

# Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-2'-Methyl-4'-Nitro-Aniline Complexes with $Y^{3+}$ , $La^{3+}$ , $Pr^{3+}$ , $Nd^{3+}$ , $Gd^{3+}$ and $Dy^{3+}$

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“Potentiometric studies have been carried out on metal complexes of  $Y^{3+}$ ,  $La^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Gd^{3+}$  and  $Dy^{3+}$  with 2-hydroxy-1-naphthalidene-2'-methyl-4'-nitroaniline. The dissociation constants ( $pK_1 + pK_2$ ) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at  $25 \pm 0.1^\circ$  and at an ionic strength  $0.1M$  in 75 : 25 percent (v/v) dioxan-water medium. The validity of Born's relation was examined by studying the plot of  $Z^2/r$  vs  $\log k$  values of rare earth complexes of the ligand.

In the present communication the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-2'-methyl-4'-nitroaniline with various trivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti<sup>1</sup>.

The Corning Model 12, a precision research pH meter with combined glass electrode and a calomel reference electrode was used for pH measurements. The calomel electrode was replenished with the supplied saturated KCl solution from time to time. Both electrodes dip into the titrating mixture, without vitiating any results. The meter has an arrangement for normal and expanded scale. The changes in the pH can be measured with an accuracy of 0.005 pH unit.

## Experimental

The ligand 2-hydroxy-1-naphthalidene-2'-methyl-4'-nitroaniline was prepared by dissolving 10 gm of 2-hydroxy-1-naphthaldehyde (Fluka) in 50 ml of absolute ethanol. To this was added equimolar quantity of *o*-methyl-*p*-nitroaniline. This reaction mixture was refluxed on a water bath for half an hour. After cooling, the solution was filtered to get the crude product, which was repeatedly crystallised from alcohol to get analytically pure compound. The m.p. observed was  $191^\circ$ .

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

The medium of titration was 75 : 25 percent dioxan-water (v/v) mixture. Sodium perchlorate was added to maintain a constant ionic strength.

The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solutions. The free acid, the free acid plus the ligand and the mixture of metal ion containing the acid plus the ligand were titrated against standard carbonate free sodium hydroxide. Metal ion solutions of Yttrium Gadolinium and Neodymium were prepared by taking the metal nitrates of A.R. grade. Metal ion solutions of Dysprosium, Praseodymium and Lanthanum were prepared by taking the metal carbonates of A.R. grade. All metal nitrates and carbonates were supplied by S.D. Lab. Chem. Industry, Bombay. All these were standardised complexometrically<sup>3</sup> by EDTA titrations. All the measurements were carried out at  $25 \pm 0.1^\circ$ .

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.07M) solution :

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

The experimental method of Irving and Rossotti<sup>1</sup> was applied to find out the values of  $\bar{n}$  and  $pL$ . The titrations were performed in duplicate to test for the reproducibility.

**Results and Discussion**

It may be pointed out here that the ligand used in this study did not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in the pH even after one hour.

In the ligand it is the phenolic (OH) group that takes part in the complex formation and the ligand behaves as monoprotic.

From the titration curves using the solutions (i) and (ii),  $\bar{n}_A$  values at various 'B' values (pH meter readings), were calculated and a curve between 'B' and the corresponding  $\bar{n}_A$  values was plotted (Fig. 1). The value of  $pK_1^H$  was evaluated by half integral method as well as from the plot of  $\log \left[ \frac{\bar{n}_A}{1 - \bar{n}_A} \right]$  vs 'B' (Fig. 2). Both these values agree quite well.

From the titration curves of solutions (ii) and (iii)  $\bar{n}$  and  $pL$  value were calculated. The  $\bar{n}$  values were plotted against the corresponding  $pL$  values to get the formation curves of the metal complexion equilibria. From this  $\log K_1$  and  $\log K_2$  values were evaluated by half integral method. Since the difference between the  $\log K_1$  and  $\log K_2$  values was found to be less than 1.78 log unit, the same were calculated by least square method.

The most representative values as calculated by the least square method are recorded in Table 1. The order of stability of the trivalent metal chelates was found to be  $Y^{3+} > Nd^{3+} > Gd^{3+} > La^{3+} > Dy^{3+} > Pr^{3+}$ .

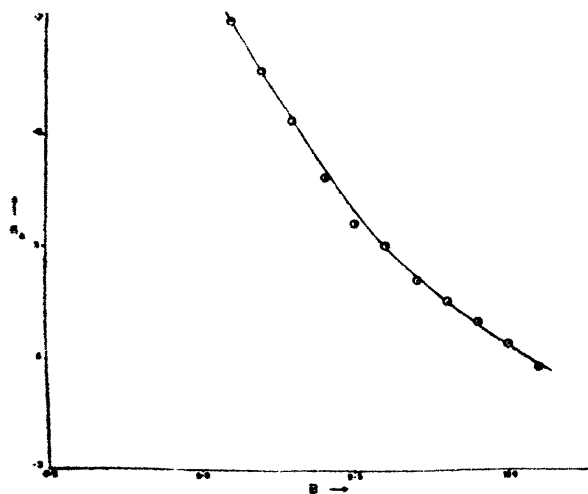


Fig. 1. Formation curve of 2-Hydroxy-1-Naphthalidene-2'-Methyl-4'-Nitroaniline. Plot of  $\bar{n}_A$  vs B.

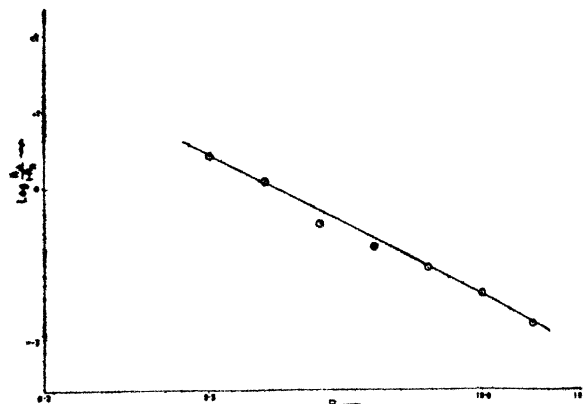


Fig. 2. 2-Hydroxy-1-Naphthalidene-2'-Methyl-4'-Nitroaniline. Plot of  $\log \frac{\bar{n}_A}{1 - \bar{n}_A}$  vs B

TABLE I—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES\*

Cations	$t = 25^\circ C$						
	$H^+$	$Y^{3+}$	$La^3$	$Pr^{3+}$	$Nd^{3+}$	$Dy^{3+}$	$Gd^{3+}$
$\log K_1$	9.6	7.00	6.20	5.98	6.67	6.02	6.39
$\log K_2$	—	5.92	5.00	4.75	6.32	5.80	5.06

\* For proton association ( $H^+$ ),  $K_1$  corresponds to the species  $LH$ , while for metal ions  $K_1$  and  $K_2$  correspond to the species  $ML_1$  and  $ML_2$  respectively.

The rare earth metal ions differ from each other in the number of electrons in the 4f orbitals which are effectively shielded from the interaction with ligand orbitals by electrons in 5s and 5p orbitals. Hybridization would involve normally unoccupied higher energy orbitals (e.g. 5d, 6s, 6p) and this may be expected to occur with the most strongly coordinated ligands. Rare earths, therefore, normally form ionic compounds. The possibility of covalent interaction, however, cannot be completely excluded as reported in the case of acetylacetonone chelates of rare earths<sup>4</sup>.

If the bonds are ionic, the Born relation  $E = \frac{Z^2}{2r} \left[ 1 - \frac{1}{D} \right]$  should hold for the energy change on complexation of a gaseous ion of charge 'Z' and radius 'r' in a medium of dielectric constant 'D'. Since the stability constant is related directly to this energy, the  $\log K$  values should increase linearly with  $Z^2/r$ .

The plots of  $Z^2/r$  vs  $\log K_1$  values of the rare earth complexes do not exhibit any linear increase of  $\log K_1$  with increase in  $Z^2/r$ . The probable explanation of non-linearity could be that the

assumption about ionic character of metal-ligand bond on which the linearity relation is based is not valid. The other probable causes are (i) coordination number of metal ion greater than six, and (ii) steric factor.

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