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Effect of triton-X100 on ternary complexes of cobalt(II), nickel(II), copper(II) & zinc(II) with aspartic and citric acids

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A computer based investigation has been made pH-metrically on the chemical speciation of mixed ligand complexes in ternary systems consisting of cobalt(II), nickel(II), copper(II) and zinc(II) with aspartic and citric acids in various concentrations (0.0–2.5% v/v) of the triton-X 100 surfactant solution maintaining an ionic strength of 0.16 mol dm^{-3} with sodium hydroxide at 303.0+0.1 K. These ligands interact with the metal ions to form MLXH^{2-}, MLX$_2$H^{4-} and MLX^{3-} species. The trend of the variation in log β values with changing dielectric constant as well as with mole fraction of the surfactant is explained based on the electrostatic interactions of the side chains of the ligands, charge neutralization, chelate effect, stacking interactions and hydrogen bonding. The existence of different ternary species is established from modelling studies using the computer program MINIQUAD75. Distribution diagrams with different pH-compositions of surfactant and structures of plausible ternary complexes are also presented.

Keywords: Triton-X 100, Stability constant, Citric acid, Aspartic acid, Ternary complexes

Citric acid (Cit), a naturally occurring complexing agent, is used in the separation of actinides and in the extraction of toxic metals and radionuclides from wastes, sledges, sediments, and contaminated soils[1]. It forms soluble metal‒citrate complexes with transition metals and actinides[2,3]. In the presence of more than one metal, a ternary complex is formed with citric acid due to the bonding of the metals with both the carboxyl[4] and hydroxyl groups. Citric acid is a ubiquitous molecule, essential for aerobic life. The activity of citric acid as a metal chelator is central to its importance in living systems[5,6]. Citric acid accumulation in substantial amounts depends on both the strain as well as certain environmental parameters. It is accumulated when several nutrient factors are present[7].

L-aspartic acid (Asp) is a ubiquitous acid present in many foods, either in its free form or in peptides and proteins. Aspartate impairs neuronal calcium extrusion while reducing sodium[8,9] gradient. Aspartate-induced intracellular calcium changes and neurotoxicity in cortical neurons in vivo was studied[10]. A thorough study of all the species existing in every natural system is impossible due to limitations of the available experimental methods. Hence, modelling studies involving ternary complexes have gained[11-13] popularity (Sasikumar et al., 2019; Rawda et al., 2019; Sujay Mahata et al., 2019).

The micellar effect[14] on metal ligand equilibria of magnesium(II) and calcium(II) with L-arginine and the binary complex equilibria of L-arginine and L-histidine with nickel(II)[15] in cetyltrimethylammonium bromide (CTAB) micellar media have also been studied in our laboratory. Ternary complexes of essential metal ions with L-arginine and succinic acid in cationic surfactant medium have been studied[16] recently. The physiological activities of L-arginine, L-histidine and nickel(II) are associated with the metabolic processes in the liver[17] was studied. The ternary complexes containing a metal ion and two different ligands have been studied[18-21] previously (Kayali & Berthon, 1980; Brookes & Petit, 1977; Alemadaroglu & Berthon, 1981; Sivasankaran Nair et al., 1982). The present paper reports a pH-metric study of the speciation of ternary complexes of aspartic and citric acids with cobalt(II), nickel(II), copper(II) and zinc(II) in triton –X100 micellar media of varying compositions.

The importance of this study is to confirm the species formed under the present experimental conditions and to validate the models by statistical treatment of the data. The ternary stability constants of aspartic and citric acids have been determined. In particular, applications[22] considered are to extraction metallurgy, the nuclear energy industry, analytical methods, and to medical, environmental, and industrial research. These applications all require stability constant values of high reliability and sources of critically evaluated published constants are referenced. Stability constant is useful physical entity, which explains the importance[23] and function of various complexes in biological systems. Further scope of this work lies in the better evaluation of p*K* values using pH study. Micellar-water mixtures, which are comparable to those of the physiological fluids, are chosen in these studies. These solutions are expected to mimic the physiological conditions.

Materials and Methods

Aqueous solutions of cobalt, nickel, copper, zinc chlorides, aspartic acid and citric acid (E. Merck, G.R.) were prepared using triple-distilled water. Aqueous solutions of triton-X100 were also prepared using triple-distilled water. The alkali metric titrations were carried out in a medium containing varying compositions of TX-100 (0.5–2.5% v/v) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium hydroxide at 303.0+0.1 K. An ELICO (Model L1-120) pH-meter (readability 0.01 pH units) pH meter was used. The glass electrode was equilibrated in a well-stirred micellar solution containing an inert electrolyte. The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of the glass electrode were taken into account in the form of a correction factor[24] which was computed from the simulated acid-base titration data calculated by SCPHD program[25] for each of the solvent compositions.

A correction was applied to the pH meter dial reading to account for the solvent effect on pH. Strong acid was titrated with alkali at regular intervals to check whether complete equilibrium was achieved. The calomel electrode was refilled with micellar solution of equivalent composition as that of the titrand. In each titration, the titrand consisted of mineral acid (HCl) of approximately 1 mmol in a total volume of 50 cm^3. Titrations of solutions containing different ratios of metal to primary (Cit) and secondary (Asp) ligands with different ratios (M:L:X= 1:2:2, 1:2:4 and 1:4:2) were carried out with 0.5 mol dm^{-3} sodium hydroxide solution.

Modelling strategy

The best-fit chemical models consisting of stoichiometric coefficients and logarithm of stability constants were arrived at by using a computer program MINIQUAD75[26]. Some heuristics[27] were followed in the refinement of stability constants and validation of models[28].

Results and Discussion

Complex equilibria

The models containing different number of species were tested from the primary alkali metric data. Only a few species were refined while other species were rejected by MINIQUAD75. Existence of species was determined by performing exhaustive modelling. Models containing various numbers and combinations of species were generated using an expert system package CEES[29] and these models were refined using MINIQUAD75. The final model in Triton-X100-water media for ternary complexes of cobalt(II), nickel(II), copper(II) and zinc(II) with citric and aspartic acids contained the species MLX, MLXH and MLX_2H. The parameters of the best-fit models are given in Table 1. A very low standard deviation in log β values indicates the precision of these parameters.

The small values[30] of U_{corr} indicate that the model is consistent with the experimental data. The kurtosis values between 2.25 and 8.82 indicate that the residuals form a mesokurtic pattern. The values of skewness between -3.74 and 1.01 show that the residuals form a part of normal distribution and hence a least squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic R-values, which indicate the need for inclusion of additional species in the model χ^2 is a special case of ϒ distribution which measures the probability of residuals forming a part of standard normal distribution. The details of these statistical parameters can be found elsewhere[31].

Effect of micelles

The variation of the stability constants of ternary complexes of Asp and Cit with mole fraction of surfactants (Triton-X100) is shown in Fig. 1. The non-linear decrease in the stability of ternary complexes with mole fraction of the surfactant indicates the dominance of non-electrostatic forces over electrostatic forces and decreased dielectric constant with increased surfactant concentration.

The species should be stabilized in the micellar medium with opposite charges due to electrostatic

Table 1 — Parameters of best fit chemical models of ternary complexes of Cit and Asp in Triton x100-water mixtures; Temperature = 303 K, Ionic strength = 0.16 mol dm^{-3}

% v/v	Logβ (SD)			NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Triton -X100	MLX	MLXH	MLX_2H							
Co(II)										
0.0	10.74(8)	16.85(20)	22.97(32)	197	9.63	-1.27	54.02	0.0821	5.84	1.7-7.5
0.5	10.25(6)	15.83(11)	21.85(26)	122	5.54	0.33	49.49	0.0393	2.98	2.8-6.5
1.0	9.76(7)	15.46(10)	--	127	5.96	0.41	60.66	0.0532	3.03	2.5-6.5
1.5	9.45(5)	15.87(12)	21.45(26)	121	2.71	0.95	58.32	0.0074	3.85	2.5-6.5
2.0	9.78(7)	15.09(11)	21.33(25)	117	7.75	1.01	77.11	0.0062	5.15	2.5-6.6
2.5	9.16(8)	14.56(10)	20.15(24)	119	6.83	0.88	37.54	0.0414	4.32	2.5-6.6
Ni(II)										
0.0	14.73(9)	18.59(18)	23.58(25)	174	1.38	0.21	66.09	0.0972	6.01	2.0-6.7
0.5	14.05(6)	18.06(14)	22.78(28)	100	9.01	-0.98	59.74	0.0698	5.42	2.5-6.0
1.0	13.75(6)	17.56(15)	-	98	4.10	-0.44	27.84	0.0574	8.82	2.5-6.0
1.5	13.89(5)	17.91(13)	-	95	3.75	-0.39	36.75	0.0556	7.42	2.6-6.0
2.0	13.44(5)	--	22.56(30)	100	9.56	-0.27	49.74	0.0432	4.34	2.5-6.2
2.5	13.07(8)	17.25(15)	22.09(32)	104	7.32	-1.02	81.52	0.0098	6.66	2.5-6.5
Cu(II)										
0.0	12.86(10)	15.82(18)	20.74(28)	189	3.37	0.44	22.32	0.0815	8.21	1.7-8.0
0.5	11.53(6)	15.36(9)	19.86(28)	98	1.57	-2.24	50.21	0.0452	2.25	2.0-6.5
1.0	11.84(7)	14.56(15)	--	95	2.39	-1.79	48.34	0.0395	5.94	2.0-6.5
1.5	11.23(5)	14.76(18)	19.52(28)	91	1.93	-2.88	39.41	0.0786	4.74	2.0-6.5
2.0	10.89(6)	14.09(17)	19.25(27)	88	8.58	-3.74	98.46	0.0532	3.98	2.0-6.5
2.5	10.24(5)	13.86(18)	18.79(28)	97	4.78	-2.98	77.67	0.0793	2.79	2.0-6.5
Zn(II)										
0.0	13.52(5)	17.82(10)	25.96(30)	147	0.41	-1.14	51.04	0.0824	5.02	1.7-7.5
0.5	13.05(9)	17.24(15)	25.43(25)	125	1.06	0.24	44.39	0.0432	2.98	2.5-6.5
1.0	12.85(10)	16.58(17)	--	127	2.03	0.44	59.74	0.0531	3.08	2.5-6.5
1.5	12.31(10)	16.82(15)	--	120	2.54	0.39	54.38	0.0834	2.98	2.5-6.5
2.0	11.89(9)	16.38(18)	24.57(28)	119	9.39	0.87	49.75	0.0792	2.77	2.5-6.5
2.5	11.58(8)	16.06(15)	24.06(28)	115	1.51	0.65	39.79	0.0034	2.32	2.5-6.5

U_{corr} = U/(NP-m) X 10^8, m= number of species; NP = number of experimental points

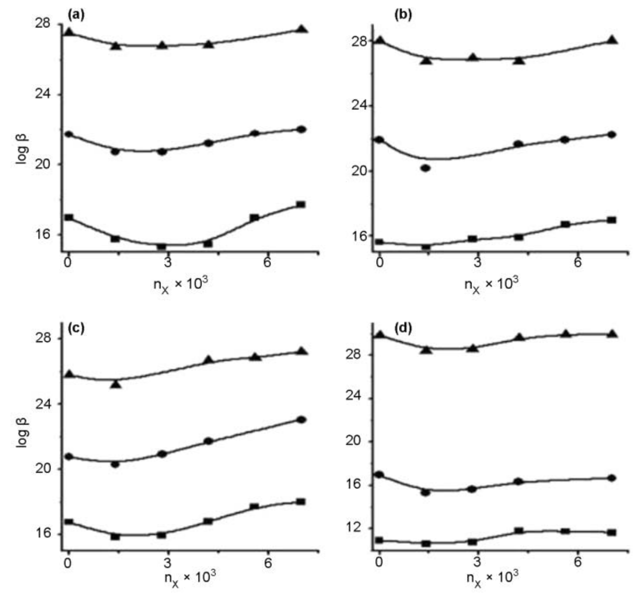

Fig. 1 — Variation of stability constants of ternary complexes of Cit- Asp with mole fraction in Triton-X100-water mixtures; (a)Co(II), (b) Ni(II), (c) Cu(II) and (d) Zn(II), Symbols used: (■) logβ MLX, (●) logβ MLXH, (▲) logβ MLX_2H

interactions but these charged species should be destabilized due to the decreased dielectric constant of the medium. The stabilization of some of the species is due to stacking interactions between NH_3^+ of one ligand and the oxygen dipole of the neighboring ligand. The reason for the extra stability of ternary complexes may be due to interactions outside the coordination sphere[32] such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization and chelate effect. This can be due to the decreased dielectric constant of the medium by which the charged species $MLXH^+$ and MLX_2H^+ are more destabilized where as the uncharged MLX remains unaffected.

Extra stability of ternary complexes compared to binary complexes

The change in the stability of the ternary complexes as compared to their binary analogues was quantified[33-35] based on the disproportionate constant (logX) given by Eqn (1), corresponding to the equilibrium given in Eqn (2).

$$logX = 2logK^{M}_{MLX} - logK^{M}_{ML_2} - logK^{M}_{MX_2} \quad \ldots (1)$$

$$\mathrm{ML_2 + MX_2 \ = 2MLX} \quad \ldots (2)$$

The stability of ternary complexes is based on the difference in stability (Δ log K) for the reactions ML with X and M (aq) with L and X, where L is primary ligand (Cit) and X is the secondary ligand (Asp). It is compared with that calculated purely on statistical grounds. Eqn (3) can be formulated based on the properties of the cyclic systems reported earlier[36] from which it is clear that both the ligands in the ternary complex influence mutually to the same extent.

$$\Delta\mathrm{logK} = \ \mathrm{logK^{M}_{MLX} - logK^{M}_{ML} \ - logK^{M}_{MX}} \quad \ldots (3)$$

This approach relates the stability of the mixed-ligand complex to the simple complexes according to the Eqns. (3–9)

$$\mathrm{M + X \Leftrightarrow MX\ K^{M}_{MX} = [MX]/[M][X]} \quad \ldots (4)$$

$$\mathrm{ML + X \Leftrightarrow MLX\ K^{ML}_{MLX = [MLX/ML]/[X]}} \quad \ldots (5)$$

$$\Delta log\ K = logK^{ML}_{MLX} \ - logK^{M}_{MX} \quad \ldots (6)$$

$$= \mathrm{logK^{MX}_{MLX} \ - logK^{M}_{ML}} \quad \ldots (7)$$

$$\Delta\mathrm{logK = log\beta_{MLX} - (log\beta_{ML} + log\beta_{MX})} \quad \ldots (8)$$

Generalizing for any mixed- ligand complex $\mathrm{log\beta M_{L1X_x}}$

$$\Delta\mathrm{logK = log\beta M_{L1X_x}\text{- }(log\boldsymbol{\beta} M_{L1}+log\boldsymbol{\beta} M_{Xx})} \quad \ldots (9)$$

The value of Δ log K should be negative as the ligand L or X coordinates more easily to the free metal ion compared to the binary complex. This is normally observed in simple binary systems where log K_1 is always greater than log K_2. On the contrary in the case of mixed-ligand complexes, Δ log K is positive for certain combination of ligands.

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 $\mathrm{K^{M}_{ML}}$ > $\mathrm{K^{ML}_{MLX}}$ applies. This suggests that Δ log K should be negative, although several exceptions[37] have been found. The statistical values of Δ log K for bidentate L and X are -0.4, -0.6, respectively and for octahedral, square planar and distorted octahedral complexes the values are between -0.9 and -0.3. Negative values Δ log K can be understood as the secondary ligand forms a more stable complex with hydrated metal ion than with ML.

Whenever the experimental values of Δ log K exceed the statistical values, it can be inferred that the ternary complex is formed as a result of interaction of ML with X or MX with L. Δ log K values of ternary complexes containing bipyridyl as the primary ligand are positive for O-donors (malonic acid, pyrocatechol etc.), negative[38] for N-donors (ethylene diamine) and intermediate or negative for amino acids with both N and O co-ordination sites. However, a very high negative value (-2.3) for Cu(en)(iminodiacetic acid) and a positive value (0.82) for Cu (O-phen)- (6,7-dihydroxynaphthaline-2-sulphonate) was also observed.

Calculations

$$\mathrm{logX_{MLX} = 2log\beta_{MLX} \ - log\beta_{ML2} - log\beta_{MX2}} \quad \ldots (10)$$

$$\mathrm{logX_{MLXH} = 2log\beta_{MLXH} - log\beta_{ML2H} - log\beta_{MX2H}} \quad \ldots (11)$$

$$\mathrm{= 2log\beta_{MLXH} - log\beta_{ML2} - log\beta_{MX2H2}} \quad \ldots (12)$$

$$\mathrm{logX_{MLX2H} = 2log\beta_{MLX2H} \ - log\beta_{ML2H2} - log\beta_{MX4}} \quad \ldots (13)$$

$$\mathrm{= 2log\beta_{MLX2H} - log\beta_{ML2} \ - log\beta_{MX4H2}} \quad \ldots (14)$$

$$\Delta\mathrm{logK_{MLX2H} = log\beta MLX2H \ - log\beta_{MLX} - log\beta_{MX2}}. \quad \ldots (15)$$

The log X and Δ log K values calculated from binary and ternary complexes are included in Table 2. These values could not be calculated for some systems due to the absence of relevant binary species. In the present study, the Δ log K values range from -3.96 to 9.59 for Cit-Asp in Triton X100-water, The log X values range from 3.02 to 12.01 for Cit-Asp in Triton-X100 water-mixtures. Some Δ log K values and log X values are found to be more than the theoretical values which account for the extra stability of the ternary complexes

Distribution diagrams

In the pH range of the present study, L-aspartic acid (2.0-10.0) exists[39] as LH_3^+, LH_2, LH^- and L^{2-} while citric acid (1.7-8.0) exists[40] as XH_3, XH_2^-, XH^{2-} and X^{3-}. These ligands interact with the metal ions to form $\mathrm{MLX}H^{2--}$, $\mathrm{MLX_2\ H^{4--}}$ and $\mathrm{MLX^{3-}}$ species. Some typical distribution diagrams of these species are given in Fig. 2. The lower concentrations

Table 2 — Log X and Δ log K values from stability constants of ternary complexes of Cit and Asp in Triton-X100-water mixtures

% v/v Surfactant	$\log X_{MLX}$	$\log X_{MLXH}$	$\Delta \log K_{MLX_2H}$	$\log X_{MLX}$	$\log X_{MLXH}$	$\Delta \log K_{MLX_2H}$
		Co(II)			**Ni(II)**	
0.0	7.27	9.59	9.59	-0.64	9.75	9.90
0.5	3.02	8.26	0.40	7.97	9.46	6.18
1.0	4.24	7.34	--	9.28	8.62	--
1.5	5.17	8.06	-0.64	9.92	9.03	--
2.0	5.86	8.99	0.86	10.25	10.69	7.28
2.5	8.32	9.84	-0.28	11.00	11.37	7.42
		Cu(II)			**Zn(II)**	
0.0	7.11	6.6	6.6	-1.22	12.01	12.45
0.5	5.92	4.75	-2.45	9.99	9.69	9.84
1.0	5.80	5.21	-2.57	9.21	9.03	--
1.5	6.29	4.94	--	10.44	8.86	--
2.0	8.39	5.99	3.99	10.48	10.42	9.75
2.5	8.32	7.10	-3.96	11.26	10.77	9.48

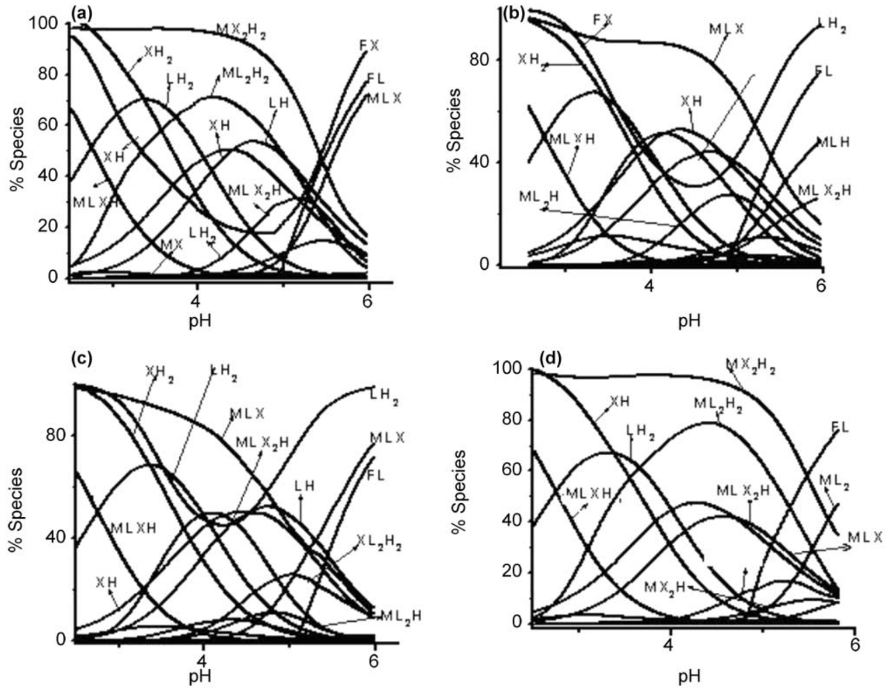

Fig. 2 — Distribution diagrams of Cit and Asp with (a) Co(II), (b) Ni(II), (c) Cu(II) and (d) Zn(II) in 1.0 % v/v Triton-X100-water mixtures

of binary species than those of the ternary species indicate the higher stability of ternary complexes. The formation of the ternary species is discussed below.

$MLXH^{2-}$ might have formed due to the following equilibria in the pH range 2.0-4.0.

$$M(II) + LH_3 + XH_2 \Leftrightarrow MLXH^{2-} + 4H^+ \quad \dots (16)$$

$$M(II) + LH_{2-} + XH^- \Leftrightarrow MLXH^{2-} + 2H^+ \quad \dots (17)$$

The formation of MLX^{3-} in the pH region 4.0-8.0 can be represented by the following equilibria:

$$M(II) + LH_3 + XH_2 \Leftrightarrow MLX^{3-} + 5H^+ \quad \dots (17)$$

$$M(II) + LH_3 + XH_2 \Leftrightarrow MLX^{3-} + 3H^+ \quad \dots (18)$$

$$MX + LH^{2-} \Leftrightarrow MLX^{3-} + H^+ \quad \dots (19)$$

$$MLXH^{2-} \Leftrightarrow MLX^{3-} + H^+ \quad \dots (20)$$

The formation of MLX_2H^{4-} in the pH region 4.0-6.0 can be represented by the following equilibria:

$$M(II) + LH_3 + 2XH_2 \Leftrightarrow MLX_2H^{4-} + 6H^+ \quad \dots (21)$$

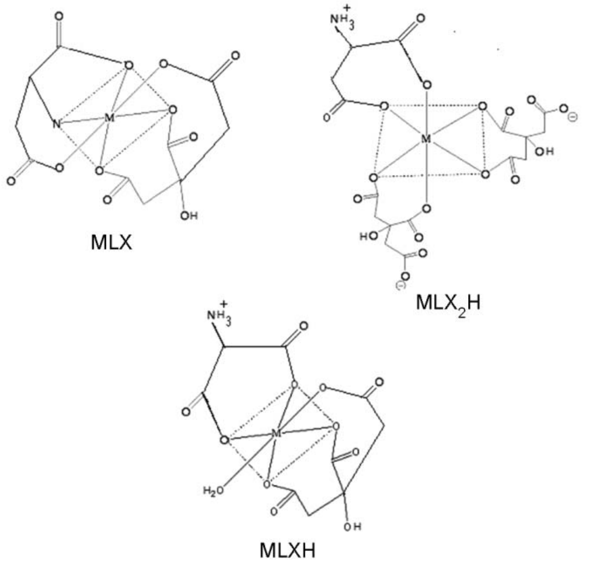

Fig. 3 — Structures for ternary complexes of Co(II), Ni(II), Cu(II) and Zn(II) with L- aspartic acid and citric acid

$$\mathrm{M(II)} + \mathrm{LH}_{2-} + 2\mathrm{XH}^{-} \Leftrightarrow \mathrm{MLX}_2\,\mathrm{H}^{4-} + 3\mathrm{H}^{+} \quad \ldots (22)$$

$$\mathrm{MLX}H^{2-} + \mathrm{XH}^{-} \Leftrightarrow \mathrm{MLX}_2\mathrm{H}^{4-} + \mathrm{H}^{+} \quad \ldots (23)$$

The concentration of binary complexes in all the systems studied was negligible. Based on the above equilibria, the possible structures of the complexes can be represented as given in the Fig. 3.

Conclusions

A study of the chemical speciation of ternary complexes of Co(II), Ni(II) ,Cu(II) and Zn(II) with Cit and Asp in miceller medium reveals the compartmentalization of metabolic reactions. The following conclusions can be drawn from the modelling studies. The models for the ternary species contained $\mathrm{MLX}H^{2--}$, $\mathrm{MLX}_2\,\mathrm{H}^{4--}$ and MLX^{3-}, where L is aspartic acid and X is citric acid. The change in the stability of the ternary complexes as compared to their binary analogues shows that the ternary complexes are more stable than the binary complexes due to the interactions outside the coordination sphere. The decreased stability of complexes with the increase in surfactant concentration indicates the destabilisation of these species. The most predominant ternary species is MLXH under the prevailing experimental conditions indicating the presence of protonated species in the corresponding biological systems. The higher stability of neutral complex than the charged species clearly indicates that the uncharged species are formed predominantly in bio fluids. The decreased stability of the charged binary species compared to the corresponding ternary complexes observed in the present study can also be extended to the various ternary metal complexes formed in the biological systems. Finally, the study gives an insight into the metal availability /metal transport in bio fluids. The ternary complexes are more amenable for ‘‘metal transport’’ because of their extra stability and the binary complexes make the ‘‘metal available’’ in biological systems due to their decreased stability.

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