



Mixed-ligand complex formation equilibria of nickel(II) with picolinic acid and some amino acids (glycine, α -alanine, β -alanine, and proline) studied in $1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ NaCl}$ at $25 \text{ }^\circ\text{C}$



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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 $25 \text{ }^\circ\text{C}$ and ionic strength $1.0 \text{ mol} \cdot \text{dm}^{-3} \text{ NaCl}$. 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 glucose-lowering 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

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 now, 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

NiCl₂·6H₂O (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 $100.0 \text{ mmol} \cdot \text{dm}^{-3}$ Titrisol Merck ampoules. The NaOH solution was standardized against potassium hydrogen phthalate (Merck p.a., recrystallized and dried at $120 \text{ }^\circ\text{C}$) 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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