Share Your Innovations through JACS Directory

Journal of Advanced Chemical Sciences

Visit Journal at http://www.jacsdirectory.com/jacs

ISSN: 2394-5311

Speciation of Ternary Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Citric and Succinic Acids in Micellar Medium

S.R. Pedada[1,*], N.R. Gollapalli[2]

[1]*Gayatri Vidya Parishad College of Engineering For Women, Visakhapatnam – 530 048, Andhra Pradesh, India.*
[2]*School of Chemistry, Andhra University, Visakhapatnam – 530 003, Andhra Pradesh, India.*

ARTICLE DETAILS

Article history:
Received 15 February 2017
Accepted 22 March 2017
Available online 26 June 2017

Keywords:
Chemical Speciation
Micelles
Ternary Complexes

ABSTRACT

The ternary complexes MLX, MLXH and MLX_2H have been identified in citric and succinic acid complexes of Co(II), Ni(II), Cu(II) and Zn(II) in (0.0-2.5% w/v) anionic, cationic and neutral micellar media at an ionic strength of 0.16 $moldm^{-3}$ ($NaNO_3$) and 303 K temperature. These species were selected based on statistical parameters and residual analysis. Extra stability of the ternary complexes compared to their binary complexes was believed to be due to electrostatic interactions of the side chains of ligands, charge neutralization, chelate effect, stacking interactions and hydrogen bonding. The species distribution, effects of micelles and dielectric constant of the medium have been discussed.

1. Introduction

Considerable attention has been paid in recent years on the study of the coordination of bio ligands with metal ions in biochemistry [1-4]. Citric acid (Cit) plays an important role in enzyme-catalyzed chemical reactions of central importance in all living cells that use oxygen as part of cellular respiration. In eukaryotes, the citric acid or tricarboxylic acid cycle occurs in the matrix of the mitochondrion. In aerobic organisms, the citric acid cycle as a possible substitute for poly phosphates added to solid detergents and these applications are based on formation of stable complexes with metal ions [5]. It has been regarded as being on a side is part of a metabolic pathway involved in the chemical conversion of carbohydrates, fats and proteins into carbon dioxide and water to generate a form of usable energy. Citrates have been traditionally used as masking agents in ion-exchange chromatography. Recently citrate has been considered path in the Krebs cycle [6]. Succinic acid (Suc) is involved in citric acid cycle and glyoxalate cycles, in which two-carbon acetyl units are converted into four-carbon succinate units for energy production and biosynthesis. Succinic acid is used [7, 8], in the manufacture of medicaments and nutritional supplements effective for treating of insulin resistance in mammals, preferably in non-insulin dependent diabetic humans.

From these facts it is obvious that the physiological activities of Cit and Suc with some essential metal ions are associated with the catabolic and anabolic processes. Hence, speciation studies of citric acid and succinic acid with Co(II), Ni(II), Cu(II) and Zn(II) ions in surfactant-water mixtures have been studied.

2. Experimental Methods

2.1 Materials and Methods

AR sample of sodium laurylsulphate (SLS, Qualigens, India), cetyltrimethylammonium bromide (CTAB, AR, Qualigens, India) and Triton X100 (TX 100, E-Merck, Germany) were dissolved in triple distilled water. Their purity was checked by determining the Critical Micellar Concentrations (CMC) conductometrically. CMC values of SLS, CTAB and TX 100 were $8.1x10^{-3}$, $9.2x10^{-4}$ and 0.54 vol%, respectively at 298 K. GR Grade (Merck, India) samples of citric acid, succinic acid, Co(II), Cu(II), Ni(II) and Zn(II) chlorides, nitric acid, sodium hydroxide and sodium nitrate were prepared by dissolving then in triple distilled water. All the metal solutions have been standardized by usual standard methods [9].

To increase the solubility of Cit and Suc and to suppress the hydrolysis of metal salts, nitric acid concentration was maintained at 0.05 $moldm^{-3}$. 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 strengths of alkali and acid were determined using the Gran plot method [10].

2.2 Apparatus

An ELICO (Model L1-120) pH meter (readability 0.01) was used to monitor the changes in H^+ concentration. The pH meter was calibrated as mentioned in our earlier papers [11] .The glass electrode was equilibrated in a well stirred water-surfactant solution containing the inert electrolyte ($NaNO_3$). The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of the correction factor [12].

2.3 Procedure

The 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 $moldm^{-3}$ with sodium nitrate at 303.0±0.1 K. The strong acid was titrated with alkali at regular intervals to check whether complete equilibration was achieved. Free acid titrations were carried every day prior to the mixed-ligand titrations to calculate the correction factor. In each of the titrations, the titrand consisted of approximately 1 mmol, of mineral acid, metal ion, ligands and the inert electrolyte 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 metal to primary ligand to secondary ligand were carried out with 0.4 $moldm^{-3}$ sodium hydroxide solution. Other experimental details are given elsewhere [13].

2.4 Modelling Strategy

The approximate stability constants of ternary complexes were calculated with the computer program SCPHD [14]. Different models containing varied number of ternary species were generated using the expert systems CEES [15]. The best fit chemical models for each ternary system were investigated by using MINIQUAD75.

*Corresponding Author
Email Address: raosrp@gmail.com (S.R. Pedada)

3. Results and Discussion

3.1 Complex Equilibria

A preliminary investigation of alkali metric titrations of mixtures containing different mole ratios of Cit and Suc in the presence of mineral acid and inert electrolyte inferred that no condensed species are formed [16]. The binary metal complexes were fixed in the refinement of ternary complexes in testing various chemical models using computer program MINIQUAD75 [17]. The best fit models were chosen as that with low standard deviation in the formation constants and minimum U_{corr}(sum of 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 χ^2, R-factor, skewness and kurtosis given in Tables 1-3. The species detected for Co(II), Ni (II),Cu (II)and Zn (II) ions are MLX^{3-}, $MLXH^{2-}$ and MLX_2H^{4-}, where L is the primary ligand (Cit) and X is the secondary ligand (Suc).

A very low standard deviation in 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 most of the residuals are leptokurtic and a few form mesokurtic patterns. The values of skewness recorded in the tables are between -2.98 to 1.70. These data evince 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)-Cit – Suc complexes in CTAB-water mixtures

% w/v CTAB	Logβ(SD) MLX	MLXH	MLX_2H	NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Co(II)										
0.0	10.74(8)	16.85(20)	22.97(32)	197	9.63	-1.27	54.02	0.0821	5.84	1.75-7.50
0.5	10.92(9)	16.98(18)	23.02(31)	195	8.16	-2.20	51.05	0.0732	4.48	1.75-7.50
1.0	11.04(7)	17.12(22)	--	189	7.41	-1.74	49.09	0.0844	3.72	1.75-8.00
1.5	11.25(7)	17.26(18)	23.56(32)	183	2.72	-1.99	46.97	0.0755	6.08	1.75-7.00
2.0	11.63(8)	17.54(17)	23.78(30)	180	5.08	-1.84	37.34	0.0842	7.84	1.75-7.00
2.5	11.91(9)	17.81(20)	24.02(31)	178	1.37	-1.77	29.97	0.0731	6.93	1.75-7.00
Ni(II)										
0.0	14.73(9)	18.59(18)	23.58(25)	174	1.38	0.21	66.09	0.0972	6.01	2.00-6.70
0.5	14.96(7)	19.05(15)	23.97(22)	189	2.80	0.39	61.79	0.0700	5.04	2.007.70
1.0	15.26(8)	19.45(18)	24.15(26)	187	3.60	0.09	57.39	0.0625	3.07	2.00-7.70
1.5	15.89(8)	19.24(14)	--	181	7.80	0.74	49.07	0.0071	1.22	2.00-7.70
2.0	16.08(5)	19.78(16)	--	179	2.55	0.33	39.09	0.0082	2.97	2.00-7.70
2.5	16.45(6)	20.23(15)	24.79(25)	171	0.48	0.21	37.25	0.0097	3.45	2.00-6.70
Cu (II)										
0.0	12.86(10)	15.82(18)	20.74(28)	189	3.37	0.44	22.32	0.0815	8.21	1.75-8.00
0.5	12.95(8)	16.04(19)	21.09(32)	184	3.92	0.97	25.09	0.0717	6.31	1.75-8.00
1.0	13.16(8)	16.28(15)	--	179	0.48	0.07	31.72	0.0741	5.49	1.75-8.00
1.5	13.46(7)	16.49(18)	21.56(26)	177	5.78	0.37	35.94	0.0815	3.52	1.75-8.00
2.0	13.25(9)	16.87(15)	21.82(24)	170	3.41	0.50	41.04	0.0710	4.72	1.75-7.00
2.5	13.87(7)	17.17(17)	22.09(25)	175	7.50	0.79	48.09	0.0011	5.92	1.75-8.00
Zn(II)										
0.0	13.52(5)	17.82(10)	25.96(30)	147	0.41	-1.14	51.04	0.0824	5.02	1.75-7.50
0.5	13.89(7)	17.94(12)	26.04(32)	148	2.21	-1.94	59.08	0.0721	4.29	1.75-8.00
1.0	14.02(6)	18.01(15)	-	142	3.38	-1.33	63.71	0.0844	3.92	1.75-7.00
1.5	14.25(5)	18.35(16)	-	149	0.82	-1.74	68.78	0.0753	4.87	1.75-8.00
2.0	14.54(6)	18.69(15)	26.69(36)	138	8.81	-1.97	49.81	0.0774	5.92	1.75-7.70
2.5	15.03(5)	19.12(18)	27.09(38)	129	4.42	-1.88	74.85	0.0832	4.91	1.75-6.50

Table 2 Parameters of best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)-Cit – Suc complexesinTX100-water mixtures

% v/v TX100	Logβ (SD) MLX	MLXH	MLX_2H	NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Co(II)										
0.0	10.74(8)	16.85(20)	22.97(32)	197	9.63	-1.27	54.02	0.0821	5.84	1.75-7.50
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	1.75-8.0
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	1.75-7.5
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

Table 3 Parameters of best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)-Cit – Suc complexes in SLS-water mixtures

% w/v SLS	Logβ (SD) MLX	MLXH	MLX_2H	NP	U_{corr}	Skew-ness	χ^2	R-Factor	Kurtosis	pH-Range
Co(II)										
0.0	10.74(8)	16.85(20)	22.97(32)	197	9.63	-1.27	54.02	0.0821	5.84	1.75-7.5
0.5	9.21(5)	15.86(17)	21.56(32)	98	6.73	0.21	38.38	0.0322	2.45	2.5-6.5
1.0	9.45(4)	15.42(18)	21.76(28)	95	4.02	0.35	34.32	0.0343	3.34	2.5-6.5
1.5	9.65(8)	15.63(17)	21.84(27)	96	4.19	0.44	45.85	0.0415	2.21	2.5-6.5
2.0	9.82(7)	15.74(15)	22.02(25)	94	4.94	0.84	39.81	0.0931	3.45	2.5-6.5
2.5	10.74(8)	15.95(14)	22.15(32)	97	1.06	0.74	49.84	0.0757	2.75	2.5-6.5
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	13.26(9)	17.23(14)	22.56(28)	105	5.75	-1.35	40.82	0.0721	3.82	2.5-6.5
1.0	13.58(7)	17.46(15)	--	107	7.05	-1.48	48.82	0.0831	4.42	2.5-6.5
1.5	13.65(6)	17.65(18)	--	100	9.80	-1.37	37.32	0.0621	3.37	2.5-6.5
2.0	13.819(7)	18.02(17)	22.87(23)	103	3.19	-1.22	41.02	0.0321	3.20	2.5-6.5
2.5	14.04(7)	18.19(14)	23.05(25)	102	1.50	-1.94	37.09	0.0441	3.22	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	1.75-8.0
0.5	10.86(6)	13.98(17)	18.56(35)	100	3.81	-1.25	50.14	0.0025	4.42	2.5-6.5
1.0	10.95(7)	14.02(15)	18.92(30)	107	2.59	-1.29	39.15	0.0056	5.52	2.5-6.5
1.5	11.26(8)	14.26(17)	19.25(34)	102	0.80	-1.27	29.15	0.0026	4.32	2.5-6.5
2.0	11.58(6)	14.54(15)	19.43(32)	105	1.96	-1.39	34.12	0.0543	4.22	2.5-6.5
2.5	11.74(7)	14.83(17)	19.81(35)	101	7.16	-1.49	38.15	0.0581	3.39	2.5-6.5
Zn(II)										
0.0	13.52(5)	17.82(10)	25.96(30)	147	0.41	-1.14	51.04	0.0824	5.02	1.75-7.5
0.5	11.89(9)	15.92(15)	23.98(35)	90	9.88	1.22	39.82	0.0418	3.42	2.5-6.0
1.0	11.99(7)	16.02(18)	--	97	7.65	1.34	45.92	0.0317	4.72	2.5-6.5
1.5	12.31(7)	16.23(16)	24.31(34)	92	2.58	1.09	42.22	0.0418	3.72	2.5-6.5
2.0	12.52(8)	16.54(16)	24.58(32)	99	3.95	1.24	54.54	0.0319	2.82	2.5-6.5
2.5	12.75(8)	16.78(15)	24.85(35)	101	9.59	1.70	64.32	0.0013	3.34	2.5-6.5

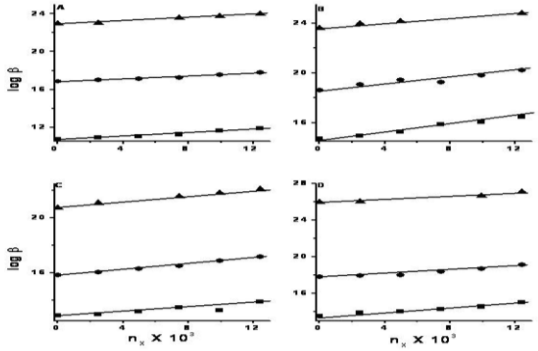

Fig. 1 Variation of stability constant values of complexes with mole fraction of CTAB (A) Co(II), (B) Ni(II), (C) Cu(II) and (D) Zn(II) (■) $\log\beta_{MLX}$, (●) $\log\beta_{MLXH}$, (▲) $\log\beta_{MLX2H}$

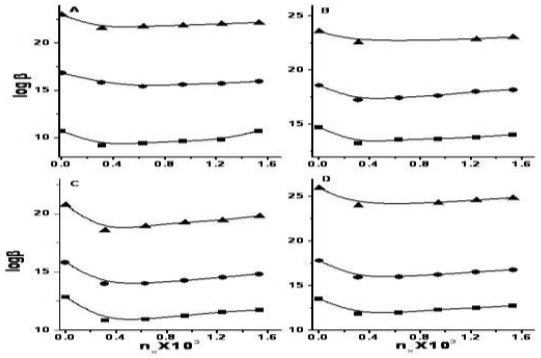

Fig. 2 Variation of stability constant values of complexes with mole fraction of SLS (A) Co(II), (B) Ni(II), (C) Cu(II) and (D) Zn(II) (■) $\log\beta_{MLX}$, (●) $\log\beta_{MLXH}$, (▲) $\log\beta_{MLX2H}$

3.2 Effect of Micelles

The variations in the magnitudes of the formation constants of ternary complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Cit and Suc in different compositions of the surfactants (CTAB, SLS, TX 100) are shown in Figs. 1-3. In the case of SLS and TX 100 stabilities of the complexes decrease linearly with increase in surfactant concentration. This is due to the destabilization [18], of these negatively charged species MLX^{3-}, $MLXH^{2-}$ and MLX_2H^{4-} with increasing surfactant content. The destabilization is due to the decreased dielectric constant of the medium and negatively charged polar heads of SLS. The observed linear increase in the stabilities of the complexes with increase in CTAB concentration is due to the stabilization of these negatively charged species. This trend is Similar to their corresponding binary complexes [19, 20].

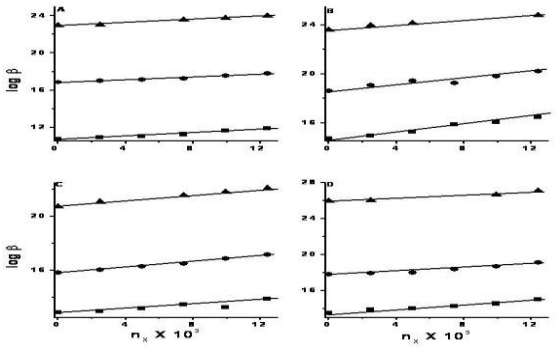

Fig. 3 Variation of stability constant values of complexes with mole fraction of TX 100 (A)Co(II),(B)Ni(II), (C) Cu(II) and (D) Zn(II) (■) $\log\beta_{MLX}$, (●) $\log\beta_{MLXH}$, (▲) $\log\beta_{MLX2H}$

3.3 Extra Stability of Ternary Complexes

The change in the stability of the ternary complexes as compared to their binary analogues was quantified [21-24], based on the disproportionation constant (log X) given in Eq. (1), corresponding to the equilibrium given in Eq. (2),

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

$$ML_2 + MX_2 \rightleftharpoons 2\,MLX \quad (2)$$

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 [25], to be 0.6. A value greater than this accounts for the extra stability of MLX. Another approach [26], to quantify the stability of ternary complexes was based on the difference in stability (Δ logK) 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 Eq. (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 $K_{ML}^{M} > K_{MLX}^{ML}$ applies. This suggests that Δ logK should be negative, although several exceptions [27], have been found. The stastical values of Δ logK 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 Δ logK 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 logK 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 logK values of ternary complexes containing bipyridyl as the primary ligand are positive [28], for O-donors (malonic acid, pyrocatechol etc.), negative [29], for N-donors (ethylene diamine) and intermediate or negative [30], 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.

The logX and Δ logK values calculated from binary and ternary complexes are included in Tables 4-6. These values could not be calculated for some systems due to the absence of relevant binary species. In the present study, the log X values range from 33.17 to 0.31 surfactant some of which are higher than those expected on statistical basis (0.6). These higher values account for the extra stability of the ternary complexes. The values of Δ logK are also found to be higher than -0.4. The reason[31, 32], 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.

Table 4 Variation of stability of ternary complexes of Cit and Suc in CTAB-water mixtures

% w/v CTAB	log X_{MLX}	log X_{MLXH}	log X_{MLX2H}	Δ log K $_{MLX2H}$	log X_{MLX}	log X_{MLXH}	log X_{MLX2H}	Δ log K $_{MLX2H}$
	Co(II)				**Ni(II)**			
0.0	7.17	12.09	21.63	-6.67	10.91	8.62	19.73	-4.02
0.5	8.17	9.58	24.62	2.31	13.76	8.66	21.89	-5.79
1.0	9.03	9.01	-	-	14.30	6.54	22.24	5.87
1.5	9.14	8.99	24.52	-3.65	15.66	6.34	-	-
2.0	9.48	9.91	24.83	2.56	15.79	7.11	-	-
2.5	9.57	10.47	24.68	1.25	17.43	9.80	24.12	-7.19
	Cu(II)				**Zn(II)**			
0.0	15.10	10.03	14.43	1.85	12.45	10.03	28.38	-
0.5	10.39	8.78	17.01	-4..32	15.62	8.78	30.80	-
1.0	11.06	11.52	-	-	15.87	11.52	-	-
1.5	12.06	8.23	18.75	-2.87	16.70	8.23	-	-
2.0	11.41	9.55	18.78	-4.20	17.90	9.55	33.17	-
2.5	12.57	9.25	19.29	1.23	18.17	9.25	25.43	-

Table 5 Variation of stability of ternary complexes of Cit and Suc in TX 100- water mixtures

% v/v TX100	log X_{MLX}	log X_{MLXH}	log X_{MLX2H}	Δ log K $_{MLX2H}$	log X_{MLX}	log X_{MLXH}	log X_{MLX2H}	Δ log K $_{MLX2H}$
	Co(II)				**Ni(II)**			
0.0	7.69	8.20	20.24	4.52	11.12	20.56	2.24	-2.53
0.5	6.40	7.42	-	-5.23	8.82	18.52	3.52	-4.52
1.0	5.79	8.54	19.70	-	9.55	16.48	4.29	-
1.5	7.71	7.69	20.25	-4.26	-	19.77	2.57	-
2.0	5.70	7.06	20.60	-3.24	9.49	-	2.82	3.22
2.5	5.70	7.06	20.60	2.15	9.49	19.17	2.12	4.02
	Cu(II)				**Zn(II)**			
0.0	9.11	7.51	16.51	1.53	12.33	28.71	-	3.58
0.5	10.37	6.29	14.59	-2.58	10.15	25.34	-	-4.28
1.0	8.67	5.94	15.46	-	10.04	23.42	-	-
1.5	8.61	5.09	16.11	2.58	10.01	26.48	-	-
2.0	7.63	5.16	15.02	0.97	9.33	25.33	-	3.56
2.5	7.69	8.20	20.24	-3.48	11.12	20.56	2.24	0.58

Table 6 Variation of stability of ternary complexes of Cit and Suc in SLS-water mixtures

% w/v SLS	log X_{MLX}	log X_{MLXH}	log X_{MLX2H}	Δ log K_{MLX2H}	log X_{MLX}	log X_{MLXH}	log X_{MLX2H}	Δ log K_{MLX2H}
Co(II)					**Ni(II)**			
0.0	7.27	9.59	21.63	-0.64	9.90	9.75	2.03	2.23
0.5	3.02	8.26	18.93	0.40	7.97	9.46	0.31	-3.84
1.0	4.24	7.34	20.06	0.62	9.28	8.62	1.01	-
1.5	5.17	8.06	20.78	0.64	9.92	9.03	1.56	-
2.0	5.86	8.99	21.51	-0.86	10.25	10.69	2.79	-6.53
2.5	8.32	9.84	22.34	0.28	11.00	11.37	3.99	2.57
Cu(II)					**Zn(II)**			
0.0	7.11	6.6	16.44	1.22	12.45	12.1	28.38	-1.28
0.5	5.92	4.75	11.18	-2.45	9.99	9.69	25.43	3.57
1.0	5.80	5.21	11.95	2.57	9.21	9.03	25.93	-
1.5	6.29	4.94	12.49	-3.36	10.44	8.86	26.95	-1.94
2.0	8.39	5.99	13.45	4.99	10.48	10.42	-	-2.15
2.5	8.32	7.10	14.26	5.96	11.26	10.77	27.84	1.96

Calculations:-

$\Delta \log X_{MLX} = 2\log\beta_{MLX} - \log\beta_{ML2} - \log\beta_{MX2}$

$\Delta \log X_{MLXH} = 2\log\beta_{MLXH} - \log\beta_{ML2H2} - \log\beta_{MX2}$

$\Delta \log X_{MLX2H} = 2\log\beta_{MLX2H} - \log\beta_{ML2} - \log\beta_{MX2}$

$\Delta \log K_{MLX2H} = 2\log\beta_{MLX2H} - \log\beta_{MLH} - \log\beta_{MX2}$

3.4 Distribution Diagrams

Since the present study is confined to a pH range of 1.7-8.0, citric acid exists [33] , as LH_3, LH_2^-, LH^{2-} and L^{3-} while succinic acid exists as XH_2, XH^-, X^{2-} (2.5-6.5). A perusal of the distribution diagrams (Fig. 4) reveals that at very low pH the concentration of mixed ligand complexes are less than those of protonated ligands. As the pH is increased the concentrations of the ternary species are increased. The protonated ternary species, MLX^{3-}, $MLXH^{2-}$ and MLX_2H^{4-} (Fig. 5) are distributed at higher pH. The smaller concentrations of binary species than those of ternary species indicate the extra stability of the ternary complexes. The formation of the complex species can be represented by the following equilibria. The species MLX^{3-} formed in the pH region 4.0-8.0 can be represented by the following equilibria:

$M(II) + LH_3 + XH_2 \leftrightarrow MLX^{3-} + 5H^+$

$M(II) + LH_2 + XH^- \leftrightarrow MLX^{3-} + 3H^+$

$M(II) + LH + X^{2-} \leftrightarrow MLX^{3-} + H^+$

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

$M(II) + LH_3 + XH_2 \leftrightarrow MLXH^{2-} + 4H^+$

$M(II) + LH_2 + XH^- \leftrightarrow MLXH^{2-} + 2H^+$

$M(II) + LH + X^{2-} \leftrightarrow MLXH^{2-}$

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

$M(II) + LH_3 + 2XH_2 \leftrightarrow MLX_2H^{4-} + 6H^+$

$M(II) + LH_2 + 2XH^- \leftrightarrow MLX_2H^{4-} + 3H$

$M(II) + LH + 2X^{2-} \leftrightarrow MLX_2H^{4-}$

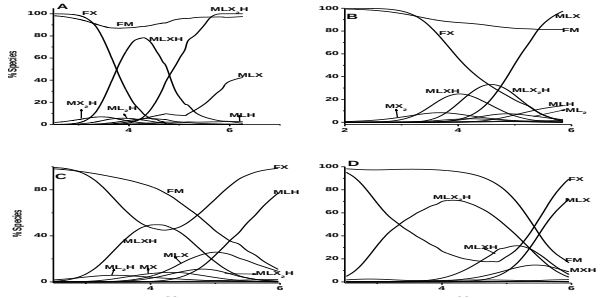

Fig. 4 Distribution diagrams of ternary complexes of Cit and Suc in 1.5% w/v CTAB water mixture (A) Co(II), (B) Ni(II), (C) Cu(II) and (D) Zn(II)

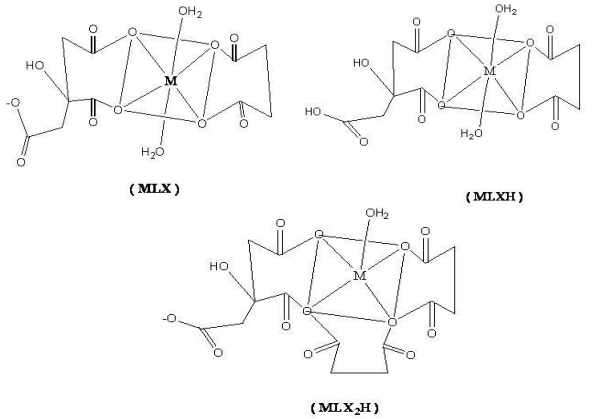

Fig. 5 Plausible structures of ternary complexes of citric acid (L) and succinic acid (X) with Co(II), Ni(II), Cu(II) and Zn(II)

4. Conclusion

The following conclusions result from the modeling studies: The models for the ternary species contained MLX^{3-}, $MLXH^{2-}$, MLX_2H^{4-} where L is citric acid and X is succinic 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 linear variation of log β value of complexes with mole fraction of the surfactant indicates that electrostatic forces dominate the non-electrostatic forces. The decreased stability of the charged binary species compared to the corresponding ternary complexes observed in the present study is useful to understand the various ternary metal complexes formed in the biological systems.

References

[1] K.V. Lavanya, V.M. Rao, G.N. Rao, Speciation of ternary complexes of Ca(II) and Mg(II) with L-arginine and L-histidine in micellar media, Oxidat. Commun. 31 (2008) 398-409.

[2] G.N. Rao, K.G. Sudarsan, Effect of micelles on speciation of ternary complexes of Ni(II) with L-arginine and L-histidine, Chem. Speciat. Bioavail. 18 (2006) 71-76.

[3] S.B. Ronald, G.N. Rao, Speciation of ternary complexes of calcium(II) and magnesium(II) of L-glutamine and succinic acid in acetonitrile-water mixtures, Proc. Nat. Acad . Sci. Ind. 72 (2002) 301-313.

[4] B.B.V. Sailaja, T. Kebede, G.N. Rao, M.S. Prasada Rao, Effect of micelles on speciation of ternary complexes of uranyl(VI) with oxalic and malonic acids, Proc. Nat. Acad. Sci. Ind. 74A (2004) 399-412.

[5] C. Qiyuan. X. Zhang, W. Chien-hsien, G. Loren, Calorimetric investigation of complex formation in the aqueous Fe(III)-citrate system, Can. J. Chem. 71 (1993) 937-941.

[6] M.F. Utter, H. Rudney, M. Cook, The enzymatic formation of citric acid studied with c^{14} –labeled oxalacetate, J. Biol. Chem. 185 (1950) 689-699.

[7] J.T. Beatty, H. Gest, Biosynthetic and bioenergetic functions of citric acid cycle reactions in *Rhodopseudomonas capsulate*, J. Bacteriol. 148 (1981) 584-593.

[8] H.E. Melendez, T.G. Waddell, M. Cascente, The puzzle of the Krebs citric acid cycle assembling the pieces of chemically feasible reactions and opportunism in the design of metabolic pathways during evolution, J. Mol. Evol. 43 (1996) 293-303.

[9] V.M. Rao, M.P. Latha, T.S. Rao, G.N. Rao, Mixed ligand complexes of toxic metal ions with L-glutamic acid and l-methionine in urea-water mixtures, Chem. Speciat. Bioavailab. 18 (2006) 143-151.

[10] G .Gran, Equivalence volumes in potentiometric titrations, Anal. Chim. Acta. 206 (1988) 111-123.

[11] J.S. Sukumar, G.N. Rao, K.V. Ramana, M.S. Rao, Effect of denaturants on the speciation of amino acid complexes-computer augmented modeling studies VI: Protonation equilibria of L-ornithine and L-glutamic acid in anionic micellar media, Ind. J. Chem. 35 (1996) 121-126.

[12] M.P. Latha, V.M. Rao, T.S. Rao, G.N. Rao, Chemical speciation of Pb(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) binary complexes of L-methionine in 1,2 propanediol-water mixtures, Bull. Chem. Soc. Ethiop. 21 (2007) 363-372.

[13] M. Padmaja, M.S. Babu, G.N. Rao, R.S. Rao, K.V. Ramana, Effect of urea on the speciation of 1,10-phenanthroline complexes of toxic metal ions computer augmented modeling studies, Polyhedron 9 (1990) 2497-2506.

[14] G.N. Rao, Complex equilibria of some biologically important metal ions in aqua-organic media Ph.D. Thesis, Andhra University, Visakhapatnam, India, 1989.

[15] A. Braibanti, R.S. Rao, A.R. Babu, G.N. Rao, CEES: Expert system for complex equilibria I MODGENML: Model generation for metal-ligand equilibria in solution phase, Ann. Chim. Italy 85 (1995) 17-29.

[16] G.N. Rao, S.B. Ronald, Effect of solvent on protonation equilibria of L-glutamine and succinic acids, J. Ind. Chem. Soc. 79 (2002) 416-419.

[17] P. Gans, A. Sabatini, A. Vacca, An improved computer program for the computation of formation constants from potentiometric data, Inorg. Chim. Acta. 18 (1976) 237-239.

[18] V.U.S. Sagar, G. Himabindu, K.G. Sudarsan, G.N. Rao, Speciation studies of binary complexes of nickel(II) with L-arginine and L-histidine in micellar medium, J. Ind. Chem. Soc. 82 (2005) 598-601.

[19] P.S. Rao, B. Srikanth, V.S. Rao, C.K. Sastry, G.N. Rao, Micellar effect on metal-ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with citric acid, Bull .Chem. Soc. Ethiop. 23(3) (2009) 347-358.

[20] B. Srikanth, P.S. Rao, V.S. Rao, C.K. Sastry, G.N. Rao, Effect of micelles on the chemical speciation of binary complexes of Co(II), Ni(II), Cu(II) and Zn(II) with succinic acid, J. Serb. Chem. Soc. 74(7) (2000) 745-754.

[21] R. Griesser, H. Sigel, Ternare komplexe in Losung II, Einfluss von 2,20-bipyridyl auf die stabilitat des Cu_2þ-Glycin-1:1-complexes, Helv. Chim. Acta. 50 (1967) 1842-1845.

[22] R. Greisser, H. Sigel, Ternary complexes in solution XI: complex formation between the cobalt(II)-, nickel(II)-,copper(II)- and zinc (II)-2, 20-bipyridyl 1 : 1 complexes and ethylenediamine, glycinate or pyrocatecholate, Inorg. Chem. 10 (1971) 2229-2232.

[23] R. Greisser, H. Sigel, Ternary complexes in solution XVI: Influence of the size of the chelate rings on the stability of mixed ligand copper(II) complexes containing aliphatic ligands, Inorg. Chem. 13 (1974) 462-465.

[24] H. Sigel, P.R. Huber, R. Greisser, B. Prijs, Ternary complexes in solution XV mixed-ligand copper(II) complexes with 2,2 0-bipyridyl or 1,10-phenanthroline and pyrocatecholate or derivatives thereof, Inorg. Chem. 12 (1974) 1198-1200.

[25] S. Kida, Investigation on mixed complexes I Spectrophotometric study of mixed complexes formed by cupric ion and bidentate ligands, Bull. Chem. Soc. Japan 29 (1956) 805-811.

[26] R.B. Martin, R. Prados, Some factors influencing mixed complex formation, J. Inorg. Nucl. Chem. 36 (1974) 1665-1670.

[27] H. Sigel, Ternary Cu^{2+} complexes stability structure and reactivity, Angew. Chem. Int. Ed. Engl. 14 (1975) 394-402.

[28] R. Greisser, H. Sigel, Ternary complexes in solution VIII: complex formation between the copper(II) -2, 20-bipyridyl 1:1 complex and ligands containing oxygen and (or) nitrogen donor atoms, Inorg. Chem. 9 (1970) 1238-1243.

[29] H. Sigel, Ternary complexes in solution, Chim. 21 (1967) 489-500.

[30] R. Griesser, H. Sigel, Ternare komplexe in Losung II Einfluss von 2,2 0-bipyridyl auf die stabilitat des Cu_2þ-Glycin-1:1-complexes, Helv. Chim. Acta. 50 (1967) 1842-1845.

[31] T. Sakurai, O. Yamauchi, A. Nakahara, Mixed ligand copper(II) complexes of a-amino acids with ligand-ligand interactions, Bull. Chem. Soc. Japan 49 (1976) 169-173.

[32] T. Sakurai, O. Yamauchi, A. Nakahara, Stereoselectivity in mixed ligand copper(II) complexes with electrostatic ligand-ligand interactions, Applications to optical resolution of a-amino acids with a charged side chain, Bull. Chem. Soc. Japan 50 (1977) 1776-1779.

[33] P.S. Rao, B. Srikanth, V.S. Rao, C.K. Sastry, G.N. Rao, Protonation equilibria of L-aspartic acid, citric acid and succinic acid in anionic micellar media, E-J. Chem. 6 (2009) 561-568.

Cite this Article as: S.R. Pedada, N.R. Gollapalli, Speciation of ternary complexes of Co(II), Ni(II), Cu(II) and Zn(II) with citric and succinic acids in micellar medium, J. Adv. Chem. Sci. 3(2) (2017) 457–461.