Formation constants and thermodynamic parameters of bivalent metal ion complexes with 3-amino-5-methyl isoxazole Schiff bases and N, N; N, O and O, O donor ligands in solution

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ABSTRACT

The formation constants of binary and ternary complexes of Schiff bases MEMIIMP, MIIMP, BMIIMP, CMIIMP, MMIIMP, MIIBD and some N,O; N,N; O,O donor ligands with Co (II), Ni (II), Cu (II) and Zn (II) have been determined by potentiometrically at 0.1M KNO₃.in aqua organic medium. The effects of temperature and ionic strengths on binary systems have been studied. All these metalions form 1:1 and 1:2 binary complexes and 1:1:1 ternary complex. The thermodynamic parameters ΔG, ΔH and ΔS of binary complexes have been determined and discussed. The stabilities of ternary complexes are discussed on the basis of $\Delta \log K$.

Keywords: Isoxazole Schiff bases; potentiometrically, formation constants, thermodynamic parameters, $\Delta \log K$.

INTRODUCTION

Schiff bases are important intermediates in a number of enzymatic reactions involving interactions of an enzyme with an amino or a carbonyl group of the substrate [1]. Schiff bases have the highest degree of hydrolysis at pH-5 and the solubility in water is also highest at this pH [2]. Schiff base ligands are able to coordinate with many different metals and stabilize them in various oxidation states [3]. Azomethine and their transition metal complexes have remarkable potential for inhibiting growth of various pathogenic micro organisms [4]. The dissociation constants of HBMI, HCBMI, HBBMI and HDBMI and stability constants of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes were determined potentiometrically at 303K and at 0.1 M KNO₃ ionic strength in 70% v/v acetone-water medium and reported earlier. The order of PKa values and stability constants were found to be HBMI > HBBMI > HCBMI > HDBMI. This was attributed to increasing order of –I effect of substituent. The stability constants of these complexes with respect to bivalent transition metal ions followed the order $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$. This order was in accordance with Irving-Williams natural order [5].

However not much of work has been carried out on the chelating tendencies of 3-(2-hydroxybenzylideneamino)-5-methyl isoxazole and its substituted derivatives with different bivalent transition metal ions. Therefore an attempt has been made to study the interaction of MEMIIMP, MIIMP, BMIIMP, CMIIMP, MMIIMP and MIIBD and some N, O; N, N; O, O donor ligands with bivalent metal ions such as Co (II), Ni (II), Cu (II) and Zn (II) in solution.
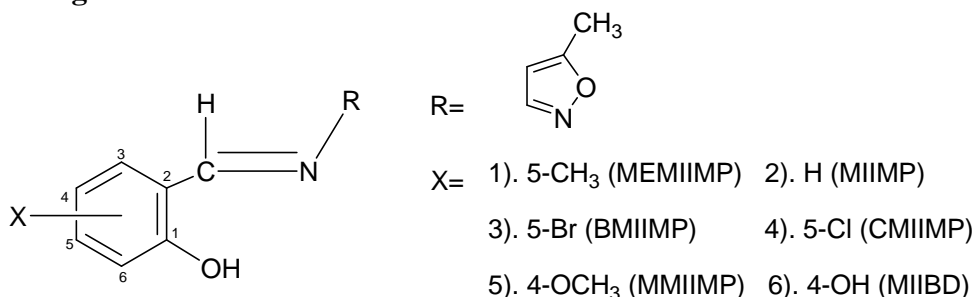
EXPERIMENTAL SECTION

Synthesis of ligands
MEMIIMP / MIIMP / / BMIIMP/ CMIIMP / MMIIMP / MIIBD
A mixture of 3-amino-5-methyl isoxazole (0.05mol) and salicylaldehyde / 5-methyl salicylaldehyde / 5-Bromo salicylaldehyde / 5-Chloro salicylaldehyde / 4-methoxy salicylaldehyde / 4-hydroxy salicylaldehyde (0.05mol) was taken in methanol and refluxed for 2 hours. The yellow coloured Schiff bases obtained were recrystallized from petroleum ether and methanol. Purity of the compounds was checked by TLC. Yield: 80-85%.

Structures of ligands

1). 5-CH_3 (MEMIIMP)   2). H (MIIMP)

3). 5-Br (BMIIMP)   4). 5-Cl (CMIIMP)

5). 4-OCH_3 (MMIIMP)   6). 4-OH (MIIBD)

Reagents and materials
The ligand solutions were prepared by dissolving a known weight of the solid in methanol (Analar). Metal ion solutions were prepared from metal nitrates samples (BDH) in double distilled water and standardized with EDTA [6] Solution of HNO_3 and 1M KNO_3 were also prepared in doubly distilled water. A carbonate free potassium hydroxide solution was used as the titrant and standardized against Analar Potassium hydrogen phthalate.

Potentiometric measurements
The apparatus, general conditions and methods of calculation were the same as reported earlier [4]. The following mixtures were prepared and titrated potentiometrically against standard 0.1M KOH at three different temperatures and three different ionic strengths. For each solution mixture the volume was made up to 50 ml with double distilled water before the titration. The following titrations were carried out.

1. HNO_3 (4.0 x 10^{-3} M)
2. HNO_3 (4.0 x 10^{-3} M) + ligand (1.0 x 10^{-3} M)
3. HNO_3 (4.0 x 10^{-3} M) + ligand (1.0 x 10^{-3} M) + metal ion (2.0 x 10^{-4} M)

A constant temperature was maintained using a high precision constant temperature bath (Baheti Enterprises). The pH measurements were made using a digital Digisun Electronic model DI-707 pH meter in conjunction with a combined glass and calomel electrode. The instrument could read pH in the range of 0 -14 with a reading accuracy of ± 0.1 pH units. The pH-meter readings were corrected by Van Uitert and Hass relation [7].

RESULTS AND DISCUSSION

Acid dissociation constants

The average number of protons, $\bar{n}_A$, associated with the ligand at different pH values were calculated from the titration curves of the acid in the absence and presence of ligand. The formation curves ($\bar{n}_A$ vs. pH) for the acid systems were constructed and found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that the all ligands have one dissociable proton (phenolic proton). Different computational methods were applied to evaluate the stepwise dissociation constants. The average values obtained are listed in Table-1. The data in the table-1 reveal that the order of dissociation constants with respect to the ligands was found to be MEMIIMP>MIIMP>BMIIMP>CMIIMP>MMIIMP>MIIBD. This order is in accordance with the basicity of the ligands.

Table-1: Dissociation constants and stepwise stability constants of metal complexes at 303K and 0.1 M. ionic strength in aqueous medium

Ligand/ Metal ion	pKa	Stability Constants		Standard Deviation
		Log K_1	Log K_2	
MEMIIMP	8.4			
Co(II)		3.48	3.39	± 0.03
Ni(II)		4.74	3.78	± 0.02
Cu(II)		6.08	5.45	± 0.03
Zn(II)		4.28	3.92	± 0.02
MIIMP	8.36			
Co(II)		3.24	3.1	± 0.03
Ni (II)		3.96	3.48	± 0.02
Cu (II)		5.9	4.97	± 0.03
Zn (II)		3.59	3.4	± 0.02
BMIIMP	7.25			
Co(II)		3.44	3.3	± 0.04
Ni(II)		4.34	3.69	± 0.02
Cu(II)		6.35	5.8	± 0.03
Zn(II)		3.9	3.5	± 0.02
CMIIMP	7.18			
Co (II)		3.18	2.8	± 0.03
Ni (II)		3.626	3.12	± 0.02
Cu (II)		4.397	3.63	± 0.03
Zn (II)		3.48	3.16	± 0.02
MMIIMP	7.1			
Co(II)		3.39	3.26	± 0.03
Ni(II)		4.09	3.57	± 0.03
Cu(II)		5.52	3.91	± 0.04
Zn(II)		3.74	3.3	± 0.03
MIIBD	6.9			
Co(II)		3.3	3.2	± 0.02
Ni(II)		3.92	3.41	± 0.03
Cu(II)		5.05	3.85	± 0.04
Zn(II)		3.57	3.26	± 0.03

Metal ligand stability constants
The formation curves for the metal complexes were obtained by plotting the average number of the ligand attached per metal ion ($\bar{n}$) vs. the free ligand exponent (pL), according to the Irving and Rossetti [8].These curves were analyzed and the successive stability constants were determined using different computational methods [9]. The stability constants log K_1 and log K_2 are given in Table -1. From the data it is found that:

i.   The maximum value of $\bar{n}$ was about two indicating the formation of 1:1 and 1:2 (metal: ligand) complexes only [10].
ii. The order of stability constants with respect to the ligands were found to be MEMIIMP>MIIMP>BMIIMP>CMIIMP>MMIIMP>MIIBD. This order is in accordance with the basicity of the ligands.
iii. The increasing order of the stability constants with respect to the metalions were found to be Co(II)<Ni(II)<Cu(II) > Zn(II), which is also in agreement with Irving and Williams order. This order largely reflects the changes in the heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal ion [11] and the crystal field stabilization energies [12].

Effect of temperature
The dissociation constant and the stability constants of MEMIIMP, BMIIMP, MMIIMP and MIIBD with bivalent metal ions have been studied at three different temperatures 303, 313 and 323K at constant 0.1M KNO_3 ionic strength. The representative related to MEIIMP is given in Table-2. The slope of the plot (log K vs. 1/T) was utilized to evaluate the enthalpy change (ΔH) for the complexation process. From Gibbs energy change (ΔG) and (ΔH) values one can deduce the entropy change (ΔS) using the well known relationships. The thermodynamic parameters ΔH, ΔG and ΔS were presented in Table-2.

It is evident from the data that dissociation constants and the stability constants decrease with rise in temperature, indicating that the formation equilibrium is exothermic in nature. The data in table-2 reveals that all the metal complexes are accompanied by negative enthalpy (ΔG) changes suggesting that the metal-ligand bonds are fairly strong.

Table-2: Stability constants and thermodynamic parameters of memiimp with transition metalions at 0.1 M. KNO_3

Metal ion	Temp (K)	pKa	Log K_1	Log K_2	- Δ G kJ/mole	- Δ H kJ/mole	Δ S J/mole
Co(II)	303 K	8.4	3.48	3.39	20.18	25.42	17.27
	313 K	8.1	3.34	3.24			
	323 K	7.93	3.29	3.20			
Ni(II)	303 K	8.4	4.74	3.78	27.51	107.13	-262.79
	313 K	8.1	4.15	3.33			
	323 K	7.93	3.86	3.23			
Cu(II)	303 K	8.4	6.08	5.45	35.27	124.38	-294.11
	313 K	8.1	5.39	4.65			
	323 K	7.93	5.10	4.33			
Zn(II)	303 K	8.4	4.28	3.92	24.83	54.47	-97.84
	313 K	8.1	3.98	3.64			
	323 K	7.93	3.81	3.53			

Positive entropy changes accompanying a given reaction are due to the release of bound water molecules from the metal chelates. During formation of metal chelates, water molecules from the primary hydration sphere of the metal ion are displaced by the chelating ligand. Thus there is an

increase in the number of particles in the system i.e., randomness of the system increases as shown in the following equation.

$$M^{+2} (aq) + L^-(aq) \; === \; ML^+ (aq) + nH_2O$$
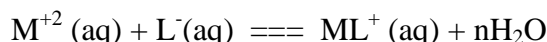
For some complexes negative entropy values are observed, which indicates that the complex largely retains the primary solvation sphere of the metal ion [13] Williams [14] has pointed out that usually a high entropy value is associated with the combination of positive and negative ions combination of a metal ion with a negatively charged ligand always involves displacement of water molecules, which then become part of the solvent. Since the water molecules bound to the metal ions are highly distorted and oriented, the entropy is low. Large negative entropy values are associated with large negative values of enthalpy. For this, the solvent and ligand field – central ion interactions [15] and also π interactions [16] may be possible contributing factors.

Effect of ionic strength
The effect of variation of ionic strength on the stabilities of transition metal complexes of MEMIIMP, BMIIMP, MMIIMP and MIIBD has been determined. For this purpose the proton ligand and metal-ligand stability constants of these ligands have been evaluated at three different ionic strengths (0.1, 0.15 and 0.2M) using potassium nitrate as a supporting electrolyte at constant temperature (303K). For some representative systems the data is summarized in Table-3 are given**.** From the data it is observed that the dissociation constant and stability constants decrease with raise in ionic strength.

Log K values were plotted against square root of μ as per the Debye-Huckel equation. The plots of log K_1 vs $\sqrt{\mu}$ for all systems were found to be linear, the slope values observed in all cases were less than the values expected on the basis of Debye-Huckel equation. This indicates that the ligands in the present investigation interact both in dissociated and undissociated forms and thus various species co-exist in the solution [17].

Table-3: Stepwise stability constants of metal complexes of memiimp at different ionicstrength and at 303 K temperatures

| Metal ion	Stability constants	Ionic strength		
		0.1M	0.15M	0.2M
H$^+$	pKa	8.40	8.14	8.12
Co(II)	Log K_1	3.48	3.40	3.34
	Log K_2	3.39	3.30	3.20
Ni(II)	Log K_1	4.74	3.82	3.42
	Log K_2	3.78	3.60	3.22
Cu(II)	Log K_1	6.08	5.72	5.65
	Log K_2	5.45	4.82	4.53
Zn(II)	Log K_1	4.28	3.94	3.83
	Log K_2	3.92	3.60	3.50

Ternary systems
The stability constants of mixed ligand complexes of Ni(II)-L-A and Co(II)-L-A [where L= Isoxazole Schiff bases MEMIIMP,MIIMP, BMIIMP,CMIIMP, MMIIMP and MIIBD; A= Glycine (Gly) , Phenyl alanine (PA) N,O donors; 1,10-Phenanthroline (1,10-phen), 2,2'-bipyridyl (2,2'-bipy); N,N donors , Oxalic acid (OA), Salicylic acid (SA), O,O donors; and Thioglycollic acid (TGA)] have been determined potentiometrically at 303K and 0.1 M KNO$_3$ ionic strength.

The representative potentiometric titration curves are shown in the Fig-1 and Fig-2. The ternary complexes were formed at different pH regions as compared to their binary complexes, as evidenced from the species distribution curves obtained for the systems using the computer program BEST. The concentration profiles of various species suggest that at lower pH range the binary complex formation predominates over ternary, at higher pH range the ternary complex formation predominates over binary complex formation. Following are some of the salient features that confirm the formation of ternary chelates in solution.
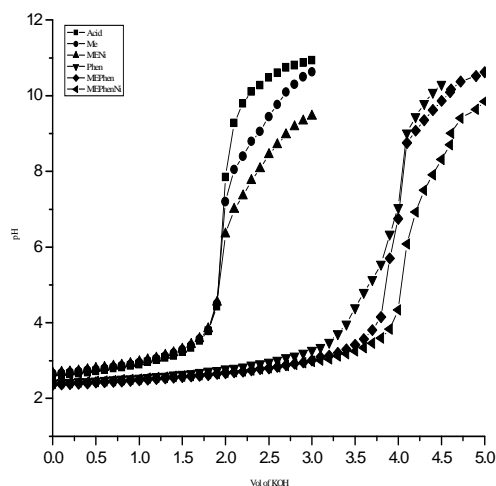
Fig-1: pH titration curves of Ni (II)-1, 10 Phen-MEMIIMP ternary systems in aqueous medium at 303K and 0.1M. Ionic strength.
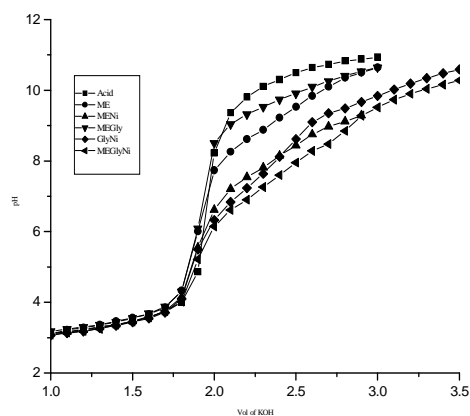
Fig-2: pH titration curves of Ni (II)-MEMIIMP-Gly ternary system in aqueous medium at 303K and 0.1M. Ionic strength.

In all these systems studied, the complex formation occurred in stepwise equilibria. The pH titration curves corresponding with ternary systems indicate that the isoxazole Schiff bases (L) act as primary ligand in the presence of Gly and PA whereas in the presence of 1,10-phen , 2,2'-bipy , OA, SA and TGA they act as secondary ligands. Thus the formation of ternary complexes was stepwise equilibria. The stability constants of ternary complexes were calculated by known equations [18] and presented in table-4. These stabilities were expressed in terms of Δlog K (Table 4) which is the difference between stability constant of ternary complexes and 1:1 binary stability constant of secondary ligand. In the case of Co (II) and Ni (II)-L-Gly / PA/1, 10-phen/2, 2'-bipy/TGA systems positive ΔlogK values were observed indicating the ternary complexes were more stable than 1:1 binary of secondary ligand. This may be due to ligand-ligand

interactions, effective charge neutralization and lesser electrostatic interactions in the case of Gly & PA systems and $d\pi - p\pi$ back bonding interaction in the case of 1,10-phen & 2,2'-bipy systems. In the case of Co (II) and Ni (II)-L-OA / SA systems negative Δ logK values were observed indicating ternary complexes are less stable than 1:1 binary of secondary ligand. This may be due to formation of negatively charged ternary complexes, which involves in greater electrostatic repulsions.

Table-4: Stability constants log of K_{MAL}^{MA} Co (II) / Ni (II) Ternary complexes of MEMIIMP in aqueous medium at 303K and 0.1M ionic strength

| Ligand | pKa | Stability Constants | | | Standard Deviation |
		Binary 1:1	Ternary 1:1:1	Δlog K	
N-O Donors:					
Co-MEMIIMP-Gly	9.83	3.48	4.06	0.58	± 0.03
Ni-MEMIIMP-Gly	9.83	4.74	5.75	0.71	± 0.04
Co-MEMIIMP-PA	9.15	3.48	4.15	0.67	± 0.04
Ni-MEMIIMP-PA	9.15	4.74	5.83	0.79	± 0.03
N-N Donors:					
Co-1,10 Phen –MEMIIMP	8.40	3.48	3.91	0.43	± 0.04
Ni-1,10 Phen-MEMIIMP	8.40	4.74	5.56	0.08	± 0.03
Co-2,2'- bipy –MEMIIMP	8.40	3.48	3.78	0.30	± 0.04
Ni-2,2'- bipy-MEMIIMP	8.40	4.74	5.47	0.43	± 0.02
O-O Donors:					
Co-SA –MEMIIMP	8.40	3.48	3.42	-0.54	± 0.05
Co-OA –MEMIIMP	8.40	3.48	3.36	-0.112	± 0.04
Ni-OA-MEMIIMP	8.40	4.74	4.96	-0.072	± 0.02
S-O Donors:					
Co-TGA –MEMIIMP	8.40	3.48	3.86	0.38	± 0.03
Ni-TGA-MEMIIMP	8.40	4.74	5.60	0.56	± 0.04

CONCLUSION

In conclusion, the order of stability constants of binary and ternary complexes with respect to ligands at different temperatures and different ionic strengths was found to be MEMIIMP>MIIMP>BMIIMP>CMIIMP>MMIIMP>MIIBD. The order of stability constants with respect to metal ions is Co (II) < Ni (II) < Cu (II) > Zn (II) which is in accordance with Irving- Williams natural order. In the case of Co II)/ Ni(II) - L - Gly/PA/1,10-phen/ 2,2'-bipyridine /TGA systems positive Δ log K values were observed indicating the ternary complexes were more stable than 1:1 binary complex of secondary ligand.

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