

Research Article

Electrochemical Behavior of Ni(II)-Salen at the Mercury Electrode

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Received 4 February 2013; Revised 26 March 2013; Accepted 1 April 2013

Academic Editor: Angela Molina

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The complex Ni(II)-salen has been studied using cyclic and square-wave cathodic stripping voltammetry at the static mercury drop electrode in an aqueous media of phosphate and Hepes buffers (at pH 7.0). The resulting voltammograms consist of a totally irreversible one-electron transfer attributable to the coupling of Ni(II) salen/Ni(I) salen via an EC mechanism. The mean value for the transfer coefficient α in both supporting electrolytes was calculated as 0.35 ± 0.05 . The amount of reactant adsorbed after 60 s of accumulation at -700 mV was calculated to be 2.8×10^{-8} mol·cm⁻². The detection limit for nickel determination was found to be 3.4×10^{-9} mol L⁻¹.

1. Introduction

The effective clinical use of cis-diammine dichloro platinum(II) complex and other platinum complexes in the treatment of human cancer has stimulated studies in the interaction of DNA with different metal complexes. While some metal complexes possess potential antitumor activities, many others are persistent environmental hazards. The understanding of the precise nature of the interaction of different metal complexes with DNA is crucial to better predict their utilization for diverse purposes such as pharmacology, controlling genetic information, and the elucidation of protein-DNA contacts or gene therapy [1].

Several areas of chemistry have taken great interest in salen-type Schiff bases and their complexes with transition metals. This is mainly due to their biological activity [2, 3], optical [4, 5], catalytic [6–9], chromophoric [10], thermochromic [11], and photochromic [12] properties.

In analytical chemistry, this class of compounds has been used to impregnate ion exchange resins for the study of Cu(II), Co(II), and Ni(II) complexes [13], in the fluorescent analysis of some amines [14] and amino acids [15] and

in solvent extraction of Ga(II) and Fe(III) complexes [16]. Ni(II)-selective ion sensors of salen-type Schiff base chelates have also been developed [17].

Recently, it was found that some transition metal complexes, such as manganese [1, 18], nickel [19–23], iron [24], ruthenium [25], and copper [26], with ligands of the salen type can selectively modify DNA and RNA [27–29]. The oxidative and reductive chemistry of nickel(II) complexes with Schiff bases of salen type has been studied extensively in organic solvents with different coordinating strength [30–37]. In the present work, the electrochemical behavior of Ni(II)-salen (Figure 1) at a mercury electrode in an aqueous phosphate and Hepes buffers (pH 7.0) by cyclic and square-wave stripping voltammetry has been examined. The phosphate and Hepes buffers are widely used in studies using biological samples and were chosen for their ability to establish the pH 7.0 in aqueous solutions and they do not interact or affect ions involved in biological reactions. A comparison between the two is that the Hepes has a molecular structure more complex (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid) than the phosphate buffer, which is prepared at pH 7 using only monosodium phosphate and

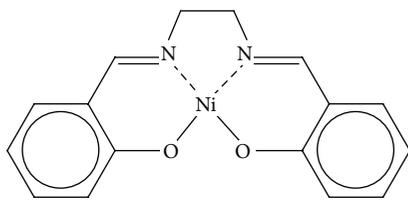


FIGURE 1: Structure of Ni(II)-salen complex.

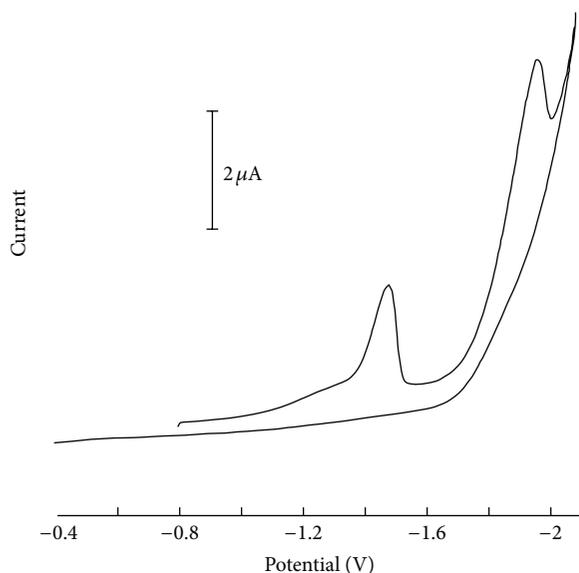


FIGURE 2: Staircase cyclic voltammograms for $1.7 \times 10^{-6} \text{ mol L}^{-1}$ of Ni(II)-salen complex in phosphate buffer (0.02 mol L^{-1} , pH 7.0). Equilibrium time: 30 s at -800 mV . Scan rate: $300 \text{ mV} \cdot \text{s}^{-1}$.

its base combined, disodium phosphate. The techniques of cyclic and square-wave voltammetry are highly convenient to understand the redox behavior of Ni(II)-salen complex in aqueous solution proposed in this paper; in addition square-wave stripping voltammetry technique is very sensitive and ideal for the development of an analytical method for the measurement of Ni(II)-salen at trace levels.

2. Experimental

2.1. Apparatus. All measurements were obtained with a BAS-50 W voltammetric analyzer with a hanging mercury drop electrode. The sample cell (10 mL of volume) was fitted with an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode and a platinum wire auxiliary electrode. A magnetic stirrer and a stirring bar provided the convective transport during the preconcentration step on the voltammetric stripping techniques.

2.2. Chemicals and Solutions. All chemicals were of analytical grade. The Ni(II)-salen complex was prepared by refluxing a 0.1 mol L^{-1} solution of nickel acetate with an equal quantity of the ligand salen in ethanol for 2 hours. The precipitate

was filtered, washed twice with ethanol and acetone, and dried in a desiccator containing phosphorous pentoxide. The stock solution of the Ni(II)-salen complex was prepared by dissolving the crystalline complex in dimethylformamide (DMF) up to a solution containing 1.0 mg L^{-1} . Dilutions were made with DMF or with the appropriated stock buffer solution.

The stock buffer solutions of potassium dihydrogen phosphate and 4-(2-hydroxyethyl)-1-piperazine ethanesulfonic acid (Hepes) (0.02 mol L^{-1}) were prepared by dissolving the suitable quantities of the reagents (Sigma) in water followed by adding NaOH (0.2 mol L^{-1}) to adjust the desired pH. All solutions were prepared with water distilled and purified by the Milli-Q purification system.

2.3. Procedure. A known volume (10 mL) of the supporting electrolyte solution (0.02 mol L^{-1} phosphate or Hepes buffers at pH 7.0) was added to the cell and degassed with nitrogen for 8 min (and for 30 s before each square-wave stripping cycle). The preconcentration potential (-700 mV) was applied to the electrode for a selected time, while the solution was stirred. The stirring was then stopped, and after 30 s the voltammogram was recorded by applying a negative-going potential scan. The scan was terminated at -1500 mV , and the square-wave stripping cycle was repeated with a new mercury drop. After the background stripping voltammograms had been obtained, aliquots of the Ni(II)-salen standards were introduced. The entire procedure was automated, as controlled by the BAS stripping analyzer. Throughout this operation, nitrogen was passed over the solution surface. The staircase cyclic voltammograms started at -800 mV and the potential was reversed at -2200 mV . All data were obtained at ambient temperature.

3. Results and Discussion

The electrochemical reduction of $\text{UO}_2(\text{II})$ and $\text{Cu}(\text{II})$ -salen in buffered aqueous solution of phosphate or Hepes at hanging mercury drop electrode (HMDE) was studied in our laboratory [38, 40]. In connection with such studies, the present work reports an electrochemical behavior of nickel(II) complexed with the Schiff base $\text{N,N}'$ -ethylenebis(salicylideneimine), Ni(II)-salen, using cyclic and square-wave voltammetry.

3.1. Cyclic Voltammetry. Cyclic voltammetry (CV) is widely used for the initial characterization of electrochemically active systems. Figure 2 illustrates a typical staircase cyclic voltammogram obtained for $1.7 \times 10^{-6} \text{ mol L}^{-1}$ of Ni(II)-salen complex in an unstirred phosphate 0.02 mol L^{-1} buffer (pH 7.0). The forward potential scan was started at -800 mV and its direction was reversed at -2200 mV . A first cathodic peak current was obtained at -1400 mV and is due to the reduction of Ni(II)-salen complex. A second cathodic peak, which only appears at a higher scan rate ($>200 \text{ mV s}^{-1}$), was observed at -2000 mV . This signal is probably due the disproportionation of Ni(I)-salen (an irreversible chemical reaction) [38, 39]. No

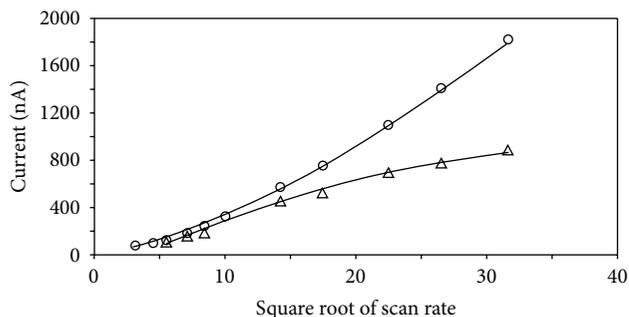


FIGURE 3: Dependence of peak current on square root of scan rate by staircase cyclic voltammetry for $1.7 \times 10^{-6} \text{ mol L}^{-1}$ of Ni(II)-salen complex in phosphate buffer (circle) and Hepes (triangle) buffers (0.02 mol L^{-1} , pH 7.0). Equilibrium time of 30 s at -800 mV .

peak potential was observed in the reverse scan. The absence of peaks in the backward scan can be related to irreversible processes and also to the presence of a chemical step (EC mechanism).

Cyclic voltammograms also were recorded at a series of potential scan rates between 5 and 1000 mV s^{-1} at a mercury electrode for $1.7 \times 10^{-6} \text{ mol L}^{-1}$ of Ni(II)-salen complex. For both phosphate and Hepes aqueous media, a nonlinear relationship between reduction peak current (Ni(II)-salen) (i_p) and the square root of the scan rates ($\nu^{1/2}$) was observed (Figure 3). A linear plot of i_p against $\nu^{1/2}$ should be obtained when the electrode process is a fully reversible or irreversible process at macroelectrodes; deviations from this behavior can be due to radial diffusion, quasi-reversible kinetics, and/or coupled chemical reactions/adsorption [41].

The relationships between i_p and scan rate (ν) also was examined for both supporting electrolytes. A linear plot of i_p against ν should be obtained when the electrode process is an adsorption-controlled process [42].

For the phosphate buffer, the relationships between i_p and ν for both ranges of scan rate ($5\text{--}100$ and $100\text{--}1000 \text{ mV s}^{-1}$) examined suggested a mixed adsorption- and diffusion-controlled process at the electrode surface. The plots of i_p versus ν were linear with different slope values. The slope of the $\log i_p$ versus $\log \nu$ plot over the total range of scan rates examined was 0.72. This average slope clearly indicates that the process has more than one step. This slope is between the theoretical values of 0.5 and 1.0 for diffusion- and adsorption-controlled electrode process, respectively.

In the Hepes buffer, the height of the cathodic peak for the complex in the range of scan rate ($5\text{--}100 \text{ mV s}^{-1}$) examined is not directly proportional to either the value of the scan rate or the square root of this value. A theoretical treatment [42] of these results suggests that there is a complex overall process controlled by diffusion and adsorption of the Ni(II)-salen species to the electrode surface. From 100 to 1000 mV s^{-1} the i_p versus $\nu^{1/2}$ plot showed a straight line suggesting a diffusion-controlled reduction process. Moreover, the slope of the $\log i_p$ versus $\log \nu$ plot was 0.43 which is very close to

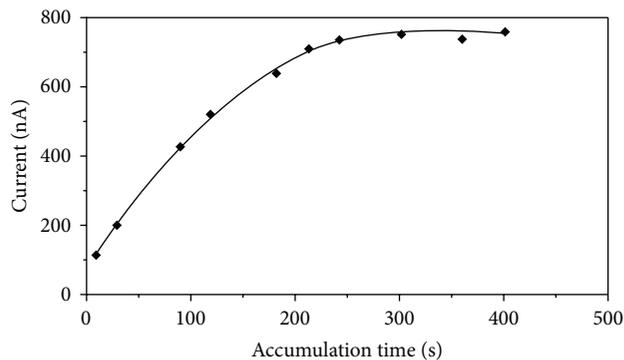


FIGURE 4: The effect of accumulation time on the current of the square-wave stripping peak for $2.1 \times 10^{-7} \text{ mol L}^{-1}$ Ni(II)-salen complex in phosphate buffer (0.02 mol L^{-1} , pH 7.0). Accumulation time at -700 mV with stirring. Potential step height (E -step): 4 mV . SW- a : 30 mV and SW- f : 30 Hz .

the theoretical of 0.5 for the diffusion-controlled electrode process.

The dependence of reduction peak potential (E_p) on the decimal logarithm of the scan rate ($\log \nu$) must be a straight line [slope = $(59/n\alpha)$] mV to allow the determination of the charge coefficient transfer, α [40]. In phosphate buffer when E_p is plotted against $\log \nu$ we obtain a linear relationship (correlation coefficient = 0.999) with slopes of 59 mV and 120 mV for scan rates on the ranges of $10\text{--}200 \text{ mV s}^{-1}$ ($\alpha = 0.50$) and of $200\text{--}1000 \text{ mV s}^{-1}$ ($\alpha = 0.25$), respectively. This demonstrates an increase in the irreversibility of the electrode process with scan rate. Again, the data seems to point out to a process with more than one step.

For the Hepes buffer, the E_p against $\log \nu$ plot was allowed to estimate the value of α as 0.30 over all ranges of scan rates studied.

In the phosphate buffer, from 20 to 100 mV s^{-1} , the $i_p/\nu^{1/2}$ value is constant. This also establishes the electrode process as diffusion controlled. For Hepes buffer, this $i_p/\nu^{1/2}$ value is constant for $\nu > 100 \text{ mV s}^{-1}$.

3.2. Square-Wave Stripping Voltammetry (SWV). SWV also is a powerful technique for electroanalytical purposes and for the elucidation of the redox mechanism and adsorption studies [43]. The relationships of peak potential and current with the square-wave frequency, SW- f , and pulse amplitude, SW- a , give the characteristics of the redox mechanism [44]. The adsorptive accumulation of the Ni(II)-salen complex was initially developed by square-wave stripping voltammetry (experimental conditions: $2.1 \times 10^{-7} \text{ mol L}^{-1}$ of Ni(II)-salen complex in an phosphate buffer (0.02 mol L^{-1} , pH 7.0); accumulation for 60 s at -700 mV with stirring; potential step height (E -step): 4 mV ; SW- a : 30 mV , and SW- f : 30 Hz). The results of the voltammograms showed similar behavior to those obtained on the staircase cyclic voltammetry (Figure 2—forward direction). The first reduction current peak of Ni(II)-salen also was observed at -1400 mV .

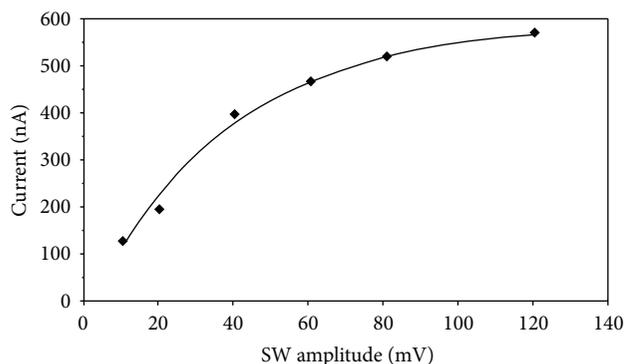


FIGURE 5: The effect of SW amplitude on the current of the square-wave stripping peak for $1.7 \times 10^{-7} \text{ mol L}^{-1}$ Ni(II)-salen complex. Other conditions as in Figure 4.

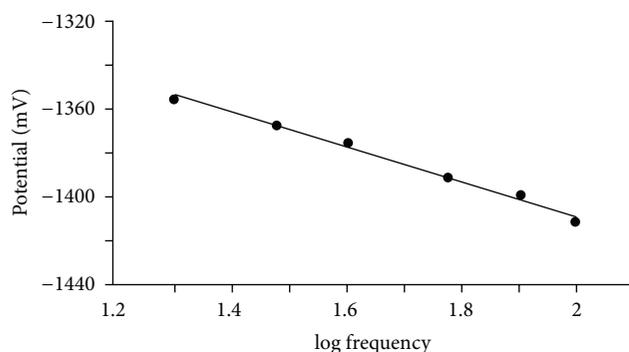


FIGURE 6: The effect of decimal logarithm of the SW frequency on the potential of the square-wave stripping peak for Ni(II)-salen. Other conditions as in Figure 4.

Figure 4 shows the effect of an accumulation time on the square-wave stripping peak current (at -1400 mV) of the Ni(II)-salen complex. The current is seen to increase from 0 until leveling off at 210 sec. Such time-dependent profiles represent the mercury drop saturated with a stable layer of the complex adsorbed. With higher Ni(II)-salen concentration the reduction current reaches a plateau after a shorter accumulation time.

The relations between the peak current (Ni(II)-salen) and the parameters of the square wave were studied to the better comprehension of irreversibility on the electrode process. The effect of the square-wave amplitude on stripping current is shown in Figure 5. The current increases linearly with the amplitude at first and then levels off. This fact can be characteristic of a totally irreversible redox reaction, but several other systems show similar behavior [45]. Square-wave amplitudes greater than 80 mV yield no additional sensitivity for analytical purposes.

The peak width at half-height was observed and is a crucial parameter for assessing the reversibility or irreversibility of the electrode process. For totally irreversible redox reactions $\Delta E_{p/2}$ does not depend on the SW amplitude. A separate experiment using the same conditions as Figure 5 also was realized. The results of the voltammograms show

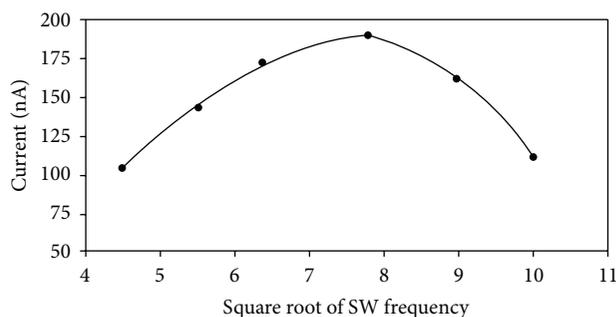


FIGURE 7: The effect of the square root of the SW frequency on the current of the square-wave stripping peak for Ni(II)-salen. Other conditions as in Figure 4.

which $\Delta E_{p/2}$, after SW amplitude of 10 mV , remains constant. This fact is also characteristic of a totally irreversible redox reaction with the adsorption of the reactant [45, 46].

The dependence of the reduction peak current of the Ni(II)-salen complex on the SW amplitude (Figure 5) also shows that the initial slope is $(\Delta i_p / \Delta a)_{a < 40} = 3.9 \text{ nA mV}^{-1}$. According to the following equation [45]

$$i_p = 500q\alpha n^2 F a f \Delta E \Gamma, \quad (1)$$

where a is the SW amplitude, q is the surface area of the electrode, f is the frequency, and ΔE the scan increment (E -step), the amount of the adsorbed reactant can be calculated from the slope $\Delta i_p / \Delta a$, using the values $\alpha = 0.37$, $n = 2$, $q = 0.016 \text{ cm}^2$, $f = 30 \text{ Hz}$, ΔE is 4 mV , and Γ is the surface concentration of the complex. The calculated amount of the adsorbed reactant is $\Gamma = 2.8 \times 10^{-8} \text{ mol cm}^{-2}$ with Ni(II)-salen concentration of $1.7 \times 10^{-7} \text{ mol L}^{-1}$ in phosphate buffer (pH 7.0) and using accumulation time of 60 s at -700 mV .

Precise information about the electrode reaction mechanism arises from the dependence of the reduction current on the SW frequency. At higher frequencies the signal tends to lose its definition as the influence of the charging current becomes increasingly important [47]. Was verified in Figure 6 which the peak potential (E_p) shifts linearly to more negative potential values on the increasing frequency, with indicative for totally irreversible electrode processes and adsorption of the product. The least-squares analysis yielded a slope of $78.8 \text{ mV} \cdot \log f^{-1}$ and a correlation coefficient of 0.992.

The transfer coefficient (α) can be calculated, as the peak potential depends linearly on the logarithm of the SW-frequency as shown in Figure 6. The slope is $\Delta E_p / \Delta \log f = 59 / n\alpha$ [48]. The half-peak width is independent of the SW-frequency. In theory, these characteristics are attributed to the totally irreversible reduction processes with adsorption of the reactant. Other systems can show this same behavior.

Using large step heights (E -step) greatly increases the net currents, which is also characteristic of irreversible systems [45]. A linear dependence was observed over the range from 2 to 10 mV of step heights. The least-squares analysis yielded a slope of $26.9 \text{ nA} \cdot \text{mV}^{-1}$ and a correlation coefficient of 0.988. A linear dependence of (E -step) on the E_p also was observed.

TABLE 1: Comparison of Ni(II)-, Cu(II)-, and UO₂(II)-salen complexes in an aqueous medium.

Metal-salen complex	Electrode	Supporting electrolyte (at pH 7.0)	Detection limit (mol L ⁻¹)	Cathodic peak potential, E_{pc} , (mV)
Nickel	Hanging mercury drop	Hepes and phosphate	3.4×10^{-9}	-1400 and -2000
Copper [38, 39]	Hanging mercury drop	Phosphate	1.0×10^{-8}	-160, -530, -990 and -1100
Uranyl [38, 40]	Hanging mercury drop	Hepes	1.0×10^{-8}	-590, -950 and -1140

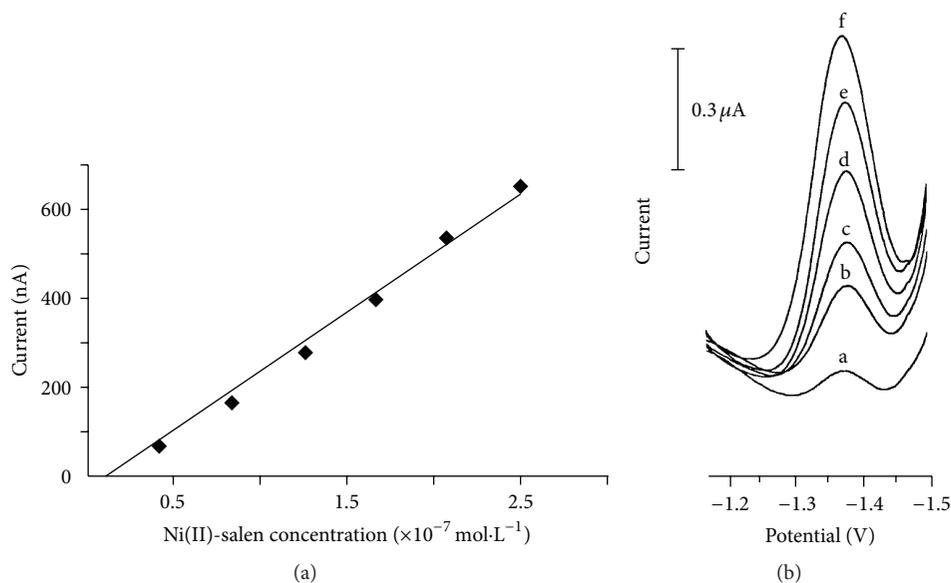


FIGURE 8: Square-wave stripping voltammograms (b) obtained for solutions of increasing Ni(II)-salen concentration from 4.2×10^{-8} to 2.5×10^{-7} mol L⁻¹ (a-f). Other conditions as in Figure 4. Also shown is the resulting calibration plot (a).

The least-squares analysis yielded a slope of -6.8 and a correlation coefficient of 0.993 .

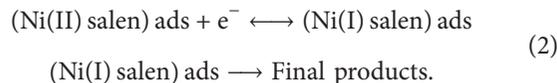
The effect of the square root of the SW-frequency on the peak current of the Ni(II)-salen complex also was evaluated (Figure 7). The highest peak current was observed using a frequency of approximately 60 Hz.

Adsorptive stripping square-wave analysis has been shown as an important method in trace analysis because of its broad scope of applications and relative simple instrumentation. It was established that the Ni(II)-salen complex adsorbs at the electrode surface and by accumulation of the complex at -700 mV the detection of lower concentration is possible. The sensitivity of the square-wave stripping voltammetric response increases with accumulation time and is dependent on the character of the electrode process. Figure 8 shows the voltammograms obtained by varying the Ni(II)-salen concentration from 4.2×10^{-8} to 2.5×10^{-7} mol L⁻¹. The resulting calibration curve, shown as the inset, is seen to be linear up to 2.5×10^{-7} mol L⁻¹ (correlation coefficient = 0.987). The detection limit was estimated to be 3.4×10^{-9} mol L⁻¹ ($S/2N$) with 10 s of accumulation time.

Table 1 compares the voltammetric behavior of Ni(II)-, Cu(II)-, and UO₂(II)-salen complexes in an aqueous medium.

4. Conclusions

In the phosphate buffer, the electrode process seemed to be a mixed adsorption- and diffusion-controlled one, whereas in the Hepes buffer a diffusion-controlled electrode process takes place. These results indicate that Ni(II)-salen and the product of its reduction adsorb at the electrode surface with a one-electron reduction through an EC mechanism. Thus the following redox reaction could be suggested:



Similar results were obtained by Sweeny and Peters [49] using CV, organic supporting electrolyte, and glassy carbon as working electrode. Azevedo et al. [50] reported that in organic media the reduction of the Ni(II)-salen complex is with one-electron, diffusion-controlled, and reversible reduction process. In addition, the present study describes an effective assay for the determination of trace levels of nickel(II) in presence of salen. The detection limit of 3.4×10^{-9} mol L⁻¹ is comparable to that seen for other adsorptive stripping methods [39, 40]. The Ni(II)-salen polymeric film could be applied as a sensor in the determination of dissolved

oxygen, dipyrone and as an electrochemical energy storage system [51–53]. As the solution of Ni(II)-salen in DMF is water-soluble, we are trying to study the effect of the complex solution on DNA cleavage. This metal complex can also be immobilized on a bismuth film/glassy carbon surface or used to modify a carbon paste electrode in order to study its interactions with DNA.

Acknowledgments

The authors gratefully acknowledge the CNPq and CNEN of the Government of Brazil and PUC-Rio for support of this work. In addition, they thank J. C. Moreira and M. Lovric for their helpful discussion. The experimental assistances of A. B. Neves and A. T. da Silva are also appreciated.

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