Thermochimica Acta, 18 (1977) 329–331
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

Note

Stability constants of chelates of 3-hydroxynaphthalene-2-carboxylic acid with yttrium(III), cerium(III) and lanthanum(III)

S. S. SANDHU, J. N. KUMARIA AND R. S. SANDHU
Department of Chemistry, Guru Nanak Dev University, Amritsar (India)
(Received 2 June 1976)

3-Hydroxynaphthalene-2-carboxylic acid is an efficient complexing agent. The hydroxy group being *ortho* to the carboxylic acid group forms well defined complexes with several metal ions[1–6]. Amongst the trivalent metals, yttrium(III) by virtue of its resemblance to rare earth metal ions, is expected to form strong complexes. Recently, complexes of few lanthanides with 3-hydroxynaphthalene-2-carboxylic acid have been prepared in which coordination through the oxygen of the hydroxyl group of the acid has been indicated with the help of UV, visible and IR spectra[7]. Thermodynamic stability constants of Y(III), Ce(III) and La(III) complexes with the same ligand in aqueous dioxane (50%, v/v) at 30°C and four different ionic strengths has already been reported by us[8].

In the present investigation, the stability constants of the chelates of 3-hydroxynaphthalene-2-carboxylic acid with Y(III), Ce(III) and La(III) have been determined in aqueous dioxane (50%, v/v) at 20, 30 and 40°C and at ionic strength 0.1M KNO_3 using the Irving and Rossotti titration technique[9].

EXPERIMENTAL

Dioxane was purified by the recommended procedure[10]. The double distilled CO_2 free water was used in all experimental work. The solution of the ligand (0.05 M) was prepared by dissolving it in dioxane.

Photovolt digital pH-meter type M-120, having an accuracy of ±0.002 units was calibrated by suitable buffers before use. All experiments were performed at 20, 30 and 40°C and at $\mu = 0.1$ M (KNO_3) in (50%, v/v) aqueous dioxane mixture.

The three solutions (total volume 50 ml in each case) were prepared as follows: (A) 1.0×10^{-2} M HNO_3; (B) 1.0×10^{-2} M $HNO_3 + 5.0 \times 10^{-2}$ M ligand; (C) 1.0×10^{-2} M $HNO_3 + 5.0 \times 10^{-2}$ M ligand $+ 1.0 \times 10^{-2}$ M metal ion solution, such that the concentrations of the common ingredients were identical in different cases. An appropriate quantity of potassium nitrate solution (1.0 M) was added to maintain the ionic strength at 0.1 M. The above solutions were titrated against standard potassium hydroxide solution prepared in aqueous dioxane (50%, v/v). The shapes of the titration curves were as usual.

The concentrations were corrected for the changes in volume produced by the addition of alkali during titrations.

RESULTS AND DISCUSSION

Values of formation functions $\bar{n}_A$, $\bar{n}$ and pL were calculated using the standard expressions[9].

Log pK_2^H was obtained from the formation curve plotted between $\bar{n}_A$ vs. pH by interpolation at half $\bar{n}_A$ value. It has also been calculated by interpolation at various $\bar{n}_A$ values.

In the case of 3-hydroxynaphthalene-2-carboxylic acid, since there are very few values of $\bar{n}_A <$ one, the value of log pK_1^H has been obtained by using the following relationship:

$$\log pK_1^H pK_2^H = 2\,\text{pH}\ (\text{at}\ \bar{n}_A = 1)$$

The plots of $\bar{n}$ vs. pL for the complexes indicate that the values of $\bar{n}$ obtained are of the order of 2, at an apparent pH 6.5 which is approximately the hydrolysis region of the rare-reath metal ion. Regions above this value were not employed for calculations. It may thus be inferred that 1:1 and 1:2 metal chelates of 3-hydroxynaphthalene-2-carboxylic acid with Y(III), Ce(III), and La(III) are formed by the metal ion and the oxygen of the *o*-hydroxy group as well as the carboxylic acid group.

Stability constants of the metal complexes (log K_1, log K_2) were obtained from the $\bar{n}$ vs. pL formation curves and treated by interpolation at half $\bar{n}$ values[11], inter-

TABLE I

VALUES OF PROTONATION CONSTANTS, STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS AT THREE TEMPERATURES

Cation	*Constants*	*Temp. (°C)*			*−ΔG° (kcal mol⁻¹)*			*ΔH° (kcal mol⁻¹) at 30°C*	*ΔS° (kcal mol⁻¹ degree⁻¹) at 30°C*
		20	*30*	*40*	*20°C*	*30°C*	*40°C*		
H(I)	log pK_1^H	11.52	11.25	10.95					
	log pK_2^H	2.78	2.65	2.45					
	log $p\beta_2^H$	14.30	13.90	13.40					
Y(III)	log K_1	8.70	8.55	8.30					
	log K_2	8.37	8.13	8.00					
	log β_2	17.07	16.68	16.30	22.88	23.13	23.35	−16.8	21.0
Ce(III)	log K_1	8.67	8.52	8.21					
	log K_2	7.87	7.52	7.36					
	log β_2	16.54	16.04	15.57	22.17	22.24	22.30	−20.3	6.3
La(III)	log K_1	8.51	8.20	7.98					
	log K_2	7.78	7.57	7.39					
	log β_2	16.29	15.77	15.37	21.84	21.86	22.01	−19.5	7.8

polation at various $\bar{n}$ values and graphical method[12] and extended to an aqueous dioxane mixture by Van Uitert and Haas[13].

The error limits are ±0.05 for log K_1 and log K_2 values.

The mean values of protonation constants (log pK_1^H, log pK_2^H) and formation constants (log K_1, log K_2) are reported in Table 1.

The values of overall changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) accompanying complexation have been determined using the temperature coefficient and Gibbs-Helmholtz equation[14] (Table 1).

The accuracy of $\Delta G°$, $\Delta H°$ and $\Delta S°$ values is ±0.08 kcal mol^{-1}, ±0.1 kcal mol^{-1} and ±0.3 cal $degree^{-1}$ mol^{-1}, respectively.

The values of protonation constants and formation constants decrease with increase of temperature. The order of overall stability (log β_2) is Y(III)>Ce(III)>La(III) as expected on the basis of their electronic configuration. The free energies of formation ($\Delta G°$) of the complexes have more negative values with increase of temperature showing that complex formation is a spontaneous process. The enthalpy change ($\Delta H°$) being negative in all cases is favourable for the formation of these complexes. The entropy change ($\Delta S°$) being positive in all cases also favours the formation of complexes.

REFERENCES

1 R. P. Aggarwal and R. C. Mehrotra, *J. Less-Common Metals*, 3 (1961) 398.
2 M. N. Desai, *Curr. Sci.*, 34 (1965) 312.
3 S. L. Gupta and R. N. Soni, *J. Indian Chem. Soc.*, 43 (1966) 473.
4 O. Makitie, *Suomen Kemistil. B*, 39 (1966) 26, 175.
5 S. L. Gupta and R. N. Soni, *J. Indian Chem. Soc.*, 44 (1967) 195.
6 S. S. Sandhu, J. N. Kumaria and R. S. Sandhu, *J. Indian Chem. Soc.*, 53 (1976) 435.
7 Y. H. Deshpande and V. R. Rao, *J. Inorg. Nucl. Chem.*, 35 (1973) 3626.
8 S. S. Sandhu, J. N. Kumaria and R. S. Sandhu, *Thermochim. Acta*, 16 (1976) 245.
9 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1954) 2904.
10 A. I. Vogel, *A Text-Book of Practical Organic Chemistry*, Longmans Green, London, 1961, p. 177.
11 J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, P. Haase and Son, Copenhagen, 1941, p. 298.
12 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1953) 3397.
13 L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 75 (1953) 451.
14 K. B. Yatsimirskii and V. P. Vasil' Ev, *Instability Constants of Complex Compounds*, Van Nostrand New York, 1960, p. 63.