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

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The proton-ligand stability constant (pK^H) of the ligand, N-(2-hydroxy-5-phenylbenzylidene) -phenylhydrazine and its metal-ligand stability constants with Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mg^{2+} and Zn^{2+} ions have been determined potentionmetrically at 30.0 ± 0.1°C in dioxane-water medium (75:25 v/v) and at constant ionic strength (0.1 M $NaClO_4$) in a nitrogen atmosphere. The order of stability constants (log K_1) was found to be:

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

Which is an agreement with Murakami's order. Plots of stability constants (log K_1) vs different parameters like second ionisation potentials, electrongativities and reciprocal of ionic radii were drawn to explore the possible correlations.

From the survey of the literature it is observed that no work on the solution stability constants of N-(2-hydroxy-5-phenylbenzylidene)-phenylhydrazine and its bivalent metal chelates has been reported so far. Hence present investigation was undertaken to determine the stability constants of the complexes of Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mg^{2+} and Zn^{2+} metal ions with the title ligand.

EXPERIMENTAL

The ligand N-(2-hydroxy-5-phenylbenzylidene)-phenylhydrazine was synthesised by refluxing equimolar quantities of 4-hydroxy-3-aldehydobiphenyl and phenylhydrazine in alcohol. The crude product obtained was repeatedly crystallised to obtain an analytically pure compound(observed m.p. 202°C). The purity of the sample was tested by TLC and elemental analysis.

The solutions of the metal perchlorates were prepared using metal carbonates or oxides of A.R grade. All these were standardised complexometrically by EDTA titrations (2). The pH measurements were carried out with Elico-Model LI-15 precision pH meter. During the titrations, oxygen free nitrogen presaturated with solvent mixture was bubbled through the solution. Experiments were carried out at 30 ± 0.1°C. The medium used was 75:25% v/v dioxane - water mixture.

The fllowing solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.0526 M) solution.

(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 accurately weighed reagent to give 0.004 M reagent concentration in the final solution + 30 ml. dioxane.

(iii) 5 ml. of (0.64 M) $NaClO_4$ + 5 ml. of metal perchlorate (0.008 M) in (0.16 M) $HClO_4$ + requisite amount of reagent accurately weighed to give 0.004 M reagent concentration in final solution + 30 ml. of dioxan.

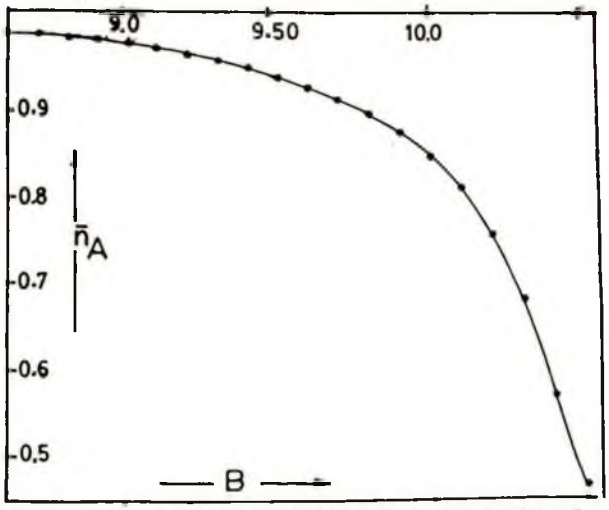


Fig. 1 Formation Curve of N-(2-Hydroxy-5-Phenyl-Benzylidene)-Phenylhydrazine.

RESULTS AND DISCUSSION

The $\bar{n}_A$ values for the ligand were calculated using the method of Irving and Rossotti (1) pK^H value of

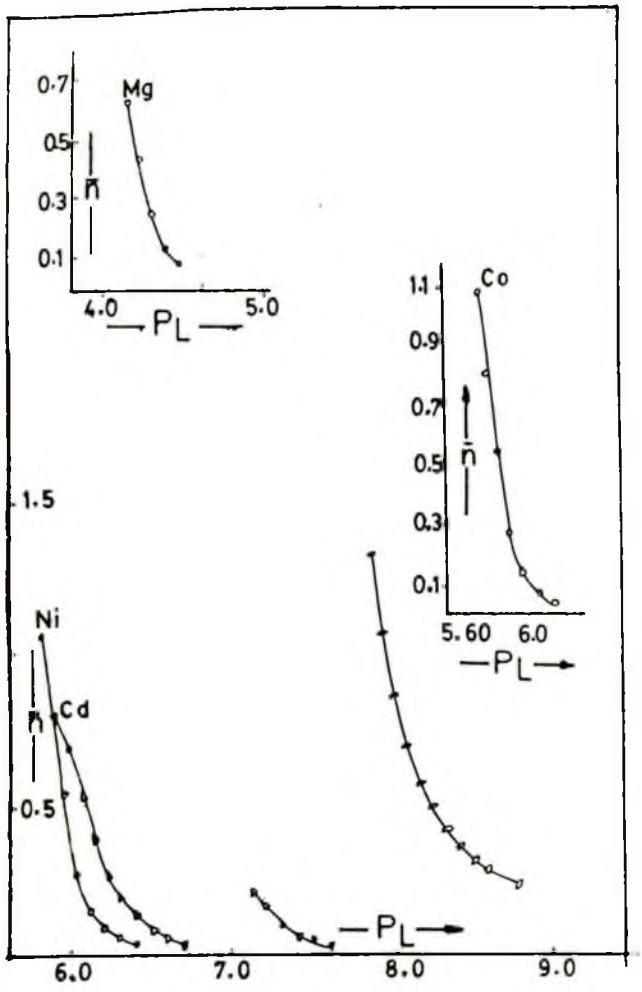


Fig. 2 n - PL plots for metal ligand systems of Metal-Ligand systems of N-(2-Hydroxy-5-Phenylbenzylidene)-Phenylhydrazine.

the reagent was determined from the formation curve ($\bar{n}_A$ vs B) (Fig.1) as well as from the plot log ($\bar{n}_A/1-\bar{n}_A$) vs B. This value agrees quite well with that obtained by half integrat method.

From the titration curves using solutions (ii) and (iii) $\bar{n}$ (average number of ligand molecules attached per metal ion) and pL (free ligand exponent) values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of metal complex ion equillibria (Fig.2). From the formation curves, the values of stability constants (log K) of 1:1 complex were determined. The plot of log ($\bar{n}/1-\bar{n}$) vs pL were also drawn for these systems to

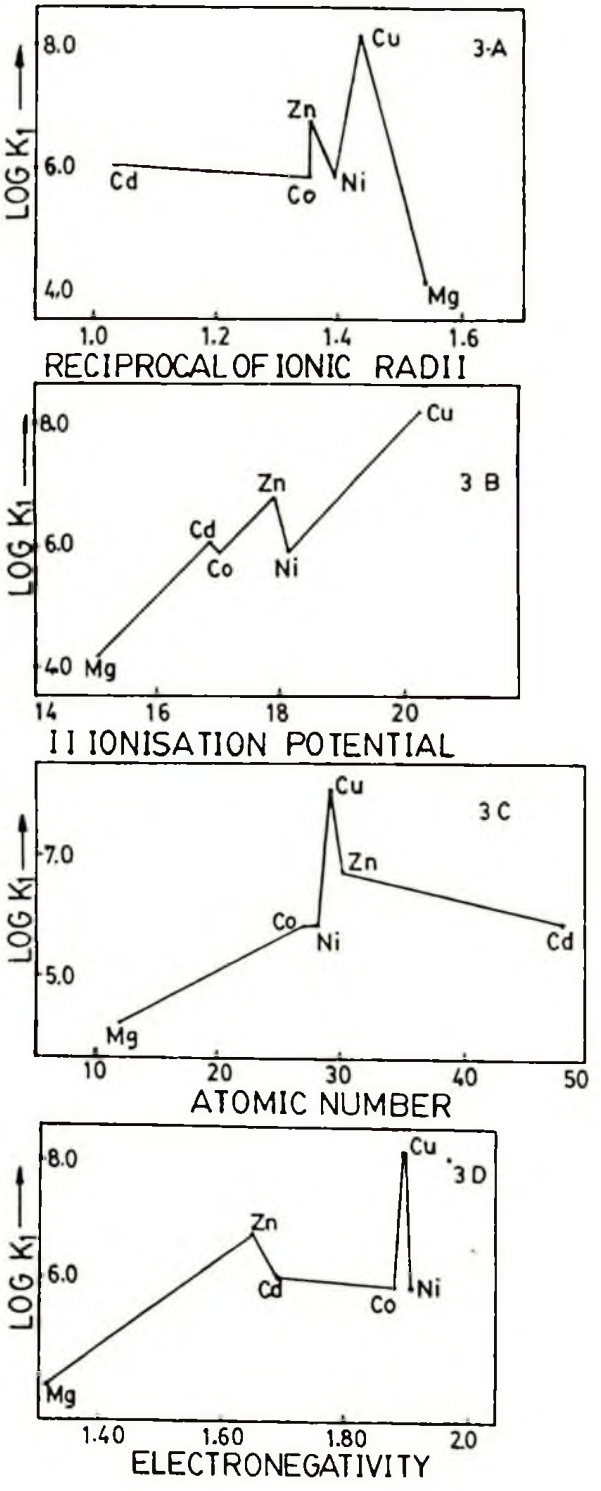


Fig. 3 Relation ship of the stability constant with ionic/atomic parameter of the metal.

corroborate the values obtained by half integral method. The values obtained from both the methods agree quite well. The most representative values are recorded in Table - I.

The order of stability constants was found to be :

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

which is in agreement with Murakami's order.

TABLE 1

STABILITY CONSTANTS OF VARIOUS COMPLEXES*

t = 30 ± 0.1°C. M = 0.1 M

	H^+	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Mg^{2+}
$Log k_1$	10.465	8.22	6.78	6.05	5.93	5.94	4.19

* For proton association , K_1 corresponds to the species LH, while for metal ions K_1 corresponds species ML .

In the present work a graph of stability constants of the bivalent metal ions with the title ligand was plotted against reciprocal of ionic radii of the elements (Fig.3-A).

A correlation between 2nd Ionisation potential and stability of the complex was pointed out by Irving and Williams (4), Schwarzenbach (5) and Calvin and Melchoir (6). A similar relation was observed in the present case in the plot of log K_1 of the various metal chelates vs. Second ionisation potential of the metal ions (Fig.3-B).

A similar correlation as in the above case was also observed between electronegativity and complex stability in the present study (Fig.3-D).

Plot of log K_1 vs atomic number (Fig.3-C) of the elements shows a monotonic rise to a maximum of Cu followed by a lower value of Zn. A similar relationship was observed by Irving and Williams (7) . The above plot also confirms the observation that stability seems to decrease with increase in basicity of the metal, i.e. weakly basic metal Cu forms stronger chelates and strongly basic metal like Mg forms weaker chelates (8).

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