Modern Electroanalytical Methods

An International Conference to Mark the 40th Anniversary of the Award of the Nobel Prize to Professor Jaroslav Heyrovský, September 19 - 23, 1999, *Juniorcentrum* Seč, Czech Republic

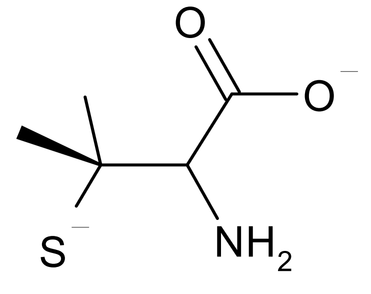
Poster PO / 2

ELECTROANALYTICAL INVESTIGATIONS IN THE NICKEL(II) – PENICILLAMINE SYSTEM

Florinel Gabriel Bănică[1] and Ana Ion[2]

1) Department of Chemistry, Faculty of Chemistry and Biology,
Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway
2) Department of Analytical Chemistry an Instrumental Analysis, Faculty of Industrial Chemistry, POLITEHNICA University of Bucharest, Calea Griviței 132, Bucharest, Romania

1. INTRODUCTION



Penicillamine (Pen, L^{2-})

PENICILLAMINE STRUCTURE - related to that of the naturally occurring amino acid **Cysteine** (**CySH**). **Pen** is a product of penicillin alkaline hydrolysis

BIOLOGICAL RELEVANCE

- Used as a drug for Wilson disease, rheumatoid arthritis, and cystinuria.
- Antidote in heavy metal poisoning (including **Ni(II)** intoxication) owing to its chelating properties.

Ni(II) COMPLEXATION BY PEN

Like Cys, Pen form square planar complexes involving *N, S* coordination. The steric hindrance due to the methyl substituents prevents the formation of polynuclear complexes, as it happens in the case of Cys or cysteamine. That is why the complexation scheme in the case of Ni(II) – Pen system involves only two species: [NiL] and $[NiL_2]^{2-}$.

AIM OF THIS WORK

Investigation of the cathodic electrode processes in the Ni(II)-Pen system by making appropriate correlations between the parameters of the polarograhic waves and complex species concentrations calculated by means of available equilibrium constants (D. D. Perin et al., *J. Chem. Soc. A* **1968**, 53).

EXPERIMENTAL METHOD: DC polarography

Author's papers related to this topic

- Ion A., Bănică F. G., Luca C.: *Collect. Czech. Chem. Commun*. **63** (1998) 187.
- Bănică F. G., Ion A., Collect. *Czech. Chem. Commun*. **63** (1998) 995.
- Bănică F. G., Ion A., Collect. *Czech. Chem. Commun*. **65** (2000) 995.

Other related publications

- F. G. Banica, A. G. Fogg, A. Ion, J. C. Moreira, "Cathodic stripping voltammetry of sulphur-containing amino acids and peptides in the presence of nickel ion. Catalytic and inhibiting effects". *Analyt. Lett.*, **29**, 1415 (1996).

- Ion, F. G. Banica, A.G. Fogg, H. Kozlowski, "Cathodic stripping voltammetry of D-penicillamine and N- acetylcysteine in the presence of nickel ion." *Electroanalysis*, **8**, 40 (1996).

2. POLAROGRAPHIC CATHODIC WAVES IN THE Ni(II) – Pen SYSTEM

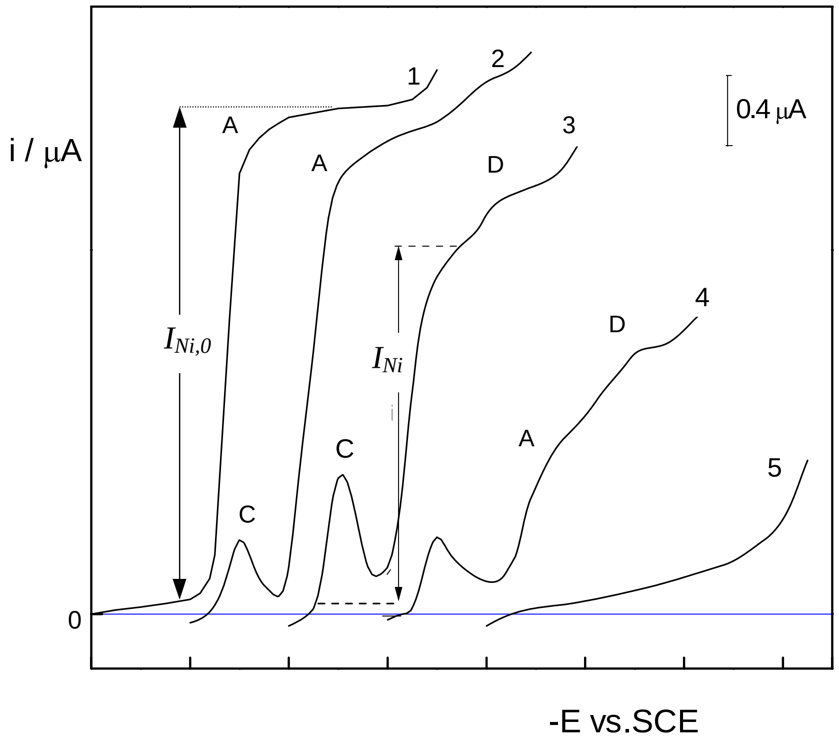


FIG. 1. Effect of Pen concentration on the nickel waves at pH 6.52 in the phosphate-acetate buffer. Ni^{2+}, 0.6 mM. Pen (mM): 1) 0; 2) 0.12; 3) 0.44; 4) 0.87; 5) 1.4. Initial potential, -0.400 V; abscissa scale, -0.400 V/div.

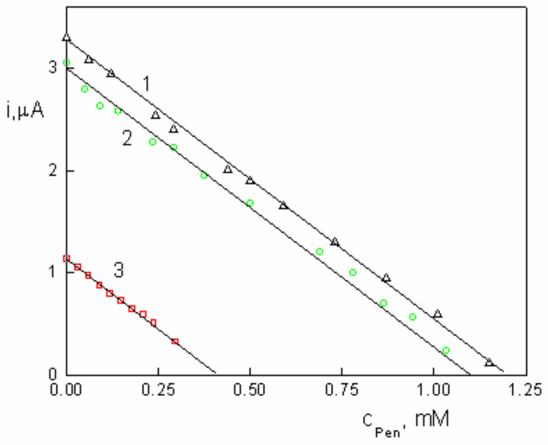
Waves assignation

A: Ni^{2+} reduction (diffusion controlled)
C: Catalytic Ni(II) Pre-wave (CNiP)
D: Catalytic Hydrogen Pre-wave (CHP)

Penicillamine effect in Ni(II) polarography

- Decrease in wave A limiting current till complete disappearance at a slight excess of Pen
- Occurrence of the catalytic Ni(II) and H$^+$ waves in the same way as in the Ni(II) –CySH system
- In contrast with the CySH system, both catalytic waves vanish at a slight excess of Pen.

3. Pen EFFECTS ON THE Ni(II) DIFFUSION WAVE



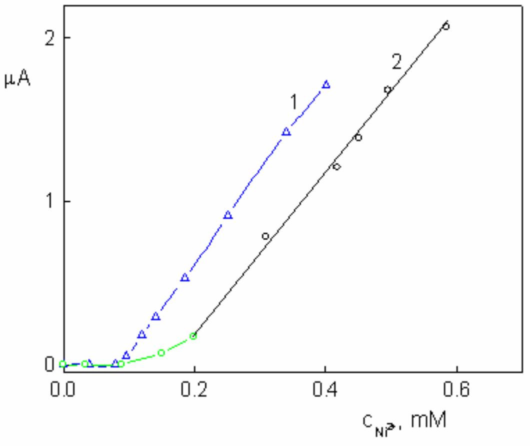


FIG. 2. Effect of Pen concentration on nickel diffusion current in the phosphate - acetate buffer at pH 6.52. Ni^{2+} (mM): 1) 0.59_5; 2) 0.57; 3) 0.20.

FIG. 3. Effect of Ni^{2+} concentration on the diffusion current at constant pH (6.52) and various Pen concentration: **0.2 mM Pen** (curve 1); **0.5 mM Pen** (curve 2).

Comments

In the presence of Pen, Ni(II) diffusion wave occurs only if [Pen]/[Ni(II)] < 2.It results that the [NiL$_2$]$^{2-}$ species is both chemically and electrochemically inert, in contrast with the pertinent CySH complex, which is labile. Wave A current is proportional to the sum concentrations of Ni^{2+} and [NiL] species.

4. Ni^{2+} REDUCTION CATALYZED BY Pen (WAVE C, Fig. 1)

Objective: Finding the composition of the nickel complex, which acts as the electron acceptor in the catalytic nickel reduction.

Procedure: Compare the effects of the experimental parameter on wave current and nickel species distribution.

FIG. 4

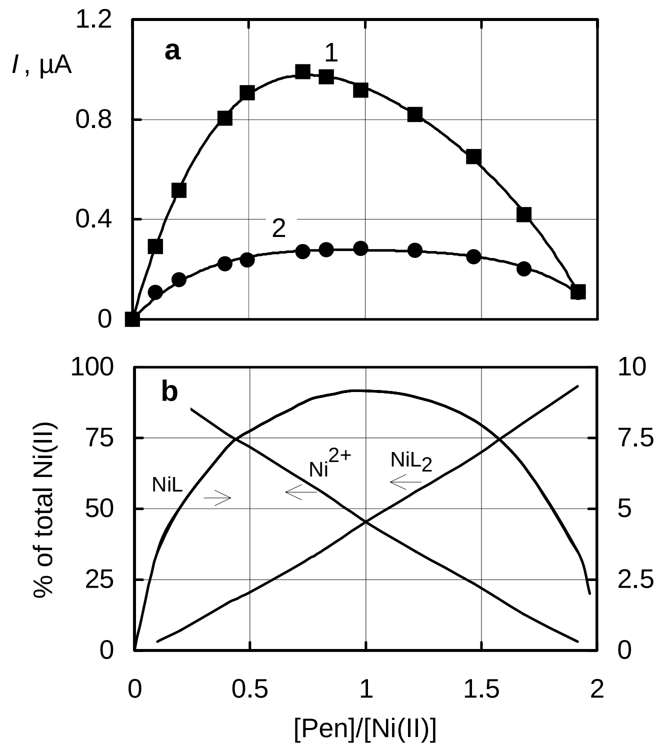


FIG. 4. Effect of the [Pen]/ $[Ni^{2+}]_t$ ratio at constant $[Ni(II)]_t$ (0.6 mmol l^{-1}) and pH 6.52. a) Wave C current. *1*) Experimental; *2*) hypothetical diffusion current of [NiL]. b) Nickel species distribution under the same conditions.

Rem.: Wave C current curve parallel the change in [NiL] concentration. The current (curve 1) is much higher than the expected diffusion current of [NiL] (curve 2) proving the **catalytic character** of this wave.

FIG. 5

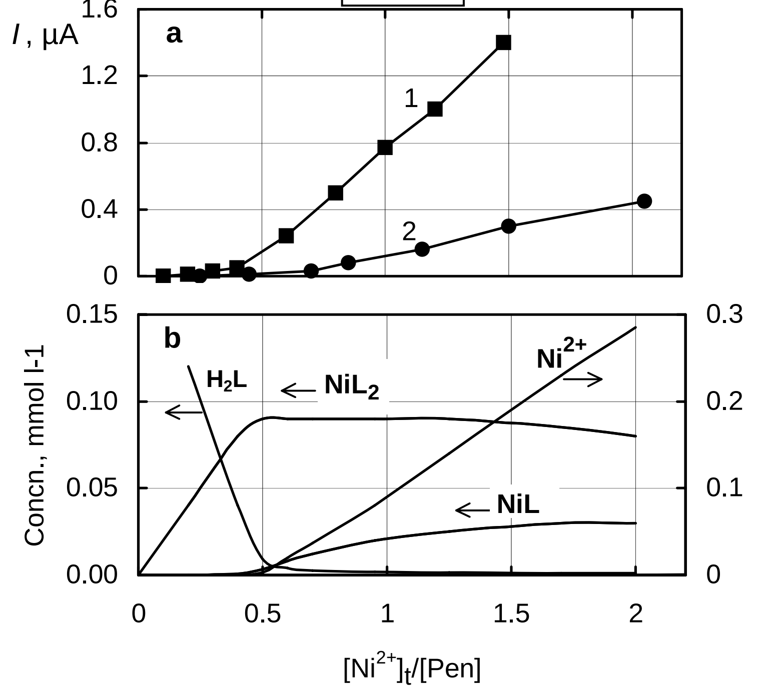


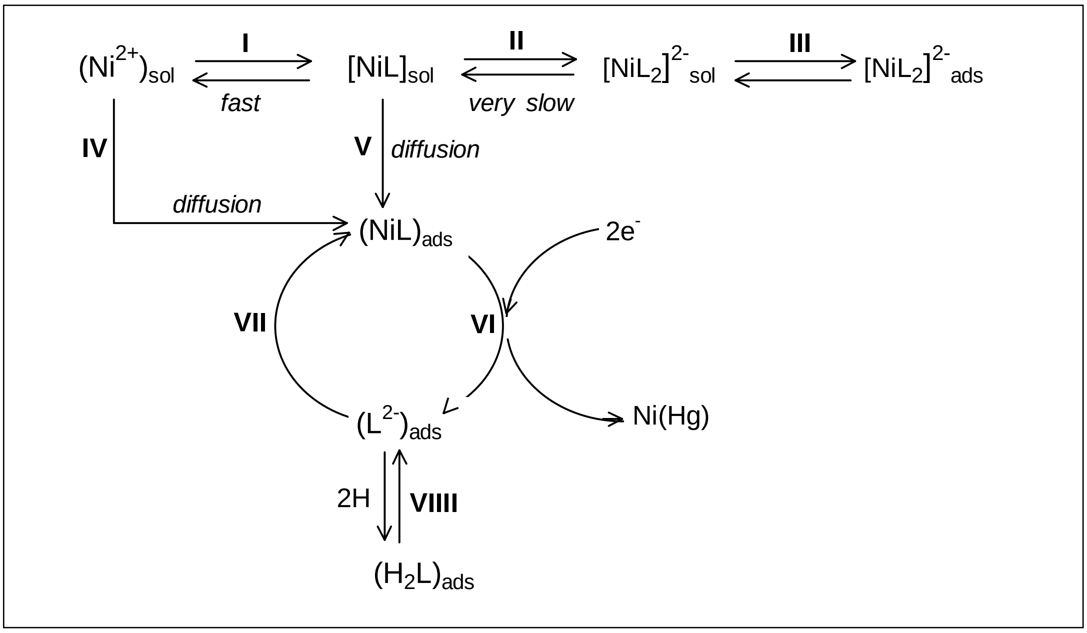
FIG. 5. Effect of the $[Ni^{2+}]_t$/[Pen] ratio at pH 6.52. a) CNiP current; Pen: *1*) 0.5; *2*) 0.2 mmol l^{-1}. b) Nickel species distribution at 0.2 mmol l^{-1} Pen.

CONCLUSIONS

The complex form that is reduced in the potential region of the wave C is **[NiL]** (Section 5).

An analogous complex take part in the CNiP induced by CySH. The main difference consists in the capacity of the **labile** $[Ni(CyS^-)_2]^{2-}$ complex to provide nickel ions that enter the catalytic process.

5. REACTION MECHANISM FOR Ni(II) REDUCTION CATALYZED BY Pen



SOME IMPORTANT FEATURES

- Catalytic nickel reduction occurs in the absence of the free ligand. Occurrence of the free ligand implies masking of nickel in the form of the inert $[NiL_2]^{2-}$ complex.

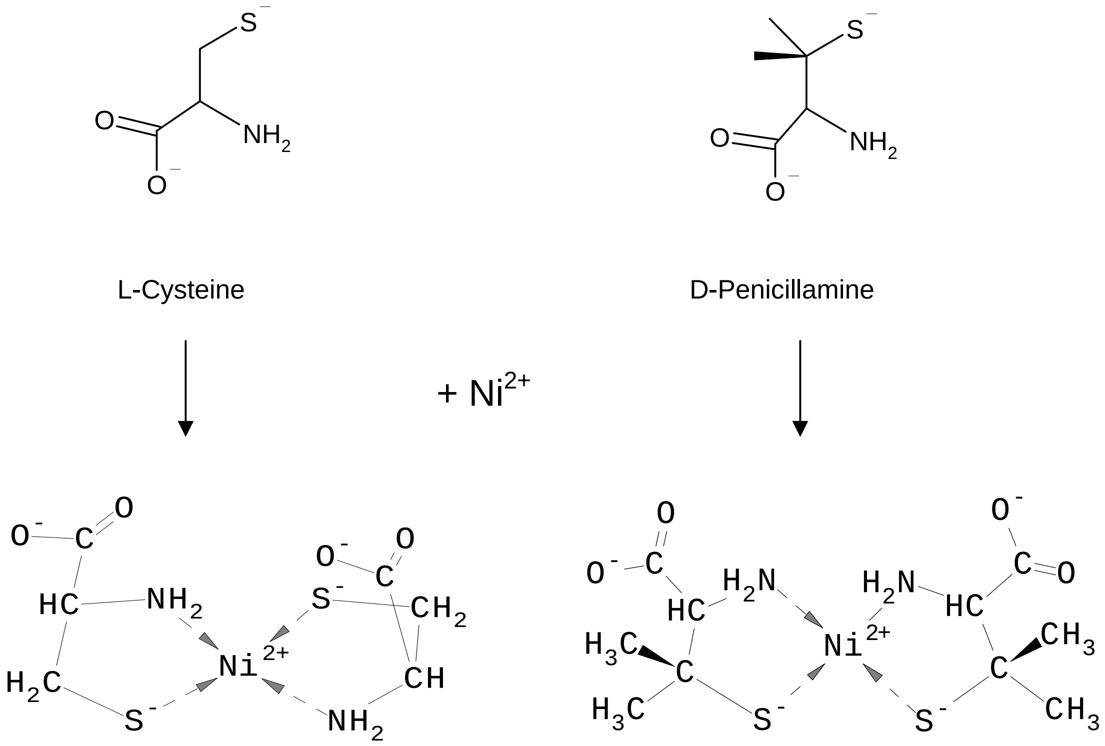
- Reduction occurs in the adsorbed state, as proven by electrocapillary curves (not shown). The surface coverage strongly decreases while shifting the potential in the negative direction. This account for the particular shape of the catalytic nickel wave (Fig. 1) and also makes the peak C current not to be an actual limiting current.

- The process is initiated by the reduction of $[NiL]_{ads}$ (step VI) that is followed by the regeneration of the reducible species (step VII) with the participation of the Ni^{2+} ion. Ni^{2+} diffusion (VI) could be influence the overall reaction rate provided the wave C current is higher than about 20% of nickel diffusion current (wave A).

- The maximum catalytic nickel currents depends on (1) [NiL] concentration in the bulk of the solution; (2) reaction rate for the step (VII); rate of Ni^{2+} transport towards electrode surface; (3) surface coverage by the catalyst, both as free molecule and bound in the nickel complex.

6. Pen AND CySH AS AGENTS FOR Ni(II) DETOXIFICATION

Previous data on the **kinetic stability** of $[NiL_2]^{2-}$ complexes (where L states for either cysteine or penicillamine) provide a rationale for understanding the mechanism of Ni(II) detoxification by a chelating agent.



log β_2 = 20.158

Labile complex:

$[NiL_2] \rightarrow Ni^{2+} + 2\,L^{2-}$ (very **fast**)

Poor detoxifying effect

log β_2 = 22.886

Inert complex:

$[NiL_2] \rightarrow Ni^{2+} + 2\,L^{2-}$ (extremely **slow**)

Strong detoxifying effect

(**Sources**: complexes structures: N. Baidya et al., *Inorg. Chem.*, **1991**, *30*, 2448; 3967; formation constants: D. D. Perin, *J. Chem. Soc. A* **1968**, 53).

Comments. Despite the close values of the formation constants for the pertinent Ni(II) complexes, Pen proved to be much more efficient than CySH in nickel detoxification (M.M. Jones et al., *J. Inorg. Nucl. Chem*. **1981**, 43, 1705). This difference can be accounted for by the extremely high kinetic stability of the Pen complex, as demonstrated in this work. **Consequently, kinetic rather than thermodynamic stability of the nickel complex may be responsible for the detoxifying capacity**.

The inert character of the nickel complex with the chelating agent may be the answer to the puzzling conclusion that “there seems no definite relationship exists between the structure of the chelating agent examined and their ability to counteract the [toxic] effects of nickel” (S. K. Tandon et al. *Fund. Appl. Toxicol.*, **1996**, *31*, 141).

7. CATALYTIC HYDROGEN PRE-WAVE (WAVE D IN Fig. 1)

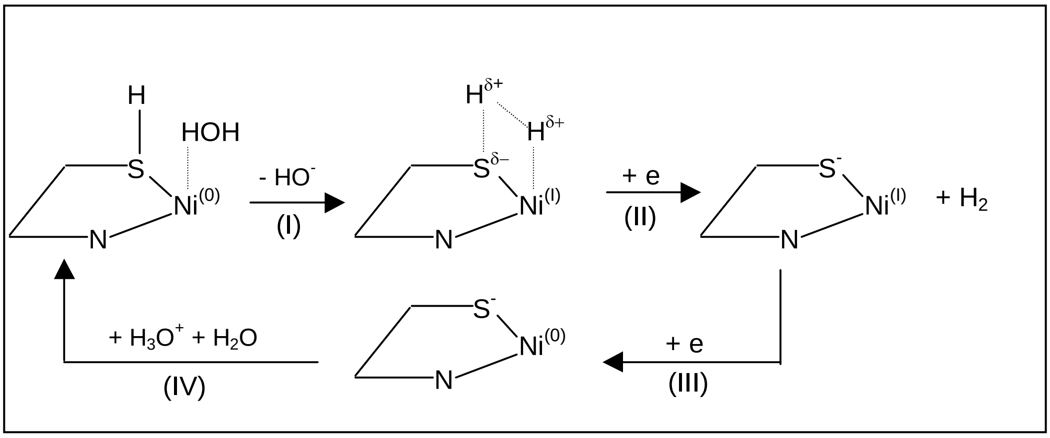
The CHP occurs in the presence of Ni(II) and a ligand like CySH or some of its derivatives and analogous, including Se-cysteine. The Table below summarizes the main characteristics of the CHP and point out the fundamental distinctions of the CHP as compared with the *Brdička* catalytic hydrogen wave produced by thiol ligands in the presence of Co(II) or Ni(II).

A COMPARISON OF THE *CHP* AND *BRDIČKA* WAVE

Parameter	***Catalytic Hydrogen Pre-wave***	***Brdička Wave***
Shape	In accord with the equation of the **irreversible wave**, with a distinct limiting current (Fig. 1, wave D)	**Maximum shaped**; no distinct limiting current occurs.
Characteristic potential	$E_{1/2}$ between **-1.2 and -1.3 V** vs. SCE, slightly dependent on the ligand structure. For a given ligand, $E_{1/2}$ is almost independent on pH and ligand concentration	Maximum potential at about **-1.6** V
Ligand structure	The occurrence of vicinal -SH and $-NH_2$ functions is compulsory	Beside the -SH function, a second coordinating group (e.g. $-NH_2$, $-COO^-$ or -SH) must be present to form a 5 member chelate ring with Co^{2+}. Exceptions: non-sulfur ligand.
Metal ion effect	The typical behavior is observed in the presence of Ni(II). Co(II) induces analogous patterns, but additional processes occur and make the polarograms more complicate	Both Co(II) and Ni(II) give the Brdička wave, but, under identical conditions, the wave current is higher for Co(II).
Optimum pH range	Around **7** (acetate or acetate-phosphate buffer); the CHP vanishes at pH > 8 and pH < 5	Around **9.5** (ammonia or borate buffer)
Interface effects	No adsorption detected in the potential region of the CHP.	No direct proof for adsorption, but it is assumed that the shape of the wave is due to the potential effect on the surface concentration of the ligand.

Conclusions resulting from the investigation of the CHP yielded by Pen:

- CHP occurrence depends on the presence of the **[NiL] complex**. Formation of $[NiL_2]^{2-}$ results in CHP current depression. CHP vanishes when a slight excess of Pen brings about the conversion of all existing Ni(II) into the $[NiL_2]^{2-}$ form.
- The close analogy of the CHP yielded by Pen and CySH allows one to infer that the same kind of complex is responsible for the occurrence of the CHP in the presence of the last one, although the $[Ni(CyS^{2-})_2]^{2-}$ is labile and some polynuclear complexes also occurs in this case.
- The CHP is a fair model process for **hydrogen reduction catalyzed by Ni-containing hydrogenases.**



Catalytic Hydrogen Pre-wave: Proposed Mechanism