

Cationic surfactant influence on ternary complexes of CoII, NiII, CuII and ZnII ions with aspartic and citric acids

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ABSTRACT

A potentiometric titration study has been undertaken to determine the cationic surfactant influence on mixed ligand complexes in ternary systems consisting of cobalt (II), nickel (II), copper (II), and zinc (II) with aspartic and citric acids at various concentrations (0.0–2.5% w/v) of the CTAB (Cetyltrimethyl ammonium bromide)-surfactant solution while maintaining an ionic strength of 0.16 mol L⁻¹ (NaCl) at 30 °C. Titrations were performed in the presence of different ratios (M:L:X = 1:2:2, 1:4:2, and 1:2:4) of metal (M) and aspartic acid (L) to citric acid (X) using sodium hydroxide. Model systems were developed based on statistical parameters and residual analysis. For Co(II), Ni(II), Cu(II), and Zn(II), the species detected were MLXH₂, MLX₂H₅, and MLX₃. The electrostatic relationship of the ligands' side chains, charge neutralization, chelate effect, stacking interactions, and hydrogen bonding are used to explain the trend in the variation of logarithm of stability constants (log β) values with changing dielectric constant and mole fraction of the surfactant. The variation in species distribution as a function of pH and surfactant composition is also presented and discussed, as are plausible equilibria for the formation of the species and structures of the ternary complexes are also presented and discussed.

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1. Introduction

L-aspartic acid (Asp) is a naturally occurring amino acid with an extra carboxylic group in the side chain¹. Asp is a component of the active centre of some enzymes² and forms complexes with metal ions via its three binding sites. Chelation via the amino and α-carboxylate groups occurs readily and studies of metal binding have been undertaken to deduce whether side chain carboxylates are also coordinated to the metal ion³⁻⁴. Potentiometric studies on vanadium (III) complexes with L-alanine and Asp were carried out by Bukietynska et al⁵. Bottari studied⁶ copper (II) complexes with aspartate and glutamate. The stability constants of biomolecules and amino acid-mixed ligand complexes with Ni(II) were investigated using the potentiometric titration method by Phase et al⁷. Ternary transition metal complexes with an azo-imine ligand and 2,2'-bipyridine characterization, computational calculations, and acetylcholinesterase inhibition activities were studied by Serbest et al⁸. Mononuclear pyrazine-2-carbohydrazone metal complexes: Synthesis, structural assessment, thermal, biological, and electrical conductivity studies were carried out by Ashish Bansod et al⁹.

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid (Cit) ions occur in small amounts in most living organisms and act as bioactive ligands in many biochemical processes¹⁰⁻¹⁴. Due to their capacity to form thermodynamically stable complexes with a variety of metal ions, they have found widespread use in food, pharmaceutical industries, and medicinal

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formulations. Recently, much attention has been focused on the synthesis of nanomaterials using metal citrates as precursors^(15–18). Also, modelling studies involving ternary complexes have gained^{19–21} popularity [Sasikumar et al., 2019; Rawda et al., 2019; Sujay Mahata et al., 2019] in the context of understanding the role of metal ions in physiological systems.

The significance of the present study is to identify the metal complex species formed under the given experimental conditions and to validate the associated models by statistical treatment of the data obtained relating to the ternary stability constants of aspartic and citric acids. Surfactant-water mixtures are used in these studies to mimic physiological fluid media. These data are useful in extraction metallurgy, nuclear energy, and medical, environmental, and industrial research²². In general, stability constant data are useful in understanding the role and activity of metal complexes in biological systems²³.

2. Experimental

Solutions of Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II} sulphates (0.1 mol L^{-1}) were prepared by dissolving AR-grade (Merck, India) salts in triple-distilled water. Aqueous solutions of Asp and Cit (Merck, India) were also prepared. To increase the solubility of Asp and Cit and suppress the hydrolysis of the metal salts, the mineral acid concentration in the above solutions was maintained at 0.05 mol L^{-1} . CTAB (Merck, India) was used as received. A 2.0 mol L^{-1} sodium chloride (Qualigens, India) solution was prepared to maintain the ionic strength in the titrand. A 0.2 mol L^{-1} hydrochloric acid (Merck, India) solution and a 0.5 mol L^{-1} sodium hydroxide (Merck, India) were prepared. To eliminate the errors associated with the determination of the concentrations, the data were subjected to an analysis of variance for one-way classification (ANOVA). The alkali concentration was determined using the Gran plot method²⁴.

2.1 Apparatus

All titrations were performed in media containing varying concentrations of CTAB while maintaining an ionic strength of 0.16 mol L^{-1} with sodium chloride at $30 \text{ }^\circ\text{C}$. A Systronics pH system (model 335) (readability 0.001) was used. The glass electrode was homogenised in a well-stirred CTAB–water mixture containing an inert electrolyte. A correction factor calculated from replicated acid-base titration data calculated by the SCPHD program^{25–27} was used to compensate for variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error, and dissolved carbon dioxide on the response of the glass electrode. A correction factor has been applied to the pH metre dial reading. Titrations of a strong acid with alkali were undertaken at regular intervals to check the complete equilibration of the electrode. The calomel electrode was refilled with a cationic CTAB–water mixture of composition equivalent to that of the titrant. In each titration, the titrant consisted of mineral acid (HCl) of approximately 1–5 mmol in a total volume of 50 cm^3 . Titrations of solutions containing different ratios of metal to primary (Asp) and secondary (Cit) ligands with different ratios (M:L:X = 1:2:2, 1:4:2, and 1:2:4) were carried out with a 0.5 mol L^{-1} sodium hydroxide solution.

2.2 Modelling strategy

The computer programme MINQUAD75²⁸ was used to generate the best-fit chemical models relating stoichiometric coefficients to the logarithm of stability constants ($\log \beta$). Some heuristics were followed in refining stability constants and validating models^{29–30}. The formation constants for acid–base equilibria and those for binary metal complexes of Asp and Cit were determined in the refinement of the mixed ligand stability constants using MINQUAD75.

3. Results and Discussion

3.1 Complex equilibria

In the presence of a mineral acid and an inert electrolyte, alkali-metric titrations of mixtures containing different mole ratios of Asp and Cit revealed that MLXH^2 , MLX_2H^5 , and MLX^3 species are formed for $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Zn}(\text{II})$. The parameters of the best-fit models and statistical parameters are given in Table I. The very low standard deviation in the $\log \beta$ values reflects the precision of these parameters. This indicates that the generated models appropriately fit the experimental data. The small values of U_{corr} indicate that the model is consistent with the experimental data³¹. The majority of the systems had kurtosis values around 3, and hence, the residuals form a meso-kurtic pattern.

For some systems, the kurtosis values are greater than 3 (leptokurtic pattern). The values of skewness between -0.02 and 1.98 indicate that the residuals form a part of a normal distribution, and hence the least squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic R -factor values, which indicate the need for the inclusion of additional species in the model. χ^2 is a special case of a γ -distribution that measures the probability of residuals forming a part of standard normal distribution.

Table 1. Parameters of best fit chemical models of ternary complexes of Asp and Cit in CTAB-water mixtures; Temperature = 30 °C, Ionic strength = 0.16 mol L⁻¹

%w/v	Log β (SD)			NP	U _{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
	MLX	MLXH	MLX ₂ H							
0.0	16.97(15)	21.73(25)	27.53(32)	137	8.29	-0.94	101.32	0.0014	5.02	2.00-
0.5	15.42(18)	20.87(24)	25.78(30)	125	7.15	-0.87	121.30	0.0832	4.98	2.00-
1.0	15.53(16)	20.73(20)	25.43(29)	129	9.36	-0.67	125.27	0.0741	5.39	2.00-
1.5	15.74(20)	20.59(28)	25.57(34)	137	9.38	-0.77	117.05	0.0863	4.74	2.00-
2.0	15.82(21)	20.46(30)	25.49(34)	145	0.67	-0.02	107.29	0.0772	6.09	2.00-
2.5	15.64(13)	20.57(22)	25.59(30)	142	3.44	-0.09	131.20	0.0911	4.44	2.00-
Ni(II)										
0.0	15.63(08)	21.92(19)	27.97(26)	158	9.80	0.85	54.32	0.0811	3.29	2.00-
0.5	13.98(12)	19.47(20)	25.79(32)	133	3.23	0.76	39.09	0.0774	4.71	2.00-
1.0	13.53(09)	19.43(16)	--	137	9.55	0.54	42.07	0.0655	5.29	2.00-
1.5	13.79(15)	19.35(22)	25.58(28)	149	9.60	0.34	39.77	0.0421	6.33	2.00-
2.0	13.64(06)	19.11(26)	25.47(26)	139	0.48	0.70	21.78	0.0625	7.42	2.00-
2.5	13.75(14)	19.23(25)	25.54(36)	140	0.52	0.81	25.04	0.0500	6.30	2.00-
Cu(II)										
0.0	16.74(11)	20.73(20)	25.98(26)	120	0.37	-1.88	72.44	0.0824	5.48	2.00-
0.5	15.76(16)	19.93(24)	24.96(35)	112	2.70	1.92	25.02	0.0732	4.43	2.00-
1.0	15.83(12)	19.75(22)	24.47(32)	114	2.72	-1.22	32.06	0.0844	3.97	2.00-
1.5	15.74(12)	19.54(24)	24.38(36)	117	0.29	-1.04	49.97	0.0759	4.08	2.00-
2.0	15.98(14)	19.64(25)	24.25(36)	121	9.71	1.90	51.04	0.0011	5.07	2.00-
2.5	15.75(15)	19.53(27)	24.94(38)	125	7.19	1.98	29.07	0.0024	4.37	2.00-
Zn(II)										
0.0	10.93(06)	16.94(14)	29.82(28)	148	2.58	0.22	101.23	0.0813	6.20	2.00-
0.5	8.49(08)	15.23(16)	27.02(36)	152	5.03	0.34	121.02	0.0715	7.02	2.00-
1.0	8.41(07)	15.34(15)	27.14(30)	138	8.81	0.49	117.05	0.0625	4.09	2.00-
1.5	8.70(10)	15.47(15)	27.08(25)	136	1.84	0.89	114.52	0.0741	3.99	2.00-
2.0	8.54(12)	15.97(19)	27.45(30)	130	0.94	0.74	110.59	0.0835	4.72	2.00-
2.5	8.96(10)	15.87(22)	27.93(34)	128	8.00	0.60	107.21	0.0661	4.87	2.00-

U_{corr} = U/(NP-m) × 10⁸, m= number of species; NP = number of experimental points

3.2 Effect of micelles on stability of complexes

The linear variation of the Asp and Cit complexes of Co(II), Ni(II), Cu(II), and Zn(II) in cationic CTAB-water mixtures with mole fraction (Fig. 1) indicates that electrostatic forces dominate the equilibrium process under the experimental conditions used. The stability of a complex depends on the charge of the Stern layer³², the polarity of the medium, and the electrostatic attraction or repulsive forces operating between the complex species and the micellar surface. This linear decrease³³ is caused by the medium's decreasing dielectric constant as surfactant content³⁴ increases. The charged species will be destabilised due to the decreased dielectric constant of the medium and increasing surfactant concentration. The stability of the neutral mixed complexes (Fig. 1) is not influenced by CTAB. CTAB acts as a denaturant for macromolecules by interacting with the peptide groups. Hence, the stability of the species decreases with increasing CTAB content, and the decreased stability of the ternary complexes is related to the ligation power of CTAB

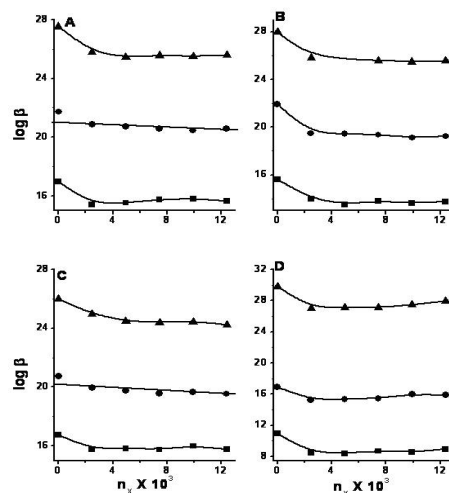


Fig. 1. Variation of stability constants of ternary complexes of Asp-Cit with mole fraction in CTAB water mixtures; (A) Co(II), (B) Ni(II), (C) Cu(II) and, (D) Zn(II) (■) log β_{MLX} , (●) log β_{MLXH} and (▲) log β_{MLX_2H}

3.3 Stability of the ternary complexes

The change in ternary complex stability as correlated to their binary analogues has been quantified³⁵⁻³⁶. One approach compares the variation in stability ($\Delta \log K$) for the two reactions ML with X and M (aq) with X were calculated solely on statistical grounds. Eqs. (1, 2) and can be rationalised using the previously reported cyclic system properties, which show that both ligands in the ternary complex have reciprocal influence to the same extent³⁷⁻³⁸. The value of $\Delta \log K$ should be negative as the ligand L or X coordinates more easily with 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, $\Delta \log K$ is positive for certain combinations of ligands.

$$\Delta \log K = \log K_{MLX}^{ML} - \log K_{MX}^M \quad (1)$$

$$= \log K_{MLX}^{MX} - \log K_{ML}^M \quad (2)$$

Both the electrostatic theory of binary complex formation and statistical arguments clearly indicate that, in the case of a given multivalent hydrated metal ion, more coordination positions are available for the first ligand than for the second one. As a result, the order of stability applies, which means that $\Delta \log K$ is negative, with a few exceptions³⁹. The statistical values of $\Delta \log K$ for bidentate L and X are -0.4 and -0.6 for octahedral and square planar complexes, respectively, whereas for distorted octahedral complexes, these values vary between -0.9 and -0.3 . Negative values of $\Delta \log K$ can be rationalised as the secondary ligand forming a more stable complex with the hydrated metal ion than with ML, which does not mean that the ternary complex is absent.

Table 2. $\log X$ and $\Delta \log K$ values from overall stability constants of Asp and Cit in surfactant (CTAB)-water mixtures

% w/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	8.10	10.07	-0.24	8.54	5.61	-3.02
0.5	5.17	9.51	-1.31	10.76	4.66	-2.79
1.0	9.03	8.01	-2.52	12.30	6.54	--
1.5	3.14	5.99	-0.65	15.66	3.34	-5.42
2.0	8.48	7.91	-3.05	13.79	7.11	-2.49
2.5	4.57	9.42	-3.51	15.40	8.80	-4.78
	Cu(II)			Zn(II)		
0.0	5.32	5.59	-0.64	7.93	11.75	-4.28
0.5	4.02	8.26	1.40	7.97	9.12	-4.18
1.0	5.21	4.34	-3.24	10.28	8.62	-0.25
1.5	5.13	8.06	-0.64	5.92	9.05	-5.34
2.0	4.86	9.90	1.86	10.25	10.69	-7.28
2.5	5.32	7.84	-0.27	9.02	7.37	-2.84

Calculations

$$\log X_{MLX} = 2 \log \beta_{MLX} - \log \beta_{ML_2} - \log \beta_{MX_2} \quad (4)$$

$$\log X_{MLXH} = 2 \log \beta_{MLXH} - \log \beta_{ML_2} - \log \beta_{MX_2} = 2 \log \beta_{MLXH} - \log \beta_{ML_2} - \log \beta_{MX_2H_2} \quad (5)$$

$$\log X_{MLX_2H} = 2 \log \beta_{MLX_2H} - \log \beta_{ML_2H_2} - \log \beta_{MX_4} = 2 \log \beta_{MLX_2H} - \log \beta_{ML_2} - \log \beta_{MX_4H_2} \quad (6)$$

$$\Delta \log K_{MLX_2H} = \log \beta_{MLX_2H} - \log \beta_{MLH} - \log \beta_{MX_2} \quad (7)$$

When the experimental value of $\Delta \log K$ exceeds the statistical value, it can be inferred that the ternary complex is formed by the interaction of ML with X or MX with L. Sigel postulated that the $\Delta \log K$ values of ternary complexes with bipyridyl as the primary ligand were positive for *O*-donors (malonic acid, pyrocatechol, *etc.*), negative for *N*-donors (ethylene diamine), and intermediate or minor negative values for amino acids with both N and O coordination sites⁴⁰⁻⁴¹. Cu(en) (iminodiacetic acid) had a very high negative value (-2.3), while Cu(o phen) (6,7-dihydroxynaphthalene-2-sulfonate) had a positive value (0.82). Some $\Delta \log K$ values and $\log X$ values are found to be greater than the theoretical values, which account for the extra stability of the ternary complexes.

The formulas for the calculation of $\Delta \log K$ values are given in Table 2. The $\Delta \log K$ values calculated for the binary and ternary complexes are given in Table 2. Co (II), Ni (II), Cu (II), and Zn (II) ions form octahedral complexes with Asp and Cit. For most of the systems in Table 2, the values of $\Delta \log K$ are found to be higher than those expected on statistical grounds (-0.4). The increased stability of the ternary complexes can be due to interactions outside the coordination sphere, such as the existence of hydrogen bonds between the coordinated ligands. In addition, a similar stabilising effect may

likewise be exerted by electrostatic interactions between non-coordinated, charged groups of the ligands, such as the NH_3^+ of Asp and the COO^- of Cit.

3.4 Effect of influential parameters on stability constants

Any variation in the parameters (the concentrations of the chemicals) affects the measurements of the equilibrium constants. Such parameters are called influential parameters. In order to rely on the best-fit a chemical model for critical evaluation and application under a variety of experimental conditions distinct accuracies of data acquisition, a study was undertaken by inserting pessimistic errors in the concentrations of alkali, acid, ligands, metal ions and correction factor. The results in Table 3, indicate that the errors in the concentrations of alkali and acid affect the stability constants to a greater extent than the errors associated with the ligands and the metal ion

Table 3. Effect of errors in influential parameters on the stability constants of ternary complexes of Ni(II) with Asp-Cit in 1.0 % w/v CTAB-water mixture

Ingredient	% Error	log β (SD)		
		MLX	MLXH	MLX ₂ H
	0	15.63(8)	21.92(19)	27.97(26)
Alkali	-5	Rejected	Rejected	Rejected
	-2	16.05(7)	21.03(19)	28.06(41)
	+2	15.92(6)	21.25(25)	Rejected
	+5	15.85(9)	Rejected	Rejected
Acid	-5	15.22(8)	Rejected	Rejected
	-2	15.42(7)	20.52(16)	27.35(38)
	+2	15.35(8)	Rejected	Rejected
	+5	Rejected	20.23(19)	27.23(39)
Asp	-5	15.77(10)	Rejected	28.18(47)
	-2	15.45(8)	21.38(25)	28.42(37)
	+2	15.24(5)	20.65(22)	27.94(34)
	+5	16.04(7)	20.93(20)	Rejected
Cit	-5	16.13(7)	Rejected	27.99(48)
	-2	15.85(9)	20.64(24)	27.42(32)
	+2	15.72(10)	21.08(21)	27.27(37)
	+5	15.59(9)	Rejected	Rejected
Metal	-5	Rejected	21.01(25)	Rejected
	-2	Rejected	20.85(24)	28.58(37)
	+2	16.25(6)	21.33(24)	28.15(28)
	+5	15.78(5)	Rejected	27.77(40)
log F	-5	16.07(7)	21.12(22)	28.09(42)
	-2	16.20(8)	20.74(20)	28.39(34)
	+2	15.65(6)	Rejected	Rejected

3.5 Distribution diagrams

L-aspartic acid (2.0-10.0) exists⁴² as LH_3^+ , LH_2 , LH^- and L^{2-} in the pH range of the current study, whereas citric acid (1.7-8.0) exists as XH_3 , XH_2^- , XH^{2-} and X^{3-} . These ligands interact with metal ions to form the MLXH^{2-} , $\text{MLX}_2\text{H}^{5-}$ and MLX^{3-} species. Some typical distribution diagrams of these species are given in **Fig. 2**. The lower concentrations of binary species compared to those of ternary species indicate the higher stability of ternary complexes.

The formation of MLXH^{2-} in the pH region 2.0-4.0 can be represented by the following equilibria.



LH_3^+ and XH^{2-} forms of aspartic and citric acids, respectively, interact with the metal ion to form MLXH^{2-} (Equilibrium 7). MLXH^{2-} can also be formed due to the interaction of the metal ion with LH_2 and XH_3 forms of ligands (Equilibrium 8).

The species $\text{MLX}_2\text{H}^{5-}$ is proposed to form through the following equilibria in the pH region 4.0-6.0.



MLX_2H^{5-} may be formed due to the interaction of the metal ion with LH_2 and XH^{2-} (Equilibrium 10). MLX_2H^{5-} can also be formed due to equilibria 11 and 12. For Co(II), Ni(II) and Cu(II) complexes the concentration of MLX_2H^{5-} species is increased as the concentration of $MLXH^{2-}$ is decreased (Equilibrium 11).

The species MLX^{3-} formed in the pH region 4.0-8.0 can be represented by the following equilibria.



The MLX^{3-} is formed by the interaction of LH^- and XH^{2-} (Equilibrium 13) or by the de protonation of $MLXH^{2-}$ (Equilibrium 14). In the case of Cu(II) (Fig. 2), MLX^{3-} species is increased as the concentration of $MLXH^{2-}$ species is decreased.

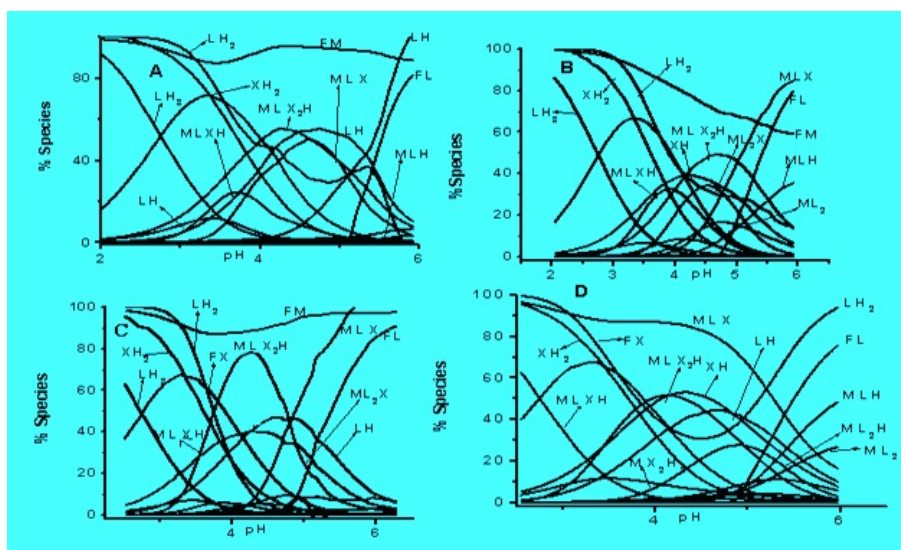


Fig. 2. Distribution diagrams of (Asp) Cu (Cit) in (A) 0.5 (B) 1.0 (C) 1.5 and, (D) 2.0 % w/v CTAB-water mixtures

The possible structures of these ternary complexes are proposed in **Fig. 3**.

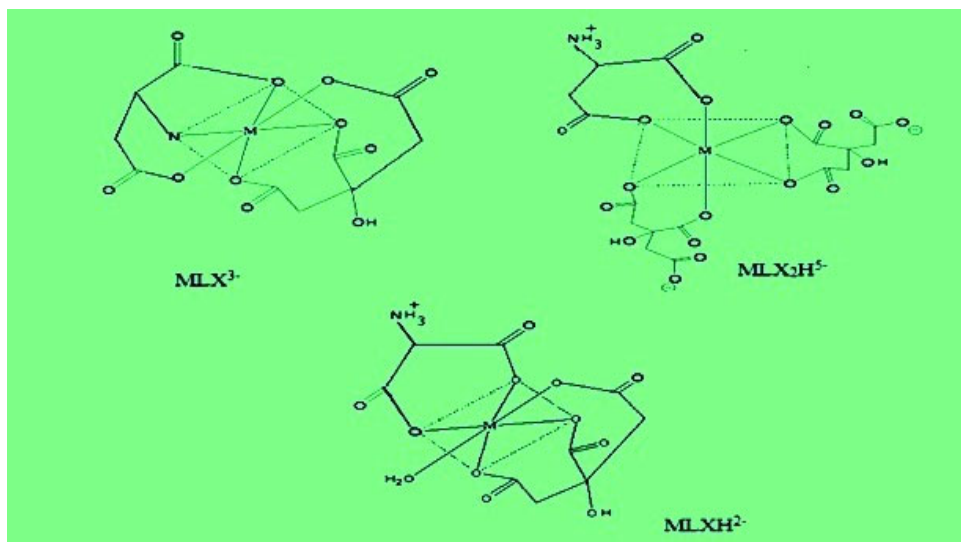


Fig. 3. Structures for ternary complexes of Co(II), Cu(II), Ni(II), and Zn(II) with L-aspartic acid and citric acid

4. Conclusions

The following conclusions derive from the studies of the speciation of ternary complexes of Co (II), Ni (II), Cu (II), and Zn (II) with Asp and Cit in CTAB-water media:

The detected species were $MLXH^{2-}$, MLX_2H^{5-} and MLX^{3-} . The trend of the variation in the $\log \beta$ values with changing dielectric constants along with the mole fraction of the surfactant is explained based on the electrostatic interactions of the side chains of the ligands. The change in 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 creation of hydrogen bonds between the coordinated ligands, charge neutralization, and the chelate effect. MLX_2H^{5-} species is increased as the concentration of $MLXH^{2-}$ is decreased. MLX^{3-} species is increased as the concentration of $MLXH^{2-}$ species is decreased. This analysis also gives an insight into the bioavailability and bioaccumulation of these metals. The ternary complexes are more responsible for metal transport because of their extra stability, whereas the binary complexes make the metal bioavailable due to their decreased stability.

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