Spectrophotometric Studies of the Complexes of Phenylazochromotropic Acid Formed with Thorium

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Various *o*-substituted-*o'*-hydroxyazo compounds having functional groups in the ortho position have been synthetized, and their behaviors as analytical reagents have been studied[1-6]. Among these compounds a series of azo compounds coupled with chromotropic acid are most interesting as the reagents for the spectrophotometric determination of various metals.

The present paper describes the basic studies of the reaction of phenylazochromotropic acid with thorium.

Experimental

Reagents.—*Phenylazochromotropic Acid*[6,7]. — Diazotized aniline was coupled with chromotropic acid, and the pure azo compound was obtained in the form of diacid dihydrate after recrystallization from concentrated hydrochloric acid, followed by that from water. Solutions of 2.5×10^{-4} and 3×10^{-4} mol./l. were prepared and stored in the dark.

Thorium Perchlorate Solution. — Purified thorium nitrate[8] was dissolved in water, the hydroxide was precipitated with sodium hydroxide, and then it was dissolved in perchloric acid. The stock solution was standaridized gravimetrically with oxalate[9]. It contained 17.6 mg. of thorium per milliliter and was diluted to an appropriate concentration for each experiment.

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

5.8∼7.0 pH values, acetic acid and sodium acetate.
8.0∼9.8 pH values, ammonia and ammonium chloride.

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

Apparatus.—The absorbance was measured with a Shimadzu spectrophotometer, QR-50 type, and a Hitachi automatic recording spectrophotometer, EPS-2 type, with 1 cm. cells; the pH value was measured with a Horiba glass electrode pH meter, model M-3.

Results and Discussion

Absorption Spectra of the Reagent and its Thorium Complex. — For the measurement of absorption spectra of the reagents and its thorium complex, the following procedure was used. All solutions were prepared in a dark room, for the absorption of the reagent decreases in daylight, especially at higher pH values. Five milliliter of a 2.5×10^{-4} or a 3×10^{-4} mol./l. reagent solution was placed in a 50 ml. volumetric flask, followed by the addition of an adequate volume of 0.2 M perchloric acid in order to adjust the pH value of the solution to 1∼5, of a 0.2 M sodium hydroxide solution in order to adjust the pH value of the solution to 11∼13, or of 5 ml. of a buffer solution of the pH 5.8∼9.8. The ionic strength was maintained at 0.1 by an appropriate addition of a 1 M sodium perchlorate solution, and then the volume was made up to 50 ml. with water.

Thorium complex solutions were prepared similarly: 5 ml. of a 2.5×10^{-4} mol./l. reagent solution was placed in a 50 ml. volumetric flask, followed by the addition of 0.2 M perchloric acid in order to adjust the pH value of the solution to 1∼3.2, of a 1 M sodium perchlorate solution to maintain the ionic strength at 0.1, and of 5 ml. of a 2.5×10^{-2} mol./l. thorium perchlorate solution, then the

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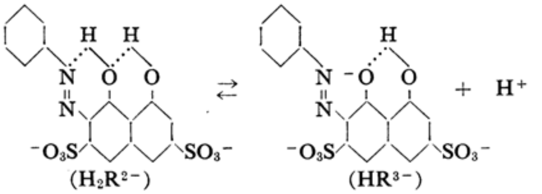
[1] K. Emi, K. Tôei and H. Miyata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 78, 736 (1957).
[2] K. Emi, K. Tôei and N. Takemoto, ibid., **78**, 741 (1957).
[3] K. Emi, K. Tôei and H. Miyata, ibid., **78**, 977 (1957).
[4] K. Emi, K. Tôei and H. Miyata, ibid., **78**, 979 (1957).
[5] K. Emi, K. Tôei and K. Furukawa, ibid., **79**, 681 (1958).
[6] T. Iwachido, H. Miyata and K. Tôei, This Bulletin, **33**, 95 (1960).
[7] Color Index 16570, Acid Red 29.
[8] R. L. Swan, *J. Chem. Soc.*, **125**, 781 (1924).
[9] W. W. Scott, "Standard Methods of Chemical Analysis", D. van Nostrand Co., Inc. (1939), p. 953.

volume was made up to 50 ml. with water. The solutions were allowed to stand for one hour or more at 25°C, after which the absorbance was measured in a 1 cm. cell against water.

In the pH value range higher than 4, thorium hydroxide was precipitated, so absorption measurements were not possible.

In Fig. 1 it is seen that, on the addition of thorium to the reagent solution, the absorption maxima shifted towards the longer wavelengths. Curve VII shows an absorption maximum at 565 mμ.

Dissociation Constant of Phenylazochromotropic Acid. — Judging from the presence of the isosbestic points (348∼350, 392∼394, 460∼462 and 560∼562 mμ), two structures (H_2R^{2-} and HR^{3-})[10,11] may be expected to exist (Fig. 1).



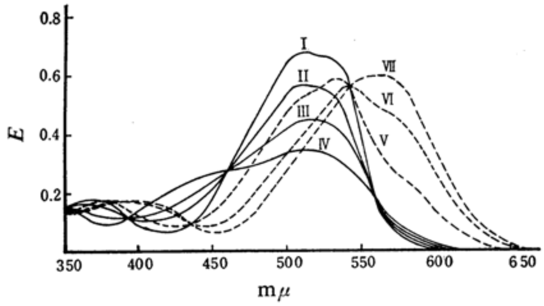


Fig. 1. Absorption spectra of phenylazochromotropic acid (I—IV) and its thorium complex (V—VII).
I 2.5×10^{-5} mol./l., pH 1.8∼6, $\mu=0.1$, 25°C; II pH 8.3; III pH 9.3; IV pH 11∼12.4; V pH 1.0; VI pH 1.42; VII pH 3.2

The constant of the above dissociation, K_{a_1}, was calculated by the following equation from the absobance vs. the pH value curve at 510 mμ (25°C, $\mu=0.1$) shown in Fig. 2.

In the following equations $[H_2R]$ and $[HR]$ represent the concentrations of H_2R^{2-} and H^{3-} respectively:

$$K_{a_1}=[H]\,[HR]/[H_2R]$$

$$pK_{a_1}=-\log[H]-\log\{[HR]/[H_2R]\}$$

$$=-\log[H]-\log\{(E_{H_2R}-E)/(E-E_{HR})\}$$

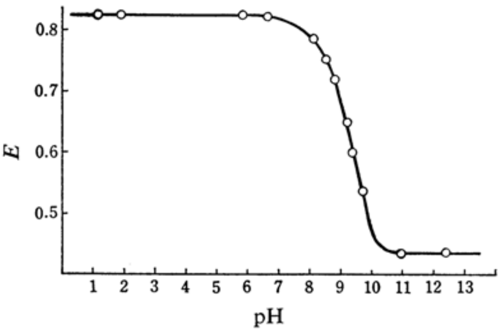


Fig. 2. Absorbance at 510 mμ vs. pH for phenylazochromotropic acid (3×10^{-5} mol./l.).

where E_{H_2R} and E_{HR} represent the absorbance in the 1∼6 and 11∼12 pH value ranges respectively and E, the absorbance at a pH value of 8∼10 (Fig. 2).

In Fig. 3, the values of $\log\{(E_{H_2R}-E)/(E-E_{HR})\}$ were plotted against the pH value, and the value of pK_{a1} was estimated graphically to be 9.30. A value of 9.29 for the same dissociation constant has been reported by Schwarzenbach[12].

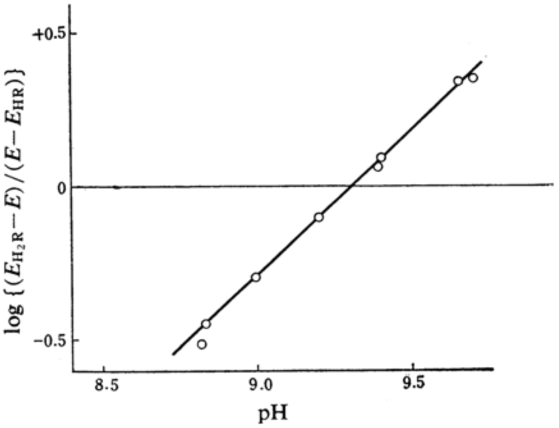


Fig. 3. Relationship between pH and $\log\{(E_{H_2R}-E)/(E-E_{HR})\}$.

Chemical Composition of the Thorium Complex. — *Continuous Variation Method.* — The absorbances at 580 mμ of solutions with various $[Th]/([Th]+[H_2R])$ ratios were measured one hour after the solutions had been prepared; the results indicated the formation of a 1 : 1 complex of thorium with the reagent (Fig. 4).

Mole Ratio Method. — The results obtained indicate the formation of a 1 : 1 complex within the range of experimental error. The measurement was made at 580 mμ and at a pH value of 3.1 (Fig. 5).

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[10] H. Zollinger and W. Büchler, *Helv. Chim. Acta*, **34**, 591 (1951).

[11] J. Heller and G. Schwarzenbach, ibid., **34**, 1876 (1951).

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

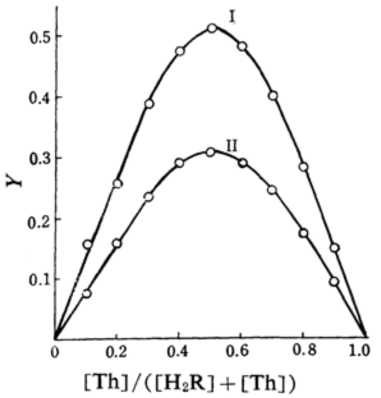

Fig. 4. Continuous variation method.
pH 3.4, $\mu=0.1$, 25°C, 580 mμ
I Th=H$_2$R=4.5×10^{-5} mol./l.
II Th=H$_2$R=3.0×10^{-5} mol./l.

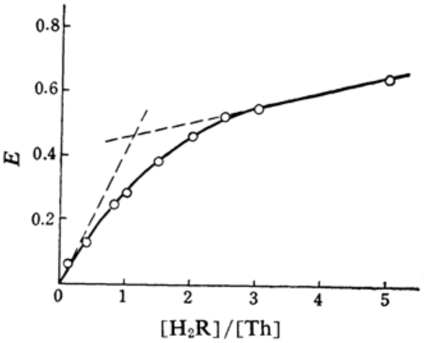

Fig. 5. Mole ratio method.
pH 3.1, $\mu=0.1$, 25°C, 580 mμ
Thorium concn.=3×10^{-5} mol./l., reagent concn. varied.

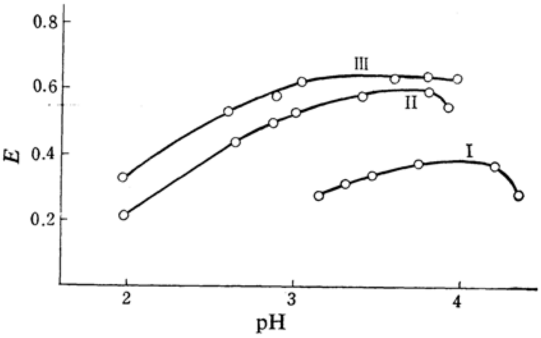

Fig. 6. Effect of pH on absorbance values of the thorium complex.
I H$_2$R : Th=1 : 1
II H$_2$R : Th=1 : 5
III H$_2$R : Th=1 : 10

Both methods show that a 1 : 1 complex is formed between thorium and the reagent in the pH value range studied.

Effect of pH Value on the Color of the Complex.—The pH values of solutions containing thorium and the reagent (3.0×10^{-5} mol./l.) in the molar ratios 1 : 1, 5 : 1 and 10 : 1 were adjusted to 2∼4.2 by perchloric acid, and the absorbances were measured (Fig. 6).

The curves in Fig. 6 show that the absorption increases with the increase of the thorium : reagent ratio and that it tends to be constant over a wide pH value range.

Effect of Time. — The relationship between the absorbance at 580 mμ and the lapse of time after the mixing of thorium with the reagent in various pH value ranges is shown in Fig. 7. The color of the thorium complex is fully developed in a few minutes after mixing, and the absorbance remained constant for two hours.

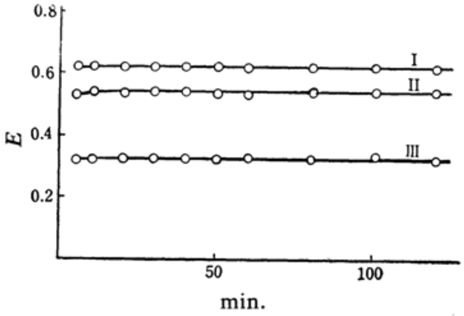

Fig. 7. Effect of reaction time.
I pH 3.5 II 2.59 III 1.95

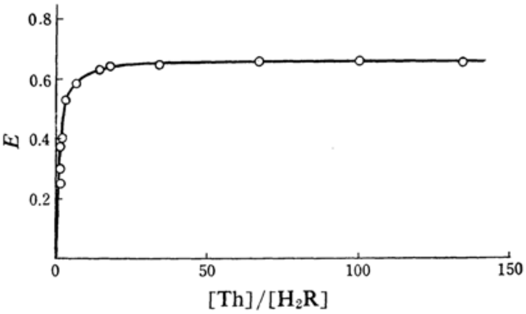

Fig. 8. Effect of excess thorium concentration on the absorbance of the complex.
pH 3.2, $\mu=0.1$, 25°C, 580 mμ
Reagent concn.=3×10^{-5} mol./l.

Effect of an Excess Thorium Concentration.—The effect of an excess thorium concentration on the absorbance is shown in Fig. 8, other experimental conditions being kept constant.

The curve indicates that the absorbance reaches a constant value when the molar ratio of thorium to the reagent exceeds 60.

The Apparent Stability Constant* of the Thorium Complex.—The existence of the isosbestic points (346∼347, 436 and 542 mμ) is

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* Conditional stability constant suggested by A. Ringbom, *J. Chem. Educ.*, 35, 282 (1958).

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

pH	E	C_R	C_{Th}	[ThHR]	K'
1.98	0.215	3×10^{-5}	15×10^{-5}	0.86×10^{-5}	0.28×10^{4}
2.01	0.203	6×10^{-5}	6×10^{-5}	0.65×10^{-5}	0.23×10^{4}
2.40	0.638	3×10^{-5}	300×10^{-5}	2.87×10^{-5}	0.73×10^{4}
2.50	0.379	12×10^{-5}	2.5×10^{-5}	1.16×10^{-5}	0.80×10^{4}
2.68	0.085	3×10^{-5}	1×10^{-5}	0.24×10^{-5}	1.17×10^{4}
3.0	0.348	2.7×10^{-5}	6.3×10^{-5}	1.51×10^{-5}	2.63×10^{4}
3.1	0.616	3×10^{-5}	40×10^{-5}	2.76×10^{-5}	3.13×10^{4}
3.2	0.274	2.4×10^{-5}	3.6×10^{-5}	1.17×10^{-5}	3.94×10^{4}
3.4	0.317	2.4×10^{-5}	3.6×10^{-5}	1.38×10^{-5}	6.05×10^{4}
3.4	0.428	2.7×10^{-5}	6.3×10^{-5}	1.89×10^{-5}	5.27×10^{4}

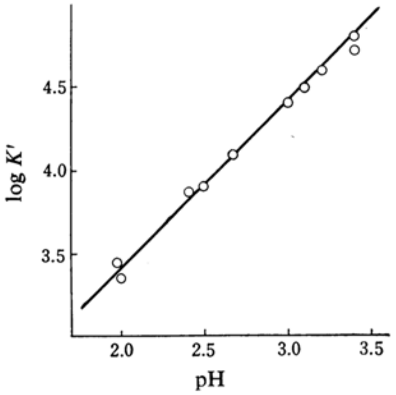

Fig. 9. Relationship between pH and log K'.

excellent evidence that only two structures are present, H_2R and a single complex in the 1.0~3.4 pH value range (Fig. 1).

The value of the apparent stability constant of the thorium complex may be estimated by assuming that the formation of the thorium complex is in accordance with the following equation:

$$Th^{4+} + H_2R^{2-} \rightleftarrows ThHR^{+} + H^{+}$$

The equilibrium constant, K, is given by:

$$K = [ThHR]\,[H]/[Th]\,[H_2R] \qquad (1)$$

the ionic charge being neglected for the sake of convenience. The total concentrations of the reagent and thorium are given by:

$$C_R = [H_2R] + [HR] + [R] + [ThHR] \qquad (1)$$

$$C_{Th} = [Th] + [ThHR] \qquad (2)$$

respectively. At pH values lower than 4, [HR] and [R] can be disregarded. Substitution of Eqs. 2 and 3 into Eq. 1 leads to the following equation:

$$K = [ThHR]\,[H]/$$
$$(C_{Th} - [ThHR])(C_R - [ThHR]) \qquad (4)$$

The absorbance, E, of the thorium complex at 580 mμ may be expressed as:

$$E = \varepsilon_{H_2R}[H_2R] + \varepsilon_{ThHR}[ThHR] \qquad (5)$$

The molar absorptivities at 580 mμ, ε_{H_2R} and ε_{ThHR}** were found to be 1.11×10^3 and 2.33×10^4 respectively.

From Eqs. 2 and 5.

$$E = \varepsilon_{H_2R}(C_R - [ThHR]) + \varepsilon_{ThHR}[ThHR]$$
$$= \varepsilon_{H_2R}C_R - [ThHR](\varepsilon_{H_2R} - \varepsilon_{ThHR})$$

Hence,

$$[ThHR] = \varepsilon_{H_2R}C_R - E/(\varepsilon_{H_2R} - \varepsilon_{ThHR}) \qquad (6)$$

The apparent stability constant, K' (Table I), of the thorium complex was estimated at 2~3.5 pH values using Eqs. 6 and 7:

$$K' = K/[H] = [ThHR]$$
$$/(C_{Th} - [ThHR])(C_R - [ThHR]) \qquad (7)$$

In Fig. 9, 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.

Summary

The dissociation constant of phenylazochromotropic acid, pK_a, has been estimated spectrophotometrically to be 9.3_0 (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, $\log K'$, has been estimated to be 3.4~4.9 in the 2~3.5 pH value range.

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** The absorbance has reached a constant value when the molar ratio of thorium to the reagent exceeds 60 (Fig. 8). In this case, the formation of the complex was considered to be complete, and the value of ε_{ThHR} was obtained from the absorbance of the solution containing the reagent and thorium in the molar ratio of 1 : 100.