

Potentiometric Study of Mixed Ligand Chelates of Transition Metal Ions with 5-Chlorosalicylidene-2-chlorobenzylamine as the Primary Ligand and 5-Chlorosalicylidene-4-aminobenzenesulphonamide as the Secondary Ligand

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Binary and ternary complexes of the type M-L and MXL [M = Cu(II), Ni(II), Co(II), Mn(II) and Fe(III)]; X = 5-chlorosalicylidene-2-chlorobenzylamine and L = 5-chlorosalicylidene-4-aminobenzenesulphonamide have been examined pH-metrically at 27 °C and $\mu = 0.1$ M (KCl) in 75 / 25 % v/v dioxane-water mixture. The logarithms of the values of formation constants for M-L and MXL systems [M = Cu(II), Ni(II), Co(II), Mn(II) and Fe(III)] are calculated as 7.64 and 5.96; 8.05 and 4.71; 7.86 and 4.60; 7.95 and 4.66; 10.07 and 8.88, respectively.

Key Words: Potentiometric, Mixed ligand chelates, Transition metal, 5-Chlorosalicylidene-2-chlorobenzylamine, 5-Chlorosalicylidene-4-aminobenzenesulphonamide.

INTRODUCTION

The importance of Schiff bases and their complexes with transition metals have been well emphasized by researchers¹⁻³. Many attempts have been made to evaluate the stability constants of the Schiff bases and the different factors affecting the stability of metal chelates⁴⁻⁶. The protonation constants of Schiff bases obtained from 5-chlorosalicylaldehyde and their Ni(II) complexes have been determined potentiometrically⁷.

We report here the results of our studies on mixed ligand complexes of Cu(II), Ni(II), Co(II), Mn(II), Fe(III) with 5-chlorosalicylidene-2-chlorobenzylamine as primary ligand and 5-chlorosalicylidene-4-aminobenzenesulphonamide as secondary ligand in 75/25 % v/v dioxane water mixture employing modified form of Irving-Rossotti⁸ pH-metric titration technique. Under identical conditions the binary metal complexes of 5-chlorosalicylidene-4-aminobenzenesulphonamide have been investigated.

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EXPERIMENTAL

The pH titrations were carried out on an expanded scale pH-meter model No. EQ-614 supplied by Euiptronics, a precision research pH-meter with a wide range glass electrode and a calomel reference electrode. The pH meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale is 0.01-pH unit.

Synthesis of Schiff base

5-Chlorosalicylidene-2-chlorobenzylamine: 5-Chlorosalicylaldehyde and 2-chlorobenzylamine was taken in stoichiometric ratio in a round bottom flask and refluxed in methanol using a waterbath. TLC monitored the reaction. After the reaction was over, the excess solvent was distilled and a solid product was obtained on cooling. This was filtered under suction and recrystallized from methanol to obtain the pure compound.

5-Chlorosalicylidene-4-aminobenzenesulphonamide: 5-Chlorosalicylaldehyde and 4-aminobenzenesulphonamide taken in stoichiometric ratio was refluxed in methanol. TLC monitored the reaction. The solid product obtained was recrystallized from methanol. The pH-meter was standardized with buffer solutions of pH 7 and 4.

The ligand solutions were prepared in dioxane. All the metal solutions were prepared and standardized by conventional procedures⁹. A solution of potassium hydroxide was prepared (0.2 M) in double distilled carbonate free water and standardized using standard succinic acid. All the titrations were carried out in an inert atmosphere of nitrogen. All measurements were carried out at a temperature of 27.0 ± 0.5 °C. The method of Bjerrum and Calvin as modified by Irving and Rossitti was used to determine \bar{n} and pL values. All the chemicals and solvents used in the experiment were of analytical grade.

pH-metric titrations: For the determination of proton-ligand stability constant of the secondary ligand and metal ligand stability constant of the binary and ternary complexes the following set of solutions were prepared keeping the total volume $V_0 = 40$ mL. All the titrations were carried out in 75 % (v/v) dioxane-water at ionic strength $\mu = 0.1$ M. The solutions were titrated against standard 0.2 M KOH solution.

Binary system: (i) 4.0 mL of 0.16 M HCl + 3.36 mL of 1 M KCl + 2.64 mL distilled water + 30 mL dioxane. (ii) 4.0 mL of 0.16 M HCl + 3.36 mL of 1 M KCl + 2.64 mL distilled water + 4.0 mL of 0.04 M secondary ligand solution (to give final concentration = 0.004 M) + 26 mL dioxane. (iii) (i) 4.0 mL of 0.16 M HCl + 3.24 mL of 1 M KCl + requisite amount of metal chloride solution (to give 0.001 M concentration in final solution) + requisite amount of distilled water + 4.0 mL of 0.04 M secondary ligand solution + 26 mL dioxane. (In case of Fe(III)-ligand system 1 M KCl required to adjust ionic strength = 3.12 mL).

Ternary system: (i) 4.0 mL of 0.16 M HCl + 3.36 mL of 1 M KCl + 2.64 mL distilled water + 30 mL dioxane. (ii) 4.0 mL of 0.16 M HCl + 3.24 mL of 1 M KCl + requisite amount of metal chloride solution (to give 0.001 M concentration in final solution) + requisite amount of distilled water + 4.0 mL of 0.01 M primary ligand solution + 4.0 mL of 0.01 M secondary ligand solution + 22 mL dioxane.

The ratio of metal (M): secondary ligand (L) was maintained at 1:4 in each of the binary system and the ratio of metal: primary ligand (X): secondary ligand (L) was maintained at 1:1:1 in each of the ternary system.

RESULTS AND DISCUSSION

Proton-ligand stability constants: The plot of volume of alkali (KOH) against pH values was used to evaluate the proton-ligand stability constants of 5-chlorosalicylidene-4-aminobenzenesulphonamide (CSABS). The deviation of the secondary ligand titration curve from the free acid titration curve ($V_2 - V_1$) was used to evaluate the formation constant \tilde{n}_A . The proton ligand formation curve was then obtained by plotting the values of \tilde{n}_A vs. pH values. The values of $\log K_1^H$ and $\log K_2^H$ were evaluated graphically by half-integral method (A). In a similar way, the values of $\log K_1^H$ and $\log K_2^H$ were evaluated by the graphical method (B) wherein the graphs $\log \tilde{n}_A/1 - \tilde{n}_A$ vs. pH values and $\log 2 - \tilde{n}_A/1 - \tilde{n}_A$ vs. pH values are plotted. The values are given in Table-1.

TABLE-1
PROTON LIGAND STABILITY CONSTANTS

| Ligand | $\log K_1^H$ | $\log K_2^H$ | $\log K_1^H$ | $\log K_2^H$ | $\log \beta^H$ | |
|--------|------------------------|--------------|----------------------|--------------|----------------|-------|
| | Half integral method A | | Graphical method (B) | | (A) | (B) |
| CSABS | 8.80 | 2.75 | 8.8 | 2.75 | 11.55 | 11.55 |

CSABS = 5-Chlorosalicylidene-4-aminobenzenesulphonamide.

Metal-ligand stability constants of binary complexes: The metal-ligand stability constant of binary complexes were evaluated assuming that no hydrolyzed products or polynuclear complexes are formed. An examination of titration curves indicates that complexes formation has taken place in the solution on the following grounds: (i) the metal titration curves showed displacement with respect to ligand titration curves along the volume axis. This indicates the affinity of ligand with metal ions, which release protons and produce the volume difference ($V_3 - V_2$), (ii) the colour change of the ligand in presence of metal ions appeared showing the formation of new species, (iii) the hydrolysis of the metal ions was suppressed due to the complex formation and the precipitation did not appear during the titrations.

From the ligand and metal titration curves the values of \bar{n} and from that the values of pL were evaluated. The formation curves obtained were used to evaluate the metal ligand stability constants by methods (A) and (B) and are presented. The values are given in Table-2.

TABLE-2
METAL-LIGAND STABILITY CONSTANTS OF
BINARY COMPLEXES

| System | log K ₁ method | | log K ₂ method | | log β | |
|-----------------|---------------------------|-------|---------------------------|------|-------|-------|
| | (A) | (B) | (A) | (B) | (A) | (B) |
| [Mn(II)-CSABS] | 7.95 | 7.89 | 2.75 | 2.76 | 10.70 | 10.65 |
| [Co(II)-CSABS] | 7.86 | 7.85 | 2.85 | 2.90 | 10.71 | 10.75 |
| [Cu(II)-CSABS] | 7.64 | 7.66 | 3.95 | 3.99 | 11.59 | 11.65 |
| [Ni(II)-CSABS] | 8.00 | 8.05 | 3.61 | 3.60 | 11.61 | 11.65 |
| [Fe(III)-CSABS] | 10.02 | 10.07 | – | – | – | – |

The variation of \bar{n} was found to be 0 to 2 for complexes of Mn(II), Co(II), Cu(II) and Ni(II) which indicated that the composition of complexes was 1:2 in solution. In case of Fe(III) complexes the variation of \bar{n} was found to be 0 to 1 indicating the formation of 1:1 complexes hence log K₂ could not be determined.

Metal-ligand stability constants of ternary complexes

(1) The titration curves for all mixed ligand systems containing metal 5-chlorosalicylidene-2-chlorobenzylamine (CSCBA) and 5-chlorosalicylidene-4-aminobenzenesulphonamide (CSABS) *i.e.*, M-CSCBA-CSABS were drawn. The titration curves for the ternary complexes M(II)-X-L where M = Cu(II), Ni(II) coincided with those for the 1:L [M(II)-X] binary complexes in the pH region < 6.2, where 1:1 [M(II)-X] binary complexes were formed. This indicates the formation of only [M(II)-X] complexes and the non-coordination of L with M(II) ion in this region. Beyond pH 6.5 the mixed ligand [M(II)-X-L] curve diverges from the binary [M(II)-X] curve suggesting the coordination of L as a secondary ligand in presence of X.

However the ternary titration curve [M(II)-X-L] where M = Co(II), Mn(II) runs to the left of the [M(II)-X] binary complexes curve upto pH~6.5. This shows the simultaneous formation of binary complexes of the secondary ligand with the metal ion. In case of [Fe(III)-X-L] system the ternary curve coincides with 1:1 [Fe(III)-X] curve upto pH~3.5 and then separates which indicates that the [M-X] binary complexes is stable upto pH 3.5 and beyond pH 3.5 ternary complex is formed.

Hence the formation of [M(II)-X-L] ternary complex could be considered in a stepwise equilibria eqns. 1 and 2.



where X and L are Schiff bases and contain N, O⁻¹ donor sites.

(2) The horizontal distance measured between ternary complexes curves and secondary ligand curve (V₃-V₂) show the positive difference which proves the earlier release of protons in the formation of ternary complexes.

(3) The titration curves indicate that the hydrolysis of metal ions was suppressed and precipitation did not result.

The values of \bar{n} vary from 0 to 1, thus confirming the formation of 1:1:1 mixed ligand complexes. the values of $\log K_{MXL}^X$ have been evaluated from the formation curves (\bar{n} vs. pL). At $\bar{n} = 0.5$, in the formation curve, pL = log K. The log K values were also evaluated by the graphical method (B) and are presented in Table-3.

TABLE-3
METAL-LIGAND STABILITY CONSTANTS OF
TERNARY COMPLEXES

| System | log K Method A | log K Method B |
|----------------------|----------------|----------------|
| [Mn(II)CSCBA-CSABS] | 4.68 | 4.66 |
| [Co(II)CSCBA-CSABS] | 4.58 | 4.60 |
| [Cu(II)CSCBA-CSABS] | 5.96 | 6.01 |
| [Ni(II)CSCBA-CSABS] | 4.70 | 4.71 |
| [Fe(III)CSCBA-CSABS] | 8.88 | 8.90 |

The values for metal-ligand stability constants $\log K_{MXL}^X$ are found to be less than for binary complexes. This is because in the formation of ternary complexes lesser no. of sites are available for incoming ligand as compared to binary complexes. The Irving-Williams natural order of stability of complexes is Mn(II) < Co(II) < Ni(II) < Cu(II) < Fe(III). In present study of the ternary complexes the order determined is Co(II) < Mn(II) < Ni(II) < Cu(II) < Fe(III).

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(Received: 12 December 2006; Accepted: 29 September 2007) AJC-5921