 0.4666| 9.58 x10<sup>-4</sup> | 0.1161  | 3.009 x10<sup>-6</sup> |
| 2    | 1.0                | 1.50      | 0.4175| 2.37 x10<sup>-5</sup> | 0.1298  | 3.037 x10<sup>-8</sup> |

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

(each curve starts at -0.6 volts, 1 div = 0.2 volts)
Logarithmic analysis of curves of cobalt (II) and varying concentration of of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-4 (Fig .5)

Table 7:-

| S.No | - E<sub>de</sub> (Volts) | log<sub><i>i</i><sub>id</sub>-<i>i</i><sub>0</sub>-0.546 log t | 0.546 log t | log<sub><i>i</i><sub>id</sub>-<i>i</i><sub>0</sub>-0.546 log t | E<sub>1/2</sub> (Volts) |
|------|-----------------|--------------------------|-----------|--------------------------|------------------|
| 1    | 1.11            | -0.1940                  | 0.2410    | -0.4350                  |                 |
| 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                  | -1.215          |
| 5    | 1.19            | +0.1232                  | 0.2352    | -0.1120                  |                 |
| 6    | 1.21            | +0.2028                  | 0.2338    | -0.0310                  |                 |

Table 7:-

| S.No | - E<sub>de</sub> (Volts) | log<sub><i>i</i><sub>id</sub>-<i>i</i><sub>0</sub>-0.546 log t | 0.546 log t | log<sub><i>i</i><sub>id</sub>-<i>i</i><sub>0</sub>-0.546 log t | E<sub>1/2</sub> (Volts) |
|------|-----------------|--------------------------|-----------|--------------------------|------------------|
| 1    | 0.91            | -0.1915                  | 0.2505    | -0.4420                  |                 |
| 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                  | -0.940          |
| 5    | 0.94            | +0.2927                  | 0.2426    | +0.0501                  |                 |

Table 7:-

| S.No | - E<sub>de</sub> (Volts) | log<sub><i>i</i><sub>id</sub>-<i>i</i><sub>0</sub>-0.546 log t | 0.546 log t | log<sub><i>i</i><sub>id</sub>-<i>i</i><sub>0</sub>-0.546 log t | E<sub>1/2</sub> (Volts) |
|------|-----------------|--------------------------|-----------|--------------------------|------------------|
| 1    | 1.01            | -0.1412                  | 0.2477    | -0.0985                  |                 |
| 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                  | -1.05           |
Table 7:

| S.No | $-\text{E}_{dc}$ (Volts) | $\log \frac{i_d-i}{i_d}$ | 0.546 log t | $\log \frac{i_d-i}{i_d}$ - 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 | $h_{\text{effective}}$ | $h_{1/2\text{effective}}$ | $I_d$ (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 $\alpha_n$ and $k_{f,h}^o$

| S.No | Con. of ligand (mM) | Intercept $E_{1/2}$ | Slope | $D_{0}^{1/2}$ | $\alpha_n$ | $k_{f,h}^o$ |
|------|---------------------|---------------------|-------|---------------|------------|------------|
| 1    | 0.5                 | 0.940               | 0.1785| $4.821 \times 10^{-4}$ | 0.3036 | $9.245 \times 10^{-8}$ |
| 2    | 1.0                 | 1.05                | 0.1666| $2.575 \times 10^{-4}$ | 0.3253 | $6.790 \times 10^{-9}$ |
| 3    | 1.5                 | 1.06                | 0.1764| $1.560 \times 10^{-4}$ | 0.3072 | $6.452 \times 10^{-9}$ |

Fig. 5: Polarogram of solutions of cobalt sulphate and varying concentration of 4-methoxybenzaldehyde thiosemicarbazone.
Fig. 6: Logarithmic plot of $-E_{d.e}$ vs $[\log \frac{i}{i_d-i}]$ corresponding to curves 1-4, Fig. 5.

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

Table 10:-

| S.No | $-E_{d.e}$ (Volts) | $\log \frac{i}{i_d-i}$ | $-E_{1/2}$ (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:-

| S.No | $-E_{d.e}$ (Volts) | $\log \frac{i}{i_d-i}$ | $-E_{1/2}$ (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:-

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

Table 11: - Effect of height of mercury column

| S.No | $h_{\text{effective}}$ | $h_{1/2}$ effective | $I_{d} (\mu A)$ |
|------|------------------------|-------------------|----------------|
| 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 $\alpha_n$ and $k_{o,f,h}^o$

| S.No | Con.of ligand (mM) | Intercept $E_{1/2}$ | Slope | $D_0^{1/2}$ | $\alpha_n$ | $k_{o,f,h}^o$ |
|------|-------------------|-------------------|-------|-------------|------------|--------------|
| 1    | 0.5               | 0.505             | 0.5500| 2.821 x 10^{-3} | 0.0985   | 7.605 x 10^{-3} |
| 2    | 0.75              | 0.540             | 0.4857| 2.352 x 10^{-4} | 0.1115   | 4.700 x 10^{-4} |
| 3    | 1.25              | 0.560             | 0.6470| 1.106 x 10^{-4} | 0.0837   | 2.901 x 10^{-4} |

Fig. 7: - Polarogram of solutions of cobalt sulphate and varying concentration of 4-methoxybenzaldehyde thiosemicarbazone
Logarithmic analyses of curves of Zinc sulphate and varying concentration of 4-methoxybenzaldehyde thiosemicarbazone corresponding to curve 1-4 (Fig. 9)

Table 13:-

| S.No | $-E_{dc}$ (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        |                |
| 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:-

| S.No | $-E_{dc}$ (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        |                |
| 6    | 1.19            | +0.4070         | 0.2245         | +0.1825        |                |
Table 13:

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

Table 13:

| S.No | \(-E_{de}\) (Volts) | \(\log \frac{i}{i_{d-i}}\) | 0.546 \(\log t\) | \(\log \frac{i}{i_{d-i}} - 0.546 \log t\) | \(E_{1/2}\) (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 | \(h_{\text{effective}}\) | \(h_{1/2\text{effective}}\) | \(I_d (\mu A)\) |
|------|--------------------------|-----------------------------|-----------------|
| 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 \(\alpha_n\) and \(k^o_{r,h}\)

| S.No | Con.of ligand (mM) | Intercept \(E_{1/2}\) | Slope | \(D_{1/2}^{1/2}\) | \(\alpha_n\) | \(k^o_{r,h}\) |
|------|---------------------|------------------------|-------|-------------------|--------------|---------------|
| 1    | 0.4                 | 1.22                   | 0.7000| 5.18x10^{-4}      | 0.0774       | 2.011x10^{-3} |
| 2    | 0.8                 | 1.18                   | 0.6481| 2.45x10^{-4}      | 0.0836       | 8.555x10^{-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.
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 $\log i_{i_d} - i_{corr}$ corresponding to curves 1-4, Fig 9.

Because of the irreversible character of the reduction of the complex at d.m.e only kinetic parameters $\alpha_n$ and $k^0_{f,h}$ 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

$$E_{d,e} = E_{1/2} - \frac{0.542}{\alpha_n} \cdot \frac{\log i_{i_d} - i_{corr}}{i_{i_d} - i_{corr}}$$

with $E_{1/2} = -0.2412 + \frac{0.05915}{\alpha_n} \cdot \log \frac{1.349}{D_0^{1/2}}$ $k^0_{f,h}^{1/2}$

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 $\alpha_n$ and $k^0_{f,h}$ are

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

and $$E_{d,e} = E_{1/2}^0 - \frac{0.542}{\alpha_n} \cdot (\log \frac{i_{i_d}}{i_{corr}} - 0.546 \log t)$$

The values of $\alpha_n$ and $E_{1/2}^0$ are obtained from the plot of $E_{d,e}$ vs $E_{d,e}$, Fig 9. 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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