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Short Communication

Effect of Dielectric constants of Dioxane-Water mixtures on Proton-Ligand Dissociation constants (pK) and formation Constants of Cu (II) complexes with 1, 3-Diphenyl Thiazines pH-metrically at 0.1M ionic strength

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Abstract

The interactions between Cu(II) and nitro-phenyl thiazine(L_1), chlorodiphenyl-thiazine (L_2), chloro, 1,3.thiazine (L_3), 1,3 phenyl thiazine (L_4), and 1,3 diphenyl thiazine (L_5), have been investigated by pH-metric technique at 0.1M ionic strength and in different percentage of dioxone-water mixture with Cu(II)-1,3, diphenyl thiazine data obtained can be used to study the effect of dielectric constants on proton–ligand stability constant. It showed that Cu (II) forms 1:1 and 1:2 complexes with substituted thiazines. It could be also seen that pK and log k values are found to be increased with increasing the percentage of dioxane-water mixtures.

Keywords: Substituted thiazine, Cu (II) metal ion and dioxane.

Introduction

Substituted thiazines are antibiotic drugs and good chelating agents due to presence of electron donor nitro, phenyl and chloro groups. A survey of literature reveals that metal-ligand stability constants[1] of Aminoacids, Adific acid, sulphonic acid and salicylic and their derivatives have seen studied by many workers. Proton-ligand and metal-ligand stability constants of Lanthanide Metal ions with substituted Pyrazolines and Pyrazoles have been studied by Bansod[2] Narwade etal[3] have investigated the stability constants of Lanthanide metal ions with some substituted sulphonic acids spectrophotometrically. Sandawale and Narwade[4] have studied the influence of dielectric constants of methanol-water mixtures on formation constants of Cu(II). Glycyl-Glycyl-Glycine peptide complexes. In a view of analytical applications and antibiotic drugs it is worthwhile to know the physico-chemical properties of metal ion complexes and effect of dielectric constants of solvents on stability constants. Therefore, the present work is undertaken to make of systematic study of Cu(II) complexes with substituted thiazines. Rare earth ions are used as probe in biochemistry of calcium. Birnhanm etal[5] showed that lanthanide ion could substitute the calcium ion to produce active enzymine system. Use of unnatural diacting agents in biological system is reported by Narwade[6]. The role of binary complexes in storage and transport for physiological activity of substances has been studied[7]. The biological properties of transition metal ion complexes have been reported by Sharma etal[8].

Material and Methods

Experimental: Standard solution of 0.2M NaOH, 1M.KNO_3 and 0.1M.KNO_3 were prepared by using A.R. grade reagents. The aqueous solution of 0.01M of Cu(II) was prepared in double distilled water and its concentration was checked by standard solution of EDTA(0.01M). The solutions of 1, 3 all above substituted thiazine is prepared in 70% dioxane-water mixture as a solvent.

Calvin-Bjerrum Titration Process: Titrations are carried out in an inert atmosphere of nitrogen gas, in order to keep away CO_2 and removal of dissolved oxygen.

Three sets of titrations are performed as follows: i. Free acid titration nitric acid (1 x 10^{-1}M), ii. Free acid nitric acid (1 x 10^{-1}M) + ligand (20 x 10^{-4} M), iii. Free acid, nitric acid (1 x 10^{-1}M) + ligand (20 x 10^{-4} M) + Metal ion Cu(II), (4 x 10^{-4} M).

Above three sets were titrated against standard solution of 0.2M NaOH and 0.1M ionic strength was maintained constant by adding an appropriate amount of 1M KNO_3 solution. Titrations were carried out by bubbling nitrogen gas for removal of dissolved oxygen gas.

pH values were corrected by the use of Van-Vitart and Hass equation[10].

Metal-ligand Stability Constants (log k_1 and log k_2): The deviation of (acid + ligand metal ion) curves from (acid + ligand) curves was found around pH 2.75 and increased continued for all the systems. This indicated the commencement of complex formation between ligand and metal ion before hydrolysis. The values (n^-) metal-ligand formation numbers were evaluated by the use of Irving-Rossetti's expression". The values of log k_1 for 1:1 complex and log k_2 f or 1:2 complex were evaluated and presented in table 1.

The values of stability constant increased with increasing the percentage of dioxane-water mixture. Table 2 There is no an appreciable change in log k_1 and log k_2 values this may be due to fact of the effect of dixane –bulk solvent that indicates the formation of simultaneously complexes. The deviation between ligand curve and metal ion curve indicated the commentment of complex formation morever the change in colour during titration also indicated the formation of complex between metal ion and ligand.

The Plots of pK/log k vs 1/D (D-Dielectric Constant)

The plots between pK /log k and 1/D showed linear relationship.

Water is recognized by all workers in solution field as being a unique structure having three dimensional like frame work. The dielectric constant of a medium is not solely responsible for the extent of dissociation. There is at least an additional factor for the chemical role of solvent in most cases.

Table-1
Metal ligand stability constant between Cu(II) and substituted thiazines at 0.1m ionic strength

S.N.	System	Log k_1	Log k_2
1	Nitrophenyl thiazine(L1)	5.15	4.85
2	Chloro diphenyl thiazine(L2)	5.05	4.65
3	Chloro 1,3 thiazine(L3)	5.25	4.95
4	1,3-phenil thiazine(L4)	4.95	4.75
5	1,3,diphenil thiazine(L5)	5.00	4.65

Results and Discussion

Calculation of Proton-ligand stability constant (pK). Existance of proton-ligand equilibria corresponds to dissociation of proton from -OH group of legand. $HL = H^+ + L^-$. The deviation between acid titration curve and legand titration curve showed to start the dissociation of -OH group of ligand. The average number of proton-associated with legand ($\bar{n}_A$) were determined from deviation employing using Irving-Rossotti's expression". Formation curves were obtained by plotting $\bar{n}_A$ vs pH in different percentage of dioxane-water mixture and pK values were obtained at $\bar{n}_A = 0.5$. The pK values were found to be increased with increasing the percentage of dioxane-water mixture. That may be due to the effect of bulky solvent[12-14].

Conclusion

It is also observed that from the above results are clearly indicates that the interaction of ligands with metal ions will directly affect the complex formation and due to that changes occur in log K values. *It could be also seen that pK and log k values are found to be increased with increasing the percentage of dioxane-water mixtures.*

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Table-2
The values of pK and log k in different percentage of dioxane-water mixture of Cu (II) - 1,3 diphenyl complex

% Dioxane	Dielectric Constant D	1/D	Mole Fraction	pK	log k_1	log k_2
50	34.26	0.02910	0.1735	5.75	4.65	4.55
55	30.10	0.03322	0.2041	6.50	4.70	4.60
60	25.85	0.03868	0.2395	7.15	4.85	4.65
65	21.80	0.04587	0.2805	7.75	4.95	4.72
70	17.69	0.05652	0.3288	8.00	5.15	4.85
75	14.4	0.06944	0.3864	8.50	5.30	4.93

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