

Determination of Stability constants of Cobalt (II)-ADP and Cobalt (II)-ATP Complexes using Ionophoretic Technique

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Abstract: Ionophoretic technique is studied as a novel tool for the study of binary metal complexes of Cobalt (II)-ADP and Cobalt (II)-ATP. The stability constants of Cobalt (II)-ADP and Cobalt (II)-ATP Complexes equilibria in simple and mixed ligand systems in solutions. Are found to be $10^{4.68}$ and $10^{5.50}$ respectively. These values are determined at 25°C and at ionic strength equal to 0.1M (NaClO_4). The specially designed electrophoretic tube (1) has been used for investigation of these complexes in the solution.

Keywords: Ionophoretic technique, Electrophoretic tube, Stability, ADP, ATP, nucleotides

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I. Introduction

The investigation of interaction of the metal ions with nucleotides is of increasing interest owing to the importance of these processes in biology. Nucleotides dependent energy systems play a key role in all metabolic aspects. Keeping this in view we have made an attempt to study the stability of cobalt (II)-ADP and cobalt (II)-ATP Complexes using a very simple and novel technique called Ionophoretic Technique. The dissociation constants of ADP and ATP were determined by Yadav et al using paper electrophoresis (2). The dissociation constants for our investigation were taken from literature (3) and used for evaluating the stability constants.

Experimental:

Binary cobalt (II)-ADP and cobalt (II)-ATP Complexes:

A set of 15 ml solution each containing 1×10^{-3} Co(II), 0.1M HClO_4 and 1×10^{-2} M ADP/ATP were prepared at different pH values (by adding NaOH solution). A 10 ml of the solution is taken in the electrophoretic tube and thermostated at 25°C . The tube (18 cm & 5 cm diameter) with a stopper in the middle was fused perpendicularly at the ends with short wider tubes of 1.2 mm diameter. The position of the tube was adjusted in such a way that the level of the solution in one wide end arm reached a circular mark on it. This adjustment fixed the volume of the solution on both sides of the middle stopper. Two (0.5 cm x 0.5cm) platinum electrodes were dipped in each arm cup and 50V potential difference was applied between them. Electrolysis of the solution was allowed for 45 minutes after which the middle stopper of the tube was closed. The solution of the anodic compartment was taken out in a 15 ml flask. The Co(II) content of the solution was converted to Co(II) – thiocyanate complex(4). and absorbance was measured at 625 nm was measured using spectrophotometer.

II. Results And Discussion

Figure 1 shows the relationship between absorbance difference and the pH's and thus gives an idea of the change of overall mobility of metal ion species with change in hydrogen ion status of the systems containing Cobalt (II)-ADP and Cobalt (II)-ATP. It is clear from the figure that the overall mobility of the Cobalt (II) ions against the PH of the background electrolyte containing the ligands (ADP and ATP) gives a curves with two plateaus in each case. A plateau is an indicator of a pH range over which mobility is practically constant. This could be possible only when a particular complex species is formed in abundance. Thus each plateau indicates the formation of a certain complex species. The first plateau correspond to a region where metal ions are uncomplexed. It is present in the lower pH region and thus it is concluded that this species of ligating acids are non complexing. Beyond this region metal ions have progressively decreasing mobility and hence complexation of metal ion should be taking place with deprotonated ionic species of ADP/ATP whose concentration gradually increases with increase in pH. The second plateau in each case corresponds to the abundant formation of ML complex which is very likely a 1:1 complex. The second plateau in each case of ADP/ATP shows a negative mobility and slightly a higher negative mobility in ATP which shows the formation of anionic complexes of Cobalt (II)-ADP and Cobalt (II)-ATP. Further increase in pH has no effect on the mobility of metal ions, hence

it is clear that the complexing species for ADP is L^{3-} and for ATP is L^{4-} . If other non protonated anionic species of the ligands could also interact, there would have another intermediate plateau in lower pH range. The overall, mobility (U) is a composite parameter contributed by different ionic species of the metal ion and is given by the following equation 1.

$$U = \frac{u_0 + u_1 k_1 [L] + u_2 k_1 k_2 [L]^2 + \dots}{1 + k_1 [L] + k_1 k_2 [L]^2 + \dots}$$

Where K' s are the stability constants of complexes and [L] is the concentration of ADP/ATP anion. u's are the ionic motilities of the different species of the metal ions which can be assessed from the plateaus of the figure(1) In the region between first and second plateau the system contains overwhelmingly a mixture of free metal ion 1:1 complex. From Figure 1 it is evident that there is no formation of 1:2 complex, hence the third term in the numerator and the denominator of the above equation (1) is neglected. U would be equal to $(U_0 + U_1 / 2)$ provided $k_1[L]=1$.

Accordingly the pH corresponding to the average value of U_0 and U_1 is found from the figure. With the knowledge of the dissociation constants of ADP/ATP ($pK_1= 6.40, pK_2= 3.96$ for ADP)³ and ($pK_1= 6.51, pK_2= 4.66$ for ATP)³, the concentration of ligands at this pH are calculated. Its reciprocal gives the stability constants of the complexes. The calculated values are given in table - 1.

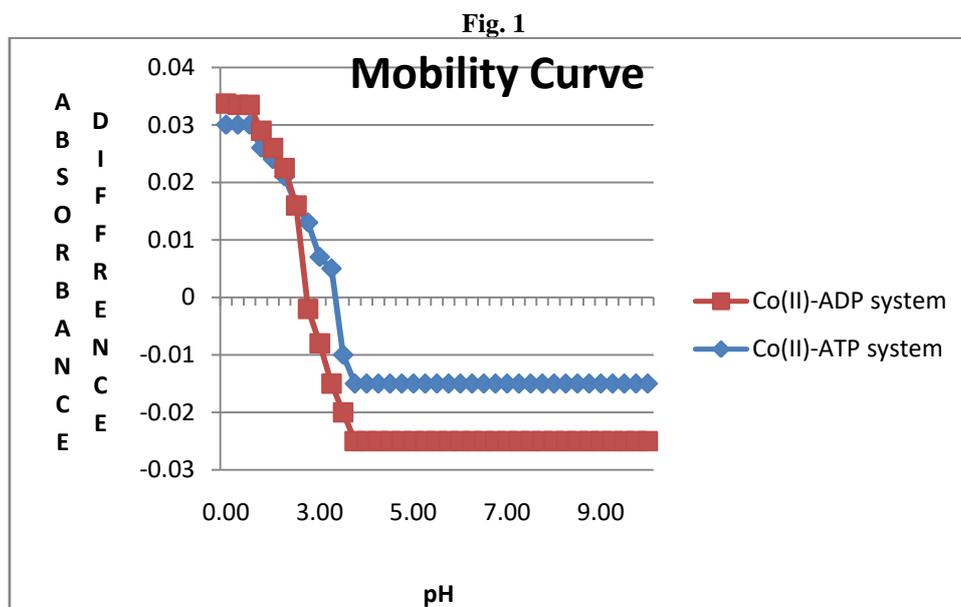


Table 1: Stability constants of 1:1 Cobalt (II)-ADP and Cobalt (II)-ATP complexes. Ionic Strength = 0.1 M, Temp. = 25°C.

Metal complexes	Calculated values	Literature values ³
Co(II) - ADP	4.68	4.20
Co(II) - ATP	5.50	4.63

References

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