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

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o-Carboxyphenyl-azo-chromotropic acid was synthesized as a colorimetric reagent for thorium. The acid dissociation constants of the reagent have been determined spectrophotometrically at 25°C and $\mu=0.1$ ($NaClO_4$). The pK_1 (for the dissociation of the carboxyl group) and the pK_2 (for the dissociation of the naphtholic hydroxyl groups) were 3.20 and 10.17 respectively. The reagent forms a violet 1 : 1 complex with thorium, showing an absorption maximum at 565 mμ in an acidic solution. The apparent stability constant of the thorium complex was measured spectrophotometrically.

In the course of our studies of the thorium complex formed with ortho-substituted phenyl-azo-chromotropic acid,[1-4] the behavior of the carboxyl group upon the complex formation has been studied. The reagent, *o*-carboxyphenyl-azo-chromotropic acid, was synthesized in our laboratory

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

2) H. Miyata, *ibid.*, **36**, 127 (1963).

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

4) K. Tôei, H. Miyata and T. Mitsumata, *ibid.*, **38**, 1050 (1965).

and was used as a spot-test reagent for calcium.[5]

Majumdar and Savariar have reported that the reagent forms a 1 : 2 blue-violet thorium complex[6] or a 2 : 3 complex.[7] They used it as a metal indicator in the complexometric titration of thorium at pH values from 2 to 3.6 or of zirconium at pH values from 1.4 to 2.5, and also as a reagent in the spectrophotometric determination of thorium at pH values from 2.7 to 3.4 and aluminum at pH values from 4.8 to 5.0.

This paper will report the results of more detailed studies of the dissociation of the reagent, and of the stability of its complex with thorium.

Experimental

Reagents. *o-Carboxyphenyl-azo-chromotropic Acid.* Diazotized anthranilic acid was coupled with chromotropic acid, and a pure azo compound as free acid was obtained in the form of reddish-brown needles after recrystallization from a concentration hydrochloric acid.

Thorium Perchlorate Solution. Thorium hydroxide prepared from the purified nitrate[8] is dissolved in perchloric acid, and the concentration of thorium is determined gravimetrically by precipitating it as oxalate.[9]

The other reagent were of a guaranteed reagent grade.

Apparatus. The visible spectra of the reagent and the thorium complex were measured with a Hitachi EPS-2-type recording spectrophotometer, while, the absorbance was measured with a Shimadzu QR-50-type spectrophotometer, using 1 cm cells.

The pH value was measured with a Toa-Denpa glass electrode pH meter, Model HM-8A.

Procedure. The measurements of the absorption spectra at various pH values were made as follows: Five milliliters of a 3×10^{-4} mol/*l* reagent solution were placed in a 50 m*l* volumetric flask, and an adequate amount of 1 M perchloric acid, 1 M sodium hydroxide, or a buffer solution (an acetic acid - sodium acetate or an ammonia - ammonium chloride buffer) was added in order to adjust the pH value. One-tenth milliliter of a 0.01 M EDTA solution was added to mask trace amounts of calcium or magnesium contained in the sodium hydroxide or ammonium chloride, because definite isosbestic points can not be obtained in the absence of EDTA, especially at higher pH values. Then a 1 M sodium perchlorate solution was added to maintain the ionic strength at 0.1, and the volume was made up to 50 m*l* with deionized, distilled water.

The thorium complex solution was prepared similarly: Five milliliters of a 3×10^{-4} mol/*l* reagent solution were placed in a 50 m*l* volumetric flask, followed by the addition of a perchloric acid or sodium hydroxide solution in order to adjust the pH value of the solution and a 1 M sodium perchlorate solution to maintain the ionic strength at 0.1. Then 5 m*l* of a 3×10^{-4} mol/*l* thorium perchlorate solution was added, and the volume was made up to 50 m*l* with water.

The solutions were allowed to stand for one hour at 25°C, after which the absorbance was measured against water.

Results and Discussion

Absorption Spectra. The absorption spectra of the reagent and its thorium complex are shown in Fig. 1.

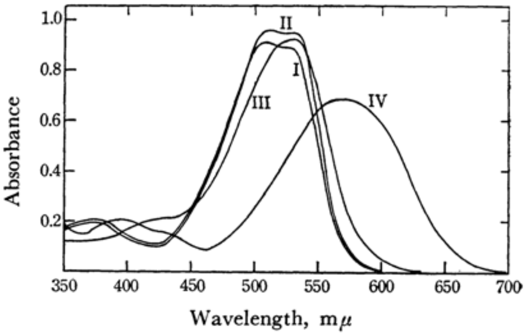

Fig. 1. Absorption spectra of *o*-carboxyphenyl-azo-chromotropic acid and its thorium complex.
I 3.0×10^{-5} mol/*l* reagent solution at pH below 1
II 3.0×10^{-5} mol/*l* reagent solution at pH 5.5 to 7.5
III 3.0×10^{-5} mol/*l* reagent solution at pH above 13
IV the thorium complex (Thorium concn. to the reagent concn. = 7 : 1) at pH 2.60

Curve I, with peaks at 508 and 528 mμ, shows an absorption spectrum of the reagent in the pH range below 1. In this pH range, the dissociation of the carboxyl group does not occur.

Curve II shows an absorption spectrum in the pH range from 5.5 to 7.5, while, Curve III shows another absorption spectrum, this one in the pH range above 13.

It seems that the change in the absorption spectra between pH 1 and 5.5 corresponds to the dissociation of the carboxyl group. There is one isosbestic point, at 497 mμ, as may be seen in Fig. 2. On the other hand, the change of the absorption spectra between pH 7.5 and 13 seems to correspond to the dissociation of one of the naphtholic hydroxyl groups. The isosbestic points occur at 394, 453, and 542 mμ, as may be seen in Figs. 1 and 3.

By adding thorium to the reagent solution, the peaks of the reagent shift toward longer wavelengths and the spectrum (IV) shows an absorption maximum at 565 mμ.

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5) K. Emi, K. Tôei and N. Takemoto, *Nippon Kagaku Zassi*, *(J. Chem. Soc. Japan, Pure Chem. Sect.)* **78**, 743 (1957).

6) A. K. Majumdar and C. P. Savariar, *Z. anal. Chem.*, **174**, 197 (1960).

7) A. K. Majumdar and C. P. Savariar, *ibid.*, **174**, 269 (1960).

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

9) W. W. Scott, "Standard Methods of Chemical Analysis," D. van Nostrand Co., Inc., New York, N. Y. (1939), p. 953.

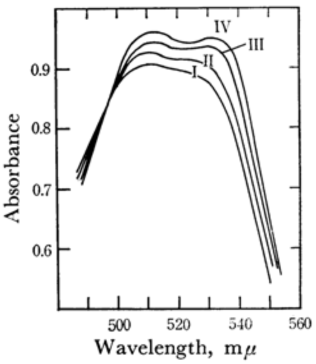

Fig. 2. Absorption Spectra of H_3R, H_2R and their mixture.
I pH below 1, H_3R
II 2.94
III 3.54
IV 5.5 to 7.5, H_2R

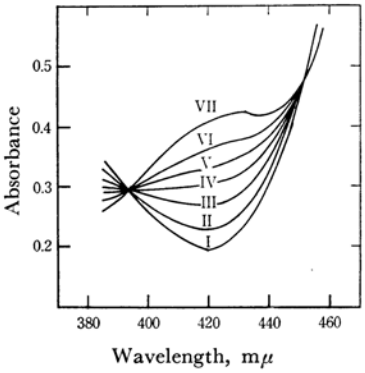

Fig. 3. Absorption spectra of H_2R, HR and their mixture.
I pH 5.5 to 7.5, H_2R (the reagent concn. = 6.0×10^{-5} M); II 9.50; III 9.91; IV 10.20; V 10.46; VI 10.79; VII above 13, HR

The Acid Dissociation Constant. The acid dissociation constants reported here for the reagent were determined spectrophotometrically at 25°C and at an ionic strength of 0.1.

The reagent, *o*-carboxyphenyl-azo-chromotropic acid (Abbr. H_5R), is dissociated in water as follows:

$$H_3R^{2-} = H_2R^{3-} + H^+$$

and $$H_2R^{3-} = HR^{4-} + H^+$$

The first acid dissociation constant, K_1, corresponds to the dissociation of a hydrogen atom from the carboxyl group, while the second, K_2, corresponds to that of one of the hydrogen atoms from two naphtholic hydroxyl groups of chromotropic acid. These may be expressed as:

$$K_1 = [H][H_2R]/[H_3R]$$
$$K_2 = [H][HR]/[H_2R]$$

The ionic charge is neglected for the sake of convenience, the square brackets denote the concentration in moles per liter.

Therefore,

$$pK_1 = pH - \log[H_2R]/[H_3R]$$
$$= pH - \log(E_{H_3R} - E)/(E - E_{H_2R}) \quad (1)$$

and $$pK_2 = pH - \log[HR]/[H_2R]$$
$$= pH - \log(E'_{H_2R} - E')/(E' - E'_{HR}) \quad (2)$$

where E_{H_3R} and E_{H_2R} represent, respectively, the absorbances in the pH range below 1 and from 5.5 to 7.5 at 540 mμ; where E represents the absorbance of their mixed solution at an arbitrary pH value at 540 mμ (Fig. 2), where E'_{H_2R} and E'_{HR} represent, respectively, the absorbances in the pH range from 5.5 to 7.5 and above 13, and where E' represents the absorbance of their mixture at 420 mμ (Fig. 3).

However, the third acid dissociation constant, K_3, corresponding to the dissociation of another hydrogen atom of the naphtholic hydroxyl group, could not be obtained, because the dissociation occurs above pH 14. In the case of phenyl-azo-chromotropic acid, the pK_a value corresponding to this dissociation is 14.64.[10]

The values of pK_1 and pK_2 were estimated from Eqs. (1) and (2) to be 3.20 and 10.17 respectively.

The Effect of pH on the Formation of the Thorium Complex. The effect of the pH value on the formation of a thorium complex was studied with solutions with pH values varying from 2.0 to 3.4. The curves in Fig. 4 show that the absorbance at 565 mμ increases with an increase in the pH value.

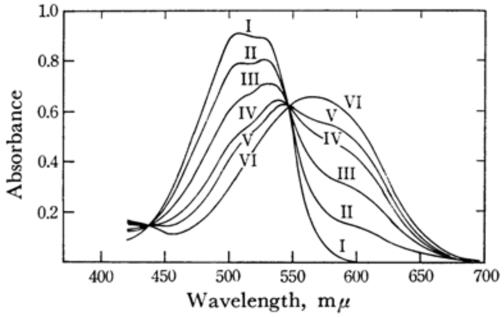

Fig. 4. Effect of pH value on the absorption spectra of the system of thorium and the reagent.
I 3.0×10^{-5} M reagent solution at pH 0.55
II Absorption curve of the mixture pH 2.08
III Absorption curve of the mixture pH 2.40
IV Absorption curve of the mixture pH 2.73
V Absorption curve of the mixture pH 2.86
VI Absorption curve of the mixture pH 3.35
(Thorium concn. to the reagent concn. = 1 : 1)

The Stability of the Thorium Complex. The effect of the standing time after the thorium is

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[10] J. Bjerrum *et al.*, "Stability Constants, Part I. Organic Ligands," The Chemical Soc., London (1957), p. 95.

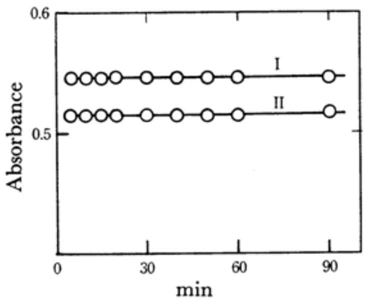

Fig. 5. Effect of time standing on the color of the thorium complex.
I pH 2.99; II 2.93

mixed with the reagent at various pH values was measured at 570 mμ; it is shown in Fig. 5. The color of the complex reached its maximum with a few minutes after mixing; thereafter, the absorbance remained almost constant for at least 90 min.

The Composition of the Thorium Complex. In order to confirm the mole ratio of the throium complex, two methods were employed, the continuous-variation (Fig. 6) and mole-ratio methods (Fig. 7). As is shown in Figs. 6 and 7, the results indicate the formation of a 1 : 1 complex.

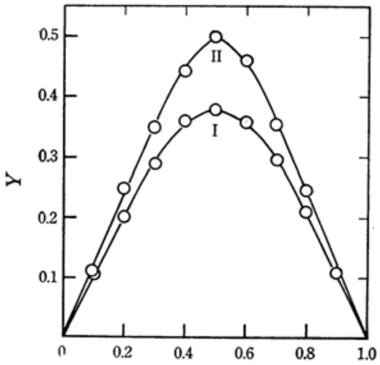

Fig. 6. Continuous variation method.
at 570 mμ, pH 3.0 (I) and 3.3 (II)
Thorium and reagent concn.$=6\times10^{-5}$ mol/l

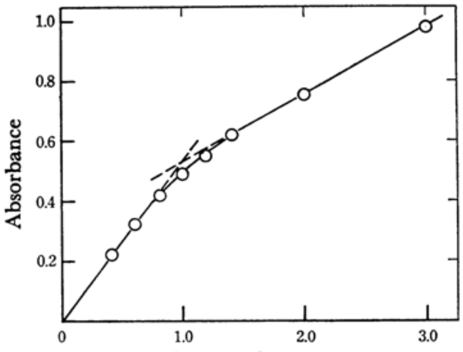

Fig. 7. Mole ratio method.
at 570 mμ, pH 2.7
Thorium concn.$=3\times10^{-5}$ mol/l
The reagent concn. varied

The Apparent Stability Constant 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:

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

and
$$Th^{4+} + H_2R^{3-} \rightleftarrows ThHR + H^+ \qquad (2)$$

$$K' = [ThHR]/[Th][H_3R+H_2R] \qquad (3)$$

$$K_1 = [H][H_2R]/[H_3R] \qquad (4)$$

K' is the apparent stability constant of the complex, and K_1 is the first acid dissociation constant of the reagent.

The total concentrations of the reagent and thorium at pH values lower than 4 are given by:

$$C_R = [H_3R] + [H_2R] + [ThHR] \qquad (5)$$

$$C_{Th} = [Th] + [ThHR] \qquad (6)$$

[ThHR] in Eqs. (5) and (6) can be obtained from the absorbance of the complex solution: the thorium ion gives no absorption in the visible region, and ε_{Th} [Th] can be neglected.

$$E = \varepsilon_{H_3R}[H_3R] + \varepsilon_{H_2R}[H_2R] + \varepsilon_{ThHR}[ThHR] \qquad (7)$$

where ε_{H_3R} (3.71×10^3) and ε_{H_2R} (4.33×10^3) are the molar absorption coefficients of H_3R and H_2R at 570 mμ; these values were calculated from the absorbances of the reagent solution at pH below 1 and from 5.5 to 7.5 respectively, at 570 mμ. ε_{ThHR} (2.33×10^4) is the molar absorption coefficient of ThHR at 570 mμ; its value was calculated from the absorbance of the complex that was considered to be completed by adding an excess amount of thorium to the reagent. Therefore, the concentration of [ThHR] is:

$$[ThHR] = C_R - A \qquad (8)$$

where:

$$A = B(1 + K_1/[H])$$

And $[H_3R]$, $[H_2R]$ and [Th] are given by:

$$[H_3R] = B = (E - \varepsilon_{ThHR}\cdot C_R)/\{\varepsilon_{H_3R} + \varepsilon_{H\ R}(K_1/[H]) - \varepsilon_{ThHR}(1 + K_1/[H])\} \qquad (9)$$

$$[H_2R] = B(K_1/[H]) \qquad (10)$$

$$[Th] = C_{Th} - (C_R - A) \qquad (11)$$

The apparent stability constant in Table 1 was estimated from the following equation by substituting Eqs. (8)—(11) into Eq. (3):

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

In Fig. 8, the value of log K' is plotted against the pH value. The experimental data obtained were in good agreement with the curve whose

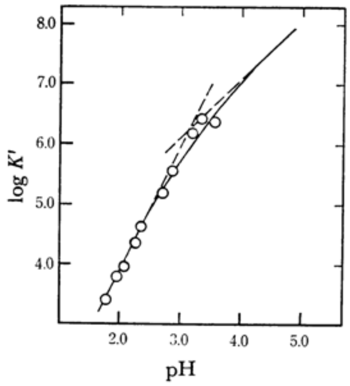

Fig. 8. Relationship between pH and log K' at 25°C, $\mu=0.1$.

slopes were 2 (below pK_1) and 1 (above pK_1) This supports the assumption in Eqs. (1) and (2), indicating that only a ThHR complex is formed under the present experimental conditions.

From a comparison of the apparent stability constant of the complex of the present reagent with that of phenyl-azo-chromotropic[12] and chromotropic acids[11], it seems most reasonable to conclude that the contribution of the carboxyl group in the ortho position is stronger than that of the azo and the naphtholic hydroxyl groups in the formation of the thorium complex.

TABLE 1. APPARENT STABILITY CONSTANT OF THE THORIUM COMPLEX
(25°C, $\mu=0.1$)

pH	E	C_R	C_{Th}	log K'
1.78	0.188	3×10^{-5} M	6×10^{-5} M	3.42
1.96	0.257	3×10^{-5} M	6×10^{-5} M	3.79
2.08	0.220	3×10^{-5} M	3×10^{-5} M	3.96
2.27	0.301	3×10^{-5} M	3×10^{-5} M	4.36
2.35	0.357	3×10^{-5} M	3×10^{-5} M	4.61
2.70	0.484	3×10^{-5} M	3×10^{-5} M	5.19
2.71	0.488	3×10^{-5} M	3×10^{-5} M	5.21
2.86	0.545	3×10^{-5} M	3×10^{-5} M	5.54
3.21	0.622	3×10^{-5} M	3×10^{-5} M	6.21
3.35	0.635	3×10^{-5} M	3×10^{-5} M	6.38
3.54	0.633	3×10^{-5} M	3×10^{-5} M	6.35

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11) M. Sakaguchi, A. Mizote, H. Miyata and K. Tôei, This Bulletin, **36**, 885 (1963).

12) H. Miyata, *ibid.*, **36**, 382 (1963).