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NOTE

Potentiometric Studies of Copper(II) Complexes with 3-Chloro-2-hydroxy Propiophenone

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In the present paper, the proton-ligand and metal-ligand stability constant of Cu(II) with 3-chloro-2-hydroxy propiophenone is reported.

Key Words: Potentiometric studies, Cu(II) complex, 3-Chloro-2-hydroxy propiophenone.

Complexation studies are very important from the point of view of analytical and biochemical researchers. This study has received the attention of many researchers[1–3]. The extent to which the ligand binds to a metal ion is expressed in terms of stability constants[4, 5] and determined by potentiometric study. The general method for determining the stepwise stability constants for complexes containing simple non-chelating ligands was first described by Bjerrum.

All the chemicals, *viz.*, phenol, NaOH, propionic anhydride, aluminium chloride, hydrochloric acid, ethanol, transition metal salts, perchloric acid, sodium perchlorate etc. were of analytical grade. The concentration of metal ions in the solutions was determined by standard procedure[6–8].

Halogen substituted phenol were prepared by Fries migration reaction of phenol and halogen sub-phenol. The stability constants of binary complexes from the experimental data consists of the following three steps:

- Titration of $HClO_4$ + $NaClO_4$ against the standard NaOH solution
- Titration of $HClO_4$ + $NaClO_4$ + ligand in 60% (v/v) ethanol-water mixture against the standard NaOH solution.
- Titration of $HClO_4$ + $NaClO_4$ + ligand + metal ion in 60% ethanol-water mixture.

The ionic strength of each solution was maintained constant at 0.1 M by adding $NaClO_4$ solution.

Determination of proton-ligand stability constants was carried and verified by least-square method (Table-1).

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The ionization of 3-chloro-2-hydroxy propiophenone can be represented as:

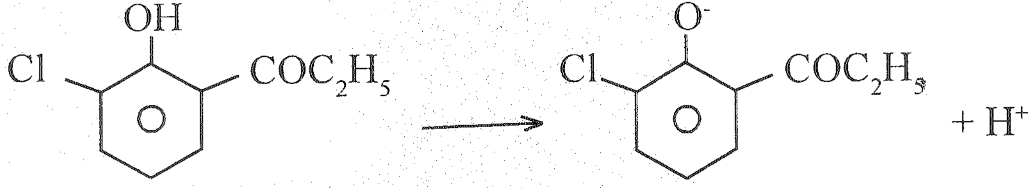

TABLE-1
CALCULATION FOR PROTON-LIGAND STABILITY CONSTANT
(pK) FOR 3-CHLORO-2-HYDROXY PROPIOPHENONE

pH	na	pK
7.75	0.7968	8.3434
7.80	0.7714	8.3281
7.85	0.7201	8.2614
7.90	0.6698	8.2071
7.95	0.6444	8.2082
8.00	0.6191	8.2108
8.05	0.5937	8.2147
8.10	0.5683	8.2192
8.15	0.4921	8.2492
8.20	0.4667	8.2942
8.25	0.3905	8.3306
8.30	0.3651	8.3759
8.35	0.3144	8.4161
8.40	0.2636	8.4553
8.45	0.2128	8.4931

The ligand contains only one replaceable hydrogen atom. Hence, only one pK value is observed. The metal-ligand stability constant for some transition metals and 3-chloro-2-hydroxy propiophenone is given in Table-2.

The proton-ligand and metal-ligand stability constants

The acid + ligand curve deviates from acid curve from pH = 7.75 indicating the deprotonation of phenolic OH group in this pH range. From these curves (figures not shown) the values of $\overline{nA}$ for various pH were calculated and found to be in the range 0.2–0.8 indicating the presence of only one pK for each ligand. pK values calculated by pointwise calculations and half integral methods were found to be in good agreement.

TABLE-2
FORMATION CONSTANTS OF TRANSITION METAL IONS WITH LIGANDS
IN 60% (v/v) ETHANOL-WATER MIXTURE

Temp. = 25 + 0.1°C $\mu = 0.1$ M $NaClO_4$

	Co(II)	Ni(II)	Zn(II)	Cu(II)	Mn(II)
log k_1	6.8166	6.9963	7.1544	7.1222	7.2503
log k_2	5.3957	5.3925	5.6283	5.7171	5.8608
log β	12.2123	12.3888	12.7827	12.8394	13.1111

The displacements of metal titration curve along volume axis (figure not shown) indicate the formation of complex species and lie in the pH region where hydrolysis is not expected the probability of formation of polynuclear complex was ruled out as the metal concentration were very dilute.

Effect of ligand basicity: The effect of the factors such as ligand basicity and metal ions on the stability have also been examined. The relation log k = a pK + b was tested since the ligands used in the present work form a close series as they have identical binding sites and hence the plot of log k *vs.* pK is expected to be linear. The validity of linear relationship has been examined to case of transition metal complexes of substituted ligands by plotting pK *vs* log β. Since the differences between log k_1 and log k_2 are very small, the linear relationship indicates idential binding sites in the ligands.

The slope values of Mn(II) and Cu(II) are near about 1.0. This is in agreement with the suggestion of Narwade *et al.*[8]. The complexes of all other metals have less than one. This is similar to the observation of Jones *et al.*[9] who suggested that the deviation of slope from unity is due to the π-bonding in the chelate formation.

One would expect that a larger difference between log k_1 and log k_2 values is due to the possible steric hindrance to the linking of second ligand to metal ion and the smaller difference is due to the *trans* structure. The ratio of log k_1/log k_2 is small in all cases. Separation factors between the first and second formation constant are well within the expected range and absence of high values implies that there is little or no steric hindrance to the addition of second ligand.

Effect of metal ion: The stability constants of bivalent metal complexes derived from similar type of ligands generally follow the Irving-Williams order.

The present complexes follow the order of stability as Mn > Cu > Zn > Ni > Co.

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