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Voltammetric and Polarographic Studies of Eriochrome Black T - Nickel(II) Complex

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The electrochemical behaviour of complexes of Eriochrome Black T (EBT) with Ni(II) was studied. It was observed that EBT forms 1:1 and 1:2 complexes with Ni(II) in 0.1 M phosphate buffer at pH 6.0 by using Square-wave voltammetry (SWV), Cyclic voltammetry (CV), Direct Current Polarography (Sampled DCP) and Controlled Potential Coulometry (CPC). It was found that the reduction processes of Ni(II)-EBT complexes are irreversible. The stability constants of the Ni(II)-EBT complexes were evaluated with the DeFord-Hume procedure at different ligand concentrations using SWV. The logarithm values of stability constants of 1:1 and 1:2 Ni(II)-EBT complexes are 8.17 and 11.17, respectively.

Key Words: Eriochrome Black T-Ni(II) complex, voltammetry and polarography.

Introduction

EBT is a carcinogenic azo-compound. It is well known that EBT has chelating properties. Therefore, EBT has been widely used for the determination of calcium, magnesium, manganese, zinc, zirconium, nickel, copper, thulium and cobalt[1−5]. Literature surveys have shown that extensive polarographic, spectroscopic and colorimetric studies on some metal complexes with EBT have been carried out[4−13].

The review of the literature indicates that the compositions and the electrochemical behaviour of the Ni(II)-EBT complexes has not been studied systematically so far[1−16]. No one has described the stability constants and the decomposition of the Ni(II)-EBT complexes. Therefore, the purpose of the present paper was to determine the stability constants and the composition of the Ni(II)-EBT complexes, using the polarographic and voltammetric techniques, in order to obtain detailed information on the interaction of the metal ion and the ligand. Voltammetry (especially SWV) is a very suitable technique because of its high selectivity and sensitivity and shorter analysing time[17]. Also, the importance of this study comes from the application of EBT as a dye stuff and metal indicator.

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Experimental

Instrumentation

Voltammograms and polarograms were obtained with an EG&G Princeton Applied Research 384 B Polarographic Analyser. The working electrode was a PARC Model 303 A Static Mercury Drop Electrode. The sample cell was fitted with an Ag/AgCl (saturated potassium chloride) reference electrode and a platinum wire auxiliary electrode. The instrument settings were as follows: medium drop size; equilibrium time, 5 s; potential scan rate, 400 mVs^{-1}; and scan increment, 4 mV. A DMP-40 Series Digital Plotter was used for the collection of experimental data. All experiments were carried out at the ambient temperature (approximately 20°C).

Reagents

$NiCl_26H_2O$ (Merck) and Eriochrome Black T (Merck) were used without further purification. All other reagents were of analytical grade. 0.1 M phosphate buffer (pH 6.0) was used as the supporting electrolyte. Stock solutions were prepared with double distilled and deionized water.

Procedure

The experiments were performed using a 2×10^{-5} M Ni(II) ions concentration while the ligand concentration was from 2.5×10^{-6} M to 4×10^{-5} M. A stream of pure nitrogen was used for 300 s to remove the dissolved oxygen in the solution before voltage scanning.

Method of calculation

The modified method of DeFord and Hume[18] was used to determine the stability constants of the irreversible complexes according to the equation

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

where β_{MLp} is the stability constant of the MLp complex (where M, metal; L, ligand), C_L is the concentration of ligand, ΔE_p is the distance of the peak potentials of the free metal ion and the complex, p is the ligand/metal value, and $(i_p)_M$ and $(i_p)_C$ are the peak currents of the free metal ion and the complex, respectively. Since no shift was observed in the peak potential in the complexes of EBT with Ni(II) ions (where ΔE_p is constant), p values were calculated from the slopes of the plots of $-\log[(i_p)_M/(i_p)_C]$ versus −log[EBT].

Results and Discussion

The nature of the electrode reaction

The nature of the electrode process was studied by CV. In the presence of 2×10^{-4} M Ni(II), the cyclic voltammogram of 2×10^{-5} M EBT is shown in Fig. 1. As a result of the interaction of Ni(II) with EBT, a new peak (peak b) was observed on the voltammograms. Normally, the complexed metal ions are reduced at a more negative potential than that of its free ion state. However, the potential of the Ni(II)-EBT complex is more positive with regard to free Ni(II) ion. Therefore, it can be thought that the EBT in the complex is reduced.

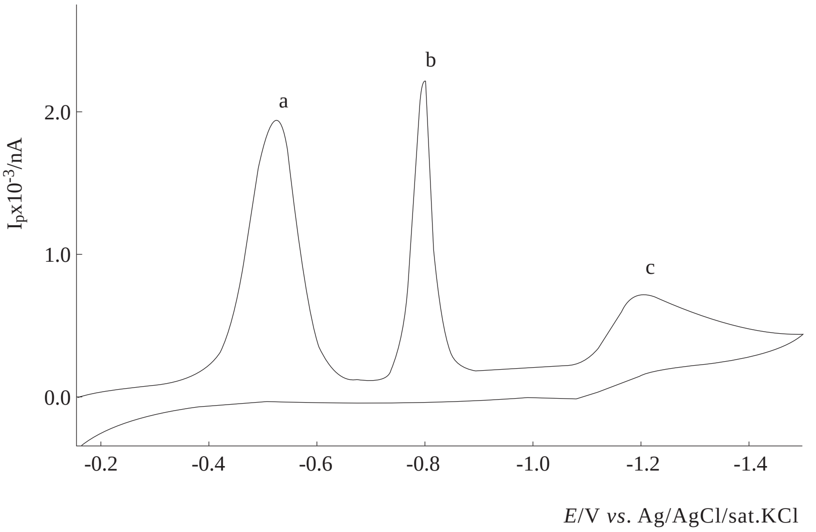


Figure 1. CV voltammogram of 2×10^{-5} M EBT in the presence of 2×10^{-4} M Ni(II) at 0.1 M phosphate buffer (pH 6.0). **a**, free EBT; **b**, Ni(II)-EBT complex and **c**, free Ni(II).

As may be seen in Fig. 1, the reduction process of the complex (peak b) is irreversible owing to no being present peak in the anodic branch. Therefore the charge-transfer coefficient (αn) of the complex was calculated by equating the slope of the plot of E versus log $[i/(i_d - i)]$ to $-0.0581/\alpha n$ (at 20°C) (where E is potential, i is current and i_d is diffusion controlled limiting current) on the polarogram obtained by means of Sampled DCP. Thus, the αn value was calculated to be 0.534. These results are agreement with those of Laviron[14].

SWV-Voltammetry

As has been previously demonstrated[19], EBT exhibits one peak which corresponds to its irreversible six-reduction at 0.1 M phosphate buffer (pH 6.0) supporting electrolyte. The addition of EBT (from 2.5×10^{-6} M to 4×10^{-5} M) to a 2×10^{-5} M Ni(II) solution results in a new peak (peak b) and a gradual decrease in the peak current of free Ni(II) ions (Fig. 2). An increase in peak b is also observed, indicating the complexation of Ni(II) with EBT. The data are listed in the Table. The modified DeFord-Hume method is used to determine the stoichiometries and stability constants of irreversible Ni(II)-EBT complexes. As the peak potential of the complex does not shift with the addition of EBT, the ΔE_p value (316 mV) does not change. A plot of the logarithm value of $(i_p)_M/(i_p)_C$ against the logarithm of the EBT concentration yields two straight lines (Fig. 3), which indicates the formation of two complexes. The slopes of these lines allow the determination of the coordination numbers (p) of 0.99 and 1.78 by applying the modified DeFord-Hume equation, meaning that metal-to-ligand complexes of 1:1 and 1:2 are formed. The overall stability constants were determined to be log $\beta_{1:1} = 8.17$ and log $\beta_{1:1} = 11.17$.

Table. SWV data for different ligand concentrations in Ni(II)EBT solution at 0.1 M phosphate buffer (pH 6.0)^a.

C_L/M	$(i_p)_M/nA$	$(i_p)_M/nA$	$-\log[(i_p)_M/(i_p)_C]$	$-\log C_L$	p	$\Delta E_p/V$	$\log \beta_{MLp}$
2.5×10^{-6}	52	92	0.262	5.602	1	0.340	8.786
5.0×10^{-6}	86	87	0.005	5.301	1		8.228
7.5×10^{-6}	122	82	0.173	5.125	1		7.874
1.0×10^{-5}	161	72	0.349	5.000	1		7.573
1.25×10^{-5}	212	70	0.481	4.903	2		12.247
1.50×10^{-5}	247	66	0.573	4.824	2		11.997
1.75×10^{-5}	291	63	0.665	4.757	2		11.771
2.00×10^{-5}	346	59	0.768	4.699	2		11.550
2.25×10^{-5}	441	55	0.904	4.648	2		11.312
2.50×10^{-5}	494	52	0.978	4.602	2		11.148
2.75×10^{-5}	504	50	1.003	4.560	2		11.040
3.00×10^{-5}	665	44	1.179	4.522	2		10.788
3.25×10^{-5}	734	53	1.141	4.488	2		10.757
3.50×10^{-5}	845	49	1.237	4.456	2		10.597
3.75×10^{-5}	886	46	1.285	4.426	2		10.489
4.00×10^{-5}	962	41	1.370	4.398	2		10.348

^{a}[Ni(II)] $= 2 \times 10^{-5}$ M; pulse amplitude = 20 mV; C_L corresponds to the total EBT concentration

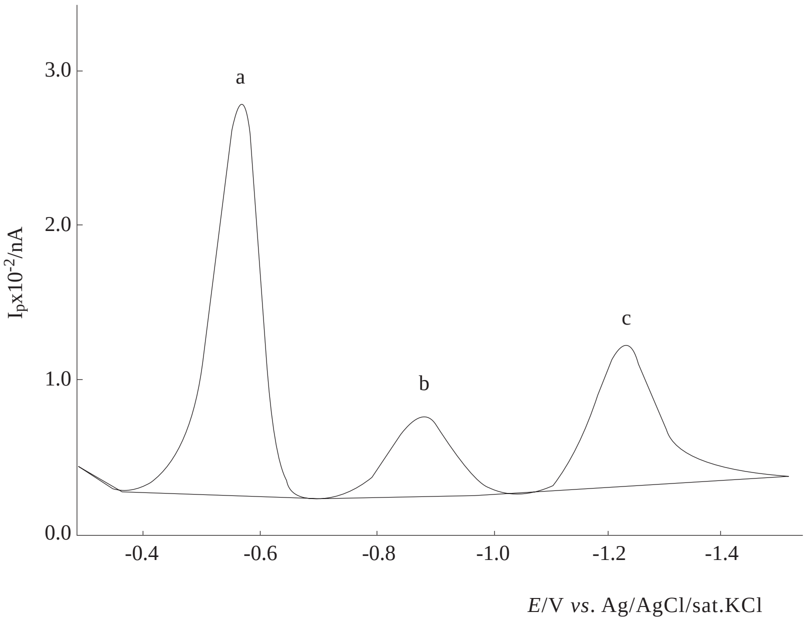


Figure 2. SWV voltammogram of 2.5×10^{-6} M EBT in the presence of 2×10^{-5} M Ni(II) at 0.1 M phosphate buffer (pH 6.0). **a**, free EBT; **b**, Ni(II)-EBT complex and **c**, free Ni(II).

We think that both the O atoms of hydroxyl groups and the N atoms of azo group in EBT molecule participate in the complex formation. As the peak potential of the complex is more positive than that of free Ni(II) ions, the electrode mechanism of the complex should involve the reduction of the complexed EBT. CPC results show that the six-electron is consumed per EBT molecule in the complexes, as can be seen in the Scheme.

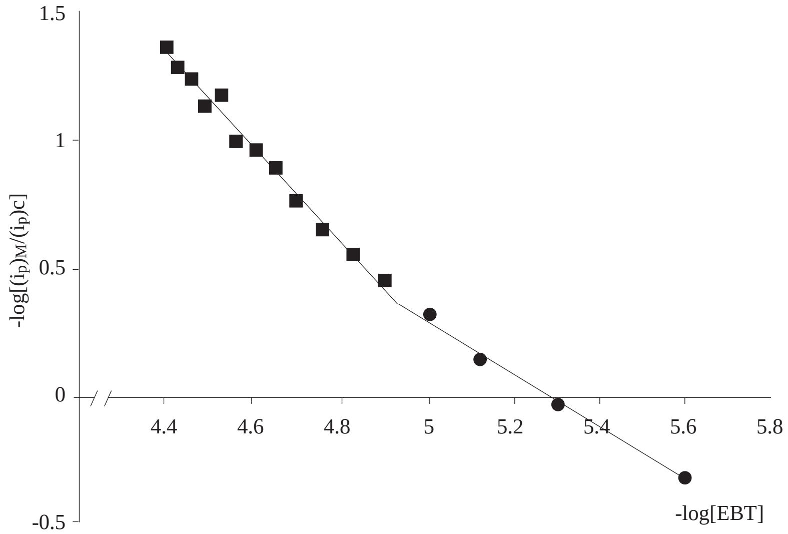
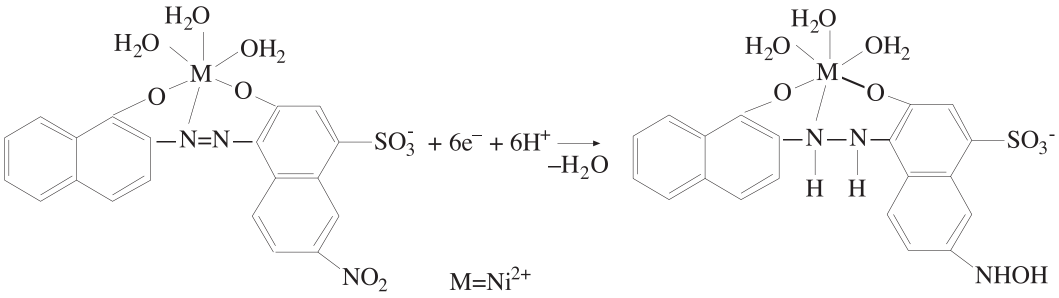


Figure 3. Plot of $-\log[(i_p)_M/(i_p)_C]$ versus $-\log[\text{EBT}]$.



Scheme

Conclusion

The complexation reaction occurring between Ni(II) ions and EBT can be followed using SWV, DCP, CV and CPC, which allow the identification of the complexes formed as well as the determination of their stability constants. In addition, the results show that the DeFord-Hume method is applicable even in the presence of irreversible complexes. Also, SWV is a fast, cheap and sensitive technique for the study of the formation of complexes.

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