Electrochemical Investigation of Complexation and Speciation of Zinc with 1,10-Phenanthroline in Aqueous Solution using Mercury Film Coated Glassy Carbon Electrode

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Abstract:- Electrochemical investigation of complexation and speciation of zinc with 1,10-Phenanthroline (phen) in aqueous solution have been performed by an electrochemical technique, DPASV, using Mercury Film Coated Glassy Carbon Electrode (MFGCE). The work was carried out at constant pH and ionic strength. The overall formation constants of different complexes of zinc with phen were measured by applying Leden, DeFord and Hume model. It was found that three (1:1, 1:2 & 1:3; metal:ligand) complexes were formed with phen under the experimental conditions used in this work. The overall formation constant of complexes, $\beta_{Zn(phen)n}$ which can be defined as $\beta_{Zn(Phen)n} = [Zn(Phen)_n]/[Zn^{2+}][Phen]^n$ [where, 'Phen' is the complexing ligand and 'n' is an integer]. The values of the formation constants were found to be $10^{6.66}$, $10^{12.30}$ and $10^{17.44}$ for Zn(Phen), $Zn(Phen)_2$ and $Zn(Phen)_3$, respectively (for simplicity charges of the complexes were omitted). Using the values of formation constants of metal ligand complexes and the hydrolysis constant of zinc, the % of all species were computed. Finally it is concluded that electrochemical technique, specially DPASV is a simple and powerful tool to investigate the metal organic interaction in aqueous solution. Thin mercury film coated glassy carbon electrode acts as an ultra-microelectrode which is more sensitive than any other hanging mercury or dropping mercury electrode.

Keywords:- *DPASV, Complexation, Speciation, Mercury Film Coated Glassy Carbon Electrode.*

I. INTRODUCTION

Zinc ion plays an important role in biological system. It exists in the active sites of many enzymes as structural ions and regulates the catalytic function of enzymes. It is an extraordinary important trace metal for well-functioning immune system in human health[1]. Only a trace quantity of zinc plays an important role in biological process in human body[2].

The interaction of zinc ion with organic ligand having N, O or S donor atoms plays a significant importance in the biological system as well as coordination chemistry of zinc. The organic ligand, 1,10-Phenanthroline (phen) is a typical N-containing heterocyclic compound shown in Figure-1. It acts as a classical bi-dentate ligand for many transition metals in coordination chemistry[3-5]. A number of investigations have done on phen and its derivatives highlighted on their catalytic and biological activities as well as their supramolecular chemistry[6-9]. In biological system, phen acts as an inhibitor of metallopeptidases, especially carboxypeptidase A[10]. It has much affinity towards zinc metallopeptidases and much lower affinity for calcium [11].

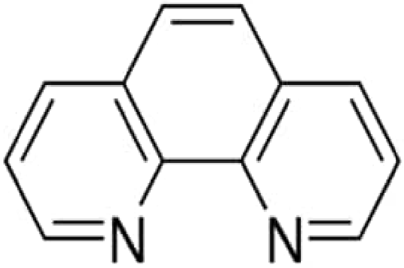

Fig. 1: Structure of 1,10-Phenanthroline (phen)

Since both zinc and phen are important in biological system. Hence it is necessary to know the interaction of zinc ion with 1,10-Phenanthroline (phen) at low concentration. The main objective of this investigation is to know the interaction between zinc ion with organic ligand like phen and determine the stability constants or formation constant of various complexes in aqueous solution. The stability constants of zinc complexes with 1,10-phenanthroline are necessary to calculate different chemical species exist in aqueous system at low concentration.

In the present research project, electro-analytical technique has been used to study the complexion and speciation of zinc ion with organic ligand. Among the electro-analytical techniques available, differential pulse anodic stripping voltammetry (DPASV) is a powerful technique to study the speciation of zinc with selected organic ligand in aqueous solution at ppb level. The technique has been used for qualitative and quantitative applications in analytical chemistry since its invention. The development of new method has expanded its utility to study the stability constant of metal complexes with selected organic ligands. This method is attractive in analytical chemistry owing to its high precision and accuracy at low concentration. Extensive works have been done in our laboratory to investigate the interaction between various organic ligands and metal ions[12-14]. DPASV is suitable to investigate the physicochemical behavior of metal ion at low concentration in aquatic environment.

The proposed electrochemical investigation was performed at ionic strength, $I = 0.1$ mol dm^{-3} (99.9% $NaNO_3$) at ambient temperature (30 °C). The solution pH was 9.10 and it was kept constant by the addition of borate buffer. Leden-DeFord-Hume model was applied to calculate the stability constants of zinc complexes with phen using the difference of peak potential between free and complexed metal ions and their diffusion currents.

II. MATERIALS AND METHODS

A. Reagents:

To prepare a mercury film, 0.5 M mercury(II) stock solution was prepared by dissolving required amounts of $HgCl_2$ (99.5%, Merck Germany) in 0.1M HCl (37%, Merck, Germany). A 100 µg/mL stock solution of zinc (Zn) was prepared weekly from 1000µg/mL Zn standard solution (Sigma-Aldrich) for atomic absorption spectrometry (AAS) in 0.1 M HNO_3 (65%, Merck, Germany). A 0.01 M stock solution of 1,10-phenanthroline (99.0%, Sigma-Aldrich) was prepared by deionized water which was ultra-filtered through 0.45 µm membrane filter to remove any particle before use. To maintain ionic strength of the solution, $NaNO_3$ (99.99%, Merck, Germany) was used. All the chemicals were used as it is without any further purification. Other necessary standard solutions were prepared by dilution of the stock solutions.

B. Equipments:

The major instrumental analysis for complexation was carried out by HQ-2040, computerized electrochemical analyzer (AA, USA). It was connected with computer controlled electrochemical cell and a magnetic stirrer. The electrochemical cell was assembled with three electrodes: (i) working electrode (mercury film coated glassy carbon electrode), (ii) Ag/AgCl. Sat KCl reference electrode and (iii) Pt wire counter electrode. The digital pH meter (JENWAY 3505) was used to measure solution pH.

C. Preparation of mercury film:

A thin mercury film (TMF) was prepared on commercially available glassy carbon electrode (GCE) which was polished with fine alumina and washed with a plenty of water before use. The film was prepared in 10 mL of 0.001 M $HgCl_2$ solution which was purged with 99.9% pure N_2 for 10 minutes to remove oxygen from mercury solution before use. The electrochemical cell was coupled with the analyzer and carefully removed bubbles from the electrode surface if necessary. The mercury (Hg) film was prepared on the surface of the GCE by the deposition of mercury at –400 mV for 6 minutes using DPV program.

D. DPASV measurements:

At first, 10.0 mL of aqueous solution which was buffered at pH = 9.10 ± 0.10 and I = 0.10 ($NaNO_3$) at ambient temperature was poured into the cell. Then oxygen was removed from this solution by purging it with 99.9% pure N_2. The blank voltammogram was recorded using the conditions as follows:

Method: DPASV; potential range: -1250 mV to -500 mV; gain (1-20): 10; time: 120 s; delay: 30 s.

To check linearity of the calibration curve of the metal ion, several voltammograms were recorded after successive addition of standard metal solution maintaining similar experimental conditions. A linear calibration for zinc ion was obtained in the range 0-100 µg/L of zinc in aqueous solution.

The formation of zinc complexes with phen has been investigated using the 3.06 µM aqueous solution of zinc (I=0.10M $NaNO_3$ and pH = 9.10). The voltammogram of free Zn(II) ion was recorded after removal of oxygen from aqueous solution. Precision of the method was checked by triplicate measurements. When the precision of the measurements is quite good then a small amount of phen was added to the aqueous solution of zinc. The equilibrium time was set for 60 seconds. The voltammogram was recorded again using the same experimental parameters. The peak current of the voltammogram was reduced and potential was shifted due to the addition of phen. The successive addition of phen into the aqueous solution of zinc was continued until no change was observed in the voltammogram.

E. Theoretical treatment:

The free zinc ion forms stepwise complexes with phen as follows:

$$M^{n+} \overset{L}{\rightleftharpoons} ML^{n+} \overset{L}{\rightleftharpoons} ML_2^{n+} \;.....\; ML_j^{n+} \qquad (1)$$

Where L represents the free form of selected organic ligand 1,10-phenanthroline (phen) and M represents zinc metal. The peak current and peak potential obtained by increasing phen concentration were used to determine the formation constant of zinc complexes in solution using Leden-DeFord-Hume model [15-16] as follows:

$$F_0 = \exp\left(-\frac{nF}{RT}\Delta E + 1n\frac{I_{free}}{I_{complexed}}\right) = 1 + \sum_{i=1}^{N}\beta_i[L]^i \qquad (2)$$

Where, F_0 is the zero-order Leden function, △E = $(E)_s$ - $(E)_c$, is the change in peak potential in free metal ion, $(E)_s$ and complexed metal ion, $(E)_c$; n is the number of electron, F is the Faraday constant, R is gas constant, I_{free} represents the peak current of uncomplexed metal ion, $I_{complexed}$ is the peak current of complexed metal ion and [L] is the free ligand concentration. The value of [L] was computed by the following equation (equation 3) using the pk values (protonation constants) of phen reported in the literature [17]. Thus,

$$[L] = C_L(1 + [H^+]K_1 + [H^+]^2K_1K_2)^{-1} \qquad (3)$$

Where, C_L = total concentration of phen and K_1 is the first protonation constant and K_2 is the second protonation constants of phen.

From equation 2, it is shown that the F_0 can be evaluated from the variation of peak currents as well as peak potential for any values of [L] in the experiment. In this study, the overall formation constants (β_i) are evaluated by conventional polynomial fitting program on Equation 2.

III. RESULTS AND DISCUSSION

The interaction of zinc with phen has been investigated by DPASV using TMFGCE. Experimental parameters i.e. pH, deposition time, potential range, etc. were optimized at constant ionic strength (I = 0.1M) for the complexation of zinc with selected organic ligand (phen). Under optimum conditions, peak current of zinc is directly related with [Zn(II)] in aqueous solution shown in Figure 2. The linear plot of peak current vs. [Zn(II)] indicates that reduction of zinc to Zn(Hg) is diffusion controlled.

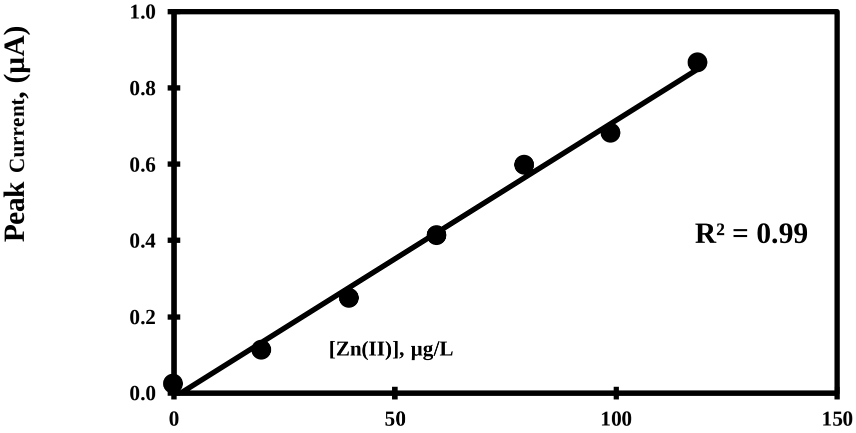

Fig. 2: A linear plot of peak current vs. [Zn(II)] in aqueous solution

A voltammogram of free (uncomplexed) zinc ion and its change with [phen] is shown in Figure 3. The voltammogram of Zn(II) shows that zinc ion appeared at -1090 mV. The current of uncomplexed zinc ion gradually decreased with increase of [phen] indicating the formation of Zn-phen complexes shown in Figures 4. The complexes formed in this case are electro-inactive in nature.

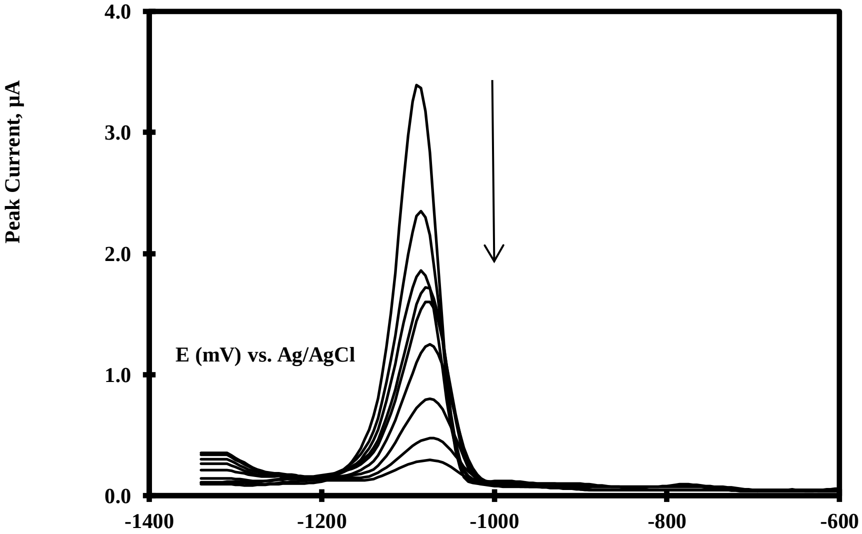

Fig. 3: Voltammograms of zinc and zinc-phen complexes when [Zn(II)] = 3.06×10^{-6} M, $[\text{phen}]_{\text{total}}$ = 0.00 to 8.10×10^{-6} M (top to bottom trace) sequentially added to the solution at pH = 9.1 ± 0.1 and I = 0.1 M ($NaNO_3$

In the present DPASV technique, the reduction of zinc ion on MFE to form zinc amalgam, Zn(Hg) and the process is reversible. The linear relationship between potential (E) and log $i/(i_d\text{-}i)$ (Figure-4) confirming the reversible process under present experimental conditions.

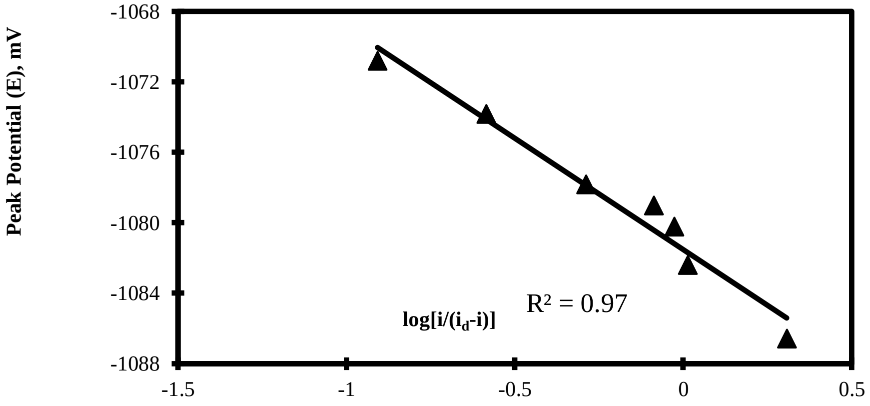

Fig. 4: Plot of peak potential (E) vs. log[i/(i_d-i)]

Again, a smooth curve obtained by plotting potential (E) vs. log$[phen]_{total}$ for Zn(II) ion (Figure 5) indicating more than one complexes are formed.

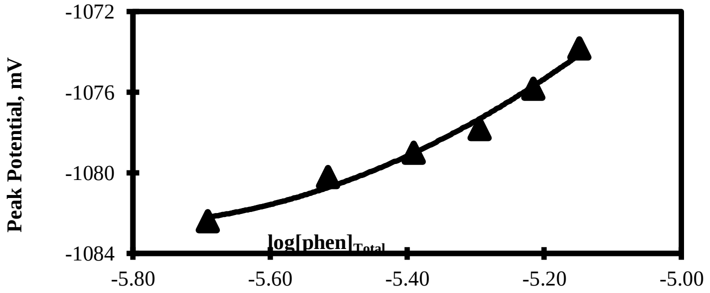

Fig. 5: Plot of peak potential (E) vs. log $[phen]_{total}$

The value of F_0 was plotted against $[phen]_{free}$ and obtained a third order polynomial curve shown in Figure 6 indicating three complexes are formed with zinc ion. The value of the formation constant of three complexes, Zn(phen), $Zn(phen)_2$, and $Zn(phen)_3$ are calculated using polynomial fitting program.

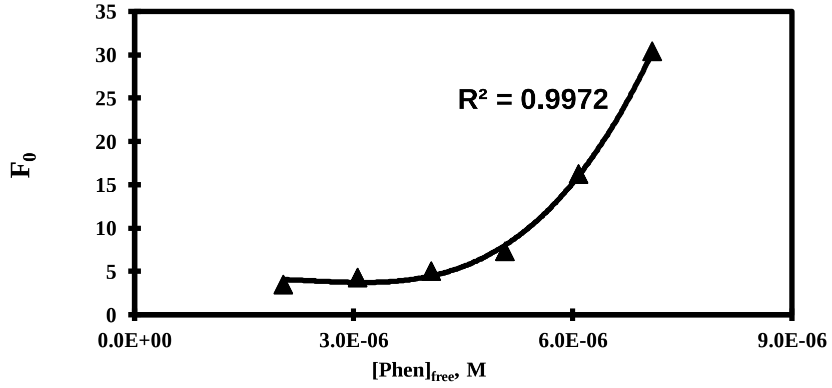

Fig. 6: The plot of F_0 vs. $[phen]_{free}$

In the present experiment, selected organic ligand (L) can be monoprotonated (HL) or diprotonated (H_2L) as shown in Figure 7 depending on pH and the protonation constant.

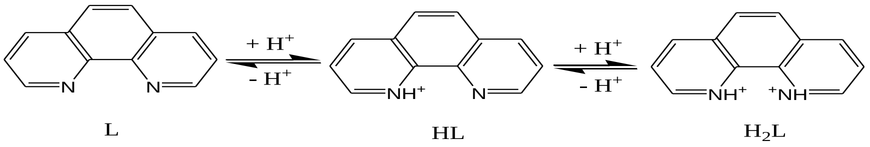

Fig. 7: Protonation of 1,10-Phenanthroline (phen)

The values of the protonation constants of phen were found in the literature as: $K_1 = [HL][H^+]^{-1}[L]^{-1} = 10^{4.93}$ and $K_2 = [H_2L][HL]^{-1}[H^+]^{-1} = 10^{1.5}$ [15]; where K_1 and K_2 are the 1st and 2nd protonation constant. Using these values, % of each species of phen was calculated and plotted in Figure 8. The result revealed that 99.99% of phen exists as free form at pH 9.10.

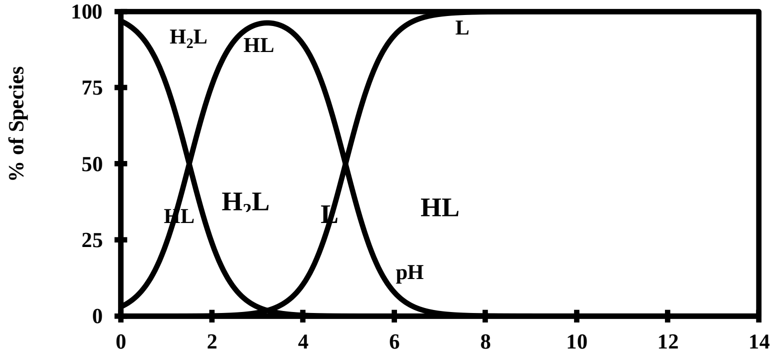

Fig. 8: Species distribution of 1,10-phenanthroline (phen) as a function of pH.

Thus it is confirmed that zinc forms three complexes with free phen (not bound with proton) and their ratio was 1:1, 1:2 and 1:3 (Zn: phen). The logarithmic values of overall formation constant (stability constant) of zinc complexes with phen are found to be 6.65, 12.31 and 17.44 for Zn(phen), $Zn(phen)_2$ and $Zn(phen)_3$, respectively. The values of the overall formation constant are very similar to the literature values published before as shown in the Table 1.

Table 1: Comparison of the overall stability constants of zinc complexes with 1,10-phenanthroline (phen) with reported values

Metal Complexes	**Ionic strength**	**Temperature, °C**	**logβ1**	**log β2**	**log β3**	**References**
	0.10	30	6.66	12.30	17.44	This work
Zinc complexes	0.10	25	6.40	12.20	17.10	[17]
	0.00	25	6.20	12. 10	17.30	[17]

Zinc may hydrolysed at pH 9.1 in aqueous solution. Using hydrolysis constants of zinc and formation constants of zinc phen complexes, the % of all species of zinc were calculated. It was found that 19.0% aqua Zn2+, 25.1% ZnOH+, 52.4% Zn(OH)2 and 3.5% Zn(OH)3- exist at pH 9.1 before complexation of zinc with phen. After the addition of phen, zinc forms three complexes and their overall formation constants were calculated as described above. Among three complexes, Zn(phen)3 is the most stable complex due to its octahedral structure.

The % of all possible species of zinc present under experimental conditions are calculated and shown in Figure 9.

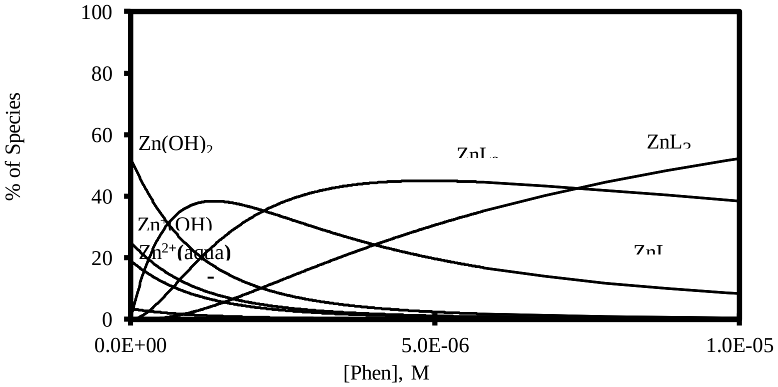

Fig. 9: Speciation of zinc as a function of [phen] at pH 9.1

IV. CONCLUSION

The electrochemical investigation of complexation and speciation of zinc with phen has been carried out in aqueous solution by DPASV using mercury film electrode. The results revealed that zinc forms three complexes with phen depending on its concentration. The formation constants of zinc-phen complexes are very much similar to the reported values indicating the suitability of the method. Mercury film coated glassy carbon electrode acts as microelectrode and its sensitivity is higher than conventional mercury electrode in polarography. Thus the method is suitable for the study of metal complexation at ppb level and is useful for environmental and biological systems.

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