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Stability Constants of Lanthanoid(III) Complexes with 7-Bromo-8-hydroxy-5-quinolinesulfonic Acid

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Stability constants of the tervalent yttrium and lanthanoid complexes with 7-bromo-8-hydroxy-5-quinolinesulfonic acid have been determined in aqueous medium containing 0.100 M sodium perchlorate at 25±1 °C by means of pH-titration. The trends in the order of the stability constants of these complexes are also discussed.

The metal complexes of 8-quinolinol have been extensively investigated, but those of 7-bromo-8-hydroxy-5-quinolinesulfonic acid do not appear to have been investigated in detail. This is especially the case with complexes with the tervalent lanthanoid ions. The present communication describes the results of pH-titration for the determination of stoichiometric stability constants K of the tervalent yttrium and the lanthanoid complexes with 7-bromo-8-hydroxy-5-quinolinesulfonic acid in aqueous solutions containing 0.100 M sodium perchlorate at 25° (±1°)C. The results indicate a stepwise formation of 1 : 1, 1 : 2, and 1 : 3 metal : ligand complexes. The $\log K_3$ values could not be determined with an accuracy better than ±0.8 because of the precipitate formation around $\bar{n}=1.9$—2.2.

Experimental

7-Bromo-8-hydroxy-5-quinolinesulfonic Acid was prepared from 8-quinolinol.[1] *Lanthanoid(III) perchlorate* solutions were prepared by dissolving 84—100 mg of the oxides (Johnson, Matthey & Co. Ltd., Specpure grade) in 5 ml of warm 0.84 M perchloric acid, and diluting the solutions to 100 ml with water. The concentration of perchloric acid in the metal solutions was determined by Gran's titrimetric method.[2] A 0.50 M sodium perchlorate (B.D.H.) solution was used to keep the concentration of the perchlorate ions at 0.100 M in the final solutions used for titration. *Sodium hydroxide* solution, free from carbonate, was prepared from sodium hydroxide pellets (B.D.H.) and standardized against potassium hydrogen phthalate.

Titration Procedure. The following solutions were prepared for the titration of a set of metal — ligand concentrations:

(1) 5.00 ml of E molar perchloric acid, 4.00 ml of 0.50 M sodium perchlorate, and 11.00 ml water,

(2) 5.00 ml of E molar perchloric acid, 4.00 ml of 0.50 molar sodium perchlorate, 1.00 ml of water, and 10.00 ml of T_L molar 7-bromo-8-hydroxy-5-quinolinesulfonic acid,

(3) 5.00 ml of T_M molar metal solution (prepared in E' molar perchloric acid) adjusted to E molar acid concentration (using sodium hydroxide or perchloric acid), (4.00—10 E') ml of 0.50 molar sodium perchlorate (10 E' ml of 0.50 molar sodium perchlorate solution compensating the perchlorate ions present in metal solutions, *i.e.*, for 5.00 ml of E' molar perchloric acid; E' was in the range 0.0437—0.0213 M for different metal solutions), (1.00+10 E') ml of water and 10.00 ml of T_L molar 7-bromo-8-hydroxy-5-quinolinesulfonic acid.

The value of E was kept at 1.00×10^{-3} M. Solution (1), (2), or (3) was then titrated against 1 M molar sodium hydroxide,

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[1] R. G. W. Hollingshead, "Oxine and Its Derivatives," Butterworths Scientific Publications (1959), Vol. 3.

[2] G. Gran, *Analyst*, **77**, 661 (1962).

and the equilibrium pH of the solution at each addition of alkali was recorded. Each titration was repeated till the equilibrium pH of the solutions after each addition of alkali was found to be within 0.02 pH units. Titration of solution (3) was, however, discontinued at the appearance of opalescence in solution.

Calculations

The plots of $\bar{n}$, the ligand number, *vs.* pL, L being the equilibrium concentration of the ligand, for a metal complex were calculated from the results of titration using equations similar to those proposed by Irving and Rossotti:[3]

$$\bar{n}_{\mathrm{h}} = \left(yT_{\mathrm{L}} + \frac{(V_1 - V_2)(N+E)}{V^0 + V_1}\right) / T_{\mathrm{L}} \tag{1}$$

$$\bar{n} = \frac{(V_3 - V_2)(N+E+(y-\bar{n}_{\mathrm{h}})T_{\mathrm{L}})}{(V^0 + V_2)\bar{n}_{\mathrm{h}} T_{\mathrm{M}}} \tag{2}$$

and

$$\mathrm{p}L = -\log L = \log \frac{\sum_0^J \beta_j^{\mathrm{H}} (\mathrm{H}^+)^j}{T_{\mathrm{L}} - \bar{n} T_{\mathrm{M}}} \times \frac{V^0 + V_3}{V^0} \tag{3}$$

where the symbols have their usual meanings.[3]

As the formation function for mononuclear complexes can be given by

$$\bar{n} = \frac{K_1 L + 2K_1K_2L^2 + 3K_1K_2K_3L^3}{1 + K_1L + K_1K_2L^2 + K_1K_2K_3L^3} \tag{4}$$

the corresponding stability constants K_n were calculated from the experimental points from the linear plots of the equations

$$\frac{\bar{n}}{1-\bar{n}} \cdot \frac{1}{L} = K_1 + \frac{2-\bar{n}}{1-\bar{n}} \cdot K_1K_2L \tag{5}$$

and

$$\left(\frac{\bar{n}}{2-\bar{n}} \cdot \frac{1}{L} + \frac{\bar{n}-1}{2-\bar{n}} \cdot K_1\right)\frac{1}{L} = K_1K_2 + \frac{3-\bar{n}}{2-\bar{n}} \cdot K_1K_2K_3L. \tag{6}$$

Results and Discussion

Assuming the ligand to be the bivalent anion of the unionized molecule (obtained by the ionization of the sulfonic acid and the hydroxyl groups), the *proton association constants* for the ligand were determined to be $\log K_1^{\mathrm{H}} = 7.32 \pm 0.03$, $\log K_2^{\mathrm{H}} = 4.38 \pm 0.03$, and $\log K_3^{\mathrm{H}}$ less than 2 in aqueous solutions containing 0.100 M sodium perchlorate at 25 °C. The stability constants for yttrium(III) and lanthanoid(III) complexes with 7-bromo-8-hydroxy-5-quinolinesulfonic acid are given in Table 1.

TABLE 1. STOICHIOMETRIC STABILITY CONSTANTS OF 7-BROMO-8-HYDROXY-5-QUINOLINESULFONATE COMPLEXES AT 25°C AND AT $\mu = 0.100$ M ($NaClO_4$)

Lanthanoid(III) ion	$\log K_1$[a]	$\log K_2$[b]	$\log K_3$[c]
La	4.68	4.03	3.4
Ce	4.81	4.19	3.6
Pr	4.97	4.30	3.9
Nd	5.09	4.43	4.0
Eu	5.43	4.70	4.3
Sm	5.30	4.57	4.2
Gd	5.21	4.64	4.0
Tb	5.32	4.77	4.1
Dy	5.45	4.85	4.1
Ho	5.59	4.89	4.1
Er	5.69	4.81	4.0
Tm	5.82	4.73	3.9
Yb	5.93	4.64	3.8
Lu	5.82	4.50[d]	
Y	5.50	4.86	4.2

a) ±0.04 b) ±0.08 c) ±0.8 d) ±0.15

We see that for the lanthanoid(III) complexes, $\log K$ increases regularly with the atomic number of the lanthanoid from lanthanum to europium, the values for gadolinium complexes being lower than those for the europium complexes, a trend established for the lanthanoid complexes.[4] In case of heavy lanthanoid complexes, however, two trends are observed:

(1) $\log K_1$ increases regularly from gadolinium to ytterbium,

(2) $\log K_2$ increases from gadolinium to holmium and then drops for the next members of the series.

The first trend is very common for the lanthanoid complexes. The less common second trend is also observed. This might be due to the steric factors involved in the introduction of the second ligand molecule to the 1 : 1 complex.

The $\log K$ values for lutetium complexes are lower than those for ytterbium complexes, probably due to the same factors as responsible for the gadolinium-break.

As a result of their observations on the stability constants of the lanthanoid and yttrium complexes with a common ligand, Yoneda *et al.*[5] concluded that the $\log K$ for yttrium complex is comparable to that for light lanthanoid complexes in case of monodentate ligands, but of the heavy lanthanoid complexes for multidentate ligands forming chelate structure. As expected for the present ligand, the stability constants for yttrium(III) complexes are among those of the heavy lanthanoid complexes.

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[3] H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, **1954**, 2904.

[4] T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Fiestel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

[5] H. Yoneda, G. R. Choppin, J. L. Bear, and A. J. Graffeo, *Inorg. Chem.*, **4**, 244 (1965) and references therein.