

## Stability Constants of Transition Metal Complexes of 2-Hydroxybenzilidine-*p*-Chloroaniline

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Proton dissociation constant of the ligand and the stability constants of the complexes of the metal ions Co(II), Ni(II), Cu(II) and Zn(II) with 2-hydroxy-benzilidine *p*-chloroaniline have been determined potentiometrically at  $30 \pm 0.1^\circ\text{C}$  and at ionic strength 0.1 M in 75 : 25 (v/v) dioxane-water medium.  $\log K_1$  and  $\log K_2$  values have been determined. The stabilities of the chelates follow the order  $\text{Zn} > \text{Co} > \text{Cu} > \text{Ni}$ .

**Key words:** Stability constants, Transition metal, Complexes, 2-Hydroxybenzilidine-*p*-chloroaniline.

### INTRODUCTION

In the present communication, the successive stability constants of the complexes of 2-hydroxybenzilidine-*p*-chloroaniline with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration techniques adopted by Irving and Rossotti<sup>1</sup>.

### EXPERIMENTAL

Measurements of pH were made on an expanded scale pH meter model No. EQ-614 supplied by EQUIP-TRONICS, a precision research pH meter with a wide range glass electrode and a calomel reference electrode. The pH meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale is 0.01 pH unit.

The ligand 2-hydroxybenzilidine-*p*-chloroaniline was synthesized in the laboratory and crystallized to get an analytically pure sample.

The medium of titration was dioxane-water mixture containing 75% (v/v) of dioxane. The dioxane used for the experiments was purified by the method described by Vogel<sup>2</sup>. Distilled water, redistilled over alkaline potassium permanganate made free from carbon dioxide by boiling, was used throughout the investigation.

Sodium perchlorate was added to maintain a constant ionic strength (0.1 M). The titrations were carried out in an inert atmosphere by bubbling nitrogen gas through the solutions. All the metal perchlorate solutions were standardized complexometrically<sup>3</sup> by EDTA 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 M) solution keeping the total volume 40 mL.

- (i) 5 mL of 0.16 M  $\text{HClO}_4$  + 5 mL of (0.64M)  $\text{NaClO}_4$  + 30 mL of dioxane.

- (ii) 5 mL of 0.16 M  $\text{HClO}_4$  + 5 mL of 0.64 M  $\text{NaClO}_4$  + requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution + 30 mL of dioxane.
- (iii) 5 mL of 0.64 M  $\text{NaClO}_4$  + 5 mL of (0.001 M) metal salt solution in 0.16 M  $\text{HClO}_4$  + requisite amount of the reagent accurately weighed to give 0.004 M reagent concentration in the final solution + 30 mL of dioxane.

The method of Irving and Rossotti<sup>1</sup> was applied to find out the values of  $n$  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.

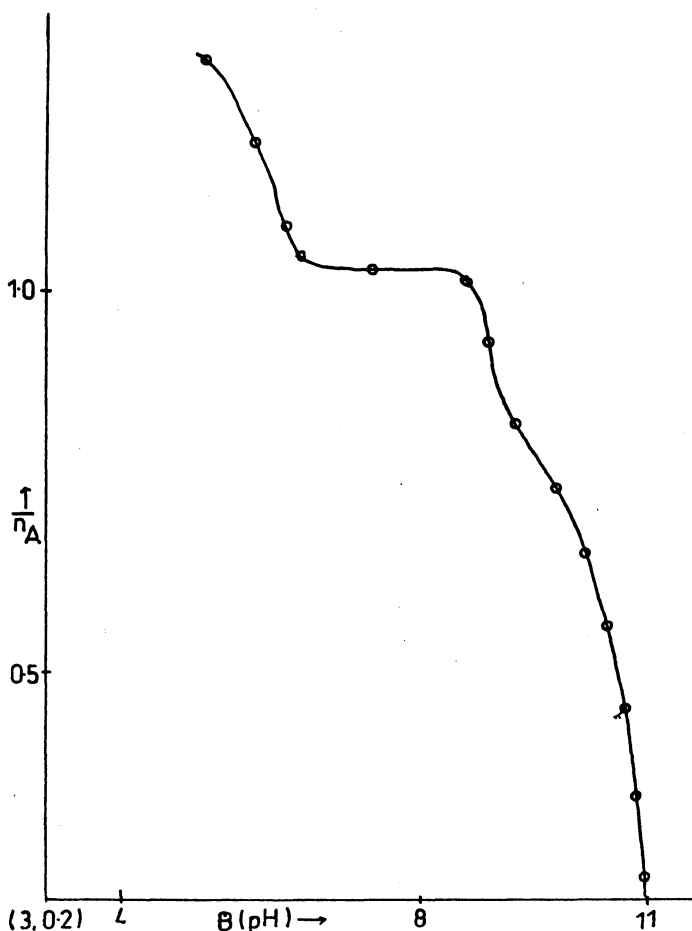


Fig. 1. 2-Hydroxy-benzilidene-*p*-chloroaniline formation curve

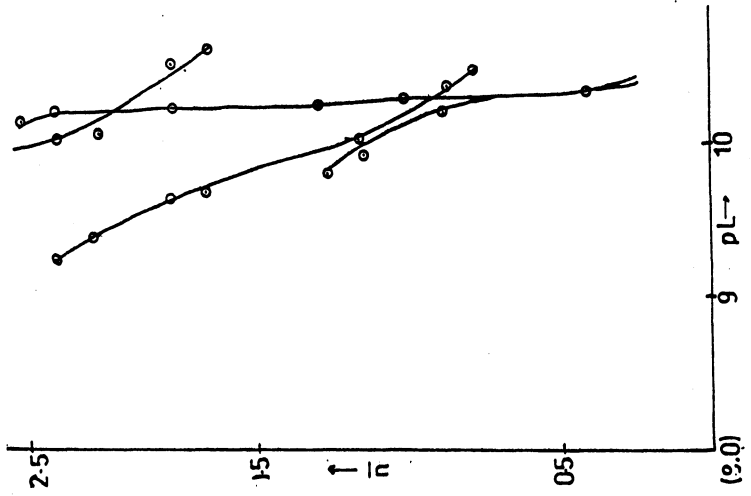


Fig. 3. Metal-ligand systems of 2-Hydroxy-benzylidene-*p*-chloroaniline formation curves

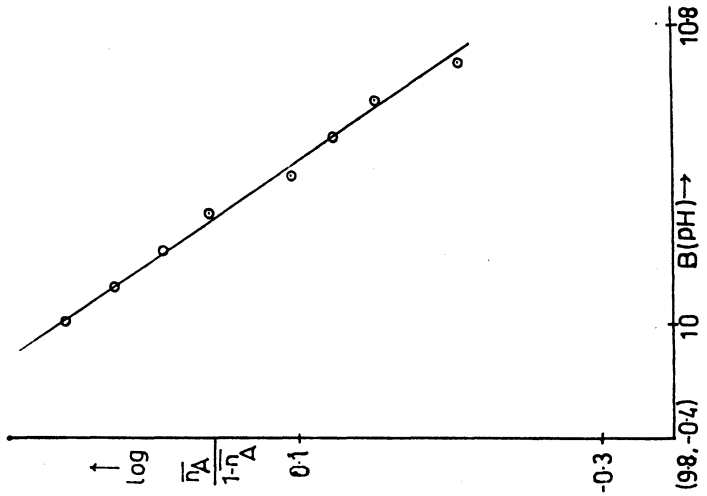


Fig. 2. 2-Hydroxy-benzylidene-*p*-chloroaniline

From the titration curves of the solutions (i) and (ii),  $nA$  values at various 'B' values (pH meter readings) were calculated, and the curve between 'B' and the corresponding  $nA$  values was plotted (Fig. 1). The formation curve extends over a range  $0.2 < nA < 1.3$  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. The value of  $pK_1H$  only could be evaluated from half integral point at  $nA = 0.5$ .

The value of  $pK_2H$  could not be found by half integral and graphical methods.

A plot of  $\log [\bar{n}A/(1 - \bar{n}A)]$  against 'B' was also drawn (Fig. 2). From this curve the value of practical  $pK_1H$  was evaluated. The two values agree fairly 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 (Fig. 3) to get the formation curves of the metal complex ion equilibria. 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  $\bar{n} = 0.5$  and  $1.5$  respectively. In addition, the least square method was also applied to calculate  $\log K_1$  and  $\log K_2$  in the case of Co(II) and Ni(II) chelates. The most representative values are recorded in Table-1.

TABLE-1  
STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES<sup>a</sup>

Temperature (T) = 303 K		Ionic strength ( $\mu = 0.1$ M)			
Cations	H <sup>+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
$\log K_1$	10.55	10.32	10.72	—	—
$\log K_2$	—	10.21	9.09	9.82	11.06

<sup>a</sup>H<sup>+</sup> correspond to the species  $LH_1$  and  $LH_2$  respectively, while for the metal ions  $K_1$  and  $K_2$  correspond to the species  $ML_1$  and  $ML_2$  respectively.

## REFERENCES

1. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
2. A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd Edn., Longmans, p. 177.
3. G. Schwarzenbach, *Complexometric Titrations*, Methuen & Co. Ltd., London, p. 60 (1956).

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