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# Formation constants of chelates of 7-bromo-8-hydroxy-quinoline-5-sulphonic acid with yttrium and some lanthanides

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**Abstract.** Formation constants and thermodynamic parameters of chelation $\triangle F$ $\triangle H$ and $\triangle S$ for chelates of 7-bromo-8-hydroxy-quinoline-5-sulphonic acid with yttrium, lanthanum, praseodymium, neodymium, gadolinium, terbium, dysprosium and holmium are reported and discussed.

**Keywords.** Rare-earth chelates; 7-bromo-8-hydroxyquinoline-5-sulphonic acid; formation constants.

## 1. Introduction

Chang *et al* (1964) published detailed procedures for synthesis of a number of derivatives of 8-hydroxyquinoline-5-sulphonic acid including the 7-bromo-one. The procedure was subsequently reported by Banerji and Srivastava (1967) and used in studies on metal complexes. However, recent work has aroused doubts on these procedures and a definite route for the synthesis of 7-bromo-8-hydroxyquinoline-5-sulphonic acid (Gershon *et al* 1969) has been suggested.

As work on the interaction of 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BrHQS) with rare earth metal ions has not been reported earlier the present studies were undertaken by using a sample of the reagent prepared according to the procedure detailed by Gershon *et al* (1969).

These studies deal with data obtained on formation constants of chelates of $Y^{3+}$ and $La^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$ and $Ho^{3+}$ with BrHQS at 30°, 40° and 50°C at fixed ionic strength. The thermodynamic parameters of chelation are also reported in this paper.

## 2. Experimental

Ligand stock solution of concentration between $3{\cdot}45\times10^{-3}$—$4{\cdot}42\times10^{-3}$ M was obtained by dissolving requisite quantity of BrHQS in freshly boiled double distilled water. Appropriate quantities of rare earth chlorides were dissolved in 0·1 M perchloric acid (Riedel, Germany) to obtain the rare earth metal ion stock solutions. Rare earth oxides (purity 99·9% supplied by Indian Rare Earths) were used to get rare earth chlorides. The metal ion content in the stock solution so obtained was

**Table 1.** Chelate formation constants and thermodynamic functions of yttrium and some lanthanides with 7-bromo-8-hydroxyquinoline-5-sulphonic acid.

Ionic Strength: $\mu$=0·1 Temp.: 30°C

| Metal ion | $n$ in $K_n$ | Log $K_n$* | $-\Delta F$ kcal/mole | $-\Delta H$ kcal/mole | $+\Delta S$ cal/mole |
|---|---|---|---|---|---|
| $H^+$ | 1 | 7·41 | 10·27 | 5·01 | 17·35 |
| | 2 | 2·42 | 3·35 | 2·00 | 4·45 |
| $Y^{3+}$ | 1 | 6·72 | 9·32 | 5·80 | 11·61 |
| | 2 | 5·79 | 8·03 | 6·03 | 6·60 |
| | 3 | 5·24 | 7·26 | 6·25 | 3·33 |
| $La^{3+}$ | 1 | 6·55 | 9·08 | 6·03 | 10·06 |
| | 2 | 5·93 | 8·22 | 6·25 | 6·50 |
| | 3 | 5·50 | 7·62 | 6·48 | 3·76 |
| $Pr^{3+}$ | 1 | 6·80 | 9·43 | 6·92 | 8·28 |
| | 2 | 6·05 | 8·39 | 7·14 | 4·12 |
| | 3 | 5·81 | 8·06 | 7·36 | 2·31 |
| $Nd^{3+}$ | 1 | 7·04 | 9·76 | 5·80 | 13·06 |
| | 2 | 5·78 | 8·01 | 6·02 | 6·57 |
| | 3 | 5·05 | 7·00 | 6·25 | 2·48 |
| $Gd^{3+}$ | 1 | 6.89 | 9.55 | 6·03 | 11·61 |
| | 2 | 5·61 | 7·78 | 6·28 | 4·95 |
| | 3 | 5·41 | 7·50 | 6·49 | 3·33 |
| $Tb^{3+}$ | 1 | 6·40 | 8·87 | 6·44 | 8·02 |
| | 2 | 5·56 | 7·71 | 6·70 | 3·33 |
| | 3 | 5·25 | 7·28 | 6·90 | 1·25 |
| $Dy^{3+}$ | 1 | 7·23 | 10·03 | 7·14 | 9·54 |
| | 2 | 6·40 | 8·87 | 7·35 | 5·01 |
| | 3 | 5·92 | 8·21 | 7·59 | 2·05 |
| $Ho^{3+}$ | 1 | 6·32 | 8·76 | 5·80 | 9·76 |
| | 2 | 5·20 | 7·21 | 6·00 | 3·99 |
| | 3 | 4·84 | 6·71 | 6·25 | 1·50 |

*Accuracy of log $K$ values was $\pm$ 0·05 for the first step and $\pm$0·07 for the second and third steps respectively.

between $1{\cdot}27\times10^{-3}$—$1{\cdot}56\times10^{-3}$ M and was analysed by standard procedure (Topp 1965). Sodium perchlorate solutions of appropriate strength were used for maintaining an ionic strength of 0·1 in three solutions prepared according to the experimental procedure reported earlier (Kane and Joshi 1974). The results are presented in table 1.

## 3. Results and discussion

$\bar{n}_A$ values for the ligand and $\bar{n}$ values for the metal chelate were calculated using the standard procedure (Irving and Rossotti 1954). The highest $\bar{n}_A$ value of 1·9 indicated the presence of two dissociable protons in the ligand. Table 1 gives the proton ligand stability constant values corresponding to the formation of the —OH and —$NH^+$ groups. The highest value obtained for $\bar{n}$ for the metal chelate was 2·9 indicating formation of a 3-step complex. The usual decrease in the magnitude for the forma-

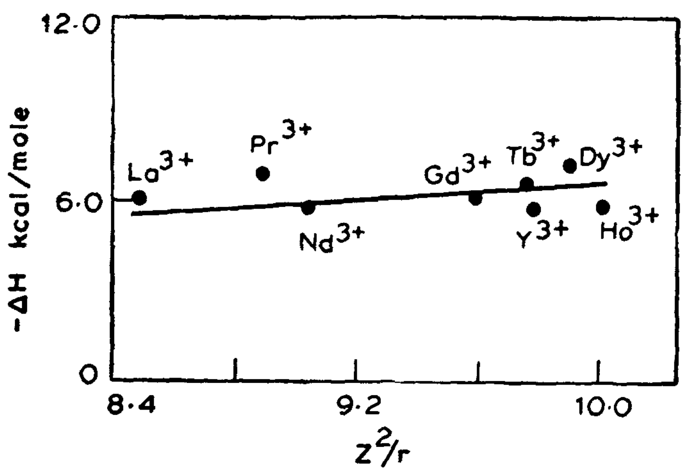


**Figure 1.** Plot of negative enthalphy values against $z^2/r$

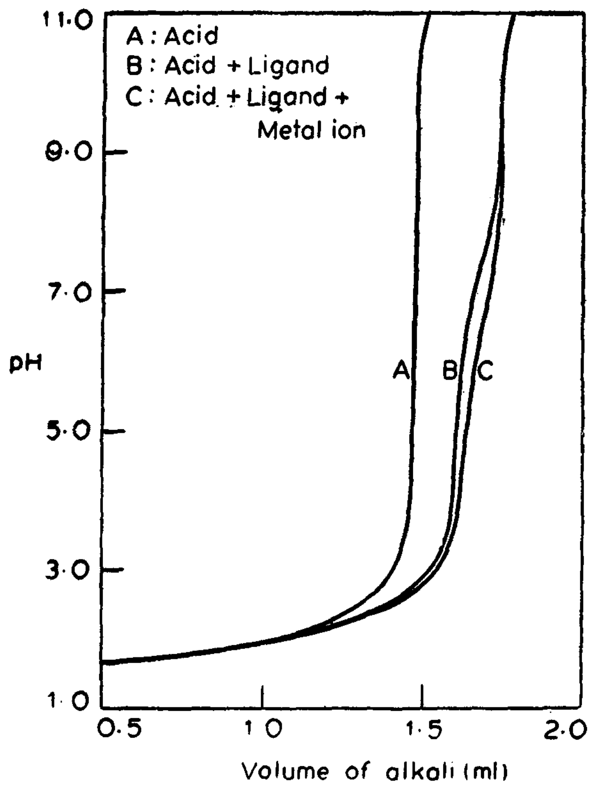


**Figure 2.** $La^{3+}$—BrHQS system, 30°C, $\mu$=0·1

tion constants of the first, second and third steps of chelation was obtained. The formation constant values for the BrHQS chelates are low as compared to the corresponding chelates with 8-hydroxyquinoline-5-sulphonic acid. As the basicity of

BrHQS is less than that of 8-hydroxyquinoline -5-sulphonic acid, the lower formation-constant values of the chelates of BrHQS are understandable.

Values of log $K_1$ for the metal chelate vary linearly with $z^2/r$ for the metal ions which agree with the observations of Williams (1954). $\triangle H$ values (table 1) indicate that the chelates are formed exothermically. $\triangle H$ is primarily seen to be a function of inverse radius of the metal ions. This is indicated by the plot of negative enthalpy values against $z^2/r$ (figure 1). The positive entropy values indicating increase of entropy during complexation, can be explained on the assumption of partial displacement of water of hydration frozen to the metal ions, when chelate formation takes place.

Hydrolysis of the metal ions, under the experimental conditions, is ruled out in the light of the nature of metal ion ligand titration curves (see figure 2).

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