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FORMATION CONSTANT OF TRANSITION METAL CHELATES WITH 2,2' BIPYRIDYL AMINE , 1-2 AND 1-3 DIAMINO PROPANE

M.P.BRAHMBHATT AND L. S. BHUTADIYA

SHETH M. N. SCIENCE COLLEGE, PATAN - 384 265

art_kinjal@yahoo.co.in

ABSTRACT:

Formation of 1:1:1 ternary complex species (MAL) has been inferred and the relevant equilibrium has been established using potentiometric technique on the basis of interaction of M^{2+} ions {M= Cd(II) } with ligand A [A= 2,2'Bipyridyl amine] in the presence of the ligand L [L = 1-2 ,1-3 Diamino propane] in aqueous medium at constant ionic strength of 0.2 Mole dm^{-3} and temperatures 25⁰C .An attempt has been made to for obtain the extent of metal ion distribution among the various species over the entire pH-range of study.

KEY WORDS : *Transition metal, Diamines, Formation constant.*

INTRODUCTION:

Transition metal chelates of different ligand with oxygen and nitrogen donors have been reported^{1,2}. The transition metals have tendency to form coordination compounds with Lewis bases, with groups which are able to donate an electron pair. Amino acids are well known chelating agents, their importance in biological system and in industry has earned attention of chemist for their metal complexes³⁻⁶. During past several decades, diamines and their derivatives are studied for important applications as stable complexes in fields like biotechnology, environmental science and biochemistry etc⁷⁻⁹.

In the present study an attempt has been made to determine the stability constant of ternary complexes of Cd(II) with diamines. Various Factor influencing the formation and stabilities of ternary complexes have been discussed.

MATERIALS AND METHODS:

EXPERIMENTAL :-

Conductivity water was used trough the work. Distilled water was redistilled over alkaline potassium permanganate. The pH of this water was found to be ~6.8 . Digital μ -361 pH meter

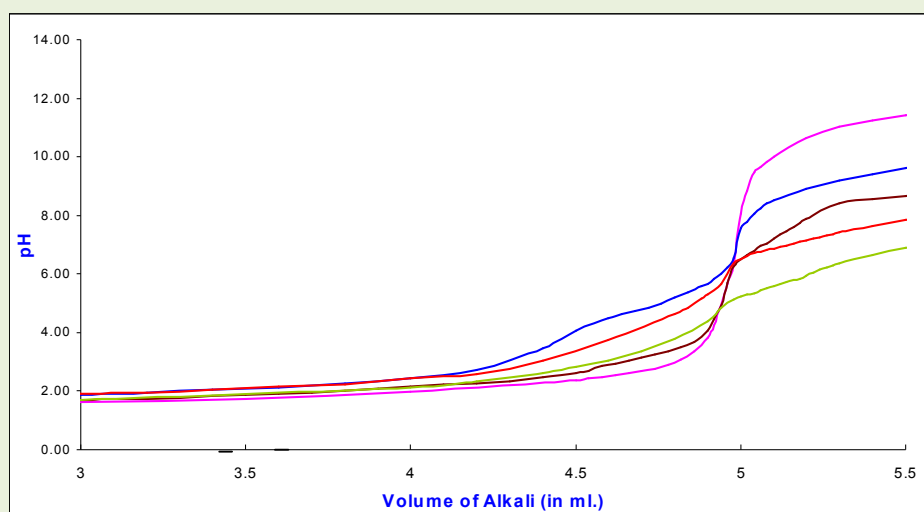
with readability ± 0.01 with combined glass calomel electrode has been used for potentiometry.

All the ligands used were of A.R. grade. They were obtained from different chemical companies and their purities were checked by noting their boiling points. Stock solution of Cd(II) perchlorate solutions were standardized by complexometric EDTA titration.¹⁰ Carbonate free NaOH solution was standardized by reported method¹¹. Stoichiometrically 1:1:1 concentration of Cadmium (II) A and L is maintained in the solution. Five sets of the solutions were prepared containing:

- (1) known amount of free HClO_4 .
- (2) free HClO_4 + known amount of primary ligand.
- (3) free HClO_4 + known amount of secondary ligand.
- (4) free HClO_4 + known amount of primary ligand + known amount of metal perchlorate.
- (5) free HClO_4 + known amount of primary ligand + known amount of secondary ligand + known amount of metal perchlorate.

Total volume of each mixture was raised to 50 ml using conductivity water. Some representative pH titration curves are presented in fig. 1. The titration curves are shown in fig. as under nH, n and pL were calculated using computer programme on the basis of literature¹²⁻¹³.

Fig. :- 1



RESULT AND DISCUSSION:

The order of formation constants for the mixed ligand chelates in the 1:1:1 and 1:1:2.5 proportions is similar as that for Ni(II) chelates with the same primary and secondary

significantly lower than 1:1:1 ratio. It shows that maximum possibility and optimum conditions for mixed ligand formation constant is in 1:1:1 ratio.

The order can be explained in terms of basicity of secondary ligand. The value of mixed ligand formation constants can be explained on the basis of special behavior of 2,2'-bipyridylamine. Beside that there is also π -bond formation by the back donation of electrons from M \rightarrow N. The $d\pi$ - $P\pi$ interaction has been observed in metal – 2,2' bipyridylamine complexes. The N \rightarrow M σ -bonding, there exists strong M \rightarrow N π -interaction due to back donation of electrons from metal $d\pi$ orbital to the vacant delocalized π -orbitals over the 2,2' bipyridylamine molecule. The presence of M \rightarrow N π bond has been confirmed by various investigations¹⁴⁻¹⁷.

As a result of π -interaction in M \rightarrow N bond, the concentration of electrons around the metal ion in $[M(2,2'\text{bipy.A.})]^{+2}$ complex does not increase significantly and electro negativity of the metal ion in $[M(2,2'\text{bipy.A.})]^{+2}$ remains the same as in $[M(\text{H}_2\text{O})]^{+2}$ and even in presence of higher concentration of ligand. So it is expected that $\log K_{\text{MAL}}^{\text{MA}}$ should be nearly equal to $\log K_{\text{ML1}}^{\text{M}}$

But in this case, it is observed that the mixed ligand formation constant values in case of excess ligand are significantly lower. This indicates that the excess concentration of ligand, play an important role, and create non favorable situation for MAL formation. Due to higher concentration of L the electron density is more surrounding the metal ion. Hence its tendency to accept back electron is also reduced. Therefore, M \rightarrow N, $d\pi$ - $p\pi$ interaction may not be strong as observed in case of 1:1:1 ratio. This may be the reason in lowering of the $\log K_{\text{MAL}}^{\text{MA}}$ values in presence of excess L. This is very interesting and it needs further investigation.

Table

Mixed Ligand Formation Constants of Cd(II)		
Temp : 25 ⁰ ± 0.1 ⁰ C		
$\mu = 0.2 \text{ M (NaClO}_4\text{)}$		
Ligand	$\log K_{\text{Cd.A.L}}^{\text{Cd.A}}$ 1 : 1 : 1	$\log K_{\text{Cd.A.L}}^{\text{Cd.A}}$ 1 : 1 : 2.5
Ethylene diamine	6.20*	3.82
1,2 diamino propane	6.39*	3.56
1,2 diamino propane	6.06*	4.35

*Reported

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