

# Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-Thiosemicarbazone Complexes with $\text{Be}^{2+}$ , $\text{Y}^{3+}$ , $\text{Pr}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Dy}^{3+}$ , $\text{Gd}^{3+}$ and $\text{UO}_2^{2+}$

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Potentiometric studies have been carried out on metal complexes of  $\text{Be}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{UO}_2^{2+}$  with 2-hydroxy-1-naphthalidene-thiosemicarbazone. The proton-ligand 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  $25 \pm 0.1^\circ$  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.

**I**N the present communication the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-thiosemicarbazone with various 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. 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-thiosemicarbazone was synthesised and repeatedly crystallised to get an analytically pure sample with m.p.  $276^\circ$ . Literature m.p. is  $275^\circ$ .<sup>2</sup>

The dioxan used for experimental work was purified by the method described by Vogel<sup>3</sup>. Distilled water redistilled over alkaline potassium permanganate was used throughout the investigation.

The medium of titration was 75 : 25 per cent 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 which were converted to their respective carbonates and then to their perchlorates. Metal ion solutions of dysprosium and praseodymium were prepared by taking the metal carbonates

of A. R. grade which were then converted to their respective perchlorates. These metal nitrates and carbonates were supplied by S. D. Lab. Chem. Industry, Bombay. Metal ion solutions of uranyl and beryllium were prepared by using AnalaR grade uranyl nitrate and AnalaR grade beryllium oxide, supplied by B.D.H.  $\text{UO}_2^{2+}$  and  $\text{Be}^{2+}$  were estimated gravimetrically as  $\text{U}_3\text{O}_8$  and  $\text{Be}_2\text{P}_2\text{O}_7$ ; the others were standardised complexometrically<sup>4</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 ( $1.025M$ ) solution.

- (i) 5 ml of ( $0.16M$ )  $\text{HClO}_4$  + 5 ml of ( $0.64M$ )  $\text{NaClO}_4$  + 30 ml of dioxan.
- (ii) 5 ml of ( $0.16M$ )  $\text{HClO}_4$  + 5 ml of ( $0.64M$ )  $\text{NaClO}_4$  + requisite amount of reagent accurately weighed to give  $0.004M$  reagent concentration in the final solution + 30 ml of dioxan.
- (iii) 5 ml of ( $0.64M$ )  $\text{NaClO}_4$  + 5 ml of metal salt ( $0.008M$ ) solution in ( $0.16M$ )  $\text{HClO}_4$  + 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 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 (Fig. 1) 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. 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'. Both these values agree quite well.

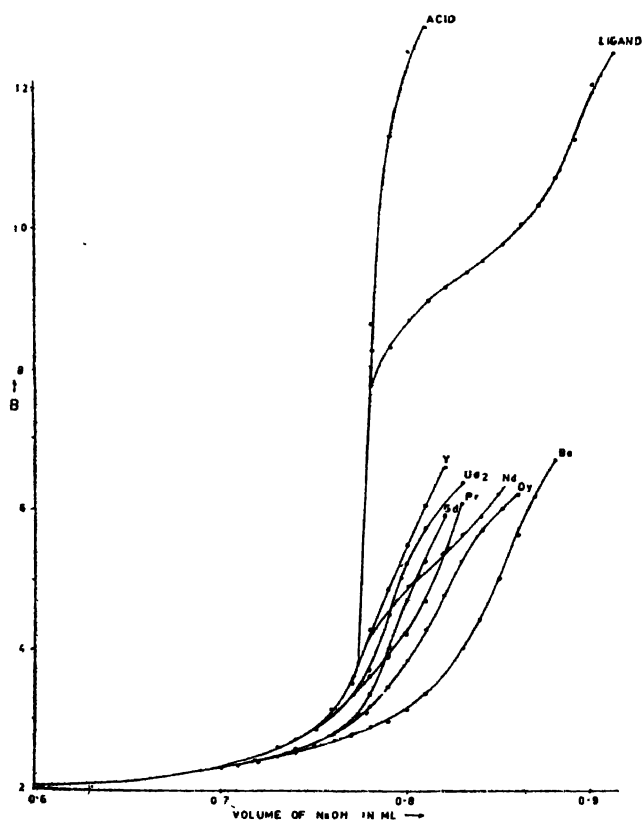


Fig. 1. Titration curves of 2-hydroxy-1-naphthalidene thiosemicarbazone.

From the titration curves of 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 metal complexion equilibria. From this  $\log K_1$  and  $\log K_2$  values were evaluated by the half integral method. In the case of beryllium, neodymium and dysprosium metal systems, since the difference between  $\log K_1$  and  $\log K_2$  values was found to be less than 1.78 log unit, the same were calculated by the least square method and are reported. The values of standard deviation and limits of error<sup>7</sup> were 0.039 and 0.012 respectively.

The most representative values are recorded in Table 1. The order of stability of the various metal chelates was found to be  $Be^{2+} > Dy^{3+} > Pr^{3+} > Gd^{3+} > Nd^{3+} > UO_2^{2+} > Y^{3+}$ .

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES\*

Cations	$t=25^\circ$							
	$H^+$	$Be^{2+}$	$Y^{3+}$	$Pr^{3+}$	$Nd^{3+}$	$Dy^{3+}$	$Gd^{3+}$	$UO_2^{2+}$
$\log K_1$	10.14	10.24	7.59	8.76	7.90	9.13	8.44	7.88
$\log K_2$	—	8.83	—	—	7.10	7.39	—	—

\* 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.

Rare earths, normally form ionic compounds. The possibility of covalent interaction, however, cannot be completely excluded as reported in the case of acetylacetonate chelates of rare earths<sup>8</sup>. If the bonds are ionic, the Born relation  $E = \frac{Z}{2r} \left[ 1 - \frac{1}{D} \right]$  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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