

FORMATION CONSTANTS OF THE CHELATES OF 2-HYDROXY-1-NAPHTHALIDENE-*p*-METHOXYANILINE WITH SOME DIVALENT METAL IONS

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ABSTRACT

Potentiometric studies have been carried on the metal complexes of Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Mg^{+2} with 2-hydroxy-1-naphthalidene-*p*-methoxyaniline. 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 $30 \pm 0.1^\circ \text{C}$. The order of stability is found to be $\text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Cd} > \text{Mg}$.

LITERATURE survey indicates that no systematic study on the stabilities of 2-hydroxy-1-naphthalidene-*p*-methoxyaniline and its metal chelates with bivalent metal ions has been carried out. In the present communication, the successive stability constants of the complexes of 2-hydroxyl-1-naphthalidene-*p*-methoxyaniline with various divalent metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti¹.

EXPERIMENTAL

The Corning Model 12, a precision research pH meter was employed throughout the work for pH determinations. The ligand was synthesised and repeatedly crystallised to get an analytically pure sample (m.p. 109°C)².

The medium of titration was dioxan-water mixture containing 75% (v/v) of dioxan. The dioxan used for the experiments was purified by the method described by Vogel³. Conductivity water was used throughout the investigation. Sodium perchlorate was added to maintain constant ionic strength (0.1 M). The titrations were carried out in an inert atmosphere by bubbling the nitrogen gas through the solutions. All the metal perchlorate solutions were standardised complexometrically⁴ by E.D.T.A. titrations. All measurements were made at $30 \pm 0.1^\circ \text{C}$.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.092 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 dioxan.
- (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 0.01 M reagent concentration in the final solution + 30 ml of dioxan.
- (iii) 5 ml of (0.64 M) NaClO_4 + 5 ml of (0.024 M) metal salt solution in (0.16 M) HClO_4 + requisite amount of the reagent

accurately weighed to give 0.01 M, 0.05 M and 0.03 M reagent concentration in the final solution in the case of (Cu^{+2} , Co^{+2} , Ni^{+2} , Zn^{+2}); Mg^{+2} and Cd^{+2} respectively + 30 ml of dioxan.

All titrations were performed in duplicate to test for reproducibility.

The experimental method of Irving and Rossotti¹ was applied to find the values of \bar{n} and pL.

RESULTS AND DISCUSSION

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

From the titration curves using the solutions (i) and (ii) \bar{n}_A values at various 'B' values (pH meter readings) were calculated and the curve between 'B' and the corresponding \bar{n}_A values was plotted (Fig. 1). The formation curve extends over a range $0.85 < \bar{n}_A < 1.8$ and is wavelike. This indicates the formation of the species HL and H_2L , i.e., the protonated nitrogen and the phenolic hydrogen are completely dissociable in steps separable.

Three methods known as half integral, graphical and least square⁷ are suitably employed here to calculate the stability constants.

In the half integral method, the values of pL at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ were taken as $\log K_1$ and $\log K_2$ respectively from the formation curves extending over a range of $0 < \bar{n} < 2$. In the cases where stepwise formation of complexes is indicated by the flattening of the formation curves at integer values of \bar{n}_A or \bar{n} , the different portions of 1:1 and 1:2 complexes were treated separately and the respective pK^H and $\log K$ values were determined by graphical method from the linear plots of, $\log \frac{\bar{n}_A}{(1 - \bar{n}_A)}$ or $\log \frac{(2 - \bar{n}_A)}{(1 - \bar{n}_A)}$ versus 'B' (pH meter

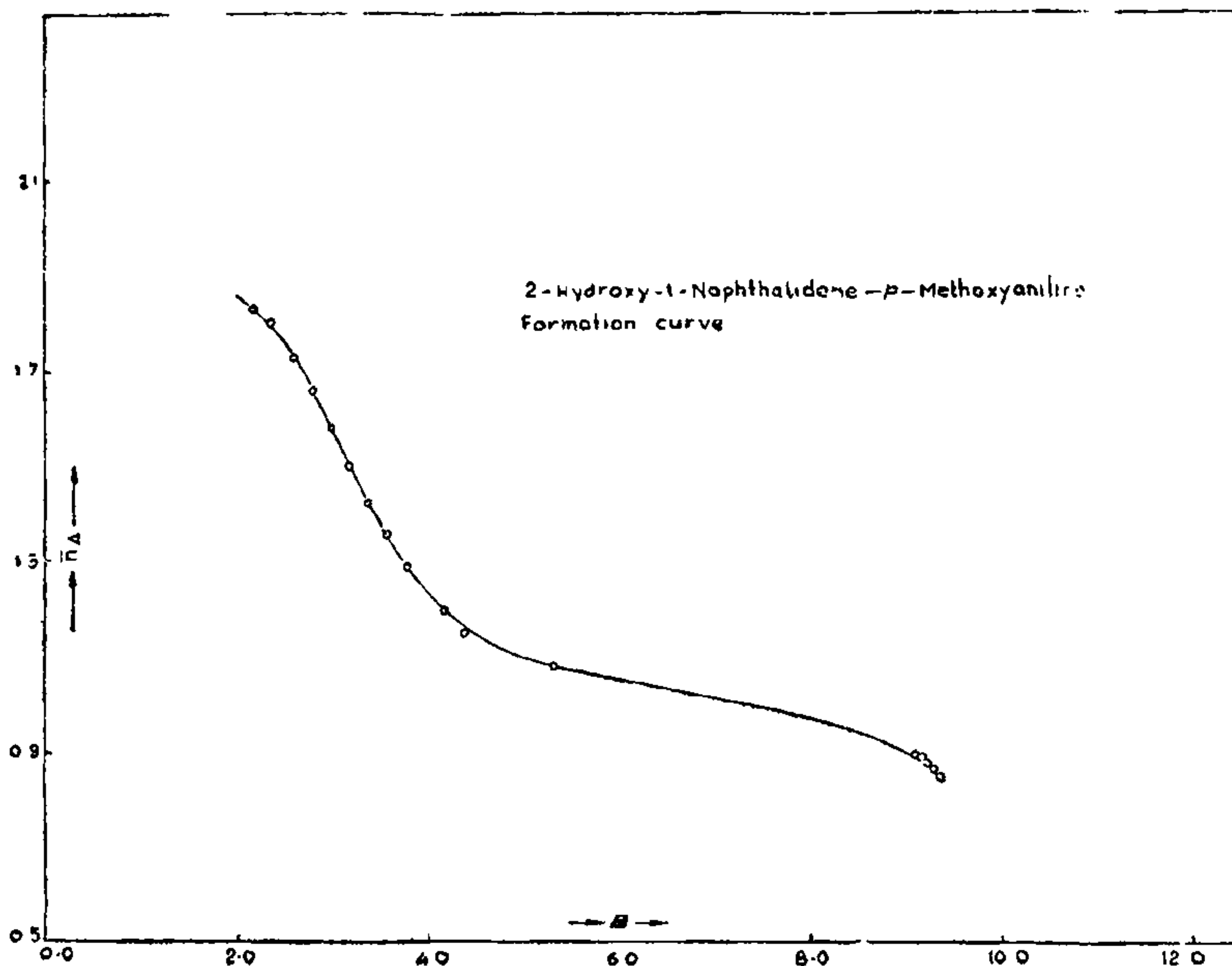


FIG. 1

readings) and $\log \bar{n}/(1 - \bar{n})$ or $\log \frac{(2 - \bar{n})}{(1 - \bar{n})}$ versus pL as the case may be by employing the relation

$$\bar{n}_A + (\bar{n}_A - 1) \cdot pK_2^H \cdot \frac{1}{\text{antilog } B} = 0$$

and

$$(\bar{n}_A - 1) - (2 - \bar{n}_A) pK_2^H \cdot \frac{1}{\text{antilog } B} = 0$$

and

$$\log K = \log \frac{\bar{n} - (i - 1)}{(i - \bar{n})} + pL$$

In the cases where the formation curves are incomplete in the sense that they do not reach the value of $\bar{n} = 1.5$ and in the cases in which the formation curves are not wavelike indicating that the formation of the second complex starts before the completion of the 1:1 complex, $\log K$ values are calculated by the least square method:

$$\bar{n} = \frac{K_1(L) + 2K_1K_2(L)^2 + \dots + NK_1K_2 \dots K_N(L)^N}{1 + K_1(L) + K_1K_2(L)^2 + \dots + K_1K_2 \dots K_N(L)^N}$$

This equation for 1:1 and 1:2 complexes can be written in the linear form as:

$$\frac{\bar{n}}{(\bar{n} - 1)L} = \frac{(2 - \bar{n})}{(1 - \bar{n})} \cdot (L) K_1K_2 - K_1$$

knowing the quantities $\frac{\bar{n}}{(\bar{n} - 1)(L)}$ and $\frac{(2 - \bar{n})}{(\bar{n} - 1)} \cdot (L)$

For each point on the formation curve the above equation is solved by the least square method to get the values of K_1 and K_2 . The value of pK_2^H only could be evaluated from half integral point at $\bar{n}_A = 1.5$. The value of pK_1^H could not be found by half integral methods. It was however determined by least square method.

A plot of $\log \left[\frac{2 - \bar{n}_A}{1 - \bar{n}_A} \right]$ against B was also drawn but is not included here for economy of space. From this curve the value of practical pK_2^H was evaluated. The two values agree quite well.

From the titration curves of the 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 complexation equilibria (Fig. 2). From these formation curves the values of stability constants $\log K_1$ were determined which correspond to the pL values at $\bar{n} = 0.5$. The least square method was applied to calculate $\log K_1$ and $\log K_2$ in the case of Co^{+2} and Mg^{+2} . The most representative values are recorded in Table I.

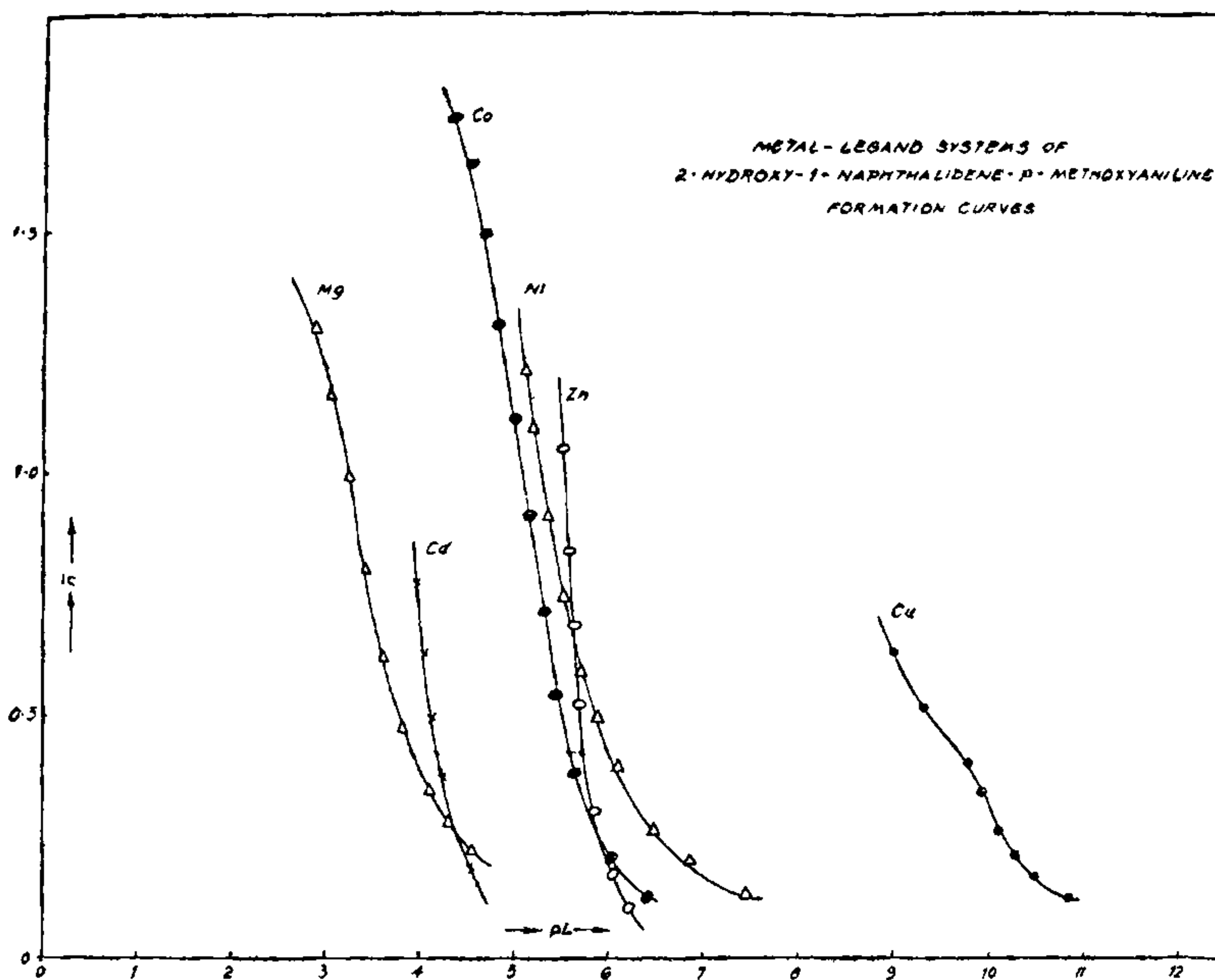


FIG. 2

TABLE I

Stepwise formation constants of various complexes

Metal ions	H ⁺	Cu ⁺²	Ni ⁺²	Co ⁺²	Zn ⁺²	Cd ⁺²	Mg ⁺²
log K ₁	10.00	9.35	5.84	5.37	5.66	4.10	3.77
log K ₂	3.22	4.80	2.67

The order of stability of bivalent metal chelates was Cu > Ni > Zn > Co > Cd > Mg.

The order in the case of Zn⁺² complex is reversed with respect to Co⁺² as compared to that observed by Maley and Mellor⁵. The reversal of the order in the case of cobalt and zinc may be attributed to the closeness of the values in the present investigation.

A parallelism between log K and second ionisation potential (I.P.) is also observed in the present case as has been suggested by Irving and Williams⁶. This is verified graphically by plotting the (stability

constants) formation constants and the ionisation potentials as a function of the atomic number.

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1. Irving, H. M. and Rossotti, H. S., *J. Chem. Soc.*, 1954, p. 2904.
2. Savich, I. A., Zelentsov, V. V. and Spitsyn, I., *Ser. Mat. Mekh. Astron. Fiz. Khim.*, 1956, No. 1, 233; *Chem. Abstr.*, 1959, 53, 1264.
3. Vogel, A. I., *A Text Book of Practical Organic Chemistry*, Longmans, III Edition, p. 177.
4. Schwarzenbach, G., *Complexometric Titrations*, Methuen and Co., Ltd., London, 1956, p. 60.
5. Maley and L. E. and Mellor, D. P., *Nature*, 1947, 159, 370.
6. Irving, H. and Williams, R. J. P., *Ibid.*, 1948, 162, 746; *J. Chem. Soc.*, 1953, p. 3192.
7. — and Rossotti, H. S., *J. Chem. Soc.*, 1953, p. 3397.