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Speciation studies of binary complexes of nickel(II) with L-arginine and L-histidine in micellar medium

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A computer assisted investigation has been made on the nature of complexes of nickel(II) with L-arginine and L-histidine. The formation constants have been determined experimentally by monitoring hydrogen ion concentration. The distribution of the metal ion amongst the complexes formed with the above amino acids has also been computed. The formation constants have been refined with the computer program, MINIQUAD75 using the primary alkalimetric data. The distribution pattern of different species varies with the relative concentrations of the metal ion and the ligand. Influence of the micelles on the speciation is discussed based on the dielectric constant of the medium and distribution of various species in the Stern layer and in the bulk solvent. The probable structures of the complexes are also given.

Nickel(II) is associated with several enzymes[1–3] and any variation in its concentration leads to metabolic disorders[4]. The physiological activities of L-arginine, L-histidine and nickel(II) are associated with the metabolic processes in liver[5,6]. Hence, there is every likelihood for this metal ion and amino acids to interact in the hepatic cells. Amphiphilic molecules influence the bulk properties of physiological systems. They can solubilise, concentrate and compartmentalize ions and molecules[7]. They can also modify complex and acid-base equilibria, redox properties and reaction rates. The protonation equilibria of L-arginine and L-histidine have been studied in cetyltrimethylammonium bromide (CTAB), sodium lauryl sulphate (SLS) and Triton X-100 micellar media[8]. The complexation of L-arginine with magnesium(II) and calcium(II) has also been studied in our laboratory[9]. The present paper reports a pH metric study of the binary complex equilibria of L-arginine and L-histidine with nickel(II) in CTAB micellar media of varying compositions.

Results and discussion

Complex equilibria :

There are several instances where different species were reported for the same chemical system by different research workers[10–14]. The probes utilized and computational procedures adopted were some times the same and some times different. In order to rationalize the contradicting models reported above, greater details regarding the (1) ingredient concentration, (2) method of pruning the primary data for the refinement, (3) pH range and the number of points in each sub range and (4) proportion of the points corresponding to each species in the model are required. Further, different species proposed for the same metal-ligand system are many a time judged based on the best-fit criteria.

The models containing different number of species were tried from the primary alkalimetric data. Only a few species were refined while other species were rejected by the computer program MINIQUAD75[15]. Then models with combination of different species at a time were also tested. After arriving at a valid model, the species rejected in the preliminary scrutiny were again tried. Some species were removed from the model if their percentage concentration was less than 10. Existence of species was determined by performing exhaustive modeling[16]. Models containing various number and combination of species were generated using an expert system package CEES[17] and these models were refined using MINIQUAD75.

The final model in CTAB-water media for L-histidine complexes of nickel(II) contained the species ML, ML_2 and ML_2H and that for L-arginine complexes contained ML, MLH and ML_2H. The parameters of the best-fit models are given in Table 1.

Table 1. Best fit chemical models of nickel(II)-arginine (or histidine) complexes in CTAB micellar media

μ = 0.16 mol dm^{-3}; pH range = 2.0–11.0; temp = 303 K

%w/v	log β_{mlh} (SD)			NP	U_{corr} × 10^8	Skewness	Kurtosis	χ^2	R
	110	**111**	**121**						
				L-Arginine					
0.0	13.57(6)	21.15(15)	28.93(5)	78	4.73	1.00	4.86	29.79	0.006
0.5	14.13(2)	20.86(1)	30.36(6)	92	144.94	1.24	4.12	28.41	0.039
1.0	11.35(3)	18.56(9)	25.14(8)	82	66.58	1.08	4.81	68.41	0.028
1.5	11.00(3)	17.05(3)	23.02(3)	77	43.91	1.22	5.49	76.15	0.024
2.0	9.95(2)	15.02(9)	21.30(1)	91	8.29	1.10	19.27	173.8	0.009
2.5	9.04(5)	13.03(2)	20.01(9)	92	29.66	0.35	5.10	139.7	0.018
				L-Histidine					
	110	**120**	**121**						
0.0	8.16(6)	14.55(15)	19.33(5)	58	1.63	0.69	4.40	14.41	0.008
0.5	7.95(6)	14.11(1)	19.14(7)	63	44.94	–0.98	6.12	25.48	0.007
1.0	7.50(3)	13.20(2)	18.77(4)	62	52.58	–3.30	16.47	67.05	0.022
1.5	7.40(3)	13.00(3)	18.71(5)	65	43.91	1.22	5.49	76.15	0.024
2.0	6.95(2)	13.22(8)	18.09(9)	83	8.29	–1.10	19.27	173.8	0.009
2.5	7.00(6)	13.01(4)	18.00(7)	92	29.66	0.35	5.10	139.7	0.018

NP = Number of experimental points.

A very low standard deviation in log β values indicates the precision of these parameters. The small values of U_{corr} (sum of squares of deviations in concentrations of ingredients at all experimental points corrected for degrees of freedom[18]) indicate that the model can represent experimental data. The Kurtosis values between 4.12 and 19.27 indicate that the residuals form Platykurtic pattern. The values of Skewness between 3.30 and 1.24 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. They decide the need for inclusion of additional species in the model. χ^2 is a special case of γ distribution which measures the probability of residuals forming a part of standard normal distribution. The details of these statistical parameters can be found elsewhere[19].

Effect of micelles :

The variations in the magnitudes of formation constants of the complex species formed due to the interaction between nickel(II) and arginine or histidine with percentage composition of the surfactant (CTAB) are shown in Fig. 1. From the figure, it can be seen that the stabilities of the complexes are decreasing linearly (R^2 = 0.98) with increasing CTAB content. The decreased stability of the complexes may be due to the following reasons :

(1) With increased surfactant concentration, the concentration of micelles increases and the dielectric constant decreases. The lower dielectric constant of the medium destabilizes the charged complex species.

(2) The Stern layer[20] of the cationic micelles (CTAB) has positively charged head groups and anions shall be present in Gouy-Chapman double layer Hence, the positively charged complexes cannot be stabilized on the surface of the micelles and they are thrown into the bulk of the solution.

(3) The hydrophobic groups of the amino acids make them to be drawn into the core of the micelle and metal ions are present in the bulk solution. This makes the non-availability of ligands to the metal ions for the formation of complexes.

Distribution diagrams :

L-Arginine has one dissociable carboxylate proton and its amino and guanidyl groups can associate with one proton each. The forms of the ligand are LH_3^{2+}, LH_2^+ and LH in the pH regions 1.5–3.5, 2.5–9.0 and 8.0–11.5, respectively[8]. L-Histidine has one dissociable carboxylate proton and its amino and imidazole groups can associate with one proton each. The forms of the ligand are LH_3^{2+}, LH_2^+ and LH in the pH regions 1.5–3.0, 2.0–7.0 and 5.0–9.0, respectively[8].

Since the present study is confined to a pH range of 2.0–

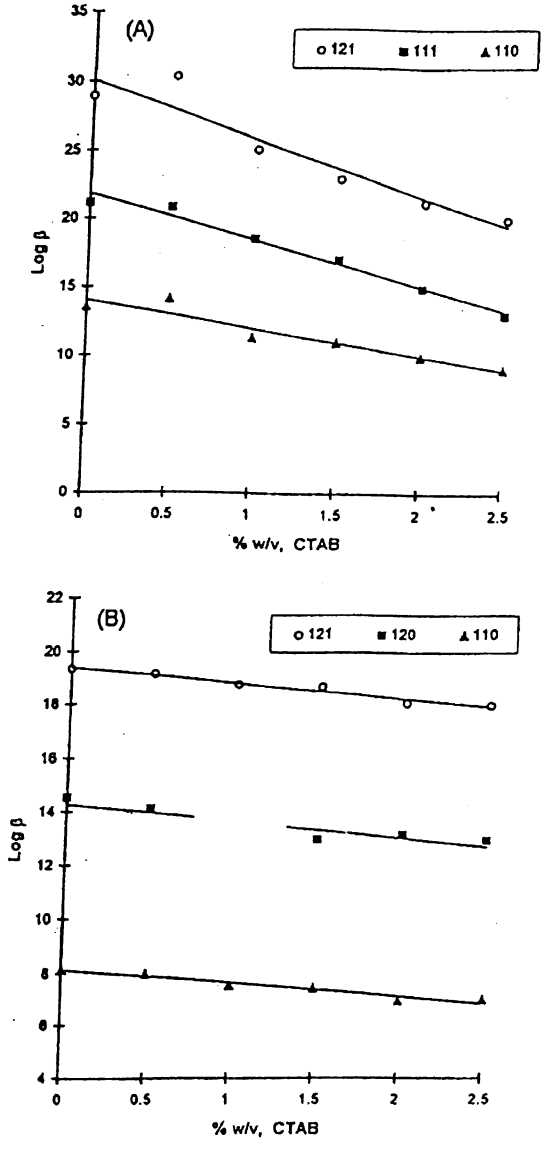

Fig. 1. Variation of magnitude of stability constants (log β) with CTAB content : (A) nickel-arginine complexes (regression coefficient values, R^2 : **110** : 0.906, **111** : 0.977, **121** : 0.903), (B) nickel-histidine complexes (regression coefficient values, R^2 : **110** : 0.943, **120** : 0.749, **121** : 0.956).

11.0 for the complexes of nickel(II) with both the ligands, the formation of the complex species in this pH region can be represented as the following equilibria :

(i) $M(II) + LH_2^+ \rightleftharpoons MLH^{2+} + H^+$

(ii) $M(II) + 2\,LH_2^+ \rightleftharpoons ML_2H_2^{2+} + 2H^+$ (minor process)

(iii) $MLH^{2+} + LH_2^+ \rightleftharpoons ML_2H_2^{2+} + H^+$ (minor process)

(iv) $ML_2H_2^{2+} \rightleftharpoons ML_2H^+ + H^+$

(v) $MLH^{2+} \rightleftharpoons ML^+ + H^+$

(vi) $ML_2H^+ \rightleftharpoons ML_2 + H^+$

(vii) $ML^+ + LH \rightleftharpoons ML_2 + H^+$

Since $ML_2H_2^{2+}$ species is not refined in the present study, either the (ii) and (iii) processes are minor or ML_2H^+ is readily formed from $ML_2H_2^{2+}$ (process (iv)).

Typical distribution diagrams are given in Fig. 2, for Ni-Arg and Ni-His complexes. Unprotonated complexes (ML and ML_2) are the major species for Ni-His complexes and the protonated complexes (MLH and ML_2H) are the major species for Ni-Arg complexes. The predominance of protonated species in arginine complexes is due to very high

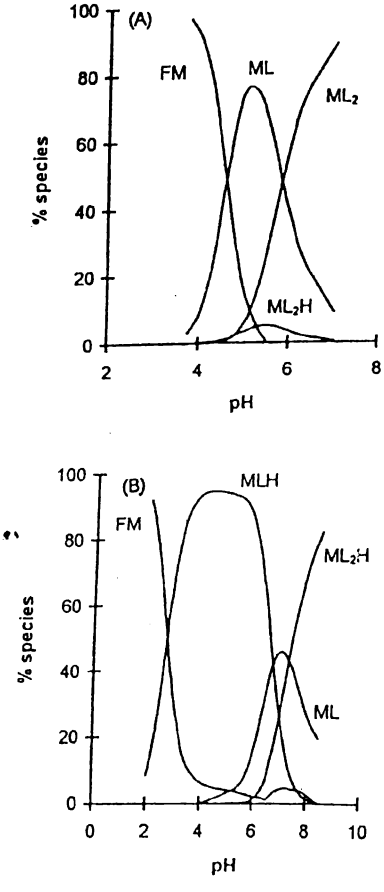

Fig. 2. Distribution diagrams of binary complexes of nickel with (A) histidine in aqueous medium, (B) arginine in 0.5% w/v CTAB medium. $[Ni^{2+}] = 4.0 \times 10^{-3}$ mol dm^{-3}; [His] = [Arg] = 8.0×10^{-3} mol dm^{-3}.

pKa value of guanidyl group of arginine[8]. In the pH range of study arginine exists as LH_2^+ and it loses third proton above a pH of 11.

Experimental

Solutions of nickel chloride, L-arginine and L-histidine (E. Merck, G.R.) were prepared in triple-distilled water. Aqueous solutions of CTAB (B.D.H.) were also prepared in triple-distilled water.

The alkalimetric titrations were carried out in the medium containing varying compositions of CTAB (0.5–2.5%, w/v) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium chloride at 303.0 ± 0.1 K. A Systronics (Model 335) pH meter was used. The glass electrode was equilibrated in a well-stirred micellar solution containing inert electrolyte. The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and/or dissolved carbon dioxide on the response of the glass electrode were taken into account in the form of correction factor[16] (log *F*). It was computed from the simulated acid-base titration data calculated by SCPHD program[21] for each of the solvent compositions. A correction was applied to 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 with different ratios (1 : 2 and 1 : 4) of metal-to-ligand were carried out with 0.4 mol dm^{-3} sodium hydroxide.

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. Some heuristics[22] were followed in the refinement of stability constants and validation of models[23].

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