

CHEMOMETRIC INVESTIGATION OF COMPLEX EQUILIBRIA OF L-ORNITHINE WITH Ca(II), Mn(II) AND Zn(II) IN PEG-400 AND TBAB MICELLAR MEDIA

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Abstract:

Mononuclear complexes of L-Ornithine (Orn) with Ca(II), Mn(II) and Zn(II) have been investigated pH metrically in Polyethyleneglycol-400 (PEG-400, neutral) and Tetrabutyl-ammonium bromide (TBAB, cationic) micellar media at constant temperature (298 K) and ionic strength (0.16 mol dm⁻³). Stability constants and best fit model for metal complexes were obtained by MINQUAD75 computer program on the basis of statistical parameters. The species identified were MLH, ML, ML₂H and ML₂. The stabilization/destabilization equilibria of the binary system (MLn) for the model species in micellar media were attributed to dielectric constant and other intrinsic interaction properties of PEG-400 and TBAB surfactant-water mixtures. Distribution diagrams of the species at different compositions of PEG-400 and TBAB are also presented.

Keywords: Complex equilibria, Metal ions, L-Ornithine, PEG-400, TBAB, MINQUAD75

1. INTRODUCTION

Speciation study of essential metal ion complexes is useful to understand the role played by the active sites in biological molecules and the bonding behavior of amino acid residues of proteins with the metal ion and can be used to mimic metalloproteins [1]. Metal complexes of L-Ornithine (Orn), a tridentate ligand [2], [3] are insoluble in water and soluble in most organic solvents [4]. Orn is known to form several stable complexes with Co(II), Ni(II) and Cu(II) [5], [6] and Cd(II), Sn(IV), Ce(IV) and Pd(II) [7], [8] in a variety of solvents differing in the degree of solubility. Orn complexes of bio-essential metals play an important role in chemotherapeutic

applications [9]. Orn helps to build muscles, reduces body fats, removes toxic ammonia in urea cycle from liver [10] and is the source of polyamines in maintaining physiological system. Orn is one of the products of the action of arginase on L-arginine, creating urea. Hence, Orn is central of the urea cycle, which allows the disposal of excess nitrogen. The nitrogen donor atoms can associate with hydrogen ions in the physiological pH range. Hence, there is often significant competition between hydrogen and metal ions for these donor sites that leads to the existence of a number of equilibria. This phenomenon may result in successively protonated complexes.

Calcium plays an important role in the cell membranes, in muscle contraction and as a structural component [11]. It helps in blood clotting, nerve signaling and the release of certain hormones. Ca²⁺ ions are essential components of plant cell walls and cell membranes and are used to balance organic anions in the plant vacuole [12]. High calcium intake or absorption results in the development of kidney stones but vitamin D is needed to absorb calcium [13]. Manganese is an essential trace nutrient in all forms of life. It is mostly concentrated in the liver and kidneys [14]. In the human brain, it is bound to manganese metalloproteins, such as glutamine synthetase in astrocytes [15]. Its deficiency in human beings causes skeletal deformities due to impaired bone growth and reduced reproductive functions. Zinc plays vital role in biosystems [16], [17]. It supports normal growth and development during pregnancy, childhood and adolescence and is required for proper sense of taste and smell [18], [19].

Polyethylene glycol (PEG) is a polyether with many applications, from industrial

manufacturing to medicine. PEG is also known as polyethylene oxide or polyoxyethylene, depending on its molecular weight. PEG is the basis of a number of laxatives. When attached to various protein medications, PEG allows a slowed clearance of the carried protein from the blood [20]. It has a low toxicity and is used in a variety of products [21]. The polymer is used as a lubricating coating for various surfaces in aqueous and non-aqueous environments [22]. Tetrabutyl-ammonium bromide (TBAB) has a positively charged head group with common types including alkyl pyridinium halides and alkyl ammonium halides, such as cetyltrimethyl-ammonium bromide or cetyltrimethyl-ammonium chloride [23], [24].

Micellar media are chosen in these studies to maintain the dielectric constants of the medium comparable to those of the physiological fluids since the polarity of the active sites should generally be applicable, to compare ligand binding to the metal ion in protein and mixed solvent environments. The studies carried out on these systems under the present experimental conditions are useful to understand the role played by the active site cavities in biological molecules. Hence, speciation studies of Orn with Ca(II), Mn(II) and Zn(II) in PEG-400 and TBAB–water mixtures are reported in this paper.

2. EXPERIMENTAL

All chemicals used were of analytical reagent grade from which corresponding solutions were prepared in triple distilled water free of dissolved oxygen and carbon dioxide via purging the solutions with nitrogen gas. Solutions of 0.05 mol dm⁻³ L-Ornithine (Sigma-Aldrich, India), 0.4 mol dm⁻³ sodium hydroxide and 0.2 mol dm⁻³ hydrochloric acid (Merck, India) were prepared. Carbonate error in the concentration of NaOH solution was determined through Gran titration. NaOH was standardized against potassium hydrogen phthalate and used to standardize HCl solution before use. 0.1 mol dm⁻³ solutions of Ca(II), Mn(II) and Zn(II) (E-Merck, Germany) were prepared from the corresponding chloride salts and standardized by complexometric titration method. The ligand solutions (to increase their solubility) and metal solutions (to repress their hydrolysis) were prepared in 0.05 mol dm⁻³ HCl. Polyethylene-glycol-400 (Merck, India) and

tetrabutylammonium bromide were used as received.

3. METHODS AND EQUIPMENT

Potentiometric titrations were conducted for the determination of stability constants of binary metal ligand complexes by modified Calvin-Wilson [25] titration technique in micellar media by using Metrohm 877 titrino plus auto-titrator (Switzerland) in conjunction with 0-14 pH reading electrode (readability 0.001). The electrode was calibrated with 0.1 mol dm⁻³ potassium hydrogen phthalate (pH 4.01) and 0.05 mol dm⁻³ borax solutions (pH 9.18). The electrode was equilibrated in appropriate surfactant solution with regular checking by initial titration of strong acid with alkali solution. After equilibration of the electrode, the data obtained by the three replicate titration measurements were reproducible and found to differ by not more than 0.02 units.

50 mL of the titrand contained different percentages of surfactants (0.5-2.5 v/v %), ligand and metal ions in an ionic strength of 0.16 mol dm⁻³ NaCl (Merck, India) and 298 K. The metal to ligand ratios were kept to be 1:1, 1:2 and 1:3 to form mononuclear complexes. The titrations were performed with 0.05 mL aliquots of sodium hydroxide (0.4 mol dm⁻³) at regular intervals under purified nitrogen atmosphere [26]. The titrimetric data generated were automatically saved in the instrument (Metrohm 877 titrino plus auto-titrator).

4. DATA PROCESSING FOR SELECTION OF BEST FIT MODELS

The effect of variations in liquid junction potential, asymmetry potential, dielectric constant, sodium ion error, dissolved carbon dioxide and activity coefficient on the response of the electrode were accounted for by correction factor which was calculated using SCPHD computer program [27]. The program also outputs the approximate stability constants of the binary complexes, which are inputted to MINQUAD75 computer program [28] that refines the stability constants. The correction factor, values of K_w and protonation constants of the ligand were fixed during refinement. The relative compositions of chemical species (their complexes and free forms) formed by the interactions between metal ions and L-Ornithine at the given set of experimental conditions (pH,

temperature and ionic strength) were also determined.

5. RESULTS AND DISCUSSION

5.1 MODELING OF CHEMICAL SPECIES

The outcomes of the best fit models that represent the different types of chemical species, their stoichiometric ratio and stability constant values for Orn complexes are given in Tables I and II in PEG-400 and TBAB media, respectively. The validity and sufficiency of the chemical models that represent the metal-ligand system to qualify as best fit model to experimental data have been tested based on sum of squares of residuals in mass balance equations 'U', the standard deviations in refined overall stability constants, chi-square,

skewness, kurtosis and crystallographic R-factor. These statistical parameters satisfy the requirements for the least squares method to be applied to the data presented. The small values of standard deviations ensure that the parameters employed are precise. The residuals with skewness values of -0.07 to -0.21 for Ca(II)-Orn, -0.08 to -0.31 for Mn(II)-Orn and -0.19 to -0.36 for Zn(II)-Orn systems form part of the Gaussian (normal) distribution for M(II)-Orn system. The values of kurtosis show both meso and slight leptokurtic patterns for Mn(II)-Orn and leptokurtic pattern (> 3.0) for Zn(II)-Orn systems and platykurtic pattern for Ca(II)-Orn (< 3) in the model distribution. The very small values of crystallographic R-factor (less than the critical value) further strengthen the adequacy of the model to represent the chemical species.

Table I. Parameters of Best Fit Chemical Models of Ca(II), Mn(II) and Zn(II)-Orn Complexes in PEG-Water Mixtures

% PEG	log β_{MLH} (SD)				NP	U_{corr}	χ^2	R factor	Skewness	Kurtosis
	110	111	120	121						
Ca(II)(pH range 1.45-10.5)										
0.0	10.69 (17)	16.82 (10)	19.91 (9)	26.73 (12)	121	1.09	12.12	0.00112	-0.21	2.98
0.5	10.60 (12)	16.74 (12)	19.83 (18)	26.57 (14)	91	1.04	11.13	0.00071	-0.19	2.23
1.0	10.55 (11)	16.68 (13)	19.74 (11)	26.50 (23)	95	1.21	15.85	0.00181	-0.18	1.12
1.5	10.50 (22)	16.60 (11)	19.66 (14)	26.43 (22)	145	2.01	11.12	0.00113	-0.09	1.20
2.0	10.42 (11)	16.56 (20)	19.59 (11)	26.35 (16)	134	2.03	11.78	0.00123	-0.16	2.21
2.5	10.36 (10)	16.54 (12)	19.48 (15)	26.31 (11)	98	1.05	17.61	0.00235	-0.07	2.32
Mn(II)(pH range 1.60-10.8)										
0.0	13.53 (18)	17.45 (14)	25.42 (18)	29.45 (26)	105	1.12	58.31	0.00150	-0.31	4.23
0.5	13.41 (12)	17.43 (11)	25.40 (19)	29.36 (19)	118	1.32	42.89	0.00152	-0.20	3.56
1.0	13.34 (15)	17.41 (18)	25.38 (14)	29.33 (11)	107	1.03	14.27	0.00114	-0.61	3.45
1.5	13.28 (11)	17.39 (15)	25.35 (11)	29.35 (12)	95	1.35	13.57	0.00161	-0.15	3.23
2.0	13.11 (13)	17.33 (12)	25.32 (19)	29.34 (11)	84	1.40	19.17	0.00151	-0.09	3.19
2.5	13.02 (15)	17.31 (11)	25.29 (15)	29.31 (11)	99	1.30	22.12	0.00201	-0.08	3.42
Zn(II)(pH range 1.55-10.5)										
0.0	14.83 (22)	18.65 (16)	27.74 (25)	32.91 (29)	124	1.04	15.12	0.00121	-0.36	1.42
0.5	14.79 (11)	18.63 (15)	27.67 (17)	32.85 (20)	119	1.09	12.16	0.00119	-0.20	1.89

1.0	14.75 (15)	18.62 (11)	27.69 (19)	32.83 (19)	110	1.01	15.27	0.00982	-0.24	2.14
1.5	14.73 (11)	18.60 (12)	27.64 (18)	32.81 (11)	109	1.06	11.12	0.00155	-0.18	1.83
2.0	14.70 (18)	18.59 (18)	27.63 (19)	32.80 (12)	95	1.85	10.13	0.00182	-0.28	1.89
2.5	14.68 (11)	18.55 (11)	27.61 (10)	32.77 (12)	116	1.96	21.12	0.00149	-0.19	2.12

$U_{corr} = U/(NP-m) \times 10^8$, where m = number of species; NP=Number of experimental points; SD=Standard deviation

Table II. Parameters of Best Fit Chemical Models of Ca(II), Mn(II) and Zn(II)-Orn Complexes in TBAB-Water Mixtures

% TB AB	log β_{MLH} (SD)				NP	U_{corr}	χ^2	R factor	Skewness	Kurtosis
	110	111	120	121						
Ca(II)(pH range 1.5-10.5)										
0.0	10.69 (17)	16.82 (10)	19.91 (9)	26.73 (12)	123	2.12	6.92	0.001	-0.13	2.78
0.5	10.65 (10)	16.76 (17)	19.81 (9)	26.69 (11)	99	3.11	4.03	0.00059	-0.14	1.98
1.0	10.63 (14)	16.71 (15)	19.78 (10)	26.65 (12)	101	2.74	8.33	0.00166	-0.1	2.87
1.5	10.55 (12)	16.63 (9)	19.75 (10)	26.63 (12)	148	2.12	9.01	0.00081	-0.04	3.05
2.0	10.53 (20)	16.55 (11)	19.72 (9)	26.60 (8)	136	2.70	8.68	0.00108	-0.14	2.96
2.5	10.51 (16)	16.53 (8)	19.70 (10)	26.59 (7)	101	3.12	11.3	0.00103	-0.08	2.07
Mn(II)(pH range 1.65-11.0)										
0.0	13.53 (18)	17.45 (14)	25.42 (18)	29.45 (26)	107	2.13	38.21	0.00138	-0.23	3.03
0.5	13.45 (19)	17.35 (19)	25.31 (12)	29.25 (20)	123	1.20	20.59	0.0014	-0.25	2.31
1.0	13.32 (12)	17.22 (24)	25.28 (14)	29.18 (17)	109	2.54	11.07	0.00099	-0.53	3.21
1.5	13.18 (18)	17.09 (17)	25.16 (17)	29.03 (18)	103	4.15	5.27	0.00029	-0.1	1.98
2.0	13.05 (17)	16.94 (28)	25.03 (21)	28.88 (19)	88	2.12	14.57	0.00136	-0.07	1.94
2.5	12.91 (11)	16.83 (25)	24.91 (12)	28.43 (17)	104	2.21	18.6	0.00069	-0.09	3.17
Zn(II)(pH range 1.6-10.2)										
0.0	14.83 (22)	18.65 (16)	27.74 (25)	32.91 (29)	129	1.16	9.92	0.00109	-0.28	3.22
0.5	14.73 (19)	18.60 (21)	27.65 (11)	32.87 (18)	126	2.11	5.06	0.00107	-0.15	4.64
1.0	14.61 (20)	18.47 (14)	27.43 (14)	32.65 (14)	117	2.71	7.75	0.00967	-0.16	1.89
1.5	14.38 (18)	18.26 (17)	27.30 (14)	32.48 (17)	111	2.15	9.23	0.00023	-0.13	3.58
2.0	14.15 (12)	18.01 (18)	27.19 (10)	32.37 (11)	98	3.25	7.03	0.00167	-0.26	2.64
2.5	13.93 (17)	17.89 (25)	26.97 (16)	32.15 (32)	122	4.53	14.81	0.00017	-0.2	1.87

5.2 CHEMICAL SPECIATION AND SPECIES DISTRIBUTION PLOTS

Chemical speciation is determined through various analytical methods in combination with mathematical model in order to get the number, types, compositions and distributions as a function of pH and to assess stability of the species under specified experimental conditions of constant temperature and ionic strength. In this connection, metal-Orn complexes were studied by determining the overall stability constants and data were subjected to refinement to arrive at the chemically reasonable speciation model that provide satisfactory best fit to the experimental data.

Orn is a tridentate ligand having two associable amino protons and one dissociable carboxylate proton. It exists as LH_3^{2+} , LH_2^+ , LH and L^- in the pH ranges, 2.0-3.5, 2.0-9.0, 8.0-11.0 and 10.0-12.0, respectively. Based on the ligand information and metal-Orn interactions, the plausible chemical species predicted and refined are MLH , ML , ML_2H and ML_2 for $Ca(II)$, $Mn(II)$ and $Zn(II)$ in micellar media. The electron pair donor N-atom on α -amino and terminal amine functional groups of Orn has strong affinity towards hydrogen ions in the physiological pH ranges. As a result of the high competition between the metal ion and hydrogen ion for N-site, protonated species were formed as well. The most likely equilibria for the binary species formation are given as follows for which charges of species are omitted for simplicity:

$M(II) + LH_3$	\rightleftharpoons	$MLH + 2H$	1	Scheme (1)
$M(II) + LH_2$	\rightleftharpoons	$MLH + H$	2	
$M(II) + LH_3$	\rightleftharpoons	$ML + 3H$	3	Scheme (2)
$M(II) + LH_2$	\rightleftharpoons	$ML + 2H$	4	
MLH	\rightleftharpoons	$ML + H$	5	Scheme (3)
$M(II) + 2LH_2$	\rightleftharpoons	$ML_2H + 3H$	6	Scheme (4)
$ML + LH_2$	\rightleftharpoons	$ML_2H + H$	7	
$MLH + LH$	\rightleftharpoons	$ML_2H + H$	8	
ML_2H	\rightleftharpoons	$ML_2 + H$	9	Scheme (5)

$M(II)+2L$ H	\rightleftharpoons	$ML_2 + 2H$	10	Scheme (6)
$ML + LH$	\rightleftharpoons	$ML_2 + H$	11	

The refined data (relative abundance, types and nature of chemical species) obtained from SIM computer program were drawn in the form of distribution diagrams by using Origin 8.5. The interaction of the metal ions of interest with Orn progressively depleted the essential metal ions resulting in the formation of stable $M(II)$ -Orn binary complex species.

At lower pH, MLH species is formed by the interactions of LH_3 and LH_2 with free metal ion [Equilibria 1,2, Scheme1]. ML can be formed by the interactions of LH_3 and LH_2 with the free metal ion [Equilibria 3,4, Scheme2] and also by the deprotonation of MLH [Equilibrium5, Scheme 3]. ML_2H species could be formed by Equilibria 6-8 [Scheme 4]. With increasing pH, deprotonation of ML_2H species gives corresponding ML_2 species [Equilibrium 9, Scheme 5], and also it is formed when LH interacts with free metal ion and ML , respectively [Equilibria 10,11, Scheme 6].

The concentration distribution diagrams of $M(II)$ -Orn binary complexes are given in Figs. 1, 2 in PEG-400-water and TBAB-water mixtures, respectively. This co-existence of MLH/ML and ML_2H/ML_2 with deprotonation/ protonation dynamic equilibria might be ensured by the increase in concentration of ML and ML_2 progressively with decreasing concentration of MLH and ML_2H in all the $M(II)$ -Orn system. The decrease in the concentration of the free metal to lower values and to zero values at extreme higher pH indicates its strong participation in the complexation equilibria. The concentration of the free ligand drastically increases with the complete depletion of the metal ions in the post active pH regions.

5.3 EFFECT OF SURFACTANT

Dielectric constant is one of the most and prominent solvent properties that could be altered by surfactants in the given titration media. The anisotropic water distribution within micellar structure causes non-uniform micro polarity, microviscosity and degree of hydration within the micellar media [29], [30]. The degree of stability of complexes could be measured in terms of the

magnitude of the overall stability constant ($\log \beta$) of each species formed in metal ligand dynamic equilibria. The variations in the magnitude of the stability constants of metal-ligand complexes are due to electrostatic and non-electrostatic opposing factors. In the present study, the stability constants are found to decrease linearly as the percentage of surfactant increases. The destabilization of the metal ligand complexes could be attributed mainly to the low dielectric constant of the surfactant media (PEG-400 and TBAB) compared to aqueous medium. The plots of $\log \beta$ against % of surfactant (Figs. 3, 5) show linear trend observed in both the media. On the other hand, the proton accepting ability of the ligand increases in acidic environment. As a result, the proton ligand stabilization process is also competing and the stability of the complex and values of the stability constant seems to decrease slightly in PEG-400 and TBAB-water mixtures. The stability constants were found to be in the order $\text{Ca(II)} < \text{Mn(II)} < \text{Zn(II)}$ which is in accordance with the Irving-Williams series same as shown in Figs. 4, 6.

5.4 INTERPRETATION OF SYSTEMATIC ERRORS

Changing experimental conditions and the concentrations of ingredients of the titration mixture alter the position of complex equilibria between the metal ion and the ligand. It, in turn, significantly affects the magnitudes of stability constants. Deliberate introduction of pessimistic errors in concentrations of alkali, mineral acid, ligand and metal ions, most commonly known as influential parameters in the study of M(II)-Orn system in 2.5 % v/v TBAB–water mixture was made to ensure the appropriateness of the experimental conditions and the choice of the best fit models given in Tables I and II.

The destabilization/stabilization complex equilibria have been assessed from the magnitude of the overall stability constants and their corresponding standard deviation for acceptance/rejection of certain species refined by MINIQAD75. The values of the stability constants due to incorporation of the errors in the concentrations of alkali and acid were found to be more significantly affected but less affected by those of ligand and metal ions (Table III). This is noted from the high standard deviation in the $\log \beta$ values and rejection of more species in the alkali

and acids compared to the metal and ligands. This observation signifies the appropriateness of the model and relative precision of the analytical concentrations.

6. STRUCTURES OF COMPLEXES

It is noted that Ca(II) , Mn(II) and Zn(II) ions form octahedral complexes. It is also evident that amino nitrogen electron donor sites have high tendency to associate with potential electron pair acceptors in the physiological pH range. The metal and hydrogen ions, therefore, compete for these donor sites. As a result, several protonated and unprotonated complex species co-exist in the metal ligand equilibria. Orn has two associable amino and one dissociable (exchangeable) carboxylate protons which make it to act as tridentate chelating agent. At higher pH region, both the α -amino and terminal nitrogen atoms and oxygen atom of the carboxylate functional group coordinate preferentially with the metal ion resulting in the formation of unprotonated complexes; while at lower pH, only the terminal N- and carboxylate O-atoms preferentially coordinate with the metal ion leaving lone pair electrons in α -amino N-atom donated to H-ion. This situation ensured the formation of MLH , ML_2H complexes at lower pH and ML , ML_2 complexes at higher pH. Thus, on the basis of integrated chemical knowledge (educational speculation) and literature reported data, the most likely structures of these complexes are given in Fig. 7.

7. CONCLUSIONS

Orn forms MLH and ML_2H species at low pH and ML and ML_2 species at higher pH. The species detected were validated by statistical data. Protonated species were found to deprotonate to give unprotonated species with increasing pH of titration mixture. Pessimistic errors introduced in the influential parameters showed that the errors in the concentrations of alkali and mineral acid affected the overall stability constants of the complex more significantly than those in ligand and metal. $\log \beta$ values were found to decrease linearly with increasing percentage of TBAB and PEG-400 suggesting the dominance of electrostatic interactions over the non-electrostatic interactions.

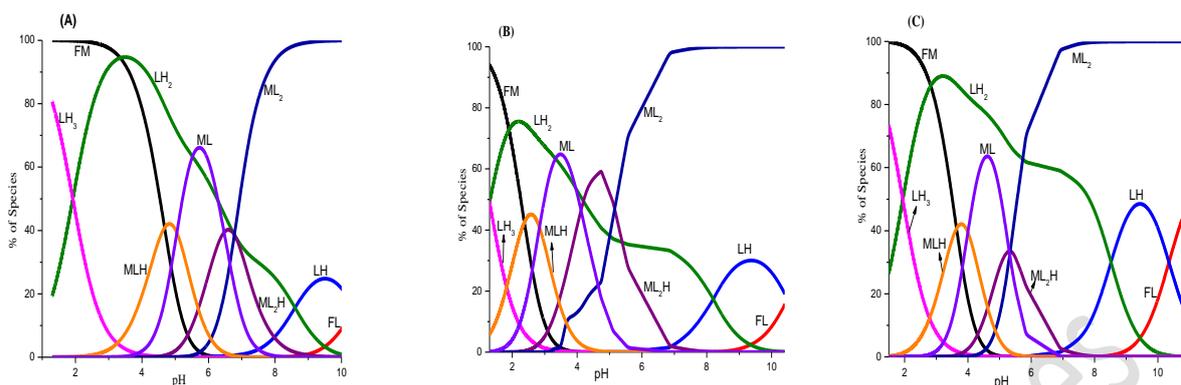


Fig. 1: Concentration distribution diagrams of M(II)-Orn complexes in 1.5 % v/v PEG-water mixture. M(II)= (A) Ca(II) (B) Mn(II), and (C) Zn(II).

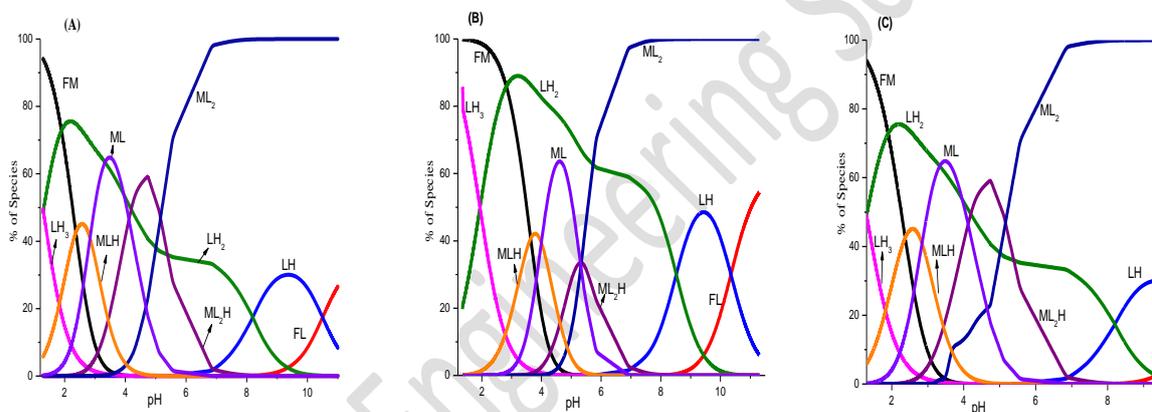


Fig. 2: Concentration distribution diagrams of M(II)-Orn complexes in 1.5 % v/v TBAB-water mixture. (A) Ca(II) (B) Mn(II), and (C) Zn(II).

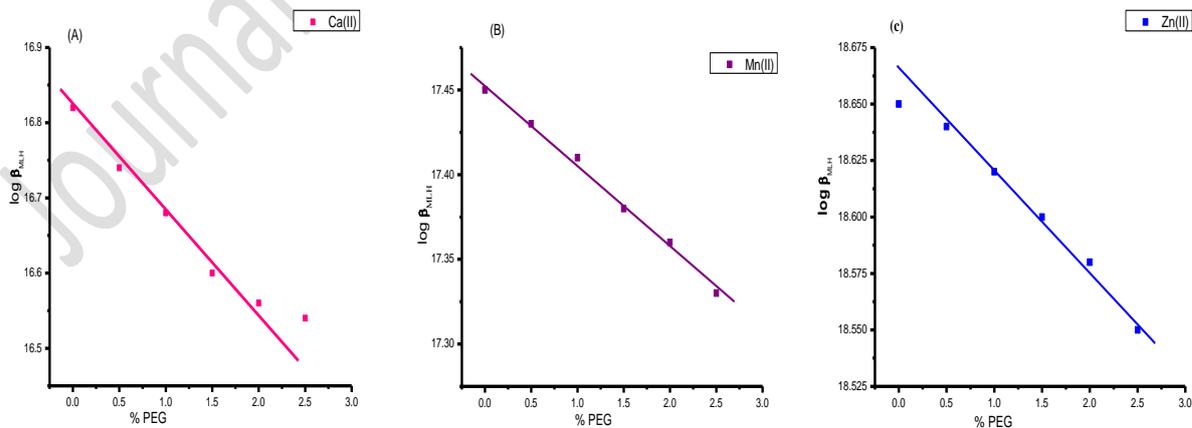


Fig. 3: Variation of log β_{MLH} of Orn complexes of (A) Ca(II), (B) Mn(II) and (C) Zn(II) with percentage of PEG-400

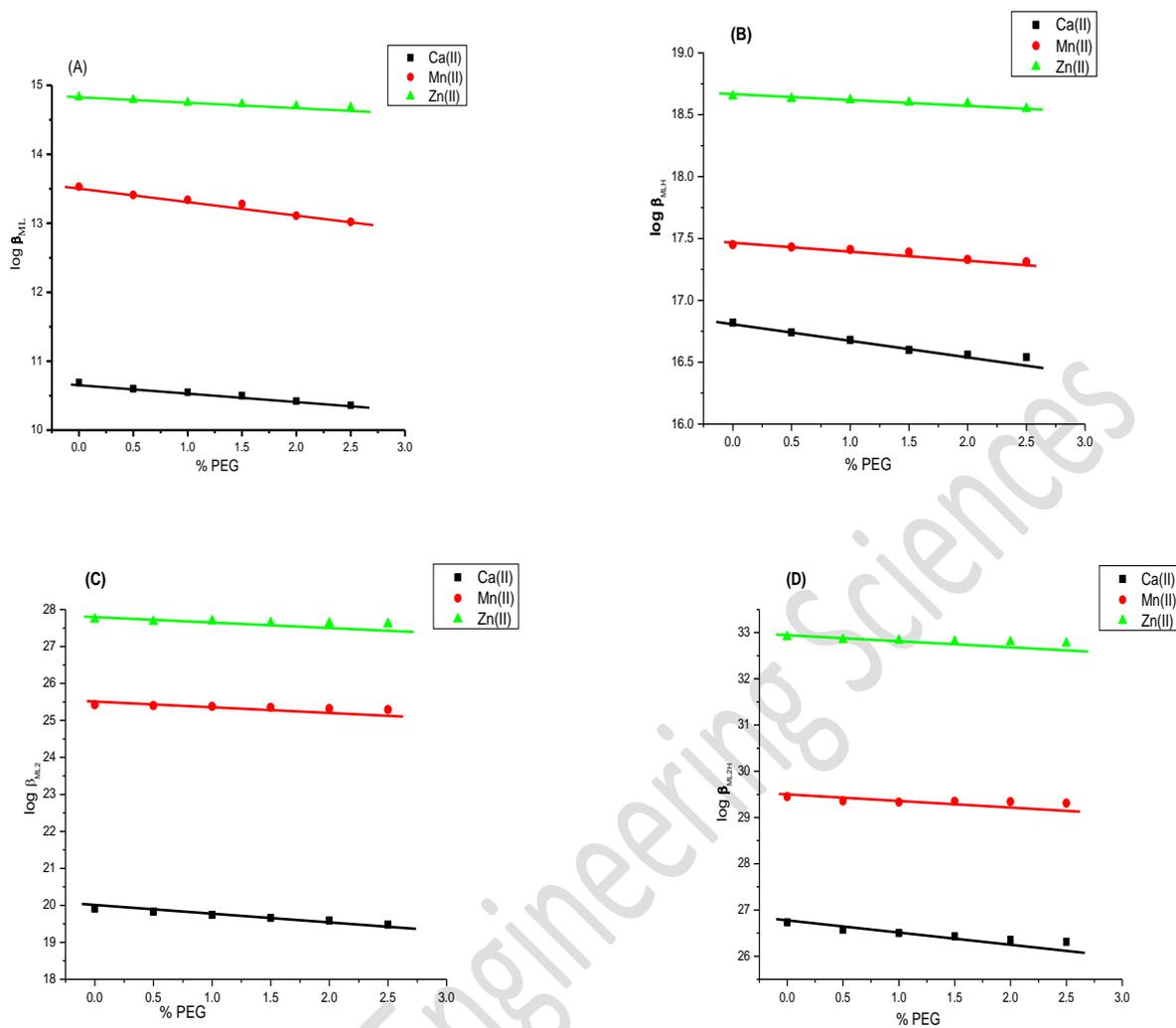


Fig. 4: Variation of stability constants of M(II)-Orn with % of PEG. M(II)= Ca(II), Mn(II) and Zn(II). (A) $\log \beta_{ML}$, (B) $\log \beta_{MLH}$, (C) $\log \beta_{ML2}$, (D) $\log \beta_{ML2H}$

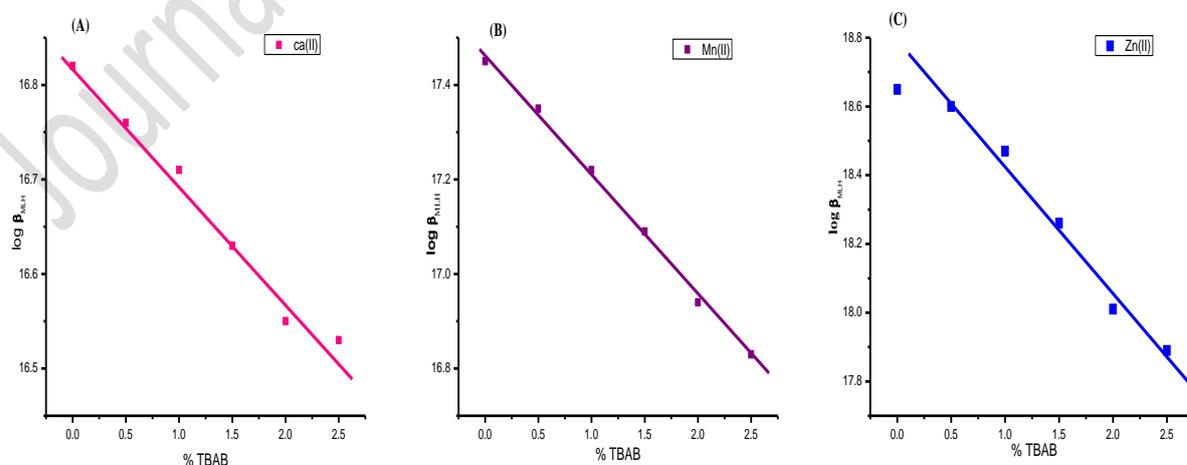


Fig. 5: Variation of $\log \beta_{MLH}$ of Orn complexes of (A) Ca(II), (B) Mn(II) and (C) Zn(II) with percentage of TBAB

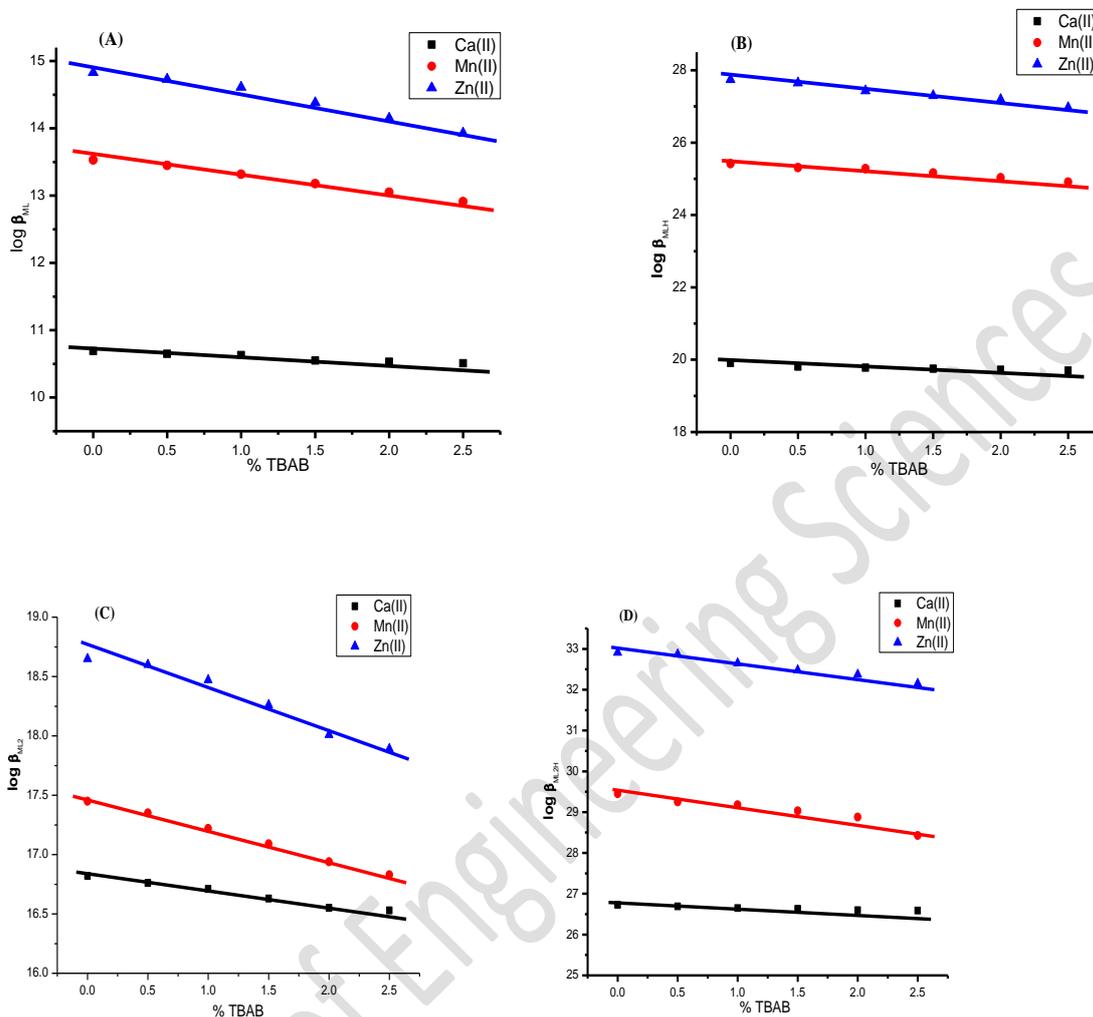


Fig. 6:

Variation of stability constants of M(II)-Orn with % of TBAB M(II) = Ca(II), Mn(II) and Zn(II). (A) $\log \beta_{ML}$, (B) $\log \beta_{MLH}$, (C) $\log \beta_{ML2}$, (D) $\log \beta_{ML2H}$

Table III: Effect of Errors in Concentrations of Components on Stability Constants of Ca(II)-Orn Complexes in 2.5 % w/v TBAB-Water Mixtures

Component	% of error	$\log \beta_{mlh}(SD)$			
		110	111	120	121
Ca(II)-Orn					
Acid	0	10.51 (16)	16.53 (8)	19.70 (10)	26.59 (7)
	-2	10.49 (19)	16.51 (14)	19.68 (16)	26.55 (14)
	-5	10.40(27)	16.42(45)	19.57(17)	Rejected
	+2	10.59(17)	16.71(35)	19.67(32)	Rejected
	+5	10.65(23)	16.80(17)	Rejected	26.65(31)
Alkali	-2	10.46(17)	16.53(15)	19.66(21)	26.59(19)
	-5	10.41(26)	16.42(32)	19.63(31)	26.48(23)

	+2	10.56(34)	16.56(37)	Rejected	26.63(39)
	+5	10.66(37)	Rejected	19.67(19)	Rejected
Ligand	-2	10.48 (31)	16.50 (17)	19.68 (77)	26.56 (19)
	-5	10.46(21)	16.48(32)	19.65(71)	26.53(37)
	+2	10.58(27)	16.58(24)	19.68(32)	26.56(98)
	+5	10.59(19)	16.59(13)	19.70(85)	26.58(47)
Metal	-2	10.50 (16)	16.49 (19)	19.67 (19)	26.58 (74)
	-5	10.49(18)	16.48(53)	19.65(11)	26.55(91)
	+2	10.54(32)	16.52(19)	19.69(12)	26.60(31)
	+5	10.56(19)	Rejected	19.72(56)	Rejected

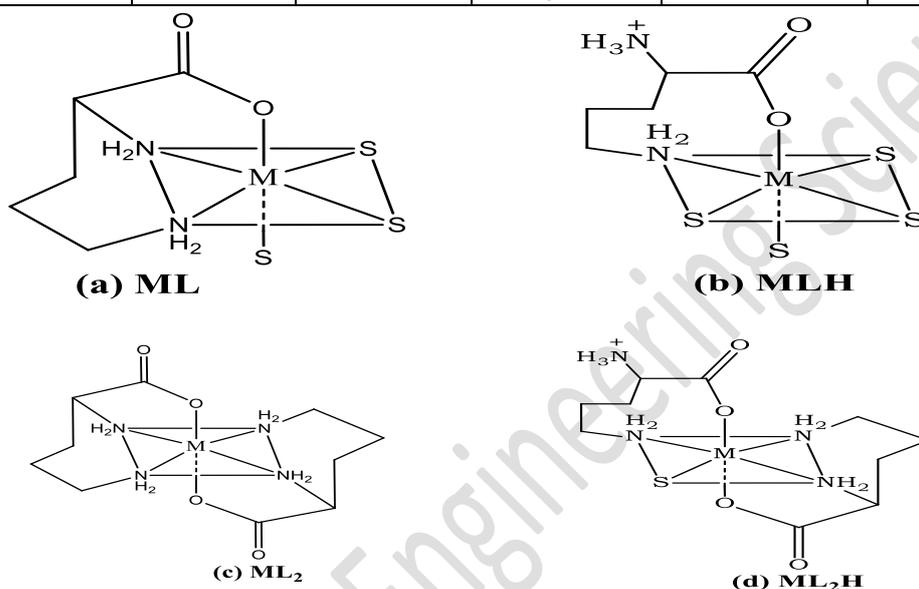


Fig. 7: Proposed structures of M(II)-Orn complexes where M = Ca(II), Mn(II) or Zn(II) and S is either surfactant or water molecule

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