Journal of Electroanalytical Chemistry 637 (2009) 55–62

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Interaction of niacin with nickel(II) ions

Jadwiga Urbańska, Halina Podsiadły *

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland

ARTICLE INFO

Article history:
Received 20 July 2009
Received in revised form 15 September 2009
Accepted 28 September 2009
Available online 2 October 2009

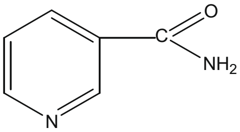
Keywords:
Nickel(II) complexes
Nicotinamide
Nicotinic acid
Stability constants
Electrode reduction mechanism

ABSTRACT

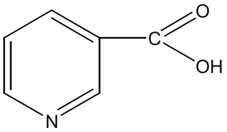
The interaction of Ni(II) ions with nicotinamide and nicotinic acid in aqueous solution were examined by potentiometric, dc polarographic and spectroscopic techniques. The stoichiometry of the species reduced on a mercury electrode, and their electrochemical parameters were determined. In both systems the ML complex is reduced on the electrode at less negative values of potentials and more reversible than aquaion of Ni(II). The stability constants of the nicotinate and nicotinamide complexes were determined in 0.1 M $NaClO_4$ and 20 °C. It was shown that the polarographic technique is able to detect the complex species which are not seen in potentiometric titration and to determine its stability constants as well as potentiometric method. The relationship between the complex structure and its electrochemical reactivity is also discussed.

1. Introduction

Niacin, a water-soluble type of vitamin B, is generic name for both nicotinic acid (pyridine 3-carboxylic acid) and nicotinamide (pyridine 3-carboxylic acid amide). Although the two compounds are identical in their vitamin functions, their pharmacological and toxic effects are different.



Nicotinamide (ANA)



Nicotinic acid (HNA)

Nicotinic acid is not free in the body. It is converted *in vivo* to nicotinamide which is a component of two related coenzymes: nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) indispensable for enzymatic catalysis of several vitally important redox processes.

Niacin has unique pharmacological properties. Research has demonstrated its remarkable benefits for arthritis, asthma, diabetes, heart disease, stress, stroke and recently as an anti-aging nutrient [1–4].

Nicotinamide itself is mainly used to treat the vitamin deficiency syndrome known as pellagra and is an effective agent in treating some neurodegenerative diseases [5].

Nicotinamide and nicotinic acid can interact with a number of metal ions. Therefore the interaction of transition and heavy metal ions with these ligands is important for evaluating their potential beneficial and deteriorative effects. Some of nicotinamide complexes are biologically active as antifungicidal [6], antitumoral [7] and insulin enhancing agents [8].

In recent years a number of various nicotinamide and nicotinate metal complexes have been synthesized in solid state and their physico-chemical properties were characterized by spectroscopic, crystallographic and thermal methods [9–22]. Different coordination mode of ligands in these complexes were proposed. Nicotinamide and nicotinate ions act as a monodentate ligands with two potential binding sites – a pyridine nitrogen atom and a carbonylate/carboxylate oxygen atom in monomeric complexes or as a bridging ligands in polymeric complexes example [12,17,18,22].

A small number of potentiometric studies on estimation the formation constants of these complexes in the solution has been found [23–27].

The polarographic methods have been used seldom in coordination equilibria (speciation) studies [28–30], although in some favourable cases, the polarographic measurements can indicate complexes formed in the solution in minor quantities, which are often overlooked by potentiometric calculations [31].

Both studied ligands are polarographically active. Their reduction mechanism is characterized by the presence of several waves depending on pH of the medium [32–36]. The reduction waves of ligands may superimpose with the reduction waves of some metal ions or their complexes. This phenomenon complicate significantly the determination of the proper mechanism of electrode process in those systems.

---

* Corresponding author. Tel.: +48 71 3757437; fax: +48 71 328 23 48.
E-mail address: ph@wchuwr.pl (H. Podsiadły).

0022-0728/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2009.09.030

In this paper we present the results of the coordination abilities of niacin towards Ni(II) ions. The interaction of nicotinic acid with Ni(II) ion, to our knowledge, was not studied polarographically, whereas that with nicotinamide was partly examined by some authors [29,30], but still the kinetics and electrode reduction mechanism in this system is not satisfactorily explained. Therefore, the first aim of our work was to describe the coordination equilibria occurring in the aqueous solution, as well as to determine the stoichiometry of the complex species reduced on a mercury electrode and finally, to establish the relationship between the complex structure and its electrochemical reactivity. Secondly, we wish to show that polarographic method can indicate the existence of 1:1 complex which could not be established in potentiometric calculations and to determine its stability constant quite precisely.

2. Experimental

The potentiometric measurements were performed using an EMU/0 (electrochemical universal meter) produced by Technical University of Wrocław. This instrument was combined with automatic burette and appropriate computer set. The potentiometric measurements were carried out by means of the cell SCE ||S|GE, where SCE = Hg|Hg_2Cl_2| saturated NaCl solution; S-equilibrium solution and GE the glass electrode ("pHG 211–8 Radiometer"). The glass electrode was calibrated using $HClO_4$ and NaOH (free CO_2) solutions (I = 0.1 M ClO_4^-). The calibration procedure was described in Ref. [37]. Anaerobic conditions were maintained both in the titration vessel and in the titrant solution by circulating nitrogen. The purities and exact concentrations of the ligands solutions were determined by NaOH potentiometric titrations (by the Gran method) [38]. The sodium hydroxide solution was standardized against potassium hydrogen phthalate. The HYPERQUAD computer program [39] was used for calculations of protonation constants of ligands and stability constants of Ni(II) complexes.

The polarographic measurements were made on a Radelkis OH-105 polarograph, using a dropping mercury electrode as working electrode (drop lifetime 6.0 s at a height of 70 cm and m = 1.056 mg s^{-1}). The saturated calomel electrode (SCE) was used as the anode and reference electrode; it was connected with the solution under examination *via* a salt bridge filled with sodium perchlorate. The large area of the anode (mercury pool) allows to keep its constant potential.

The resulting current was measured as the difference between the total current and the residual current (supporting electrolyte and ligand currents at the same potential). The pH values were checked by means of a Radelkis OP-211 digital pH meter. The pH was adjusted to the desired value by means of sodium hydroxide or perchloric acid solutions. The solutions were deaerated with nitrogen gas before each experiment.

UV–VIS spectra were recorded on Cary 50-Varian spectrophotometer in the range 190–900 nm.

All stock solutions were prepared from analytical-reagent grade chemicals. In potentiometric measurements the total metal concentrations varied from 1.66×10^{-3} mol L^{-1} to 7.5×10^{-3} mol L^{-1}. The ligand to metal ratios varied from L/M 1–10. The concentration of nickel(II) (as $NiSO_4$) in polarographic measurements was 1×10^{-4} mol L^{-1} and those of nicotinamide and nicotinate ions used are given in the respective tables together with obtained results. In spectroscopic measurements the concentration of Ni(II) varied within the range $2–5 \times 10^{-3}$ mol L^{-1} and L/M varied from 1 to 10. A constant ionic strength of 0.1 mol L^{-1} was maintained by adding sodium perchlorate. All measurements were performed at 20 °C.

3. Results and discussion

3.1. Potentiometric measurements

Although the protonation constants of nicotinic acid and nicotinamide have already been reported we determined them under our experimental conditions by potentiometric titration in the pH range 1.8–12. The HYPERQUAD computer program were used for calculations [39]. The obtained values are listed in Table 1 together with the literature data for comparison. A good agreement with earlier published data for both ligands is obtained [24,26,27], considering the differences in ionic strength and ionic medium. The $pK_{N\text{-}py}$ values correspond to a proton dissociation from nitrogen atom of the pyridine ring of both ligands and pK_{COOH} to the dissociation of a proton from the carboxylic group of nicotinic acid.

In the presence of Ni(II) ions a weak interaction between the metal ions and both ligands were stated. Only 1:2 nicotinamide and 1:1 nicotinate complexes were identified in the pH range 3.5–6.5 with the stability constants $\log \beta_2 = 4.28$ (0.06) and $\log \beta_1 = 2.66$ (0.05), respectively (Table 1). We were not able to identify 1:1 species in Ni(II)–nicotinamide system. Above pH 7 the insoluble species precipitate from a solution in both systems (probably the $Ni(OH)_2$).

3.2. Polarographic measurements

3.2.1. Ni(II)–nicotinamide system

Ni(II) ions in 0.1 M $NaClO_4$ in the absence of nicotinamide exhibits a single, irreversible, 2-electron diffusion-controlled wave at −0.967 V. The addition of very small amount of nicotinamide to the solution of Ni(II) ions causes the appearance of the new wave (prewave), at −0.7 V (Fig. 1). This prewave increases in height with increasing concentration of ligand in the solution up to 0.01 M and moves somewhat towards more positive potentials, whereas Ni(II) wave continually decreases and finally disappears. The full development of this prewave coincides with the most positive potential which occurs at −0.680 V vs. SCE. Its maximum limiting current is equal to 93% of the limiting current of free $Ni(II)_{aq}$ ion wave and remains constant up to 0.06 M of nicotinamide. Further increase of nicotinamide concentration above 0.06 M shifts this prewave to slightly more negative potentials and considerable reduces its height. The influence of the nicotinamide concentration over the range 10^{-5}–0.6 M on Ni(II) wave is shown in Fig. 1. The values of limiting current of the registered waves as a function of logarithm of the free ligand concentration are presented in Fig. 2.

The concentration of free ligand is related with its total concentration by equation:

$$[L] = C_L/[1 + \beta_1 C_{Ni} + C_{H+}/K_{N\text{-}py}]$$

where β_1 is the stability constant of the complex, C_{H+}, C_{Ni} and C_L are the total hydrogen, nickel(II) ions and ligand concentrations in the bulk solution, respectively, $K_{N\text{-}py}$ the protonation constant of N-py of ligand. As the pH of the solutions are higher more than 2 log unit from protonation constant of nicotinamide the concentration of protonated form is negligible.

The appearance of the Ni(II)-prewave suggests the formation of at least one complex species between Ni(II) and ANA which is reduced at a lower potential than Ni(II) aquaion. Diagram of logarithmic analysis of the waves shows that the slope (2.303 $RT/\alpha nF$) of well-developed Ni(II)-ANA prewave is equal to 34 mV in its lower part (in the upper part is somewhat higher) whereas the slope of Ni(II) aquaion wave is 68 mV.

Afterwards the influence of different variables, such as pH of the solution, the concentrations of $NaClO_4$ (ionic strength) and that of