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# A Spectrophotometric Study on the Thorium Complex of *o*-Hydroxyphenyl-azo-chromotropic Acid*[1]

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*o*-Hydroxyphenyl-azo-chromotropic acid was used as a colorimetric reagent for thorium. The acid dissociation constants of the reagent have been determined by the pH titration method. The $pK_1$ (for the dissociation of the phenolic hydroxyl group) and $pK_2$ (for that of the naphtholic hydroxyl group) were found to be 7.60 and 10.60 respectively at 25°C and $\mu=0.1$. The reagent forms a violet 1 : 1 complex in an acidic solution, and its apparent stability constant is measured spectrophotometrically.

In the course of our studies on the thorium complex formed with ortho-substituted phenyl-azo-chromotropic acid,[1] the effect of the phenolic hydroxyl group on the complex formation has been studied. In the present paper, the method of preparing *o*-hydroxyphenyl-azo-chromotropic acid and the results of the determination of the acid dissociation constants of the reagent by the pH titration method will be described. The thorium complex of the reagent will be studied spectrophotometrically, and the reaction scheme will be presented from the point of view of the relation between the apparent stability constant and the pH value.

## Experimental

**Reagents.** *o-Hydroxyphenyl-azo-chromotropic Acid.*[2] *o*-Aminophenol was dissolved in 99% ethanol, and then concentrated hydrochloric acid was added. The solution was cooled in ice and diazotized with an equivalent

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

2) Colour Index No. 16670.

amount of isoamylnitrite. A coupling reaction was carried out by adding the diazonium salt solution to an ice-cooled chromotropic acid solution. The azo compound thus obtained was purified from a concentrated hydrochloric acid solution.

In order to prepare the sodium salt of the reagent, the purified azo compound was dissolved again in water, and then salted out. The pure disodium salt of the reagent was obtained as reddish-brown needles with a metallic lustre.

*Thorium Perchlorate Solution.*[1] This solution was prepared by dissolving purified thorium hydroxide in perchloric acid. The concentration of thorium was determined gravimetrically through the use of oxalate.

*Potassium Hydroxide Solution.* This solution was prepared from potassium hydroxide (Tokyo Ohkakogyo Co., marked SV) and was standardized against potassium biphthalate (Merck Co.) without any further purification. All the other reagents used were of a guaranteed grade.

**Apparatus and Procedure.** In the pH titration, the pH value was measured with a Hitachi-Horiba glass electrode pH meter, Model P.

The same apparatus and procedure as in the preceding report[3] were used for the spectrophotometric measurements.

## Results and Discussion

**The Acid Dissociation Constant.**[4] The reagent, *o*-hydroxyphenyl-azo-chromotropic acid, was dissociated in water as follows:

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

and:

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

$K_1$ and $K_2$[5] represent, respectively, the dissociation of the phenolic hydroxyl group and that of the naphtholic hydroxyl group in the reagent.

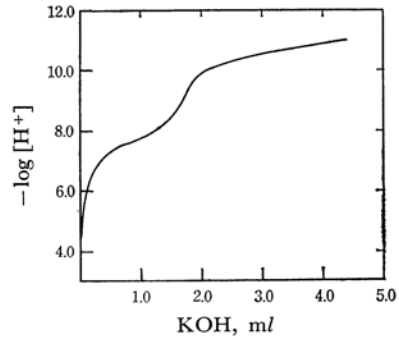


Fig. 1. Titration curve of the reagent.
25°C, $\mu=0.1$

The constants, $K_1$ and $K_2$, reported here were estimated by pH titration: 100 m*l* of a $1.694\times10^{-3}$ mol/*l* reagent solution were titrated with a 0.1 N potassium hydroxide solution. From the titration curve given in Fig. 1, the values of $pK_1$ and $pK_2$ are found to be 7.60 and 10.60 respectively.

**Absorption Spectra.** The absorption spectra of the solutions containing thorium and the reagent in a molar ratio of 1 : 1 are shown in Fig. 2 over the pH range from 1.95 to 3.62. The absorbance at around the peaks of the reagent becomes lower with an increase in the pH value. There are three isosbestic points, at 362, 410, and 470 m$\mu$.

**The Composition of the Complex.** Attempts to determine the composition of the complex were carried out by two methods, the continuous variation method and the mole ratio method.

As is shown in Figs. 3 and 4, the results indicate that thorium forms a 1-to-1 complex with the reagent.

**The Apparent Stability Constant of the Complex.** The apparent stability constant, $K'$,

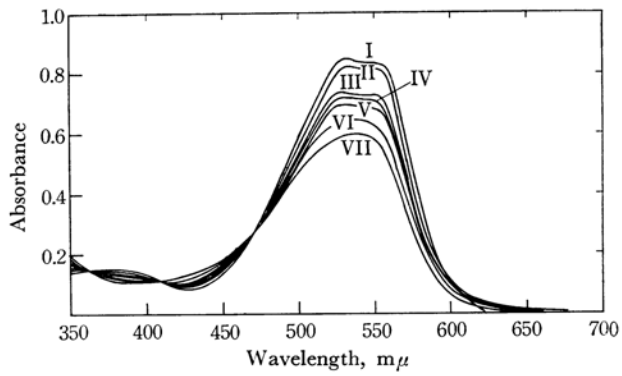


Fig. 2. Absorption spectra of the solutions containing the reagent and thorium.
I $2.5\times10^{-5}$ M reagent solution at pH 2.02.
II to VII The solution containing thorium and the reagent (1 : 1) at pH's 1.95, 2.69, 2.78, 2.90, 3.18 and 3.62 respectively.

3) K. Tôei, H. Miyata and T. Harada, submitted to this Bulletin for publication.
4) Y. Murakami, K. Nakamura and M. Tokunaga, This Bulletin, **36**, 670 (1963).
5) K. Tôei, H. Miyata and S. Nakashima submitted to this Bulletin for publication.

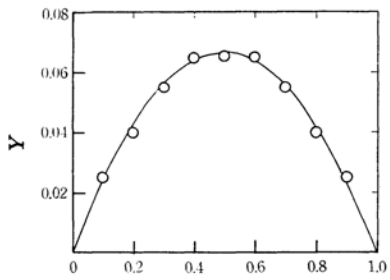


Fig. 3. Continuous variation method.
520 m$\mu$, pH 3.2
[Th]+[Reagent]=$5.0\times10^{-5}$ mol/$l$

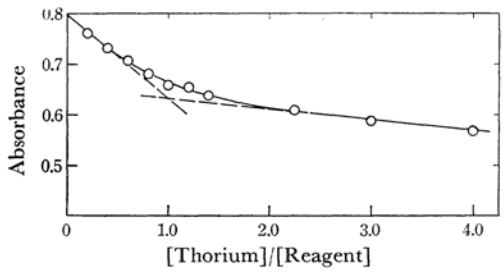


Fig. 4. Mole ratio method.
520 m$\mu$, pH 3.1
The reagent concn.=$2.5\times10^{-5}$ mol/$l$
Thorium concn. varied

of the thorium complex may be obtained by assuming the formation of the complex in accordance with the following equation:

$$Th^{4+} + H_3R^{2-} \rightleftarrows ThHR + 2H^+ \quad (1)$$

$K'$ is the apparent stability constant of the complex:

$$K' = [ThHR]/[Th][H_3R] \quad (2)$$

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

$$C_R = [H_3R] + [H_2R] + [HR] + [R] + [ThHR] \quad (3)$$

$$C_{Th} = [Th] + [ThHR] \quad (4)$$

respectively. At pH values lower than 4, $[H_2R]$, [HR] and [R] can be disregarded.

The substitution of Eqs. (3) and (4) into Eq. (2) leads to the following equation:

$$K' = [ThHR]/(C_{Th} - [ThHR])(C_R - [ThHR]) \quad (5)$$

[ThHR] in Eq. (5) can be obtained from the absorbance of the system of the reagent and the complex solution:

$$E = \varepsilon_{H_3R}[H_3R] + \varepsilon_{ThHR}[ThHR] + \varepsilon_{Th}[Th] \quad (6)$$

$\varepsilon_{Th}[Th]$ can be neglected, for thorium ions do not show any absorption in the visible region. The molar absorptivity of $H_3R$ at 520 m$\mu$, $\varepsilon_{H_3R}$, was calculated from the absorbance of the reagent solution in the pH range below 4; it was found to be $3.20\times10^4$. Also, the value of $\varepsilon_{ThHR}$, the molar absorptivity of ThHR, was calculated from the absorbance of the complex that was considered to be completed by adding the excess amount of thorium to the reagent; it was found to be $2.19\times10^4$. Hence,

$$[ThHR] = (\varepsilon_{H_3R}\cdot C_R - E)/(\varepsilon_{H_3R} - \varepsilon_{ThHR}) \quad (7)$$

The apparent stability constants in Table 1 could be calculated by substituting Eq. (7) into Eq. (5).

Table 1. Apparent stability constants of the thorium complex
(25°C, $\mu$=0.1)

| pH | $E$ | $C_R$ $\times10^{-5}$ M | $C_{Th}$ $\times10^{-5}$ M | log $K'$ |
|---|---|---|---|---|
| 1.95 | 0.772 | 2.5 | 5.0 | 3.42 |
| 2.69 | 0.717 | 2.5 | 2.5 | 4.47 |
| 2.78 | 0.699 | 2.5 | 2.5 | 4.66 |
| 2.90 | 0.676 | 2.5 | 2.5 | 4.89 |
| 3.62 | 0.585 | 2.5 | 2.5 | 6.25 |
| 2.17 | 0.791* | 2.5 | 2.5 | 3.64 |
| 2.34 | 0.772* | 2.5 | 2.5 | 3.97 |
| 2.58 | 0.742* | 2.5 | 2.5 | 4.32 |
| 3.18 | 0.638* | 2.5 | 2.5 | 5.38 |
| 3.25 | 0.627* | 2.5 | 2.5 | 5.53 |

* $E$ was measured at 530 m$\mu$, and $\varepsilon_{H_3R}$ and $\varepsilon_{ThHR}$ were $3.26\times10^4$ and $2.20\times10^4$ respectively.

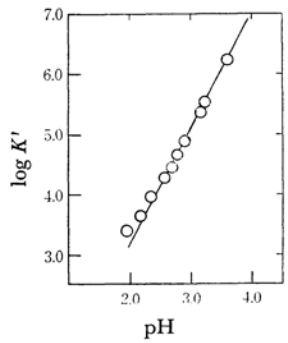


Fig. 5. Relationship between pH and log $K'$.
25°C, $\mu$=0.1

In Fig. 5, the value of the logarithm of the apparent stability constant is plotted against the pH value. All the results are seen to be satisfactory except for the plots of the lower pH values.