Note

Thermodynamic stability constants of yttrium(III), cerium(III), and lanthanum(III) complexes with 3-hydroxy naphthalene-2-carboxylic acid

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Stability constants can be used to predict the conditions required for the complete formation of a given complex. Reliable information of this type is of great importance in planning analytical and separation procedures. Amongst the trivalent metals, yttrium(III), by virtue of its resemblance to rare earth metal ions, is expected to form strong complexes. The complexes of 3-hydroxy naphthalene-2-carboxylic acid with different metal ions have been studied earlier by various workers under different experimental conditions[1–5]. Recently, complexes of lanthanides with 3-hydroxy naphthalene-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[6]. In the present study the stability constants of Y(III), Ce(III) and La(III) with 3-hydroxy naphthalene-2-carboxylic acid have been determined in 50% (V/V) dioxane–water medium at 30°C at four different ionic strengths of 0.05, 0.10, 0.15 and 0.20 M KNO_3. The study reveals the formation of both 1:1 and 1:2 complexes. Thermodynamic formation constants have also been determined and free energy values have been evaluated from them.

EXPERIMENTAL

For the investigations of metal–ligand equilibria, it becomes necessary to control the free ligand concentration in order that various equations can be applied. This can be achieved either by changing the total ligand concentration or by varying the total acid in the system with the addition either of an acid or of alkali. The pH titration technique of Bjerrum[7] and Calvin[8] as modified by Irving and Rossotti[9] has been employed in the present investigations.

All chemicals used were of B.D.H. AnalaR quality. Twice-distilled CO_2 free water was used in all experimental work. Dioxane was purified by the method described by Vogel[10]. The pH was measured on a Digicord pH meter having a sensitivity of ±0.002 and was calibrated by suitable buffers before use. The thermostat bath temperatures were maintained at 30±0.1 °C and titrations were carried out in 50% (V/V) dioxane–water medium.

The three solutions 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 common ingredients were identical in different cases. An appropriate quantity of potassium nitrate solution was added to maintain the desired ionic strength, i.e., $\mu = 0.05$, 0.10, 0.15 and 0.20 M. The initial volume of the solution was 50 ml in all the cases. The above solutions were titrated with standard potassium hydroxide solution prepared in 50% (V/V) dioxane–water mixture.

Three titration curves were obtained which were referred to as (i) acid titration curve; (ii) ligand titration curve; (iii) complex titration curve.

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

RESULTS AND DISCUSSION

Since the solutions employed were dilute, the probability of the existence of hydrogen and hydroxyl bearing complexes and the complexes with anions present can reasonably be considered to be negligible under the experimental conditions of our present investigation and have been ignored. The hydrolysis of the metal ion is accompanied by liberation of protons and as such a displacement of the metal titration curve is possible, even in the absence of any reaction with the reagent. In order to avoid the error all calculations were made below the pH at which any precipitate occurred.

$\bar{n}_H$, $\bar{n}$ and pL were calculated by employing the relationships derived by Irving and Rossotti[9].

The practical proton ligand stability constant, $\log {}^P K_2^H$ was obtained from the proton–ligand formation curve plotted between $\bar{n}_H$ vs. pH, as Bjerrum's half-integral value at 1.5 $\bar{n}_H$. The same has also been calculated by interpolation at various $\bar{n}_H$ values using the following equation:

$$\log {}^P K_2^H = pH + \log (\bar{n}_H - 1)/(2 - \bar{n}_H)$$
(for all points above $\bar{n}_H = 1$)

In the case of 3-hydroxy naphthalene-2-carboxylic acid, since there are few values of $\bar{n}_H$ lower than one, the value of $\log {}^P K_1^H$ has been obtained by using the following relationship:

$$\log {}^P K_1^H \, {}^P K_2^H = 2pH \text{ (at } \bar{n}_H = 1).$$

The plots of $\bar{n}$ vs. pL for the complexes indicate that the values of $\bar{n}$ obtained are of the order of 2. This suggests that Y(III), Ce(III) and La(III) form two types of complexes in the proportion of 1:1 and 1:2 with the ligand.

Metal–ligand stability constants $\log K_1$ and $\log K_2$ were calculated from the formation curves obtained by plotting graphs of $\bar{n}$ vs. pL, using Bjerrum's half integral method[7], pointwise calculation or interpolation at various $\bar{n}$ values and the

graphical method[11], and extended to dioxane–water mixture by Van Uitert and Haas[12]. Since the ratio of succesive constants is less then 10^4, i.e., $K_1/K_2 < 10^4$, the method of successive approximations[11] was used to refine the values of $\log K_1$ and $\log K_2$.

The error limits are ± 0.05 for $\log K_1$ and $\log K_2$ values of stability constants.

The differences in the values of $\log K_1$ and $\log K_2$ for Y(III), Ce(III) and La(III) complexes with the ligand in each case are less than 1.5, thus suggesting that formation of two types of complexes ML and ML_2 proceeds simultaneously and the metal–ligand equilibria can be expressed as:

$$M^{3+} + 2H_2L \rightleftharpoons ML_2 + 4H^+$$
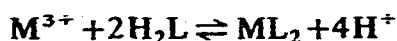
The metal–ligand stability data at various μ values (Table 1) reveal that $\log \beta_2$ values decrease with an increase in the ionic strength of the medium. According to Hückel[13], the activity of the metal ion for its interaction with other molecular species varies in inverse proportion to the ionic strength of the medium in which the reactions were studied. On this basis, the decrease in stabilities for 3-hydroxy naphthalene-2-carboxylic acid complexes of Y(III), Ce(III) and La(III) in solutions of increasing ionic strength is justified.

The order of stability is Y(III) > Ce(III) > La(III) for $\log \beta_2$ values as expected on the basis of their electronic configuration.

The values of log step formation constants at various ionic strengths, extrapolated to zero ionic strength gave step thermodynamic formation constant[14]. These values are shown in Table 2 as $\log K_1^{\mu=0}$, $\log K_2^{\mu=0}$. Their sum is shown as calculated

TABLE 1

VALUES OF THE PROTONATION CONSTANTS OF THE LIGAND
AND CONCENTRATION STABILITY CONSTANTS OF COMPLEXES AT 30°C

Cation	Constants	Method	$\mu = 0.05$	$\mu = 0.10$	$\mu = 0.15$	$\mu = 0.20$
H(I)	$\log {}^rK_1^H$		11.30	11.25	11.20	11.15
	$\log {}^rK_2^H$		2.70	2.65	2.60	2.55
	$\log {}^r\beta_2^H$		14.00	13.90	13.80	13.70
Y(III)	$\log K_1$	(I)	8.75	8.53	8.43	8.33
		(II)	8.75	8.53	8.43	8.33
		(III)	8.79	8.60	8.39	8.31
		Mean	8.76	8.55	8.42	8.32
		(IV)	8.46	8.22	8.11	8.03
	$\log K_2$	(I)	8.30	8.13	7.97	7.84
		(II)	8.30	8.13	7.97	7.84
		(III)	8.27	8.12	7.95	7.81
		Mean	8.29	8.13	7.96	7.83
		(IV)	8.59	8.46	8.29	8.14
	$\log \beta_2$		17.05	16.68	16.38	16.15

TABLE 1 *(continued)*

Cation	Constants	Method	$\mu = 0.05$	$\mu = 0.10$	$\mu = 0.15$	$\mu = 0.20$
Ce(III)	log K_1	(I)	8.63	8.52	8.45	8.30
		(II)	8.63	8.52	8.45	8.30
		(III)	8.62	8.51	8.41	8.30
		Mean	8.63	8.52	8.44	8.30
		(IV)	8.53	8.41	8.31	8.16
	log K_2	(I)	7.58	7.58	7.50	7.42
		(II)	7.58	7.58	7.50	7.42
		(III)	7.55	7.40	7.47	7.40
		Mean	7.57	7.52	7.49	7.41
		(IV)	7.67	7.63	7.62	7.55
	log β_2		16.20	16.04	15.93	15.71
La(III)	log K_1	(I)	8.33	8.20	8.10	8.02
		(II)	8.33	8.20	8.10	8.02
		(III)	8.29	8.20	8.13	8.04
		Mean	8.32	8.20	8.11	8.03
		(IV)	8.12	7.97	7.90	7.83
	log K_2	(I)	7.62	7.58	7.45	7.31
		(II)	7.62	7.58	7.45	7.31
		(III)	7.61	7.55	7.41	7.33
		Mean	7.62	7.57	7.44	7.32
		(IV)	7.83	7.81	7.66	7.52
	log β_2		15.94	15.77	15.55	15.35

(I)   = Bjerrum's half-integral method;
(II) = graphical method;
(III) = interpolation at various $\bar{n}$ values or pointwise calculation method;
(IV) = method of successive approximations.

TABLE 2

VALUES OF THERMODYNAMIC STABILITY CONSTANTS AND FREE ENERGIES AT 30 °C

	Metal ion		
	Y(III)	Ce(III)	La(III)
log $K_1^{\mu=0}$	8.93	8.73	8.42
log $K_2^{\mu=0}$	8.45	7.63	7.73
Calcd. log $K^{\mu=0}$	17.38	16.36	16.15
Exptl. log $K^{\mu=0}$	17.38	16.36	16.15
ΔF_1^0 (kcal mol^{-1})	-12.38	-12.10	-11.67
ΔF_2^0 (kcal mol^{-1})	-11.71	-10.58	-10.72
Calcd. ΔF° (kcal mol^{-1})	-24.10	-22.68	-22.39
Exptl. ΔF° (kcal mol^{-1})	-24.10	-22.68	-22.39

$\log K^{\mu=0}$. The values of overall stability constant $\log \beta_2$ at various ionic strengths were likewise extrapolated to zero ionic strength and the overall thermodynamic stability constants thus obtained have been symbolised as experimental $\log K^{\mu=0}$.

Ligational standard free energy was obtained from the expression:

$$\Delta F^\circ = -2.303\ RT \log K^{\mu=0}$$

where $K^{\mu=0}$ is the value of formation constant at zero ionic strength.

The precision of ΔF° value is ± 0.08 kcal mol^{-1}.

REFERENCES

1 R. P. Aggarwal and R. C. Mehrotra, *J. Less-Common Metals*, 3 (1961) 398.
2 M. N. Dessai, *Current Sci.*, 34 (1965) 312.
3 S. L. Gupta and R. N. Soni, *J. Indian Chem. Soc.*, 43 (1966) 473.
4 O. Makitie, *Suomen Kem.*, 1339 (1966) 26, 175.
5 S. L. Gupta and R. N. Soni, *J. Indian Chem. Soc.*, 44 (1967) 195.
6 Y. H. Deshpande and V. R. Rao, *J. Inorg. Nucl. Chem.*, 35 (1973) 3626.
7 J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*. Haase & Son, Copenhagen, 1941, p. 298.
8 M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 67 (1945) 2003.
9 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1954) 2904.
10 A. I. Vogel, *Textbook of Practical Organic Chemistry*. Longmans Green, London.
11 H. Irving and H. S. Rossotti, *J. Chem. Soc.*, (1953) 3397.
12 L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 75 (1953) 451.
13 E. Huckel, *Phys. Z.*, 26 (1925) 93.
14 F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants*, McGraw-Hill, New York, 1961.