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Investigations on Multidentate Ligand Complexes with Some Late Transition Metal Ions

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Formation of the species MHA (M = Ni^{2+}, Cu^{2+}, Pd^{2+}, Cd^{2+}), MA, MA(OH), M_2A (M = Cu^{2+} or Pd^{2+}), $Pd_2A(OH)$, MHB (M = Ni^{2+}, Zn^{2+}, Pd^{2+}, Ag^{+} or Cd^{2+}) and MB (M = Ni^{2+}, Zn^{2+}, Pd^{2+} or Ag^{+}) [where A = pentaanion of 1-hydroxy-8-(2-hydroxy-naphthylazo)-2-(sulphonaphthylazo)-3,6-disulphonic acid and B = tetraanion of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid] has been inferred in aqueous solution in pH-metric experimental measurements of the corresponding metal-ligand mixtures. Equilibrium constants related to the complex species present have been evaluated at 25°C (μ = 0.10 M KNO_3) and involvement of the ligand donor groups in coordination, under different ratios of the reactants and pH variations of the reaction mixtures, have been discussed.

INTRODUCTION

Multidentate ligands are useful in demonstrating new complexing properties of the individual ligand donor groups using the technique of incorporating different metal-ligand ratios, based on the positions and basicity of the functional groups, in the reaction mixtures[1]. Many new protonated, nonprotonated and hydroxo species are identified in solutions. Sometimes, unusual and nonconventional coordinating groups bind the metal in a suitable pH range through the structural changes in the complexes formed at other pH values[2,3].

1-Hydroxy-8-(2-hydroxynaphthylazo)-2-(sulphonapthylazo)-3,6-disulphonic acid (FSB, H_5A) and 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (HSA, H_4B), which possess many biological, industrial and analytical applications[4], are expected to yield new complexes in solution due to presence of polyfunctional complexing groups. Thus, the complexation reactions of these polydentate ligands involving the late transition metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Ag^{+} and Cd^{2+} have been investigated, employing pH-metric experimental procedure[5], over a wide pH range (2.8–11.0) in mixtures containing 1:1, 1:2 and 2:1 metal-ligand ratios.

EXPERIMENTAL

Materials

Standard solution of 0.1306 N NaOH, 1.0 M KNO_3 and 0.00146 N HNO_3 were prepared using analytical grade reagents, 5.0×10^{-3}M solutions of $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $Cd(NO_3)_2 \cdot 4H_2O$, (all

from BDH) and $PdCl_2$ (CDH) were obtained by dissolving the corrresponding compounds. Metal contents except Pd^{2+} were determined by EDTA titration method[6]. Pd^{2+} was estimated gravimetrically. Aqueous solution of 1-hydroxy-8-(2-hydroxynaphthylazo)-2-(sulphonaphthylazo)-3,6-disulphonic acid (trisodium salt) and 2-hydroxy-1-(2-hydroxy-4-sulpho-1-napthylazo)-3-naphthoic acid (both Loba) were prepared by direct weighing. A known amount of alkali was added to the measuring flask of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid to obtain monosodium salt solution of the ligand.

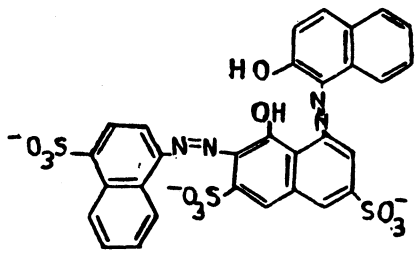
Procedure

A number of mixtures (i) HNO_3, (ii) 5.0×10^{-4}M ligand + (i); (iii) 5.0×10^{-4} M metal ion + (ii), (iv) 2.5×10^{-4} M metal ion + (ii); (v) 1.0×10^{-3} M metal ion + (ii) were prepared, and titrated against the NaOH solution, keeping the initial volume of each mixture 50 cm^3 (25°C, $\mu = 0.10$ M KNO_3) using EC digital pH-meter-5652 with combined electrode system. From the experimental data titration curves (pH vs. moles of alkali used per mole of ligand, 'a') were obtained and analysed as described earlier[7], for obtaining informations on metal-ligand interactions, and the corresponding equilibrium constants were evaluated.

RESULTS AND DISCUSSION

Proton-ligand dissociation constants

A green colour of the diprotonated FSB solution does not change on addition of alkali, and also the pH vs. volume of alkali curves for the acid and acid + ligand mixtures almost coincide throughout the entire experimental pH values. The pH vs. 'a' curve for the ligand is a vertical straight line at $a = 0$ (Fig. 1), and thus, proton-ligand dissociation constants of the two phenolic groups could not be obtained.



(H_2A^{3-})

The mixture (ii) for ligand HSA is red and turbid below pH *ca.* 3.2 Beyond this pH the red solution gradually changes to violet and subsequently to blue in the pH range 6.0–11.0. These colour changes are expected due to dissociation of the two phenolic protons of the ligand molecule. The proton from carboxylic group is completely ionised below pH *ca.* 6.0. The pH vs. 'a' curve (Fig. 1) also

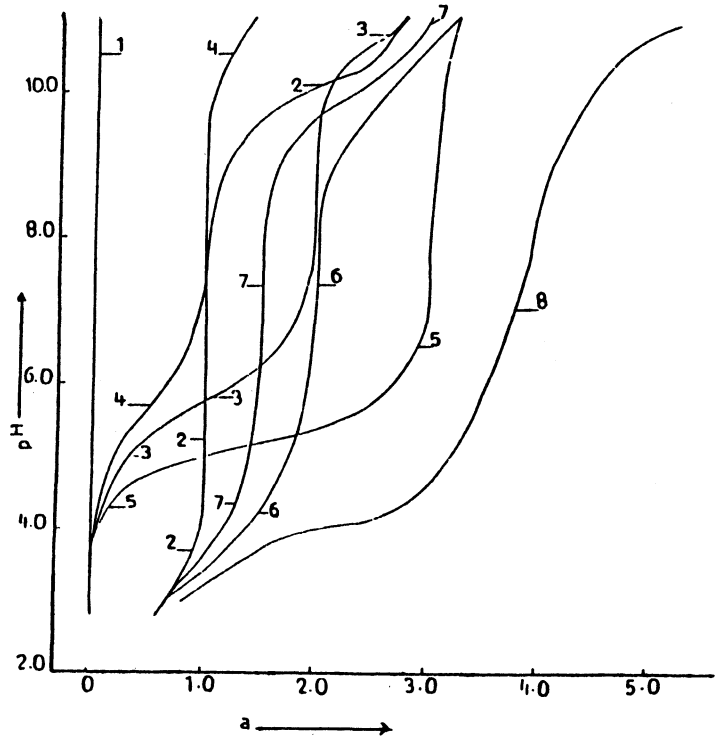
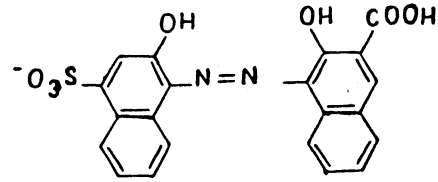


Fig. 1 pH vs. a curves for Pd^{2+}-FSB and Pd^{2+}-HSA complexes (25°C, $\mu = 0.10$ M KNO_3), total initial ligand concentration = 5.0×10^{-4} M): curves, 1-FSB, 2-HSA, 3-Pd^{2+}-FSB (1:1), 4-Pd^{2+}-FSB (1:2), 5-Pd^{2+}-FSB (2:1), 6-Pd^{2+}-HSA (1:1), 7-Pd^{2+}-HSA (1:2), 8-Pd^{2+}-HSA (2:1).

indicates dissociation of these protons from the ligand. The proton-ligand dissociation constants K_2^H, K_3^H and K_4^H (Table-1) were calculated as described earlier[7]. The values reported in water non-aqueous solvent mixtures by Kosak and Ballezo[8] [$K_1^H = 10^{-2.68}$, $K_2^H = 10^{-4.39}$ (in 50% methanol); $K_3^H = 10^{-7.60}$, $K_4^H = 10^{-14.35}$ (in 25% methanol)] slightly deviate from the present results probably due to change in experimental method temperature and medium of the reaction mixture.



(H_3B^-)

TABLE-1
EQUILIBRIUM CONSTANTS OF METAL-FSB AND METAL-HSA COMPLEXES
(25°C, μ = 0.10 M KNO_3)

Reaction	log K
$Ni^{2+} + H_2A^{3-} \rightleftarrows NiHA^{2-} + H^+$	−6.79 ± 0.08
$Cu^{2+} + H_2A^{3-} \rightleftarrows CuHA^{2-} + H^+$	−2.85 ± 0.11
$Cu^{2+} + H_2A^{3-} \rightleftarrows CuHA^{3-} + 2H^+$	−8.92 ± 0.07
$CuA^{3-} + OH^- \rightleftarrows CuA(OH)^{4-}$	3.43 ± 0.18
$2Cu^{2+} + H_2A^{3-} \rightleftarrows Cu_2A^- + 2H^+$	−5.62 ± 0.37
$CuHA^{2-} + Cu^{2+} \rightleftarrows Cu_2A + H^+$	−2.77
$Pd^{2+} + H_2A^{3-} \rightleftarrows PdHA^{2-} + H^+$	−1.85 ± 0.04
$Pd^{2+} + H_2A^{3-} \rightleftarrows PdA^{3-} + 2H^+$	−7.68 ± 0.05
$PdA^{3-} + OH^- \rightleftarrows PdA(OH)^{4+}$	3.30 ± 0.15
$2Pd^{2+} + H_2A^{3-} \rightleftarrows Pd_2A^- + 2H^+$	−3.67± 0.05
$Pd_2A + OH^- \rightleftarrows Pd_2A(OH)^{2-}$	9.45 ± 0.12
$PdHA^{2-} + Pd^{2+} \rightleftarrows Pd_2A + H^+$	−1.82
$Cd^{2+} + H_2A^{3-} \rightleftarrows CdHA^{2-} + H^+$	−7.03 ± 0.05
$H_3B^- \rightleftarrows H_2B^{2-} + H^+$	−2.66 ± 0.02
$H_2B^{2-} \rightleftarrows HB^{3-} + H^+$	−9.57 ± 0.05
$HB^{3-} \rightleftarrows B^{4-} + H^+$	−10.51 ± 0.01
$Ni^{2+} + H_3B^- \rightleftarrows NiHB^- + 2H^+$	−3.78
$Ni^{2+} + H_2B^{2-} \rightleftarrows NiHB^- + H^+$	−1.12
$Ni^{2+} + HB^{3-} \rightleftarrows NiHB^-$	8.45 ± 0.04
$NiHB^- \rightleftarrows NiB^{2-}$	−9.96
$Ni^{2+} + H_3B^- \rightleftarrows NiB^{2-} + 3H^+$	−13.54
$Ni^{2+} + H_2B^{2-} \rightleftarrows NiB^{2-} + 2H^+$	−10.88
$Ni^{2+} + HB^{3-} \rightleftarrows NiB^{2-} + H^+$	−1.31
$Ni^{2+} + B^{4-} \rightleftarrows NiB^{2-}$	9.20 ± 0.02
$Zn^{2+} + H_3B^- \rightleftarrows ZnHB^- + 2H^+$	−4.31
$Zn^{2+} + H_2B^{2-} \rightleftarrows ZnHB^- + H^+$	−1.65
$Zn^{2+} + HB^{3-} \rightleftarrows ZnHB^-$	−7.92 ± 0.02
$ZnHB^- \rightleftarrows ZnB^{2-} + H^+$	−9.36
$Zn^{2+} + H_3B^- \rightleftarrows ZnB^{2-} + 3H^+$	−13.67
$Zn^{2+} + H_2B^{2-} \rightleftarrows ZnB^{2-} + 2H^+$	−11.01
$Zn^{2+} + HB^{3-} \rightleftarrows ZnB^{2-} + H^+$	−1.44
$Zn^{2+} + B^{4-} \rightleftarrows ZnB^{2-}$	−9.07 ± 0.02
$Pd^{2+} + H_3B^- \rightleftarrows PdHB^- + 2H^+$	−3.26
$Pd^{2+} + H_2B^{2-} \rightleftarrows PdHB^- + H^+$	−0.6
$Pd^{2+} + HB^{3-} \rightleftarrows PdHB^-$	8.97 ± 0.03
$PdHB^- \rightleftarrows PdB^{2-} + H^+$	−9.76
$Pd^{2+} + H_3B^- \rightleftarrows PdB^{2-} + 3H^+$	−13.02
$Pd^{2+} + H_2B^{2-} \rightleftarrows PdB^{2-} + 2H^+$	−10.36
$Pd^{2+} + HB^{3-} \rightleftarrows PdB^{2-} + H^+$	−0.79

Reaction		log K
$Pd^{2+} + B^{4-}$	$\rightleftarrows PdB^{2-}$	9.72± 0.01
$Ag^{+} + H_3B^{-}$	$\rightleftarrows AgHB^{2-} + 2H^{+}$	−7.76
$Ag^{+} + H_2B^{2-}$	$\rightleftarrows AgHB^{2-} + H^{+}$	−5.10
$Ag^{+} + HB^{3-}$	$\rightleftarrows AgHB^{2-}$	4.47± 0.03
$AgHB^{2-}$	$\rightleftarrows AgB^{3-} + H^{+}$	−10.29
$Ag^{+} + H_3B^{-}$	$\rightleftarrows AgB^{3-} + 3H^{+}$	−18.05
$Ag^{+} + H_2B^{2-}$	$\rightleftarrows AgB^{3-} + 2H^{+}$	−15.39
$Ag^{+} + HB^{3-}$	$\rightleftarrows AgB^{3-} + H^{+}$	• −5.82
$Ag^{+} + B^{4-}$	$\rightleftarrows AgB^{3-}$	4.69± 0.06
$Cd^{2+} + H_3B^{-}$	$\rightleftarrows CdHB^{-} + 2H^{+}$	−8.05
$Cd^{2+} + H_2B^{2-}$	$\rightleftarrows CdHB^{-} + H^{+}$	−5.39
$Cd^{2+} + HB^{3-}$	$\rightleftarrows CdHB^{-}$	4.18± 0.02

(a) 1:1 *Metal-ligand complexes*: 1:1 Ni^{2+}-FSB titration mixture changes blackish green from pH *ca.* 9.0 and subsequently turns turbid from pH *ca.* 10.0. No conclusion could be drawn on the nature of 1:1 metal-ligand complex from the shape of pH vs. 'a' curve. The curve does not show any inflection at a = 1 or 2. However, from the colour change, existence of 1:1 metal-ligand species appears almost certain. Involvement of only one phenolic group in coordination may be expected on the basis of results of Cu^{2+} and Pd^{2+} interactions with FSB (discussed later on). For the evaluation of equilibrium constant of the expected reaction (1), relations (2)–(4) were used.

$$M + H_2A \rightleftarrows MHA + H^{+}; \quad K_1 = [MHA][H^{+}]/[M][H_2A] \tag{1}$$

$$[H_2A] = C_A(1 - a) \tag{2}$$

$$[M] = [H_2A] \tag{3}$$

$$[MHA] = C_M — [M] \tag{4}$$

(charges have been omitted for simplicity)

No calculation was possible beyond pH *ca.* 10.0 due to existence of turbidity.

The titration mixture of 1:1 Cu^{2+}-FSB system, with green colour (almost identical with the colour of ligand) below pH *ca.* 6.3 gradually changes to blue between pH *ca.* 6.3 and 9.81. Beyond pH *ca.* 9.8 the colour of solution further turns pinkish black. A comparison of colour changes with titration curve indicates existence of monoprotonated species $CuHA^{2-}$ between a = 0 and 1 and CuA^{3-} between a = 1 and 2. The steep inflection in pH vs. 'a' curve at a = 2 shows independent formation of the non-protonated species CuA^{3-}:

$$M + H_2A \rightleftarrows MA + 2H^{+}; \quad K_1' = [MA][H^{+}]^2/[M][H_2A] \tag{5}$$

Concentrations of different species were obtained using the following relations derived from mass and charge balance equations:

$$\left(\frac{K'}{H}\right)[H_2A]^2 + 2[H_2A] - C_A(2 - a) = 0 \tag{6}$$

(for [M] eqn. (3) has been used)

$$[MA] = C_M - [M] - [MHA] \quad (7)$$

Increase in 'a' value, beyond a = 2, is expected because of attachment of OH^- ion with the nonprotonated complex.

$$MA + OH \rightleftarrows MA(OH); \quad K_1'' = [MA(OH)]/[MA][OH] \quad (8)$$

The K_1'' value was obtained after calculating [M], $[H_2A]$ and [MA(OH)] with the help of eqns. (3), (9) and (10), respectively.

$$(2K_1[H^+] + K_1')[HA]^2 + 3[H^+]^2[H_2A] - C_A(3 - a)[H^+] = 0 \quad (9)$$

$$[MA(OH)] = C_M - [M] - [MHA] - [MA] \quad (10)$$

The corresponding equilibrium constants (eqns. (1), (5) and (8)) are given in Table-1.

Formation of turbidity in 1:1 Zn^{2+}-FSB system in the entire pH conditions did not allow any calculation.

Existence of green $PdHA^{2-}$ species is indicated by pH vs. 'a' curve between 'a' = 0 and 1 in 1:1 Pd^{2+}-FSB mixture. A steep inflection at 'a' = 2 in titration curve shows similarity with the interaction of Cu^{2+} ion with the ligand. Thus, between 'a' = 1 and 2, formation of PdA^{3-} species is expected. The pH vs. 'a' curve and colour observation in titration mixture also show existence of blackish green hydroxo complex beyond 'a' = 2.0 (pH *ca.* 9.6).

The ligand FSB does not coordinate with Ag^+ ion as indicated by the 1:1, metal-ligand titration curve, which coincides with ligand titration curve. Cd^{2+}-FSB 1:1 titration mixture gradually changes to dark green between 'a' = 0 and 1 and subsequently to blackish red turbidity beyond 'a' *ca.* 1.0.

Comparison of equilibrium constants (K_1) for different metals in complex (MHA) follows the order $Pd^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+}$. A similar trend of equilibrium constant values in PdA and CuA complexes has also been observed.

As expected, the 1:1 Ni^{2+}-HSA mixture is initially in turbid form due to presence of unionised free ligand. The red colour gradually changes into a purple solution between 'a' = 1 and 2 (pH *ca.* 8.5) and the corresponding pH vs. 'a' curve shows a steep inflection at 'a' = 2. Thus, below 'a' = 2 equilibrium (ii) involving the coordination of ligand with the metal ion, through carboxylic acid and one phenolic oxygen, is expected to exist.

$$M + HB \rightleftarrows MHB; \quad K_1 = [MHB]/[M][HB] \quad (11)$$

The K_1 value was calculated using the following equations:

$$[HB] = \frac{C_B(2 - a)}{a_1} \quad (12)$$

$$[M] = a_2[HB] \quad (13)$$

$$[MHB] = C_M - [M] \quad (14)$$

where $a_1 = \frac{2[H^+]^2}{K_2^H K_3^H} + \frac{[H^+]}{K_3^H}$, $a_2 = \frac{[H^+]^2}{K_2^H K_3^H} + \frac{[H^+]}{K_3^H} + 1.$

The reaction mixture appears red and turbid from pH *ca.* 9.4 which finally yields a dark red precipitate with further increase in 'a' value. Beyond 'a' = 2 and before turbidity formation, nonprotonated complex NiB^{2-} is expected to occur in solution. Thus, for evaluation of equilibrium constant of reaction (15), eqns. (16)–(18) were utilized.

$$M + B \rightleftarrows MB; \quad K_1' = [MB]/[M][B] \tag{15}$$

$$\frac{K_1 a_4[H^+]}{K_4^H}[B]^2 + a_3[B] - C_B(3 - a) = 0 \tag{16}$$

$$[M] = a_4[B] \tag{17}$$

$$[MB] = C_M - [M] - [MHB] \tag{18}$$

where $a_3 = \frac{3[H^+]^3}{K_2^H K_3^H K_4^H} + \frac{2[H^+]^2}{K_3^H K_4^H} + \frac{[H^+]}{K_4^H}$, $a_4 = \frac{[H^+]^3}{K_2^H K_3^H K_4^H} + \frac{[H^+]^2}{K_3^H K_4^H} + \frac{[H^+]}{K_4^H} + 1.$

The titration mixture for Cu^{2+} system remains in turbid form (violet) in the pH range 3.8–11.0. The deviation of the ligand and complex titration curves from very low pH value (pH *ca.* 3.5) and the colour of the mixture (complex system) indicate the metal ligand inteaction. But, the turbidity formation did not allow the calculations.

The 1 : 1 Zn^{2+}-HSA mixture remains red in the pH range 2.8–11.0. Beyond pH *ca.* 10.0 (a = 3.0) the solution changes into a reddish purple turbidity. The pH vs. 'a' curve shows a steep inflection at 'a' = 2 (pH *ca.* 8.0) indicating formation of monoprotonated red complex. Further, between 'a' = 2 and 3 (pH *ca.* 10.0) equilibrium (15) is expected to exist involving the formation of ZnB^{2-} (red) species.

The reaction mixture for Pd^{2+} system yields a pinkish purple precipitate beyond pH *ca.* 9.5 ('a' = 2.55). It remains as reddish purple solution below pH of precipitation. The titration curve also shows a steep inflection at 'a' = 2 as in case of Ni^{2+} and Zn^{2+} systems.

From pH vs. 'a' curve and the colour change from violet to yellow between pH *ca.* 7.0 and 9.4 ('a' = 2.0) for Ag^+ system, existence of equilibrium (ii) can be concluded. The yellow colouration is due to formation of $AgHB^{2-}$ complex. Intensity of the yellow colour increases between 'a' = 2 and 3 as result of proton dissociation from the complex molecule. Beyond pH *ca.* 10.7 ('a' *ca.* 3) the solution turns into a brownish purple and tubid mixture.

The 1 : 1 Cd^{2+}-ligand mixture titration indicates the formation of reddish purple $CdHB^-$ complex between pH *ca.* 7.2 and 9.3. However, the mixture remains as reddish purple and turbid between pH *ca.* 9.2 and 11.0

(b) 1 : 2 *Metal-ligand complexes*: None of the metal ions chosen for the study forms 1 : 2 metal-FSB complex as evident by the corresponding titration curve. Their titration curves almost coincide with the composite curves obtained from the ligand and corresponding 1 : 1, metal-FSB systems. A similar trend has been noted in HSA systems. Also, the colour change in the titration mixture with change of pH has been observed as the mixed colour of ligand and 1 : 1, metal-ligand

mixture. The pH of precipitation or turbidity formation is almost identical with the corresponding 1:1, metal-ligand system. Thus, it has been concluded that under the descibed experimental condition, 1:2 metal-ligand complexes of FSB or HSA with the metal ions under study are not formed in solution.

(c) 2:1 *Metal-ligand complexes*: The 2:1 metal-FSB reaction mixtures of Ni^{2+}, Zn^{2+} and Cd^{2+} systems remain in turbid form from the pH of deviation of their corresponding titration curves from the ligand curve. Therefore, it is not possible to have any calculation on their metal-ligand equilibria. The titration mixture of Cu^{2+} system gradually changes to bluish green from pH *ca.* 6.2 to 7.0 ('a' *ca.* 2). This colour change may reasonably be considered due to formation of a new species. Existence of only 1:1 metal-ligand species along with the uncomplexed metal ion cannot be expected as such a mixture would appear blue and also turbid due to metal hydrolysis. The evaluated equilibrium constant obtained for reaction (19) using eqns. (20)–(22) is given in Table-1.

$$2M + H_2A \rightleftarrows M_2A + 2H^+; \quad K = [M_2A][H^+]^2/[M]^2[H_2A] \tag{19}$$

$$(X_2 - 2X_1)[H_2A]^2 + (2 + X_1X_3)[H_2A] - 2X_3 = 0 \tag{20}$$

$$[M] = \frac{2[H_2A]}{1 - X_1[H_2A]} \tag{21}$$

$$2[M_2A] = C_M - [M] - [MHA] - [MA] \tag{22}$$

where $X_1 = \frac{K_1}{[H^+]} + \frac{K'_1}{[H^+]^2}$, $X_2 = \frac{2K_1}{[H^+]}$, $X_3 = C_A(2 - a)$.

Between pH 7.0 and 11.0 the reaction mixture remains in turbid form. A colour change in 2:1 mixture of Pd^{2+}-FSB system (from green to blackish green) is also observed between 'a' = 1 and 2. The blackish green colour persists between pH 5.4 and 8.5 ('a' = 3.0). Thus, formation of Pd_2A, $Pd_2A(OH)^{2-}$ is expected between 'a' = 1 and 2, 2 and 3, respectively. Nature of titration curve of Pd^{2+} system is different from that of Cu^{2+} beyond 'a' = 2. The titration curve indicates a steep inflection at 'a' = 3.0 and the titration mixture remains turbid (black) from pH *ca.* 9.5. The following expressions, including eqn. (21) derived from mass and charge balance relations, were used for calculation of equilibrium constant of the reaction (23) existing between 'a' = 2 and 3:

$$M_2A + OH \rightleftarrows M_2A(OH); \quad K = [M_2A(OH)]/[M_2A][OH] \tag{23}$$

$$(X_6 - X_1X_5 - X_1X_4 + 3X_1^2)[H_2A]^3 + (X_4 + X_5 - 6X_1 - X_7X_1^2)[H_2A] + (3 - 2X_1X_7)[H_2A] - X_7 = 0] \tag{24}$$

$$[M_2A(OH)] = C_M - [M] - [MHA] - [MA] - [M_2A] \tag{25}$$

where $X_4 = \frac{4K_1}{[H^+]}$, $X_5 = \frac{2K'_1}{[H^+]^2}$, $X_6 = \frac{4K}{[H^+]^2}$, $X_7 = C_A(3 - \text{'a'})$.

Greater value of equilibrium constant in the coordination of second metal ion

with the ligand is exhibited in case of Pd^{2+} complex than the corresponding value of Cu^{2+} complex similar to their 1:1 metal-ligand complex systems.

The titration curve of Ni^{2+}-HSA system indicates that 2:1 metal-ligand species is not formed in solution. The colour of the titration mixture is also identical with 1:1, metal-ligand mixture below pH *ca.* 9.20. Beyond this pH the mixture turns into pinkish purple precipitate. The titration mixture of Cu^{2+} system remains in violet turbid form almost in the entire range of experimental pH. The existence of light red purple turbidity in the 2:1, Zn^{2+}-HSA mixture from pH *ca.* 8.5 also did not allow the calculation for M_2B complex. The reddish purple solution of 2:1, Pd^{2+}-HSA mixture yields a red precipitate from pH *ca.* 4.0 ('a' = 2). From the pH vs. 'a' curve formation of Pd_2B species may be expected but it would have not been possible to evaluate the equilibrium constant due to turbidity formation. Ag^+ system remains in brown turbidity form in the entire range of pH of metal-ligand interaction (pH 7.0–11.0). Similarly, no calculation could be made on 2:1, Cd^{2+}-HSA complex beyond 'a' *ca.* 2, where attachment of second metal with the 1:1 metal-ligand complex is expected, as the reaction mixture remains turbid (purple) between pH *ca.* 8.8 and 11.0

In the complex MHA there are three possible positions of attachment of metals with the ligand: (i) phenolic group (1) of naphthalene ring with two $—SO_3H$ groups—azo group (2) between the two naphthalene rings, both with $—SO_3H$ groups, (ii) phenolic group (1)-azo group (3) between the two naphthalene rings, one with no $—SO_3H$ group and the other with two $—SO_3H$ groups and (iii) phenolic group (4) of naphthalene ring with no $—SO_3H$ group-azo group (3). Coordination through positions (3) and (4) are expected more favourable owing to their ability to form five-membered chelate ring and the poor inductive effect on account of $—SO_3H$ group. The other phenolic group (1), instead of being in free ionized form at higher pH values, appears to be coordinated with metal in MA. Under this new stuctural arrangement, involving ligand coordination through two phenolic and one azo groups, the FSB would behave as a tridentate ligand. Further, in 2:1, metal-ligand complex (M_2A) the two metals are expected to be attached with the ligand at separate positions: phenolic oxygen (1)-azo group (2) and phenolic oxygen (4)-azo group (3). Similarly, during dissociation of proton from MHB, where metal is attached through oxygen donors of carboxylic and phenolic groups (in *ortho* position), bonded metal is expected to be further complexed through the azo and the other phenolic group. But, unlike corresponding FSB complex here one of the coordinated groups $—COO^-$ is expected to remain free in MB due to unfavourable position of the two phenolic, $—COO^-$ and azo groups to act as a tetradentate ligand. Thus, in this nonprotonated complex the metal is to be bonded through the azo and the two phenolic donors. Parallel structural changes involving decoordination of some donors at higher pH value on account of coordination saturation of some oligopeptide derivative complex with transition metal ions have also ben reported by Martell and Motekaitis[2].

Maximum % M associated with different species, the corresponding pH and the pH range of their existence in significant amount in 1:1, 2:1 metal-FSB and 1:1 metal-HSA complex systems were obtained (Table-2) from the distribution curves plotted between percentage of metal distributed among various species

TABLE-2
MAXIMUM % M-DISTRIBUTED IN DIFFERENT SPECIES, THE CORRESPONDING pH and the pH RANGE OF THEIR EXISTENCE IN SIGNIFICANT AMOUNT IN DIFFERENT METAL-FSB/HSA RATIO SYSTEMS

Metal-ligand system	*Maximum % M distributed in the species						
	M	MH_2B	MHA/MHB	MA	MA(OH)	M_2A	$M_2A(OH)$
Ni-FSB (1:1)	97.1 (9.0, 9.0–. . .)	—	43.0 (10.0, 9.4–. . .)	—	—	—	—
Cu-FSB (1:1)	99.2 (4.6, 4.6–8.0)	—	55.0 (6.2, 4.8–8.0)	46.0 (9.8, 6.6–. . .)	73.0 (10.8, 9.8–. . .)	—	—
Cu-FSB (2:1)	93.5 (6.0, 6.0–. . .)	—	6.3 (6.8, 6.8–. . .)	34.0 (6.8, 6.8–. . .)	—	34.8 (6.8, 6.8–. . .)	—
Pd-FSB (1:1)	100.0 (3.6, 3.6–8.2)	—	42.1 (5.6, 3.6–8.2)	100.0 (8.8, 5.0–. . .)	62.9 (10.8, 9.4–. . .)	—	—
Pd-FSB (2:1)	100.0 (3.8, 3.8–7.4)	—	16.5 (4.8, 3.8–6.6)	2.5 (5.4, 4.4–7.0)	—	.12.5 (5.0, 4.0–6.6)	100.0 (7.4, 4.8–. . .)
Cd-FSB (1:1)	98.2 (9.4, 9.4–. . .)	—	58.0 (10.4, 9.6–. . .)	—	—	—	—
Ni-HSA (1:1)	98.6 (3.4, 3.4–7.6)	95.0 (6.8, 3.4–. . .)	22.3 (9.2, 8.8–. . .)	—	—	—	—
Zn-HSA (1:1)	97.8 (3.8, 3.8–8.0)	94.4 (7.4, 4.0–. . .)	73.1 (9.8, 8.2–. . .)	—	—	—	—
Pd-HSA (1:1)	100.0 (3.0, 3.0–7.4)	100.0 (7.4, 3.0–. . .)	30.1 (9.4, 8.0–. . .)	—	—	—	—
Ag-HSA (1:1)	98.4 (7.0, 7.0–. . .)	78.3 (9.6, 7.2–. . .)	56.3 (10.6, 9.8–. . .)	—	—	—	—
Cd-HSA (1:1)	100.0 (7.2, 7.2–. . .)	60.0 (9.2, 7.4–. . .)	—	—	—	—	—

*Under the experimental pH condition.
(. . ., . . . –. . .) pH of Maximum % M distribution. pH-range of existence of the species, respectively.

and pH (Fig. 2 Pd^{2+}-FSB/HSA system; others omitted). Fig. 2 shows that a

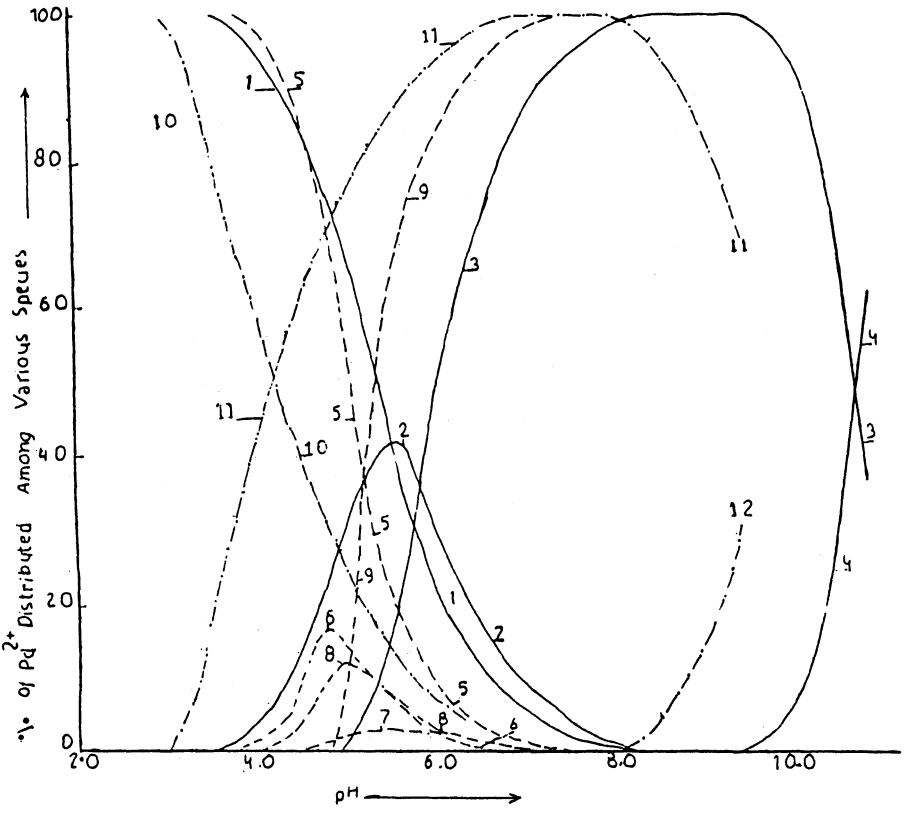


Fig. 2 Distribution of Pd^{2+} in various species with pH: Curves—1 : 1, metal-FSB system [1-Pd^{2+}, 2-PdHA, 3-PdA, 4-PdA(OH)], 2 : 1, metal-FSB system [5-Pd^{2+}, 6-PdHA, 7-PdA, 8-Pd_2A, 9-$Pd_2A(OH)$]; 1 : 1, metal-HSA sytem [10-Pd^{2+} 11-PdH_2B, 12-PdHB], respectively.

progressive decrease in percentage of free Pd^{2+} ion is accompanied by an increase in pH in all the systems. Amount of free metal ion in 1 : 1 metal-FSB mixture is insignificant beyond pH *ca.* 8.2. At the same time formation of PdHA occurs. It increases up to pH 5.6. Further beyond this pH concentration of PdHA decreases owing to dissociation of proton, forming nonprotonated PdA complex. Appreciable quantity of PdA(OH) lies in the pH range 9.4– . . . . Gradual decrease in free metal percentage with increase of pH is also visible (Fig. 2) in case of 2 : 1, Pd^{2+}-FSB system. Above pH *ca.* 7.4 it becomes negligeble due to formation of 2 : 1 complex species. Maximum percentages of PdHA, PdA, Pd_2A, $Pd_2A(OH)$ formed in mixture are 16.5, 2.5, 12.5 and 100% respectively under the experimental 2 : 1 metal-ligand ratio and pH conditions.

In 1 : 1 Pd^{2+}-HSA system also amount of free metal becomes negligible at pH

ca. 7.4 due to formation of 1 : 1 complexes (PdH_2B and PdHB). Maximum amount of PdH_2B and PdHB present in solution has been recorded as 100% (pH 6.8), 30.1 (pH 9.4) respectively.

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