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Research Paper

Potentiometric Studies of Bivalent Metal Ions with Adenine and Nitrilotriacetic Acid

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Abstract: A potentiometric titration technique has been used to determine the stability constants of the various bivalent metal ions, Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) with biologically important nucleobases (Adenine) and aminopolycarboxylic acid (Nitrilotriacetic acid) at 30 ± 1 °C and ionic strength $I = 0.1$ M (NaNO₃). The acid-base properties of both ligands were investigated and discussed. The protonation constants of ligands Adenine (A) and Nitrilotriacetic acid (B) were determined and used for determination of stability constants of the ternary (1:1:1) and quaternary (1:1:1:1) systems in aqueous solution. The observed concentration of species formation of ternary and quaternary complexes of metal complexes obtained by SCOGS computer program and represented in graphical form using ORIGIN 6.1. The species formation curves of various ternary and quaternary complexes reveal that the complex formation was found to occur in simultaneously manner. The Stability constants of ternary and quaternary complexes were calculated by SCOGS computer program using potentiometric pH-metric titration values. The order of stability constant of quaternary system has been discussed and found that the complex species MA, MB, MAB and M₁M₂AB type followed the Irving William order of stability constants. The species formation curves of each metal complexes occurring at different physiological pH has been shown in figures and discussed briefly.

Keywords: Adenine, Quaternary system, Stability Constant, SCOGS.

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Introduction

The research on the complexation reactions has always been of great interest because of the numerous applications of the complexes, which have certain properties different from those of its components^[1]. The metal ions in presence of organic and inorganic ligands are playing a crucial role in the field of analytical chemistry^[2], catalysis^[3], biology^[4], medicine^[5], chemical protection of radiation in the study of metalloproteins and metalloenzymes^[6,7]. Moreover, the ternary and quaternary complexes play an important role in biological processes e.g., enzymes are known to be activated by metal ions^[8]. Mixed-ligand, mixed-metal complexes involving more than one metal ions of the same or different types may prove as better models for multimetal-multiligand equilibrium^[9] occurring in the biological systems^[10,11]. Such complexes are of importance in the study of bio-fluids particularly when hyper accumulated metal ions

are present for physiological or pathological nature^[12]. Mutual influences between metal ions may be of antagonist or of synergistic nature. Complexes of nitrilotriacetic acid (NTA) have been widely adopted in biology and are gaining increasing uses in biotechnology, particularly in protein purification techniques known as immobilized metal ion affinity chromatography (IMAC)^[13]. Nitrilotriacetic acid has gained, recently, popularity as metal chelator in IMAC^[14]. The metal complexes of adenine (Ade) have considerable interest in the design of model complexes involving purines which could mimic three interactions of metal ions with DNA. Complexes of adenine also show significant anti-inflammatory activity, antitumor activity^[15] and different animal cancer^[16]. The present investigation, therefore, is an attempt to gather facts leading to a better understanding of the complexation pattern of metal chelates and multinuclear chelates towards some bivalent transition metal ions. The

species distribution with pH at different compositions, formation constants of binary, ternary, quaternary complexes and possible equilibria for the formation of species are reported in this paper.

Material and Methods

All the reagents were used of AR/GR grade and their solutions were prepared in double distilled carbon dioxide free water. Metal nitrate solutions were prepared and standardized by EDTA titration^[17]. The ligand NTA dissolved consuming two moles of alkali solution. Adenine was prepared by constant stirring in double distilled water. Solution of NaOH and HNO₃ were prepared in ultra distilled water and standardized against standard oxalic acid solution as usual.

The other experimental details have been described elsewhere^[18]. The ratio of M₁:M₂:Ade:NTA (1:1:1:1) and the total volume 50 ml were kept in all experimental condition. All the mixtures were titrated with carbonate free standard 0.1 M NaOH solution at fixed temperature 30° C and maintaining a fixed ionic strength I=0.1 M NaNO₃. The total volume 50 ml of solution were maintain in following manner.

Acid solution

A: 5 ml NaNO₃ (1.0M) + 5 ml HNO₃ (0.02 M) + H₂O

Ligand solution

B: 5 ml NaNO₃ (1.0M) + 5 ml HNO₃ (0.02 M) + 5 ml A/B (0.01) + H₂O

Binary solution (1:1)

C: 5 ml NaNO₃ (1.0M) + 5 ml HNO₃ (0.02 M) + 5 ml M (0.01) + 5 ml A/B (0.01M) + H₂O

Mixed ligand ternary solution (1:1:1) (M:A:B)

D: 5 ml NaNO₃ (1.0M) + 5 ml HNO₃ (0.02 M) + 5 ml M (0.01) + 5 ml A (0.01M) + 5 ml B (0.01M) + H₂O

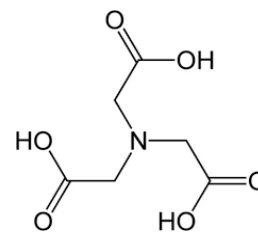
Mixed Metal-Mixed Ligand quaternary solution (1:1:1:1) (M₁:M₂:A:B)

E: 5 ml NaNO₃ (1.0M) + 5 ml HNO₃ (0.02 M) + 5 ml M₁ (0.01) + 5 ml A (0.01M) + 5 ml M₂ (0.01 M) + 5 ml B (0.01M) + H₂O

Where M=M₁=M₂= Co(II), Ni(II), Cu(II), Zn(II),Pb(II) and Cd(II) metal ions and A is Adenine and B is Nitrilotriacetic acid (NTA)

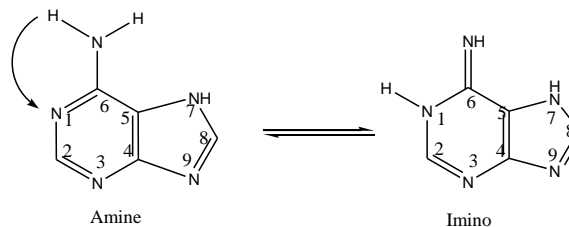
Results and Discussion

NTA is non toxic aminopolycarboxylic acid. It is a tripodal tetradentate trianionic ligand. NTA behaves as a tri or quardidentate ligand, coordination taking place from one nitrogen atom and two or three carboxyl oxygen atom. It is colorless solid that is used as a chelating agent to control of polyvalent metal ions in aqueous solutions by sequestration^[19].



Structure of NTA

Adenine is chemically 6-amino purine, is one of the most common nucleic acid base found in the DNA and RNA, which is directly involved in protein synthesis and in the transfer of the genetic information. The heterocyclic molecules in solution generally yield a mixed population of species in equilibrium when the hydrogen atoms attached to nitrogen are able to migrate to other free nitrogen or oxygen within the same molecule (prototropic change). This kind of tautomerism depends on the dielectric constant of the solvent and on the pK value of the heteroatoms. The tautomeric forms of Adenine are the *amine* and *imino* form respectively.



Tautomerism in adenine

Although Adenine can undergo a change from an amine to an imino form, the amine form is strongly favored being more difficult to detect even traces of the imino form in the naturally occurring DNA. The ionization constants have been determined using potentiometric technique^[20] and calculated using SCOGS computer program that employs a least square method^[21]. These values are listed in Table 1, which are in good agreement with those reported in the literature.

Sayce^[22] developed a new computer program SCOGS (Stability constant of generalized species) which employs the conventional non linear least square approach. It is capable of calculating simultaneously or individually, association constants for any of the species formed in the system containing up to two metals and two ligands, provided that the degree of complex formation is pH-dependent. Thus, SCOGS may be utilized to analyze appropriate pH titration data to yield metal-ion hydrolytic constants, stability constants of simple complexes (MA, MB and MAB etc.).

Table1: Proton ligand and metal ligand binary, ternary and quaternary constants (log β_{pqrst}) in aqueous solution

$I = 0.1 \text{ M (NaNO}_3\text{)}, \text{ temp} = 30 \text{ }^\circ\text{C [A = Ade; B = NTA]}, \text{ Limits of error in the constants} = \pm (0.1 - 0.2) \text{ in log unit.}$

Species	Protonation Constant (Log β_{pqrst})							
	Ligand		Metal Hydrolytic		Metal Complexes			
	A	B	M(OH) ₊	M(OH) ₂	MA	MB	M-A-B	M ₁ -M ₂ -A-B
LH3		13.93	-	-	-	-	-	-
LH2	10.88	12.13	-	-	-	-	-	-
LH	7.02	9.65	-	-	-	-	-	-
Co	-	-	-8.23	-17.83	6.84	10.38	17.75	-
Ni	-	-	-8.10	-16.87	4.32	11.5	17.53	-
Cu	-	-	-6.29	-13.10	6.18	12.94	18.22	-
Zn	-	-	-7.89	-14.92	4.06	12.84	18.85	-
Cd	-	-	-6.89	-14.35	5.88	9.78	15.95	-
Pb	-	-	-9.84	-15.54	4.05	11.34	15.84	-
Cu-Co	-	-	-	-	-	-	-	23.15
Cu-Ni	-	-	-	-	-	-	-	24.12
Cu-Zn	-	-	-	-	-	-	-	25.52
Cu-Cd	-	-	-	-	-	-	-	23.12
Cu-Pb	-	-	-	-	-	-	-	22.12

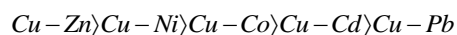
SCOGS may also be used to calculate constants for "mixed" complexes containing two different metals and two different ligands. The overall stability constants (β_{pqrst}) of complexes under studied are expressed by the general equation in aqueous solutions as follows:

$${}_pM_1 + {}_qM_2 + {}_rA + {}_sB + t(OH) \leftrightarrow (M_1)_p (M_2)_q (A)_r (B)_s (OH)_t$$

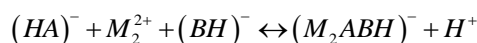
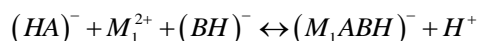
$$\beta_{pqrst} = \frac{[(M_1)_p (M_2)_q (A)_r (B)_s (OH)_t]}{[M_1]^p [M_2]^q [A]^r [B]^s [OH]^t}$$

Where, integer s is positive for a hydroxo species, negative for a protonated species and zero for a neutral species. The evaluation and refinement of stability constant of the complexes formed have been done and species distribution curves were obtained by plotting % concentration v/s pH.

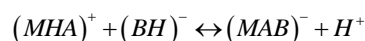
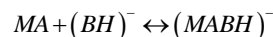
Comparing the speciation curves of systems under studied, it will be found that quaternary species is dominated among all the species formed at higher pH range. Quaternary system observe the presence of Multinuclear complex species, protonated ligand species; AH₂, AH, BH₃, BH₂, BH, binary and ternary complex species viz. [M1(II)-A-BH]-and [M2(II)-A-BH]-The overall stability constants of mixed-metal mixed ligand [M1(II)-M2(II)-Ade-NTA] (1:1:1:1) quaternary systems form a composite Irving-Williams order and the trend is found to be as:



A skim of species distribution diagram (fig 1-5) reveals that at very low pH the concentration of binary and ternary complexes are less than those of protonated ligands because in aqueous solution there is competition between metal ions and hydrogen ions for ligands, so that the apparent metal-binding ability of a ligand decreased at lower pH. The concentration of ternary species increased with increasing pH in each of the system studied. The extra stability of ternary complexes is due to interaction outside the coordination sphere. This may sometimes be due to formation of hydrogen bonds between the coordinated ligands. The simultaneous formation of ternary complex may be explained as per the following equilibria:



The alternative method for the formation of ternary complex is expressed by the following equilibria:



Similarly, the quaternary complexes occur in larger concentrations than the ternary complexes at higher pH. Multimetal-multiligand complex shows its maximum abundance $\approx 62\%$ to 82% in the pH range ≈ 4.5 to 7 and at still higher pH there is a gradual fall in its concentration.

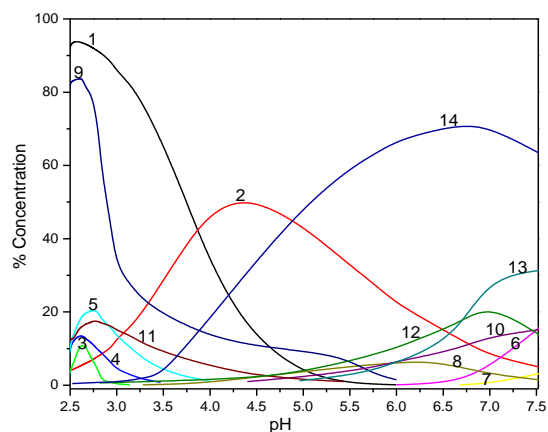


Figure 1: Species distribution diagram of (1:1:1:1)Cu(II)-Pb(II)-Adenine(A)-NTA(B) system: (1)H₂L₁ (2)HL₁ (3)H₃L₂ (4)H₂L₂ (5)HL₂ (6)Cu(OH)₂ (7)Pb(OH)₂ (8)CuA (9)CuB (10)PbA (11)PbB (12)Cu-A-B (13)Pb-A-B (14)Cu-Pb-A-B

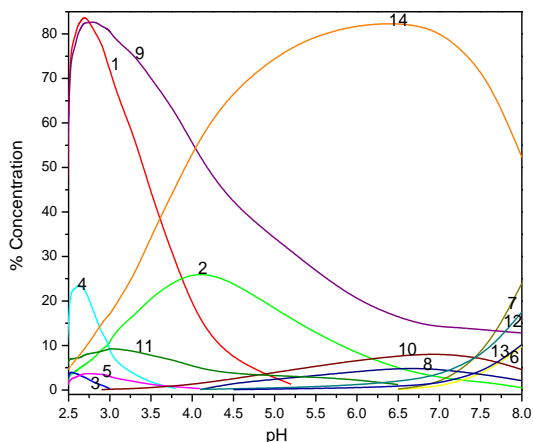


Figure 2: Species distribution diagram of (1:1:1:1)Cu(II)-Cd(II)-Adenine(A)-NTA(B) system: (1) H₂L₁ (2)HL₁ (3)H₃L₂ (4)H₂L₂ (5)HL₂ (6)Cu(OH)₂ (7)Cd(OH)₂ (8)CuA (9)CuB (10)CdA (11)CdB (12)Cu-A-B (13)Cd-A-B (14)Cu-Cd-A-B

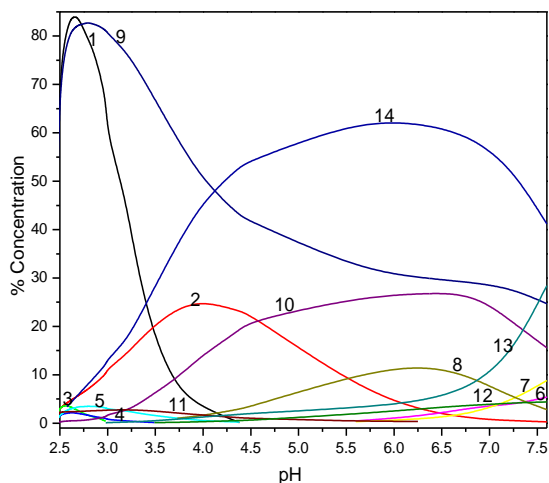


Figure 3: Species distribution diagram of (1:1:1:1)Cu(II)-Co(II)-Adenine(A)-NTA(B) system: (1)H₂L₁ (2)HL₁ (3)H₃L₂ (4)H₂L₂ (5)HL₂ (6)Cu(OH)₂

(7)Co(OH)₂ (8)CuA (9)CuB (10)CoA (11)CoB (12)Cu-A-B (13)Co-A-B (14)Cu-CO-A-B

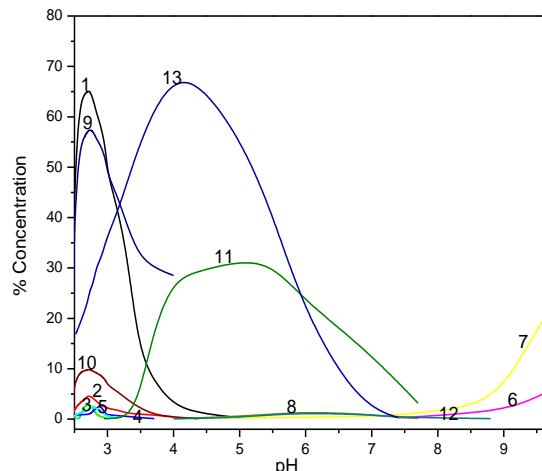


Figure 4: Species distribution diagram of (1:1:1:1)Cu(II)-Ni(II)-Adenine(A)-NTA(B) system: (1)H₂L₁ (2)HL₁ (3)H₃L₂ (4)H₂L₂ (5)HL₂ (6)Cu(OH)₂ (7)Ni(OH)₂ (8)CuA (9)CuB (10)NiB (11)Cu-A-B (12)Ni-A-B (13)Cu-Ni-A-B

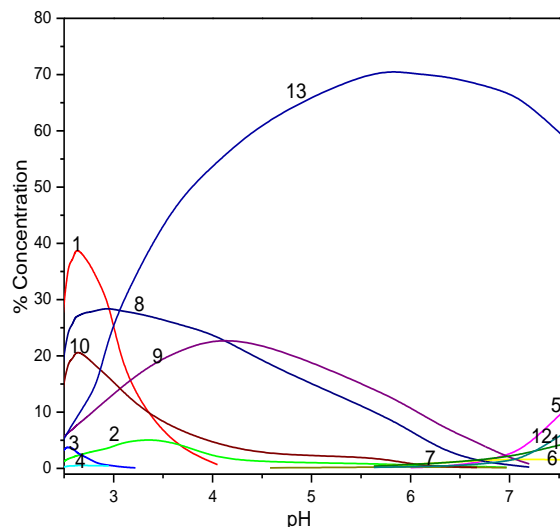
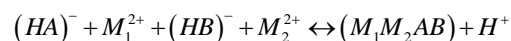


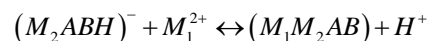
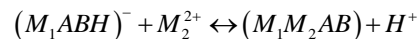
Figure 5: Species distribution diagram of (1:1:1:1)Cu(II)-Zn(II)-Adenine(A)-NTA(B) system: (1)H₂L₁ (2)HL₁ (3)H₂L₂ (4)HL₂ (5)Cu(OH)₂ (6)Zn(OH)₂ (7)CuA (8)CuB (9)ZnA (10)ZnB (11)Cu-A-B (12)Zn-A-B (13)Cu-Zn-A-B

There is occurrence of maxima of 70.9 % (at pH ≈ 6.8), 82.35 % (at pH ≈ 6.2), 62.12 % (at pH ≈ 6), 67% (at pH ≈ 4.5) and 70.5 % (at pH ≈ 5.8) for Cu-Pb-Ade-NTA, Cu-Cd-Ade-NTA, Cu-Co-Ade-NTA, Cu-Ni-Ade-NTA and Cu-Zn-Ade-NTA (1:1:1:1) quaternary species respectively. There is a decline in the concentration of quaternary complex which may also be attributed to the formation of hydroxo species as the buffer region corresponding to the complexation equilibria has been found to be overlapping with the hydrolytic equilibria of metal ions in solution.

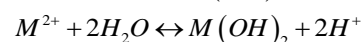
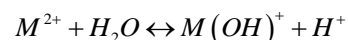
The simultaneous formation of quaternary complex may be expressed as:



Another form of equilibria may be represented as:



Dissociation of the quaternary complex and appearance of hydroxo species at higher pH region may be expressed as:



Conclusion

It is concluded that in all the system under studied, complexation occurs through simultaneous process in all the $M_1(II)$ - $M_2(II)$ -Ade-NTA (1:1:1:1) quaternary systems covering the entire pH region. In term of complex species, the order was quaternary > ternary > binary, which can be explained based on the increased number of fused rings and the extra stabilization caused by ligand-ligand interactions.

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