FORMATION CONSTANTS OF Co (II), Ni (II), Cu (II), Zn (II), Cd (II), UO_2 (II) AND VO (II) CHELATES OF THE SCHIFF BASE DERIVED FROM PYRROLE-2-CARBOXALDEHYDE AND β-ALANINE

A SURVEY[1,2] of the literature has revealed that no work has been done on the metal-complexes of 3-(2-pyrrolideneimino)-propionic acid (H_2PP) Schiff base derived from pyrrol-2-carboxaldehyde and β-alanine. Hence the work on the potentiometric studies of its chelates with Co (II), Ni (II), Cu (II), Zn (II), Cd (II), UO_2 (II) and VO (II) was undertaken. The measurements were carried out by Calvin-Bjerrum pH-titration technique[3,4] at 25° C, 30° C and 35° C in aqueous medium (0·1 M $NaClO_4$).

Precision pH-meter type OP : 205 No. 837 with glass-calomel assembly was used. H_2PP was synthesised by a procedure similar to that reported earlier[5], m.p. 172° C, found C, 57·49; H, 5·98; N, 16·72; Calcd. for $C_8H_{10}N_2O_2$, C, 57·83; H, 6·02; N, 16·86%. All the chemicals used were either BDH or Ridiel reagents. The standard solutions of H_2PP, metal-nitrates and sodium perchlorate were prepared in doubly distilled water.

H_2PP was titrated in the absence and in the presence of the metal-ions of interest with 0·1 M sodium hydroxide solution at 25° C, 30° C and 35° C and the titration curves had the usual shapes.

In the case of H_2PP, the formation curves extend upto $\bar{n}_A \simeq 2{\cdot}0$, indicating that two protons respectively from carboxylic and imino groups are dissociated. The mean values of dissociation constants obtained by different methods (algebraic and interpolation at half $\bar{n}_A$ values) are pK_1, 8·91, 8·85 and 8·81 and pK_2, 10·12, 10·06 and 10·01, at 25° C, 30° C and 35° C respectively.

A perusal of the pK_1 values suggest that the proton of the carboxylic group in the ligand is present as a Zwitter-ion in solution.

The formation curves for all the metal-ligand systems attain their maxima at $\bar{n} < 1{\cdot}0$ which indicate the formation of 1 : 1 chelates only.

The values of log K_1 obtained for Co (II), Ni (II), Cu (II), Zn (II), Cd (II), UO_2 (II) and VO (II) complexes are 8·50, 10·35, 11·95, 5·55, 4·35, 13·10 and 14·20 at 25° C, 8·55, 10·40, 11·99, 5·57, 4·37, 13·15 and 14·25 at 30° C and 8·60, 10·45, 12·05, 5·60, 4·40; 13·20 and 14·30 at 35° C respectively. The sequence of stability constants, VO (II) > UO_2 (II) > Cu (II) > Ni (II) > Co (II) > Zn (II) > Cd (II) is in agreement with the Irving-Williams rule[6].

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1. Cotton, F. A., *Prog. Inorg. Chem*, 1966, 7, 88.
2. Perry, Christopher, L., Weber. and James Harold, *J. Inorg. Nucl. Chem.*, 1971, 33, 1031.
3. Calvin, M. and Wilson, K. W., *J. Am. Chem Soc.*, 1945, 67, 2003.
4. Bjerrum, J., "Metal amine formation in aqueous solution" (P. Haase & Sons, Copenhagen), 1941.
5. Mehta, R. K. and Gupta, R. K., *Ind. J. Chem.*, 1973, 11, 56.
6. Irving, H. and Williams, R. J. P., *Nature*; 1948, 162, 746; *J. Chem. Soc.*, 1953, p. 3192.

PYROLYTIC STUDIES ON BUFFALO MILK CASEIN

IN order to evaluate the nutritive significarce of milk and milk products prepared under different thermal conditions, systematic studies on the effect of heat on buffalo casein at different intervals of time were studied. In addition, pyrolytic studies on H_2O_2 treated buffalo milk casein were also investigated as low concentrations of H_2O_2 have been found to preserve milk[1].

Previous studies on pyrolytic effect of cow casein have indicated the destruction of certain amino acids and the release of phosphopeptides[2] and free amino acids. Fujimaki *et al.*[3] observed that the roasted casein exhibits a decrease in biological value due to partial destruction and racemisation of peptides and amino acids. Osner *et al.*[4] have observed the denaturation of casein above 130° C and also severe destruction of certain amino acids at elevated temperatures.

Buffalo casein from fresh buffalo milk and caseins from H_2O_2 treated buffalo milk were isolated by isoelectric precipitation technique[5].

Hundred mg each of the (i) fresh casein (unheated); (ii) heated casein; (iii) H_2O_2 treated buffalo milk casein, and (iv) H_2O_2 treated and heated buffalo milk casein were hydrolysed using 6N HCl at 120° C.

The hydrolysates were spotted on Whatmann No. 1 filter-paper and irrigated with *n*-butanol, water, acetic acid (4:1:1) by employing ascending paper chromatographic technique. The separated amino acids were identified by treatment with ninhydrin in 95% aqueous acetone and quantitatively estimated using densitometer. For overlapping amino acids such as lysine, histidine, serine, glycine, aspartic acid, etc., the two-dimensional development technique was employed using phenol-water in the ratio 4:1 as the second solvent. Similar experiments were carried out with the other

TABLE I

Percentage loss of various amino acids in Buffalo milk casein

(Average values of three samples)

Amino acids	Average % loss of heated B.M.C.* for 1 h	Average % loss of heated B.M.C.* for 24 h	Average % loss of H_2O_2 treated and heated B.M.C.* for 1 h			
			concentration of H_2O_2			
			0·02%	0·04%	0·08%	0·10%
1. Lysine	2·8	67·2	13·2	27·0	54·1	67·6
2. Histidine	2·7	65·3	13·4	26·8	53·4	66·8
3. Arginine	2·3	56·1	12·9	22·5	42·4	56·1
4. Serine	2·1	50·4	13·6	23·4	38·4	49·2
5. Glycine	1·8	42·7	8·6	17·4	34·1	42·8
6. Aspartic acid	2·4	57·6	12·6	24·4	50·8	62·0
7. Threonine	2·6	62·6	17·1	26·2	48·2	59·5
8. Alanine	2·1	50·6	12·7	17·5	35·1	50·4
9. Tyrosine	2·4	58·8	12·1	24·2	49·2	60·4
10. Valine	2·9	69·6	13·6	26·2	54·4	69·4
11. Methionine	2·6	62·4	13·7	26·8	52·4	68·2
12. Phenylalanine	2·3	56·6	13·8	22·9	44·8	53·6
13. Leucines	1·7	40·8	8·2	16·4	33·1	40·6

B.M.C.*—Buffalo milk casein.

samples of the hydrolysates prepared under identical conditions. The developed chromatogram was used for the estimation of amino acids densitometrically. The results are given in Table 1.

RESULTS AND DISCUSSION

From the above results it is clearly indicated that thermally treated casein for a period of 1 h at 110°C has undergone a small decrease (2·5%) in most of the amino acids. When casein is heated for 24 h under identical conditions the loss is over 50%.

In the case of casein isolated from milk treated with H_2O_2, it is observed that even at a very low concentration of 0·02%, there is over 10% loss of amino acids on heating for an hour at 110°C. At higher concentrations of H_2O_2 (0·1% by wt/v) there is a marked decrease of amino acids over 60%.

H_2O_2 treated casein on pyrolysis at 110°C readily turns brown releasing gaseous products. So the H_2O_2 treated samples (0·02 wt/v) should not be heated for over 30 min. at 110°C.

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1. Srinivasan, A. and Gopalan, S., *Curr. Sci.*, 1975, 44 (12), 423.
2. Lorient, D. and Alais, C., *Int. Dairy Cong.*, 1970, 1E, 54.
3. Fujimaki, M., Kato, H. and Hayase, F., *Agri. Biol. Chem.*, 1972, 36 (3), 416.
4. Osner, R. C. and Johnson, R. M., *J. Food. Tech.*, 1974, 9 (3), 301.
5. Ganguly, N. C., Prabhakaran, R. J. V. and Iya, K. K., *J. Dairy Sci.*, 1964, 47, 13.

ON THE REPLANTATION OF HUMAN MOLARS

MODERN operative dental practice involves *replantation* of the traumatically displaced teeth as well as *intentional replantation*[1,2], attempting to treat and retain the permanent teeth affected with caries—in such cases where *in vivo* endodontic surgery is not feasible. *In vitro* endodontic treatments are carried out in the shortest possible time thus maintaining the viability of the supporting structures of the extracted teeth[3]. Further, the limitation of endodontic therapy of the carious teeth, extent of coronal destruction and periodontal involvement and, oral hygiene are some of the important criteria to be considered while attempting an *intentional replantation* towards a conservative management. Present study was undertaken with