

Study of metal complexes of glycil glycine by paper electrophoresis

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(Received: January 01, 2010; Accepted: February 01, 2010)

ABSTRACT

A recent technique involving the use of paper electrophoresis is described for the study of the equilibria in binary complex systems in solutions. The stability constants of ML, ML₂ and ML₃ complex species of some ions Th(IV), Cr(III) & Al(III) with Glycil were determined at an ionic strength of 0.1 perchloric acid and 35°C.

Key words : Paper electrophoresis, Metal complex, Glycil Glycine.

INTRODUCTION

Amino acids are essential constituents of biological systems and play an important role in the metabolism of living organisms. The thermodynamic changes which occur in biological systems are difficult to measure and even more difficult to interpret owing to the complexity of naturally occurring compounds. Studies of simpler systems, however, yield unambiguous results from which the behaviour of more complex molecules may be inferred. It is well known that many enzymes are inactive in the complete absence of metal ions, but get activated by their presence even in traces. These ions may bind substrates to active centres by means of chelation or complexation reactions since both the active centre of the enzyme and the substrate are usually multidentate. In the simplest case, a metal ion may be attached to a terminal amino acid group of an enzyme or to an intrachain amino acid. Thus useful information may be obtained from stability data relating to metal ions and simple acids and peptides. The present paper reports stability constants of glycil glycine complexes of Th(IV), Cr(III) & Al(III) by paper electrophoresis,

EXPERIMENTAL

Instruments

Systronics paper electrophoresis equipment horizontal cum vertical type No. 604 (India) have been used. The apparatus consisted of a PVC moulded double tank vessel. In our laboratories significant change has been made for controlling the temperature. Two hollow metal plates covered with thin polythene plates have been used. For controlling the temperature, thermostated water supply has been made through hollow plates. The tank is closed with a transparent PVC moulded lid. The whole assembly is tight which prevents moisture changes, which may upset the equilibrium in the paper.

This assembly design thus keeps to a minimum, the disturbing effects of evaporation from the unwanted liquid flow in the water.

Each electrolyte vessel containing a separate electrode chamber in which the anode and cathode are placed respectively. The auxiliary unit is a specially designed one, which can be operated upon either voltage mode or on current mode. The

voltage can be changed through three ranges Viz, 0-100, 100-200 and 200-300 volts.

Filter Paper Strips

Strips of Whatman No. 1 filter paper for chromatography (30 × 1) cm² were used and the potential gradient was 7.7V/cm.

pH- Indicator and Accessories

CP 901 Century digital pH-meter having glass electrode assembly and working on 220volts/50 cycles stabilized A.C. main was used.

Solution of the complexing reagents

Stock solutions of the complexing reagent viz, Glycyl Glycine, (BDH anal R grade) were prepared by dissolving accurately weighted amounts in water. Solution of required strength were then prepared by suitable dilution.

Electro – osmotic indicator

5.0 × 10⁻³M glucose (BDH anal R) was prepared in water and used as an electro – osmotic indicator for the correction due to electro – osmosis.

Detecting reagent for metal ions

1 – (2-pyridylazo) – 2 - naphthol (PAN): 0.1% (w/v) solution in ethanol for Th(IV), Cr(III) & Al(III).

Indicator for glucose

A saturated aqueous solution (0.9 ml) of silver nitrate was diluted with acetone to 20ml. Glucose was detected by spraying with this solution, and then with 2% ethanolic hydroxide when a black spot was formed.

Perchloric acid as background electrolyte

A stock solution (5.0M) was prepared by suitable dilution of 70% perchloric acid (SDS Anal R). the solution was standardized by titrating as suitable volume of its dilute solution against a standard sodium hydroxide solution.

Procedure

For recording observation on particular metal, ion, five strips are stopped with metal ion solution along with additional one spotted with glucose using 1.0 μ pipette and then mounted on the insulated plate. Each of two electrolyte vessel

was filled with 150 ml of background electrolyte containing 0.1 M perchloric acid and ligand (1.0 × 10⁻²) The paper was moistened with the background electrolyte and then allow to drain off excess electrolyte. The second insulated plate was placed on paper strips and then thermo stated water supply allowed to supply. The lid was then closed, placed on the electrode vessel and the chamber was made tight. It was left for ten minute and a direct current (200 volt) was applied for 60 minutes. After electrophoresis, these strips were removed from tank dried. The metal ions and glucose spot were detected by specific reagents. The leading and tailing edge were measured from the marked point and the mean were taken. The distance moved by glucose was taken into account for obtaining the correct path length. Migration towards anode and cathode were designed by – ve and +ve signs respectively.

RESULTS AND DISCUSSION

The plot of overall electrophoretic mobility of metal ion spot against pH gives number of plateaus. A plateau is obviously show pH range where mobility is practically constant. This is possible only when a particular complex is overwhelmingly formed. Thus every plateau formation of certain complex species. The first one in beginning corresponds of pH range in which metal ions are uncomplexed. It lies in low pH region where concerned of highly protonated species of amino acid is obviously maximum, hence it is concluded that this protonated species of amino acid is non – complexing, Beyond this pH range metal ion spot has progressively decreasing mobility. Complexation of metal ion should be taking place with other ionic

Table 1: Stability constants of various binary complexing systems involving glycyl glycine as ligand

Metal	Stability Constants		
	Log K ^M _{ML}	Log β _{ML2}	Log β _{ML3}
Th(IV)	5.58	-	-
Cr(III)	5.47	9.14	11.76
Al(III)	5.00	8.68	11.30

Temperature 35°C

Ionic Strength = 0.1

species of amino acids. Whose concentration increase with increase in pH. The reveals that second plateau in each case with positive mobility indicate the formation of 1:1 complex of cations nature, Further increase of pH, the mobility in case of Th (IV) remained unchanged while mobility decrease giving rise to third and fourth plateau in case of Cr(III) and Al(III). Since the mobility of third and fourth plateau lie in positive region, cationic nature of metal complex is indicated, in view of zero mobility of subsequent complex formed in the region of the fourth plateau the complexes should be 1:3 The earlier complex should consequently be 1:2 with respect to metal ion and ligand ion.

Chemical literatures {1-5} also assigns prominent liganding properties to protonated anionic species of glycil glycine ruling out any such property to zwitter ion. Further increase of pH has no effect on mobility of metal ions.

For calculating stability constants of different complexes obtained. The following equations has been utilized. Form the above discussion it is clear that complexes formed with Th(IV) is 1:1 in composition while in trivalent metal ions 1:1 1:2, 1:3 The deprotonated species L- i.e. anion of glycil glycine not been assumed to be ligand species with metal ions. Complexes of glycil glycine

with metal ions are thus formed as a result of coordination of anion of the glycil glycine in stages. The mathematical equation $U = \sum U_i f_i^{[16]}$ is simplified as :

$$U = \frac{u_0 + u_1 K_1 [L] + u_2 + K_1 K_1 [L]^2 + u_3 + K_1 K_2 K_3 [L]^3}{1 + K_1 [L] + K_1 K_2 [L]^2 + K_1 K_2 K_3 [L]^3}$$

Where u_0 , u_1 , u_2 and u_3 are mobilities of uncomplexed metal ions, 1:1 metal complex 1:2 metal complex and 1:3 metal complex respectively. For calculating the stability constant K_1 the region between first and second plateau is pertinent. The overall mobility "U" will be equal to the arithmetic mean of mobility of uncomplexed metal ion (u_0) and tha of the first complex u_1 at pH when $K_1 = \frac{1}{[L]}$

With the help of dissociation constants of glycil glycine ($\log k_1 = 10^{3.1}$, $\log k^2 = 10^8$ the concentration of anion is determined for the pH, from the which k_1 can be calculated. Similar procedure is adopted for calculation of K_2 , where 2nd and 3rd plateau and K_3 where 3rd 4th plateau are considered.

The calculated value of stability constants are given in Table 1.

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