*Spectrophotometric Studies of the Complexes of o-Sulfobenzeneazochromotropic Acid Formed with Thorium**

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Azo compounds having arseno, $-AsO_3H_2$⁽¹⁾, or phosphono, $-PO_3H_2$⁽²⁾, groups in the ortho position have been applied as reagents for the determination of thorium, zirconium and uranium. These groups are most interesting as functional groups for thorium, and the behavior of sulfo group, $-SO_3H$, for thorium is also attractive to the other.

The present paper describes the preparation of *o*-sulfobenzeneazochromotropic acid, and the determination of the first dissociation constant of the reagent by the spectrophotometric method. The complex of the reagent with thorium is studied spectrophotometrically, and the reaction scheme is presented from the relation between the apparent stability constant and the pH value.

Experimental

Reagents.—*o-Sulfobenzeneazochromotropic Acid***.—Diazotized *o*-aminobenzenesulfonic acid was coupled with chromotropic acid, and a pure azo compound was obtained in the form of reddish brown needles of monosodium salt after recrystallization from concentrated hydrochloric acid. A solution of 3×10^{-4} mol./l. was prepared and stored in the dark.

1 M Thorium Perchlorate Solution.—It was prepared by dissolving thorium hydroxide into perchloric acid.

1 M Sodium Perchlorate Solution.—It was prepared from twice-recrystallized $NaClO_4\cdot H_2O$.

Buffer Solutions.—The following buffer solutions were prepared from guaranteed reagents:

5.8∼7.0 pH value acetic acid and sodium acetate.

8.0∼10.6 pH value aqueous ammonia and ammonium chloride.

Procedure and Apparatus.—All solutions were made in a dark room, for the absorbance of the reagent tended to be decreased in daylight, especially at higher pH values.

Five milliliter of a 3×10^{-4} mol./l. reagent solution was placed in a 50 ml. volumetric flask, after which an adequate volume of 0.2 M perchloric acid, 0.2 M sodium hydroxide or buffer solution was added in order to adjust the pH value to the desired value. 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 ml. with water. Each of the solutions was used for the determination of the first dissociation constant of the reagent.

To prepare the complex solution, 5 ml. of a 3×10^{-4} mol./l. reagent solution was placed in a 50 ml. volumetric flask, followed by the addition of 0.2 M perchloric acid to adjust the pH value of the solution to 1∼3.4 and of a 1 M sodium perchlorate solution to maintain the ionic strength at 0.1. Five milliliter of a 4×10^{-3} mol./l. thorium perchlorate

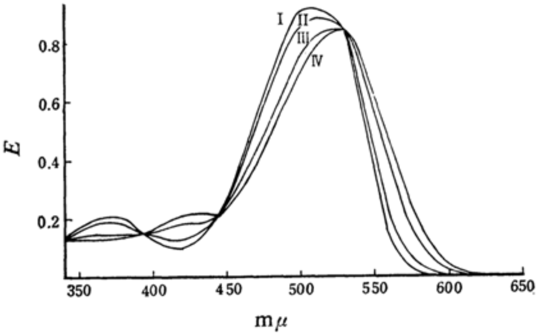

Fig. 1. Absorption curves of *o*-sulfobenzeneazochromotropic acid.
$\mu=0.1$, at 25°C 3×10^{-5} mol./l.
I pH 1∼8 II pH 9.2
III pH 10.5 IV pH 11.5∼13

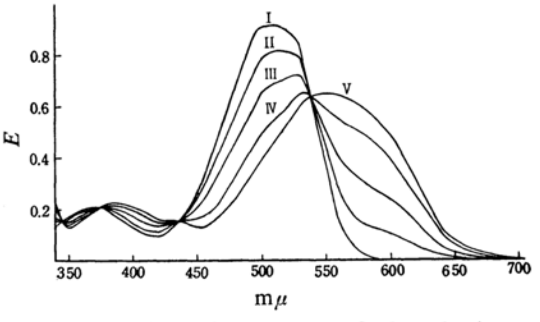

Fig. 2. Absorption curves of the thorium complex.
I Reagent, pH 1∼8, $\mu=0.1$ at 25°C
II Complex, pH 1.9
III Complex, pH 2.3
IV Complex, pH 2.9
V Complex, pH 3.4

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* Presented at the Symposium of the Analytical Chemical Society of Japan, Tokushima, October, 1962.

1) For example, A. E. Taylor and R. T. Dillon, *Anal. Chem.*, **24**, 1624 (1952).

2) A. A. Nemodruk et al., *J. Anal. Chem. USSR*, **16**, 296 (1961).

** Anal. Found: C, 36.85; H, 2.23; N, 5.20; Na, 4.4. Calcd. for $C_{16}H_{11}O_{11}N_2S_3Na$: C, 36.50; H, 2.11; N, 5.32; Na, 4.36%.

solution was added, and then the volume was made up to 50 ml. with water. The solutions were allowed to stand for one hour or more at 25°C. The absorbance was then measured with a Shimadzu spectrophotometer QR-50 type and a Hitachi automatic recording spectrophotometer EPS-2 type, with 1 cm. cells, while the pH value was measured with a Tôwa-Denpa glass electrode pH meter model HM-5A. Absorption spectra at various pH values are shown in Figs. 1 and 2.

Results and Discussion

Spectral Properties of the Reagent and its First Dissociation Constant.—Between the pH values of 1 and 8, the reagent gives identical absorption spectra, each with one absorption maximum at 507 mμ (Fig. 1). This indicates that the electrolytic dissociation of the naphtholic group does not occur. Above a pH value of 8, the maximum shifts towards another maximum (527 mμ) with an increase in the pH value, and between the pH values of 11.5 and 13 the reagent again gives identical absorption spectra.

Judging from the presence of the isosbestic points (392∼394, 442∼444 and 528∼530 mμ), two structures (H_2R^{3-} and HR^{4-}) are expected to exist.

$$H_2R^{3-} \leftrightarrows HR^{4-} + H^+$$

The constant of the above dissociation, K_{a_1}, was calculated by the following equation[3]:

$$pK_{a_1} = -\log[H] - \log\{(E_{H:R} - E)/(E - E_{HR})\}$$

where $E_{H\ R}$ and E_{HR} represent the absorbances at $-\log[H] = 1\sim8$ and $11.5\sim13$ respectively, and E represents the absorbance at $-\log[H] = 8\sim11.5$. These absorbances are measured at 560 mμ, because the difference between $E_{H\ R}$ and E_{HR} is the largest.

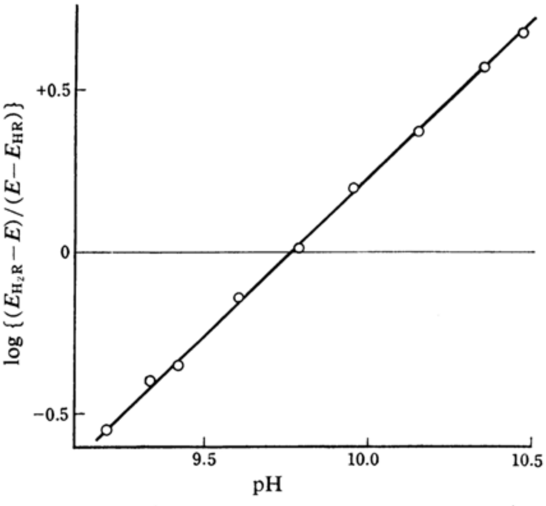

Fig. 3. Relationship between pH and log {$(E_{H_2R} - E)/(E - E_{HR})$}.
560 mμ, 25°C, $\mu = 0.1$

In Fig. 3, the values of $\log\{(E_{H:R} - E)/(E - E_{HR})\}$ are plotted against the pH value, and the value of pK_{a_1} is estimated graphically to be 9.7_6.

The Chemical Composition of the Complex.—In order to confirm the mole ratio of the complex, two methods were employed, the continuous variation and the mole ratio methods. In the former method, the measurement of the absorbances of a series of solutions containing a varying mole per cent of 6×10^{-5} M reagent and 6×10^{-5} M thorium was undertaken. As is shown in Fig. 4, the maximum absorbance of the complex was obtained when the mole ratio of thorium to the reagent was 1 : 1.

In the latter method, the absorbances of a series of solutions containing a varying concentration of the reagent to a fixed thorium concentration (4×10^{-5} mol./l.) was measured at 580 mμ. The results obtained indicate the formation of a 1 : 1 complex (Fig. 5). The results of these experiments confirm that the mole ratio of thorium to the reagent in the complex formed is 1 : 1.

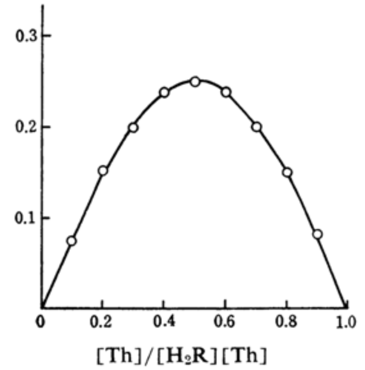

Fig. 4. Continuous variation method.
580 mμ, pH 3.1
Th = H_2R = 6×10^{-5} mol./l.

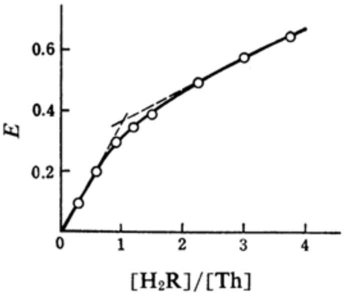

Fig. 5. Mole ratio method.
580 mμ, pH 3.35
Thorium concn. = 4×10^{-5} mol./l.
The reagent concentration varied.

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[3] H. Miyata, This Bulletin, 36, 382 (1963).

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

pH	E	C_R	C_{Th}	[ThHR]	K'
2.3	0.057	3×10^{-5}	4×10^{-5}	0.15×10^{-5}	0.14×10^{4}
2.45	0.062	3×10^{-5}	4×10^{-5}	0.17×10^{-5}	0.16×10^{4}
2.6	0.240	6×10^{-5}	8×10^{-5}	0.89×10^{-5}	0.24×10^{4}
2.9	0.355	6×10^{-5}	8×10^{-5}	1.42×10^{-5}	0.47×10^{4}
2.9	0.119	3×10^{-5}	4×10^{-5}	0.44×10^{-5}	0.48×10^{4}
3.1	0.155	3×10^{-5}	4×10^{-5}	0.60×10^{-5}	0.74×10^{4}
3.1	0.456	6×10^{-5}	8×10^{-5}	1.88×10^{-5}	0.75×10^{4}
3.15	0.154	3×10^{-5}	4×10^{-5}	0.60×10^{-5}	0.74×10^{4}
3.45	0.233	3×10^{-5}	4×10^{-5}	0.96×10^{-5}	1.56×10^{4}
3.5	0.228	3×10^{-5}	4×10^{-5}	0.94×10^{-5}	1.49×10^{4}

The Effet of Time on the Color of the Complex.—The effect of the lapse of time after the mixing of thorium with the reagent at various pH values is shown in Fig. 6. The color of the complex is fully developed in a few minutes after mixing, and the absorbance remained constant for two hours and more.

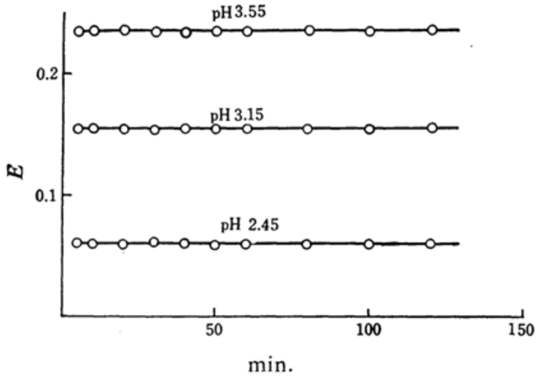

Fig. 6. Effect of reaction time.

The Effect of an Excess Thorium Concentration.—The effect of an excess thorium concentration on the absorbance is shown in Fig. 7, where the curve indicates that the absorbance reaches a constant value when the molar ratio of thorium to the reagent exceeds 110.

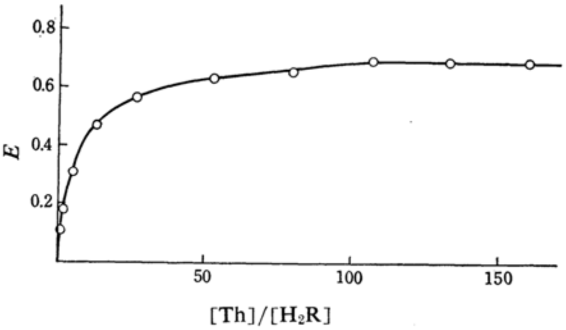

Fig. 7. Effect of excess thorium concentration 580 mμ, pH 2.9, the reagent concentration 3×10^{-5} mol./l.

The Apparent Stability Constant of the Complex. — The existence of the isosbestic points (346~347, 372~374, 435~437 and 540~542 mμ) is excellent evidence that only two structures are present, H_2R^{3-} and a single complex in the pH value range of 2~3.4 (Fig. 2). An approximate value of the apparent stability constant, K', (Table I) of the complex may be obtained by assuming that the formation of the thorium complex is in accordance with the the following equation[3]:

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

The equilibrium constant, K, is given by

$$K=[ThHR]\,[H]/[Th]\,[H_2R]$$

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

where C_R and C_{Th} represent the total concentration of the reagent and of the thorium respectively, and [ThHR] represents the concentration of the complex.

In Fig. 8, the logarithm of the apparent stability constant (log K') is plotted against the pH value. The curve indicates that thorium reacts with the reagent, displacing one hydrogen atom.

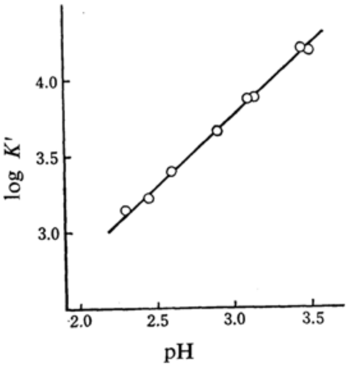

Fig. 8. Relationship between pH and log K'. 580 mμ, 25°C, $\mu=0.1$

Summary

o-Sulfobenzeneazochromotropic acid was prepared in the form of reddish brown needles of monosodium salt, and the value of the first dissociation constant, pK_{a_1}, was estimated spectrophotometrically to be 9.7_6 (25°C, $\mu=0.1$).

The reagent reacts with thorium in the molar ratio 1 : 1, displacing one hydrogen atom, and the approximate value of the apparent stability constant of the complex, $\log K'$, was estimated to be 3.2～4.2 at pH values from 2.5 to 3.5, while the concentration of thorium was about $(4\sim8)\times10^{-5}$.

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