Potentiometric Studies on Some Bivalent Metal Complexes With N-(2-Hydroxy-5-Phenylbenzylidene)-2-Amino-Benzothiazole

M.S. Mayadeo and S.V. Joshi

Department of Chemistry, Ramnarain Ruia College, Matunga, Bombay - 400 019

Potentiometric studies have been carried out on metal complexes of Cu^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, and Cd^{2+} with N-(2-hydroxy-5-phenylbenzylidene) -2- aminobenzothiazole. The dissociation constants (pK_1 and pK_2) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 30 ± 0.1°C and at ionic strength 0.1 M in 75:25 (v/v) dioxane-water medium. The order of stability constants of the chelates is found to be:

$$Mg^{2+} < Cd^{2+} < Ni^{2+} \quad Co^{2+} < Zn^{2+} < Cu^{2+}$$

Plots of stability constants (log K_1) vs different parameters like atomic number, reciprocal of ionic radii, electronegativity, second ionisation potential were drawn to explore possible correlations.

In the present communication the successive stability constants of the complexes of N-(2-hydroxy-5-phenylbenzylidene)-2-aminobenzothiazole with various bivalent metal ions have been determined potentiometrically following Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti .

EXPERIMENTAL

The ligand N-(2-hydroxy-5-phenylbenzylidene)-2-aminobenzothiazole was prepared by dissolving 5 gm. of 2-hydroxy-5-phenyl benzaldehyde in 30 ml. of ethanol. To this was added equimolar quanitty of 2-aminobenzothiazole and the reaction mixture was refluxed on a water bath for one hour. After cooling, the solution was filtered to get a crude product which was repeatedly crystallised from ethanol to get an analytically pure compound. The purity of the compound was tested by TLC and elemental analysis.

All other experimental conditions were the same as in reference 2.

RESULTS AND DISCUSSION

In the ligand it is phenolic (OH) group which takes part in complex formation and the proton is replaced by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, 'Y', the number of dissociable protons attached to each ligand molecule is one.

From the titration curves using solutions (i) and (ii), $\bar{n}$ at various 'B' values (pH meter readings) were calculated and a curve between 'B' and the corresponding n values was plotted (Fig.1). The

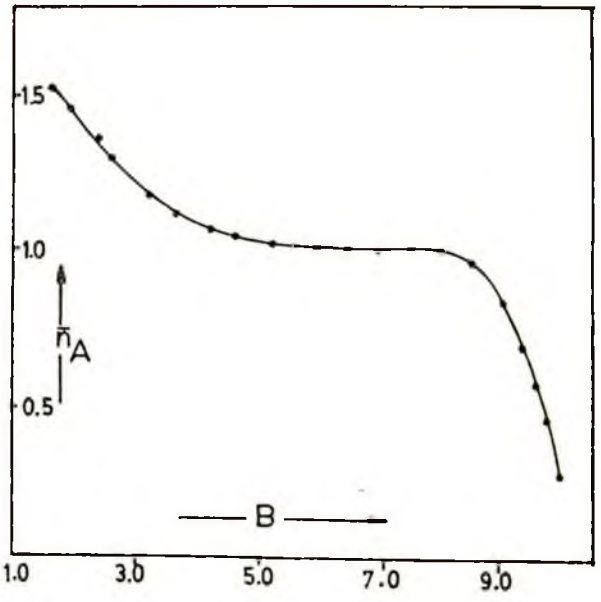


Fig. 1 N-(2-Hydroxy-5-Phenylbenzylidene)-2-Aminobenzothiazole. formation curve.

formation curve extends over a range of $0.276 < \bar{n}_A < 1.529$ and is wavelike. The value of pK_1^H which corresponds to phenolic 'H' was evaluated from the half integral point at $\bar{n} = 0.5$ while that of pK_2^H which corresponds to the association of proton to nitrogen was obtained at $\bar{n} = 1.5$.

The plots of log $(\bar{n}_A/1-\bar{n}_A)$ vs 'B' and log $(2-\bar{n}_A/\bar{n}_A$

-1) vs. 'B' were also drawn. From the former, pK_1^H was evaluated and from the later, pK_2^H was evaluated. These values agree quite well with those obtained by the half integral method. This is presented in Table 1.

TABLE 1

STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES

t = 30 ± 0.1°C μ =0.1 M

	H^+	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Mg^{2+}	Cd^{2+}
log K_1	9.625	8.03	5.33	5.80	5.43	3.66	4.74
log K_2	1.850	-	-	-	-	-	-

* For proton association K_1 and K_2 correspond to the species LH and LH_2^+ respectively, while for metal ions K_1 corresponds to the species ML

From the titration curves using solutions (ii) and (iii) $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of the metal complex equilibria (Fig.2). From these formation

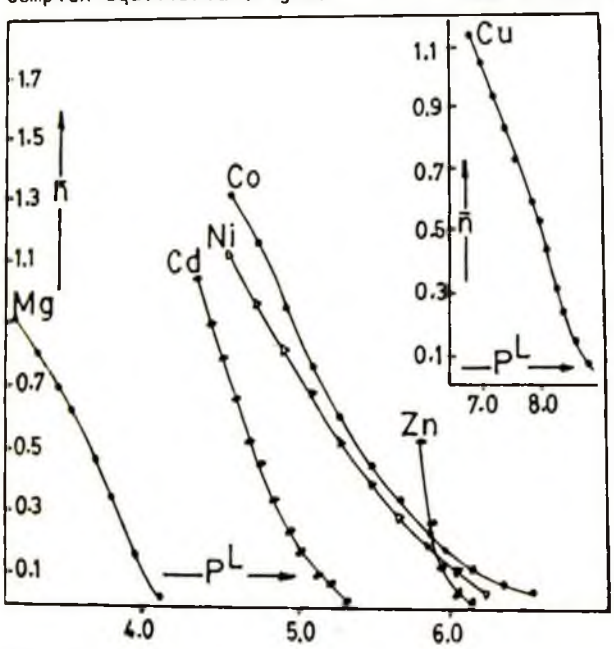
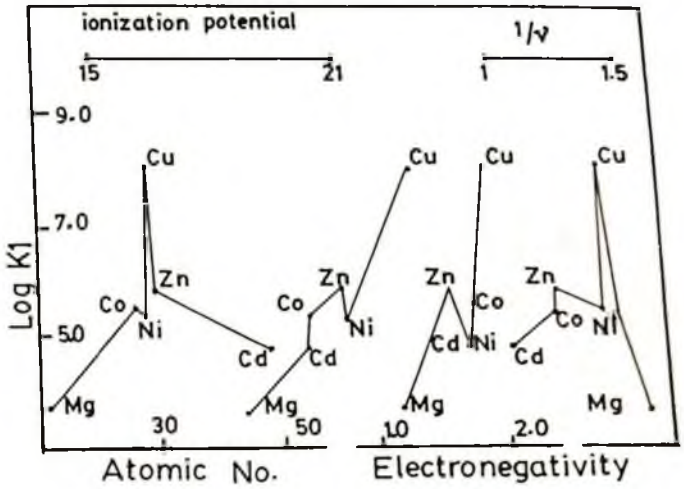


Fig. 2 Metal-ligand systems of N-(2-Hydroxy-5-Phenylbenzylidene)-2-Aminobenzothiazole. formation curves.

curves, values of stability constants log K_1 were determined which correspond to the pL values at $\bar{n}$ = 0.5. The plots of log $(\bar{n}/1-\bar{n})$ vs. pL were also drawn for these systems. In all cases values



of log K_1 evaluated from the linear plots agree quite well with those values obtained from the half integral method. The most representative values are recorded in Table-1.

The log K_2 values could not be evaluated due to precipitation.

The order of stability of the bivalent metal chelates was found to be:

$$Mg^{2+} < Cd^{2+} \quad Ni^{2+} < Co^{2+} \quad Zn^{2+} < Cu^{2+}$$

The plots of log K_1 of different metals with atomic number, ionization potential, electronegativity and reciprocal of ionic radii have been drawn. The results are similar to that observed earlier.

ACKNOWLEDGEMENT

The authors wish to record their sincere thanks to Dr. D.G. Vartak, B.A.R.C. Bombay, for his valuable suggesstions in accomplishing this work.

REFERENCES

1. H. Irving and H.S. Rossotti, J. Chem. Soc., 2904, (1954)

2. M.S. Mayadeo and S.V. Joshi, J. Electrochem. Soc. India. 34(3),(1985) 198.