Mixed Ligand Complexes of Transition Metal Ions with Selective Bio-Ligands in Surfactant-Water Mixtures

Srikanth Bathula, Krishna Kumar Kotra

Abstract— Chemical speciation of ternary complexes of L-arginine and L-aspartic acid with essential transition metal ions was studied pH metrically. The following MLX, MLXH and ML_2X ternary species are detected and reported in this paper. The existence of different ternary species is established from modeling studies using the computer program MINIQUAD75. The relative concentrations (M: L: X=1:2:2, 1:2:4, 1:4:2) and stabilities of the ternary species are compared with those of binary species. The extra stability associated with the ternary complexes is attributed to factors such as charge neutralization, chelate effect, stacking interactions and hydrogen bonding. Trend in variation of stability constants with the change in the mole fraction of the surfactant in various micellar media is explained on the basis of electrostatic and non-electrostatic forces. Distribution diagrams in relation to pH and plausible structures were presented.

Keywords: Chemical speciation; ternary complexes; surfactants; MINIQUAD75, arginine, aspartic acid.

I. INTRODUCTION

L-Arginine(Arg) is an essential amino acid, required for polyamine biosynthesis[1] in bacteria, fungi and higher eukaryotes. It also serves as precursor to nitric oxide(NO) synthesis. L-arginine containing ingredients are used for the treatment of antihypertensive in living organisms[2]. L-Aspartic acid (Asp) serves as an excitatory neurotransmitter[3] in the brain. It is one of the key components in all living things.

Cobalt performs a crucial role in several biological functions like synthesis of DNA and hemoglobin. It also activates several metelloenzymes[4] like ribonucleotide reductase (DNA synthesis), glycylglycine dipeptidase(hydrolysis of dipeptide) and glutamate mutase(amino acid metabolism). Copper is found mainly in heart, brain and liver where it is stored as copper thrionein and released as ceruloplasmin or in the form of copper serum albumin complex. For the high metabolic rate, brain, requires large number of Cu-metelloenzymes. Ni(II) was a component of the enzyme urease, it contains 6% of soluble cellular proteins and catalyses the hydrolysis of urea to yield ammonia and carbomate[5]. The role of zinc in these metelloenzymes includes participation in catalytic functions, maintenance of structural stability and regulatory functions [6]. Binary and ternary complexes of Arg, Asp, succinic acid(Suc) and citrulline(Cit) with Co(II), Ni(II), Cu(II) and Zn(II) were reported earlier[7-12]. Hence, chemical speciation of Arg and Asp with some transition metals in surfactant-water mixtures has been reported in this paper.

Revised Version Manuscript Received on 10, September 2019.

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II. METHODOLOGY

GR Grade (Merck, India) sample of L-arginine, L-aspartic acid, Co(II), Cu(II), Ni(II) and Zn(II) chlorides, nitric acid, sodium hydroxide and sodium nitrate were prepared in triple distilled water. All the metal solutions have been standardized by analytical methods[13]. Surfactant solutions like Cetyltrimethylammonium bromide (CTAB, A R, Qualigens, India), Sodium laurylsulphate (SLS, AR, Qualigens, India) and TritonX-100 (TX100, E-Merck, Germany) were used.

To increase the solubility of Arg and Asp and to suppress the hydrolysis of metal salts, nitric acid concentration has been maintained at 0.05 mol dm^{-3}. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one way classification (ANOVA). The strength of alkali was determined using the Gran plot method [14].

Apparatus

An ELICO (Model L1-120) pH-meter (readability 0.01) was used to monitor the changes in H^+ concentration. The glass electrode was equilibrated in a well stirred aqua-surfactants containing inert electrolyte. The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode are accounted for in the form of correction factor[15].

Procedure

The mixed ligand titrations were carried out in the medium containing varying concentrations of (0.0-2.5% w/v) surfactants in water maintaining an ionic strength of 0.16 mol dm^{-3} with sodium nitrate at 303.0±0.1K. The alkalimetric titrations were carried out at regular intervals to check whether complete equilibration was achieved. Free acid titrations were carried out prior to the mixed-ligand titrations to calculate the correction factor. In each of the titrations, the titrand consisted of mineral acid of approximately 1 mmol in a total volume of 50 cm^3. Titrations with different ratios (M:

L: X =1:2:2, 1:2:4, 1:4:2) of mixed-ligand were carried out with 0.4 mol dm^{-3} sodium hydroxide. Other experimental details are given elsewhere[16].

Modeling strategy

The best-fit chemical models consisting of stoichiometric coefficients and logarithm of stability constants were arrived at by using the computer program MINIQUAD75[17] and approximate complex stability constants were calculated with the computer program SCPHD[18]. Some heuristics [19] were followed in the refinement of stability constants and validation of models.

III. RESULTS AND DISCUSSION

Complex equilibria

A preliminary investigation of alkalimetric titrations of mixtures containing different mole ratios of Arg and Asp in the presence of mineral acid and inert electrolyte inferred that no condensed species are formed[20]. The binary metal complexes were fixed in the refinement of ternary complexes in testing various chemical models using computer program MINIQUAD75. The best fit models were chosen as that with low standard deviation in formation constants and minimum U_{corr} (sum of the squares of deviations in concentrations of ligands and hydrogen ion at all experimental points corrected for degrees of freedom) which was corroborated by other statistical parameters like $\chi 2$, R-factor, skewness and kurtosis given in Tables 1-3. The species detected for the metal ions are MLX, ML_2X and MLXH.

A very low standard deviation in overall formation constant (log β) values indicates the precision of these parameters. The small values of U_{corr} indicate that the experimental data can be represented by the model. Small values of mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean with little dispersion. For an ideal normal distribution, the values of kurtosis and skewness should be three and zero, respectively. The kurtosis values in the present study indicate that the most of the residuals are very nearer to leptokurtic and a few form mesokurtic patterns [21]. The values of skewness recorded in the tables are between -3.24 to 3.47. These data evinced that the residuals form a part of normal distribution; hence, least–squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic R-value recorded.

Table 1. Parameters of best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)-Arg-Asp complexes in CTAB-water mixtures

% w/v CTAB	Logβ_{mlxh} (SD) MLX	ML_2X	MLXH	NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Co(II)										
0.0	14.83(2)	18.72(4)	24.68(16)	101	2.11	0.59	39.97	0.0234	7.62	2.5-10.5
0.5	17.10(3)	19.83(7)	26.01(21)	90	5.97	0.25	31.52	0.0851	4.09	2.5-10.2
1.0	17.28(1)	19.94(7)	25.25(34)	99	4.79	0.29	39.32	0.0764	4.32	2.5-10.5
1.5	17.34(5)	19.73(8)	--	100	2.48	0.33	49.09	0.0836	3.95	2.5-10.5
2.0	17.69(3)	19.85(5)	--	104	4.40	0.42	45.42	0.0841	3.85	2.5-10.5
2.5	18.15(2)	20.09(6)	25.87(27)	107	2.40	0.91	54.51	0.0728	4.97	2.5-10.0
Ni(II)										
0.0	16.98(3)	19.52(8)	25.58(20)	108	0.19	-3.24	37.39	0.0643	3.54	2.0-11.0
0.5	17.61(2)	20.74(8)	--	98	5.68	0.94	37.34	0.0844	3.45	2.5-10.5
1.0	17.85(2)	20.93(6)	27.73(18)	104	9.50	0.88	43.52	0.0736	3.25	2.5-10.5
1.5	17.18(1)	--	27.64(6)	107	9.85	0.97	40.25	0.0848	3.15	2.5-10.5
2.0	17.78(4)	21.04(9)	27.82(21)	109	2.09	0.75	41.20	0.0932	3.10	2.5-10.5
2.5	17.93(4)	--	28.02(12)	105	2.25	0.71	22.10	0.0713	2.91	2.5-10.0
Cu (II)										
0.0	17.92(1)	21.98(3)	26.87(8)	107	5.71	-2.88	31.98	0.0549	5.92	2.0-11.0
0.5	18.94(1)	23.44(6)	28.43(12)	108	2.28	-1.67	121.34	0.0215	4.82	2.5-10.5
1.0	18.76(3)	23.77(11)	28.72(14)	105	1.47	-2.34	111.41	0.0526	5.07	2.5-10.5
1.5	18.54(2)	24.50(8)	29.05(20)	100	3.09	-2.74	131.52	0.0145	4.02	2.5-10.4
2.0	18.63(4)	24.59(15)	29.01(8)	109	3.47	-1.98	127.51	0.0372	3.05	2.5-10.5
2.5	20.12(2)	25.08(12)	29.58(21)	98	6.83	-1.73	124.72	0.0452	4.29	2.5-10.0
Zn(II)										
0.0	16.52(2)	19.42(14)	22.97(7)	100	1.54	3.47	39.82	0.0743	2.39	2.5-11.0
0.5	17.01(3)	20.13(8)	23.54(24)	97	4.73	-1.39	59.72	0.0432	4.42	2.5-10.5
1.0	17.73(2)	20.43(11)	23.78(29)	99	4.00	-1.90	67.43	0.0772	4.99	2.5-10.5
1.5	17.95(1)	--	23.90(4)	101	2.36	-1.88	53.21	0.0643	3.74	2.5-10.7
2.0	18.02(2)	--	24.05(8)	107	8.86	-1.07	29.34	0.0842	2.97	2.5-10.7
2.5	18.46(4)	21.24(18)	24.63(6)	105	1.07	-1.04	34.39	0.0951	3.01	2.5-10.8

U_{corr} = U/(NP-m)X10^8, where m = number of species; NP=Number of experimental points; SD= standard deviation

Table 2. Parameters of best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)-Arg-Asp complexes in SLS-water mixtures

% w/v SLS	Logβ (SD) MLX	ML_2X	MLXH	NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Co(II)										
0.0	14.83(2)	18.72(4)	24.68(16)	101	2.11	0.59	39.97	0.0234	7.62	2.5-10.5
0.5	13.96(1)	17.47(7)	23.58(21)	85	8.36	-0.39	100.09	0.0564	3.92	2.0-10.0
1.0	13.73(3)	17.49(14)	23.99(19)	81	6.15	-0.47	98.94	0.0732	4.82	2.0-10.0
1.5	13.84(2)	17.83(12)	23.84(24)	91	8.86	-0.59	121.31	0.0821	3.94	2.0-10.5
2.0	13.24(3)	17.29(10)	23.57(15)	89	4.23	-0.10	115.19	0.0617	2.98	2.0-10.0
2.5	13.55(3)	17.83(16)	23.42(19)	83	5.12	-0.05	110.42	0.0742	5.90	2.0-10.0
Ni(II)										
0.0	16.98(3)	19.52(8)	25.58(20)	108	0.19	-3.24	37.39	0.0643	3.54	2.0-11.0
0.5	15.61(5)	18.55(7)	24.15(13)	80	6.36	0.74	59.02	0.0731	5.42	2.0-10.0
1.0	15.73(3)	18.95(15)	24.23(25)	92	2.24	0.39	67.01	0.0052	6.39	2.0-10.2
1.5	15.94(1)	18.59(15)	24.47(8)	95	7.20	0.09	61.09	0.0443	4.44	2.0-10.2
2.0	15.76(3)	18.97(7)	24.59(18)	99	5.52	0.73	71.40	0.0334	3.29	2.0-10.5
2.5	15.68(4)	18.79(17)	24.87(10)	87	2.14	0.40	77.59	0.0654	2.97	2.0-10.2
Cu(II)										
0.0	17.92(1)	21.98(3)	26.87(8)	107	5.71	-2.88	31.98	0.0549	5.92	2.0-11.0
0.5	16.26(1)	20.30(6)	25.30(15)	80	8.44	-1.92	24.41	0.0484	2.27	2.5-10.0
1.0	16.37(3)	20.34(11)	25.31(9)	85	7.31	-1.70	20.09	0.0662	4.97	2.5-10.5
1.5	16.48(2)	20.39(7)	25.34(20)	88	9.88	-1.01	31.07	0.0112	5.02	2.0-10.5
2.0	16.65(4)	20.47(16)	25.56(18)	81	9.74	-1.24	44.07	0.0220	2.87	2.0-10.0
2.5	16.97(1)	20.86(10)	25.79(25)	83	0.58	-1.39	49.03	0.0314	3.33	2.0-10.2
Zn(II)										
0.0	16.52(2)	19.42(14)	22.97(7)	100	1.54	3.47	39.82	0.0743	2.39	2.5-11.0
0.5	15.42(2)	18.83(10)	21.77(5)	83	8.75	0.33	48.42	0.0311	9.38	2.0-10.5
1.0	15.44(3)	18.84(8)	21.65(21)	88	7.29	0.49	37.07	0.0423	7.42	2.0-10.7
1.5	15.59(2)	18.97(14)	21.92(30)	95	8.36	0.08	33.09	0.0955	6.97	2.0-11.0
2.0	15.98(4)	18.76(12)	21.87(16)	105	1.96	0.94	55.03	0.0724	5.75	2.0-11.0
2.5	15.78(2)	18.59(9)	21.63(28)	100	4.02	0.79	62.94	0.0973	5.54	2.0-10.7

Table 3. Parameters of best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)-Arg- Asp complexes in TX100-water mixtures

% v/v TX100	Logβ (SD) MLX	ML_2X	MLXH	NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Co(II)										
0.0	14.83(2)	18.72(4)	24.68(16)	101	2.11	0.59	39.97	0.0234	7.62	2.5-10.5
0.5	13.80(4)	17.72(6)	23.71(12)	96	2.50	0.22	29.98	0.0432	5.95	2.5-10.5
1.0	13.53(5)	17.59(31)	23.61(24)	95	6.95	0.85	50.32	0.0222	3.98	2.5-10.5
1.5	13.79(1)	17.83(5)	-	98	2.87	0.74	49.82	0.0445	4.28	2.5-10.5
2.0	13.32(2)	17.24(5)	23.40(17)	100	6.94	0.62	53.52	0.0323	3.48	2.5-10.5
2.5	13.07(3)	17.09(8)	22.12(12)	91	0.41	0.34	38.38	0.0043	2.32	2.2-10.2
Ni(II)										
0.0	16.98(3)	19.52(8)	25.58(20)	108	0.19	-3.24	37.39	0.0643	3.54	2.0-11.0
0.5	15.61(3)	18.54(11)	24.59(8)	100	4.53	-1.84	44.35	0.0483	2.92	2.0-11.0
1.0	15.37(2)	18.97(10)	24.20(31)	97	5.42	-2.24	39.82	0.0393	4.82	2.0-11.0
1.5	15.49(4)	18.20(8)	24.74(11)	95	0.10	-1.14	46.47	0.0741	3.39	2.5-10.5
2.0	15.67(4)	18.72(5)	-	91	0.18	-1.15	33.95	0.0832	2.54	2.0-10.5
2.5	15.21(2)	18.25(10)	24.31(15)	93	3.88	-1.94	49.95	0.0763	6.32	2.0-10.5
Cu (II)										
0.0	17.92(1)	21.98(3)	26.87(8)	107	5.71	-2.88	31.98	0.0549	5.92	2.0-11.0
0.5	16.62(3)	20.03(5)	25.03(9)	97	5.26	-1.98	34.92	0.0348	4.32	2.0-10.5
1.0	16.33(2)	20.42(10)	25.73(15)	95	7.17	-2.32	88.72	0.0034	2.95	2.0-10.5

1.5	16.84(3)	20.93(13)	25.22(15)	90	3.15	-1.54	97.18	0.0030	3.56	2.5-10.5
2.0	16.51(4)	20.72(15)	25.64(27)	85	4.22	-0.94	31.95	0.0693	3.16	2.5-10.0
2.5	16.14(2)	20.55(11)	25.19(20)	100	5.68	-0.13	16.78	0.0064	4.41	2.5-10.5
Zn(II)										
0.0	16.52(2)	19.42(14)	22.97(7)	100	1.54	3.47	39.82	0.0743	2.39	2.5-11.0
0.5	15.24(2)	18.38(15)	21.77(8)	91	2.39	1.82	48.62	0.0834	4.32	2.5-10.5
1.0	15.49(1)	18.65(13)	21.69(6)	102	4.24	1.70	105.65	0.0119	5.3	2.5-11.5
1.5	15.95(1)	18.57(7)	21.92(16)	98	3.89	1.96	35.64	0.0627	4.32	2.5-10.5
2.0	15.82(2)	18.32(8)	21.53(20)	94	7.80	2.32	30.24	0.0734	2.98	2.5-10.5
2.5	15.46(3)	18.45(6)	21.04(17)	97	9.46	3.38	32.92	0.0659	3.42	2.5-10.5

Effect of micelles

The effect of surfactant on complex equilibria and apparent shift in the magnitude of stability constants in miceller media compared to aqueous solution can be attributed to the creation of a concentration gradient of proton between the interface and the bulk solution [22].

The variation of overall stability constant values or change in free energy with co-solvent content depends upon two factors, viz., electrostatic and non-electrostatic. Born's classical treatment [23] holds good in accounting for the electrostatic contribution to the free energy change. Hence, the log β values should vary linearly as a function of the mole fraction of the medium, indicates that electrostatic forces and decreased dielectric constant of the medium [24, 25] are dominating the equilibrium process under the present experimental conditions.

The decrease or increase in the stability constants may arise primarily from the difference in the environment of the species as well as from the distribution of the micellar and bulk phase. Since, The CTAB micelles have positive surface charge, the deprotonated carboxylate ions are stabilized on the miceller surface, because the anions are more stabilized compared to the protonated forms by the cationic micelles due to the formation of ion pairs. The number of micelles increases with the concentration of surfactant and oppositely charged ions are concentrated in the Stern layer [26]. TX100 is a non-ionic surfactant having neutral charge on the micellar surface, in this medium the charged species are expected to be destabilized. Where the complex species having negative charge they shall be destabilized by the anionic micelles due to the same environment on the micellar surface. This trend is observed in the present study (Figs 1-3).

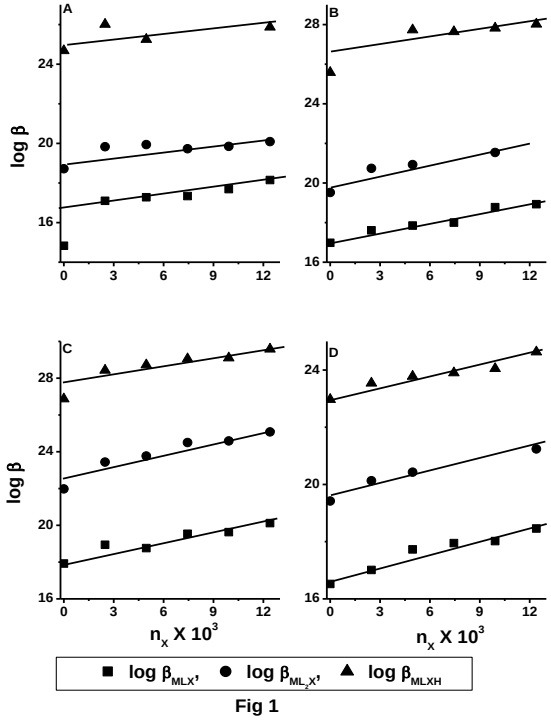


Fig. 1 Variation of stability constant of ternary complexes with mole fraction of CTAB (A) Co(II) B) Ni(II) C) Cu(II) and D) Zn(II).

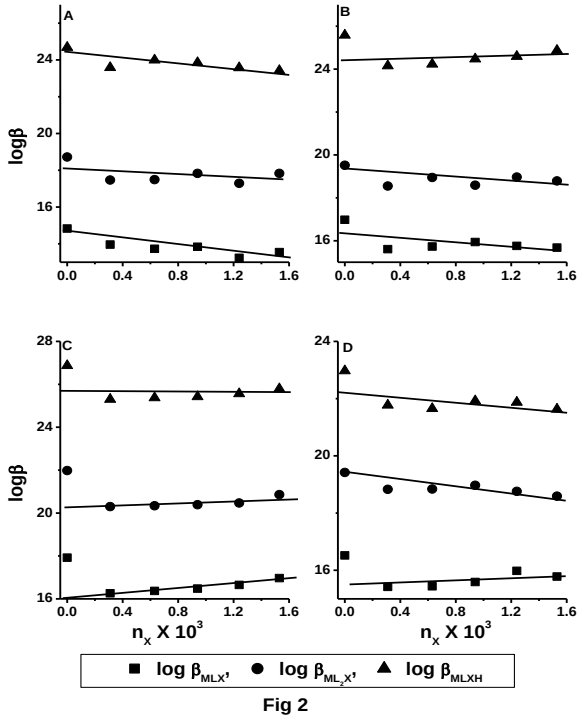


Fig. 2 Variation of stability constant of ternary complexes with mole fraction of SLS (A) Co(II) B) Ni(II) C) Cu(II) and D) Zn(II).

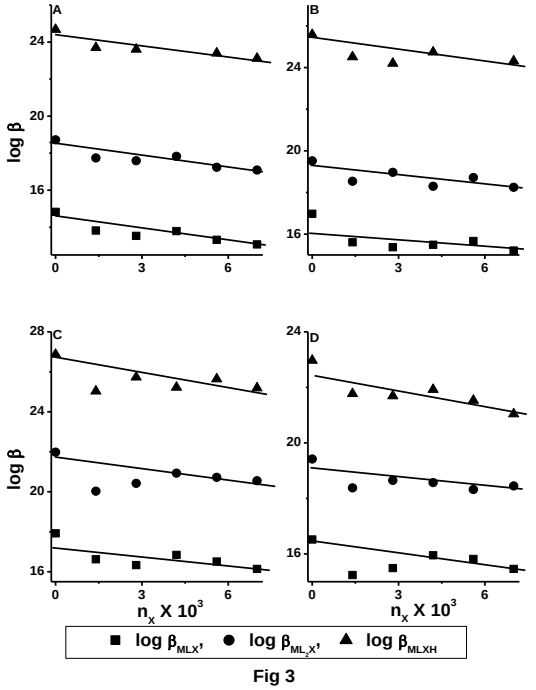


Fig. 3 Variation of stability constant of ternary complexes with mole fraction of TX100 (A) Co(II) B) Ni(II) C) Cu(II) and D) Zn(II)

Reasons for the extra stability of ternary complexes

The change in the stability of the ternary complexes as compared to their binary analogues was quantified [27-30] based on the disproportionation constant (log*X*) given by Equation 1, corresponding to the equilibrium given in Equation 2.

$$\log X = 2\log K^{M}_{MLX} - \log K^{M}_{ML_2} - \log K^{M}_{MX_2} \quad .....(1)$$

$ML_2 + MX_2$ 2 MLX ` (2)

Under these equilibrium conditions one can expect 50% ternary complex and 25% each of the binary complexes to be formed and the value of log*X* was reported [31] to be 0.6. A value greater than this account for the extra stability of MLX. Another approach [32] to quantify the stability of ternary complexes was based on the difference in stability ($\Delta \log K$) for the reactions ML with X and $M_{(aq)}$ with L and X, where L is primary ligand and X is a secondary ligand. It is compared with that calculated purely on statistical grounds as given in equation 3.

$$\Delta \log K = \log K^{M}_{MLX} - \log K^{M}_{ML} - \log K^{M}_{MX} \quad .(3)$$

The electrostatic theory of binary complex formation and statistical arguments suggest the additional coordination positions of given multivalent hydrated metal ion available for the first ligand than for the second. Hence, the usual order of stability $K^{M}_{ML} > K^{ML}_{MLX}$ applies. This suggests that $\Delta \log K$ should be negative, although several exceptions [33] have been found. The statistical values of $\Delta \log K$ for bidentate L and X are -0.4, -0.6 and between -0.9 and -0.3 for octahedral, square planar and distorted octahedral complexes respectively. Negative values of $\Delta \log K$ can be understood as the secondary ligand forms a more stable complex with hydrated metal ion than with ML.

The log*X* and $\Delta \log K$ values calculated from binary and ternary complexes are included in Table 4. These values could not be calculated for some systems due to the absence of the relevant binary species. In the present study, the log*X* values range from 0.13 to 12.46 and some values found to be higher than those expected on statistical base (0.6). These higher values account for the extra stability of the ternary complexes. The values of $\Delta \log K$ ranging from 1.06 to 3.97 for Ni(II), -1.12 to 0.23 for Cu(II). The values are found to be more than -0.4 indicates that the ternary complexes bearing extra stability. The reason for the extra stability of these complexes may be due to interactions outside the coordination sphere such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect and stacking interactions [34, 35].

Table 4.

% w/v CTAB	Log X_{MLX}	Log X_{MLXH}	Log K_{MLX}	Log K_{MLXH}	Log K_{ML2X}
Co(II)					
0.0	6.46	6.99	-	-	-
0.5	4.80	-	-	-	-
1.0	4.30	3.78	-	-	-
1.5	4.61	-	-	-	-
2.0	3.18	-	-	-	-
2.5	3.72	1.82	-	-	-
Ni(II)					
0.0	9.21	2.44	2.21	1.90	2.19
0.5	10.57	-	1.71	-	3.27
1.0	10.77	2.87	1.81	1.06	3.69
1.5	10.90	3.46	1.94	1.30	-
2.0	10.95	4.59	1.82	1.44	3.97
2.5	12.46	6.94	1.80	1.94	-
Cu(II)					
0.0	7.99	1.93	-	-0.44	0.28
0.5	5.60	-0.38	-	-0.85	-0.44
1.0	5.88	-0.29	-	-1.08	-0.42
1.5	6.06	-0.09	-	-1.12	-0.44
2.0	6.01	-0.03	-	-0.80	-0.47
2.5	7.01	0.71	-	-0.72	0.23
Zn(II)					
0.0	7.10	-0.62	-	-	-
0.5	-	0.22	-	-	-
1.0	7.84	0.13	-	-	-
1.5	8.34	0.90	-	-	-
2.0	9.54	1.22	-	-	-
2.5	9.41	1.07	-	-	-

Calculations:-

$$\log X_{MLX} = 2\log\beta_{MLX} - \log\beta_{ML_2} - \log\beta_{MX_2}$$

$$\log X_{MLXH} = 2\log\beta_{MLXH} - \log\beta_{ML_2H_2} - \log\beta_{MX_2}$$

$$\log K_{MLX} = \log\beta_{MLX} - \log\beta_{ML} - \log\beta_{MX}$$

$$\log K_{MLXH} = \log\beta_{MLXH} - \log\beta_{MLH} - \log\beta_{MXH}$$

$$\log K_{ML_2X} = \log\beta_{ML_2XH} - \log\beta_{ML_2} - \log\beta_{MX}$$

Effect of systematic errors on best fit model

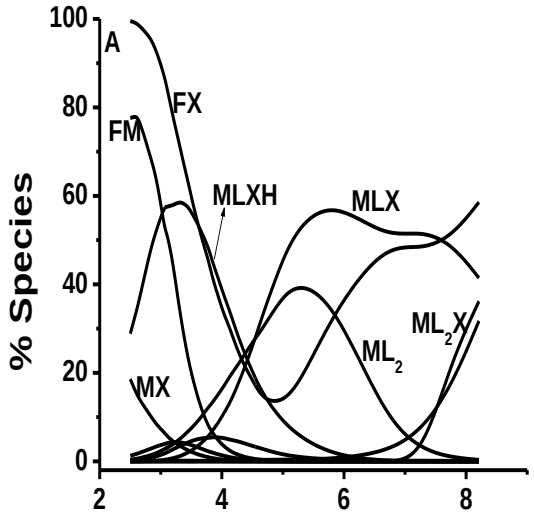
In order to rely upon the best chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was made by introducing pessimistic errors in the influential parameters like concentrations of alkali, mineral acid, ligands, metal and logF (Table 5). The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > Arg > Asp > metal > logF. Some species are even rejected when errors are introduced in the concentrations. This study confirms the appropriateness of the chosen best fit models.

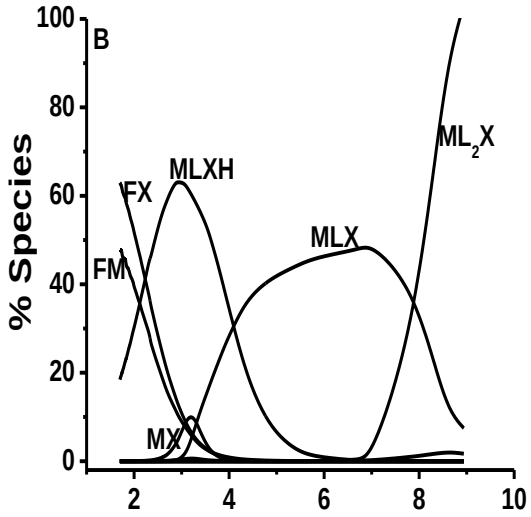
Table 5 Effect of errors in influential parameters on the stability constants of ternary complexes of Co(II) and Ni(II) with Arg-Asp in 1.0 % (v/v) TX100-water mixture

Ingre-dient	% Error	log β(SD)					
		Co(II)			Ni(II)		
		MLX	ML_2X	MLXH	MLX	ML_2X	MLXH
	0	13.53(5)	17.59(31)	23.61(24)	15.37(2)	18.97(10)	24.20(19)
Alkali	-5	14.20(55)	18.25(78)	24.24(31)	16.12(25)	19.25(41)	Rejected
	-2	Rejected	18.11(21)	21.00(25)	Rejected	Rejected	24.99(36)
	+2	14.08(42)	Rejected	Rejected	17.02(59)	19.18(20)	24.12(44)
	+5	Rejected	Rejected	Rejected	17.13(35)	Rejected	Rejected
Acid	-5	Rejected	17.62(42)	21.58(45)	16.21(59)	17.45(25)	23.42(32)
	-2	13.09(61)	Rejected	Rejected	Rejected	Rejected	23.25(58)
	+2	13.02(59)	17.51(64)	20.67(30)	15.13(24)	17.26(36)	Rejected
	+5	13.42(50)	Rejected	Rejected	Rejected	Rejected	24.07(53)
Arg	-5	13.44(29)	17.98(20)	22.89(65)	15.27(20)	18.02(38)	24.36(60)
	-2	13.59(61)	18.02(20)	22.98(26)	15.44(39)	18.43(39)	25.09(24)
	+2	13.64(35)	Rejected	20.74(14)	14.56(35)	19.02(38)	24.15(42)
	+5	Rejected	17.91(22)	Rejected	14.95(30)	18.82(38)	Rejected
Suc	-5	13.51(29)	17.88(25)	22.89(28)	Rejected	19.00(32)	23.65(60)
	-2	12.84(39)	Rejected	22.98(49)	15.32(52)	Rejected	Rejected
	+2	13.06(21)	17.89(23)	22.74(45)	15.65(33)	18.80(25)	23.74(43)
	+5	Rejected	Rejected	Rejected	16.05(46)	Rejected	23.90(55)
Metal	-5	13.64(29)	17.89(25)	23.05(36)	14.24(44)	18.45(51)	24.17(33)
	-2	12.94(45)	17.99(26)	22.92(47)	13.92(48)	18.52(42)	24.69(44)
	+2	12.72(39)	Rejected	22.77(38)	14.24(46)	18.41(34)	23.91(29)
	+5	Rejected	17.85(56)	Rejected	Rejected	18.32(33)	24.82(38)
Log F	-5	13.71(42)	Rejected	23.86(35)	15.50(49)	Rejected	24.06(21)
	-2	13.69(22)	17.89(24)	22.77(27)	15.44(50)	Rejected	Rejected
	+2	12.84(19)	18.06(42)	21.65(35)	16.08(56)	19.05(39)	23.91(55)
	+5	Rejected	Rejected	Rejected	16.03(50)	Rejected	Rejected

Distribution diagrams

A perusal of the distribution diagrams (Fig 4) reveals that the concentrations of binary species are less compared to the ternary species which indicates the existence of more stable ternary complexes. The ternary species exist in the pH ranges 2.0–5.0, 4.0-8.0 and 8-10.0 for all four metals, respectively.





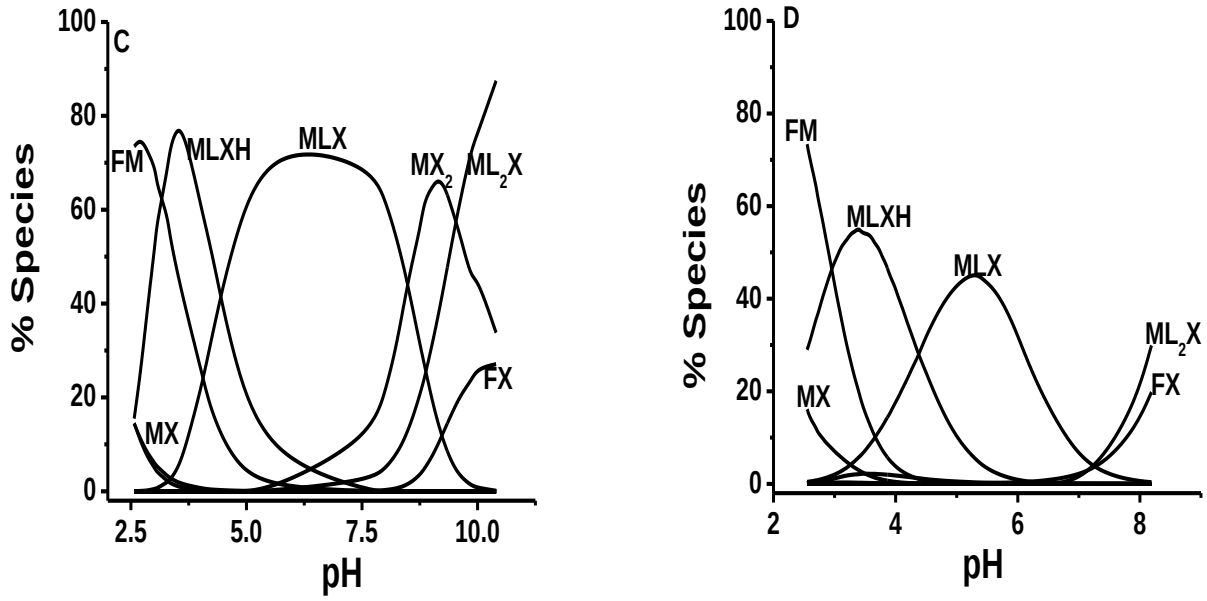


Fig 4 Distribution diagrams of ternary complexes of Arg-Asp in 1.0 % w/v SLS-water mixture (A) Co(II), (B) Ni(II), (C) Cu(II) and (D) Zn(II)

The formation of the complex species can be represented by the following equilibria.

$$M(II) + LH_3^{2+} + XH_3^{+} \Leftrightarrow MLXH_2^{+}2 + 4H^{+} \quad \rightarrow (1)$$

$$MLXH_2^{+} \Leftrightarrow MLXH + H^{+} \quad \rightarrow (2)$$

$$M(II) + LH_2^{+} + XH_2 \Leftrightarrow MLXH + 3H^{+} \quad \rightarrow (3)$$

$$MLXH \Leftrightarrow MLX^{-} + H^{+} \quad \rightarrow (4)$$

$$M(II) + LH + XH^{-} \Leftrightarrow MLX^{-} + 2H^{+} \quad \rightarrow (5)$$

$$MLXH + LH_2^{+} \Leftrightarrow ML_2XH_2 + H^{+} \quad \rightarrow (6)$$

$$ML_2XH_2 \Leftrightarrow ML_2XH^{-} + H^{+} \quad \rightarrow (7)$$

$$ML_2XH^{-} \Leftrightarrow ML_2X^{2-} + H^{+} \quad \rightarrow (8)$$

$$M(II) + 2\,LH + XH^{-} \Leftrightarrow ML_2X^{2-} + 3H^{+} \quad \rightarrow (9)$$

In the pH region 1.5-11.5, 2.0-10.5 Arg[35] and Asp[36] exist as LH_3^{2+}, LH_2^{+}, LH, L^{-} and XH_3^{+}, XH_2, XH^{-}, X^{2-}, respectively. These protonated ligands interact with the metal ion to form $MLXH_2^{+}$ (Equilibrium 1) which may successively deprotonated to form MLXH and MLX^{-} (Equilibria 2 and 4). Existence of MLXH species can be explained based on the deprotonation of $MLXH_2^{+}$ species and also due to interaction of the metal ion with ligand species (Equilibrium 3). The equilibrium 2 is more appropriate for the formation of MLXH because the concentration of MLXH increases where as that of MLX^{-}. It might have been formed from $MLXH_2$ which is formed through Equilibrium 1. $MLXH_2$ species has not been detected probably because it is less stable or quickly deprotonated to MLXH at lower pH. Where as the formation of MLX^{-} Equilibria 3 and 4 are relevant because the pH at which the concentration of MLXH decreases, MLX^{-} increases in the pH range 2.0-5.0. ML_2X is formed by the deprotonation of ML_2XH_2 (Equilibria 6, 7 and 8) and also by the interaction of metal ion with two LH species and one XH^{-} species (Equilibrium 9). Equilibrium 9 is more appropriate for the formation of ML_2X because ML_2XH_2 and its deprotonated species are not refined and during its formation the concentrations of LH and XH^{-} are decreasing. Depending on the active sites in the ligands and the nature of the metal ions, the structures were proposed for the species detected as shown in Fig 5.

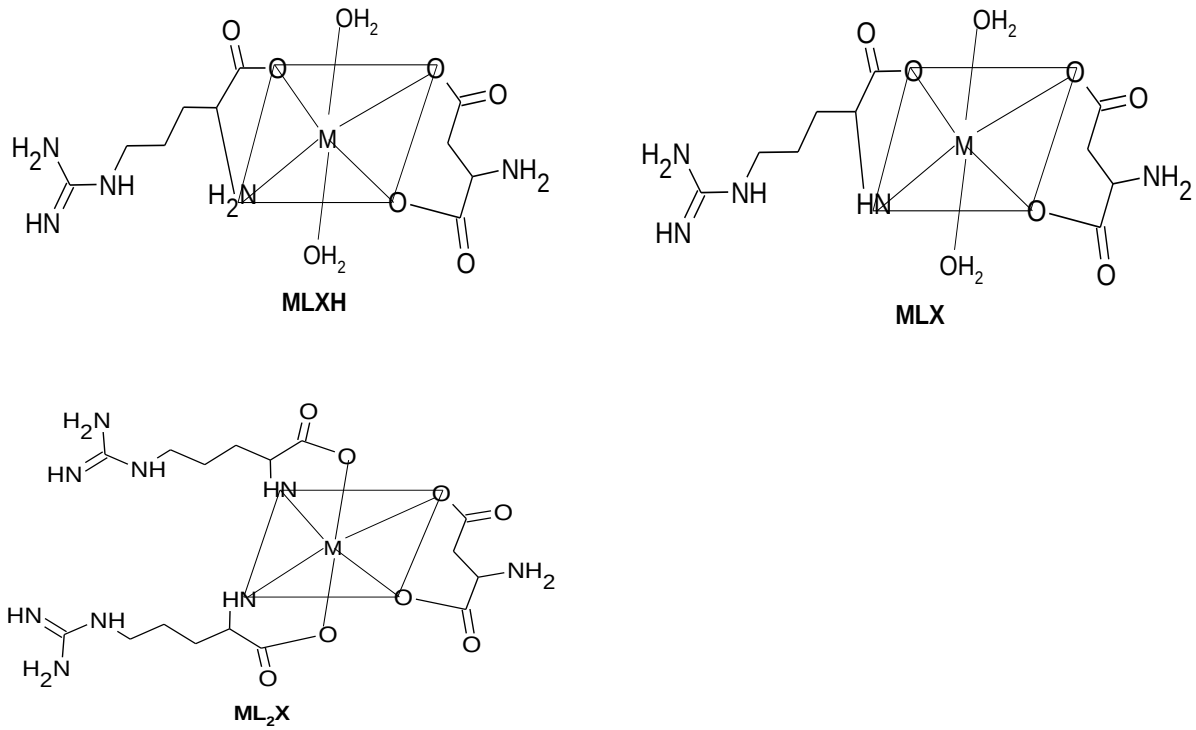


Fig 5 Plausible structures of ternary complexes of Co(II), Ni(II), Cu(II) and Zn(II) ions with L-arginine (L) and L-aspartic acid (X)

REFERENCE

1. Davis RH, Morris DR, Coffino P (1992) Microbiol Rev 56:280-290
2. Zicha J, Dobesova Z, Kunes J (2006) Hypertens Res 29:1021-1027
3. Chen EP, Geballe TM, Stansfeld JP, Johnston RA (2005) Molecular Pharmacology 67:1470-1477
4. Underwood EJ (1977) Trace elements in human and animal nutrition 4th edn. Academic press
5. Mulrooney SB, Hausinger RP (2003) Nickel uptake and utilization by micro organisms. FEMS Microbiol Rev 27: 239-261
6. Vallee BL (1988) Biofactors 1:31-36
7. Srikanth B, Rao PS, Rao VS, CK Sastry, Rao GN (2009) J Indian Chem Soc (communicated)
8. Rao VS, Srikanth B, Rao PS, CK Sastry, Rao GN (2009) Chem Spec Bioavailab 21: 71-80
9. Srikanth B, Rao PS, Rao VS, CK Sastry, Rao GN (2009) J Serbian Chem Soc (in press)
10. Srikanth B, Rao PS, Rao VS, CK Sastry, Rao GN (2009) Turk J Chem (communicated)
11. Rao PS, Srikanth B, Rao VS, CK Sastry, Rao GN (2009) J Sol Chem (communicated)
12. Rao PS, Srikanth B, Rao VS, CK Sastry, Rao GN (2009) J Iran Chem Soc (communicated)
13. Jeffery GH, Basset J, Mendham J, Denny RC (1991) Vogel's Text Book of Quantitative Chemical Analysis 5th edn. Longman, London.
14. Gran G (1988) Anal Chim Acta 206: 111-123
15. Jervis RE, Neelakanthan K (1971) J Anal Chem 43: 1206-1211
16. Padmaja N, Babu MS, Rao GN, Rao RS, Ramana KV (1990) Polyhedron 9:2497-2506
17. Gans P, Sabatini A, Vacca A (1976) Inorg Chim Acta 18:237-239
18. Rao GN (1989) Ph.D Thesis, Andhra University, Visakhapatnam, India
19. Rao GN, Rao RS (1992) J Indian Council Chem 8:12-28
20. Lavanya KV, Rao VM, Rao GN (2008) Oxid Commun 31:398-409
21. Latha MP, Rao VM, Rao TS, Rao GN (2007) Bull Chem Soc Ethiop 21:363-372
22. Hartley GS, Roe JW (1940) Trans Faraday Soc 36:101-105
23. Born M (1920) Z Phys 1:45-48
24. Singh AK, Manjula D (2001) J Indian Chem Soc 78:635-641
25. Cordes EH (1978) Pure Appl Chem 50:617-623
26. Bunton CA, Cerichelli G, Ihara Y, Supulveda L (1979) J Am Chem Soc 101:2429-2433
27. Griesser R, Sigel H (1970) Inorg Chem 9:1238-1243
28. Griesser R, Sigel H (1971) Inorg Chem 10:2229-2232
29. Griesser R, Sigel H (1974) Inorg Chem 13:462-465
30. Sigel H, Huber PR, Greisser R, Prijs B (1974) Inorg Chem 12:1198-1200
31. Kida S (1956) Bull Chem Soc Japan 29:805-811
32. Martin RB, Prados R J (1974**)** Inorg Nucl Chem 36:1665-1670
33. Sigel H (1975) Angew Chem Int Ed Engl 14:394-402
34. Sakurai T, Yamauchi O, Nakahara A (1976) Bull Chem Soc Japan 49:169-173
35. Sakurai T, Yamauchi O, Nakahara A (1977) Bull Chem Soc Japan 50:1776-1779
36. Lavanya KV, Rao GN, Rajesh M, Babu MS (2004) J Indian Chem Soc 81:384-387
37. Rao PS, Srikanth B, Rao VS, Sastry CK, Rao GN (2009) E-J Chem 6:561-568