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Equilibrium Studies of Binary and Ternary Complexes of Some Transition Metal Ions with Thiamine Hydrochloride

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Abstract

The interaction of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) metal ions with thiamine hydrochloride (TC) has been studied by pH-metric technique at 0.1 M (KNO_3) ionic strength at 302 ± 0.5 K in aqueous medium. The data obtained were used to evaluate the values of proton-ligand and metal-ligand stability constants using Irving-Rossotti titration technique. Mixed- ligand complex studies of these metal ions using aspartic acid (ASP) and glutamic acid (GLU) as primary ligands and TC as secondary ligand have been carried out pH-metrically at the same conditions.

Key Words: Ternary complexes, Transition metal ions, thiamine hydrochloride, , aspartic acid and glutamic acid.

Introduction

Recently there has been considerable interest in the study of binary, ternary and quaternary complexes by pH-metric method[1-3]. Thiamine, vitamin B_1 was the first B vitamin discovered. A deficit of this vitamin causes several diseases in children, such as beriberi and epilepsy [4-6]. Thiamine hydrochloride occurs largely in cells and its active co-enzyme from thiamine pyrophosphate whose interaction with metal ions is biologically importance as it has a wide range of coordinating sites. Hence the complexing properties of the thiamine hydrochloride have been studied with various bivalent transition metal ions and different secondary ligands[7].

Ternary complexes of Ni (II) and Cu (II) with nicotinic acid as primary ligand and imidazoles, benzimidazole, histamine and L-histidine as secondary ligands have been studied by Nair and Neekantan[8]. Patil and Mhaske[9] have studied the stability constants of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with nitrilotriacetic acid and iminodiacetic acid as primary ligands and pyridoxine hydrochloride and ethambutol hydrochloride as secondary ligands potentiometrically. Nigam and coworkers[9] have studied the ternary complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) using ASP as primary ligand and thymine as secondary ligand potentiometrically. Ternary complexes of Cu (II) using ASP and GLU as primary ligands have been reported potentiometrically by Pandeya and Patel[11]. Solution equilibia of ternary systems involving transition metal ions, hydroxomic acid, and bioligands have been studied by Khalil and Mehmoud[12]. Gazala Mohamed[13] studied ternary complexes of Co (II) involving nitrilotriacetic acid and some biologically active ligands. Patil[14] has studied ternary complexes of some transition metal ions with aspartic acid and glutamic acid as primary ligands and nicotinic acid and ascorbic acid as secondary ligands pH-merically. In this paper the stability constants of binary and ternary complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) ions with ASP and GLU as primary ligands and PHC as secondary ligand at 302 ±0.5 K and at fixed ionic strength,

μ = 0.1 M KNO_3 using modified form of Irving-Rossotti pH-metric technique[15] in aqueous medium has been studied.

Experimental

The ligand TC was obtained from Merk and was used as such. Carbonate free sodium hydroxide solution was prepared by standard method[16]. All other solutions were prepared in doubly distilled water.

The pH-metric measurements were carried out by using Elico digital pH-meter model L-120 with combined glass-calomel electrode with an accuracy of ± 0.01 of pH unit at 302 ± 0.5 K. the pH-meter was standardized against 0.05 M potassium hydrogen phthalate solution in acid medium and 0.01 M borax solution in alkaline medium. For determination of proton-ligand stability constant of the secondary ligand and the metal-ligand stability constants of binary and ternary complexes, the following set of solutions were prepared and titrated against standard alkali solution.

Binary Systems

i) 9.7 X 10^{-3} M HNO_3
ii) 9.7 X 10^{-3} M HNO_3 + 5.0 X 10^{-3} M TC
iii) 9.7 X 10^{-3} M HNO_3 + 5.0 X 10^{-3} M TC +1.0 X 10^{-3} M metal ion.

Ternary Systems

i) 9.7 X 10^{-3} M HNO_3
ii) 9.7 X 10^{-3} M HNO_3 + 1.0 X 10^{-3} M TC
iii) 9.7 X 10^{-3} M HNO_3 + 1.0 X 10^{-3} M primary ligand +1.0 X 10^{-3} M metal ion
iv) 9.7 X 10^{-3} M HNO_3 + 1.0 X 10^{-3} M primary ligand +1.0 X 10^{-3} M metal ion + 1.0 X 10^{-3} M TC

The ionic strength was maintained constant (0.1 M) by adding required volume of 1M KNO_3. The ratio of metal (M): secondary ligand (L) was maintained at 1: 5 in each of the binary systems and the ratio of metal (M): primary ligand (A): secondary ligand (L) was maintained at 1: 1: 1 in each of the ternary system.

Results and Discussion

Proton-Ligand Stability Constants: The plots of volume of alkali (NaOH) against pH-meter readings were used to evaluate the proton-ligand stability constants of TC. The deviation between free acid titration curve and secondary ligand titration curve was used to evaluate the formation functions, $\bar{n}_A$.The proton-ligand formation curves were then obtained by plotting the values of $\bar{n}_A$ versus pH-meter readings. From the graphs, the value of log K_1^H was evaluated by half integral method (method A) and point wise calculation method (method B) and presented in Table 1.

Table 1: PROTON-LIGAND STABILITY CONSTANTS

Ligand	log K_1^H	
	Method A	Method B
TC	4.82	4.83

Metal-Ligand Stability Constants of Binary Complexes

The metal-ligand stability constants of binary complexes were evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes were absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds:

1. The metal titration curves showed displacement with respect to the ligand titration curves along the volume axis. This indicated the affinity of the ligand with metal ions which released protons and produced the volume difference ($V_3 – V_2$).
2. The colour change of the ligand in presence of metal ions appeared showing the formation of new species.
3. The hydrolysis of the metal ions was suppressed due to complex formation and the precipitation did not appear during the titration.

From the ligand and metal titration curves the value of $\bar{n}$ and from that the values of pL were obtained. The formation curves obtained were used to evaluate the metal-ligand stability constants by method (A) and (B) and presented in Table 2.

Table 2: Metal-Ligand Stability Constants Of Binary Complexes

System	log K_1		log K_2		log β	
	Method A	Method B	Method A	Method B	Method A	Method B
[Mn(II)-TC]	3.18	3.17	2.28	2.30	5.46	5.47
[Co(II)-TC]	4.45	4.47	2.68	2.65	7.13	7.12
[Ni(II)-TC]	5.12	5.12	2.80	2.83	7.92	7.93
[Cu(II)-TC]	5.42	5.43	3.44	3.41	8.86	8.84
[Zn(II)-TC]	4.79	4.83	3.37	3.31	8.16	8.14

The variation of $\bar{\eta}$ was found to be 0 to 2 which indicated that the composition of complexes was 1:2 in solution.

The Irving-Williams order[17, 18]of stability constants was followed.

Metal – Ligand Stability Constants of Ternary Complexes

The metal – ligand stability constants of the ternary complexes were evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes were absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds:

1. The ternary complex titration curves show the displacement with primary complex titration curves. The horizontal distance was measured between acid curve and the secondary ligand curve(V_2 – V_1) and subtracted through the horizontal distance between ternary complex curves and primary complex titration curves (V_4 – V_3) show the positive difference which proves the earlier released of protons in the formation of ternary complexes.
2. The hydrolysis of the metal ions was suppressed and precipitation did not result.

The values of $\bar{\eta}$ varies from 0 to 0.8, thus confirming the formation of 1: 1:1 mixed ligand complexes. The values of logK^{ASP}_{MAL} and logK^{GLU}_{MAL} have been evaluated from the formation curves ($\bar{\eta}$ vs. pL). At $\bar{\eta}$ = 0.5 in the formation curve, pL = log K. The metal-ligand stability constant of PHC as secondary ligand and ASP and GLU as primary ligand are presented in Table3.

Table 3: Metal-Ligand Stability Constants Of Ternarycomplexes

System	log K									
	Mn(II)		Co(II)		Ni(II)		Cu(II)		Zn(II)	
	A	B	A	B	A	B	A	B	A	B
[M (II)-ASP-TC]	4.61	4.60	5.62	5.64	6.12	6.15	7.18	7.20	5.84	5.85
[M (II)-GLU-TC]	4.38	4.40	5.15	5.16	5.78	5.79	6.72	6.76	5.83	5.84

The Irving-Williams order[17, 18]of stability constants was observed in case of binary as well as ternary complexes which is

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

This sequence of stability of complexes with respect to metal ion is due to deceasing atomic radius and increasing the second ionization potential.

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References

[1]. A. E. Martell and R. M. Smith, Critical Constants-1: Amino acids, New York (1974).
[2]. H. Sigel, Metal Ions in Biological Systems-2, Marcel-Dekker, Inc., New York (1973).
[3]. M. T. Beck, Chemistry of Complex Equilibria, Van Nostrand, New York, pp.174-190 (1970).
[4]. The Pharmaceutical Codex, 11th Edition, The Pharmaceutical Press, London (1979).
[5]. Clarke’s Isolation and Identification of Drugs, 2nd Edition, The Pharmaceutical Press, London (1986).
[6]. Remington’s Pharmaceutical Science, 17th Edition, Mack Publishing Co., Easton, Pennsylvania (1985).
[7]. A Gayatri Devi and S. Satyanarayana, Indian J. Chem., 38A, 624(1999)
[8]. M.S. Nair and M. A. Neelkantan, Indian J. Chem., 38A, 1307(1999).
[9]. A. B. Patil and T. H. Mhaske, Asian J. Chem., Vol.14, No.1,pp. 125-129 (2002).
[10]. N. B. Nigam, P. C. Sinha, M. Gupta and M. N. Srivastava, Indian J. Chem., 22A, 818(1983).
[11]. K.B. Pandeya and R. N. Patel, Indian J. Chem., 30A, 193 (1991).
[12]. M.M. Khalil and R.K. Mahmoud, J. Chem. Eng., Data,52(2),789 (2010).
[13]. Gazala Mohamed, Res. J. Chem., Sci.,2(3), 12(2012).
[14]. A. B. Patil, Rasayan J. Chem,.6(2), 161 (2013).
[15]. H. Irving and H. S. Rossotti, J. Chem. Soc., 76, 2904(1954).
[16]. A.I. Vogel, A Text Book of Quantitative Analysis, Longman, London, pp.241 (1961).
[17]. H. Irving and R.P.J. Williams, Nature,162,746(1948)
[18]. H. Irving and R.P.J. Williams, J. Chem. Soc., 76, 31