Ternary nickel(II) complexes with histidine and glycylglycine in solution: Thermodynamic approach

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Annotation

Potentiometric study on mixed-ligand complexes of nickel(II) ion with histidine (His) and glycylglycine (GG) has been carried out in aqueous solution at 298.15 K and the ionic strength of I = 0.5 (KNO_3). Based on a com- parative analysis of the thermodynamic data on complex formation, possible coordination modes of dipeptide and amino acid residues in mixed ligand complexes are discussed.

Introduction

The ternary system, including nickel(II) ion, the simplest dipeptide glycylglycine and the amino acid histidine, is key in explaining the behavior of metal ions in enzymes. Unfortunately, the data available in periodic literature on establishing the composition of complexes formed in this system cannot be considered complete. In particular, the existence of NiHisGG, NiHHisGG and $NiHisGGH_{-1}$ (charges are omitted) mixed complexes was established earlier in paper and their stability constants were determined. Attempts to identify the formation of mixed complexes of other compositions have not been made by authors. Meanwhile, the coordination capabilities of nickel(II) allow us to talk about the ability to coordinate up to three residues of aminocarboxylate ligands. Given the importance of this system for bio-inorganic chem- istry, it was necessary to clarify the compositions of mixed complexes in aqueous solution in a wide range of pH and concentrations.

Experimental

The pH-metric titrations of solutions containing $Ni(NO_3)_2$, L-HHis, HGG and supporting electrolyte KNO_3 with carbonate-free NaOH solution have been carried out. Stock solutions of nickel(II) nitrate were prepared and standardized by titrating against EDTA. All the solutions were prepared with twice distilled water and their ionic strength was kept at 0.5 mol dm^{-3} by addition of KNO_3. The emf of the transfer chain including glass and Ag/AgCl electrodes was measured by the compensation method.

To obtain reliable values of heat effects of the above-mentioned processes calorimetric measurements using an isoperibolic ampoule flow-mixing calorimeter have been carried out.

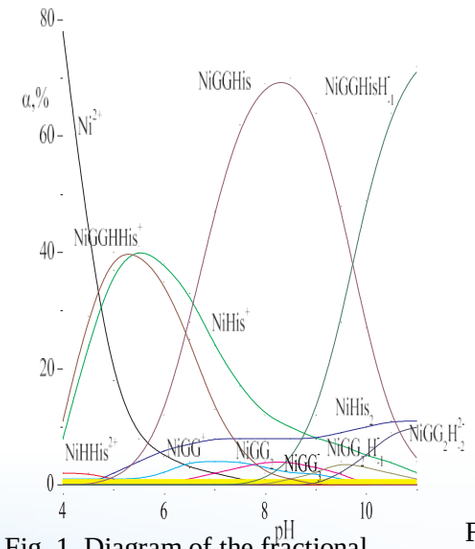

Fig. 1. Diagram of the fractional distribution of the species for the Ni–His-GG ternary system at 1:1:1 M ratio (C_{Ni} = 0.01 mol dm^{-3}).

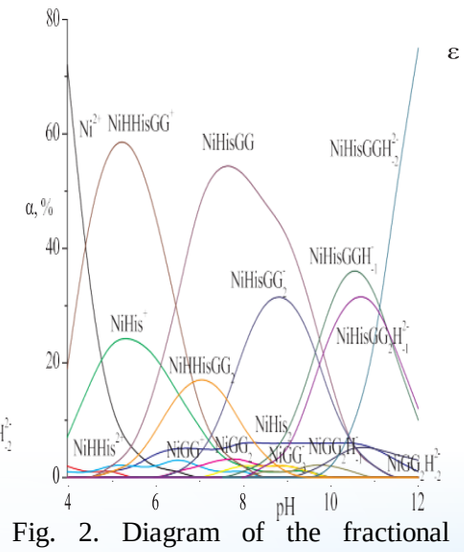

Fig. 2. Diagram of the fractional distribution of the species for the Ni–His-GG ternary system at 1:1:2 M ratio (C_{Ni} = 0.01 mol dm^{-3}).

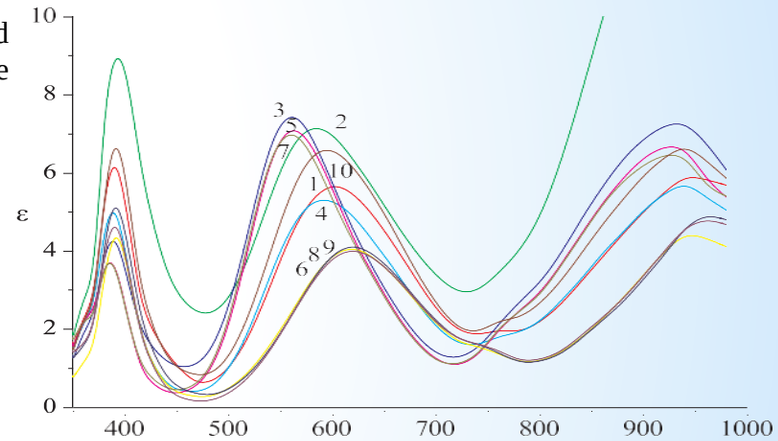

Fig. 3. pH-varied absorption spectra of solutions in the Ni-His-GG system at a) 1:1:0 M ratio and pH 7.21 (6); b) 1:2:0 M ratio and pH 7.90 (7); c) 1:1:1 M ratioand pH 8.30 (1) and 5.96 (8); d) 1:1:2 M ratio and pH 10.49 (2) and 8.93 (10);e) 1:2:1 M ratio and pH 11.23 (3); pH-varied absorption spectra of solutions in the Ni-His-Gly system [7] at f) 1:1:1 M ratio and pH 9.11 (4) and and 6.01 (9); g) 1:2:2 M ratio and pH 9.80 (5); C_{Ni} = 0.005–0.01 mol dm^{-3}; l = 5 cm, 20 °C, I = 0,5 (KNO_3).

Conclusions

Thus, careful processing of the potentiometric experiment made it possible to clarify the ionic composition of solutions in the Ni-His-GG system and to reveal the composition of different mixed complexes. A comparative analysis of thermodynamic data can be successfully used to determine the probable coordination modes of ligands. Based on the results of this analysis, the most preferred coordination schemes can be identified. This approach is quite reliable since there is an obvious correlation between the number of coordinated nitrogen atoms of the ligands and the value of heat effect, as well as the blue shift of absorption band in the region of 600 nm. To elucidate their detailed structure, it is necessary to use other physicochemical methods. The results of this work also show that the ionic composition of "traditional" systems has not been fully identified in many cases and needs to be clarified.

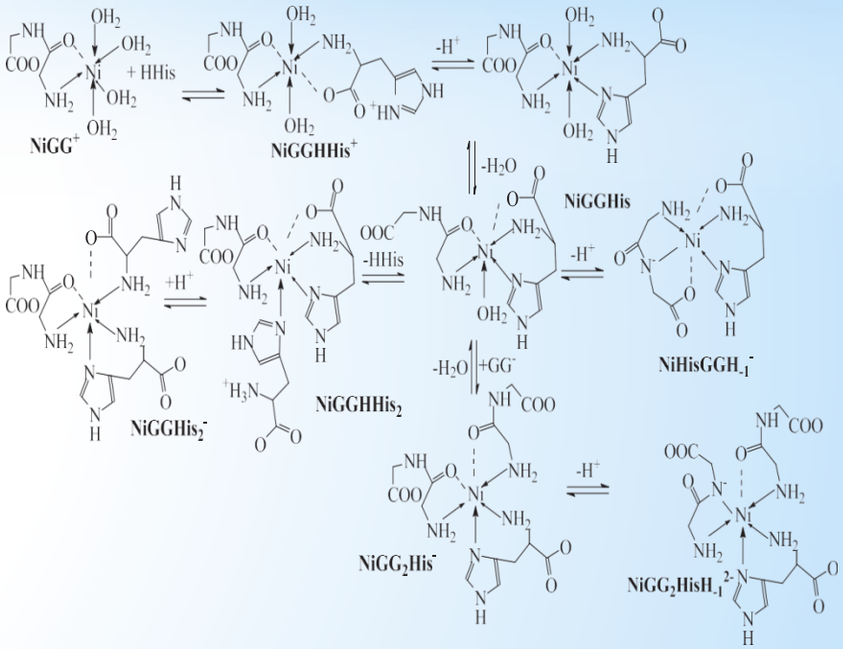

Fig. 4The probable addition of histidine to the nickel(II) glycylglycine complex.