Binary complexes of N-[2-hydroxy-1-naphthalidine]-2-chloroaniline with transition elements

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ABSTRACT

Formation of complexes of transition metals like Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand N-[2-hydroxy-1-naphthalidine]-2-chloroaniline was studied by the potentiometric technique at $27 \pm 0.1^0 C$ in 60% (v/v) dioxane – water medium at 0.1M (NaClO$_4$) ionic strength were determined by Calvin Bjerrum method as modified by Irving & Rossotti.

Key words: Transition metals, ligand, potentiometric technique, Irving & Rossotti.

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INTRODUCTION

Transition metal ion chelate complexes are employed by industry in the large-scale purification of amino acids and in the synthesis of wide range of drugs. Efficient design and optimization of these techniques therefore requires knowledge of chemical equilibria within the system and its dependence on temperature. The formation of complexes, in aqueous solution is a matter of great importance in all the fields of chemistry like inorganic analytical, biochemistry, industrial etc. There is pressing demand for the search of chelating agent which can be used in place of traditionally used compounds. The wide range of chelating agents will help for selecting suitable ligands for complexation [1-2] Potentiometric titrimetry in aqueous solution is most commonly adopted method for finding the stability constant of metal ions with different Ligands[3-4]. It is useful for the determination of equilibrium constant also. In recent years complexation is greatly influenced biological processes that are of metal ions with Ligands like drugs, amino acids, etc., coordinates biometals such as Co(II), Cu(II), Ni(II) and Zn(II) etc which affects their homeostasis[5]. Compounds with N or O donar atoms are frequently used for the formation of complexes with metal ions and have great importance in both biological and chemical applications [6-8]. The present study deals with the potentiometric studies of metals such as Mn(II), Co(II), Ni(II), Cu(II) and Zinc (II) with N-[2-hydroxy-1-naphthalidene]-2-chloroaniline.

EXPERIMENTAL SECTION

All the chemicals used for the potentiometric determination are of A.R. Grade such as HClO$_4$, NaClO$_4$, NaoH. The ligand and metal ion solution prepared in double distilled water. The distilled water obtained from metal distillation plant was redistilled over alkaline permanganate. An all glass quick fit assembly was used to prepare distilled water. Always fresh distilled water was used conductivity equal to 1.6×10^{-6} mhos. All the measurements were performed

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on solutions adjusted to an ionic strength of 0.1M with NaClO$_4$. A stream of purified nitrogen was used as the inert atmosphere in the titration cell to degus solution.

The pH-meter Elico Cl-120 standardized by using butter solutions of 4.0 and 9.2 pH. The titrations of Acid, Acid + ligand and Acid + ligand + metal ion was performed as described in the previous work[9-10]. The data was analysed and protonation constant and stability constant values were determined using computer program in Excell.

RESULTS AND DISCUSSION

The proton – ligand equilibrium constant for ligand were determined by Calvin – Bjerrem using pH metric method, which was modified by Irving – Rossotti for the calculation of $\bar{n}_A$. In Irving – Rossotti method the pH – titration of the three sets of mixture against alkali were performed.

1. Free acid – A
2. Free acid + Ligand – A + L
3. Free acid + Ligand + metal – A + L + M

The pK values were determined using half integral method. It is observed that in present investigation ligand have Cl at ortho and meta position to azomethine nitrogen of the shiff base and does not display pk_1^H values. The absence of pK is due to the electron withdrawing effect of Cl group present in the ligand.

From the titration curves metal ligand stability constat values wer determined and represented in table 1.

Cu(II)> Ni(II)> Zn(II)> Mn(II)

The stability constant values of Cu(II) complex is found to be high. This extra stability of Cu(II) complex could be attributed to the unique electronic configuration of Cu^{2+} and the John-Teller effect.[11]

There are three well known series which shows the trends in stability constants

Pfeiffer order as: Cu(II) > Ni(II) > Fe(II) > Zn(II) > Mg(II)

Irving & William order: Mn(II) < Co(II) < Ni(II) < Cu(II) < Zn(II)

Mellor and Mallay order : Cu(II)> Ni(II)>Co(II)>Zn(II)>Mn(II)

Table. 1: Formation constant of transition metal ions with Ligands 60% (v/v) dioxane – water mixture
Temp: 30 ± 0.1^{0}C   M = 0.1M (NaClO$_4$)

Log (stability Constant per unit)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
Logk$_1$	4.55	5.35	5.38	8.52	5.19
Logk$_2$	3.85	4.56	4.91	6.89	4.93
Log $^\beta$	8.4	9.91	10.29	15.41	10.12

The direct correlation of stabilities of metal complexes with ligand basicity's is based on the assumption that the base strength is a measure of the 6-bonding ability of Ligands with metal ions.

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