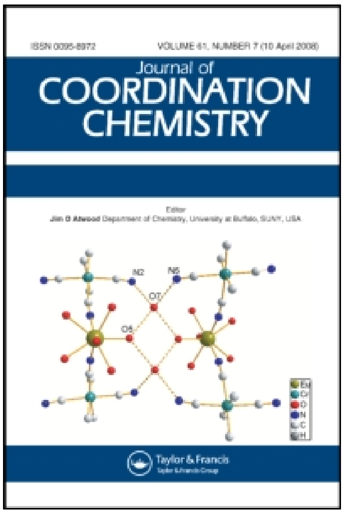

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Voltammetric study of the complexation of (2E,3E)-2H-1,4-benzothiazine-2,3 (4H)-dionedioxime, a newly synthesized oxime derivative, with nickel(II)

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In this article, the electrochemical behavior of the complexation of (2E,3E)-2H-1,4-benzothiazine-2,3 (4 H)-dionedioxime with Ni(II) is studied. The experiments were performed in DMF in the presence of tetraethylammoniumtetrafluoroborate (0.1 M) as a supporting electrolyte and studied by using square-wave voltammetry, cyclic voltammetry, and differential pulse polarography. Reductions of the complexes are irreversible. The ligand forms 1 : 1 and 1 : 2 (metal : ligand) complexes with Ni(II). Stability constants of the formed complexes were evaluated with the modified DeFord–Hume method at different ligand concentrations as $3.21(\pm 0.03) \times 10^6$ and $2.73(\pm 0.03) \times 10^6$, respectively.

Keywords: Voltammetry; Dioxime; Ni(II) complex; Stability constant

1. Introduction

Oximes have played a role in the development of coordination chemistry [1, 2] with complexes used for coordination of metal ions as neutral dioximes [2, 3], oxidation reagents [4, 5], and in medicine [6–11]. Presence of mildly acidic hydroxyl groups and slightly basic nitrogens make *vic*-dioximes amphoteric ligands that form stable complexes with transition metal ions such as Ni^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+}, and Hg^{2+} [12–15]. The chemistry of transition metal complexes with *vic*-dioxime ligands has been widely studied [16, 17], of particular interest as biological model compounds playing a significant role in stereochemistry, model systems of biochemical interest, chromatography, analytical chemistry, catalysis, stabilizers, polymers, and pigment dyes [18–24]. Many analytical procedures have been used to study Ni(II)–oxime complexes such as spectrophotometry [25], thermal decomposition [26], potentiometry using nickel-selective electrodes [27], and voltammetry [28–30].

Voltammetric techniques are fast, cheap, and sensitive analytical tools to study formation of a complex. Whereas many inorganic compounds are studied in aqueous solutions, non-aqueous solvents are finding ever-widening uses for such determinations,

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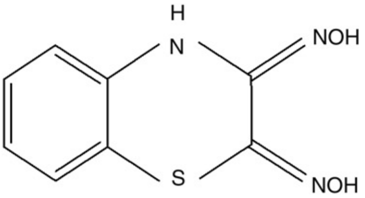

Figure 1. The chemical structure of HL.

in particular for complexes and chelates, organometallic species, and organic compounds.

In this article, interaction of Ni(II) with (2E,3E)-2H-1,4-benzothiazine-2,3 (4H)-dionedioxime (figure 1) is studied by voltammetric methods.

2. Experimental

2.1. *Instrumentation*

All voltammetric and polarographic measurements, cyclic voltammetry (CV), differential pulse polarography (DPP), square-wave voltammetry (SWV), and direct current polarography (DCP), were carried out using the three-electrode system provided by an EG&G Princeton applied research 263A polarographic analyzer potentiostat. All obtained curves were corrected for background. The working electrode was a PARC Model 303A Static Mercury Drop Electrode (SMDE). The sample cell was fitted with a Ag/AgCl (saturated KCl) reference electrode and a platinum wire as an auxiliary electrode. SWV curves were recorded with a pulse amplitude (ΔE) of 25 mV, scan rate (ν) of 50 mVs^{-1}, and frequency of 60 Hz. In DPP experiments, ΔE was 25 mV. For CV, the instrument settings were as follows: medium drop size, equilibrium time of 5 s, and ν of 85 mVs^{-1}. All experiments were carried out at ambient temperature (approximately 20°C).

2.2. *Reagents*

$Ni(NO_3)_2 \cdot 6H_2O$, *N*,*N*-dimethylformamide (DMF), supporting electrolytes of tetraethylammoniumtetrafluoroborate (TEATFB), and tetrabutylammoniumtetrafluoroborate (TBATFB) (all from Merck) were used without purification. HL, which was insoluble in aqueous solution, was synthesized and purified as described elsewhere [31]. One millilitre of NH_3(1 M)/NH_4Cl(0.1 M) was used as a buffering system in the solutions. All solutions were deaerated for 4 min with pure nitrogen gas and an inert atmosphere was maintained over the solutions during the experiments.

3. Results and discussion

3.1. *Cyclic voltammetry*

3.1.1. Cyclic voltammetry of HL. The CV of HL (5.0×10^{-5} M) in DMF was measured at a SDME. At first, the effect of the supporting electrolyte was investigated.

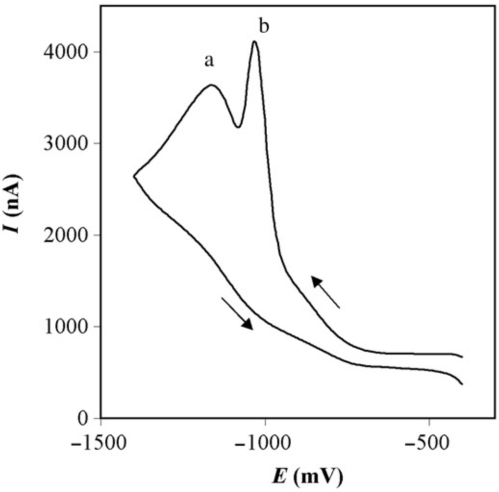

Figure 2. The CV voltammogram of HL (4.0×10^{-6} M) in the solution in the presence of 5.0×10^{-5} M Ni(II); (a) free Ni(II) ion, (b) Ni(II)–HL complex, buffered with NH_3/NH_4Cl.

For this purpose, two different concentrations of 0.1 and 0.01 M of TEATFB and TBATFB were used at a preliminary ν of 200 mVs^{-1} (Supplementary Material). The CV of HL in DMF exhibits a nearly irreversible oxidation peak. Thus, TEATFB (0.1 M), which showed a sharp and clear oxidation peak, was selected as the best supporting electrolyte for subsequent studies. The scan rate of the applied potential was also investigated (Supplementary Material, figure S2). From this figure, the ν of 85 mVs^{-1} showed the best result. Under the optimal condition HL shows an irreversible, sharp and clear oxidation peak at −620 mV.

3.1.2. CV of Ni(II)–HL complex. Figure 2 shows the CV of HL in the presence of excess Ni(II) in the buffered solution. The interaction of Ni^{2+} with HL resulted in a new peak in the voltammogram, at $E = -1036$ mV (peak b). It is obvious from this figure that the system is irreversible. The potential of the Ni(II)–HL complex is more positive than free Ni(II) ion (peak a).

A DC polarogram (figure 3) shows that HL, in the complex, has been reduced. As can be seen from figure 3, a theoretical curve (solid line) of the predicted data from the irreversible relationship between E (mV) and i (nA) [equation (1)] [32] is best fit on the experimental data from a test solution containing 3.0×10^{-4} M of HL in the presence of Ni^{2+} 1.0×10^{-4} M. The best fit is achieved with αn of 0.5.

$$E = E_{1/2} + (0.0542/\alpha n)\log[(i_d - i)/i] \text{ (at 25°C)} \qquad (1)$$

The charge-transfer coefficient (αn) of the complex was calculated from the slope of the plot of E *versus* $\log[i/(i_d - i)]$ (inset in figure 3) where E, i, and i_d are potential diffusion, current, and controlled limiting current, respectively. The value was $-0.0581/\alpha n$ (at 20.0°C). Thus, the αn value was calculated as 0.5. The $E_{1/2}$ value can be evaluated from the intercept of this plot.

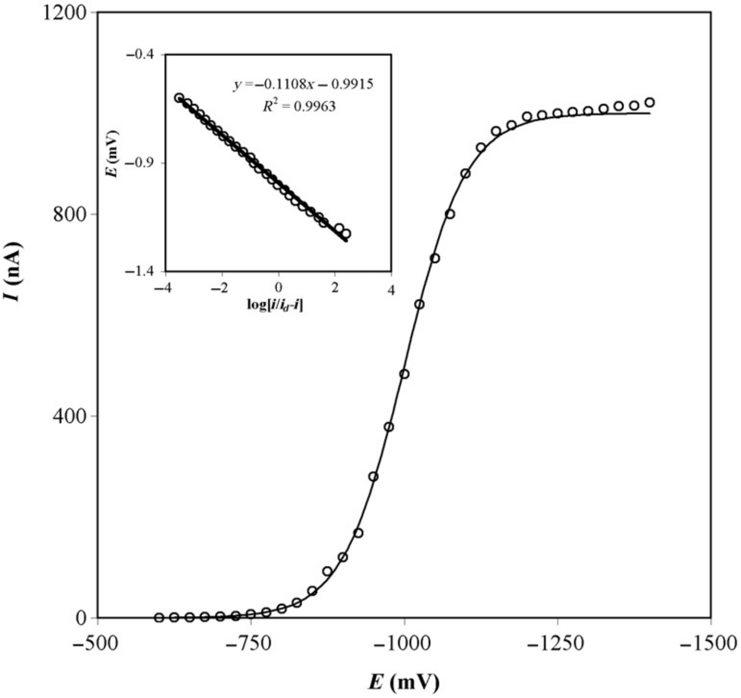

Figure 3. DC polarogram of: (circles) experimental data from a test solution containing 3.0×10^{-4} M of HL in the presence of Ni^{2+} 1.0×10^{-4} M, (solid line) a theoretical plot based on equation (2). The inset shows the plot of E (mV) *versus* $\log[i/(i_d - i)]$ for the experimental data.

3.2. *Square wave voltammetry*

The SWV analysis of the complexation process is shown in figure 4. In a typical run, the first voltammogram was recorded for a solution containing about 5.0×10^{-5} M of Ni(II) in the buffered solution, peak 'a'. Addition of excess HL resulted in curve 'b'. Various metal-to-ligand concentration ratios were prepared by addition of appropriate amounts of HL to the vessel containing a fixed Ni(II) concentration. A molar ratio plot of the peak currents (at $E = -980$ mV) of the formed complex is shown in figure 5. Two distinct inflection points about 0.5 and 1 (Ni^{2+}/HL) mole ratios reveal that two types of complexes were formed from the interaction of Ni(II) with HL in solution.

SWV experiments focused on the new peak (peak b, figure 4) that increases systematically after addition of HL. The observed increase in this peak is indicative of complexation of Ni(II) with HL. When metal complexes are consecutively formed in solution, the voltammogram peak varied in height without any shift in potential. Stability constants can be evaluated using the DeFord–Hume [33] method, originally developed for reversible electrochemical systems. However, it has been shown that this method can be applied to non-reversible systems in which reversibility does not change during metal titration with the ligand [34–37]. The modified DeFord–Hume [equation (2)] method [38] was used to determine the stoichiometry and evaluation of stability constant of the electrochemically irreversible Ni(II)–HL complex:

$$(0.434\alpha nF/RT)\Delta E_p + \log[(i_p)_M/(i_p)_C] = \log \beta_{ML_p} + p \log C_L \qquad (2)$$

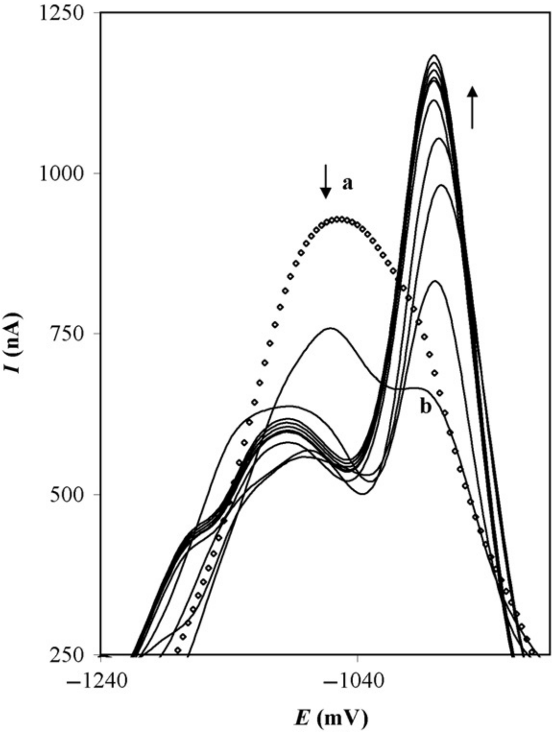

Figure 4. The SWV voltammogram of the titration of 5.0×10^{-5} M Ni(II) with 5.0×10^{-3} M HL, (a) free Ni(II), (b) Ni(II)–HL complex, buffered with NH_3/NH_4Cl.

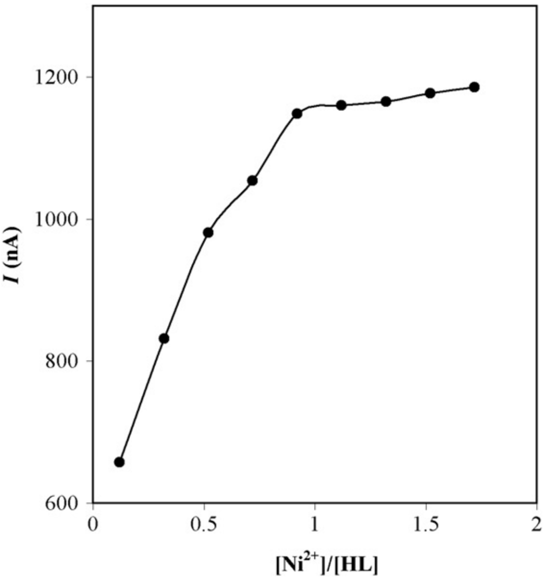

Figure 5. Determination of the stoichiometry of the resultant complexes of the interaction of HL with Ni(II) ions in the solution from the SWV data of the titration curves in figure 4, at $E = -980$ mV.

where $\beta_{\mathrm{ML}p}$ is the stability constant of the resulting complex (where M is the metal, L is the ligand), C_{L} is the concentration of the ligand, ΔE_p is the distance between the peak potentials of the free metal ion and the complex, p is the ligand/metal ratio, and $(i_p)_{\mathrm{M}}$ and $(i_p)_{\mathrm{C}}$ are the peak currents of the free metal ion and the complex, respectively. Since no shift was observed for the peak potential due to complex formation of HL with Ni(II) ions (where ΔE_p is constant), p-values could be calculated from slopes of the plots of $-\log[(i_p)_{\mathrm{C}}/(i_p)_{\mathrm{M}}]$ *versus* $-\log[\mathrm{C_{HL}}]$.

A plot of the logarithmic values of $(i_p)_{\mathrm{C}}/(i_p)_{\mathrm{M}}$ against the logarithm of the HL concentration yields two distinct straight lines (figure 6), indicating formation of two types of complexes. The slopes of these lines allow determination of the coordination number (p) of 1.10 and 0.64 by applying the modified DeFord–Hume equation, showing that metal-to-ligand complexes of 1 : 1 and 1 : 2 are formed in solution. The stability constants were determined to be $\beta_{1:1} = 3.21(\pm 0.03) \times 10^6$ and $\beta_{1:2} = 2.73(\pm 0.03) \times 10^6$. These values are close to those reported in theoretical and spectrophotometric studies [31].

3.3. *Differential pulse polarography*

To further investigate the interaction of HL with $\mathrm{Ni^{2+}}$, the electrochemical behavior of HL with Ni(II) was studied by DPP. A set of differential pulse polarograms, recorded from the Ni(II)–HL system, show a well-shaped DPP wave in which the peak height is continuously changed because of addition of HL into Ni(II) solution containing $\mathrm{NH_3/NH_4Cl}$ as buffer. The results, figure 7, are indicative of formation of a new species

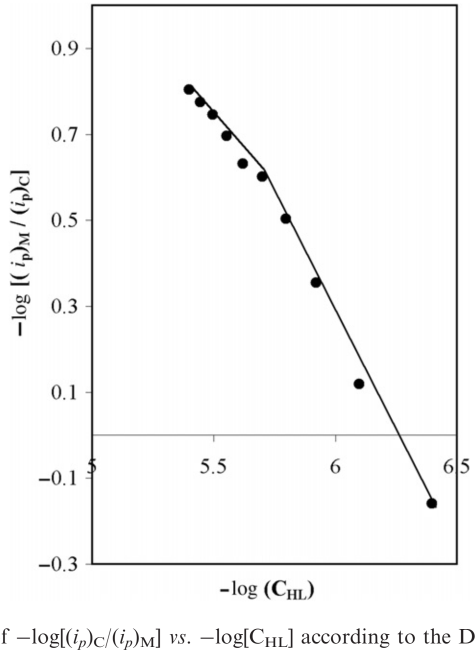

Figure 6. The plot of $-\log[(i_p)_{\mathrm{C}}/(i_p)_{\mathrm{M}}]$ *vs.* $-\log[\mathrm{C_{HL}}]$ according to the DeFord–Hume method.

in solution and demonstrate that this is an irreversible system. From the DPP data, as shown in figure 8, when we plot $(i_p)_C$ as a function of $[Ni^{2+}]/[HL]$ at $E = -984$ mV two inflection points are revealed at 0.5 and 1 (metal/ligand) molar ratios. It can be concluded that the complexes of HL with Ni^{2+} are in 1 : 1 and 1 : 2 forms. This conclusion is in good agreement with the previous results.

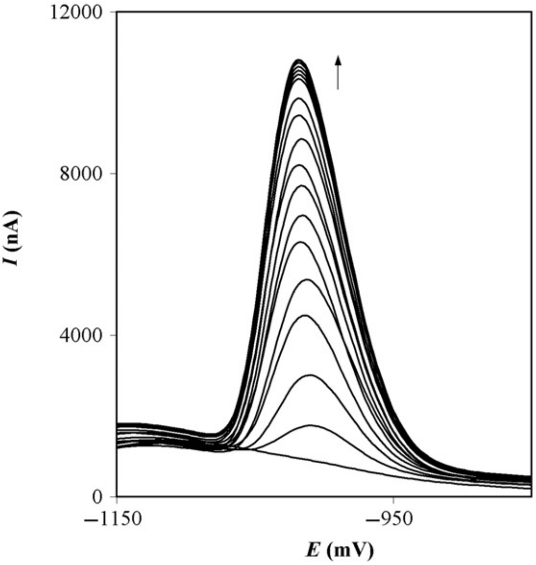

Figure 7. The DPP polarograms of the titration of Ni(II) 5.0×10^{-5} M with HL 5.0×10^{-3} M in the NH_3/NH_4Cl buffered solution.

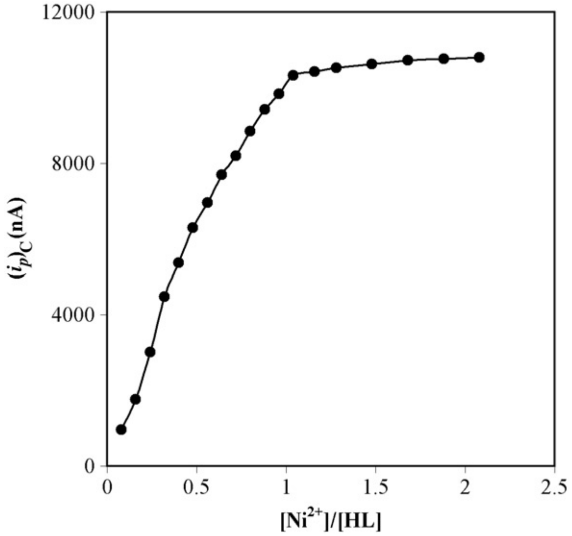

Figure 8. The DPP plot of $(i_p)_C$ *vs.* $[Ni^{2+}]/[HL]$ to determine the stoichiometry of the formed complexes from the titration curves in figure 7.

4. Conclusion

Complexation occurring between Ni(II) and (2E,3E)-2H-1,4-benzothiazine-2,3 (4H)-dionedioxime was followed using SWV, CV, and DPP which allow identification of the complexes formed as well as the determination of their stability constants. Based on the results obtained from this study, the DeFord–Hume method is applicable even in the presence of electrochemically irreversible complexes. In addition, the results show that HL interacts with Ni^{2+} forming two types of complexes with stoichiometry of 1 : 1 and 1 : 2 (metal-to-ligand). SWV is a fast, reliable and sensitive technique for study of the formation of a complex.

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