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Kinetic studies on the complexation of aqua chromium (III) with DL-leucine in aqueous acidic media

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RÉSUMÉ

La cinétique de formation de complexe 1:2 entre le chrome (III) et la DL-leucine a été étudiée spectrophotométriquement à λ_{max}=540 nm. On a trouvé que la réaction est du premier ordre pour les deux réactifs. La réaction est ralentie pour une augmentation la concentration de l'ion hydrogène de $2,5x10^{-5}$ à 10^{-3} $mol.dm^{-3}$ suivant l'équation : $k_{obs}=a+b[H^+]^{-1}$. Les paramètres d'activation ont été évalués à 38 $kJ.mol^{-1}$ et -159 $JK^{-1}.mol^{-1}$ pour l'enthalpie libre et l'entropie d'activation, respectivement. Une valeur de log K=2,9 a été obtenue à 42°C pour la constante de formation du complexe.

Mots-clés : Cinétique, complexation, Cr(III), acides aminés.

ABSTRACT

Kinetics of formation of 1:2 complex between chromium (III) and DL-leucine was studied spectrophotometrically at λ_{max}=540 nm. The reaction was found to be first order in both reactants. Increasing hydrogen ion concentration from $2.5x10^{-5}$ à 10^{-3} $mol.dm^{-3}$ decreased the reaction rate: $k_{obs}=a+b[H^+]^{-1}$. Activation parameters were evaluated to be 38 $kJ.mol^{-1}$ and -159 $JK^{-1}.mol^{-1}$, for the enthalpy and entropy of activation respectively. A value of log K=2.9 at 42°C was obtained for the formation constant of the complexe ().

Key words: Kinetics, complexation, Cr(III), amino acids.

INTRODUCTION

Recently, chromium is considered to be an essential trace element in experimental animals and probably in man, where chromium present in the trivalent state[1-3], acts biologically as cofactor in the initiation of insulin action. Chromium (III) complexation becomes very important if complexation is with ligands such as amino acids. This is because the protein of the living body consists of about twenty amino acids, ten of them are very important and deficiency in one prevents the growth of the animal and may cause death of organisms. Cr(III) complexes occurring in brewer's yeast and other food which are termed "glucose tolerance factor" were found to have an outstanding biological activity. Effort to purify this factor have led to detection of Cr(III)-nicotinic acid, glycine glutamic acid and cysteine. Synthetic Cr(III)-complexes with these ligands have a biological activity similar to those of the purified yeast fraction [4].

The kinetic of reaction between chromium(III) and glycine, L-phenylalanine, serine, valine, α-alanine, aspartic acid and DL-tryptophan was the subject of previous studies [5-14]. The present study is concerned with the kinetic of complexation of Cr(III) with DL-leucine together with the factors affecting the rate of reaction as well as measurement of the formation constant.

EXPERIMENTAL

All chemicals were of pure grade and were used without further purification. All solutions were prepared using bidistilled water. The absorbance measurements were performed using thermostated 292 Cecil spectrophotometer and pH measurements were conducted with Griffin pH meter fitted with glass-calomal electrode standardized by potassium hydrogen phthalate. Elemental analysis was carried out using Perkin Elmer 2400 C.H.N., atomic absorption spectra was performed by Perkin Elmer model 3100 and IR spectra were measured by Perkin Elmer spectrophotometer 1000 using KBr disk.

Kinetic experiments were performed by mixing thermostated solutions of DL-leucine and chromium (III) and adjusting hydrogen ion concentration to the required value with potassium hydroxide. The solution was introduced into the reaction vessel, which was previously thermostated at the desired temperature. The progress of reaction was monitored at 540nm (λ_{max} of the product), (Fig.1).

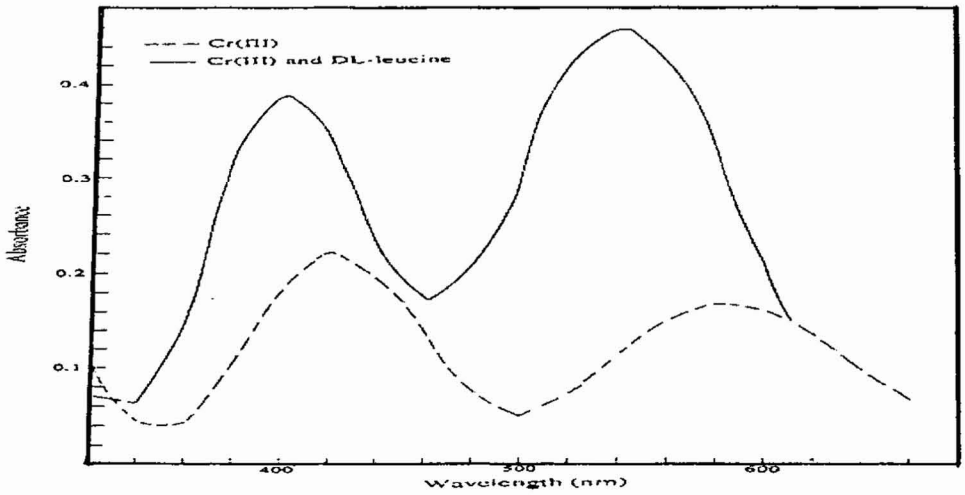

Fig.(1): Absorption spectra of chromium (III) DL-leucine.
$[Cr(III)] = 6 \times 10^{-3}$ mol dm^{-3} $[leu] = 0.12$ mol dm^{-3}
$[H^+] = 7.9 \times 10^{-5}$ mol dm^{-3} $I = 0.2$ mol dm^{-3}

Pseudo first order conditions were always maintained using at least a ten fold excess of [DL-leucine] to [Cr(III)]. Values of the observed rate constants, k_{obs}, were obtained from the slopes of the first order plots of log $(A_\infty - A_t)$ versus time (t) where A denotes the measured absorbance and subscripts refer to time of reaction. A_∞ was obtained directly after ensuring completion of the reaction. First order plots were linear for more than three half lives.

The composition of the complex formed in solution during the course of the reaction was studied by mixing different concentration ratio of Cr(III) and DL-leucine in the range from 1:8 to 1:20 (limited by the solubility of the ligand) at 42°C, $[H^+]=3.98\times10^{-5}$ mol dm^{-3} and $[Cr(III)] = 6\times10^{-3}$ mol dm^{-3}.

A solid complex was also prepared by mixing 25ml of the two reactants, $[Cr(III)]=0.05$ mol dm^{-3} and $[DL\text{-leucine}]=0.1$ mol dm^{-3} at pH = 4.8. The solution