

Potentiometric Studies on the Complexes of Some Bivalent Metal Ions with *N*-[2-Hydroxy-1-naphthalidene]-cyclohexylamine

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Potentiometric studies have been carried out on metal complexes of Cu^{II} , Ni^{II} , Co^{II} , Cd^{II} with *N*-[2-hydroxy-1-naphthalidene]-cyclohexylamine. The formation constants ($\log K_f$ and $\log K_d$) of the reagent and the dissociation constants of its metal complexes have been determined by Bjerrum method at $30 \pm 0.1^\circ$ and at ionic strength 0.1 *M* in 3 : 1 (v/v) dioxane-water medium. The order of stability constants of the chelates is found to be $\text{Cu}^{\text{II}} > \text{Co}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Cd}^{\text{II}}$.

FROM the literature available on the determination of stability constants it is seen that no work on the solution stability constants of *N*-[2-hydroxy-1-naphthalidene]-cyclohexylamine and its metal complexes has been reported so far.

The present investigation is aimed to determine the stability constants of Cu^{II} , Ni^{II} , Co^{II} , Cd^{II} with *N*-[2-hydroxy-1-naphthalidene]-cyclohexylamine.

Experimental

2-Hydroxy-1-naphthaldehyde (Fluka) (5 g) was dissolved in about 200 ml alcohol. The solution was cooled to 0° and freshly distilled cyclohexylamine, slightly in excess of equimolar quantity, was added dropwise with constant stirring. The reaction mixture was allowed to stand for 2 h at 0° . The reaction was monitored by tlc to confirm the absence of traces of aldehyde. The compound separated out on dilution was repeatedly crystallised from aqueous alcohol (30%) at 50° to get an analytically pure yellow coloured compound, m.p. 69° (Found : C, 80.55 ; H, 7.59 ; N, 5.51. $\text{C}_{17}\text{H}_{19}\text{NO}$ requires C, 80.60 ; H, 7.56 ; N, 5.53%).

Calvin-Bjerrum technique as adapted by Irving and Rossotti¹ was used to determine the dissociation constant of the reagent and formation constants of its metal complexes at $30 \pm 0.1^\circ$ in 3 : 1 (v/v) dioxane-water medium.

The Elico Li 15 model pH meter was employed for pH determinations with glass electrode for use over the pH range 0-11 (0.1 division) in combination with a dip type calomel electrode, and a temperature compensator covering a range 0° to 100° . Standardisation of the pH meter was carried out by means of buffers 0.05 *M* potassium hydrogen phthalate and 0.01 *M* borax prepared in double distilled water.

During the titration oxygen free nitrogen presaturated with solvent mixture was bubbled through the solution. The solution of metal perchlorates were prepared using metal carbonates or oxides of A.R. grade and were titrated with EDTA². The solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.08 *M*) solution.

The experimental details and computational methods are the same as described earlier³. The titrations were performed in duplicate to test the reproducibility.

Results and Discussion

The reagent does not undergo hydrolysis under the experimental conditions as indicated by the rapid attainment of equilibrium and the absence of any significant drift in the pH meter readings even after 1 h.

The phenolic (OH) group proton is replaced by the metal ion 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.

The formation curve of \bar{n}_A vs B extends over a range of $0.43 < \bar{n}_A < 2.13$, indicating the formation of species HL and H_2L . From this curve $\log K_f^{\text{H}}$ which corresponds to the association of proton to phenoxide ion of the reagent and $\log K_f^{\text{N}}$ which corresponds to the association of proton to nitrogen of the reagent were obtained at $\bar{n}_A = 0.5$ and 1.5, respectively. These values were further corroborated from 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, respectively. The two values agree quite well.

The log K_1 values for the metal systems were determined by half integral method (Fig. 1) and from the plots of \bar{n} vs pL .

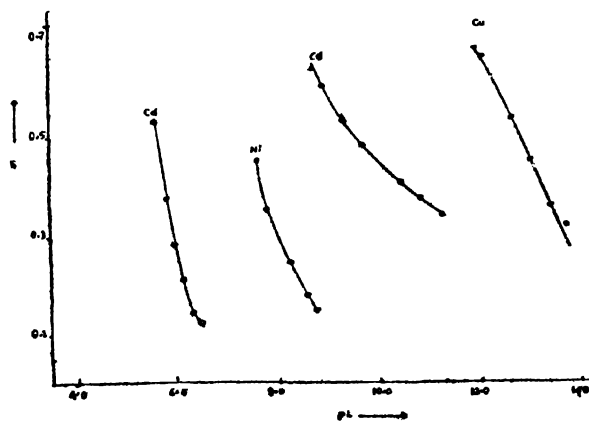


Fig. 1. Metal ligand system of *N*-[2-hydroxy-1-naphthalidene]-cyclohexylamine formation curves.

The most representative values are recorded in Table 1. The order of stability of metal chelates was found to be

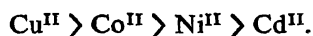


TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

Cations	Temp. = 80°				
	$\mu = 0.1 M$				
H^+	9.90	12.80	7.50	9.50	5.70
$\log K_1$	—	—	—	—	—
$\log K_2$	—	—	—	—	—

* For proton association (H^+) K_1 and K_2 corresponds to LH and LH_2^+ , respectively, for metal ions K_1 corresponds to LM . The second step formation constants for metal chelates could not be evaluated because of precipitation, probably due to metal ion hydrolysis.

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