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Research Article

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Studies on Interaction Between Cu(II), Cr(II) and Ni(II) Metal Ions and Substituted Hydroxy 1,3-Propanedione At 0.1 M Ionic Strength pH Metrically

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ABSTRACT

The interactions of Cu(II), Cr(II) and Ni(II) metal ions with 1(2'-hydroxy-5'-bromophenyl)-3(4'-aminophenyl)-1,3-propanedione (L_1) and 1(1'-hydroxy-5'-bromophenyl)-3(4'-nitrophenyl)-1,3-propanedione (L_2) have been substituted at 0.1 M ionic strength in 70 % Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Cu(II), Cr(II) and Ni(II) metal ions from 1:1 and 1:2 complexes with ligands (L_1 & L_2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k). From estimated data (pK and log k), the effects of substituents were studied.

Key words : Substituted hydroxy 1,3-propanedione, dioxane-water mixture.

INTRODUCTION

Considerable research work has been done in the past, on the study of complexes[1,2]. The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in biological kingdom. With the view to understand the bi-inorganic chemistry of metal ions, Banerjee et al[3] have synthesised a number of mixed-ligand alkaline earth metal complexes. Bjerrum's[4] dissertation has taken the initiative to develop the field. Metal complexation not only bring the reacting molecules together to give activated complex[5] but also polarised electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of complexes is determined by the nature of central metal atom and ligands. The stability of complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irving and Williams[6] had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionisation potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade et al[7] have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Many workers[8-23] have reported their results on metal-ligand stability constants. Bodkhe et al[24] have reported the metal-ligand stability constants of some β-diketones. Tekade et al[25] investigated stability constants of some substituted pyrazolines, isoxalline and diketone. Speciation of binary complexes of Ca(II), Mg(II) and Zn(II) with L-glutamic acid in DMSOwater Mixtures has been studied [26]. Thakur et al[27,28] have studied in influence of ionic strength of medium on the complexequilibria of substituted hydoxy-1-3-propandiones with Cr(III) andLa(III) metal ions and Metal-ligand stability constants of Th(III), Sm(III), Nd(III) and Pr(III) metalion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength pH metrically . Narwade et al [29] have investigated the Metal-ligand Stability Constants of Cu(II) Complexes and Measurement of Viscosity, Refractivity Index with some substituted Pyrazoles and Diketones at 0.1M Strength. Shivaraj et al [30] have studied formation constants and thermodynamic parameters of bivalentmetal ion complexes with 3-amino-5-ethyl isoxazole Schiff basesand N, N; N, O and O, O donor ligands in solution

In present work an attempt has been made to study the interactions between Cu(II), Cr(II) and Ni(II) and substituted hydroxy-1,3-propanediones at 0.1 M ionic strength, pH-metrically in 70 % dioxane water mixture.

EXPERIMENTAL SECTION

The chemicals used in the present work were of AR grade. Substituted hydroxy 1,3-propanediones (ligand 1 & 2) were synthesised by literature method in laboratory and their purity was checked by IR, NMR and M.P. techniques before used. The solutions of ligands were prepared in purified 70 % dioxane-water mixture and standardised by PH metric technique.

Systronic microprocessor based instrument with accuracy ± 0.01 unit with glass and saturated calomel electrode as used for the titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at 28 ± 0.1 ^{0}C, before processing the titrations.

Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gar.

The experimental procedure involved the titrations of

i) Free acid $HClO_4$ (0.01 M)

ii) Free acid $HClO_4$ (0.01 M) and ligand (20 x 10^{-4}M)

iii) Free acid $HClO_4$ (0.01 M) and ligand (20 x 10^{-4}M) and metal ion (4 x 10^{-4}M) against standard NaOH solution.

The ionic strength of all the solution were maintained constant (0.1 M) by adding appropirate amount of $NaClO_4$ solution. All the titrations were carried out in 70 % dioxane-water mixture and the reading were recorded for each 0.1 ml addition. The graph of volume of alkali (NaOH) against pH were plotted.

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of -OH group. Substituted hydroxy-1,3-propanedione may be considered as a monobasic acid having one replaceable H^+ ion from phenolic -OH group and can be represented as

$$HL \rightleftharpoons H^+ + L^-$$

The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A+L) and acid + ligand + metal ion curve (A+L+M)] between volume of NaOH against pH.

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Table1)

$$n_A = \gamma - \frac{(E_0+N)(V_2-V_1)}{(V_0+V_1)\,T_L^{\,0}} \qquad .....(1)$$

where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.142 mol.dm^{-3}), (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, where V_2 and V_1 are the volume of alkali added to reach the same pH reading to get accurate values of (V_2-V_1): the titration curves were drawn on an enlarged scale: E^0 and $T_L^{\,0}$ are the resultant concentration of perchloric acid and concentration of Ligand, respectively. V_0 is the initial volume of reaction mixture (50 cm^3). Proton-Ligand stability constant pk values(Table 1) of Ligand were calculated by algebraic method point wise calculation and also estimated from formation curves n_A Vs pH (Hal integral method) by noting pH at which n_A = 0.5 [Bjerrum 1957].

Metal-Ligand stability constants (log k) (Table 2&3) were determined by the half integral method by plotting n Vs pL. The experimental n values determined using expression

$$n = \frac{(E_0+N)(V_3-V_2)}{(V_0+V_2)\,T_m^0} \quad .....(2)$$

Where N, E_0, V_o and V_2 have same significance as in equation (1), V_3 is the volume of NaOH added in the metal ion titration to attain the given pH reading and T^0_M (4 x 10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture.

Table 1 Proton-Ligand stability constants (pK)

Sr. No.	System	pK	
		Half Integral method	Pointwise Calculation
1.	L_1 : 1(2'-Hydroxy-5-bromo phenyl) -3(4'-aminophenyl)1,3-propanedione	10.4500	10.4393
2.	L_2 : 1(2'-Hydroxy-5'-bromophenyl) -3(4'-nitrophenyl)1,3-propanedione	8.5100	8.4813

Table 2 Metal-ligand stability constants (log K)

System	Metal Ligand Stability Constants	
	log K_1	log K_2
Cu(II)- ligand - 1	10.1227	7.6971
Cr(II) - ligand - 1	10.3502	8.6173
Ni(II) - ligand - 1	9.9791	7.5926
Cu(II) - ligand - 2	8.3068	5.9500
Cr(II) - ligand - 2	8.5110	4.9000
Ni(II) - ligand - 2	8.4500	4.2119

Table 3 Metal-ligand Stability Constants (log K)

System	Metal Ligand Stability Constants	
	log K_1- log K_2	log K_1 / log K_2
Cu(II)- ligand - 1	2.4256	1.3151
Cr(II) - ligand - 1	1.7329	1.2010
Ni(II) - ligand - 1	2.3865	1.3143
Cu(II) - ligand - 2	2.3868	1.3961
Cr(II) - ligand - 2	3.6110	1.7369
Ni(II) - ligand - 2	4.2381	2.0062

CONCLUSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid + ligand + metal) curve for all systems started from pH = 3.0 this indicated the commencement of complex formation. Also change in colour from yellow to brown in the pH range from 3 to 8 during titration showed the complex formation between metal and ligand.

The order of pK values of ligands is found to be as pK ligand (L_1). > pK ligand (L_2).

The reduction in pK value of ligand (L_2). is attributed to presence of electron withdrawing $-NO_2$ group.

From the table 2 and 3, it is observed that sufficiently large difference between log K_1 and log K_2 values indicates the stepwise formation of complex between metal ion and ligand. The values of log K_1 and log K_2 (table 2) for Cr(II)- ligand 1 complex are higher than Cu(II) ligand 1 and Ni(II)-ligand 1 complexes. It indicates that cr(II) forms more stable complexes with ligand (L_1). than Cu(II) and Ni(II). Also Cr(II) forms more stable complex with ligand (L_2).

The higher value of ratio (log K_1 / log K_2) for Ni(II) ligand (L_2).complex indicates the more stable stepwise complex formation as compare to Cu(II) and Cr(II) complexes.

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