ELECTROCHEMICAL BEHAVIOUR OF THE Ni(II) AND Zn(II) COMPLEXES WITH A MACROCYCLIC DIIMINE CROWN ETHER: 2,3,11,12-DIBENZOL-5,9-DIAZA-4,9(10)-CISDIIMINO-1,13-DIOXACYCLOPENTADECANE

Selahattin Yılmaz[a], Ali Osman Solak[a]*, Zeynel Kılıç[a], Baki Erdoğan[b]

[a]Department of Chemistry, Faculty of Science, University of Ankara, Ankara (Türkiye)

[b]Department of Chemistry, Faculty of Arts and Science, Gazi University, Ankara (Türkiye)

Abstract

Ni(II) and Zn(II) complexes of a macrocyclic diimine crown ether, 2,3,11,12-dibenzo-5,9-diaza-4,9(10)-cisdiimino-1,13-dioxacyclopentadecane (O-en-N-tn), were prepared and their electrochemical behaviours were reported. Reduction of the complexes was studied in ethyl alcohol-water mixture (1:5 v/v) using sampled current polarographic, differential pulse polarographic, cyclic voltammetric, chronoamperometric and chronocoulometric techniques. A mechanism for the electrode reaction was proposed. Heterogeneous rate constant and the transfer coefficient of the electrode reaction were determined. Adsorptional characteristics of the complexes on mercury electrode were studied and adsorbed amounts of the complexes were found to be 10^{-11} mol/cm^2 and 10^{-12} mol/cm^2 order of magnitude in acidic and basic media respectively.

Keyword: Electrochemistry; Macrocyclic; Ni(II) and Zn(II) complexes; Diimine crown ether.

1. Introduction

The cyclic polyether crown type macromolecules form stable complexes with alkali and alkaline earth metal ions[1]. But this ligand type generally shows much less tendency to coordinate to transition metal ions[2]. The other category of macrocycle ligands containing heteroatoms such as nitrogen or sulfur form quite stable complexes

* To whom correspondence should be addressed..

with transition metal ions. Complexation ability of a macrocyclic ligand depends upon the kind of heteroatom. Such transition metal complexes of the macrocycles show special properties, which in some instances are related to those of the naturally occurring macrocyclic systems[2].

In the presence of macrocyclic crown ethers many ionic reagents are found to dissolve in solvents in which they would otherwise be insoluble[3, 4], and to exhibit enhanced anion activity. The range of synthetic application of ionic reagents is thereby extended, and this has been particularly apparent in the development of two phase reactions in which ion transfer is catalysed by crown ethers[5]. Their application to problems of ionic transports in biological systems[6], construction of ion sensitive electrodes[7], resolution of amino acids[8], or amines[9], interpretation of ion pair equilibria[10], and determination of free energies of transfer of anions[11] is further indication of their topical appeal.

It is not surprising, therefore, that during the past few years there has been a marked increase in the number of reports of effective application of macrocyclic crown ethers and their metal complexes.

Among of variety of physicochemical methods used for the study of cation-macrocycle interactions, voltammetric methods have shown their ability as a very useful means of studying the electrochemical behaviour of macrocyclic compounds and the stability and selectivity of their complexes with various cations in both aqueous and non-aqueous media. The electrochemistry of macrocyclic ligands and their complexes has been appeared in the literature mostly for crown ether type molecules. The electrochemical behavior of the crown ether dithio-carbamates and their complexes with Ni(II), Cu(II), Cr(III), Fe(II), Co(III) and Co(IV) were studied[12]. Because of the high selectivity of the macrocyclic ligands for the removal of the biologically important heavy metal ions, many appropriate binding sites and suitable cavity sizes have been designed to form selective inclusion complexes [13, 14].

In a previous publication we reported the synthesis and electrochemical behaviour of a macrocyclic diimine crown ether: 2,3,11,12 dibenzo-5,9-diaza-4,9(10)-cisdiimino-1,13-dioxacyclopentadecane(O-en-N-tn)[15]. In this paper, preparation of Ni(II) and Zn(II) complexes of the O-en-N-tn and their electrochemical behaviours are reported.
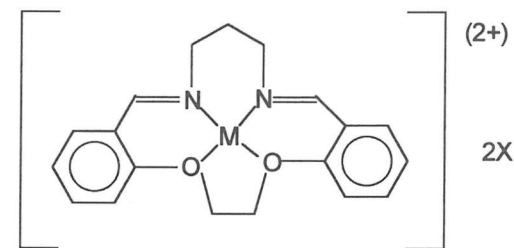
M: Ni^{2+} or Zn^{2+}

X$^-$: Cl$^-$

2. Experimental

The polarographic measurements were carried out with a BAS100B Electrochemical Analyzer equipped with a BAS 100B Cell Stand, a PAR 303A Static mercury drop electrode, a PAR Model 305 stirrer. Voltammograms were recorded on a Panasonic Model FPG-310 colour plotter. BAS 100B Electrochemical Analyser was connected to a computer and the data were processed with BAS100W.EXE program. A platinum wire as an auxiliary electrode and a Ag/AgCl/KCl(sat) electrode as a reference electrode were used. All solutions were dearated for 5-10 min. with pure nitrogen and an inert atmosphere was maintained over the solutions during the electrolysis. The pH values of the solutions were recorded by an ORION 720A pH-meter with a combined glass electrode and Ag/AgCl reference electrode. Nitrogen gas was deoxygenated by scrubbing through a solution of vanadous chloride, concentrated HCl and amalgamated zinc. In bulk electrolysis experiments, a mercury pool electrode with a surface area of 19.9 cm^2 was used. The solution was stirred with a magnetic stirrer during constant potential coulometric experiments.

O-en-N-tn was synthesized by the reactions of 1,2-bis(formylphenoxy)ethane and 1,3-diaminopropane. The ligand was purified by using column chromatography and crystallized from methanol. The structure of the resulting cyclic compound was enlightened by using UV, IR, ^{1}H-NMR, molecular weight determination and elemental analysis[16]. For the preparation of Ni(II) complex of O-en-N-tn, equimolar $NiCl_2 \cdot 6H_2O$ and O-en-N-tn solutions in methanol were mixed and boiled for about 20 minutes. After cooling, the green precipitate was filtered and crystallized from methanol[16]. Zn(II)-(O-en-N-tn) complex was prepared by the reaction of equimolar 1,2-bis(formylphenoxy)ethane, 1,3-diaminopropane and zinc chloride in methanol. After boiling the above mixture about 2 hours, the white precipitate of Zn(II)-(O-en-N-tn) complex was filtered and crystallized from methanol[16]. Acetic acid (BDH, analar), phosphoric acid (Merck), boric acid (Riedel), ammonium metavanadate (Merck), sodium hydroxide (Merck) were used without further purification. Water was distilled and deionised by ELGASTAT water purification system and was used for the preparation of solutions and solvents system with distilled ethyl alcohol. Stock solutions of nickel and zinc complexes of O-en-N-tn as 1×10^{-3} M were prepared in ethyl alcohol and diluted daily as required.

3. Results And Discussion

3.1. Characterization of the reduction processes of Ni(II) and Zn(II) complexes

The differential pulse polarographic curves for the solution of nickel and zinc complexes of O-en-N-tn at pH=2.66 are shown in Figure 1. Two peaks were observed, the first one belongs to the reduction of free O-en-N-tn ligand and the second one probably due to the reduction of free metal coming from the decomposition of the complex. For each complex solution, well-defined two electron waves were observed between pH 2-9 in ethanol/BR mixture of 1:5 v/v ratio. The potential of the peak observed in nickel complex solution is at -930 mV and that of zinc complex solution at − 1090 mV at pH of 2.66. The O-en-N-tn peaks appeared at about −200 mV and are also

shown in Figure 1. Since we have already reported the properties and electrochemical behaviour of the reduction peak of the uncomplexed O-en-N-tn[15], our concern here will be on the second peak.
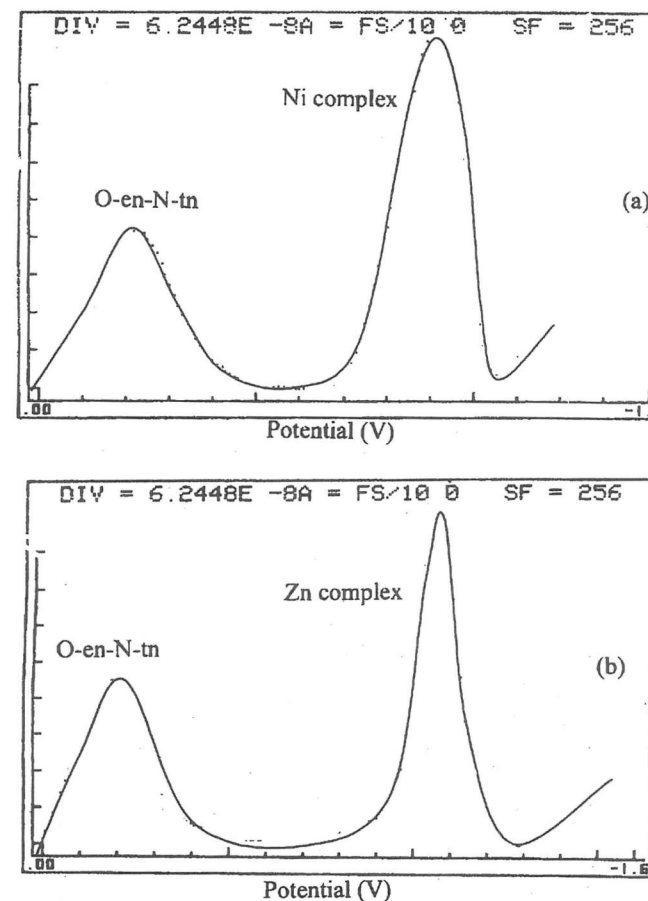

Fig. 1 - The differential pulse polarograms of the solution of nickel (a) and zinc (b) complexes of O-en-N-tn molecule in ethanol/BR mixture at pHs 2.66. Scan rate 10 mV s^{-1}, drop time 1 s, pulse ampl. 50 mV, C=1.67×10^{-4} M.

The peak potentials of the differential pulse polarograms of the second peaks are linearly dependent on pH of the medium (Fig 2). E_p - pH graphs of both complexes shifted to the negative potentials indicating that hydrogen ions are consumed in the electrode reaction. From the pH changes of the peak potentials, it is understood that both metal complexes are not stable in acidic media.
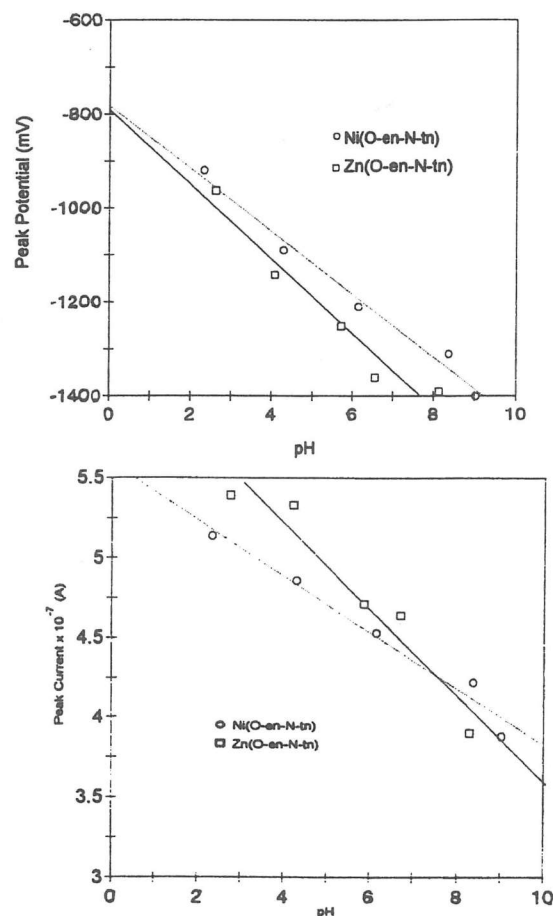

Fig. 2 - Changes of peak potential (a) (vs. Ag/AgCl) and peak current (b) with pH for differential pulse polarograms for the solution of nickel and zinc complexes of O-en-N-tn in BR-ethyl alcohol mixture. C=1.67x10⁻⁴ M.

The peak currents of the second peaks for both metal solutions decrease with the pH and are nearly suppressed at pH values greater than 9. These observations indicate that the second peaks are due to the reduction of the free nickel(II) and zinc(II) cations in the presence of O-en-N-tn. The reductions of the Ni-(O-en-N-tn) and Zn-(O-en-N-tn) complexes were not observed in the 0 V—1.5 V potential range. The reversibility of the reduction wave was tested by cyclic voltammetric criteria and logarithmic analysis. In cyclic voltammetric experiments no anodic peak resulting from reoxidation of the reduction product was observed at any scan rate or any switching potential. In addition to this criteria peak potentials were shifted to more negative values with increase in scan rate. These criteria indicate that the reductions of the Ni(II) and Zn(II) in the presence of O-en-N-tn are irreversible. As will be seen in Section 3.3, the values of the heterogeneous rate constants for both reductions also show the irreversibility of the electron transfer. The reversibility of the electrode reaction was also tested with logarithmic analysis. The slope of the $E_{1/2}$ vs. $\log[(i_d - i)/i]$ graph was constant at all pH values between 4.17-8.56 for both metal cation reductions and the average value of αn_a in this pH range was found to be 0.52 and 0.54 for nickel(II) and zinc(II) respectively.

In bulk electrolysis experiments, the potential of the mercury pool was controlled at -1,2 V vs Ag/AgCl. After suitable time of electrolysis the number of coulombs consumed in the reduction of Ni complex solution (6 mL of 1.67×10^{-4} M) was 0.6060 C (pH 4.63) and that of Zn complex solution (6 mL of 1.67×10^{-4} M) was 0.5802 C (pH 4.34). On the light of this data, the number of electrons transferred was calculated to be 6 for both Ni and Zn complex solutions. Our previous studies showed that the number of electrons consumed in the reduction of O-en-N-tn is 4 [15]. Therefore it is concluded that the second peaks correspond to a 2 electron reduction.

3.2. Adsorptional Characteristics and Charge Measurements by Chronocoulometry

For the Ni(II) and Zn(II) complex solutions, plots of the peak current for the reduction process at pH values between about 4-9, against the square root of the scan rate do not give linear relationships, indicating that the reductions were not diffusion controlled. The adsorption of the free O-en-N-tn and Ni-(O-en-N-tn) and Zn-(O-en-N-tn) complexes that may be present in the solution at these pH values on the mercury drop surface was verified by drop time measurements. Electrocapillary maximum of the solvent system containing supporting electrolyte at pH>8 was depressed and shifted to more negative potentials with the addition of 1.67×10^{-4} M Metal-(O-en-N-tn) complex. The shift and the depression of the drop time-potential curve is a very characteristic indication of adsorption[17].

From the above mentioned observations it was concluded that the Nickel and Zinc complexes of O-en-N-tn molecule and free O-en-N-tn ligand were adsorbed at pH>4 on the electrode surface. Therefore, the amount of the adsorbed metal complexes on the electrode surface was studied by chronocoulometry. In chronocoulometry, the potential of the electrode is changed from a value where no reduction takes place to a value more negative than the second peak where a faradaic current is flowing due to the reduction and the charge that flows across the electrode-electrolyte interface is measured. The measured charge contains faradaic, double layer and adsorption components, which are given in the following equation.

$$Q = 2nFAC\sqrt{Dt/\pi} + Q_{dl} + nFA\Gamma$$

In this equation the last term is due to the reactant adsorption and is the amount of adsorbed reactant in moles / cm^2 [18]. Q_{dl} is the charge of the electrical double layer. The other symbols have their usual meaning.

By applying chronocoulometric technique Q vs $t^{1/2}$ graph was drawn for both solutions in which Zn-(O-en-N-tn) complex was absent and present. From the intercept Q values of these two lines, Γ values were calculated at pHs 4.50 and 8.83 for different applied potentials. All the chronocoulometric data is shown in Table 1.

Table 1.

The adsorbed amounts of various species in the solution of Zn-(O-en-N-tn) complex on the mercury electrode at pHs 4.50 and 8.83 in different applied potentials by double potential chronocoulometry ($C=1.67 \times 10^{-4}$ M, $=250$ ms).

Potential E_2, mV	pH = 4.50			pH = 8.83		
	$Q_{dl}/\mu C$	$Q_{ads}/\mu C$	$\Gamma \times 10^{11}$ (mol·cm^{-2})	$Q_{dl}/\mu C$	$Q_{ads}/\mu C$	$\Gamma \times 10^{12}$ (mol·cm^{-2})
-1350	-0.0343	0.0889	1.95	-0.0120	0.0246	4.50
-1400	-0.0327	0.1031	2.52	-0.0252	0.0277	8.93
-1450	-0.0304	0.0989	2.45	-0.0285	0.0359	2.65
-1500	-0.0291	0.0778	1.74	-0.0369	0.0442	2.61

As can be seen from Table 1, the amount of the substance adsorbed at the electrode surface is higher at the acidic solution than that of the basic media. This is due to the adsorption of the protonated ligand in addition to the adsorption of the complex at the acidic solution. We showed in a previous paper that, only the protonated form of O-en-N-tn can be adsorbed at the electrode surface[15].

The adsorption of Ni(II) and Zn(II) complexes with O-en-N-tn was exploited for the adsorptive stripping determination of nickel and zinc at alkaline solutions. To the solution containing Ni(II) and Zn(II) ions, ligand was added and the adsorbed complexes of these ions reduced, applying differential pulse voltammetry, at sufficiently different

potentials to be determined simultaneously (Fig. 3). Details of the analytical application of nickel and zinc determination using O-en-N-tn as a ligand will be published soon.
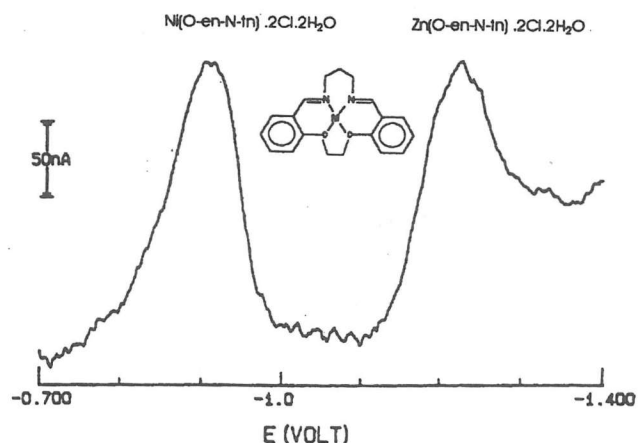

Fig. 3 - Differential pulse adsorptive stripping voltammetric peaks of the nickel and zinc complexes of O-en-N-tn in ethyl alcohol-water mixture (Concentrations of both metal complex: C=1.67x10^{-5} M, pH=4.88).

3.3. Chronoamperometric Measurements of Heterogeneous Rate Constants

Heterogeneous rate constants of Ni(II) and Zn(II) reduction were calculated at different pH values and potentials using chronoamperometric data[19]. The calculated rate constants at acidic pH values were tabulated in Table 2. As can be seen from Table 2, k_f values do not change with potentials for nickel(II) and zinc(II). The average value of k_f was found for Ni(II) to be $(2.55 \pm 0.15) \times 10^{-4}$ cm/s and that of Zn(II) was $(3.58 \pm 0.32) \times 10^{-4}$ cm/s. The k_f values indicate that the reduction of Ni(II) and Zn(II)in the presence of O-en-N-tn molecule are irreversible in nature. In calculating the heterogeneous rate constants, the diffusion coefficients were taken as 1×10^{-6} cm$^2 \cdot$s^{-1},

which is a reasonable value for most organic molecules. The average diffusion coefficients of both complexes were found from Cottrell equation as $(3.03 \pm 0.15) \times 10^{-8}$ cm^2/s and $(5.69 \pm 0.75) \times 10^{-8}$ cm^2/s for Ni(II) and Zn(II) respectively. The low diffusion coefficient values found from Cottrell equation may also indicate that the adsorption of free ligand is effective on the electrode reaction for both solutions.

Table 2.
Heterogeneous rate constants and diffusion coefficients of Ni(II) and Zn(II) ions in the presence of O-en-N-tn molecule.
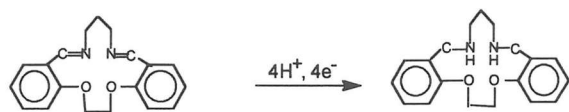
| | Ni complex | | Zn complex | |
| | pH = 4.65 | | pH = 4.77 | |
Potential E$_2$, mV	$k_f \times 10^4$, cm s^{-1}	D$\times 10^8$, cm^2 s^{-1}	$k_f \times 10^4$, cm s^{-1}	D$\times 10^8$, cm^2 s^{-1}
-1100	2.46	1.94	3.53	2.28
-1150	2.53	3.63	3.60	2.98
-1200	2.51	3.54	3.34	3.77
-1250	2.68	2.93	3.83	3.18

### 3.4. Mechanism of the Electrode Reaction

Considering the pH dependence of the reduction potential, adsorptional characteristics, number of electrons transfer and heterogeneous rate constant measurements, the electrode reaction occurs according to the following scheme.

$$ML^{2+} + 2H^+ \rightarrow H_2L^{2+} + M^{2+}$$
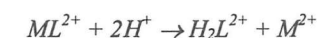
The reduction of free O-en-N-tn which occurs at about −200 mV.

Reductions of the uncomplexed Ni(II) and Zn(II) in the presence of O-en-N-tn. on the electrode surface
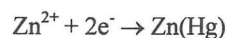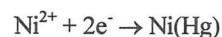
$$Ni^{2+} + 2e^- \rightarrow Ni(Hg)$$
$$Zn^{2+} + 2e^- \rightarrow Zn(Hg)$$

Acknowledgement

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