EFFECT OF SURFACTANTS ON BINARY COMPLEXES OF L-ASPARTIC ACID WITH FEW BIVALENT METAL IONS

G. NAGESWARA RAO,
Chemistry Research Laboratories, Govt. College (A), Rajahmundry-533105, India.
E-mail: gollapallinr@yahoo.com

V. SAMBASIVA RAO,
Inorganic and Analytical Chemistry Research Laboratories, School of Chemistry, Andhra University, Visakhapatnam-530003, India

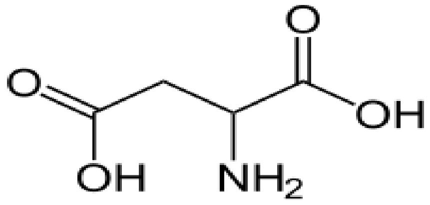
ABSTRACT

Chemical Speciation of Binary Complexes of L-Aspartic acid with Co(II), Ni(II), Cu(II) and Zn(II) was investigated pH metrically in varying concentrations (0-2.5% w/v) of the neutral surfactant (TX-100)–water mixtures at an ionic strength of 0.16 mole dm^{-3} *(*$NaNO_3$*) and temperature 303 K. The predominant complexes detected for these metal ions are ML, MLH,* ML_2H, ML_2H_2 *and* ML_2*. The trend in the variation of stability constants of the complexes with changing dielectric constant as well as composition of the medium was explained on the basis of electrostatic and non-electrostatic forces.*

Keywords: *Binary complexes, chemical speciation, stability constants, L-Aspartic acid, Triton X-100, MINIQUAD75*

INTRODUCTION

Aspartic acid (Asp) has the molecular formula, $C_4H_7NO_4$ and its structure is



Aspartic acid is a non-essential amino acid in mammals, being produced from oxaloacetate by transamination. It plays a critical role in Krebs cycle[1]. Speciation studies of essential metal ion complexes of Asp are useful[2-5] for understanding the role played by active site cavities in biological molecules and the binding behavior of protein residues with metal ions. Cobalt in the form of vitamin B_{12} is essential for animals. Vitamin B_{12} is synthesized by micro-organisms only, in particular anaerobic bacteria. Nickel is associated with several enzymes[6-8] and any variation in its concentration leads to metabolic disorders.[9] Copper is largely rejected from cells but outside the cell, it is essential for the metabolism of many hormones and connective tissue. The biological functions include electron transfer, dioxygen transport, oxygenation, oxidation, reduction and disproportionation.[10, 11] Zinc is the second most abundant essential trace metal after iron and it plays vital roles in biological systems.[12-15]

Neutral surfactant (Triton X-100, TX-100) is used as detergent, cleaning agent, emulsifier, in food, pharmaceuticals and cosmetics. Hence, speciation studies of Asp with Co(II), Ni(II), Cu(II) and Zn(II) in TX-100-water mixtures are reported in this paper.

EXPERIMENTAL

0.050 mol dm^{-3} solution of Aspartic acid (E-Merck, Germany) was prepared in triple distilled water. 0.050 mol dm^{-3}Aqueous solutions of Co(II), Ni(II), Cu(II) and Zn(II) chlorides were prepared in 0.050 mol dm^{-3} HCl, to suppress the hydrolysis of the metal salts. Triton X-100 (E-Merck, Germany) was used as supplied and the purity was checked by determined from the critical micellar concentration (CMC) conduct metrically. The CMC value of TX-100 was 0.54 vol. % at 303 K. Sodium chloride was used to maintain the ionic strength in the titrand. The strengths of alkali and mineral acid were determined using the Gran plot method.[16] the data were subjected to analysis of variance of one-way classification (ANOVA) to assess the errors that might have crept into the determination of the concentrations.

APPARATUS

The titrimetric data were obtained using a calibrated ELICO (Model LI-120) pH-meter (readability 0.01), which can monitor changes in the H_3O^+ concentration. The glass electrode was equilibrated in a well-stirred TX-100 solution containing an inert electrolyte. All the titrations were performed at 303.0±0.1 K in a medium containing varying concentrations of the surfactant (0.5–2.5 % v/v) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium chloride. The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved CO_2 on the response of glass electrode were taken into account in the form of a correction factor.[17]

PROCEDURE

For the determination of the stability constants of the binary metal–ligand species, initially titrations of a strong acid with alkali were performed at regular intervals to check whether complete equilibration had been achieved. Then the calomel electrode was refilled with micellar solution (only TX100, since it forms a precipitate with KCl) of equivalent composition to that of the titrand. In each of the titrations, the titrand consisted of approximately 1 mmol mineral acid in a total volume of 50 cm^3. Titrations with different ratios (1:2.5, 1:3.5, 1:5) of metal to ligand were performed with 0.40 mol dm^{-3} sodium hydroxide. Other experimental details are given elsewhere.[18]

MODELING STRATEGY

The computer program SCPHD[19] was used to calculate the correction factor. The binary stability constants were calculated from the pH metric titration data using the computer program MINIQUAD75[20] which exploits the advantage of a constrained least-squares method in the initial refinement and reliable convergence of the Marquardt algorithm. During the refinement of the binary systems, the correction factor and the protonation constants of Asp were fixed. The variation of stability constants with the mole fraction of TX-100 was analyzed on electrostatic grounds based on solute-solute and solute-solvent interactions.

RESULTS AND DISCUSSION

The results of the best-fit models that contain the stoichiometry of the complex species and their overall formation constants along with some of the important statistical parameters are given in Table 1. The very low standard deviation in the log values indicates the precision of these parameters. The small values of U_{corr} (sum of squares of deviations in the constituents' concentrations at all experimental points) corrected for degrees of freedom, indicate that the experimental data can be represented by the model. The small values of the 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 residuals form leptokurtic as well as platykurtic patterns[18] and very few form mesokurtic patterns. The values of skewness are between -3.32 and 1.33. 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-values. These statistical parameters thus show that the best-fit models portray the metal ligand species in neutral micellar media.

Table 1: Parameters of best fit chemical models of M (II)–Asp complexes in TX100-water medium.

%v/v TX100	Log β_{mlh} (SD)					NP	U_{corr}	Skew -ness	χ^2	R-Factor	Kurtosis	pH-Range
	ML	MLH	ML_2	ML_2H	ML_2H_2							
Co(II)												
0.0	-	13.45(4)	12.23(7)	18.93(15)	-	85	6.58	0.49	25.38	0.0067	4.41	1.80-10.5
0.5	-	13.27(2)	10.78(9)	16.98(18)	-	124	0.87	-1.58	106.3	0.0081	4.52	2.00-10.7
1.0	-	13.49(3)	10.99(8)	16.75(17)	-	97	2.08	-0.33	7.78	0.0091	2.80	2.00-9.50
1.5	-	14.35(3)	10.82(8)	15.98(14)	-	102	2.27	-0.42	6.32	0.0082	3.32	1.90-10.0
2.0	-	14.08(4)	11.05(5)	16.25(15)	-	105	4.19	-3.32	102.3	0.0055	9.29	1.70-10.0
2.5	-	13.60(4)	10.38(5)	15.84(15)	-	100	7.74	-2.21	132.3	0.0077	7.32	2.00-10.0
Ni(II)												
0.0	7.31(3)	12.08(11)	14.73(22)	-	-	137	8.53	-1.05	94.20	0.0044	5.68	1.75-10.0
0.5	7.26(5)	13.37(14)	11.59(25)	-	-	131	8.67	-1.20	84.52	0.0066	4.28	1.75-10.0
1.0	7.44(3)	13.58(9)	11.76(20)	-	-	109	2.21	-1.36	47.50	0.0031	2.96	2.50-11.0
1.5	7.66(3)	13.78(11)	11.71(28)	-	-	121	3.47	-0.98	52.64	0.0057	3.14	1.75-10.5
2.0	7.91(4)	13.92(10)	11.89(16)	-	-	135	5.94	-1.21	83.01	0.0184	6.72	1.70-10.5
2.5	8.19(2)	14.09(9)	11.93(23)	-	-	104	5.21	-1.55	45.94	0.0062	5.94	2.50-10.5
Cu(II)												
0.0	8.87(3)	13.74(7)	14.87(14)	-	-	71	6.22	0.92	48.54	0.0813	4.31	2.00-10.5
0.5	9.40(3)	12.88(7)	12.70(21)	-	-	123	2.48	-0.12	90.22	0.0046	5.90	1.75-10.0
1.0	9.52(5)	12.67(9)	12.21(23)	-	-	108	3.12	-0.87	54.51	0.0057	7.06	2.00-11.0
1.5	9.68(4)	12.39(11)	12.48(26)	-	-	139	6.52	-1.54	69.92	0.0048	6.17	1.75-11.0
2.0	9.72(2)	12.47(8)	12.84(26)	-	-	136	9.81	-1.38	73.54	0.0987	3.25	1.75-11.0
2.5	9.93(2)	12.80(12)	12.89(29)	-	-	104	4.73	-1.55	89.42	0.0035	4.59	2.50-10.0
Zn(II)												
0.0	-	-	11.73(3)	18.95(8)	25.39(15)	123	8.64	-0.38	137.1	0.0014	6.34	1.75-8.0
0.5	-	-	9.98(3)	16.98(7)	24.23(18)	122	4.05	-0.32	102.3	0.0019	3.21	1.75-9.0
1.0	-	-	8.78(2)	16.74(8)	24.83(17)	94	5.56	0.33	37.58	0.0013	6.63	2.00-10.5
1.5	-	-	8.63(3)	17.25(7)	24.93(18)	124	1.98	-0.14	61.89	0.0027	2.65	1.75-9.5
2.0	-	-	7.85(4)	17.33(8)	24.42(20)	100	2.57	-1.52	104.2	0.0086	5.32	1.90-10.5
2.5	-	-	8.84(2)	16.88(8)	25.07(21)	141	3.25	1.33	27.38	0.0043	5.52	1.65-10.0

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

EFFECT OF SURFACTANT

Variation of the stability constants (log β) with mole fraction of surfactants in neutral micellar media exhibits a non-linear decreasing trend. The stability of the complex depends on the polarity of the medium, charge on the Stern layer[21] and the electrostatic attraction or repulsive forces operating between the complex species and the neutral micellar surface. The dielectric constant of the media decreases with increasing concentration of the surfactant.[22, 23] The charged species will be destabilized due to the decreased dielectric constant of the medium with increasing surfactant concentration. The linear decrease indicates the dominance of electrostatic forces over non-electrostatic forces on the complex equilibrium.

DISTRIBUTION DIAGRAMS

The formation of various binary complex species is shown in the following equilibria.

$$M(II) + LH_2 \rightleftharpoons MLH^+ + H^+ \quad (1)$$

$$MLH^+ \rightleftharpoons ML + H^+ \quad ....(2)$$

$$M(II) + LH^- \rightleftharpoons ML + H^+ \quad ....(3)$$

$$M(II) + 2LH_2 \rightleftharpoons ML_2H_2 + 2H^+ \quad ....(4)$$

$MLH^{+} + LH_2 \rightleftharpoons ML_2H_2 + H^{+}$ ....(5)

$MLH^{+} + LH^{-} \rightleftharpoons ML_2H^{-} + H^{+}$....(6)

$ML_2H_2 \rightleftharpoons ML_2H^{-} + H^{+}$ ....(7)

$ML_2H^{-} \rightleftharpoons ML_2^{2-} + H^{+}$ ...(8)

$M(II) + 2LH^{-} \rightleftharpoons ML_2^{2-} + 2H^{+}$ ....(9)

$ML + LH^{-} \rightleftharpoons ML_2^{2-} + H^{+}$ ....(10)

Equilibria 1, 3, 4, and 9 represent the formation of complexes from metal ion and the ligand. In alkalimetric titrations, protons are removed successively from the complexes by the addition of aliquots of the alkali. Equilibria 2, 7 and 8 represent the successive deprotonation of the complexes with increasing pH of the solution during alkalimetric titrations.

Fig. 1 represents the formation of complexes. The species ML_2H and ML_2 are formed simultaneously in the pH range of 4.00-8.00. Probably Equilibria 6, 7, 9 and 10 exist simultaneously. Beyond a pH of 6 concentration of ML_2H is decreased whereas the concentration of ML_2 is increased. This indicates the formation of ML_2 from ML_2H (Equilibrium 8) where the concentration of ML species is increased while the concentration of MLH species is decreased. Equilibrium 2 is relevant in this instance. Similarly concentration of ML is decreasing as the concentration of ML_2 is increased (Equilibrium 10). The variation of concentrations of these species suggests the successive deprotonation of ML_2H_2 to ML_2.

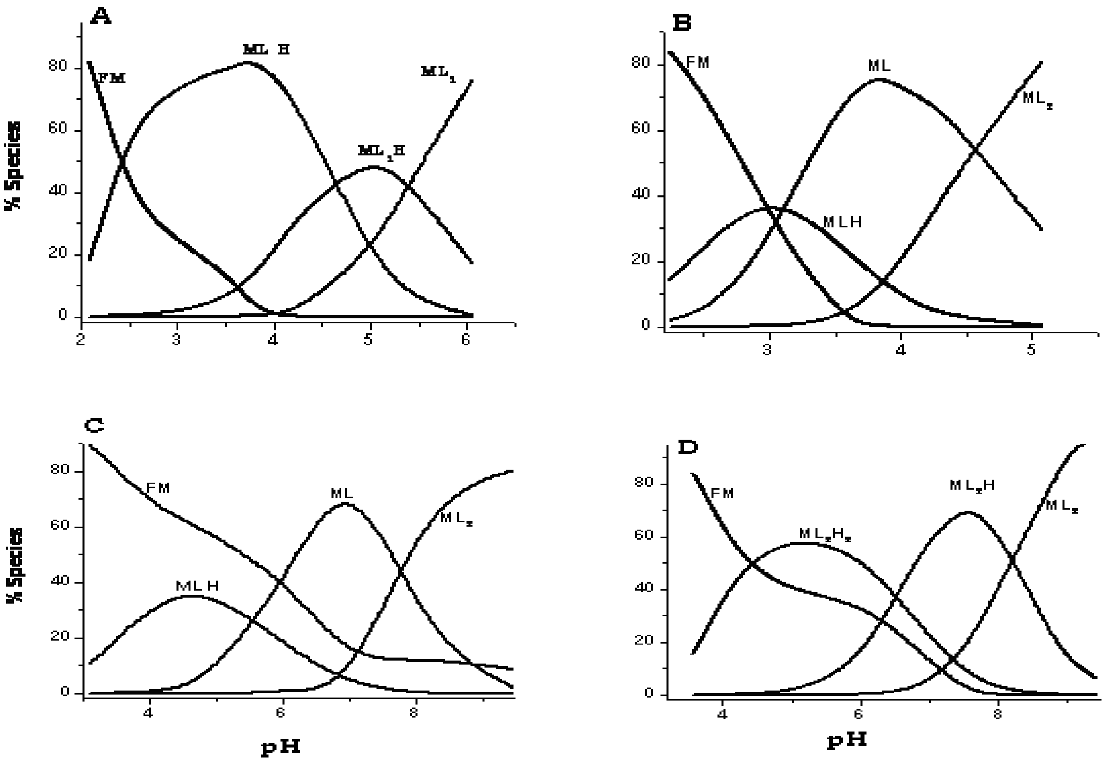


Fig. 1: Distribution diagrams of Asp complexes in 2.0 % v/v TX100-water medium. (A) Co(II), (B) Ni(II), (C) Cu(II) and (D) Zn(II).

REFERENCES

1. Lehninger, A. L., Nelson, D. L. X., Cox, M. M., *Principles of Biochemistry*, 3rd Ed. Worth Publishing, NY (2000).
2. K. V. Lavanya, V. M. Rao, G. N. Rao, Oxid. Commun. 31 (2008) 398
3. B. B. V. Sailaja, T. Kebede, G. N. Rao, M. S. Rao, Proc. Natl. Acad. Sci. India 74 (2004) 399
4. V. U. S. Sagar, G. Himabindu, K. G. Sudarsan, G. N. Rao, J. Indian Chem. Soc. 82 (2005) 598
5. G. N. Rao, A. Ramakrishna, Proc. Natl. Acad. Sci. India 75 (2005) 245
6. R. A. Poellot, T. R. Shuler, E. O. Uthes, F. H. Nielson, Proc. Natl. Acad. Sci. USA 44(1990) 80
7. M. W. W. Adams, Biochim. Biophys. Acta 1020 (1990) 115
8. R. Cammack, Nature 373 (1995) 556
9. A. K. Kolodziej, Prog. Inorg. Chem. 41 (1994) 493
10. R. H. Holm, P. Kennepohl, E. I. Solomon, Chem. Rev. (1996) 2239
11. R. Mukherjee, Comprehensive Coordination Chemistry–II: From Biology to Nanotechnology, Elsevier, 2003, p.747
12. Y. L. Lin, C. J. J. Lim, J. Am. Chem. Soc. 126 (2004) 2602
13. E. H. Cox, G. L. McLendon, Curr. Opin. Chem. Biol. 4 (2000) 162
14. J. H. Laity, B. M. J. Lee, P. E. Wright, Curr. Opin. Struct. Biol. 11 (2001) 39
15. T. Dudev, C. J. Lim, J. Chin. Chem. Soc. 50 (2003) 1093
16. G. Gran, Anal. Chim. Acta 206 (1988) 111
17. M. P. Latha, V. M. Rao, T. S. Rao, G. N. Rao, Bull. Chem. Soc. Ethiop. 21 (2007) 363
18. N. Padmaja, M. S. Babu, G. N. Rao, R. S. Rao, K. V. Ramana, Polyhedron 9 (1990) 2497
19. G. N. Rao, Ph.D. Thesis, Andhra University, Visakhapatnam, India, 1989
20. P. Gans, A. Sabatini, A. Vacca, Inorg. Chim. Acta 18 (1976) 237
21. C. A. Bunton, G. Cerichelli, Y. Ihara, L. Supulveda, J. Am. Chem. Soc. 101 (1979) 2429
22. A. K. Singh, D. Manjula, J. Indian Chem. Soc. 71 (2001) 635
23. E. H. Cordes, Pure Appl. Chem. 50 (1978) 617