



# Polarographic Study of Reduction of CO(II)-Amino Acid and Pyrimidines Complexes at Dropping Mercury Electrode

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**ABSTRACT:** The reduction of Co(II) complexes with amino acids Gly, Ala, Asn, Asp and Glu was studied polarographically. The species reduced on a mercury electrode and their electrochemical parameters were determined. It was shown that the first complex, in all studied systems, is reduced much easier, at less negative values of potentials than the aquaion. The stability constants of the complexes were also calculated. The effect of amino and carboxylate groups on the reduction mechanism of Co(II) complexes on a mercury electrode is discussed.

**KEYWORDS:** polarographic, Co(II)-amino acid, pyrimidine, complex, dropping mercury electrode

## I.INTRODUCTION

Amino acids and pyrimidines are biologically active compounds, essential for human beings and their reaction with metals have relevance to bio systems. They have good chelating ability with metal ions and also play an important role in pharmacy. Polarography plays very important role in the identification of mixed ligand complexes of different metals. Biological active metal complexes with amino acids are important in analytical, biochemical and pharmaceutical have been studied by many coworkers.<sup>1</sup>Polarographic study of mixed ligand complexes of Cadmium with L-amino acids and VitaminB5 have been studied by Khan et al. The Polarographic studies on the complexes of Copper and oxalate are reported in the literature.<sup>2</sup> A survey of literature shows that ternary complexes of Pb(II) with amino acids and MSA have not been studied so far. All polarograms were recorded on ELICO CL 375 DC Polarograph using a saturated calomel electrode (SCE) as the reference electrode and a platinum (Pt) electrode as counter electrode. The capillary had the following characteristics  $m=1.96$  mg/s,  $t = 4.10$  sec/drop and  $h = 40$  cm. The reagents MSA and amino acids were of AR grade and were used as complexing agents. KCL was used as supporting electrolyte to maintain the ionic strength at 1M. Triton X-100 of 0.001% in the final solution have been used as maximum suppresser. The temperature was maintained constant at 303 K. A glass cell is used as electrolytic cell in which all the three electrodes are immersed in test solution.<sup>3</sup> N<sub>2</sub> is used to remove the dissolved oxygen. Then increasing voltage was applied to record the current by the help of the plot between current-voltage (polarogram) the value of  $E_{1/2}$  is calculated. Polarography determines the quantitative and qualitative reductions and oxidation of electroactive substances. An electrode that is a working electrode for a polarographic analysis is known as a dropping mercury electrode. The principle of dropping mercury electrodes is that the mercury drops are weighed to determine the substance qualitatively and quantitatively.<sup>4</sup> DME or Dropping Mercury Electrode is used in Polarography to get quantitative and qualitative analyses of substances. In this electrode, the mercury is constantly dropped into the solution from a reserve with the help of capillary tubes. The diameter of these tubes is 0.03- 0.05 mm. Most analyses recommend a drop interval of 1 to 5 seconds. The use of the DME has the distinct advantage of eliminating the impacts of electrode poisoning due to the continuous regeneration of the electrode surface revealed in the test solution<sup>5</sup>. Polarography makes use of DME. It has several benefits as well as drawbacks. When using the DME, exercise caution. Only valid and doubly distilled mercury must be used in DME. When not in use, the tip of the DME should always be immersed in water and cleaned by dipping it in nitric acid. Holding the assembly in a vertical position can help to eliminate the vibrations.<sup>6</sup>

### Construction of DME

- A mercury reservoir is included in the set.
- It comprises fine capillaries with bore sizes ranging from 20 to 50 millimetres and lengths ranging from 10-15 centimetres.
- Rubber tubing joins the capillary to the mercury reservoir.



- The unknown solution is placed in a small glass electrolysis cell.
- The mercury reservoir's height allows for a drop time of 1-5 seconds.<sup>7</sup>

#### Working of the Dropping Mercury Electrode

- This electrode can be polarised and used both as a cathode and an anode.
- If the DME acts as a cathode then the mercury pool will act as Anode and vice versa. It is a counter electrode to the mercury pool.
- The counter electrode is not polarisable.
- Electrolyte, such as KCl, is added to the analyte solution at a concentration of 50-100 times that of the sample.
- To remove oxygen from the circuit, pure nitrogen or hydrogen is bubbled in the solution.
- For example, if the analyte solution contains cadmium ions, those ions are discharged at the cathode.
- The polarographic cell is then subjected to a gradually increasing voltage, and the current is measured.
- The graph depicts the relationship between applied voltage and current.
- Polarogram is the apparatus, and Polarograph is the graph obtained.<sup>8</sup>

The microelectrode in direct current (dc) polarography is a dropping mercury electrode (DME). It is made up of slight measurable declines of mercury flowing from the aperture of a capillary tube attached to a mercury reservoir. The most popular method of the model electrode is a saturated calomel electrode (SCE) with a greater surface area. Only a meagre amount of current flows as the cell's voltage increases until the substance under assay develops reduction or oxidation.<sup>9</sup>

### II.DISCUSSION

It is a branch of voltammetry in which working electrode is dropping mercury electrode called microelectrode and a reference electrode mercury pool is used. The electrolyte consists of dilute solution of active species to be determined. Active species means which reacts on electrode. Along with the base electrolyte for furnishing good current is used. On passing variable potential (current-voltage) curve is obtained called polarogram and phenomenon is called polarography. Mercury pool in presence of chemical active species using a bulk of base electrolyte to study current voltage is called polarography.<sup>10</sup> Dropping mercury electrode: It is a working micro electrode and consist of pure Hg (purified by dilute HNO<sub>3</sub>) to which a rubber tubing is attached bearing a fix glass capillary of 10-15 cm length having uniform bore with internal diameter 0.5 mm. By adjusting the height of reservoir the relative flow is adjusted. Usually a drop is formed between 1-5 seconds. It acts as a cathode and is attached along the negative terminal of battery through recorder. At anode it consists of Hg pool in contact will be a base electrolyte to which serve as reference electrode. If need is there external S.C.E may be used. It is attached to a positive terminal through potentiometer. Both cathode, anode are connected also to digital voltammeter. It is advisable that before passing current to expel oxygen dissolved in water by bubbling nitrogen or some other inert gas as interferes with C-V curve. On applying a variable potential to electrolyte current is measured at different interval of changing voltage. A plot is obtained between two to get a polarogram. A number of other micro electrodes have been used for the determination of current-voltage curve but the most satisfactory is a slow growing of dropping mercury electrode.<sup>11</sup> The dropping mercury electrode has numerous advantages: (a) The surface of an electrode is conductive, smooth and continuously renewed to give better reproducibility of the current potential curve. (b) The steady value of diffusion current is reproducible even after the each change of an applied potential. (c) The mercury drop weights can be used for the calculation of surface area. (d) Many metal ions from amalgams with mercury. (e) No contamination at the surface of dropping mercury electrode occurs. (f) No poisoning of dropping mercury electrode occurs. (g) Since hydrogen has overvoltage with respect to mercury (SCE) a large number of metallic ions can be reduced. (h) The optimum range from dropping mercury electrode is 0.4 to 2.66 and 0.4 to -2.66. (i) Moreover after the reduction many metal get dissolves in pool of mercury to form amalgam which doesn't interfere in estimation. Limitations (a) Due to the formation of mercury drop gradually surface area increases and consequently a little fluctuation in current may occur like an oscillation which may interferes estimation as an average current is considered. (b) DME can act as a good electrode between 0.4 to -2.66 V.<sup>12</sup>

Basic Principle of polarography All the factors based on theoretical concept of polarography influence the basic principle of polarography. A polarogram or a polarographic wave has represented. The slowly increasing current at the foot is known as residual current. In polarography it is necessary to use the inert base or non redox electrolyte for the correct estimation of active species. In case of only KCl (non redox electrolyte) after sweeping oxygen completely is taken a small amount of current is called as residual current is observed inspite of the fact there is no applied external voltage. This current is non-



faradic in nature and arises due to the formation of electrically double layer. The formation of double layer entirely depends upon the potential to be applied on dme either in the positive or in a negative range.<sup>13</sup> With the passage of time when potential is gradually varies before decomposition is reached a little variation in the residual current with passage of time. More dme drop falls in solution of base electrolyte more double layers formation more residual current increases. So when there is increase in potential it is sufficient to cause electrochemical reaction for the base electrolyte. Again C-V curve for KCl etc can be seen beyond -2.66 V. Sometimes base current may increase due to the other impurity present in the base electrolyte. Furthermore, the migratory current is the current observed due to the migration of ions in the solution. Migration of ions occurs under the electrostatic electric field applied which may cause little variation in the current etc. The ions may diffuse quickly once the ions have reached the respective electrode after discharging conc. gradient (low conc.) at surface electrode setup. Migratory current is due to the migration of active ions under the potential difference applied to the cell. By the diffusion current arises due to the movement of ions under practically negligible emf of the cell. It is difficult to achieve negligible voltage in the cell. So it is advisable to use excess of supporting electrolyte (non redox) in nature which will nullify the charge on electrode under such condition active ions diffuse and reach the electrode.<sup>14</sup> The current is exclusively the diffusion current. It is denoted by  $I_d$ . The diffusion current is determined by ilkovic equation:  

$$I_d = 607nD^{1/2} cm^2/3t^{1/6}$$

Where,  $n$  = number of faraday produced for active species  $C$  = concentration of electrolyte millimole/litre  $D$  = Diffusion coefficient and is measured as  $cm^2/sec$   $m$  = the amount of mercury falling per second  $t$  = time period of the drop in seconds Ilkovic equation is some correction on RHS due to diffusion of ions of active species arising from the curvature of dropping mercury electrode. It is given by here the mass of falling drop

$$1 + AD^{1/2} tm^{-1/3}$$

where,  $A$  is attraction constant,  $m$  is mass of falling mercury drop,  $D$  is diffusion coefficient<sup>15</sup>

### III.RESULTS

Factors on which diffusion current depends: (a) Temperature also effects the  $I_d$  as the ionic mobility is changed. For most of cases the temperature coefficient lies in between 1.5-2%. To control the temperature it is advisable to keep active electrolyte in a bath having a constant temperature about 25 °C. (b) Pressure also influences the  $I_d$  either by changing the mass flow of mercury and affecting its speed. This can be controlled by adjusting the height of reservoir and adjusting the speed. (c) Time alone factor doesn't affect the diffusion current because it has sixth root power coupled with mass flow, the diffusion current is affected. So, by choosing the size of capillary hole and adjusting the pressure one can get accurate result of  $I_d$ . (d) Complex formation diffusion current is also greatly affected if active species from the complex in the solution. In case anionic complex or cationic complex is formed the movement of metal ion will be different i.e. hydrated complex will show different  $I_d$  than other complexes formed. (e) Interfacial surface tension the diffusion current is effected by interfacial tension at mercury surface i.e. there is some gap between the surface of dme and solution phase containing active ions. As a result the current may decrease by decreasing the size of droplets as its interfacial tension can be reduced. (f) Diffusion coefficient diffusion coefficient is related to both viscosity and concentration of the electrolyte. Viscosity depends on temperature and concentration of active electrolyte. If concentration of solution is low the viscosity will be low and diffusion current high.<sup>16</sup> Alternatively, by increasing the temperature one can have high  $I_d$ . An empirical relation between  $I_d$  and  $\eta$  has been derived from the diffusion coefficient has been derived from stoke's Einstein formula:

$$D = RT/6\pi\eta Kr$$

Where  $R$  is gas constant

$T$  = temperature  $\Pi$  = Circle constant  $\eta$  = Coefficient of viscosity Since all other factors except  $\eta$  depend on the Brownian movement. Viscosity of solution can be decreased not only by changing the concentration of active ion but diluting it with other solvent (acetonitrile, ethanol) etc. by the addition of alcohol initially 25%  $I_d$  is increased because alcohol makes complex with metal ion which is more lyophilic at mercury surface reduces the interfacial tension current will be increased.<sup>17</sup>

Polarographic Maxima Under the ideal conditions of concentration of active ion species as well as concentration of supporting electrolyte. The polarogram gives normal C-V curve is not obtained properly. Instead an abnormal increase in current is obtained which with passage of time decreases to give plation. This abnormal increase in height of C-V curve is called polarographic maxima. These maxima may also arise besides the low concentration, pressure on dropping mercury electrode. These may vary in shape from sharp peaks to rounded heaps which gradually decrease to the normal diffusion



current curve as the applied voltage is increased. But for the measurement of exact diffusion current the value of polarographic maxima must be eliminated or suppressed.<sup>18</sup> The maxima are of two types: Strike streaming type mechanism: Such type of maxima arises due to low concentration of base electrolyte and high concentration of active species. The unique feature of such mechanism maxima is that it occurs in a very short range of applied potential to dropping mercury electrode. Due to the low concentration of base electrolyte this leads to streaming movement of CV ions which are quickly diffused due to low viscosity and high rate of diffusion. The maxima appearing in CV curve causes the difficulties in measuring the diffusion current, concentration of active electrolyte. However such type of maxima can be controlled by decreasing the concentration of active ions and increasing the concentration of a base electrolyte. Non streaming Maxima: Such type of maxima doesn't arising from streaming effect. But due to increase in pressure on reservoir attached to dropping mercury electrode the concentration of ions are reduced by the quick fall of mercury drop which will give rise to broad maxima.<sup>19</sup>  $E_{1/2}$  and  $I_d$  are not measured properly. This can be controlled or eliminated by controlling the pressure or adding surface active material. To know the exact  $E_{1/2}$ ,  $I_d$  etc there maxima must be eliminated by adding surface active material, capillary active ions, some surfactants or dyes etc. Half wave potential It is the potential of active ions when the diffusion current is half of the total current if diffusion current is  $I_d$ . At  $E_{1/2}$  diffusion current is half.  $E_{1/2}$  is the characteristic feature of the element and thus it gives the qualitative analysis, knowing the value of  $E_{1/2}$  one can predict the element present in the solution. In the usual current-voltage polarogram the total  $I_d$  current is given by the difference in height of plateau and base line current. By the convection at cathode reduction of oxidant (active ion  $Mn^{+}$ ) and is taken as the positive value while for the anode it is negative. Before the start of the experiment the concentration of active ions in the bulk as well as near dme surface is same. Sometimes when the voltage is increased decomposition of active ion or Ox this reduced component moves in the bulk of solution.<sup>20</sup>  $Ox + ne \rightarrow Red$  Since the redox phenomenon is taking place in polarography. So Nernst equation is helpful in determining the potential and current of the redox system.

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$

R = gas constant a = activity F = Faradays constant n = no. of electrons involved during the redox When the oxidant is reduced the other remaining active ions in the bulk will again diffuse to be discharged. Under such conditions current (I) at any point can be described on the basis of kinetics.<sup>21</sup>

#### IV. CONCLUSIONS

Polarographic analyses can be used directly for the determination of any substance solid, liquid, or gaseous, organic or inorganic, ionic or molecular that can be reduced or oxidized at dropping mercury electrode. One of the most important advantages of polarography is the determination of two or more substances by obtaining a single current-potential curve. In addition to analytical uses polarography is one of the most fruitful techniques of research in physical, inorganic and organic chemistry.<sup>22</sup> This technique is spreading more widely in subsidiary fields like biochemistry, pharmaceutical chemistry, environmental chemistry and others. It is that branch of Voltammetry in which changes in current, resulting from the electrolysis of the solution under study are investigated using a renewable mercury droplet as the indicator electrode (cathode). The anode of the electrolytic cell called the reference electrode consists of either a mercury pool at the bottom of the cell or a calomel electrode. The electrochemical technique Polarography used in analytical chemistry, involves measurements of current-voltage curves, obtained when voltage is applied to electrodes immersed in the solution being investigated. One of the electrodes is an indicator electrode. It is a dropping mercury electrode, consisting of a mercury drop hanging at the orifice of a fine bore glass capillary.<sup>22</sup>

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