Redox properties of the bis(2-hydroxyethyl)dithiocarbamate anion and its nickel(II) complex in aqueous solutions

H. HOFBAUEROVÁ, E. BEINROHR, and J. MOCÁK

*Department of Analytical Chemistry, Slovak Technical University,
CS-812 37 Bratislava*

The first step of the electrochemical oxidation of the bis(2-hydroxyethyl)dithiocarbamate anion (*I*) at a stationary carbon electrode is the formation of the appropriate thiuram disulfide. The voltammetric behaviour of *I* is considerably influenced by pH. The total oxidation of *I* by electrolytically generated hypobromite, involving 16 electrons per *I* molecule, was utilized in an optimized coulometric procedure for *I* determination. In electrochemical oxidation of the bis-Ni(II) complex in acidic solutions a complex with Ni(IV) central atom is formed. In neutral and alkaline solutions the corresponding thiuram disulfide is formed.

Первой стадией электрохимического окисления аниона бис(2--гидроксиэтил)дитиокарбамата (*I*) на стационарном углеродном электроде является образование соответствующего тиурамдисульфида. Вольтамметрическое поведение *I* в значительной степени зависит от pH. Полное окисление *I* электролитически генерированным гипобромитом, включающее 16 электронов на молекулу *I*, было использовано в оптимализированной кулонометрической процедуре по определению *I*. При электрохимическом окислении комплекса бис-Ni(II) в кислых растворах образуется комплекс с центральным атомом Ni(IV). В нейтральных или щелочных растворах образуется соответствующий тиурамдисульфид.

The redox properties of the N,N-disubstituted dithiocarbamic acids and their complexes with transition metals have been an object of an immense interest for a long time. It was shown [1] that dithiocarbamato ligands can stabilize higher oxidation states of various central atoms. The above-mentioned ability is due to the delocalization of the lone electron pair on the nitrogen atom of the ligand and to the corresponding π-electron density enhancement on the sulfur atoms.

The nickel(II) bis(dithiocarbamato) complexes can be oxidized both electrochemically [2] and chemically [3, 4] to complexes having Ni(III) or Ni(IV) central atoms. The oxidation reaction mechanism has not been unambiguously elucidated yet. The formation of a paramagnetic Ni(III) intermediate is probable [5].

This paper deals with the redox behaviour of nickel(II) bis(dithiocarbamato) complexes in aqueous solutions and the influence of pH on the redox process.

The potassium salt of the bis(2-hydroxyethyl)dithiocarbamic acid was chosen as a ligand since the resulting Ni(II) complex is sufficiently soluble in water (solutions of $c \approx 1 \times 10^{-4}\,mol\,dm^{-3}$ can be prepared).

Experimental

All the employed chemicals were anal. grade commercially obtained materials. Britton —Robinson and ammonia buffer solutions were used in voltammetric and chronoamperometric measurements. The base electrolyte used in coulometric titrations contained 6.12 g $Na_2B_4O_7 \cdot 10H_2O$ and 100 g KBr in 1 dm³ of aqueous solution and its pH was adjusted to 8.6 with diluted hydrochloric acid.

Cupral (Lachema, Brno), $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ was purified by recrystallization from methanol.

Bis(2-hydroxyethyl)dithiocarbamic acid, potassium salt, $(HOCH_2CH_2)_2$-$NSC_2K \cdot 0.5H_2O$, was prepared as follows: Equimolar amount of KOH was added to diethanolamine and on adding some water the resulting suspension was mixed until KOH was dissolved. On intensive cooling of the dense solution in an ice-bath equimolar amount of carbon disulfide was dropwise added. The resulting solid raw product was dissolved in water and on adding acetone to this solution the reaction product (white crystalline substance) was precipitated, filtered off and air-dried. Elemental analysis: w_i(found): 26.53 % C, 4.57 % H, 6.14 % N; w_i(calc.): 26.28 % C, 4.86 % H, 6.13 % N.

Bis(di(2-hydroxyethyl)dithiocarbamato) nickel(II) was prepared in the following way: To an aqueous solution of the potassium salt of the bis(2-hydroxyethyl)dithiocarbamic acid aqueous solution of $Ni(SO_4)_2 \cdot 5H_2O$ (in mole ratio of reactants 1 : 2) was added. The resulting green precipitate was filtered off, air-dried and purified by recrystallization from dimethylformamide. Elemental analysis: w_i(found): 28.35 % C, 4.84 % H, 6.63 % N, 14.05 % Ni; w_i(calc.): 28.65 % C, 4.80 % H, 6.68 % N, 14.00 % Ni.

The voltammetric and chronoamperometric measurements at a stationary electrode were performed using an OH-105 polarograph (Radelkis, Budapest) with three-electrode arrangement. The working electrode was a vertically arranged cylindrical carbon rod electrode, 6 mm in diameter (Elektrokarbon, Topoľčany). The area A of its active bottom surface was determined by chronoamperometric measurements of o-dianizidine [6], $A = 0.234\,cm^2$. The protecting paraffin film on the electrode was daily renewed by emerging the electrode two-three times into melted paraffin. The active surface of the electrode was carefully cleaned with fine-grained abrasive paper and polished on filter paper. The reference electrode, placed in close proximity of the working electrode, was a saturated mercurosulfate electrode. The auxiliary electrode was a large-surface paraffin-impregnated cylindrical carbon electrode.

In chronoamperometric measurements the working electrode was polarized with a potential 100 mV more positive (for oxidation) or more negative (for reduction), respectively, than the potential of the corresponding voltammetric peaks.

Coulometric titrations with electrolytically generated hypobromite were carried out with a universal OH-404 coulometric analyzer (Radelkis, Budapest) in amperostatic

mode and with biamperometric end-point detection. The working electrode used was an OH-934 platinum electrode (Radelkis) with a surface area of $5.0\,cm^2$. The auxiliary electrode was a cylindrical carbon electrode separated from the analyzed solution with a fine glass frit.

All potentials in this work are referred to the potential of the saturated calomel electrode.

Coulometric measurements at constant potential were performed with a GWP 673 multipurpose electrochemical instrument (Academy of Sciences, Berlin) using Britton —Robinson buffer solutions. The design of the PTFE coulometric cell [7] guaranteed a symmetrical potential distribution on the macroelectrode and a high electrolysis efficiency. The working electrode used was a cylindrical SU-110 graphite electrode (Elektrokarbon, Topoľčany) with an active surface of $35.3\,cm^2$. This electrode served also for the mixing of the analyzed solution. As the reference electrode a calomel electrode with NaCl solution ($4\,mol\,dm^{-3}$) was used. The auxiliary electrode was constructed from 6 cylindrical carbon electrodes (diameter 4.05 mm, length 45 mm) bound and interconnected in two levels with platinum wires to give a crown-like ring [7] with Pt wire contact.

Spectrophotometric measurements were carried out on Spekol and Specord UV VIS spectrophotometers (Zeiss, Jena).

Results and discussion

Redox properties of bis(2-hydroxyethyl)dithiocarbamate anion

The electrochemical properties of potassium bis(2-hydroxyethyl)dithiocarbamate (*I*) were studied in neutral and alkaline solutions. In acidic solutions, due to the rapid decomposition of the above compound to the corresponding amine and carbon disulfide, no reproducible results were obtained. For comparison the redox properties of sodium diethyldithiocarbamate (*II*) were also studied.
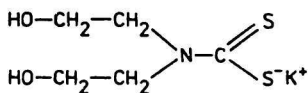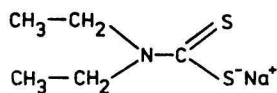
I   *II*

Cyclic voltammetric *I*—*E* curves (Fig. 1) indicate a three-step oxidation of *I*. The peak heights and position show a strong pH dependence. The second

oxidation peak of *II* is not distinct and in nonaqueous media it cannot even be observed at all [8]. After preceding anodic oxidation of *I* and *II* a peak due to the cathodic reduction was observed on the voltammetric curves (Fig. 1).
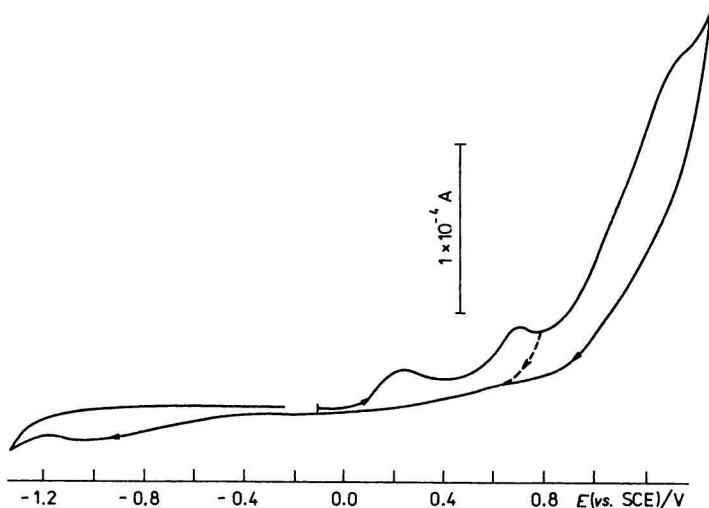

Fig. 1. Cyclic voltammetric *I—E* curves of the species *I* ($c = 5 \times 10^{-4}$ mol dm^{-3}); pH = 7.0; scan-rate 66.7 mV s^{-1}.

The dependence of anodic peaks currents and potentials on the concentration of *I* and *II* was also studied. The obtained concentration dependences were linear in a concentration range from 5×10^{-5} to 1×10^{-3} mol dm^{-3}. The E_p values were not influenced by concentration changes.

The pH dependences of oxidation peak potentials and currents for *I* are significantly different from those for *II* (Fig. 2 and Table 1). The first oxidation
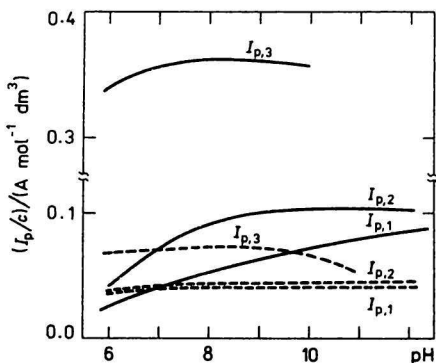

Fig. 2. Dependence of I_p/c on pH. Full line — species *I* ($c = 5 \times 10^{-4}$ mol dm^{-3}); dashed line — species *II* ($c = 2 \times 10^{-4}$ mol dm^{-3}); scan-rate 66.7 mV s^{-1}.

Table 1

Oxidation peak potentials of the bis(2-hydroxyethyl)dithiocarbamate anion ($c = 5 \times 10^{-4}$ mol dm^{-3}) and its Ni(II) complex
($c = 5 \times 10^{-5}$ mol dm^{-3})^a

pH	Ligand				Complex				
	Oxidation			Reduction	Oxidation		Reduction		
	$E_{p,1}/V$	$E_{p,2}/V$	$E_{p,3}/V$	E_p/V	$E_{p,1}/V$	$E_{p,2}/V$	$E_{p,1}/V$	$E_{p,2}/V$	$E_{p,3}/V$
2.0					0.551	0.771	−0.061	−0.291	—
3.0					0.550	0.778	−0.038	−0.286	—
4.0					0.601	0.815	−0.055	−0.291	—
5.0					0.501	0.850	−0.060	−0.302	—
6.0	0.145	0.731	1.238	−0.920					
	0.245^b	0.725^b	1.170^b	−0.900^b	0.551	0.805	—	—	−0.805
8.0	0.230	0.730	1.292	−0.925					
	0.248^b	0.720^b	1.173^b	−0.905^b	0.548	0.975	—	—	−0.862
11.0	0.282	0.730	—	−0.915					
	0.250^b	0.721^b	1.180^b	−0.905^b	0.486	—	—	—	−0.835

*a*) Scan-rate 66.7 mV s^{-1}; *b*) diethyldithiocarbamato ligand ($c = 2 \times 10^{-4}$ mol dm^{-3}) used for comparison.

peak of I is shifted to more positive potentials when increasing pH. A significant current increase is observed at the same time (Fig. 2). The first step of probably any dithiocarbamate anion oxidation is evidently a one-electron oxidation. As for other dithiocarbamates [2] we can assume also in the case of the oxidation of I the formation of a dithiocarbamate radical which rapidly dimerizes to N,N,N',N'-tetra(2-hydroxyethyl)thiuram disulfide (III)

$$R_2NCS_2^- - e^- \rightarrow R_2NCS_2^{\bullet} \tag{A}$$

$$2R_2NCS_2^{\bullet} \rightarrow (R_2NCS_2)_2 \tag{B}$$
$$(III)$$
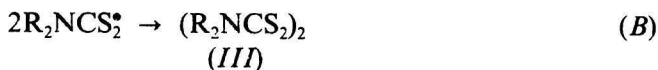
Unlike the diethyl derivative the oxidation peak potential of I increases when increasing pH. It is probably due to the presence of OH groups in I. Owing to some acidic properties of these groups, they can easily form hydrogen bonds with solvent molecules. Due to these interactions the delocalization of the lone electron pair on nitrogen atom is diminished and the resulting electron density decrease on sulfur atoms enables an oxidation at higher potentials only. At pH > 8 the peak position is evidently not pH-dependent.

The current of the first oxidation peak is practically not pH-dependent, which is in good agreement with reactions according to eqns (A) and (B). The enhancement of oxidation peak current of I when increasing pH can be accounted for by a formation of further electroactive species arising from a chemical reaction of the electrode reaction product. Such a reaction is probably the disproportionation of III according to eqn (C). The formation of colloidal sulfur when performing electrolysis at a potential beyond the first oxidation peak proved this assumption

$$(R_2NCS_2)_2 + 2OH^- \rightarrow R_2NCS_2^- + R_2NCOS^- + H_2O + S^0 \tag{C}$$
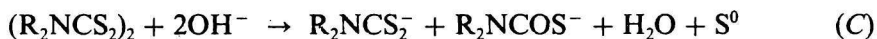
Similarly, colloidal sulfur is immediately precipitated on adding sodium hydroxide solution to III.

The released dithiocarbamate anion undergoes again an electrode reaction producing thiuram disulfide. The current intensity depends on the rate of the reaction according to eqn (C). The disproportionation can be accounted for by an interaction of OH^- anions with the carbon atom in the —CS_2— group. Due to the presence of —OH groups in I the partial positive charge on carbon atoms of III is larger than that in tetraethylthiuram disulfide, therefore III can more easily interact with OH^- ions than tetraethylthiuram disulfide. The difference in current intensities for both derivatives could also be influenced by higher solubility of III compared with that for tetraethylthiuram disulfide.

In aqueous alkaline solutions a second oxidation peak of I is observed at potentials 400 to 500 mV more positive than the potential of the first anodic

peak. Since this peak was not observed in nonaqueous media it probably originates in a reaction according to eqn (C) which was observed in aqueous alkaline solutions only. An oxidation of the monothiocarbamate anion could take place here. Owing to the lower polarizability of this anion due to the presence of an oxygen atom instead of a sulfur atom, it is oxidized not so easily as the dithiocarbamate anion. The pH dependence of the peak potential can be interpreted similarly as that for the first oxidation peak.

The current of the second oxidation peak increases rapidly when increasing pH and beyond pH = 8 it is approaching to a limiting value (Fig. 2). The origin of the second oxidation peak can be explained analogically as that of the first one

$$R_2NCOS^- - e^- \rightarrow R_2NCOS^\bullet \qquad (D)$$

$$2R_2NCOS^\bullet \rightarrow (R_2NCOS)_2 \qquad (E)$$
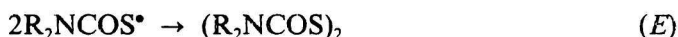
The second oxidation peak for the diethyl derivative is not distinct, which is probably due to the lower rate of reaction according to eqn (C).

In both aqueous and nonaqueous solutions a further poorly distinct peak is observed at potentials about 0.8 to 1.0 V more positive than the potential of the first oxidation peak. In nonaqueous solution this peak belongs to electrochemical oxidation of thiuram disulfide to various oxidized species [9]. As imply IR spectroscopic measurements [10], in aqueous solutions the possible electrode reaction product is bis(di(2-hydroxyethyl)carbamyl) disulfide (IV)

$$(R_2NCS_2)_2 - 4e^- + 4OH^- \rightarrow (R_2NCOS)_2 + 2S^0 + 2H_2O \qquad (F)$$
$$(IV)$$
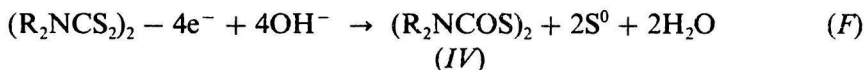
Assuming a reaction according to eqn (C) at higher pH values the high current values of the third oxidation peak are not reasonably explained by a reaction according to eqn (F) and this peak should involve therefore a deeper oxidation of IV, too.

Peaks of cathodic reduction on the voltammetric I—E curves of I appeared only after its previous anodic oxidation. The reduction currents increased when the electrode was let polarized some time (3—5 min) at a potential beyond the second oxidation peak. The peaks of cathodic reduction belong to the reduction of elemental sulfur formed in reactions according to eqns (C) and (F) [8].

Total oxidation with hypobromite

A mild oxidation of I produces low soluble thiuram disulfide. The total oxidation of I can be utilized to its sensitive determination since such a reaction involves a large number of electrons exchanged. For this purpose hypobromite

was chosen as an oxidant. The important advantage of coulometric determination of dithiocarbamates using hypobromite is in the possibility to proceed in slightly alkaline solutions where dithiocarbamates are stable.

In weakly alkaline solutions (tetraborate buffer solutions) 8 moles of hypobromite are consumed for the oxidation of 1 mole of I, the number of exchanged electrons being 16

$$R_2NCS_2^- + 8BrO^- + 4OH^- \rightarrow R_2NH + 2SO_4^{2-} + HCO_3^- + 8Br^- + H_2O \; (G)$$
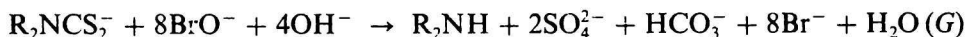
The stoichiometry of this reaction was checked by nephelometric determination of sulfate anions with Ba^{2+} in the reaction mixture.

Table 2

Results of coulometric titrations of I*

Given	Found						
$\dfrac{m}{\mu g}$	$\dfrac{m}{\mu g}$	$\dfrac{\varepsilon}{\%}$	$\dfrac{s}{\mu g}$	$\dfrac{RSD}{\%}$	$\dfrac{\tau}{\%}$	$\dfrac{I_{gen}}{mA\,cm^{-2}}$
6.85	7.04	+2.77	0.854	12.1	17.1	0.15
13.71	13.55	−1.17	0.873	6.44	9.13	0.2
27.42	27.62	+0.73	1.328	4.81	6.82	0.3
41.13	41.48	+0.85	1.468	3.54	5.13	0.3
68.55	69.11	+0.82	1.608	2.33	3.29	0.4
137.1	137.2	+0.07	2.176	1.59	2.23	0.4
274.2	271.9	−0.84	4.335	1.59	2.30	0.7
411.3	408.2	−0.75	7.800	1.91	2.75	0.8
685.5	680.3	−0.76	14.49	2.13	3.01	1.0

* ε — relative error, s — standard deviation, RSD — relative standard deviation, τ — relative width of the confidence interval, $n = n_S = n_B = 10$ (n_S — number of sample titrations, n_B — number of blank titrations), current density at biamperometric end-point indication $I_{ind} = 2\,\mu A\,cm^{-2}$.
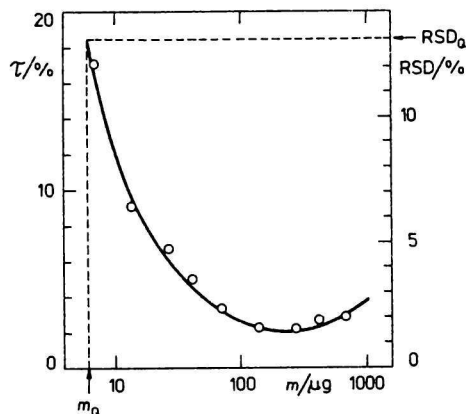

Fig. 3. Dependence of the relative width of the confidence interval τ and relative standard deviation RSD of the species I coulometric determination on the amount of I. Limit of determination $m_Q = 6.31\,\mu g$ calculated [11] using relationship $RSD_Q = 100/k_Q$ where $k_Q = 3t_{v,a}$, $v = 2n - 2$, $\alpha = 0.02$ (one-sided t-test) for 99.0 % probability.

The results obtained in coulometric titrations are listed in Table 2. The relative precision of the results expressed as the relative confidence interval τ and relative standard deviation RSD, respectively, is significantly dependent on the concentration of I (Fig. 3). The most precise and correct results were obtained for a content of $Im = 200\,\mu g$ (about $0.9\,\mu mol$) in the sample. The most suitable generating current densities for various I amounts are also listed in Table 2. The optimum indication current density was $2\,\mu A\,cm^{-2}$ and the polarization potential used for the indication electrodes was $150\,mV$.

Synthesis and properties of nickel(II) bis(di(2-hydroxyethyl)dithiocarbamate)

Nickel(II) bis(di(2-hydroxyethyl)dithiocarbamate) ([NiL_2]) was prepared as described in Experimental. The complex is readily soluble in dimethylformamide and slightly soluble in chloroform. Its solubility in methanol and water is about $10^{-4}\,mol\,dm^{-3}$. The solutions of [NiL_2] in nonaqueous solutions were stable at least for several weeks. In aqueous solutions the stability of the complex is significantly dependent on pH. The complex is rather stable in neutral and slightly alkaline solutions. On acidifying these solutions a rapid decomposition of the complex is observed with carbon disulfide, amine, and Ni^{2+} ions being released. The hydrolysis rate is strongly dependent on the H^+ ion concentration. Owing to this the acidic solutions of [NiL_2] were prepared immediately before the measurement.

In the UV region of the absorption spectrum of [NiL_2], as for other Ni(II) dithiocarbamato complexes, intensive absorption bands corresponding to inner-ligand $\pi \rightarrow \pi^*$ transfers are observed at $\lambda = 218\,nm$ and $\lambda = 245\,nm$. The next band at $\lambda = 336\,nm$ is assigned to metal to ligand charge transfer. In the near UV and VIS regions further bands corresponding to L $\rightarrow$ M type charge transfer ($\lambda = 395\,nm$) and less intensive d—d transfers ($\lambda = 490\,nm$ and $\lambda = 650\,nm$) [12] are observed.

The voltammetric behaviour of the [NiL_2] complex was followed in solutions with pH 2 to 10.

In the pH region of 2 to 5 at anodic polarization two oxidation peaks are observed. The position and height of the peaks is influenced negligibly by pH changes (Table 1). The difference $E_p - E_{p/2}$ is constant having a value of $150\,mV$. The second oxidation peak is observed at potentials at least $200\,mV$ more positive than the first one. Its position is, however, significantly shifted to more positive potentials when increasing pH. On polarizing the working electrode at a potential beyond the first anodic peak for some minutes the solution in its vicinity turned brown. After irradiating this solution with an intensive white light the original colour of the solution was renewed. An increase in current of the first anodic peak is dependent on the increase of pH.

No reduction waves were observed at an initial cathodic sweep, however, at cathodic polarization after a preceding anodic sweep two counterpeaks arose, one being 230 mV far from the other (Fig. 4).

The photochromism of the product formed at the first anodic peak implies [13] the formation of a complex of the type $[Ni(IV)L_3]^+$

$$3[Ni(II)L_2] - 4e^- \rightarrow 2[Ni(IV)L_3]^+ + Ni^{2+} \qquad (H)$$
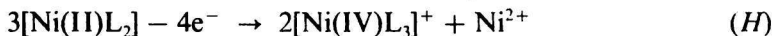
The second anodic peak belongs to a deeper oxidation of dithiocarbamato ligands (see above).

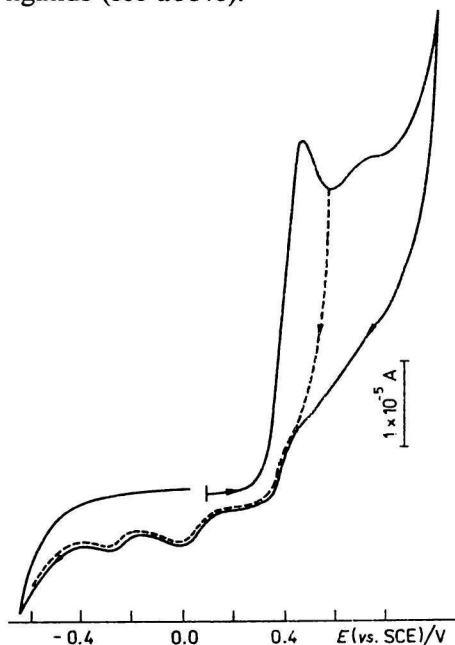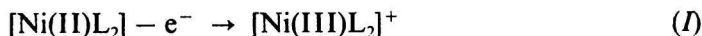
Fig. 4. Cyclic voltammetric $I—E$ curves of $[NiL_2]$ $(c = 5 \times 10^{-5}\, mol\, dm^{-3})$; pH = 5.0; scan-rate 66.7 mV s^{-1}.

The mechanism of the reaction according to eqn (H) has not been fully explained yet. The results of EPR measurements [5] and a comparison of the above observations with the chemical oxidation of Ni(II) dithiocarbamato complexes [3] imply the formation of a paramagnetic complex of the type $[Ni(III)L_2]^+$ in the first reaction step. The consecutive reaction steps probably involve the formation of a more stable tris-complex [14] followed by a disproportionation reaction

$$[Ni(II)L_2] - e^- \rightarrow [Ni(III)L_2]^+ \qquad (I)$$

$$[Ni(III)L_2]^+ + [Ni(II)L_2] \rightarrow [Ni(III)L_3] + [Ni(II)L]^+ \qquad (J)$$

$$[Ni(III)L_3] + [Ni(III)L_2]^+ \rightarrow [Ni(IV)L_3]^+ + [Ni(II)L_2] \qquad (K)$$

$$2[Ni(II)L]^+ \rightarrow [Ni(II)L_2] + Ni^{2+} \qquad (L)$$

Another possible route is *via* electrochemical oxidation of the $[Ni(III)L_3]$ intermediate

$$[Ni(III)L_3] - e^- \rightarrow [Ni(IV)L_3]^+ \qquad (M)$$
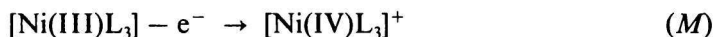
Owing to a rather low $[Ni(III)L_2]^+$ concentration the reaction pathway according to eqn (M) is more preferable than the pathway considering a reaction of $[Ni(III)L_3]$ and $[Ni(III)L_2]^+$ (eqn (K)).

In solutions with pH > 6 two anodic peaks were observed on voltammetric I—E curves, one at 0.55 V, the other in the region of 0.8 to 1.0 V. The cathodic counterpeaks observed in more acidic solutions did not appear in these solutions (Fig. 5). A single reduction wave at -0.85 V was observed when reducing the complex.
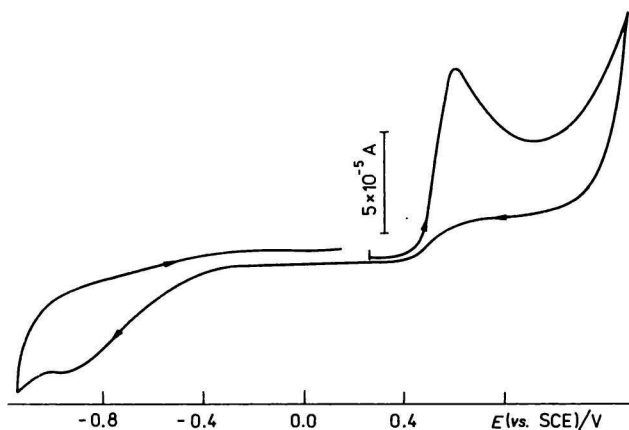

Fig. 5. Cyclic voltammetric I—E curves of $[NiL_2]$ ($c = 5 \times 10^{-5}$ mol dm^{-3}); pH = 7.0; scan-rate 66.7 mV s^{-1}.

Using potentiostatic coulometry at a potential 100 mV more positive than the first anodic peak the number of exchanged electrons was obtained, $z_1 = 2$. By means of UV spectrum assignment thiuram disulfide was identified in the electrolyzed solution.

In ammonia buffer solution (pH = 10) of $[NiL_2]$ one anodic peak at $+0.51$ V (the second one was obscured by the base electrolyte signal) and two cathodic peaks at -0.58 V and -0.94 V were observed. The last ones obviously belong to a two-step reduction of Ni(II) to Ni(I) and Ni(I) to Ni(0). The ratio of electrons exchanged in the first and second reduction step was determined from chronoamperometric measurements and was found 2:1.

The first anodic peak can be assigned to the formation of thiuram disulfide

$$[Ni(R_2NCS_2)_2] - 2e^- \rightarrow Ni^{2+} + (R_2NCS_2)_2 \qquad (N)$$
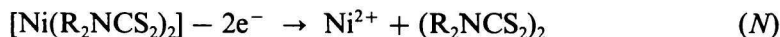
The second anodic peak is coupled with further oxidation of thiuram disulfide in analogy with the third anodic peak of the free ligand. Unlike the acidic solutions, in neutral and alkaline solutions not the central atom in [NiL$_2$] but the ligands are oxidized. Similar results were obtained at chemical oxidation of the Ni(II) bis(dithiocarbamato) complexes [15].

The potential and current of the first anodic peak are not significantly influenced by pH. The oxidation of bounded dithiocarbamato ligands in the Ni(II) complex obviously follows another pathway than that for free ligands. There is probably no replacement of sulfur atoms by oxygen atoms in ligands bound to the central atom. Thus the central atom possesses a decisive role in the oxidation pathway and furthermore a preceding oxidation of Ni(II) to Ni(III) followed by a rapid oxidation of ligands by Ni(III) is possible.

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