FORMATION CONSTANTS OF CHELATES OF 7-IODO-8-HYDROXY QUINOLINE-5-SULPHONIC ACID WITH YTTRIUM AND SOME LANTHANIDES

Y. D. KANE AND D. M. JOSHI

Chemistry Department, Institute of Science, Nagpur

ABSTRACT

Formation constants and thermodynamic parameters of chelation Δ F, Δ H and Δ S for chelates of 7-iodo-8-hydroxy-quinoline-5-sulphonic acid with yttrium, lanthanum, neodymium, gadolinium and dysprosium are reported.

7-IODO-8-hydroxy quinoline-5-sulphonic acid was first introduced by 'Yoe[1] for the colorimetric estimation of Fe^{3+}. Subsequent investigations were confined to the use of the reagent for chelatometric studies with some divalent[2,3] and trivalent[4] metal ions. Recently Chang *et al.*[5] have determined the formation constants of a number of rare earth chelates of the reagent at 25° C using water dioxane medium.

Literature survey has indicated absence of information on thermodynamic parameters of chelation on rare earth-7-iodo-8-hydroxyquinoline-5-sulphonic acid chelates. The present work hence deals with data obtained on formation constants of chelates of Y^{3+}, La^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+} with 7-iodo-8-hydroxy quinoline-5-sulphonic acid, at 30°, 40° and 50° C at fixed ionic strength. Values of thermodynamic parameters for chelation are also reported.

EXPERIMENTAL

Metal ion solutions.—All rare earth metal ion stock solutions were prepared by dissolving appropriate quantities of rare earth chlorides (obtained from the respective rare earth oxides, purity 99·9%, supplied by M/s. Indian Rare Earths, Kerala, India) in about 0·1 M perchloric acid (Riedel, Germany), as to give a stock solution with metal ion content lying between $1 \cdot 2 \times 10^{-3}$–$1 \cdot 6 \times 10^{-3}$ M. Metal ion solutions were analysed for the metal ion content as per usual procedure[6].

Ligand solution : Ligand stock solution was about 6×10^{-3} M and obtained by dissolving requisite quantity of 7-iodo-8-hydroxy quinoline-5-sulphonic acid (Fluka, Swiss, recrystallised, m.p. 259–260° C, lit. 260° C, equivalent wt. ($-SO_3H$): 351·1) in freshly boiled double distilled water.

Alkali solution : Carbonate free sodium hydroxide solution of about 1·5 M strength was used in all titrations. This solution was standardised against solid potassium hydrogen phthalate (BHD AnalaR) before every titration.

Sodium perchlorate solution : Standard sodium perchlorate solution was obtained by neutralising standard perchloric acid solution with sodium hydroxide. The strength of sodium perchlorate was adjusted so as to help in maintaining an ionic strength of 0·1 in the solutions A, B and C prepared below. This was necessary as the perchloric acid used in the metal ion solution was not always of the same strength.

Titration Technique.—The Calvin-Bjerrum titration technique as adopted by Irving and Rossotti[7] was used. Three sets of solutions for each metal ion were prepared for studies at any given temperature.

Solution A : 25 ml $HClO_4$ (0·1 M) + 50 ml H_2O + 25 ml $NaClO_4$

Solution B : 25 ml $HClO_4$(0·1 M) + 50 ml ligand solution + 25 ml $NaClO_4$.

Solution C : 25 ml $HClO_4$(0·1 M) containing metal ion + 50 ml ligand solution + 25 ml $NaClO_4$.

In all experiments the ligand to metal ratio was kept above 5.

pH titrations at any required temperature were achieved by placing the solutions in a glass thermostat (± 0·1° C) and adding sodium hydroxide (0·01 ml aliquot) the solution being stirred by a glass stirrer mechanically. Nitrogen gas (M/s. Indian Oxygen Ltd., Bombay) presaturated with water vapour at the same temperature was bubbled

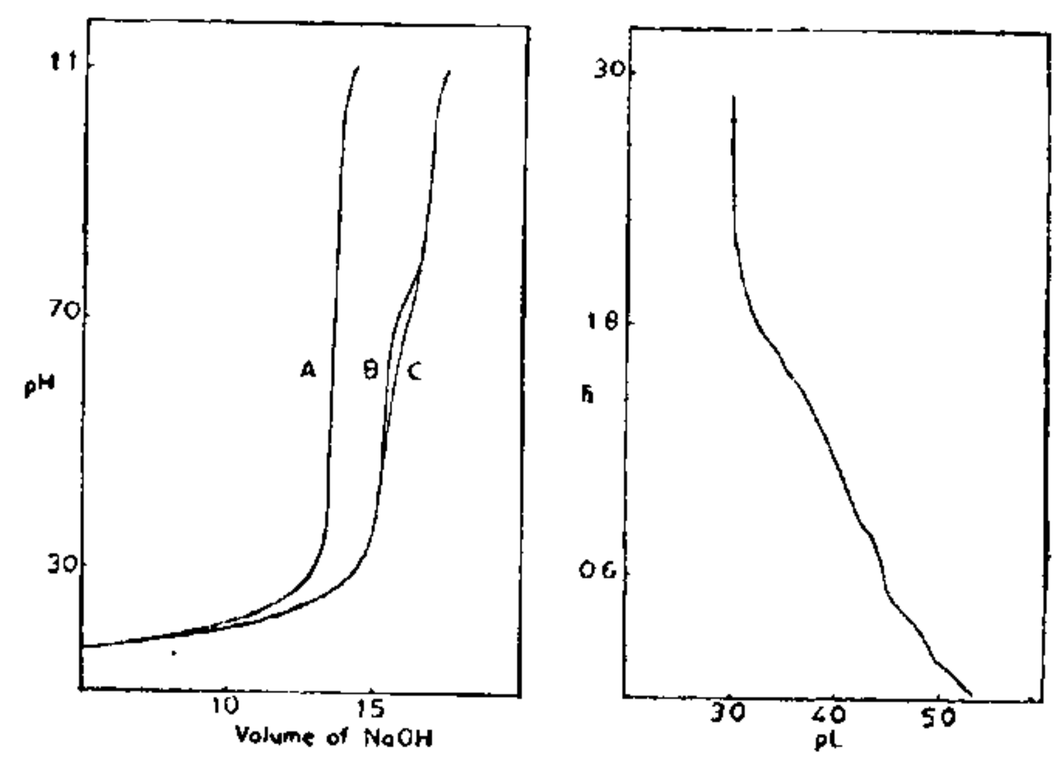

FIG. 1. La^{3+}–7I8HQ5S system ; 30° C ; $\mu = 0 \cdot 1$.

through the solution during titration. A Philips pH meter, No. PR 9405 (accuracy ± 0·05) was used, and was standardised daily at each temperature using phthalate buffer[8]. All titrations were performed in duplicate to test for reproducibility.

Values of $\bar{n}_A$, $\bar{n}$ and pL for the metal ion-ligand titrations were obtained from graphs corresponding to titrations of solutions A, B and C (Fig. 1 representative titration curve for La^{3+}) and were calculated using the following expressions[7].

$$\bar{n}_A = \left\{ yT_L^0 + \frac{(N+E^0)(V'-V'')}{(V_0+V')} \right\} \Big/ T_L^0$$

$$\bar{n} = \frac{(V'''-V'')\,[N+E^0+T_L^0(y-\bar{n}_A)]}{(V_0+V'')\,\bar{n}_A . T_m^0}$$

and

$$pL = \log \left[\frac{1+K_1(H^+)+K_1K_2(H^+)^2}{T_L^0-\bar{n}.T_m^0} \cdot \frac{V_0+V'''}{V_0} \right]$$

Values of proton ligand stability constants of 7-iodo-8-hydroxy quinoline-5-sulphonic acid were treated by (*i*) interpolations at half $\bar{n}$ values and (*ii*) interpolation at various $\bar{n}_A$ values at each temperature and the mean reported. Values of metal ligand stability constants log K_1, log K_2 and log K_3 obtained from $\bar{n}$ *vs* pL curves (Fig. 1) were refined both by (*i*) correction term method and (*ii*) graphical method and average of these reported. The results are reported in Table I. Table I also gives values of thermodynamic parameters ΔF, ΔH and ΔS for chelation calculated as per standard procedure.

Results and Discussion

Values of $\bar{n}_A$ did not go beyond 1·8 at the three temperatures indicating presence of only two dissociable protons in the ligand. Proton ligand stability constants (for –OH and NH^+ formation) are in agreement with those reported earlier[3].

Values of $\bar{n}$ for metal, in no case went beyond 2·9 indicating formation of 1 : 3 complex between metal and ligand. Stepwise formation constants for the complex log K_1, log K_2 and log K_3 reported in Table I show trends similar to those observed earlier for 8-hydroxy quinoline-5-sulphonic acid chelates with rare earths[9]. In comparison the chelates of 7-iodo-8-hydroxy quinoline-5-sulphonic acid are weaker than the corresponding chelates of 8-hydroxyquinoline-5-sulphonic acid, which may be ascribed to the lower basicity of the 7-iodo derivative. In all cases the nature of the metal titration curves served to indicate absence of hydrolysis of the metal ion.

Table I

Chelate formation constants and thermodynamic functions of yttrium and some lanthanides with 7-iodo-8-hydroxy quinoline-5-sulphonic acid

Ionic Strength : $\mu = 0 \cdot 1$ 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.	6·89	9·55	4·80	15·6
	2.	2·40	3·30	1·80	4·9
Y^{3+}	1.	5·80	8·04	2·23	19·1
	2.	4·96	6·87	2·45	14·6
	3.	4·08	5·65	2·90	9·0
La^{3+}	1.	4·52	6·26	1·56	15·3
	2.	3·64	5·04	3·34	5·6
	3.	3·00	4·16	2·90	4·1
Nd^{3+}	1.	5·01	6·94	2·45	15·1
	2.	4·10	5·68	2·45	10·6
	3.	3·02	4·18	2·90	4·2
Gd^{3+}	1.	5·34	7·40	4·24	10·4
	2.	4·42	6·13	2·68	11·3
	3.	3·21	4·45	3·57	2·9
Dy^{3+}	1.	5·17	7·17	1·34	19·2
	2.	4·11	5·70	3·12	8·5
	3.	3·00	4·16	3·35	2·6

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

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