Short Communication

A Systematic study of stability constants of binary complexes of some peptides with Mg(II), Co(II), Ni(II) and Cu(II) metal ions by analytical methods

R.B. Pawar[*], A.Y. Deshmukh and V.W. Tathe
Department of Chemistry, S.S.S.K.R. InnaniMahavidyalaya, Karanja (Lad) Dist. Washim, MS, India
dr.radhapawar@gmail.com

Abstract

A detailed study of complexes with peptides antibiotics under identical set of experimental condition which would cover many aspects of complexation is still lacking. Hence the present work is undertaken to make a systematic study of stability constant of binary complexes of some antibiotics or drugs with Mg (II), Co (II), Ni (II) and Cu (II) metal ions by PH meter.

Introduction

The linear relationship between log K and pK observed by Irving and Rossotti[1] for complexes of some metal ions with i. substituted oximes and ii. substituted salicyladehydes were attributed by Jones et al to the fact that the study was limited to two particular groups of ligands with variation of dissociation constants within a narrow range. In present investigation, the values of slopes of straight lines are found to be nearly equal to unity.

According to Ernst and Menashi[2], the effect of substituent in the ligand on the stability of metal-ligand complexes, as compared to that of proton- ligand complexes, will be i. to some extent if slope = 1, ii. to a lesser extent if slope < 1, iii. to a greater extent if slope >1.

Jones and coworkers[3] suggested that since Cu(II) and Ni(II) act as π electron donors and Fe(III) acts as an acceptor, for a series of closely related ligands, the slope of the correlation plot should be smaller than unity for Cu(II) and Ni(II) and greater than unity for Fe(III). The data reported in the literature, however, are not in full agreement with the predictions. For instance, for complexes of Fe(III) with oximes and substituted salicylicacids, the values of slopes are 0.90 and 0.75 respectively, whereas Cu(II) and Ni(II) imidoacetates and catechol complexes of Cu(II) and Ni(II) and Zn(II) gave slopes greater than one. On the other hand, for phthalicacid complexes of Cu(II) and Ni(II), the slopes less than unity have been reported. Jahagirdar and Khanolkar[4] have obtained slope values for transition metal complexes of substituted salicylicacids in the range of 0.80 to 1.00. Narwade and Khobragade[5] have studied lanthanide complexes and obtained slope values less than unity. Narwade et.al[6] have also investigated the metal-ligand stability constants of Co(II), Ni(II) and Cu(II) complexes

with p-cresol and diketones. They have obtained slope values for above complexes as 0.890. 0.785 and 0.901 respectively. The slope values nearly equal to unity indicated that the change in partial molar free energy of proton-ligand and metal-ligand complexes exactly compensated with each other.

Materials and methods

Following system are arbitrarily chosen for determining metal legand stability constant and confirmation of complexes spectrophotometrically. i. Mg(II) (L1)- Glutathione, ii. Co(II) (L2)- Carnosine, iii. Ni(II) (L3)- DLphenylalanine, iv. Cu(II) (L4)- Pentaglycine.

The Spectrophotometric study has to be do ne with a limited aim of comparing the result obtained by this technique with those of pH-metric technique.

To understand the role played by the solvent medium on stability constant of the metal complexes, Log K values for some system are evaluated in different percentage of ethanol water mixtures. Log K values are utilized to examine the relation between Log K_1 and K_2

Calvin- Bjerrum titrations: The study of complex formation of legands with metal ions has been undertaken to make the systematic study of complexes between peptides and metal ions pH-metrically by Calvin- Bjerrum titrations methods.

Metal ions uses are: Transition metal ions. Co(II). Ni(II). Cu(II). Mg(II).

pH metric titrations of : i. Nitric Acid (1.00×10^{-2}M), ii. Nitric Acid (1.00×10^{-2}M) and legand, iii. Nitric Acid (1.00×10^{-2}M) and legand (20.00×10^{-4}M) and metal salts (4.00×10^{-4}M)

against sodium hydroxide solution are carried out. Ionic strength of solution was maintained constant (μ=0.10M) by adding an appropriate amount of water and ethanol water mixtures the data log K_1 log K_2 values are utilized to examine between Pk and log K.

Results and discussion

The values of log K_1 and log K_2 calculated by pointwise calculations are presented in Table-1 for under investigation.

Salient Features of Metal Titrations Alkaline earth metal ion: Mg (II).

The departure of (A+L+M) titration curve from (A+L) titration curve started from pH 3.70. The maximum value of n is 2.15. This indicated 1:1 and 1:2 complex formation.

Transition metal ions: Co(II), Ni(II) and (Cu(II): The deviation of (A+L+M) titration curves from (A+L) titration curves for above ions commenced around pH 3.00.

Ni(II) and Cu(II) formed pale green colour and Co(II) formed light pink colour with all systems around pH 4.20. The systematic values of n are obtained upto the highest value around 2.00, indicating the formation of 1:1 and 1:2 complexes.

Validity of LogK = (a pK + b) Relation

The metal-ligand stability constants (LogK$_1$ and LogK$_2$) are evaluated for peptide complexes with metal ions as shown in Table-1.

Table-1: Metal-Ligand Stability Constants (LogK) of binary complexes by different Methods.

Sr. No.	System	Half Integral Method		Pointwise Calculation Method	
		log K_1	log K_2	log K_1	log K_2
1.	Ni(II) - L$_1$	6.2950	4.0110	6.2246	3.6017
	Ni(II) - L$_2$	9.3188	7.2431	9.0615	7.6044
	Ni(II) - L$_3$	5.7080	3.2308	7.8014	3.1608
	Ni(II) - L$_4$	6.0732	4.0110	5.9586	3.4078
2.	Co(II) - L$_1$	7.9922	3.8179	7.4916	3.2106
	Co(II) - L$_2$	9.8185	4.8417	10.1555	4.1486
	Co(II) - L$_3$	8.2990	3.4069	9.5822	3.1636
	Co(II) – L$_4$	7.0970	2.4437	7.0599	2.3935
3.	Mg(II) - L$_1$	6.0732	4.0110	5.9586	3.4078
	Mg(II) - L$_2$	7.0970	2.4437	7.0599	2.3935
	Mg(II) - L$_3$	8.1179	6.1285	10.4079	4.8196
	Mg(II) - L$_4$	6.2503	5.2506	7.1506	5.4007
4.	Cu(II) - L$_1$	5.9762	4.9168	5.7000	3.4412
	Cu(II) - L$_2$	9.3417	6.9351	9.3178	6.7017
	Cu(II) - L$_3$	8.5070	3.4049	8.0373	3.3786
	Cu(II) - L$_4$	9.8004	5.7050	9.6041	5.5532

The linear relation, LogK = (a pK + b), first used by Bjerrum[7] has been found by some workers to hold for transition metal complexes of a series of closely related ligands. In the present investigation, above relation is tested by plotting the graphs between ($pK_1 + pK_2$) against $LogK_1$ and $LogK_2$ by observing a good linear relation giving slope values 0.95 and 0.88 respectively. The same validity of linear relation is observed by Irving and Rossotti for metal complexes of a series of 8-hydroxy quinolines[8], the interaction of a metal ion with a base corresponds to the neutralisation reaction in exactly the same sense as does the corresponding reacting hydrogen ion. It is, therefore, reasonable to expect that there should be a similarity in the factors influencing the bonding of hydrogen ion and metal ions to a Lewis base and that for a closely related series, there should be a relationship between dissociating tendencies of hydrogen ions and metal ions.

Conclusion

The values of slopes of Cu(II), Ni(II) and Co(II) Mg(II) complexes in the present work are not in good agreement with the values of Jones et[9] al regarding the behaviour of π electron donors like Cu(II) and Ni(II). The disagreement may be attributed to the fact that π electron donating or accepting properties of cations may not be the only factor which influences the slope values. Other factors such as ionisation potential of metal ion, nuclear repulsion between metal ion and donor atoms, tendency of metal ion to form π bonds and ligand field stabilization may influence the slope values.

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