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SPECTROPHOTOMETRIC STUDY OF SOLUTION EQUILIBRIA BETWEEN Al^{3+} ION AND L-HISTIDINE

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Abstract

Aluminium(III) ion and L-histidine (HHis) react in water solution to yield two mononuclear binary complexes $[\text{Al}(\text{HHis})]^{3+}$ and $[\text{Al}(\text{HHis})\text{His}]^{2+}$. The over-all stability constants for these complexes were calculated by non-linear least-squares treatment of the spectrophotometric data and found to be: $\log \beta_{1,1,1} = 13.12 \pm 0.04$, $\log \beta_{1,2,1} = 20.9 \pm 0.1$, respectively. Indices refer to stoichiometric coefficients in complexation equilibrium: $p \text{ Al} + q \text{ His} + r \text{ H} \rightarrow [\text{Al}_p\text{His}_q\text{H}_r]$. The possible structures of the complexes in solution, are discussed.

Introduction

Aluminium is detrimental and toxic element. In human organism it may enter from the environment, the diet or medication. Its toxic effects are mainly exerted on brain, bone and muscle tissues. L-histidine is most metabolically active amino acid and is constituent of active site of many enzymes, proteins, oligopeptides, hemoglobin and mioglobin. Toxic effects of aluminum may arise from blocking enzyme function or modification of conformation of protein chain. Explanation of these interactions at molecular level requires the knowledge of binding properties of amino acids toward Al^{3+} ion. Hence in this report we studied the complexation behaviour of histidine with respect to Al^{3+} ion in water solution at 0.1 mol/L ionic strength adjusted with LiCl.

Experimental

The UV spectra were taken on Beckman model 5260 and GBC Cintra 40 double beam spectrophotometers. The matching pair of quartz cells were used for blank and specimen. The concentration ratios of aluminium to histidine were 1:3, 1:5 and 1:8, with the total aluminium concentration ranging from 3 to 10 mmol/L. The pH of the solutions was adjusted with standard HCl or NaOH and was varied in the interval 4.0 – 6.0. The spectra were taken in the wavelength interval 240 – 350 nm.

Results and Discussion

L-histidine shows UV absorption in far UV region of electromagnetic spectrum with a maximum at 211 nm.

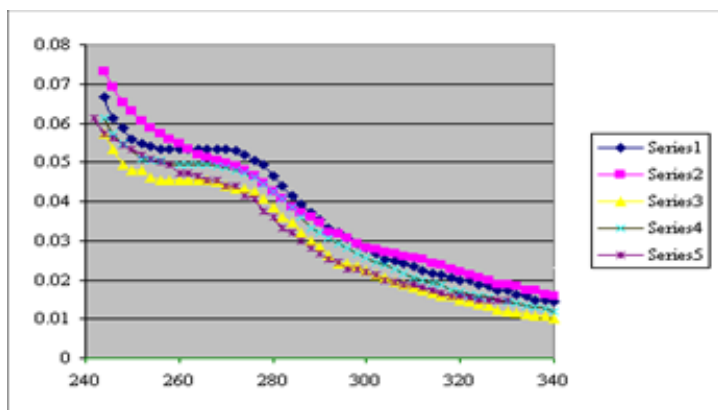


Figure 1. UVspectra of His+Al³⁺ solutions. $C_{\text{His}} = 30 \text{ mmol/dm}^3$, $C_{\text{Al}} = 3.6 \text{ mmol/dm}^3$. (1) pH= 5.10; (2) 5.24; (3) 5.54 (4) 5.63, (5) 6.0

The absorption band is symmetrical and approaches zero at wavelengths higher than 240 nm. In the presence of Al³⁺ ion the tail extending into wavelengths higher than 240 nm exhibits appreciably higher absorption than pure histidine. Raising of absorption is observable after 2-3 days of ageing of the solution. Thus, the spectra of all solutions were taken 72 h after the preparation. The obtained spectra (Fig. 1) show monotonous decrease in absorbance with increasing the wavelength. The plateau appears between 250 and 275 nm. Its position is pH dependent. The dependence of the intensity and position of the spectral bands on pH indicates the presence of several absorbing complexes in solution. In order to evaluate spectrophotometric data, the Squad [2] program was used. In Squad calculations the protonation constants of histidine and stability constants of aluminium hydrolytic complexes were taken from our previous work [1] and were not optimized while these of Al³⁺ with histidine and their molar absorptivities were varied until minimum value of the sum, S and standard deviations of the fit, SD, were obtained. During the calculations various models were tested. The finally obtained results of calculation are given in table 2.

Table 1. Calculated stability constants of Al³⁺ - His complexes. Data for protonation constants of His and hydrolytic complexes of aluminum are from ref. [1].

Species	$\log \beta_{p,q,r} \pm \sigma$
Al(HHis)(His) ²⁺	20.9 ± 0.1
Al(HHis) ³⁺	13.12 ± 0.04
Al(His) ²⁺	6.98 ± 0.15
Statistical parameters of the fit	S=2·10 ⁻³ , SD=1.0·10 ⁻³

The distribution diagram of the Al³⁺ - L-histidine complexes in solution is shown in Figure 2.

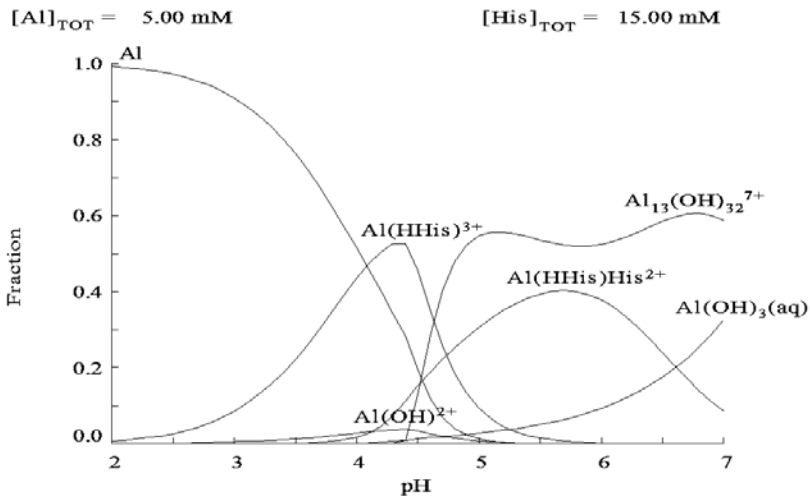
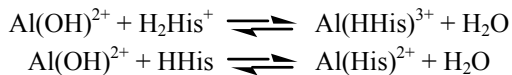


Figure 2. The distribution diagram of Histidine- Al^{3+} complexes

The distribution diagram of pure hydrolytic species [] indicates that in the pH interval 4.0 – 4.5 most important reactive species of aluminium is monohydroxo complex $Al(OH)^{2+}$ so that the probable mechanism of the formation of binary ligand complexes should be:



Bearing in mind the concentrations of the reactive species in the pH region in which $Al(His)$ complex is formed, it seems reasonable to suppose that the actual composition of the complex is $Al(OH)(HHis)$, i.e. that one of coordinated water molecules to aluminium is protolyzed and ammonium group of histidine does not dissociate.

References

- [1] P.Đurđević,R.Jelić,D.Dzajević,M.Cvijović,Metal Based Drugs, 2002, 8, 235.
- [2] D.J.Legget, Squad Stability quotients from absorbance data. In D.J.Legget (ed) Computational Methods for the Determination of Formation Constants, Plenum Press, N.Y., 1985. pp 159-220