

Studies of Influence of Ionic strengths of Cu (II) metal ion complex with Rubenic acid by P^H - metric technique.

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Abstract: The interaction of Cu (II) metal ion complex with Rubenic acid has been studied at various ionic strengths P^H - metrically. The values of P_k [Proton - Ligand stability constant] and log k [Metal - Ligand stability constant] are utilised to estimate the thermodynamic stability constant at zero ionic strength and to know the exact nature of complexation equilibria. P_k/log k values are found to be increasing with decreasing the values of ionic strengths.

Key words: Cu (II), Dithio-oxamide [Rubenic acid] Ethanol.

I. Introduction

Sumer *et al.*, [1] studies of Influence of Ionic strength of medium on the complexation equilibria of substituted hydroxy 1-3-propanodiones with Cr (III) & La (III) metal ions P^H metrically. Jaisingh *et al.*, [2] have studied the stability constant of some bivalent metal chelates with 2-4-dihydroxy valero-phenoxime at various ionic strength.

Gudadhe *et al.*, [3] have investigated the stability constant of Cu [II] Complex with some substituted propanediones at various ionic strengths potentiometrically

Mandakmone *et al.*, [4] have studied the stability constants of UO₂ (II) Complexes with some substituted Coumanins at 0.1 m ionic strength potentiometrically & spectrophotometrically.

Palaskar *et al.*, [5] have studied the effect of ionic strength and dielectric constant of cu (II)-3-nitrophthalic acid potentiometrically at various ionic strengths.

Meshram *et al.*, [6] have studied stability constants of Pr[III] complexes with substituted pynazoline. May and Jones *et al.*, [7] have applied Hammett's equation to the complex of substituted benzoic acid. Willims *et al.*, [8] the entropy term is usually favourable when ligend in anionic and generally in case of neutral ligands. Inving and Rosotiet *et al.*, [9] have a given a method for determining the metal ligand stability constant of the complex by P^H - metrically.

Sawalakhe *et al.*, [10] have investigates metal ligand stability constant of Fe(III), Cr (III) and Al (III) metal ion complexes with some substituted diketones and pyrazoles at 0.1 M ionic strength.

Narwade and Jagirdar *et al.*, [11] have determined metal ligand stability constant of di-valent and trivalent metal ions with some substitutes sulphonic acid. P. Agrawal and Narwade M. L. *et al.*, [12] have determined metal ligand stability constant at 0.1 M ionic strength.

Ali Asagar *et al.*, [13] have studied the metal ligend stability constant of some transition metal ions with the some substitutes pyrazolines and isoxazoline P^H - metrically and obtained very low values of stability constant due to weak chelating agent.

Present work deals with the determination of proton - ligand stability constant and metal - ligand stability constant of Cu (II) and Rubenic acid at different ionic strengths and at 29 ± 0.1^oc temperature.

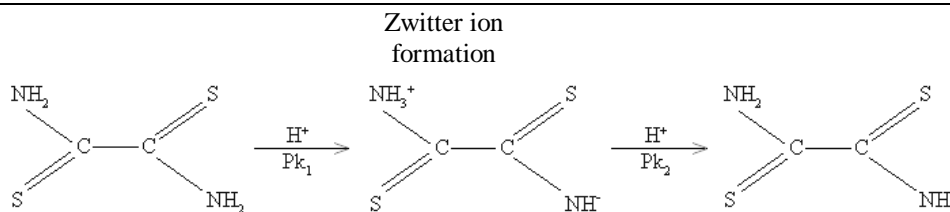
II. Experimental

Equip-tronics digital P^H meter model EQ - 610 was used [accuracy ±0.05 unit] for measuring the P^H of solution. Metal solution were prepared in double distilled water. Ligand solution is prepared in 70% ethanol - water [v/v] solution nitric acid, sodium hydroxide & nitrate used were of A.R. Grade.

The titration were conducted in an inert atmosphere of nitrogen. The ionic strength of the solution was maintained constant by adding an appropriate amount of 1 M KNO₃ solution. The values were recorded by P^H meter and converted of [H⁺] values by applying the correction proposed by Van Uitert and Hass [14].

III. Result And Discussion

Cu (II) metal ions complex with Rubenic acid may be considered as a dibasic acid having one replaced H⁺ ion from ligand can be represented as –



The titration data were used to construct the curves between volume NaOH V/s P^H. They are called acid ligand and metal titration curves.

Table - 1 : Proton ligand stability constant at various ionic strength

| Ionic strength | Pk value |
|----------------|----------|
| 0.10 | 4.30 |
| 0.08 | 4.50 |
| 0.06 | 4.80 |
| 0.03 | 4.90 |
| 0.01 | 5.10 |

Table - 2 : Metal ligand stability constant at various ionic strength.

| Ionic strength | log K ₁ | log K ₂ |
|----------------|--------------------|--------------------|
| 0.10 | 7.24 | 5.25 |
| 0.08 | 8.14 | 7.05 |
| 0.06 | 9.54 | 8.85 |
| 0.04 | 10.05 | 9.50 |
| 0.02 | 10.55 | 9.90 |

Table - 3 : Δ Z² Values for dissociation and association equilibria.

| Reaction equilibria | Constants | Δ Z ² | |
|-----------------------------------------------------------|-------------------|------------------|-------|
| | | Expected | Found |
| HL ↔ H ⁺ + L ⁻ | Pk | 2.00 | 2.65 |
| HL + Cu ²⁺ ↔ H ⁺ + CuL ⁺ | logk ₁ | -2.00 | 2.25 |
| HL + CuL ⁺ ↔ H ⁺ + CuL ₂ | logk ₂ | 0.00 | 3.00 |

H₂L = Rubenic acid

The Pk value of ligand & log k value of Cu (II) complexes at various ionic strengths was calculated by Irving & Rossotti's method and are presented in Table - 1 and Table - 2 respectively.

It could be seen from Table-2 that the stability constant values of Cu(II) are greater. This may be due to greater tendency of d-block elements to form complexes. It means Cu(II) is a good complexing agent. Also it is clear that pk/logk values are found to be decreased with increasing ionic strength. The pk/logk values were used to calculate the thermodynamic constant with the help of Bronsted equation [15].

$$\text{Logk} = \log k^0 + A \Delta Z^2 - \sqrt{\mu}$$

$$\text{and } \text{Pk} = \text{Pk}^0 - A \Delta Z^2 - \sqrt{\mu}$$

Where, A is the Debye-Huckel constant, Δ Z² is the difference in the square of charge of product and reactant ions and k⁰ is the formation constant at zero ionic strength. The values of Pk, logk₁ and logk₂ were plotted against √μ. The plot at log k/Pk v/s √μ gave straight lines. The magnitude of Δ Z² and slopes were calculated from graphs. The data obtained of Pk and logk could be utilised to know the mechanism of complexation equilibria. The expected and observed values of Δ Z² for the corresponding dissociation and association equilibria is given in Table-3.

Table-4 : Thermodynamic dissociation constant at zero ionic strength [Pk/logk]

| Plots | Ligand [Rubenic acid] | Cu(II) - Metal Rubenic Complex |
|-----------------------------------------------------------------------|-----------------------|--------------------------------|
| Pk v/s $\sqrt{\mu}$ | Pk ⁰ 7.73 | |
| Pk v/s $\sqrt{\mu} (1 + \sqrt{\mu})$ | 7.50 | |
| Pk v/s $[\sqrt{\mu} (1 + \sqrt{\mu})] - 0.3\sqrt{\mu}$ | 7.65 | |
| logk ₁ v/s $\sqrt{\mu}$ | | logk ⁰ . 12.40 |
| logk ₁ v/s $\sqrt{\mu} (1 + \sqrt{\mu})$ | | 12.33 |
| logk ₁ v/s $[\sqrt{\mu} (1 + \sqrt{\mu})] - 0.3\sqrt{\mu}$ | | 12.36 |
| logk ₂ v/s $\sqrt{\mu}$ | | 10.87 |
| logk ₂ v/s $\sqrt{\mu} (1 + \sqrt{\mu})$ | | 10.69 |
| logk ₂ v/s $[\sqrt{\mu} (1 + \sqrt{\mu})] - 0.3\sqrt{\mu}$ | | 10.14 |

It is observe from Table-3 that the slope of Pk and logk do not give a conclusive evidence regarding the magnitude of the change of reacting species. The discrepancy may be due to the limited applicability of Bronsted equation.

The plots of Pk/log k v/s $\sqrt{\mu} (1 + \sqrt{\mu})$ and $[\sqrt{\mu} (1 + \sqrt{\mu})] - 0.3\sqrt{\mu}$ are also plotted and slope values were determined. It showed that modified Debye-Huckel equation also did not show much improvement in the slope values. The discrepancy between observed and expected slope values was thought of to be due to the concentration and not the reactivity terms used in the equation of stability constant.

Thermodynamic Stability Constants [Pk/log k]

The thermodynamic constant observed from various plots at zero ionic strengths are presented in Table-4, which shows a good agreement among thermodynamic constant obtained from various plots.

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