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

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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)-benzylamine. The dissociation constants (pK_1 and pK_2) of the reagent and the formation constants of the 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:

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

Plots of stability constants (log K) vs different parameters like atomic number, elecatronegativity, reciprocal of ionic radii 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)-benzylamine with various bivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti (1).

EXPERIMENTAL

The ligand N-(2-hydroxy-5-phenylbenzylidene)-benzylamine was prepared by mixing a solution of 5 gm. of 4-hydroxy-3-aldehydobiphenyl in 30 ml. of ethanol and an equimolar quantity of benzylamine and refluxing the reaction mixture for 15 minutes on a water-bath. After cooling, the solution was filtered to get a crude product. This was repeatedly crystallised from ethanol to get an analytically pure compound. The purity was tested by TLC and elemental analysis.All other conditions of experiment were the same as in ref.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), $\bar{n}_A$ at various B values (pH meter readings) were calculated and plotted in (Fig. 1). The formation curve extends over a rnge $0.447 < \bar{n}_A$ 1.928 and is wavelike. The value of pK_1^H which corresponds to phenolic 'H' and pK_2^H which corresponds to the association of proton to nitrogen was obtained by half integral method by the value of $\bar{n}_A$=0.5 and at $\bar{n}_A$ =1.5.

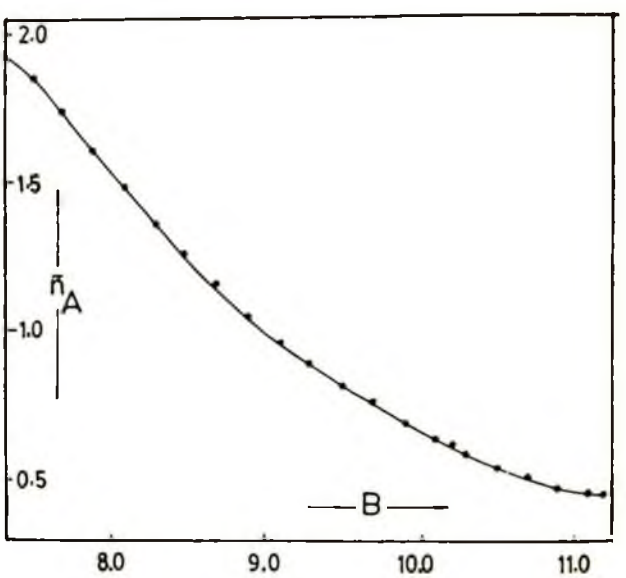


Fig. 1 Formation Curves of N-(2-Hydroxy-5-Phenylbenzylidene)-Benzylamine.

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 latter pK_2^H was evaluated. These values agree quite well with those obtained by the half integral method.

From the titration curves (ii) & (iii) the metal formation curves are constructed (Fig. 2). From these formation curves the values of stability constants log K_1 were determined which correspond to the pL values at $\bar{n}$ = 0.5 and was confirmed from the plots of log ($\bar{n}$/1-$\bar{n}$) vs pL. In case of cadmium, the maximum experimental value of

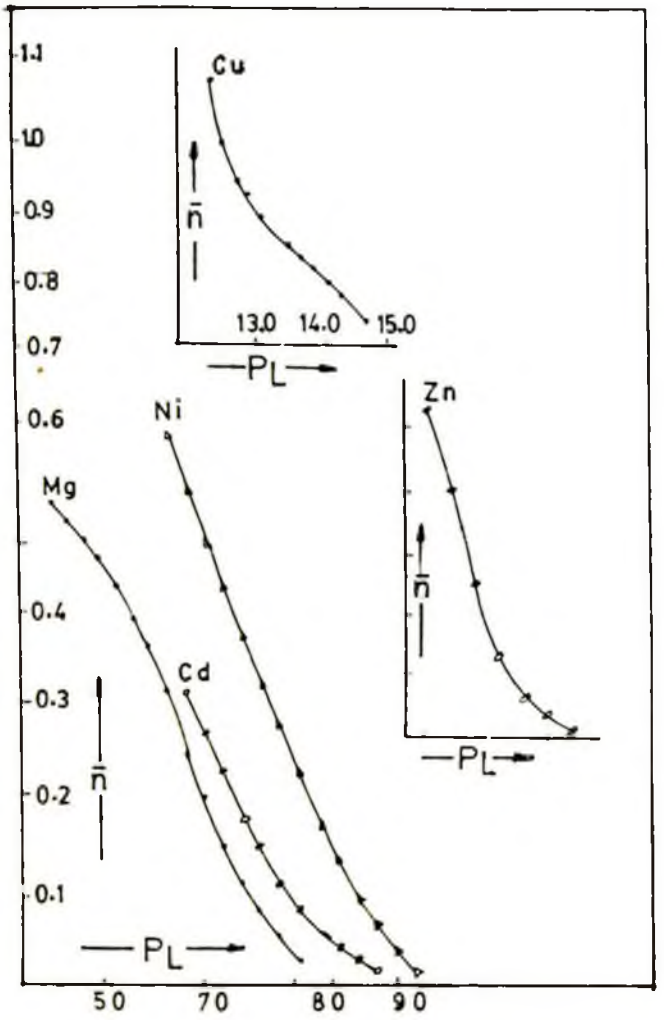


Fig. 2 Metal-Ligand systems of N-(2-Hydroxy-5-Phenylbenzylidene)-Benzylamine. Formation Curves.

$\bar{n} < 0.4$. However, in this case, complex log K_1 value was evaluated by the extrapolation of the linear plot of log $(\bar{n}/1-\bar{n})$ vs pL. In all cases values of log K_1 evaluated from the linear plots agree quite well with those values obtained by half integral method.

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

The most representative values are recorded in Table-1.

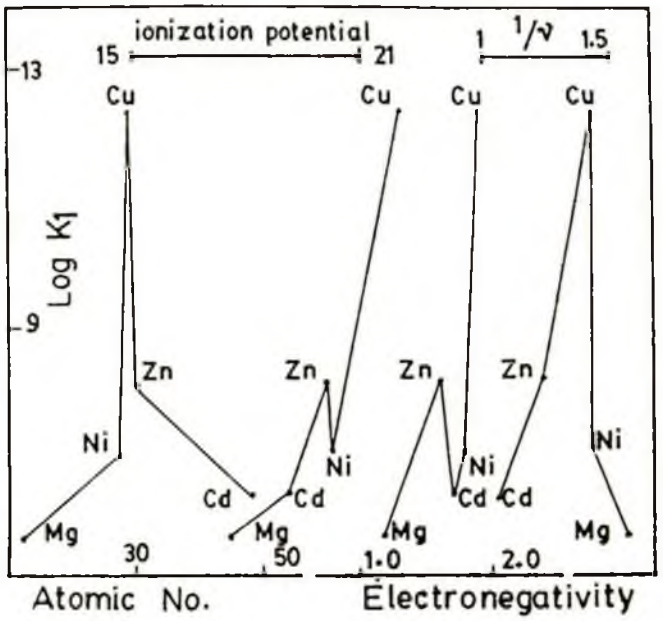


TABLE 1

STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

T = 30 ± 0.1°C μ = 0.1 M

	H^+	Cu^{2+}	Ni^{2+}	Zn^{2+}	Mg^{2+}	Cd^{2+}
log K_1	10.700	12.35	7.00	8.10	5.62	6.30
log K_2	8.075	-	-	-	-	-

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

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

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

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.

REFERENCES

1. M. 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.