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Thermodynamic, Stability, Potentiometric and Solution Studies of Mixed Metal Complexes Involving Transition Metals and EGTA Ligand

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Abstract: ***Ethylene glycol-bis (2-aminoethylether)-N, N, N', N'-tetraacetic acid [EGTA] is a multidentate ligand bear several application in medical science. In order to draw inference on their complexation behaviour and solution studies in mixed metal systems involving this ligand with Nickle , Lead, Cobalt and Copper have been carried using pH- metric titration technique in aqueous medium at three different ionic strengths (μ=0.05,0.10,0.15M) and at two different temperature 20°c and 30°C. SCOGS computer program was applied for computation. Protonated and non-protonated mixed metal ligand complexes are inferred to be formed through multiple equilibria. Distribution of various species is presented in the form of speciation curves. The two metals are coordinated to the ligand ion simultaneously in a single step. ΔlogK values support the formation of ternary complexes.***

Keywords: Ternary complexes, protonated species, non-protonated species, SCOGS

1. Introduction

In the recent time researchers have developed interest in exploring the formation of mixed metal complexes for the reason that many biological reactions involve the formation of mixed metal species. Also the mixed ionic systems often occur in nature, example natural water has ions such as H^+, Na^+, Mg^{2+} and Ca^{2+} so it becomes essential to find the general rules of stability of mixed metal complexes in comparison to simple species. As a consequence several investigations are made and interesting results are reported on mixed metal systems in recent past [1].

Equlibrium studies on mixed metal complexes of Cu(II), Ni(II) and Zn(II) with peptide and imidazole are reported by Patel and co-workers[2]-[3]. Further they have studied the equilibrium and solution structure of mixed metal and mixed ligand complexes of Cu(II), Ni(II) and Zn(II) with L-cysteine, L-threonine and imidazole by potentiometric and spectrophotometric techniques[4].Thermodynamic study of heterobinuclear complexes of transition metals have been reported [5]-[7].

The ability of polyaminocarboxylic acid to form generally stable and readily soluble complexes with a variety of metal ions is the reason for their extensive and diversified applications. EGTA is important compound of this class serving as potential ligand for many metal ions including the toxic metals. This multidentate ligand bear several applications in medical science [8]-[19].

Krishna et al. have investigated mixed metal complex formation of DTPA involving Cd(II) and alkaline earth metal ions and heterobinuclear complexes of DTPA with Hg(II) and some other metal ions [20]-[22]. Recently they studied synthesis and characterization of novel heterobinuclearHg(II)-DTPA-M(II) complexes where M(II)= Cu(II),Pb(II), Mg(II) and Ca(II) [23]. Structure of EGTA chelates of Mg(II) and Cu(II) are studied by Schauer and Anderson [24].

2. Experimental Conditions

2.1 Chemicals

Metal nitrate solution, 0.01M solution of Ni(II), Pb(II), Cu(II) and Co(II) were prepared by dissolving respective nitrates (G.R, Merck) in 0.01M nitric acid solution. Solution of disodium salt of EGTA were prepared by dissolving accurately weighted amount of acid (A.R) in two equivalents of standard sodium hydroxide (0.10M) to get a solution of 0.01M.

2.2 Instrument

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 was used for pH measurement. The pH meter was calibrated with aqueous buffers (pH 4.0 and 9.20) before and after titration.

2.3 Measuring Approach

Following sets of titration mixture were prepared by keeping total volume 50mL and titrated against 0.10M NaOH solution, ionic strengths (μ=0.05, 0.10, 0.15M) is maintained by adding different concentration of $NaNO_3$ solution to each titration mixture at temperature 20±1°C and 30±1°C. The complex of each titration mixtures is as follows:-

1) Acid titration: HNO_3 (2.0×10^{-3}M).
2) Ligand 'A' titration: HNO_3 (2.0×10^{-3}M) + Ligand 'A'(1.0×10^{-3}M).
3) Metal (M)-Ligand 'A'(1:1) titration: HNO_3 (2.0×10^{-3}M) + Ligand 'A' (1.0×10^{-3}M) + Metal nitrate (1.0×10^{-3}M).

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4) Metal´(M´)-Ligand (1:1) titration: HNO_3(2.0×10^{-3}M) + Ligand 'A'(1.0×10^{-3}M) + Metal´ nitrate (1.0×10^{-3}M)
5) Metal (M)- Metal´(M´) –Ligand (1:1:1) titration: HNO_3 (2.0×10^{-3}M) + Ligand 'A'(1.0×10^{-3}M) + Metal Nitrate (1.0×10^{-3}M) + Metal´ nitrate (1.0×10^{-3}M).

Where, ligand´A´= EGTA and M/M´= Ni(II), Pb(II), Co(II) and Cu(II)

Volume of alkali used in each set of titration is converted into moles of alkali per mole of ligand / metal and denoted as '*a*'. This is presented in the form of representative titration curves (fig.1). Results are discussed on the basis of variation in nature of titration curves with respect to '*a*'.

3. Results and Discussion

In fig.1, curve 1 shows acid titration curve and is taken as reference curve. curve 2 shows ligand 'A' (EGTA) titration curve. The curve diverges to the right of mineral acid curve 1 from pH≈7.2 which indicates strong basic nature of the two dissociable proton of EGTA. Absence of sharp inflection on the curve 2 suggests that two protons are liberated in overlapping manner.

Curve 3 and 4 depicts the titration curves of metal(II)-EGTA (1:1) and metal´(II)-EGTA (1:1) binary systems respectively. It is observed that curve 3 and 4 are displaced towards right side from the acid titration curve 1 and ligand titration curve 2 in preliminary stage of titration, thereby suggesting the strong basic nature of dissociable protons. An inflection at '*a*'=1.0 show formation of protonated metal(II)- EGTA (MAH type) of complex in the lower range and another weak inflection at '*a*'=2.0 suggest existence of non-protonated MA type of complex in higher pH range.

Table 1: Protonation Constants of Ligand (EGTA)

Parameter	20°C	30°C
log β_{HA}	9.85	9.49
log β_{H2A}	17.67	17.34

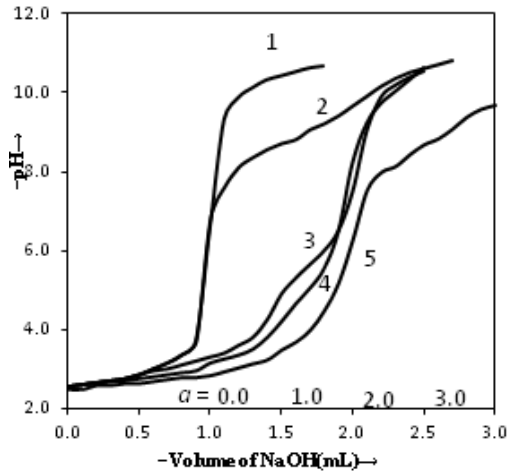


Figure 1: pH vs. Vol. of NaOH Curves for Ni(II)-Pb(II)-EGTA(1:1:1)System at 30 ºC[μ=0.10M $NaNO_3$]

All other mixed metal systems involving EGTA (i.e Ni(II)-Pb(II)- EGTA, Ni(II)- Co(II)- EGTA, Pb(II)- Co(II)- EGTA, Cu(II)- Ni(II)- EGTA, Cu(II)- Pb(II)- EGTA and Cu(II)-Co(II)- EGTA) depict the same trend.

Displacement of mixed metal titration curve (curve 5) in the same fig. towards right hand side from the ligand curve 2, metal-ligand titration curve 3 and 4, shows formation of mixed metal complex. A weak inflection in the curve near '*a*'=2.0 (pH≈6.0) indicates formation of non-protonated mixed metal complex. Curve 5 is seen to be diverging from curve 2, 3 and 4 from initial stage of titration thereby suggesting the simultaneous coordination of both the metal ions with ligand. Equilibria involved in above complexation are given here under:

Scheme 1

$$M/M' + HA \overset{0\le a\le 1}{\rightleftharpoons} MAH/M'AH$$

$$MAH/M'AH \overset{1\le a\le 2}{\rightleftharpoons} MA/M'A + H$$

$$MA + M' \overset{1\le a\le 2}{\rightleftharpoons} MM'A$$

$$M'A + M \overset{1\le a\le 2}{\rightleftharpoons} MM'A$$

$$M + A + M' \overset{0\le a\le 2}{\rightleftharpoons} MM'A$$

(Charges have been omitted for the sake of simplicity).

Calculations of proton dissociation constants and protonation constants of ligands, formation constants of binary and ternary systems were done by using algebraic method of Martell and Chaberek [25]-[26] as modified by Dey et al. [27]. All experimental values were refined by SCOGS computer program [28]-[29]. Thermodynamic formation constants were obtained by extrapolating the log β vs √μ plot to zero ionic strength. The values are reported in tables 1, 2 and 3.

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Table-2: Thermodynamic formation constants of binary complexes of M(II)/M′(II)-EGTA in equimolar systems

Parameter	Ni(II)		Pb(II)		Co(II)		Cu(II)	
	20°C	30°C	20°C	30°C	20°C	30°C	20°C	30°C
log β_{MAH}	18.08	17.65	17.80	17.14	16.64	16.37	18.25	17.36
log β_{MA}	12.25	11.82	12.51	11.94	11.59	11.05	13.94	12.93
log K^{M}_{MAH}	7.62	7.16	7.86	7.65	7.45	6.88	8.18	7.87
pK^{H}_{MAH}	6.10	5.84	5.68	5.23	5.86	5.30	5.02	4.77
Thermodynamic formation constants were obtained by extrapolating the log β vs √μ plot to zero ionic strength								

Table 3: Thermodynamic parameters of M(II) –M`(II) – ligand 'A' (EGTA) ternary complexes in equimolar systems.

Parameter	20°C		30°C		- ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	log $K_{\mu\to0}$	- ΔG° kJmol^{-1}	log $K_{\mu\to0}$	- ΔG° kJmol^{-1}		
	Ni(II) –Pb(II)- EGTA					
$\log K^{MM'}_{MM'A}$	19.06	106.0	18.54	107.5	88.36	63.21
$\log K^{MA}_{MM'A}$	8.08	45.32	7.90	45.83	30.61	50.28
$\log K^{M'A}_{MM'A}$	5.96	32.37	5.78	33.53	30.56	9.60
	Ni(II) –Co(II)- EGTA					
$\log K^{MM'}_{MM'A}$	16.90	94.81	16.38	95.02	88.39	21.90
$\log K^{MA}_{MM'A}$	5.98	33.54	5.79	33.59	32.33	4.26
$\log K^{M'A}_{MM'A}$	5.77	32.37	5.59	32.43	30.62	6.05
	Pb(II) –Co(II)- EGTA					
$\log K^{MM'}_{MM'A}$	18.91	106.0	18.55	107.6	61.15	153.2
$\log K^{MA}_{MM'A}$	5.89	33.06	5.71	33.12	30.59	8.34
$\log K^{M'A}_{MM'A}$	7.04	39.49	6.85	39.74	32.28	24.56
	Cu(II) –Ni(II)-EGTA					
$\log K^{MM'}_{MM'A}$	18.44	103.4	17.84	103.5	101.8	4.97
$\log K^{MA}_{MM'A}$	4.98	27.93	4.82	27.96	27.17	2.52
$\log K^{M'A}_{MM'A}$	7.03	39.43	6.87	39.85	27.22	41.77
	Cu(II) –Pb(II)- EGTA					
$\log K^{MM'}_{MM'A}$	17.67	99.13	17.13	99.38	91.75	25.04
$\log K^{MA}_{MM'A}$	4.84	27.15	4.69	27.20	25.48	5.64
$\log K^{M'A}_{MM'A}$	5.96	33.43	5.78	33.53	30.55	9.68
	Cu(II) –Co(II)- EGTA					
$\log K^{MM'}_{MM'A}$	20.87	117.0	20.45	118.6	71.32	155.9
$\log K^{MA}_{MM'A}$	5.73	32.14	5.66	32.83	11.83	69.10
$\log K^{M'A}_{MM'A}$	7.38	41.40	7.16	41.53	37.45	13.67

Table 4: Δlog K values for MM'A complexes

Parameter	20°C			30°C		
	Ni^{II}-Pb^{II}	Ni^{II}-Co^{II}	Pb^{II}-Co^{II}	Ni^{II}-Pb^{II}	Ni^{II}-Co^{II}	Pb^{II}-Co^{II}
$\Delta\log K_{MM'A}$	-5.7	-6.94	-5.18	-5.22	-6.49	-4.44
	Cu^{II}-Ni^{II}	Cu^{II}-Pb^{II}	Cu^{II}-Co^{II}	Cu^{II}-Ni^{II}	Cu^{II}-Pb^{II}	Cu^{II}-Co^{II}
$\Delta\log K_{MM'A}$	-7.75	-8.78	-4.66	-6.91	-7.74	-3.53

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Speciation Curves: The percent concentrations of various possible species in a particular equilibria are obtained through SCOGS computer program for ternary (1:1:1) Systems at 30°C (μ=0.10M ($NaNO_3$)). which are presented in the form of speciation curves (fig. 2-7). Percentage concentrations of binary species are very low as compared to ternary species and ternary species (MM′A) are formed as dominating species from the preliminary stage. The concentration of ternary nonprotonated (MM′A type) species increased constantly with pH. All these curves follow the similar pattern. Analysis of these curves is discussed here under:

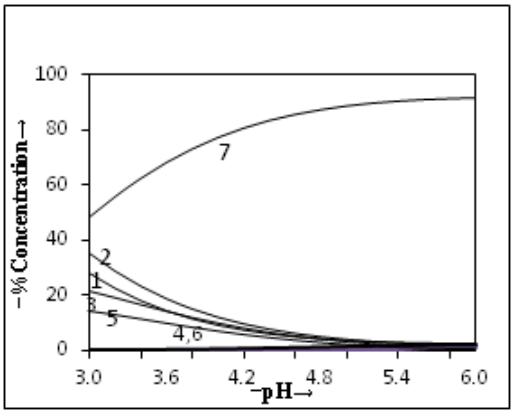


Figure 2: Speciation Curves for Ni(II) –Pb(II)-EGTA (1:1:1) System

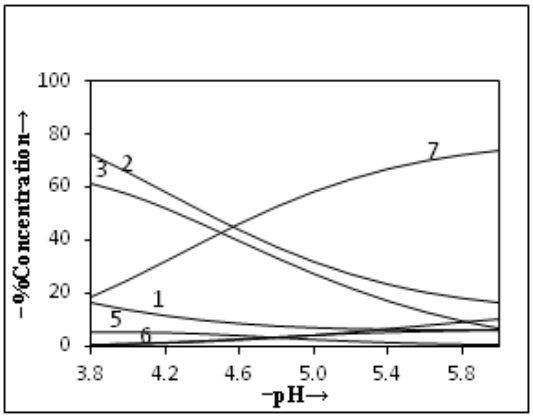


Figure 3: Speciation Curves for Ni(II) –Co(II)-EGTA (1:1:1) System

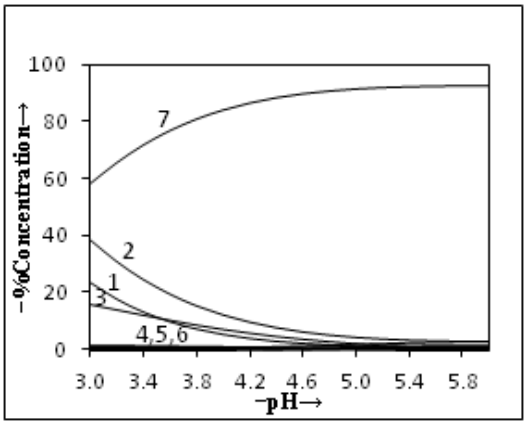


Figure 4: Speciation Curves for Pb(II) –Co(II)-EGTA (1:1:1) System

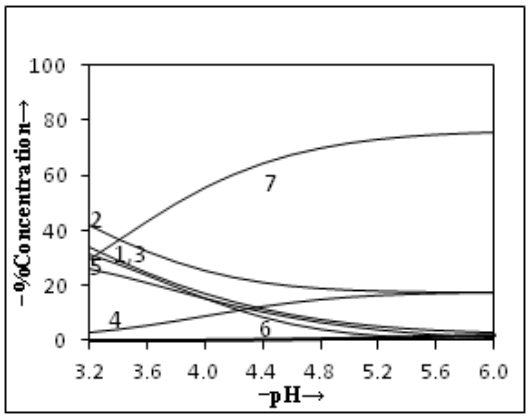


Figure 5: Speciation Curves for Cu(II) –Ni(II)-EGTA (1:1:1) System

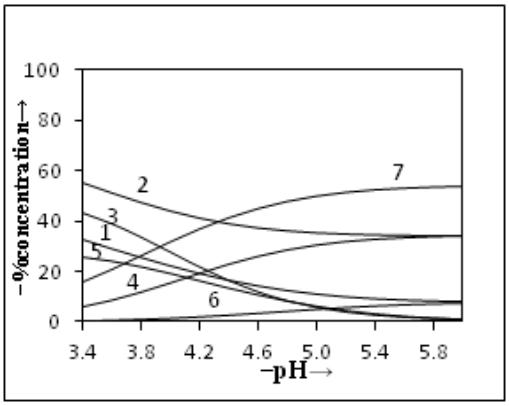


Figure 6: Speciation Curves for Cu(II) –Pb (II)-EGTA (1:1:1) System

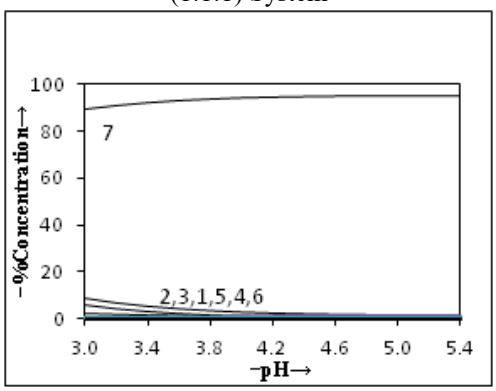


Figure 7: Speciation Curves for Cu(II) –Co(II)-EGTA (1:1:1) System

Where, Curve 1: [M]; 2 [M′]; 3[MAH]; 4 [MA]; 5 [[M′AH]; 6 [M′A]; 7 [MM′A]

4. Conclusion

The analysis of titration curves and speciation curves indicates the formation of heterobimetallic complexes through simultaneous coordination. Further the computation of different equilibrium constants were done considering the various possible equilibria as shown in scheme 1. It is observed that the values of log $\beta_{MM'A}$ and log $K^{MA}_{MM'A}$ are highest as shown in tables 3, which supports the formation of heterobinuclear complex through the following equilibria

$$M + A + M' \rightleftharpoons MM'A$$

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The metals used in present investigation are bivalent usually having coordination number four. EGTA are octadentate in nature. So it can be assumed that in binary complexes, the metal ion get coordinated to the ligand by four coordination sites, still leaving vacant coordination sites available for interaction with another metal, thus making the formation of mixed metal complex possible. In case of EGTA complex it can be presumed that each metal is coordinated to the ligand via two carboxylic groups, one nitrogen of amino group and the forth binding site being oxygen of the ether group.

The percentage formation of ternary complexes is found to be higher in comparison to the binary species. However no absolute relation could be established between percentage formation and relative thermodynamic stabilites. It is observed from the table 4, that the values of $\Delta\log K(= \log \beta_{MM'A} - \log\beta_{MA} - \log\beta_{M'A})$ are negative for all the systems which indicate the higher stability of binary over ternary. Thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were calculated and the standard free energy, enthalpy and entropy changes are reported in table 3. The negative $\Delta G°$ in each case indicates that the complexation is spontaneous. The enthalpy changes are exothermic. The positive values for $\Delta S°$ indicate that complexation reactions are entropically favoured under the experimental conditions used.

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