



RESEARCH ARTICLE

STUDY OF STABILITY CONSTANTS OF COMPLEXES OF RESORCINOL AND TYROSINE WITH COBALT (II) USING IONOPHORETIC TECHNIQUE

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ABSTRACT

Ionophoretic technique has been used to study the equilibria in simple and mixed lig and systems in solutions. For the study of ternary complexes the concentration of Resorcinol was kept constant in the case of Metal-Resorcinol –Tyrosine complex whereas tyrosine concentration is kept constant in case of Metal –Tyrosine –Resorcinol complex while that of secondary ligand tyrosine/Resorcinol is varied. The stability constant of Co(II)-Resorcinol, Co(II)-Tyrosine (1:1), Co(II)-Tyrosine (1:2), Co(II)-Resorcinol-Tyrosine and Co(II)-Tyrosine-Resorcinol complexes have been found to be $10^{12.96}$, $10^{16.21}$, $10^{9.60}$, $10^{8.20}$ and $10^{6.54}$ respectively at 0.1M (HClO₄) and 25^oC.

INTRODUCTION

In the present communication an effort has been made to assess the stability constants of metal complexes with single ligand along with the systematic study of ternary complexes formed in a system containing various electrolyte ingredients. A simple ionophoretic tube has been designed for this work, which yields better results after standardization. Cobalt is essential trace element in humans. The biological activity of Cobalt is evident from its presence in Vitamin B 12 and in some of the coenzymes hence has a wider importance for research, therapeutic, industrial, and toxicological consideration. Consequently, a variety of methods are available for its determination. Resorcinol used as one ligand has various medicinal importance as an antiseptic and a disinfectant and is also used in ointment for the treatment of skin diseases. Amino acid Tyrosine used as a ligand is one of the most vital amino acid, has use in the synthesis of structural proteins. The stability constant provides the information required to calculate the concentration of the complex in the solution. There are many areas of application in chemistry, biology and medicine.

MATERIALS AND METHODS

The technique consisted in carrying Ionophoresis in background electrolyte containing 0.1M perchloric acid and 0.01M Resorcinol / 0.01M Tyrosine with 0.001 Co (II) and for ternary complexes the concentration of Secondary ligand Tyrosine /Resorcinol ranges from 2×10^{-2} with Co(II) ions. The NaOH solution was added to produce the desired pH for the study the binary complexes. In each Ionophoretic observations, electrolysis was carried out for 45 minutes at 50 V and at 25^oC. For the study of ternary complexes the experimental procedure was slightly modified. Here the back ground electrolyte contained secondary ligand (Tyrosine/Resorcinol) in addition to primary ligand (Resorcinol/Tyrosine). For the ternary complexes the pH was always maintained at 8 (by adding NaOH solution) and the concentration of secondary ligand (Tyrosine/Resorcinol) ranged from 10^{-6} to 10^{-2} M.

Procedure for binary metal-tyrosine/resorcinol complexes

A set of 15 ml solution containing 1×10^{-3} M Co (II), 0.1M HClO₄ and 1×10^{-2} Tyrosine /Resorcinol were prepared at different pH values. A 10 ml of the solution was taken in the ionophoretic tube and thermostated at 25^oC. The tube (18 cm & 5 cm diameter) was adjusted in such a way that the level of the solution in one wide end arm reached a circular mark on it.

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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 in a 15 ml flask. The Co (II) content of the solution was converted to Co (II) – thiocyanate complex². The volume was raised up to the mark and the absorbance was measured at 450 nm with Digisunspectrocolorimeter. The Co (II) content at the anodic compartment was converted to Co (II) – thiocyanate complex and absorbance was measured at 600 nm after making up the volumes to 15 ml.

Procedure for the study of ternary complexes Metal – Tyrosine-Resorcinol and Metal- Resorcinol-Tyrosine

An appropriate reaction mixture containing Metal ions Co(II) and primary ligand Tyrosine/Resorcinol and 0.1M perchloric acid was adjusted to pH 8.0 and the secondary ligand Resorcinol/Tyrosine was added progressively and the ionophoretic mobility was recorded.

The mobility was plotted against $-\log [\text{Tyrosine/Resorsinol}]$.

RESULTS AND DISCUSSION

Co(II)-Tyrosinesystem and Co(II)-Resorcinol system

The overall mobility 'U' is a composite parameter contributed by different ionic species of the metal ion and is given by the following equation.

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

Where k 's are the stability constants of complexes and $[L]$ is the concentration of Tyrosinate anion and Resorcinol anion. u 's are the ionic mobilities of different species of the metal ion 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 in case of Co(II)-Resorcinol binary complex, hence the third term in the numerator and the denominator of the above equation can be justifiably 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 1. With the knowledge of the dissociation constants of Resorcinol ($pK_2 = 11.32$, $pK_1 = 9.15$)³ the concentration of Resorcinol ion at the corresponding pH is calculated. Its reciprocal gives the stability constants K of the 1:1 complex. The calculated values are given in table - 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 a formation of 1:2 complex in case of Co(II)-Tyrosine binary complex, hence the third term in the numerator and the denominator of the above equation should be considered. With the knowledge of the dissociation constants of Tyrosine ($pK_2 = 10.1$, $pK_1 = 9.11$)⁴ the concentration of Tyrosinate ion at the corresponding pH is calculated. Its reciprocal gives the stability constants K of the 1:1 complex and 1:2 complex in case of M-Tyrosine complex. The calculated values are given in Table - 1. The overall mobility's of the metal ion in solution in the presence of Tyrosine/Resorcinol at different PH values are represented in Fig 1. It is evident from the figure that with metal ion with Tyrosine has two plateaus and metal ion with

Resorcinol has one plateau. The stability constants of complexes ($K_{M-Tyrosine/Resorcinol}^M$) were calculated and are given in Table 1.

Table 1. Stability constants of some binary and ternary complexes of Co (II) with Tyrosine, Resorcinol Ionic Strength = 0.1 M, Temp. = 25°C

Stability constants	Co (II) value	
	Calculated values	Literature values*
$\log k_{M-Tyrosine}^M$	16.21 for 1:1 complex 9.60 for 1:2 complex	- 7.5
$\log k_{M-Resorcinol}^M$	12.96	-
$\log k_{M-Tyrosine-Resorcinol}^M$	6.54	-
$\log k_{M-Resorcinol-Tyrosine}^M$	8.20	-

* Reference no. (For column iii of Table 1) – 5

M-Tyrosine–Resorcinol Ternary complex System and M-Resorcinol-Tyrosine Ternary complex system:

This system was studied at pH 8 with a specific purpose. It was observed from mobility curves, for M-Tyrosine/Resorcinol binary System that binary complexes are formed much before pH 8. To avoid any side interactions the transformation of the M-Tyrosine/Resorcinol complexes into M-Tyrosine-Resorcinol and M-Resorcinol-Tyrosine complexes is investigated at PH. 8.0. The plots of overall mobility (Absorbance difference) against $-\log [\text{Tyrosine/Resorcinol}]$ are given in Fig –2 which shows two plateaus.

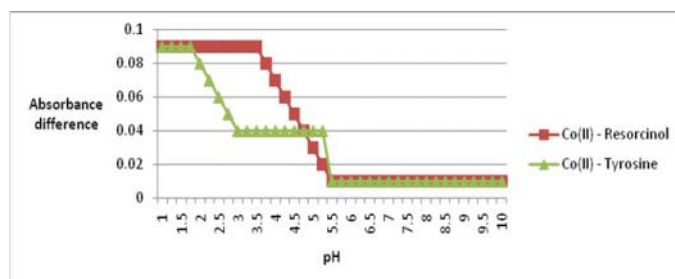


Fig. 1. Mobility Curve: Co (II)-Tyrosine system and Co (II)-Resorcinol system

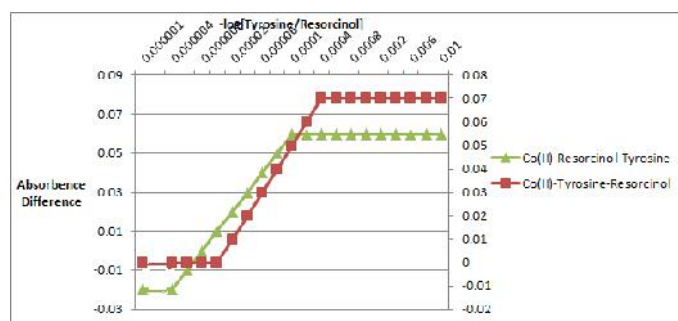
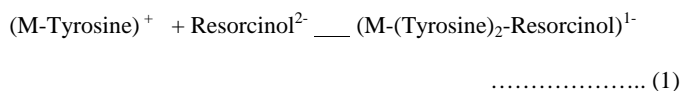


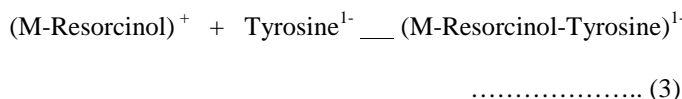
Fig. 2. Mobility Curve: Co(II)-Tyrosine-Resorcinol system and Co(II)-Resorcinol-Tyrosine system

The positive mobility in the region of first plateau is obviously due to 1:1 & 1:2 of M-Tyrosine and 1:1 M-Resorcinol complexes (ML^+) (see Fig -1). The mobility corresponding to the plateaus in Fig -2 lies in the negative region inferring that the species corresponding to these plateaus is due to the

coordination of secondary ligand Resorcinol²⁻ anion in case of Co(II)-Tyrosine- Resorcinol ternary complex and Tyrosine¹⁻ anion in case of Co(II)- Resorcinol -Tyrosine ternary complex resulting into the formation of 1:2:1(M-(Tyrosine)₂-Resorcinol)¹⁻ mixed complex and 1:1:1 (M-Resorcinol-Tyrosine)¹⁻ mixed complex. This can be shown as :



$$U = u_0 f M-Tyrosine + u_1 f M-(Tyrosine)_2-Resorcinol \quad \dots\dots\dots (2)$$



$$U = u_0 f M- Resorcinol + u_1 f M- Resorcinol-Tyrosine \quad \dots\dots\dots (4)$$

Where u_0 and u_1 are the mobilities and f M-Tyrosine/Resorcinol and f M-Tyrosine-Resorcinol/Resorcinol-Tyrosine are the mole fractions of M-Tyrosine/Resorcinol and M-Tyrosine-Resorcinol/Resorcinol-Tyrosine complexes respectively. From Fig -2 the total concentration of secondary ligand at which the overall mobility is mean of the mobilities of the two plateaus was determined. For this the concentration of secondary ligand anion at pH 8.0 was calculated. These calculated values of stability constants are also recorded in Table 1.

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