Differential Pulse Anodic Stripping Voltammetric Study of Zinc-Ethylenediamine Complex

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Abstract

Differential pulse anodic stripping voltammetric study of zinc-ethylenediamine complex has been investigated using thin mercury film coated glassy carbon electrode at 30°C. The overall work was carried out at constant ionic strength (I = 0.20 mol dm^{-3}) and pH (9.10±0.10). The electrode processes were found to be reversible and diffusion controlled. The results revealed that zinc forms three (1:1, 1:2 and 1:3- metal: ligand) complexes with ethylenediamine (en). The values of stability constant of zinc complexes were found to be $10^{6.03}$, $10^{10.16}$ and $10^{13.98}$ for ZnL, ZnL$_2$ and ZnL$_3$, respectively (the overall charges were omitted for simplicity). The percentage of all possible zinc species were calculated using the stability constant of zinc complexes and hydrolysis constant of zinc under present experimental conditions.

Keywords: DPASV, ethylenediamine, zinc, stability constant.

Introduction

Zinc is the most important essential trace element. It is known that there are about 300 enzymes in which zinc present in their active sites and plays an important role as structural ions. Zinc presents in all body tissues and fluids. It is necessary to maintain normal physiological and biochemical functions of cell. It is present in metalloenzyme superoxide dismutase, alkaline phosphatase, alcohol dehydrogenase, and DNA and RNA polymerases. Zinc ion strongly interacts with nitrogen and oxygen and forms complexes with appropriate ligands. Some of these complexes exhibit antifungal activity[1]. Some zinc containing macrocyclic compounds are very important as lipophilic carriers for anti-HIV substances. Free zinc ion in solution is highly toxic to plants, invertebrates and even vertebrate fish[2]. Although zinc is essential for human body, but excessive amount of zinc is harmful because it can suppress copper and iron absorption. Thus removal of zinc is also an interesting subject of research[3].

Zinc ion can easily interact with nitrogen containing ligand, such as ethylenediamine. In this article, we have demonstrated the formation of various complexes of zinc-ethylenediamine by differential pulse anodic stripping voltammetry (DPASV) due to its reproducibility and reliability at very low concentration[4-6]. Other methods are also available for the evaluation of complexing properties of metal ions in aqueous solution. For example, spectrophotometry[7], potentiometry[8], ion-selective electrodes[9-10], etc. However, these methods are not suitable for low concentration of metal ions (ppb or sub ppb level) in aqueous solution. Recently differential pulse anodic stripping voltammetry has been extensively used in our laboratory to determine the stability constant of the complex between metal ion at ppb level and organic ligands in aqueous solution[6,11,12].

Material and Methods

Equipment and Reagents: The differential pulse anodic stripping voltammetic measurements were performed by HQ-2040 electrochemical analyzer, Advanced Analytics, USA. The analyzer was coupled with computer controlled magnetic stirrer and electrochemical cell consisting of three electrodes: 3mm glassy carbon electrode, Ag/AgCl.KCl reference electrode and Pt counter electrode. The stock solution of mercury(II) chloride (HgCl$_2$) was prepared by dissolving required amounts of HgCl$_2$ into 0.1mol dm^{-3} HCl solution. This solution was used to prepare the mercury film on glassy carbon electrode. A 1000 ppm (1000 µg/mL) stock solution of Zn(II) was prepared by dissolving required amounts of ZnO in 0.1 mol dm^{-3} HNO$_3$ solution. Another stock solution of 0.01 mol dm^{-3} ethylenediamine was prepared by distilled and deionized water, which was filtered with 0.45 µm membrane filter before the solution was prepared. The ionic strength of the solution was maintained constant using 0.2 mol dm^{-3} NaNO$_3$ (99.99%) solution. The pH was kept constant at 9.10±0.10 by the addition of borate buffer. The required standard solutions were prepared once a week by dilution of the stock solutions. All stock solutions were stored in the refrigerator at 4°C.

Preparation of working electrode: In the present investigation, the thin mercury film coated glassy carbon electrode was used as working electrode. The thin mercury film was prepared on properly polished and washed 3 mm glassy carbon electrode in 10 mL of 1.0×10^{-3} mol dm^{-3} mercury (II) solution. The solution was purged with nitrogen for 10 minutes to remove dissolved oxygen. Then the electrodes were connected to the analyzer. Any bubbles adhering to the electrodes were removed by tapping them off. The mercury film deposition was done at -400 mV for 6 min by applying differential pulse voltammetry program as described earlier[6,11,12].

Complexation of Zn(II) with ethylenediamine (en): To measure the complexation of Zn(II) with ethylenediamine, at first the electrochemical cell was assembled with 5 mL of borate buffer having pH 9.10±0.10, 1 mL of 2 mol dm^{-3} NaNO$_3$ and 4 mL of distilled and deionized water. Then, the solution was purged with pure nitrogen for 10 minutes. The background voltammogram was obtained using the following run conditions for differential pulse anodic stripping voltammetry (DPASV):

Mode: Stripping; initial potential: 1250 mV; final potential: 500 mV; gain (1-20): 10; deposition time: 120s; quite time delay: 30s.

The voltammograms of Zn (II) were obtained after successive addition of 20 ppb (20 µg/L) of Zn (II) in the cell under the above experimental conditions. A linear calibration was obtained. To study the complexation capability of Zn (II) with ethylenedimaine, in aliquot of 10 mL solution of 300 ppb (4.59 µM) Zn(II) was prepared in borate buffer having pH 9.10±0.10 and ionic strength, I = 0.2 mol dm^{-3} (NaNO$_3$). The solution was purged with nitrogen gas for 10 minutes to remove dissolved oxygen. The voltammogram of free Zn(II) was recorded using the same run conditions for DPASV as described above. The process was repeated for 3 times to check the reproducibility. An aliquot of 10 µL of 0.1 mol dm^{-3} ethylenediamine was added to the cell and the solution was stirred for 60 seconds. The DPASV run was performed again under the same experimental conditions. The peak potential shifted to more negative value and peak height reduced due to the addition of ethylenediamine. The process was continued after successive addition of ethylenediamine in it, until constant peak height was obtained.

Theory for data treatment: In aqueous solution, the formation of a complex between metal ion, M^{n+} and organic ligand, L give the metal complex ML$_1$ (the overall charge of the complex is omitted for simplicity). The reaction occurs in several steps as follows:

$$M^{n+} \rightleftharpoons ML \rightleftharpoons ML_2 \rightleftharpoons .... \rightleftharpoons ML_i \qquad (1)$$
$$\downarrow E^{\circ}, n^{-}$$
$$M(Hg)$$
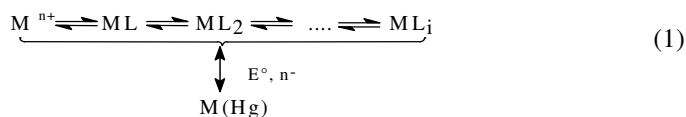
Where, i represents the number of ligand and the metal ion can be reversibly reduced on a mercury film electrode.

The differential pulse anodic stripping voltametric measurement of peak current and peak potential induced by increasing ligand concentration allows the determination of overall conditional stability constant of complexes in solution. The stability constant of various species of zinc(II) with ethylenediamine can be calculated according to the model of DeFord and Hume[13] on the basis of the change in peak potential with ligand concentration. According to their model, the overall conditional stability constant of individual complexes containing 1,2,….,i number of ligands are related to the formation function as follows:

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

Where ΔE is the change in peak portential between simple and complexed metal ions, I$_{free}$ and I$_{complexed}$ are the peak currents of simple and complexed metal ions, respectively, n = number of electrons involved in the redox reaction, F = Faraday constant, R = gas constant, [L] = free ligand concentration (not bound with proton) and i = 1, 2, …, N. The successive formation constants (β_i) are evaluated by polynomial fitting of the zero-order Leden Function F$_0$. The values of F$_0$ can be calculated from the experimental change in peak potential and peak currents for each values of [L] in the voltammetric titration using equation 2. The free ligand concentrations, [L] are computed from the protonation constants at experimental pH as follows.

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

Where, C$_L$ represents the total concentration of ligand and K_1 and K_2 are the protonation constants of ethylenediamine. The overall conditional stability constant of each species with respect to labile metal ion is determined using nonlinear fitting program on equation 2. The overall stability constant with respect to free metal ion is obtained by considering the inorganic side reaction coefficient of zine (α_{zn}) at pH 9.10±0.10.

Results and Discussion

The complexation of Zn(II) with ethylenediamine (EN) were studied by DPASV at constant ionic strength (I = 0.20) at pH 9.1 ± 0.1. From the effect of pH, deposition time and potential range, the optimum parameters were selected for Zn(II) complexation. Under the optimum parameters, a calibration curve was constructed. The calibration curve *i.e.* the plot of diffusion current against zinc concentration was found to be linear shown in figure 1, indicating the reduction of Zn to Zn(Hg) is diffusion controlled.

A typical change of voltammograms with ethylenediamine (EN) concentration is shown in figure 2. The peak of the unchelated Zn(II) appeared at − 1.08 V, under the present experimental conditions in absence of ethylenediamine. The diffusion current (I$_d$) of Zn(II) ion gradually decreased by the addition of ethylenediamine due to the formation of kinetically inert complexes shown in figure 2. The term, 'inert complex' indicates the metal-ligand complex in which kinetics of dissociation is very slow compared to the time of the DPASV measurements. The plot of peak potential (E) vs log (i/i$_d$-i) was found to be linear shown in the figure 3, indicating the reduction of Zn to Zn(Hg) on the mercury film electrode is a reversible process. The plot of peak potential (E) vs. log[EN]$_{free}$ for Zn(II) found to be a smooth curve shown in figure 4 indicating the formation of two or more complexes which are in equilibrium with each other. The zero order Leden function F$_0$ was

calculated according to the DeFord and Hume method as described above. The plot of F_0 vs. $[EN]_{free}$ shown in figure 5, gives the values of conditional stability constants of individual complexes.
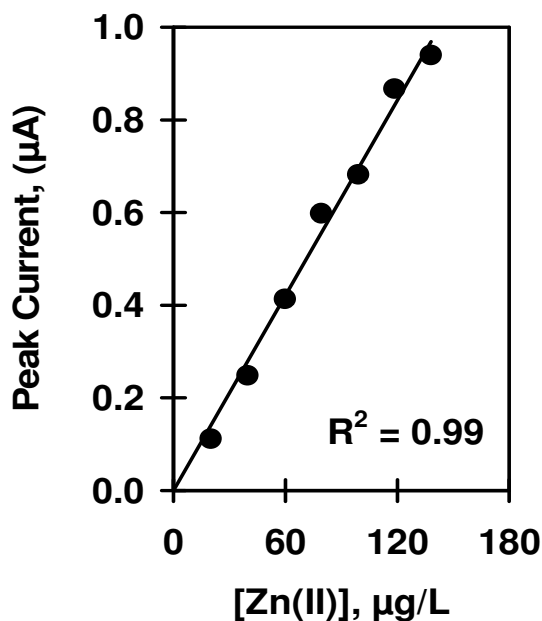

Figure-1
Calibration plot for the quantification of zinc(II) by DPASV using mercury thin film coated glassy carbon electrode in aqueous solution at pH 9.10 ± 0.10 and I = 0.20 mol dm^{-3}
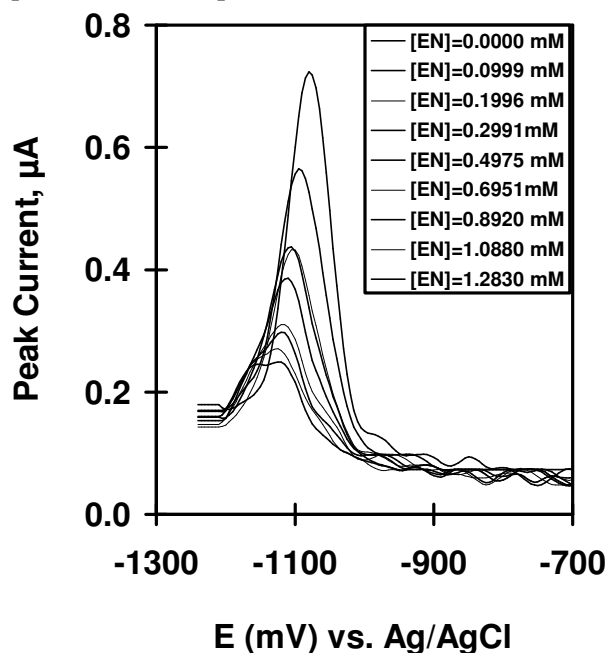

Figure-2
Voltammograms of zinc after successive addition of varying concentration of ethylenediamine (EN); [Zn (II) = 4.59 µM, [EN] = 0.00 to 1.28 mM, pH = 9.10 ± 0.1 and I = 0.20 mol dm^{-3} (NaNO$_3$)
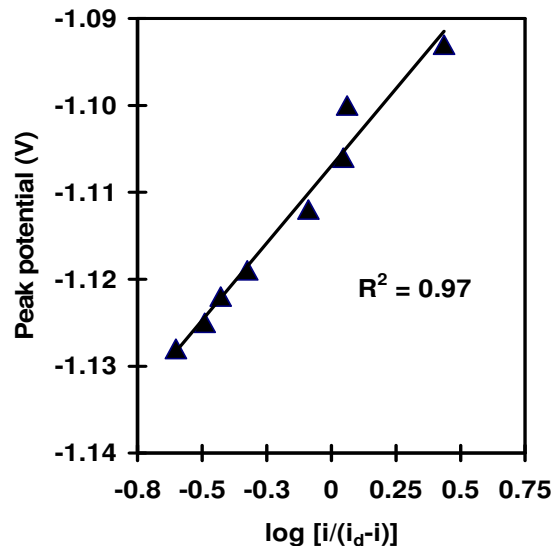

Figure-3
A plot of peak potential vs. log i/(i$_d$-i) for zinc-ethylenediamine complexes when [Zn (II)] = 4.59 µM, [EN] = 0.00 to 1.28 mM, pH = 9.10 ± 0.1 and I = 0.20 mol dm^{-3} (NaNO$_3$)
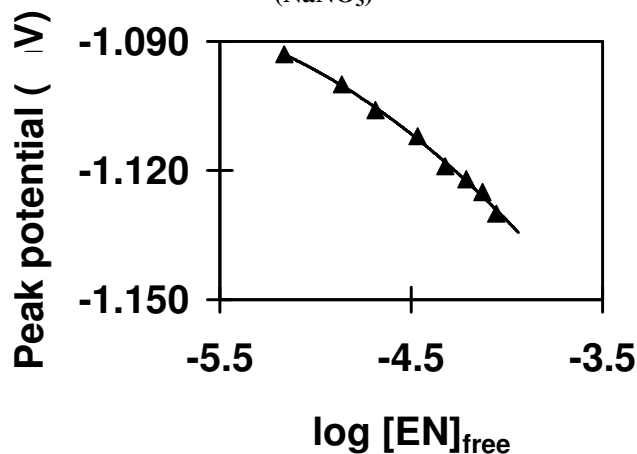

Figure-4
Plot of peak potential vs. log [EN]$_{free}$; [Zn (II)] = 4.59 µM, pH = 9.10 ± 0.1 and I = 0.20 mol dm^{-3} (NaNO$_3$)

The formation of three metal-ligand complexes, ML_1, ML_2 and ML_3 (where M represents zinc and L represents ethylenediamine) are found under the experimental conditions. In the present experiment, DPASV technique detects the labile species which consist of free hydrated form (*i. e.* aqua metal ion, M^{2+}) and hydroxo complexes (M^+OH, $M(OH)_2$ and $M(OH)_3^-$). So, it is necessary to consider the side reaction of Zn^{2+} with OH^- at experimental pH. The actual value of the overall stability constant is obtained by considering the inorganic side reaction coefficient of zinc (α_{zn}) at pH 9.10 and neglecting the hydrolyzed form. The value of α_{zn} can be computed by the following expression.

$$\alpha_{zn} = 1 + \beta_1^{OH} [OH^-] + \beta_2^{OH} [OH^-]^2 + \beta_3^{OH} [OH^-]^3 \qquad (4)$$
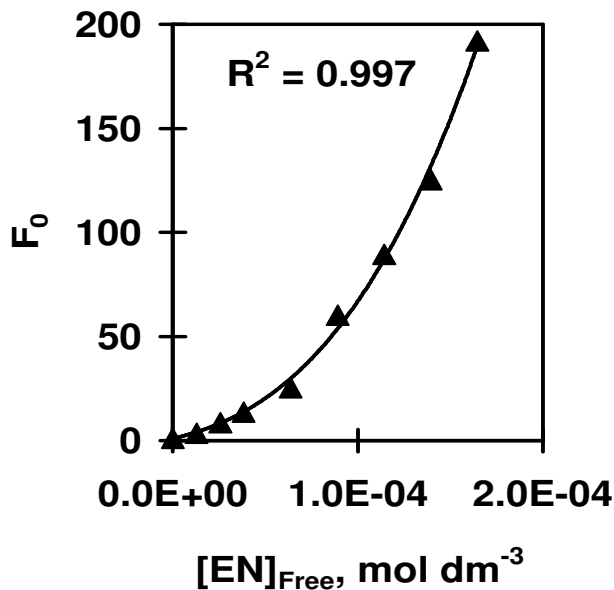
Figure-5
The variation of F_0 as a function of concentration of free ethylenediamine (EN); [Zn (II)] = 4.59 µM, pH = 9.10 ± 0.1 and I = 0.20 mol dm^{-3} (NaNO$_3$)

Where, β_1^{OH}, …β_3^{OH} are the overall hydrolysis constants of zinc. Using the hydrolysis constants of zinc, the value of the side reaction coefficient, α_{zn} was found to be 5.25 at pH 9.10.

Considering the value of α_{zn}, the stability constants were calculated and listed in table 1. The large values of overall stability constants indicate that the complexes of zinc (II) with ethylenediamine in alkaline pH are highly stable. According to the hydrolysis constants of zinc, mone-, di- and tri- hydroxyl species are possible to be formed. But in the present experimental conditions, 25.09% ZnOH$^+$, 52.42% Zn(OH)$_2$ and 3.46% Zn(OH)$_3^-$ exist at pH 9.1. The remaining part exists as aqua zinc ion (Zn^{2+}) in absence of ligand.

Ethylenediamine (EN) can exist in three different forms in solution: the monoprotonated (HL), diprotonated (H$_2$L) and free form (L) depending on pH of the solution. Since the protonation constants of ethylenediamine[14], K_1 = [HL][H$^+$]$^{-1}$[L]$^{-1}$= $10^{9.928}$ and K_2 = [H$_2$L][HL]$^{-1}$[H]$^{-1}$= $10^{6.848}$ only 12.87% free ethylenediamine is possible to exist at pH 9.10. Distribution of ethylenediamine as a function of pH in aqueous media is shown in figure 6.
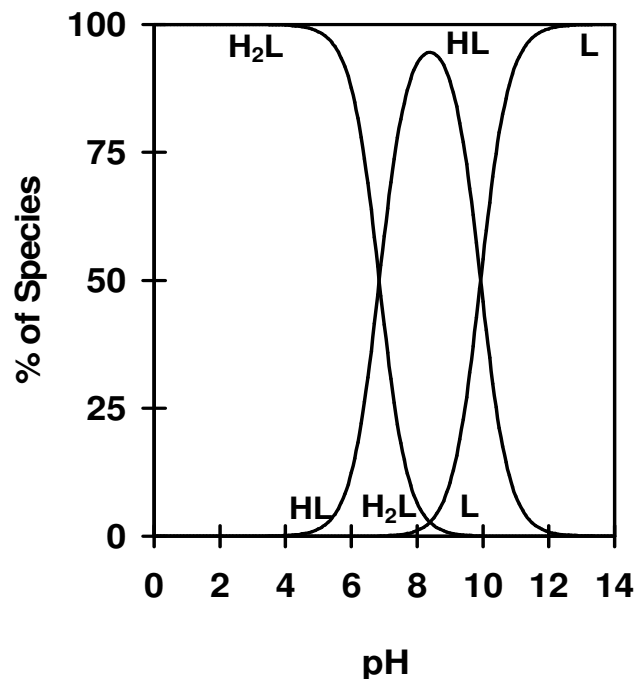

Figure-6
Species distribution of ethylenediamine (EN) as a function of pH

From the literature, it is known that zinc forms 1:1, 1:2 and 1:3 (metal: ligand) complexes with free form of ethylenediamine (L) whose stability constants have been reported[14]. In the present investigation, the logarithmic values of overall stability constant of zinc complexes with ethylenediamine are found to be 6.03, 10.16 and 13.98 for ZnL, ZnL$_2$ and ZnL$_3$, respectively. These values are very similar to the values reported before as shown in the table 1.

In this study, trace amount (300 ppb or 4.59 µM) of zinc was investigated in which free and hydrolysed forms are possible to exist in absence of ligand and hydrolysed and metal-ligand complexes are possible to exist in presence of ligand at pH 9.10. The percentage of all chemical species are caluculated and shown in figure 7 for zinc-ethylenediamine complexes. The species distribution diagram shown in figure 7 is of great help in the interpretation of voltammetric results.

Table-1
Stability constants of zinc complexes with ethylenediamine

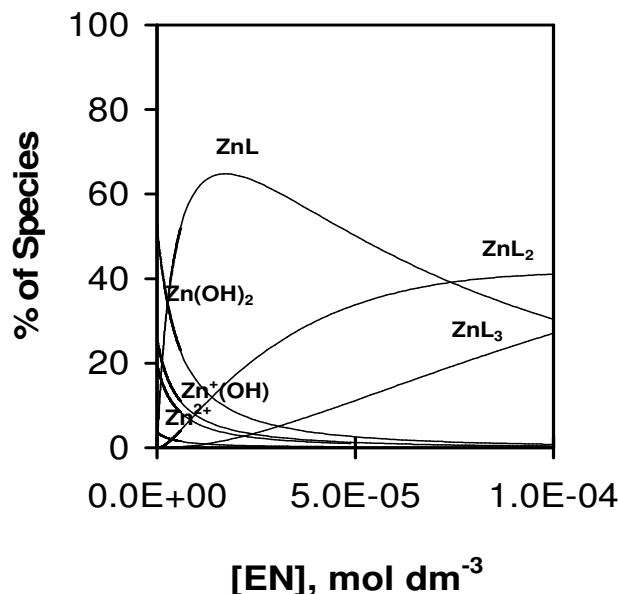| Ionic strength, mol dm^{-3}	Temperature, °C	logβ_1	log β_2	log β_3	References
0.20	30	6.03	10.16	13.98	This work
0.10	25	5.70	10.60	12.60	14
0.00	25	5.66	10.60	13.90	14

Figure-7
Species distribution of zinc as a function of concentration of ethylenediamine (EN) at pH 9.10 ± 0.1

Conclusion

Zinc-ethylenediamine complexes were investigated by DPASV. It was found that trace amount (4.59 μM) of zinc is able to form 1:1, 1:2 and 1:3 (metal: ligand) complexes with ethylenediamine (ligand) depending on pH as well as concentration of ligand. The formation constants of zinc complexes obtained in this study are in good agreement with those reported before[14]. In absence of ligand, about 52.4% zinc exists as $Zn(OH)_2$ at pH 9.10, whereas, in presence of ethylenediamine it forms different complexes depending on ligand concentration. The large values of overall stability constant indicate that the complexes are highly stable. The percentage of all species of zinc was calculated. It was found that all species of zinc co-exist within ligand concentration up to 1×10^{-4} mol dm^{-3} under the present experimental condition. All experimental information indicates that DPASV may be a powerful tool in the study of metal organic interaction in aqueous system.

Acknowledgement

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