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Mixed-ligand complex formation equilibria of nickel(II) with picolinic acid and some amino acids (glycine, α -alanine, β -alanine, and proline) studied in 1.0 mol·dm⁻³ NaCl at 25 °C



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ABSTRACT

Solution equilibria of the systems Ni(II)-Picolinic acid (HPic)- and the amino acids Glycine (HGly), Proline (HPro), α -alanine (H α Ala) and β -alanine (H β Ala) have been studied pH-metrically. The formation constants of the resulting mixed ligand complexes have been calculated at 25 °C and ionic strength 1.0 mol·dm⁻³ NaCl. Ternary complexes are formed by simultaneous reactions. The relative stability of each ternary complex was compared with that of the corresponding binary complexes in terms of $\Delta \log K''$ values. Specie distribution diagrams as a function of pH were briefly discussed.

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1. Introduction

Pyridinecarboxylic acids and their derivatives are present in many natural products. They are also of special interest to medicinal chemists because of the wide variety of physiological properties displayed by the natural and also many synthetic derivatives [1]. The 2-pyridinecarboxylic acid, for short picolinic acid (HPic), contains a carboxylic group in ortho position to the nitrogen in the pyridine ring, acting as a bidentate ligand by (N, COO⁻) co-ordination. It is formed in the body (HPic) as an intermediate in the tryptophan degradation pathway and it is also an approved food supplement. In addition, Chromax®, is the trade mark name of the Cr(Pic)₃ complex, which is currently being used as a food additive and has been shown to assist diabetic patients in maintaining glycemic control [2].

The Vanadium(IV) complex, $VO(Pic)_2$ has shown a modest glucoselowering activity [3], other metallopicolinate complexes has shown insulinmimetic activity too [4].

Sakurai et al. [5] studied in vivo coordination structural changes of a potent insulinmimetic agent, bis(picolinato)oxovanadium(IV), by electron spin-echo envelope modulation spectroscopy, and observed that the original binary complex is transformed in a ternary complex with

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a composition VO(Pic)(X), where X represents an amino acid, they said that the activity change substantially by the formation of this ternary complex. So taking into account the possible application of the metallopicolinate complexes as insulinmimetic agents, we decided to study the formation of the ternary complexes in the Nickel(II)-HPic-amino acid systems as a contribution to the knowledge of the speciation of the Nickel(II)-HPic in biofluids.

Until know, there are no reports on the speciation of the ternary complexes of Nickel(II)-HPic and the amino acids glycine (HGly), proline (HPro), α alanine (H α Ala) and β alanine (H β Ala) [6,7].

2. Experimental

2.1. Reagents

NiCl₂6H₂O (Merck p.a.), and the amino acids HGly, HPro, H α Ala and H β Ala all (Merck p.a.). Na₂EDTA·2H₂O (Merck p.a.), and bromopyrogallol Red (Merck p.a.) as indicator in order to standardize the nickel(II) stock solution were used without further purification. The HCl and NaOH solutions were prepared using 100.0 mmol·dm⁻³ Titrisol Merck ampoules. The NaOH solution was standardized against potassium hydrogen phthalate (Merck p.a., recrystallized and dried at 120 °C) using phenolphthalein as indicator, and the HCl solution was standardized with NaOH solution of known concentration [8]. The solutions were prepared using triply glass-distilled water, boiled before

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Equilibrium	HPic log β_{pr}	H α -Ala log β_{pr}	HB-Ala log β_{pr}	HGly log β_{pr}	HPro log β_{pr}
$HL + H^+ \stackrel{\scriptscriptstyle \sim}{\scriptstyle \sim} H_2 L^+$	0.90(3)	2.52(2)	3.66(1)	2.54(1)	2.09(1)
$HL = L^- + H^+$	-5.17(1)	-9.77(2)	-10.10(1)	-9.65(1)	-10.49(1)
Dispersion(σ)	0.009	0.018	0.017	0.012	0.014
Titrations	2	2	2	2	2
Ligands (mmol∙dm ⁻³)	3	3	3	3	3
pK _i					
pKa1	0.90	2.52	3.66	2.54	2.09
pKa ₂	5.17	9.77	10.10	9.65	10.49

Values of log β_{pr} and pK_i for the ligands studied (25 °C, I = 1.0 mol·dm⁻³ NaCl ionic medium).

Values in parentheses are standard deviations $[3\sigma(\log \beta)]$ on the last significant figure.

preparation of the solutions in order to remove dissolved CO₂. To prevent hydrolysis of the NiCl₂ stock solution, it contained 100 mmol·dm⁻³ HCl. NiCl₂ is hygroscopic and must be weighed as fast as possible. For that reason it is necessary to standardize the NiCl₂ stock solution using a Na₂EDTA·2H₂O solution (0.01 mol·dm⁻³) in a buffer media (pH = 10) using bromopyrogallol Red as indicator [9]. The acidity of the NiCl₂ stock solution was determined by the Gran method [10]. Potentiometric measurements were carried out in aqueous solution using 1.0 mol·dm⁻³ NaCl as ionic medium. Nitrogen free O₂ and CO₂ were used.

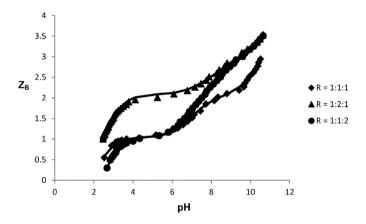


Fig. 1. Z_{B} , average number of mole of H⁺ dissociate per mole of Nickel(II) vs pH of the Nickel(II)-HPic-HGly system, in 1.0 mol·dm⁻³ NaCl at 25 °C. The lines represent theoretical curves calculated with the equilibrium constants of Table 2.

2.2. Methods

The potentiometric measurements were done using the following instruments: Thermo Orion model 520 A pH meter, Metrohm EA 876–20 titration vessel, Lauda Brinkmann RM6 thermostat bath. The sealed 100 mL thermostatted double-walled glass titration vessel was fitted with a combined Orion Ross 8102BN pH electrode with a titrant inlet, magnetic stirrer, and an inert nitrogen atmosphere inlet with outlet tubes. The temperature was maintained at (25.0 \pm 0.1) °C by constant circulation of water from the thermostat bath.

The emf (H) measurements were carried out by means of the REF//S/ GE cell, where REF = Ag/AgCl/3.0 mol·dm⁻³ KCl; S = equilibrium solution and GE = glass electrode. At 25 °C the emf (mV) of this cell follows the Nernst equation, $E = E^0 + jh + 59.16 \log h$, where *h* represents the free hydrogen ion concentration, E^0 is the standard potential and *j* is a constant which takes into account the liquid junction potential [11]. The experiments were carried out as follows: a fixed volume of 0.100 mol·dm⁻³ HCl was titrated with successive additions of 0.100 mol·dm⁻³ NaOH until near neutrality in order to get the parameters E^0 and *j*. Then, aliquots of the HPic and the amino acid under study were added and finally an aliquot of the Nickel(II) stock solution was added sequentially. And, the titration was continued with 0.100 mol·dm⁻³ NaOH. The measurements were done using a total metal concentration, $M_T = 2-3 \text{ mmol·dm}^{-3}$ and Nickel(II):HPic:amino acid molar ratios R = 1:1:1, 1:1:2 and 1:2:1.

The systems Ni²⁺-HPic-amino acids (HB) were studied according to the reaction scheme:

$$pH_2O + qNi^{2+} + rHPic + sHB \Rightarrow [Niq(OH)p(HPic)r(HB)s] + pH^+, \beta_{pars}$$

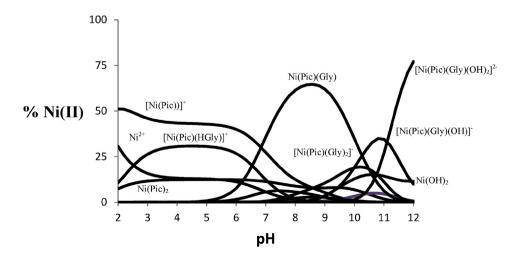


Fig. 2. Species distribution diagram as a function of pH for the Nickel(II)-HPic-HGly system in 1.0 mol \cdot dm⁻³ NaCl at 25 °C considering the conditions M_T = 2 mmol \cdot dm⁻³ and molar ratio R = 1:1:1.

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