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Formation Constants of the Chelates of 2-Hydroxybenzilidine-*o*-Aminobenzothiazole with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Ions

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Proton dissociation constant of the ligand and the stability constants of the complexes of Co(II), Ni(II), Cu(II), Zn(Il) and Cd(II) with 2-hydroxy-benzilidine-*o*-aminobenzothiazole have been determined potentiometrically at 30 ± 0.1°C and at ionic strength 0.1 M in 75 : 25 (V/V) dioxane-water medium. log K_1 and log K_2 values have been determined. The stabilities of the chelates follow the order Cu > Cd > Co > Ni > Zn.

Key Words: Formation constants, Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Chelates, 2-Hydroxybenzilidine-*o*-Aminobenzothiazole.

INTRODUCTION

The formation curve of a system of metal-ligand complexes can be obtained directly from pH-meter readings during the titration without the knowledge of hydrogen-ion concentration or activity. Simple general equations, which can be used for all ligands, which are conjugate bases to weak acids, are derived and their applications to specific systems are illustrated. The method, which is valid both in water and in mixed solvents, gives stoichiometric stability constants of metal complexes. Stoichiometric stability constants of the ligand-proton complexes can also be obtained.

EXPERIMENTAL

A precision research pH meter model No. EQ-614 supplied by Equiptronics with a wide range glass electrode and a calomel reference electrode was used for pH measurements. The pH meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale is 0.01 pH unit.

Solutions of metal perchlorates were used to avoid complexing of metal ions by anions. Metal carbonates (A.R.) or oxides were dissolved in a known volume of 1.6 M perchloric acid (E. Merck). The solutions were then made of known volume by adding distilled water. The concentrations of the solutions were determined by titrimetric method[1].

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1 M) solution keeping the total volume 40 mL.

(i) 5 mL of (0.16 M) $HClO_4$ + 5 mL of (0.64 M) $NaClO_4$ + 30 mL of dioxane.
(ii) 5 mL of (0.16 M) $HClO_4$ + 5 mL of (0.64 M) $NaClO_4$ + requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution +30 mL of dioxan.
(iii) 5 mL of (0.64 M) $NaClO_4$ + 5 mL of (0.001 M) metal salt solution in (0.16 M) $HClO_4$ + requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution + 30 mL of dioxan.

The method of Irving and Rossotti[2] was applied to find out the values of $\bar{n}$ and pL.

RESULT AND DISCUSSION

Proton ligand stability constants: The values of $\bar{n}A$ at various pH values were calculated from the acid titration curve (A) and ligand titration curve (B) by using the formula of Irving and Rossotti[2]. Proton-ligand stability constants were calculated from the plot of $\bar{n}A$ *vs.* pH (Fig. 1). The pK_1H and pK_2H values corresponding to $\bar{n}A = 0.5$ and $\bar{n}A = 1.5$ were obtained from the curve. However, the best values of pK_1H and pK_2H of the ligand were found from the plot of log nA/(1-nA) *vs.* pH and log {(2 – nA)/(1 – nA)} (Fig. 2). The two values agree fairly well.

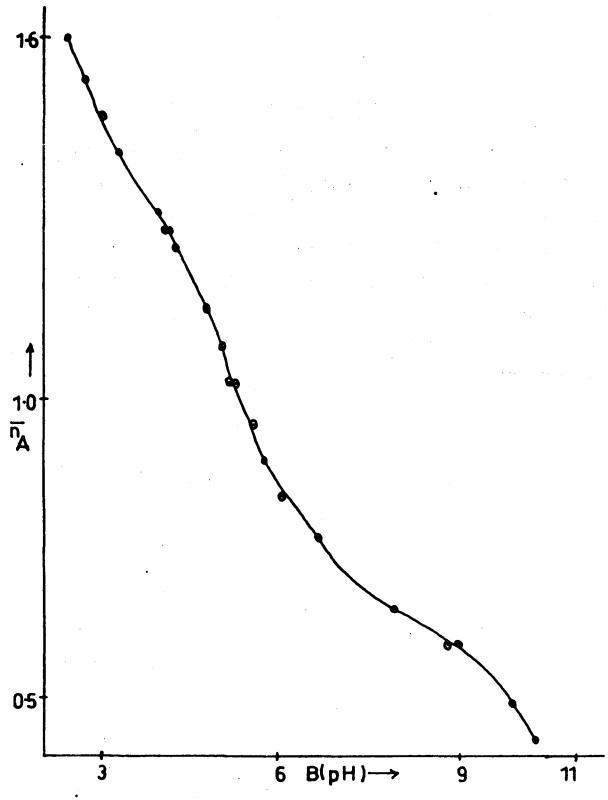

Fig. 1. 2-Hydroxy-benzilidine-*o*-aminobenzothiazole Formation Curve.

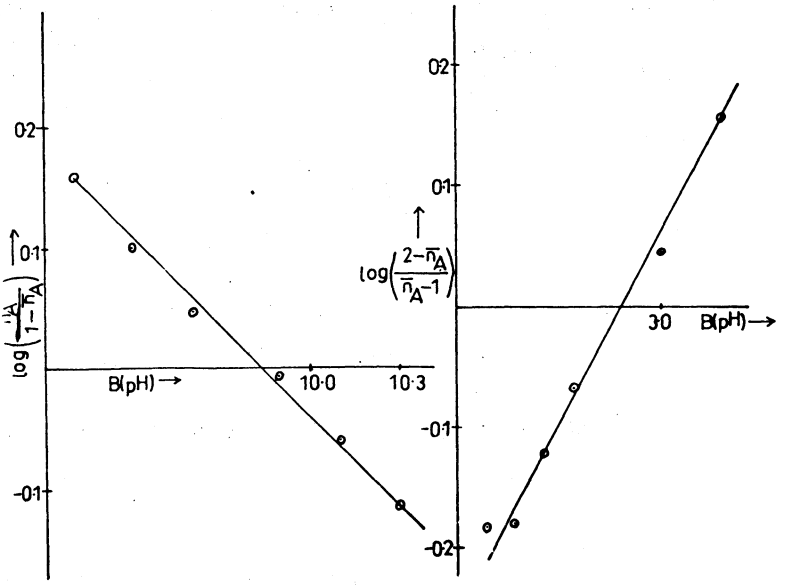

Fig. 2. 2-Hydroxy-Benzilidine-*o*-aminobenzothiazole.

Metal ligand stability constants: From the three titration curves, $\bar{n}$ values were determined at various pH values. From these data the corresponding pL values were calculated. The $\bar{n}$ values were then plotted against the corresponding pL values to get the formation curves of the metal complex equilibria (Fig. 3).

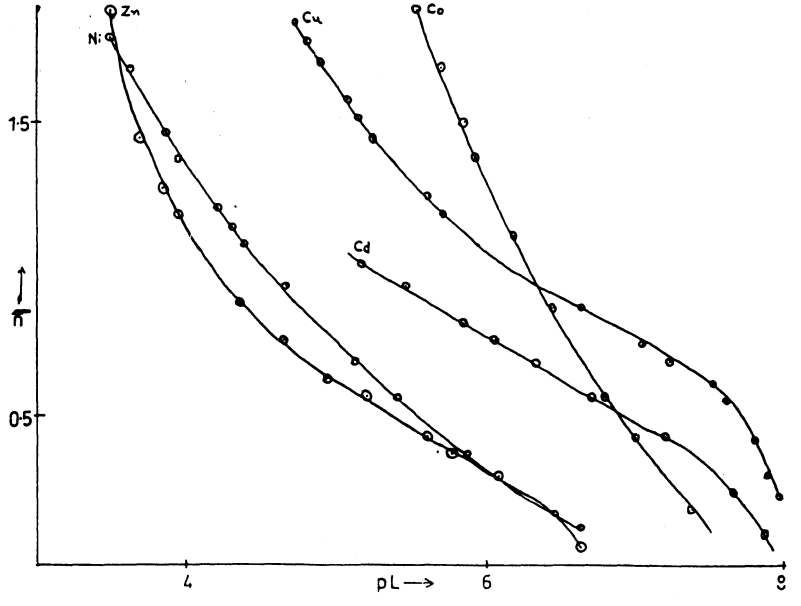

Fig. 3. Metal-Ligand Systems of 2-Hydroxy-Benzilidine-*o*-aminobenzothiazole Formation Curves.

It is observed that the metal-ligand curve is well separated from the ligand titration curves, suggesting thereby that the liberation of proton is due to chelation. From these formation curves the values of stability constants log K_1 and log K_2 were determined which correspond to the pL values at $\bar{n} = 0.5$ and 1.5 respectively. The most representative values are recorded in Table-1.

TABLE-1
STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES (a)

Temp. (t) = 30°C Ionic strength (μ) = 0.1 M

Cations	H^+	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
log K_1	9.85	6.90	5.54	7.65	5.43	6.93
log K_2	2.80	5.83	3.83	5.18	3.62	–

(a) H^+ corresponds to the species LH and LH_2 respectively, while for the metal ions K_1 and K_2 correspond to the species ML and ML_2 respectively.

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