EXPERIMENTAL

2-*Chloro benzothiazole* (2)

2-Mercapto benzothiazole (1) (0·03 mole) was suspended in chloroform and water 2:1 mixture. The mixture was cooled to 5° C. Chlorine gas was passed for 1·5 hr. Chloroform layer was tapped off and the remaining liquid was distilled under reduced pressure (yield 2·8 g). B.P. 158–162° C/50 mm.

2-*Hydrazino benzothiazole* (3)

This is prepared by condensation of 2-chloro benzothiazole with hydrazine hydiate.

Benzothiazolyl hydrazones (4)

Equimolar proportions of 2-hydrazino benzothiazole and the required aldehyde in ethanol were condensed by heating on a water bath for 20–45 min. The reaction mass was poured into water. Crude hydrazone was filtered off and recrystallised from ethanol. The yields, melting points and analytical data, etc. are included in Table I.

The hydrazones were taken in nitrobenzene and refluxed for 2 hours. Then nitrobenzene is removed by steam distillation. The products were not the cyclised *s*-triazolo (3, 4-*b*) benzothiazole derivatives '(5) but were found to be starting materials (4). Similarly ferric chloride oxidation also failed to give *s*-triazole (3, 4-*b*) benzothiazole derivatives.

Biological screening

After surface disinfection with a solution of Sodium hypochlorite (2% available chlorine) for 10 min., the seeds of *T. vulgare* and *P. deveus* were soaked for five hours in the solution. Then seeds were sown on blotter in a petri dish. The blotters were sterilized at 15 psi for 20 min. before use. The blotters were moistened with 5 ppm solution of the compounds. Along with these compounds gibberellic acid and 2, 4-dichlorophenoxy acetic acid were also used as standards and sterile water was kept as control. The results are presented in Table II.

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DETERMINATION OF STABILITY CONSTANTS OF 2-HYDROXY-1-NAPHTHALIDENE-*p*-N-DIMETHYLANILINE COMPLEXES WITH SOME BIVALENT METAL IONS

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ABSTRACT

Potentiometric studies have been carried on metal complexes of Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}. Cd^{+2} and Mg^{+2} with 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline. 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 $30 \pm 0·1° C$ and at ionic strength 0·1 M in 75:25% (v/v):dioxan-water medium. The order of stability is found to be $Cu > Co > Ni > Zn > Cd > Mg$.

L ITERATURE survey indicates that no systematic study of the stabilities of 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline and its metal chelates with bivalent metal ions appears to have been carried out.

In the present communication the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline 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 Corning Model 12, a precision research pH meter with a wide range glass electrode and a calomel reference electrode, was used for pH determination. The meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale reads 0·005 pH unit.

2-Hydroxy-1-naphthalidene-*p*-N-dimethylaniline was prepared by dissolving 10 g of 2-hydroxy-1-naphthal

dehyde (Fluka) in about 50 ml of absolute ethanol. To this solution was added equimolar quantity of *p*-N-dimethylaniline and the reaction mixture was refluxed on water-bath for about 20 to 30 minutes and then allowed to cool. On cooling, the compound separated out which was then repeatedly crystallised from ethanol to get an analytically pure compound with m.p. 168° C.

The dioxan used for the experimental work was purified by the method described by Vogel[2]. Distilled water was redistilled over alkaline potassium permanganate and made free from carbon dioxide by boiling. This water was used throughout the investigation.

The medium of titration was 75:25 dioxan-water (v/v) mixture. Perchloric acid and sodium perchlorate were added to maintain a constant ionic strength (0·1 M). The titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through the solutions. Metal ion solutions were prepared from A.R. grade metal salts. All these were standardised complexometrically by EDTA titrations[3]. All measurements were carried out at 30° ± 0·1° 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) HClO₄ + 5 ml of (0·64 M) NaClO₄ + 30 ml. of dioxan. (ii) 5 ml of (0·16 M) HClO₄ + 5 ml of (0·64 M) NaClO₄ + requisite amount of 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) NaClO₄ + 5 ml of (0·024 M) metal salt solution in (0·16 M) HClO₄ + requisite amount of the reagent accurately weighed to give 0·01 M reagent concentration in the final solution + 30 ml of dioxan.

All titrations were performed in duplicate to test for reproducibility. The experimental method of Irving and Rossotti[1] was applied to find out 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 0·51 <

$\bar{n}_A < 1·7$ and is wavelike. This indicates the formation of the species HL and H₂⁺L, *i.e.*, the protonated nitrogen and the phenolic hydrogen are completely dissociable in steps separable.
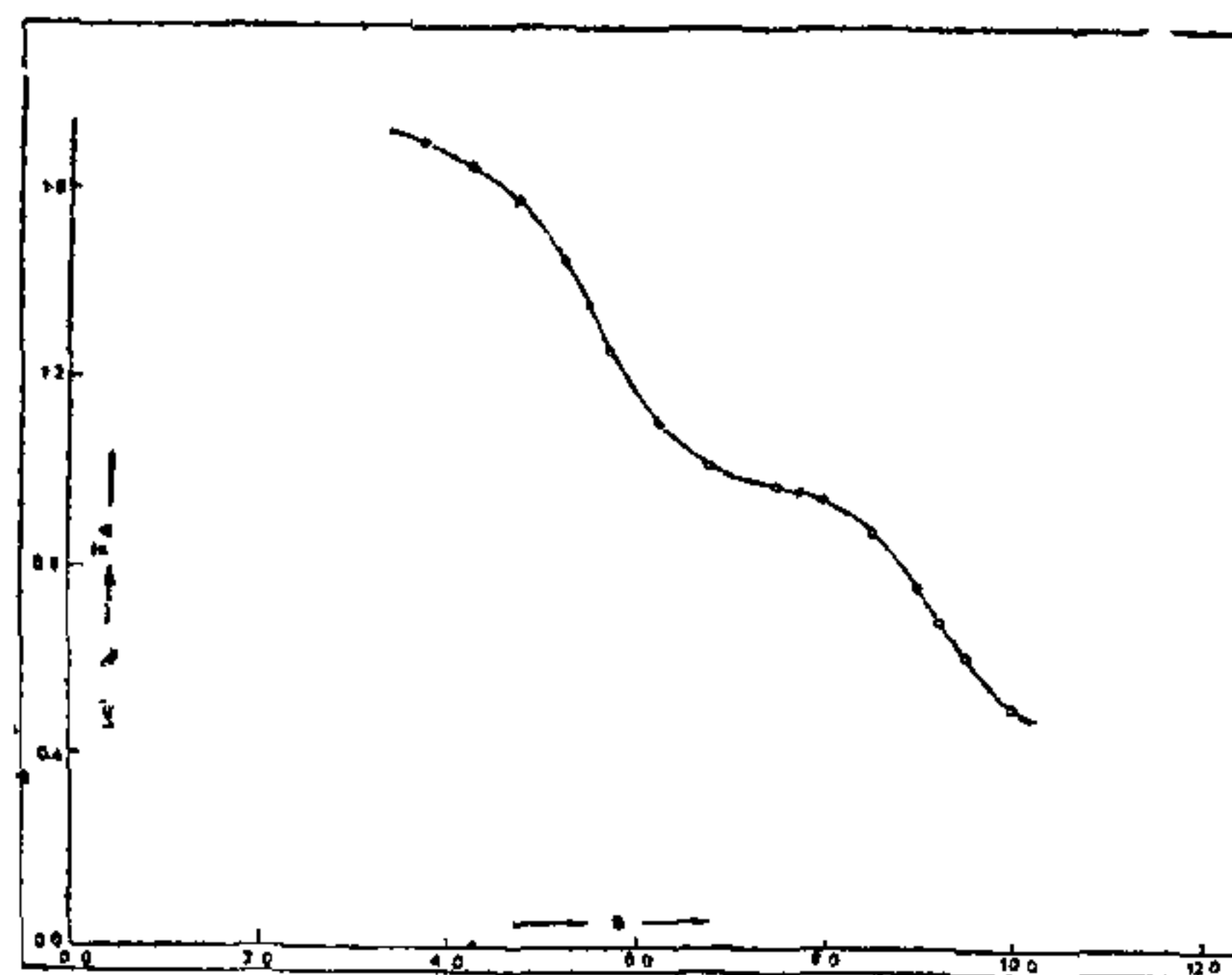

Fig. 1. 2-Hydroxy-1-naphthalidene-*p*-N-dimethylaniline formation curve.

Three methods known as half integral, graphical and least square[4] 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 the 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

$$\log \frac{\bar{n}_A}{(1 - \bar{n}_A)} \text{ or } \log \frac{(2 - \bar{n}_A)}{(1 - \bar{n}_A)} \text{ versus } B \text{ (pH meter readings) and}$$

$$\log \frac{\bar{n}}{(1 - \bar{n})} \text{ or } \log \frac{(2 - \bar{n})}{(\bar{n} - 1)} \text{ versus } p\text{L as the case}$$

may be, by employing the relation

$$\bar{n}_A + (\bar{n}_A - 1) \cdot pK_1^H \cdot \frac{1}{\text{antilog } B} = 0$$

and

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

and

$$\log K = \log \frac{\bar{n} - (i - 1)}{(i - \bar{n})} + p\text{L.}$$

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.

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

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

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

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

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 the half integral point at $\bar{n}_A = 1 \cdot 5$ in the present case. The value of pK_1^H could not be found by half integral method. It was however determined by least square method.
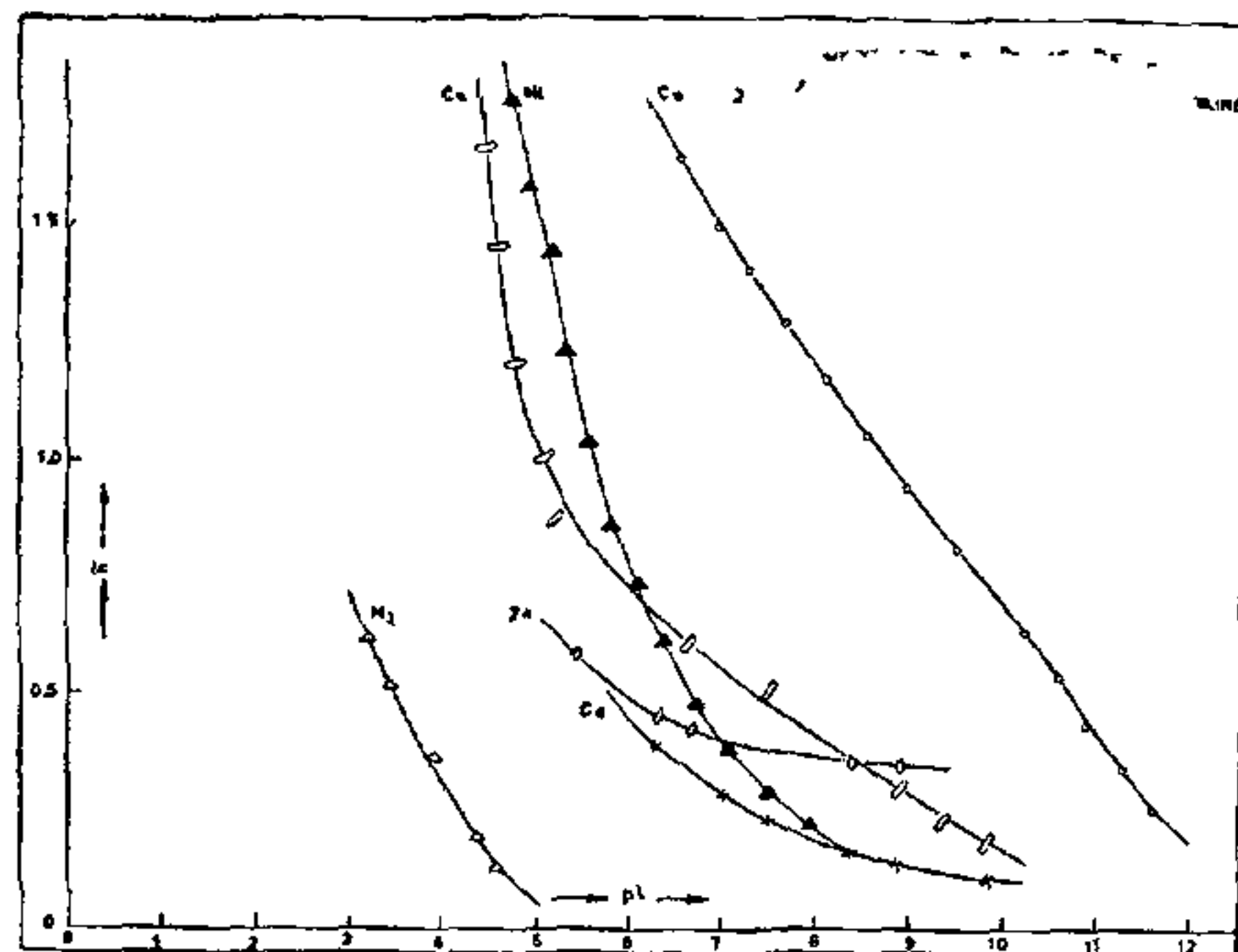
Fig. 2. Metal-Ligand system of 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline formation curves.

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 complexion equilibria (Fig. 2). 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 $\bar{n} = 0 \cdot 5$ and $1 \cdot 5$.

Two plots one of $\log \bar{n}/(1-\bar{n})$ against pL (Fig. 3) and the other of $\log (2-\bar{n})/(\bar{n}-1)$ against pL (Fig. 4) for different metal ion systems were also drawn. From these curves the values of $\log K_1$ and $\log K_2$ were evaluated. These values agree fairly well with those obtained from half integral method except in

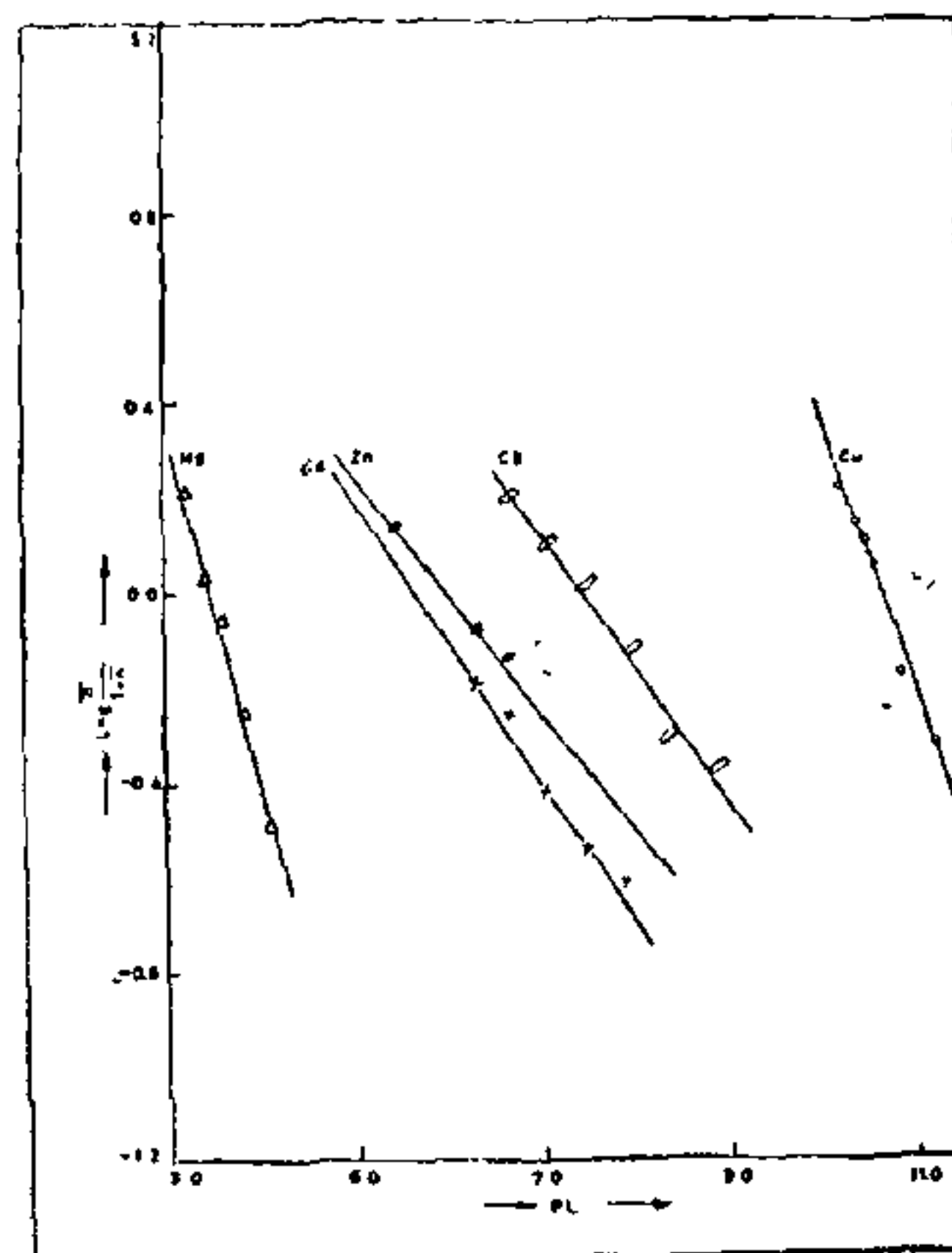the case of cadmium where the $\log K_1$ value had to be determined by graphical method on extrapolation

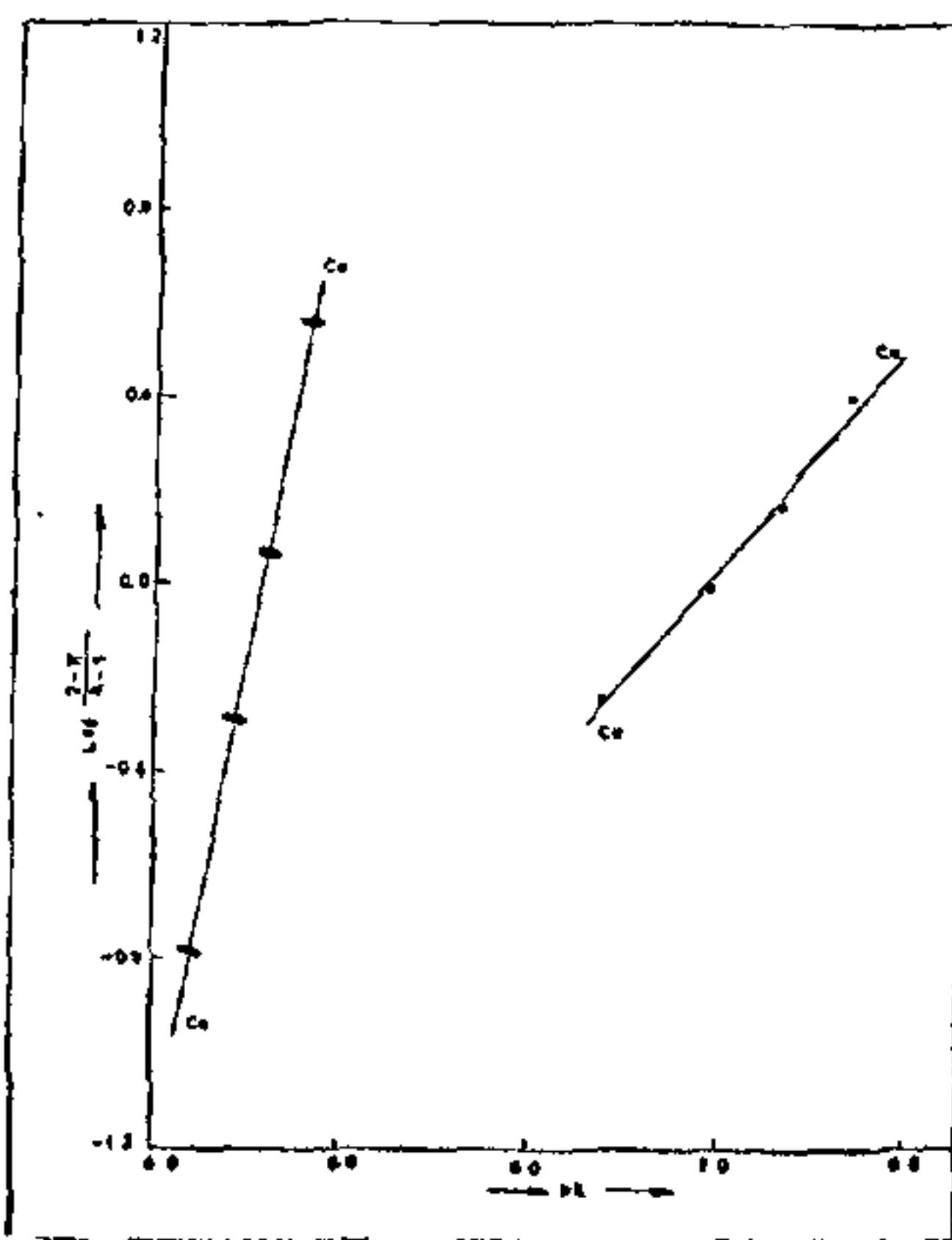Fig. 3. 2-Hydroxy-1-naphthalidene-*p*-N-dimethylaniline.

Fig. 4. 2-Hydroxy-1-naphthalidene-*p*-N-dimethylaniline.

of the curve. In addition the least square method was also applied to calculate $\log K_1$ and $\log K_2$ in the ase of Ni^{+2} and Cu^{+2}. The most representative values are recorded in Table I.

TABLE I
*Stepwise stability constants of various complexes**

$t = 30°\,C$							$\mu = 0 \cdot 1\,M$
Cations	H^+	Cu^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Mg^{+2}
$\log K_1$	9·59	10·65	6·76	7·35	5·95	5·73	3·50
$\log K_2$	5·23	6·95	4·76	4·52	..	..	...

* For H^+, K_1 and K_2 correspond 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.

The order of stability of bivalent metal chelates was $Cu^{+2} > Co^{+2} > Ni^{+2} > Zn^{+2} > Cd^{+2} > Mg^{+2}$.

The order in the case of Co^{+2} complex is reversed with respect to Ni^{+2} complex, as compared to that observed by Maley and Mellor[5].

ACKNOWLEDGEMENT

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FIRST INTERNATIONAL SYMPOSIUM ON AVIAN ENDOCRINOLOGY

THE First International Symposium on Avian Endocrinology, held at Calcutta, during January 10–15, 1977 was convened by Professor Asok Ghosh, Professor of Zoology of the University of Calcutta, and presided by Professor Donald S. Farner, the Chairman of the Department of Zoology, University of Washington, Seattle, U.S.A. The Symposium was inaugurated by Professor M. R. N. Prasad, Senior Professor of Zoology, University of Delhi. The inaugural session was presided by Dr. S. K. Mukherji, Vice-Chancellor, University of Calcutta. A number of renowned scientists from the U.S.A., U.S.S.R., Canada, U.K., Germany; Denmark, France, Holland, Hong Kong, Japan, Nepal, Bangladesh and different States of India participated in this symposium. · The total number of delegates was around two hundred.

The Scientific Programme comprised of ten separate sessions, *viz.,* I. General Organisation of the Avian Endocrine system; II. Neuroendocrine Mechanism; III. Physiology of the pineal body; IV. Pancreatic islet and carbohydrate metabolism; V. Developmental endocrinology; VI. Mechanism of Hormone action; VII. Reproduction; VIII. Adrenal gland; IX. Thyroid and Parathyroid glands; X. Renal endocrinology; and XI. Valedictory session. Altogether sixty scientific papers were presented (twenty plenary lectures and contributed papers) during the 6-day symposium.

Both theoretical and applied aspects of avian endocrinology was discussed and the role of hormones on poultry and egg prduction was emphasized. A number of papers was presented on pest birds and birds which are agriculturally beneficial and there was a general opinion that a scientific inventory on this aspect would certainly help avian endocrinologists all over the world in the biological control of pest birds and an increase in the population of the beneficial birds.