

Speciation Studies of Ternary Systems Involving Toxic Metals, Dipeptide and Catecholic Ligands

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ABSTRACT: Ternary complexes of metal M [Pb (II), Cd(II) and Hg (II)] with A (Glycylglycine) and B (o-Vanillin and 4- Methyl catechol) are investigated potentiometrically. Ligands A and B bind to metal ion M simultaneously to form 1:1:1 MAB mixed ligand complex in various equilibria. Experiments are performed in aqueous medium at three different temperatures ($20^{\circ}\text{C}\pm 1$, $30^{\circ}\text{C}\pm 1$ and $40^{\circ}\text{C}\pm 1$) and at three ionic strengths ($\mu=0.05\text{M}$, 0.10M and 0.15M) in order to calculate thermodynamic stability constants and other thermodynamic parameters. SCOGS computer program is used to obtain the speciation of various species formed in a particular equilibrium. The relative stability of ternary complexes as compared to binary species are expressed in term of $\Delta \log K$. Values of $\Delta \log K$ suggest that the formation of ternary complexes is favorable. The order of stability of the complexes with respect to metal ion is found to be $\text{Hg(II)} < \text{Cd(II)} < \text{Pb(II)}$.

KEYWORDS : glycylglycine , ternary complexes, speciation, SCOGS.

I. INTRODUCTION

Speciation studies of toxic and essential metal ion complexes are useful in order to understand the role played by the active site cavities in biological molecules and the bonding behaviour of their residues with metal ions[1-3]. The possible ligand groups in proteins are the aminoacid side chains ,the terminal amino, carboxyl ,hydroxyl and thiol groups and in some cases , the amide group in the peptide backbone. However, the study of metal-protein interactions involves complications due to the complex nature of proteins. An exact model of the metal protein system may be difficult to construct in simple biomolecules like aminoacids and peptides but such models may give a tremendous amount of information about the structure of proteins and function of biomolecules in biological systems. The interaction of metals with amino acids ,catechols ,carboxylicacids and peptides has been the subject of much interest due to the importance of metals in many biochemical processes such as respiration, metabolism and nerve transmission.[4-7]. Investigations of multiple equilibria of dipeptides and their interaction with metal ions at varying ionic strengths and temperatures throw light on the mechanism of enzyme-catalyzed reactions.The present work on the speciation of toxic metal ion complexes is useful to understand the role played by biological molecules and the bonding behavior of protein residues with the metal ion. The species refined and their relative concentrations under the experimental conditions represent the possible forms of complexes in bio fluids. Chemical speciation of metals is important for an understanding of their distribution, mobility, bioavailability, toxicity and for setting environmental quality standards [8]. Bioavailability of a particular metal depends on its complex chemical reactions of dissolution, binding and complexation with the constituents of the environmental aquatic media [9].

The present paper describes the speciation studies of mixed ligand complexes of Pb(II), Cd(II) and Hg(II) involving A= Glycylglycine and B = o-Vanillin and 4-Methylcatechol. The chosen ligands bear immense biological and medicinal importance.

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II. RELATED WORK

Dipeptides are important bioligands as they have good coordination sites for metal complexation as revealed by chemical literature [10-19]. Study of the chelating ability of glycine peptides and catecholamines, in particular diglycine with some divalent toxic metals were carried out to understand the mode of complexation of these ligands in biological systems which is used for efficacious treatment for patients with metal poisoning [20-28].

III. EXPERIMENTAL

All the reagents used were of highest purity Merck/Aldrich products. Solutions were prepared in doubly distilled CO₂-free water having pH ≈ 6.8. Solutions of metal and ligand (each 0.01M) were prepared by dissolving accurately weighed amounts in double distilled water. An Elico digital pH-meter model LI-127 with ATC probe and combined electrode type (CL-51B-Glass Body; range 0-14 pH unit; 0-100°C Automatic/Manual) with accuracy ±0.01 is employed for pH-measurement and standardized by using buffer solution of pH=4.0 and 9.20.

All the systems were investigated under equimolar concentration ratio. For each set of titration moles of alkali required per mole of ligand / metal. 'a' is determined and curves were obtained by plotting pH vs 'a'. Six sets of titration mixtures of the following compositions were prepared and titrated against standard sodium hydroxide solution (0.10M) at three different ionic strengths ($\mu = 0.05M, 0.10M$ and $0.15M$) maintained by adding different concentration of NaNO₃ solution to each titration mixture at temperatures 20°C±1, 30°C± and 40°C±1. Temperature was maintained by Siskin Julabo, thermostat model V-12B.

1. Acid titration: HNO₃(2.0×10⁻³M).
2. Ligand 'A' titration: HNO₃(2.0×10⁻³M) + Ligand 'A'(1.0×10⁻³M).
3. Ligand 'B' titration: HNO₃(2.0×10⁻³M) + Ligand 'B'(1.0×10⁻³M).
4. Metal(M)-Ligand 'A'(1:1) titration: HNO₃(2.0×10⁻³M) + Ligand 'A' (1.0×10⁻³M) + Metal nitrate (1.0×10⁻³M).
5. Metal (M)-Ligand 'B'(1:1) titration: HNO₃(2.0×10⁻³M) + Ligand 'B'(1.0×10⁻³M) + Metal nitrate (1.0×10⁻³M).
6. Metal(M) - Ligand 'A' -Ligand 'B'(1:1:1) titration: HNO₃(2.0×10⁻³M) + Ligand 'A'(1.0×10⁻³M) + Ligand 'B'(1.0×10⁻³M) + Metal nitrate (1.0×10⁻³M).

Where, M = Pb (II), Cd (II) and Hg(II)

Ligand 'A' = Glycylglycine abbreviated as (Glygly) and Ligand 'B' o-Vanillin abbreviated as (o-Van) and 4-Methyl catechol abbreviated as (4-MC).

The qualitative analysis of experimental data is subjected to computational analysis in accordance to the algebraic method of Chaberek and Martell [29-30] as modified by Dey *et.al.*[31] and refined by using SCOGS computer program[32-34]. An alternate approach for the calculation of stability constant involving simultaneous equilibria was developed by S. Ramamoorthy and M. Santappa [35-36] which is used for obtaining thermodynamic stability constants of ternary systems formed through simultaneous equilibria. Results are summarised in Table- 1 and 2.

Table-1: Thermodynamic Protonation Constant of Ligand

Parameters	Glycylglycine			Parameters	o-Vanillin			4-Methyl catechol		
	20°C	30°C	40°C		20°C	30°C	40°C	20°C	30°C	40°C
log β ₁ ^{HA}	8.52	8.32	8.20	log β ₁ ^{HB}	8.80	8.62	8.58	9.68	9.45	9.25
log β ₂ ^{H₂A}	–	–	–	log β ₂ ^{H₂B}	–	–	–	17.42	17.22	17.05

$$\log \beta_1^{HA} = pK_2^H$$

$$\log \beta_1^{HB} = pK_2^H$$

$$\log \beta_2^{H_2B} = pK_1^H + pK_2^H$$

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Table -2: Thermodynamic Formation Constants of Binary Complexes

Parameters	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
	Pb(II)-Glygly			Cd(II)-Glygly			Hg(II)-Glygly		
log β _{MA}	4.46	4.34	4.22	4.10	3.96	3.82	3.60	3.40	3.30
	Pb(II)-o-Van			Cd(II)-o-Van			Hg(II)-o-Van		
log β _{MB}	4.52	4.45	4.30	3.82	3.50	3.46	4.26	4.05	3.90
	Pb(II)-4-MC			Cd(II)-4-MC			Hg(II)-4-MC		
logK ^M _{MBH}	3.38	3.28	3.18	3.35	3.22	3.10	3.34	3.16	3.02
logK ^H _{MBH}	-6.20	-5.94	-5.40	-7.30	-7.05	-6.68	-7.32	-6.86	-6.72
logK ^H _{MB}	-7.32	-6.92	-6.65	-8.82	-8.75	-8.62	-10.85	-10.18	-9.88
log β _{MBH}	13.32	12.02	11.52	10.22	10.02	9.76	11.32	11.02	10.86
log β _{MB}	8.32	8.02	7.64	6.12	5.80	5.65	8.05	7.49	7.34

$$\log \beta_{MA} = \log K_{MA}^M$$

$$\log \beta_{MB} = \log K_{MB}^M$$

$$\log \beta_{MBH} = \log K_{MBH}^M + \log \beta_1$$

The values of the thermodynamic stability constants $\log K^{\mu \rightarrow 0}$ were used to determine the standard free energy (ΔG°) for the complexation reaction from Van't Hoff isotherm:

$$\Delta G^\circ = -2.303RT \log K^{\mu \rightarrow 0}$$

The Gibb's Helmholtz equation ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$) and Van't Hoff equation can be put in the following form:

$$\log K^{\mu \rightarrow 0} = \frac{-\Delta H^\circ}{2.303R} \frac{1}{T} + \frac{\Delta S^\circ}{2.303R}$$

The standard enthalpy change (ΔH°) and entropy change (ΔS°) have been determined by linear least square fit method by plotting a graph between $\frac{1}{T}$ vs $\log K^{\mu \rightarrow 0}$ using above equation. In the above equation:

$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R} \quad \text{and} \quad \text{Intercept} = \frac{\Delta S^\circ}{2.303R}$$

The values of ΔG° , ΔH° and ΔS° are presented in Table-3

Table-3: Thermodynamic Formation Constants and Thermodynamic Parameters of Ternary Systems

Parameter	20°C		30°C		40°C		$-\Delta H^\circ$ kJmol ⁻¹	ΔS° Jk ⁻¹ mol ⁻¹
	log K _{μ→0}	$-\Delta G^\circ$ kJmol ⁻¹	log K _{μ→0}	$-\Delta G^\circ$ kJmol ⁻¹	log K _{μ→0}	$-\Delta G^\circ$ kJmol ⁻¹		
Pb (II)-Glygly-o-Van								
logK ^{MI} _{MAB}	23.18	130.04	23.02	133.55	22.80	136.64	23.80	362.65
logK ^{MA} _{MAB}	13.22	74.16	13.06	75.76	12.86	77.07	37.47	125.99
logK ^{MB} _{MAB}	12.38	69.45	12.34	71.15	12.18	72.99	13.12	192.62
Cd (II)-Glygly-o-Van								
logK ^M _{MAB}	16.80	94.24	16.64	52.09	16.52	50.10	16.96	263.46
logK ^{MB} _{MAB}	8.98	50.37	8.85	51.34	8.70	52.13	17.36	112.59
logK ^{MA} _{MAB}	8.36	46.90	8.22	47.68	8.14	48.78	13.12	114.88

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Hg (II)-Glygly-o-Van								
$\log K_{MAB}^M$	16.22	90.99	16.10	93.14	16.01	95.94	12.72	266.91
$\log K_{MA}^M$	8.35	46.84	8.06	46.76	8.02	48.06	18.60	95.16
$\log K_{MB}^M$	8.70	48.80	8.40	48.73	8.30	48.15	23.25	86.16
Pb(II)-Glygly-4-MC								
$\log K_{MABH}^M$	23.02	129.14	22.80	132.27	22.58	135.32	27.08	348.10
$\log K_{MAB}^M$	17.18	96.38	17.10	99.20	17.04	102.12	8.47	299.84
$\log K_{MA}^M$	10.60	59.46	10.50	60.96	10.26	61.48	21.88	128.67
$\log K_{MABH}^M$	16.95	95.09	16.86	97.81	16.75	100.38	12.44	282.04
$\log K_{MBH}^M$	15.56	87.29	15.40	89.34	15.18	90.97	23.80	216.75
$\log K_{MA}^M$	17.30	97.05	17.18	99.67	17.06	102.24	14.77	280.70
$\log K_{MB}^M$								
Cd (II)-Glygly-4-MC								
$\log K_{MABH}^M$	17.52	98.28	17.40	100.94	17.28	103.56	14.77	284.91
$\log K_{MAB}^M$	10.32	57.89	10.25	59.46	10.20	59.17	7.24	172.21
$\log K_{MA}^M$	15.94	33.32	5.80	33.64	5.65	33.86	17.91	52.46
$\log K_{MABH}^M$	13.32	74.72	13.16	76.34	13.04	78.14	16.95	196.83
$\log K_{MBH}^M$	13.20	74.05	13.02	75.53	12.90	77.31	18.05	190.71
$\log K_{MA}^M$	15.34	86.05	15.18	88.06	15.04	90.13	18.32	230.91
$\log K_{MB}^M$								
Hg (II)-Glygly-4-MC								
$\log K_{MABH}^M$	22.50	126.22	22.32	129.49	22.25	133.34	14.63	380.26
$\log K_{MAB}^M$	7.68	43.08	7.72	44.78	7.64	45.78	3.28	136.38
$\log K_{MA}^M$	4.20	23.56	4.08	23.67	3.93	23.55	16.82	22.98
$\log K_{MABH}^M$	12.68	71.13	12.58	72.98	12.40	74.36	17.77	182.28
$\log K_{MBH}^M$	13.08	73.38	12.85	74.55	12.68	75.99	24.21	167.35
$\log K_{MA}^M$	20.45	86.05	20.30	88.06	20.12	90.13	20.51	321.48
$\log K_{MB}^M$								

The stability of ternary complexes over their corresponding binary complexes was evaluated by calculating the parameter $\Delta \log K$ according to the following equation and values of $\Delta \log K$ for ternary complexes are given in Table-4

$$\Delta \log K_{MABH} = \log \beta_{MABH} - (\log \beta_{MA} + \log \beta_{MBH})$$

$$\Delta \log K_{MAB} = \log \beta_{MAB} - (\log \beta_{MA} + \log \beta_{MB})$$

In general, if mixed ligand complexes are most stable than their corresponding binary complexes, the value of $\Delta \log K$ is positive [37-38]. The negative values of ΔG° indicate that the complexation is spontaneous. The negative enthalpy changes (ΔH°) suggest that all the complexation reaction are exothermic, favorable at lower temperature. The positive value of ΔS° for some metal complexes indicate that the formation of these complexes is entropically favored [39-40].

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Table-4 : Value of $\Delta \log K$ for ternary complexes

Parameters	20°C		30°C		40°C	
	$\log \beta^{\mu \rightarrow 0}$	$\Delta \log K$	$\log \beta^{\mu \rightarrow 0}$	$\Delta \log K$	$\log \beta^{\mu \rightarrow 0}$	$\Delta \log K$
Pb(II)-Glygly-o-Van						
$\log \beta_{MAB}$	23.18	14.20	23.02	14.23	22.80	14.28
Cd(II)-Glygly-o-Van						
$\log \beta_{MAB}$	16.80	8.88	16.64	9.18	16.52	9.24
Hg(II)-Glygly-o-Van						
$\log \beta_{MAB}$	16.22	8.36	16.10	8.65	16.01	8.81
Pb(II)-Glygly-4-MC						
$\log \beta_{MABH}$	29.94	12.16	29.82	13.46	29.65	13.91
$\log \beta_{MAB}$	17.18	4.40	17.10	4.74	17.04	5.18
Cd(II)-Glygly-4-MC						
$\log \beta_{MABH}$	24.61	10.29	24.56	10.58	24.45	10.87
$\log \beta_{MAB}$	10.32	0.10	10.25	0.49	10.20	0.73
Hg(II)-Glygly-4-MC						
$\log \beta_{MABH}$	22.50	7.58	22.32	7.90	22.25	8.09
$\log \beta_{MAB}$	7.90	-3.75	7.72	-3.17	7.64	-3.00

$$\log \beta_{MABH} = \log K_{MABH}^M + \log \beta_1^{HB} \qquad \log \beta_{MAB} = \log K_{MAB}^M$$

IV. RESULTS AND DISCUSSION

The experimental data is used to obtain titration curves (pH vs 'a') where, a= moles of alkali added per mole of ligand/metal. In the given Fig-1 (a-f), Curve 1 and 2 are ligand titration curves indicates strong basic nature of dissociable proton. The values of dissociation constants of Glycylglycine , o-Vanillin and 4-Methyl catechol are in close agreement with literature values [41-43] in Table-1

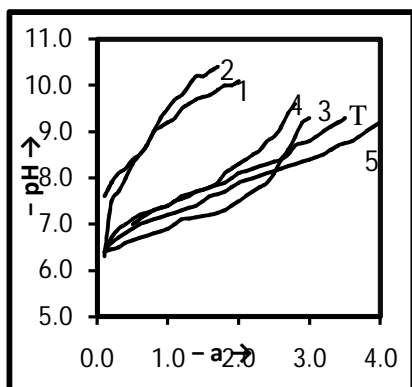


Fig-1(a)

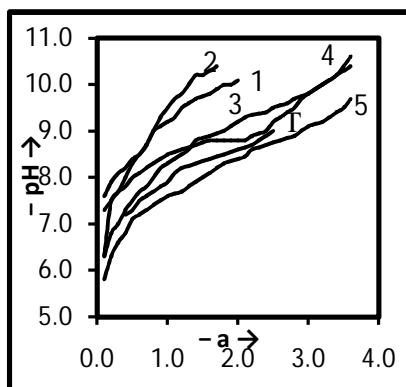


Fig-1(b)

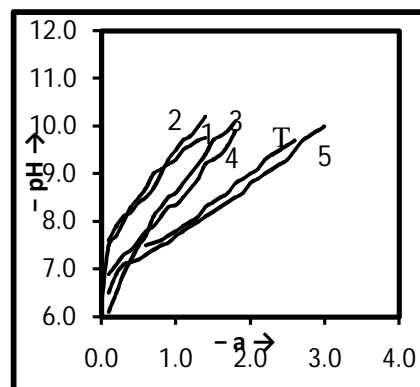


Fig-1(c)

Where, Curve : 1 [Ligand A (Glygly)] ; 2 : [Ligand B (o-Van /4-MC)] ; 3 : [Metal-LigandA (1:1)] ;
4 : [Mixed-Ligand B (1:1)] ; 5 : [Mixed-Ligand A- Ligand B] ; 6 : 'T' [Theoretical Composite Curve].

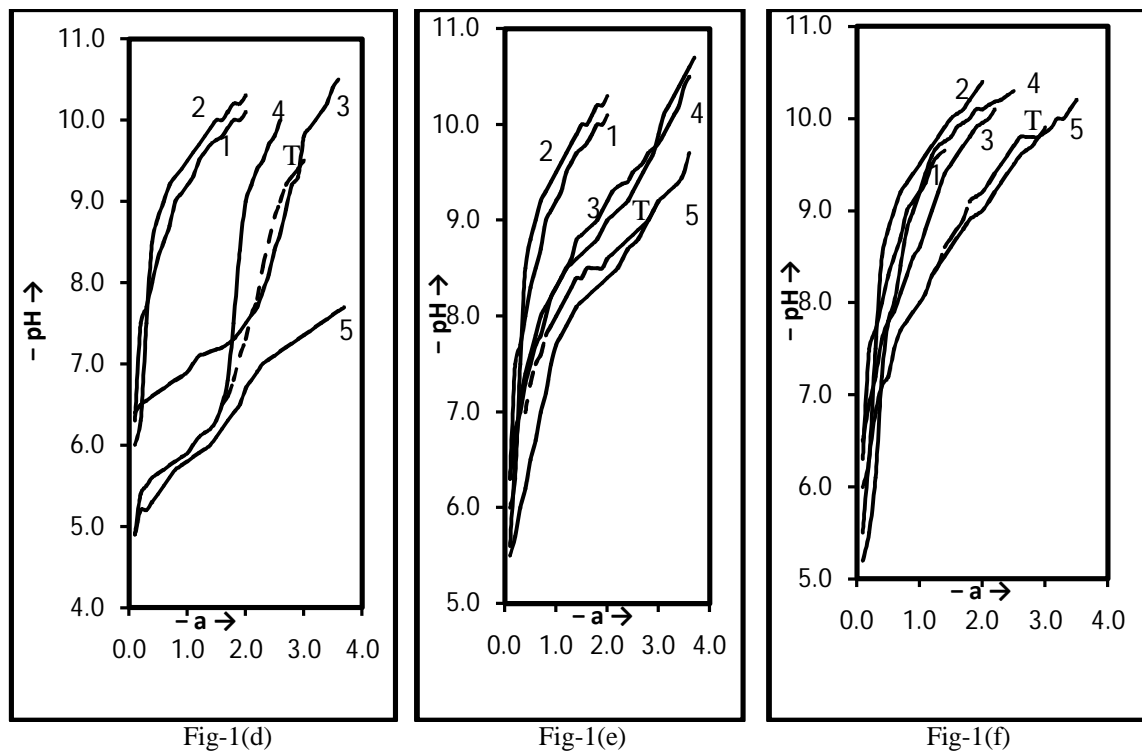


Fig-1 Titration Curves for (a) Pb(II)-Glygly-o-Van (b) Cd(II)-Glygly-o-Van (c) Hg(II)-Glygly-o-Van (d) Pb(II)-Glygly-4-MC (e) Cd(II)-Glygly-4-MC (f) Hg(II)-Glygly-4-MC Ternary systems at 30°C± [$\mu = 0.10M(NaNO_3)$].

Glycylglycine has one dissociable (carboxylate) and one associable (amino) proton. It exists as AH_2^+ , AH and A^- in the pH ranges below 5.0, 2.0–8.0 and above 5.0 respectively. This is also supported by literature report [44]. Further, deviation of curve 3 i.e., metal – ligand A and of curve 4 i.e., metal – ligand B from ligand curves suggests formation of binary complexes. Curve 5 depicts the metal-ligand A- ligand B (1:1:1) titration of Pb(II) / Cd(II) / Hg(II) – Glygly -o-Van / 4-MC ternary systems. The curve 5 in all the figs. is seen to be displaced to the right hand side of 1:1 (MA/MB) titration curves, thereby suggesting the formation of ternary complexes. This is further supported by non-superimposable nature of theoretical composite curve in the region of ternary complex formation. The theoretical composite curve is obtained by plotting the theoretical addition of the values of 'a' corresponding to ligand titration curve of one ligand to the metal – ligand (1:1) titration curve of other ligand. By the analysis of titration curves it is concluded that the two ligands are coordinated to metal ion simultaneously in a single step.

Complexation behaviour of metal and ligand is analyzed by examining curves obtained by using SCOGS computer programme. The typical species distribution curves for Pb(II), Cd(II), Hg(II) - Glygly -o-Van / 4-MC systems, which indicate the formation of Metal-Glygly-Catecholic complexes occur in higher pH region. Mixed ligand complexes of MABH and MAB have been observed that in the ternary as ligand 'B' the formation of MABH is predominated which MAB. Whereas in the case of 'B' ligand the formation of MAB is concluded. Speciation curves [Pb(II), Cd(II), Hg(II)]-Glygly-o-

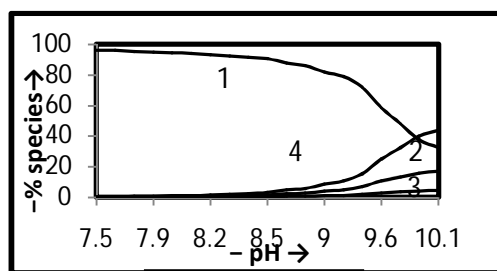


Fig-2(a)

Van are given in Fig-2 (a,b,c).

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Curve 2 and 3 show that formation of MA and MB i.e. binary non protonated complexes take place up in higher pH range with very low concentration $\approx 10-15\%$ respectively. It can be observed from the curve 1 and 4 that concentration of free metal decreases and formation of ternary species MAB comes into existence from $\text{pH} \approx 6.0$ for Cd(II) and $\text{pH} \approx 8.0$ for Pb(II) and Hg(II) then its concentration increases continuously and becomes maximum above $\text{pH} \approx 10.0$ approaching the values nearly 75% for Cd(II)-Glygly-o-Van ternary complex, also 54 % for Hg(II)-Glygly-o-Van whereas it is about 43% for Pb(II)-Glygly-o-Van.

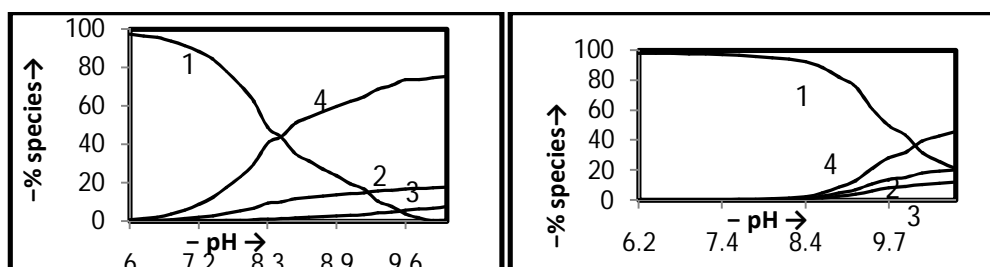


Fig-2(b)

Fig-2(c)

Fig-2 Speciation Curves for (a) Pb(II)-Glygly-o-Van (b) Cd(II)-Glygly-o-Van (c) Hg(II)-Glygly-o-Van at $30^\circ\text{C} \pm [\mu = 0.10\text{M}(\text{NaNO}_3)]$. Where, Curve 1: [M]; 2:[MA]; 3: [MB]; 4: [MAB].

Similarly, speciation curves for all the protonated and non-protonated species of M(II)-ligand A-ligand B (where $\text{M}=\text{Pb(II), Cd(II), Hg(II)}$ and ligand A=Glygly, B=4-Methyl catechol) are given in Fig-3 (a,b,c). Curve 1,2,3 in all these figures show that concentration of free metal decreases continuously and formation of MA and MBH i.e, binary non-protonated / protonated takes place from $\text{pH} \approx 4.5$ and their concentrations is $\approx 40\%$ in all the systems. The formation of

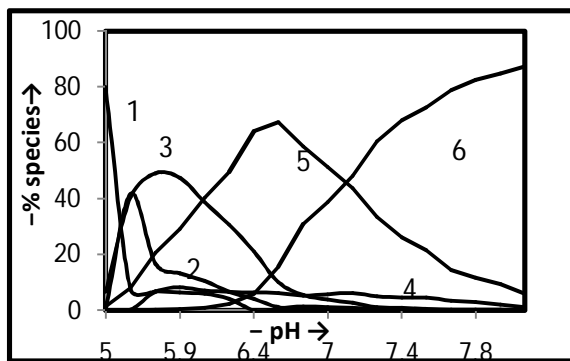


Fig-3 (a)

non-protonated MB species (curve 4) comes into existence in higher pH range and its concentration is less than 10% in all systems. Formation of ternary species takes place by simultaneous coordination of two ligands. Curve 5 show formation of protonated MABH species commences from $\text{pH} \approx 5.5$ and its concentration become maximum at $\text{pH} \approx 6.7$ in Pb(II)-Glygly-4-MC, at $\text{pH} \approx 7.9$ in Cd(II)-Glygly-4-MC and at $\text{pH} \approx 8.5$ in Hg(II)-Glygly-4-MC systems respectively and its percentage is more than 65%. Non-protonated ternary complexes MAB species (curve 6) comes into existence from $\text{pH} \approx 6.0$ in Pb(II)-Glygly-4-MC and from $\text{pH} \approx 7.5$ in Cd(II)/Hg(II)-Glygly-4-MC system as shown in fig-3(a,b,c).

The concentration of MAB ternary species is most prominent species in this system. Nature of speciation curve in Cd(II)/Hg(II)-Glygly-4-MC systems show that concentration of non-protonated MAB species increases only upto $a=3$, thereafter, percentage decreases with increase of pH as a result of dissociation of complex in the range of $3 \leq a \leq 4$ at $\text{pH} 10.0$. It is further evidenced by the occurrence of turbidity/precipitation during titration at $\text{pH} \approx 10.0$. Hence, complex of Pb(II)-Glygly-4-MC is more stable than that of Cd(II)-Glygly-4-MC and Hg(II)-Glygly-4-MC. The high thermodynamic stability of ternary complexes can be attributed to the fact that the electron densities of the metal-ligand bond in ternary systems are redistributed to increase the polarity of the complex.

The mixed ligand complex can be predicted to be formed either by simultaneous interaction of two ligands with metal ions in a single step (simultaneous equilibria) or in two different steps (stepwise equilibria). It is supported by thermodynamic parameters as tabulated in table (1-4). Thus, formation of ternary species takes place by simultaneous coordination of the two ligands in all systems except Hg(II)-Glygly-4-MC.

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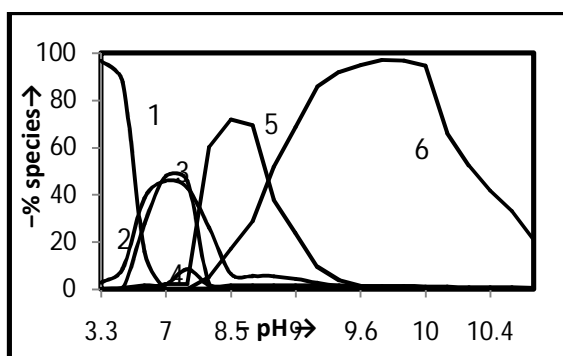
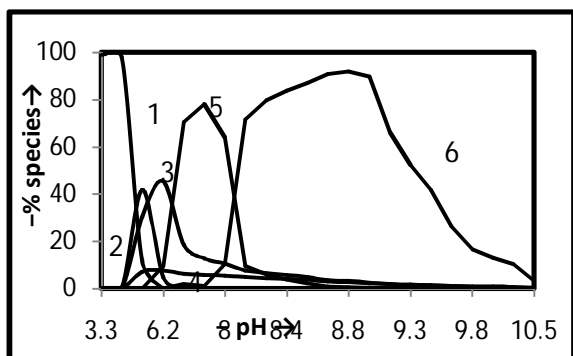


Fig-3(b)

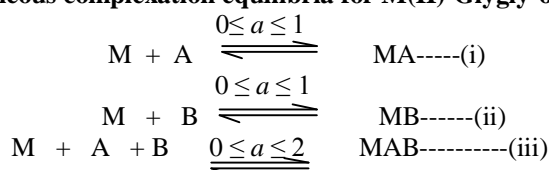
Fig-3(c)

Fig-3 Speciation curves for (a) Pb(II)-Glygly-4-MC (b) Cd(II)-Glygly-4-MC (c) Hg (II)-Glygly-4-MC systems at 30°C± [μ = 0.10M(NaNO3), Where, Curve 1 : [M]; 2 : [MA]; 3 : [MBH]; 4 : [MB]; 5 : [MABH]; 6 : [MAB]

Equilibria involved in above complexation are given in scheme 1 and scheme 2

Scheme 1

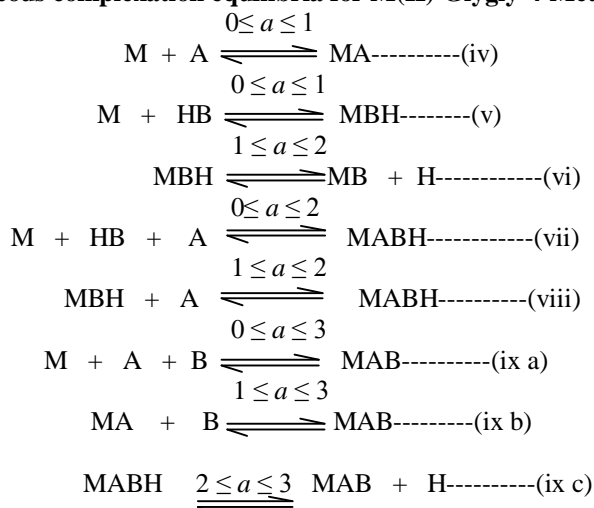
[simultaneous complexation equilibria for M(II)-Glygly-o-Vanillin]



(Charges have been omitted for the sake of simplicity)

Scheme 2

[simultaneous complexation equilibria for M(II)-Glygly-4-Methyl catechol]



(Charges have been omitted for the sake of simplicity)

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V. STRUCTURE OF COMPLEXES

The probable structure and mode of coordination suggested on the basis of the obtained results, are mentioned here under in fig.4 (a-b). Both binary and ternary glycyglycine complexes have been identified for the M(II)-Glygly - Catecholic systems of the toxic metals. The complexation behavior of metal ligand shows that the terminal carboxyl group and the terminal amino group are simultaneously coordinated to the metal ion and the amide also coordinated through the carbonyl oxygen atom to form a five-membered chelate ring. Amine nitrogen atoms can associate with hydrogen ions in the lower pH ranges. Hence, there is often significant competition between hydrogen and metal ions for the second donor site. This situation results in the simultaneous existence of equilibria producing protonated ternary complex species[45]. It is also evidenced by principle of Hard and Soft Acid and Bases (HSAB), the very soft character of Hg(II) and soft /hard character of Cd(II) and Pb(II) shows the preference for the amine nitrogen site over the harder carboxylate or amide oxygen atom. However, this needs further support of spectral studies.

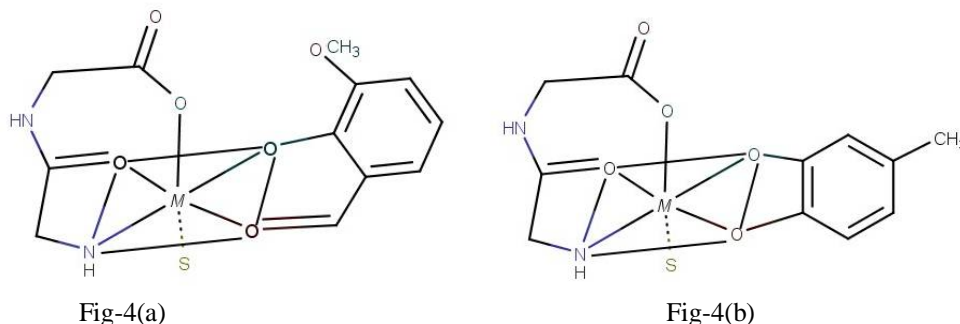


Fig-4 Proposed structures for (a) M(II) -Glygly-o-Van (b) M(II)-Glygly-4-MC ternary complexes, where S is water molecule

VI. CONCLUSION

All mixed ligand complexes formed are more stable than their corresponding binary complexes. The species detected for ternary metal complex for M-Glygly-4-MC are MABH and MAB and for M-Glygly-o-Van only MAB species formed. Stability order of complexes w.r.t metal ion is found to be Pb(II) > Cd(II) > Hg(II). The concentrations of binary (protonated and non-protonated) complexes in the presence of ternary species are less in all the systems. The higher $\Delta \log K$ observed in the study infer that the ternary complexes are more stable than the binary complexes. The higher stability of ternary complexes can be attributed to the statistical factors and electrostatic interactions between non-coordinated charged groups of the ligands. This may sometimes be due to the formation of hydrogen bonds between coordinated ligands, charge neutralization and chelate effect. The exceptional negative values in Hg(II)-Glygly-4-MC complexes is probably due to formation of complex in stepwise equilibria and less tendency of coordination of Hg(II) with O-O rather than N-O/ N-N donor ligands.

The metal-ligand stability constant $\log K$ decrease with an increase in temperature and ionic strengths. The study can be used to predict the metal availability/ metal transport in biofluids. The ternary complexes are more amenable for "metal transport" because of their stability. The trend for stability constant for binary complex species w. r. t secondary ligand is more for 4-MC than o-Vanillin due to their basicity. The probable geometry for protonated and non protonated species assumed to be octahedral.

The negative values of ΔG° in each case indicate that the complexation is spontaneous. The negative enthalpy changes (ΔH°) for the complexation suggest that all the complexation reaction are exothermic, favorable at lower temperature and the metal ligand binding process is enthalpy driven and metal-ligand bond are fairly strong. The positive value of ΔS° for some metal complexes indicate that the formation of these complexes is entropically favored.

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Bivalent toxic metals (Pb, Cd ,Hg) are common environmental pollutants in industrial area,causes major health problems.It is well known that chelation therapy is good aid to remove overtotoxicity of the metals. The ligands used in the present study are good chelating agent having strong ability to grab the toxic metals and dislodge them from tissues.So,these studies are helpful in elucidating the metabolism of nervous-renal system and range of effects induced by metals to protect living beings.

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