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A Spectrophotometric Study of the Thorium Complex of 2-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic Acid

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2-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid has been synthesized. The acid dissociation constants of the reagent have been determined spectrophotometrically at 25°C and at an ionic strength of 0.1. The reagent forms a violet 1 : 1 complex with thorium, showing an absorption maximum at 575 mμ in an acidic solution. The apparent stability constant of the thorium complex was measured over the pH range from 1 to 3.5.

In a series of investigations on *o*-substituted derivatives of phenyl-azo-chromotropic acid as reagents for thorium,1) the behavior of the oxyacetic acid group, $-OCH_2COOH$, upon the complex formation has been studied spectrophotometrically.

The preparation of the reagent, and the spectral properties of the thorium complex were described in a previous short communication.2) The application of this thorium complex to the determination of micro amounts of fluoride ions was reported in the preceding papers.3,4)

Experimental

Reagents. *2-(1, 8-Dihydroxy-3 ,6-disulfo-2-naphthylazo)-phenoxyacetic Acid.* The acetylation of *o*-aminophenol with acetic anhydride yielded the acetyl derivative, which was converted to *o*-acetaminophenoxyacetic acid5) by reaction with monochloroacetic acid in an alkaline medium. The potassium salt of *o*-aminophenoxyacetic acid6) was prepared by the reaction of potassium hydroxide with the lactam of *o*-aminophenoxyacetic acid, which had been obtained by the hydrolysis of *o*-acetaminophenoxyacetic acid with hydrochloric acid. *o*-Aminophenoxyacetic acid was also obtained by the reduction of *o*-nitrophenoxyacetic acid with iron(II) sulfate in alkaline medium. The reagent prepared by coupling chromotropic acid with diazotized potassium *o*-aminophenoxyacetate. The disodium salt of the reagent was obtained as greenish needles by recrystallization of the crude product from water.

Thorium Perchlorate Solution. Thorium nitrate was purified *via* thoriom hydroxide.7) This purified throium hydroxide was dissolved in perchloric acid, and the solution was standardized gravimetrically by oxalate.

All the other reagents used were of the guaranteed reagent grade.

Apparatus and Procedure. The same apparatus and procedure as in the preceding report8) were used for the measurements.

Calculations

Acid Dissociation Constants of the Reagent. The reagent (abbr. H_5R) is dissociated in water as follows:

$$H_3R^{2-} \overset{K_1}{\rightleftarrows} H_2R^{3-} + H^+,$$

and

$$H_2R^{3-} \overset{K_2}{\rightleftarrows} HR^{4-} + H^+$$

The constants of the above dissociation, K_1 and K_2, are:

$$K_1 = [H][H_2R]/[H_3R] \qquad (1)$$

and

$$K_2 = [H][HR]/[H_2R] \qquad (2)$$

respectively, the ionic charge being neglected for the sake of convenience. If the two dissociation steps are separated widely enough, these dissociation equilibria can be treated independently.

Therefore

$$\begin{aligned} pK_1 &= pH - \log\{[H_2R]/[H_3R]\} \\ &= pH - \log\{(E_{H_3R} - E)/(E - E_{H_2R})\} \qquad (3) \end{aligned}$$

where E_{H_3R}, E_{H_2R} and E represent, respectively, the absorbances of H_3R, H_2R and their mixture at a constant wavelength. And also

$$\begin{aligned} pK_2 &= pH - \log\{[HR]/[H_2R]\} \\ &= pH - \log\{(E'_{H_2R} - E')/(E' - E'_{HR})\} \qquad (4) \end{aligned}$$

where E'_{H_2R}, E'_{HR} and E' represent, respectively, the absorbances of H_2R, HR and their mixture at

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1) H. Miyata, This Bulletin, **36**, 386 (1963).

2) K. Tôei, H. Miyata, T. Shibata and S. Miyamura, *ibid.*, **38**, 334 (1965).

3) K. Tôei, T. Hayami, H. Miyata and Y. Shimoishi, *ibid.*, **39**, 638 (1966).

4) Y. Shimoishi and T. Hayami, *ibid.*, **40**, 1139 (1967).

5) W. A. Jacobs and M. Heidelberger, *J. Am. Chem. Soc.*, **39**, 2190 (1917).

6) A. Thate, *J. Prakt. Chem.*, **29**, 180 (1884).

7) R. L. Swan, *J. Chem. Soc.*, **125**, 781 (1924).

8) K. Tôei, H. Miyata and Takuji Harada, This Bulletin, **40**, 1141 (1967).

an another wavelength.

Apparent Stability Constants of the Thorium Complex. The apparent stability constant, K', of the thorium complex may be obtained by assuming the formation of the complex in accordance with the following equations:

$$Th^{4+} + H_3R^{2-} \rightleftarrows ThHR + 2H^+ \tag{5}$$

and

$$Th^{4+} + H_2R^{3-} \rightleftarrows ThHR + H^+ \tag{6}$$

$$K' = [ThHR]/[Th][H_3R + H_2R] \tag{7}$$

The total concentrations of the reagent and thorium are given by:

$$C_R = [H_3R] + [H_2R] + [HR] + [ThHR] \tag{8}$$

$$C_{Th} = [Th] + [ThHR] \tag{9}$$

respectively. Under the experimental conditions studied, at pH values below 4, [HR] can be disregarded, judging from the pK_2 value.

The absorbance of the complex solution, E is given by Eq. (10). The thorium ion gives no absorption in the visible region, and $\varepsilon_{Th}[Th]$ can be neglected.

$$E = \varepsilon_{H_3R}[H_3R] + \varepsilon_{H_2R}[H_2R] + \varepsilon_{ThHR}[ThHR] \tag{10}$$

where ε_{H_3R} and ε_{H_2R} are the molar absorption coefficients of H_3R and H_2R, and ε_{ThHR} is that of the throium complex, ThHR. Its value was calculated from the absorbance of the complex that was considered to be formed completely by adding an excess amount of thorium to the reagent.

The apparent stability constant, K', was estimated from the following equation by substituting Eqs. (1) and (8)—(10) into Eq. (7):

$$K' = (C_R - A)/\{C_{Th} - (C_R - A)A\} \tag{11}$$

where:

$$A = (1 + K_1/[H])(E - \varepsilon_{ThHR}\cdot C_R)/\{\varepsilon_{H_3R} + \varepsilon_{H_2R}(K_1/[H]) - \varepsilon_{ThHR}(1 + K_1/[H])\}$$

Results and Discussion

Absorption Spectra. The absorption curves of the reagent and the throium complex are shown in Fig. 1. The absorption curves vary with pH, but in the limited pH ranges below 1, from 5 to 7, and above 13, the identical curves (curves 1, 2, and 6) can be obtained.

Curve 1, in the pH range below 1, corresponds to the triprotonated species of the reagent. In this pH range, the dissociation of the oxyacetic acid group does not occur.

Curve 2, in the pH values from 5 to 7, corresponds to the diprotonated species.

The change in the absorption spectra between pH values 1 and 5 seems to correspond to the dissociation of the oxyacetic acid group. There are three isosbestic points at 353, 410 and 520 mμ.

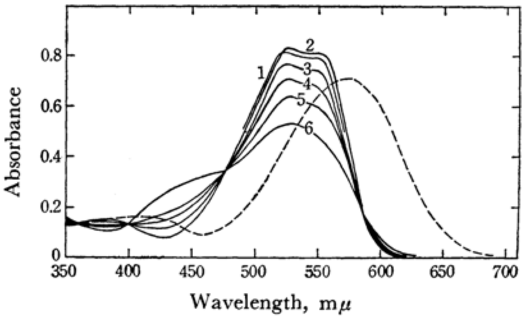

Fig. 1. Absorption spectra of the reagent and its thorium complex (broken line).
A 2.5×10^{-5} M reagent solution at: (1) pH below 1; (2) pH between 5 and 7; (3) pH 9.22; (4) pH 9.59; (5) pH 10.01; (6) pH above 12.5. Broken line: thorium concn. to the reagent solution concn. = 3.2 : 1, pH 2.55.

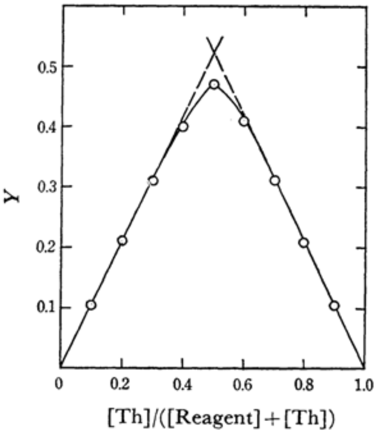

Fig. 2. Continuous-variation method.
at 600 mμ, pH 2.7
Thorium and the reagent concn. = 5.0×10^{-5} M

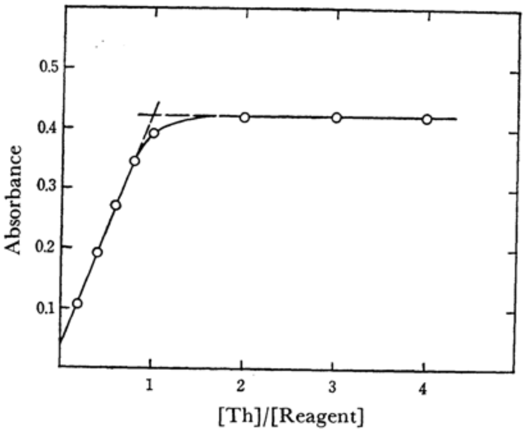

Fig. 3. Mole-ratio method.
at 600 mμ, pH 2.8
The reagent concn. = 2.0×10^{-5} M
Thorium concn. varied

TABLE 1. APPARENT STABILITY CONSTANT OF THE THORIUM COMPLEX
(25°C, $\mu=0.1$, $C_R=2.5\times10^{-5}$ M)

pH	E	C_{Th} ($\times10^{-5}$ M)	Wavelength, mμ	ε_{H_3R} ($\times10^3$)	ε_{H_2R} ($\times10^3$)	ε_{ThHR} ($\times10^4$)	log K'
1.01	0.206	2.5	580	6.41	9.34	2.75	3.61
1.39	0.294	2.5	580	6.41	9.34	2.75	4.25
2.72	0.648	2.5	580	6.41	9.34	2.75	6.77
3.08	0.672	2.5	580	6.41	9.34	2.75	7.58
1.33	0.142	2.5	600	1.02	1.70	2.10	4.20
1.90	0.335	2.5	600	1.02	1.70	2.10	5.23
0.95	0.114	8.12	600	1.02	1.70	2.10	3.45
1.31	0.290	8.12	600	1.02	1.70	2.10	4.22
1.85	0.484	8.12	600	1.02	1.70	2.10	5.28
2.43	0.521	8.12	600	1.02	1.70	2.10	6.34

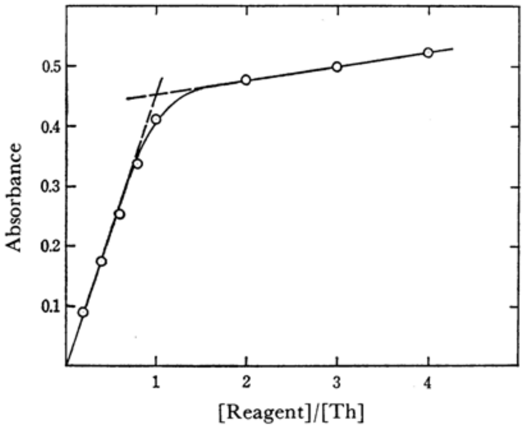

Fig. 4. Mole-ratio method
at 600 mμ, pH 3.2
Thorium concn. $=2.0\times10^{-5}$ M
The reagent concn. varied

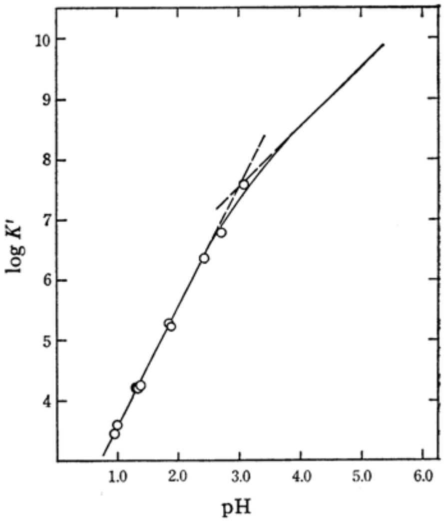

Fig. 5. Relationship between log K' and pH. at 25°C, $\mu=0.1$

Up to the pH values 12.5, the reagent gives another constant absorption curve, curve 6, corresponding to monoprotonated species. Between the curves 2 and 6, four isosbestic points exist at 361, 399, 476, and 586 mμ, as may be seen in Fig. 1. The change in the absorption spectra at pH values between 7 and 12.5 seems to correspond to the dissociation of one of the naphtholic hydroxyl groups of chromotropic acid present in the reagent.

On the addition of an excess amounts of thorium to the reagent solution, the color of the solution changes from pink to violet, and the spectrum has a maximum peak at 575 mμ.

Acid Dissociation Constant. The acid dissociation constants reported here for the reagent were determined at 25°C, and at an ionic strength of 0.1 (by sodium perchlorate). The values of pK_1 and pK_2 were measured at 578 mμ and 524 mμ, respectively, and estimated from Eqs. (1) and (2) to be 2.99 and 9.76 respectively. The third dissociation constant, K_3, corresponding to the other hydrogen atom of the naphthol hydroxyl group could not be obtained, because the dissociation occurs at pH above 14.

The Stability of the Thorium Complex. The color of the complex reached its maximum in a few minutes after mixing; then, the absorbance remained almost constant for at least 90 min.

The Composition of the Thorium Complex. Figure 2 shows the results obtained by the continuous-variation method; the maximum absorbance of the complex was obtained at a molar ratio of 1 : 1. The mole-ratio method was employed at pH 2.8 for various thorium concentrations (Fig. 3) and at pH 3.2 for various reagent concentrations (Fig. 4). The results indicated clearly the formation of a 1 : 1 complex.

Apparent Stability Constant of the Thorium Complex. The constant, log K', estimated from Eq. (11) is listed in Table 1. In Fig. 5, the values of log K' are plotted against pH values. A plot of log K' values *vs.* pH shows a slope of 2; further, H_3R^{2-} exists predominantly, hence it seems reasonable to suppose that thorium displaces two hydrogen atoms from the reagent under these conditions. Above pH 3.5, thorium hydroxide begins to precipitate so that absorption measurements are impossible.

The order of the apparent stability constant of the *o*-substituted phenyl-azo-chromotropic acids follows the sequence: the present reagent > *o*-carboxyl derivative[8] > *o*-hydroxy derivative[9] > phenyl-azo-chromotropic acid[10] > chromotropic acid[11]. It seems to be most reasonable to conclude that the oxyacetic acid group in the *o*-position will take part in the formation of the thorium complex more strongly than the other groups.

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[9] K. Tôei, H. Miyata, S. Nakashima and S. Kiguchi, This Bulletin, **40**, 1145 (1967).

[10] H. Miyata, *ibid.*, **36**, 382 (1963).

[11] M. Sakaguchi, A. Mizote, H. Miyata and K. Tôei, *ibid.*, **36**, 885 (1963).