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A Spectrophotometric Study of the Thorium Complexes of *o*-, *m*-, and *p*-Nitrophenyl-azo-chromotropic Acids*[1]

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o-, *m*-, and *p*-Nitrophenyl-azo-chromotropic acids were prepared as colorimetric reagents for thorium. The acid dissociation constants of the reagents have been determined spectrophotometrically, their pK_1 values being 8.96, 8.60, and 8.77 for the *o*-, *m*-, and *p*-compounds respectively at 25°C and when $\mu=0.1$. The reagents form violet 1 : 1 complexes in an acidic solution. The apparent stability constants have been measured spectrophotometrically. The order of the apparent stability constants of the complexes agrees with that of the first acid dissociation constants of the reagents; *m*-nitro>*p*-nitro>*o*-nitro compounds.

In the course of our studies of the thorium complex formed with ortho-substituted phenyl-azo-chromotropic acid,[1] the effect of the nitro group on the complex formation has been studied.

The present paper will describe the preparation of *o*-, *m*-, and *p*-nitrophenyl-azo-chromotropic acids as new colorimetric reagents for thorium, and will discuss their acid dissociation constants and the apparent stability constants of their complexes.

The order of their apparent stability constants agrees with that of the first acid dissociation constants of the reagents.

Experimental

Reagents. *o-, m-, and p-Nitrophenyl-azo-chromotropic Acids.*[2] Diazotized nitroanilines[3] were coupled with

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

[2] Colour Index No. 16575.

[3] K. H. Saunders, "The Aromatic Diazo-compounds and their Technical Applications," Edward Arnold & Co., London (1949), pp. 6, 311.

chromotropic acid. The pure azo compounds were obtained in the form of free acid after purification from concentrated hydrochloric acid.

Thorium Perchlorate Solution. The preparation was carried out according to the method described in a previous paper.1) All the other reagents used were of a guaranteed grade.

Spectrophotometric Measurements. The same apparatus and procedure as in a preceding paper4) were used for the spectrophotometric measurements.

All the measurements were made at 25°C and with $\mu=0.1$.

Results and Discussion

Absorption Spectra. The absorption spectra of the *o*-, *m*-, and *p*-nitro compounds and of the systems containing these compounds and thorium(IV) are shown in Figs. 1, 2, and 3 respectively.

In these figures, Curve I shows the absorption spectra of *o*-, *m*-, and *p*-compounds in the acid range below pH 5. In this pH range, the acid dissociation of one of the naphtholic groups in these compounds does not occur.

Curve IV for the *o*-compound and Curve V for the *m*- and *p*-compounds show the absorption spectra of each compound in the range above pH 12.

The change in the absorption spectra between pH 5 and 12 seems to correspond to the acid dissociation for the naphtholic group. The isosbestic points occur at 400, 457, and 545 mμ for the *o*-compound, at 398, 462, and 546 mμ for the *m*-compound, and at 403, 452, and 545 mμ for the *p*-compound.

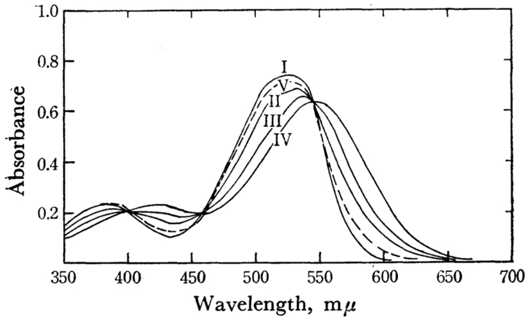

Fig. 1. Absorption spectra of *o*-nitrophenyl-azo-chromotropic acid (I—IV), and of the system containing the compound and thorium (broken line).

I 2.5×10^{-5} M reagent solution at pH <5 (H_2R)
II 2.5×10^{-5} M reagent solution at pH 8.60
III 2.5×10^{-5} M reagent solution at pH 9.31
IV 2.5×10^{-5} M reagent solution at pH >12 (HR)
V Thorium concn. to the reagent solution concn. $=10:1$, pH 3.0

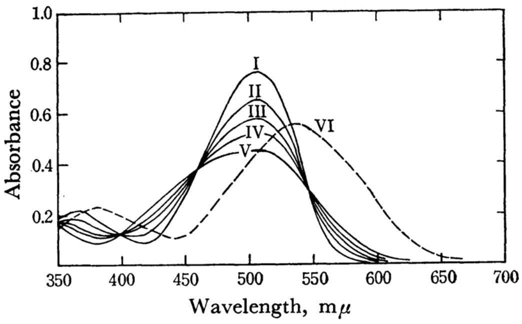

Fig. 2. Absorption spectra of *m*-nitrophenyl-azo-chromotropic acid (I—V), and of the system containing the compound and thorium (broken line).

I 2.5×10^{-5} M reagent solution at pH <5 (H_2R)
II 2.5×10^{-5} M reagent solution at pH 8.30
III 2.5×10^{-5} M reagent solution at pH 8.69
IV 2.5×10^{-5} M reagent solution at pH 9.09
V 2.5×10^{-5} M reagent solution at pH >12 (HR)
VI Thorium concn. to the reagent concn. $=10:1$, pH 3.0

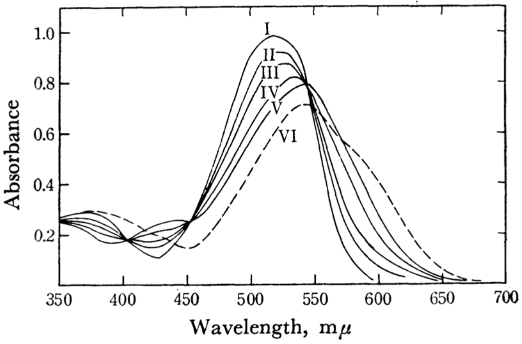

Fig. 3. Absorption spectra of *p*-nitrophenyl-azo-chromotropic acid (I—V), and of the system containing the compound and thorium (broken line).

I 2.5×10^{-5} M reagent solution at pH <5 (H_2R)
II 2.5×10^{-5} M reagent solution at pH 8.32
III 2.5×10^{-5} M reagent solution at pH 8.72
IV 2.5×10^{-5} M reagent solution at pH 9.30
V 2.5×10^{-5} M reagent solution at pH >12 (HR)
VI Thorium concn. to the reagent concn. $=10:1$, pH 3.0.

When thorium salt was added to the reagent solution, the pink color of the solution turned violet. Curve V in Fig. 1 and Curve VI in Figs. 2 and 3 show the absorption spectra of the systems containing thorium and the *o*-, *m*-, and *p*-compounds respectively.

Acid Dissociation Constant. The reagents, nitrophenyl-azo-chromotropic acids (H_4R), are dissociated in water as follows:

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

$$H_2R^{2-} \rightleftarrows HR^{3-} + H^+$$

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

K_1 was calculated by the following equation:

$$pK_1 = pH - \log\{(E_{H_2R}-E)/(E-E_{HR})\}$$

where E_{H_2R}, E_{HR}, and E[4)] represent, respectively, the absorbances of H_2R, HR, and their mixture. The second acid dissociation constant, however, could not be obtained, because dissociation would occur above pH 14.

In Fig. 4, the values of $\log\{(E_{H_2R}-E)/(E-E_{HR})\}$ are plotted against the pH values; the pK_1 values of the *o*-, *m*-, and *p*-compounds were graphically estimated to be 8.96, 8.60, and 8.77 respectively.

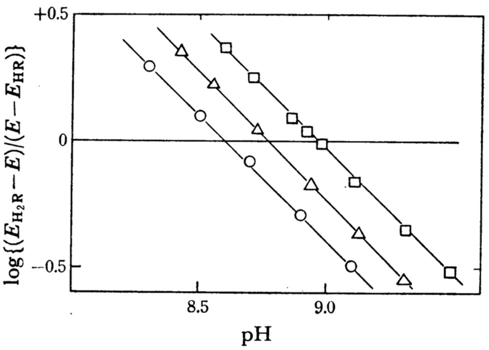

Fig. 4. Relationship between pH and $\log\{(E_{H_2R}-E)/(E-E_{HR})\}$.
-□- *o*-nitro compound
-○- *m*-nitro compound
-△- *p*-nitro compound

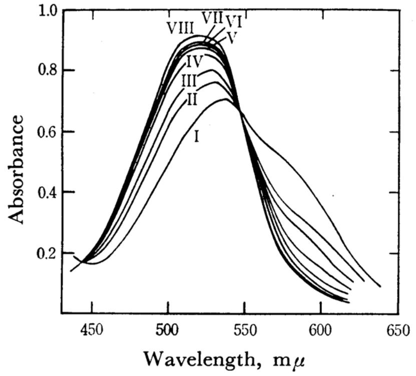

Fig. 5. Effect of the ionic strength on the absorption spectra of the system containing the *p*-compound and thorium, pH at 3.0.
the reagent concn.$=2.5\times10^{-5}$ M,
thorium concn.$=2.5\times10^{-5}$ M

I	1 M sodium perchlorate solution 0 m*l* in 50 m*l*
II	1 M sodium perchlorate solution 0.5 m*l* in 50 m*l*
III	1 M sodium perchlorate solution 1.0 m*l* in 50 m*l*
IV	1 M sodium perchlorate solution 2.0 m*l* in 50 m*l*
V	1 M sodium perchlorate solution 3.0 m*l* in 50 m*l*
VI	1 M sodium perchlorate solution 4.0 m*l* in 50 m*l*
VII	1 M sodium perchlorate solution 5.0 m*l* in 50 m*l*
VIII	1 M sodium perchlorate solution 6.0 m*l* in 50 m*l*

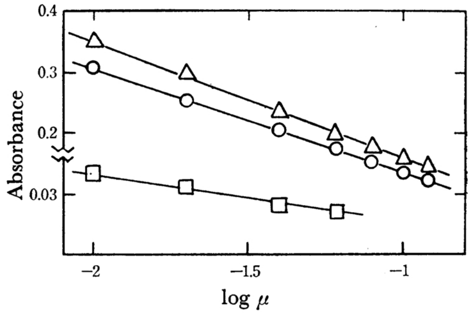

Fig. 6. Effect of the ionic strength on the system of the *o*-, *m*- *p*-compounds and thorium.
-□- *o*-compound at pH 2.5, at 590 mμ
-○- *m*-compound at pH 3.0, at 570 mμ
-△- *p*-compound at pH 3.0, at 580 mμ

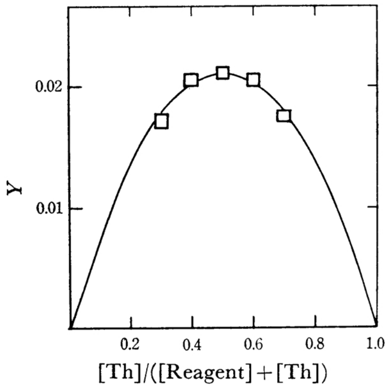

Fig. 7. Continuous variation method.
Thorium and the reagent concn.$=1\times10^{-4}$ mol/*l*
-□- *o*-compound at 590 mμ, pH 3.3

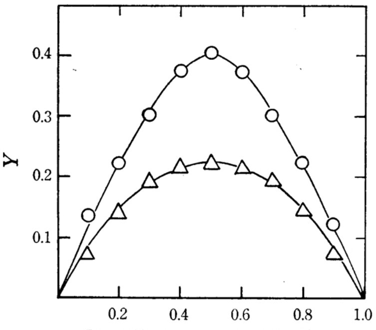

Fig. 8. Continuous variation method.
Thorium and the reagent concn.$=1\times10^{-4}$ mol/*l*
-○- *m*-compound at 570 mμ, pH 3.2
-△- *p*-compound at 580 mμ, pH 2.7

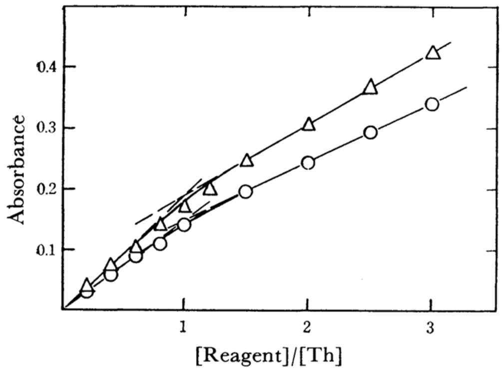

Fig. 9. Mole ratio method.
Thorium concn. $=2.5\times10^{-5}$ mol/l
The reagent concn. varied.
-○- *m*-compound at 570 mμ, pH 3.2
-△- *p*-compound at 580 mμ, pH 3.0

Thus the order of the first acid dissociation constants for these compounds follows the sequence: *m*-> *p*->*o*-compounds.

Effect of Ionic Strength. The effect of the ionic strength on the absorbances of the system in the acid region containing the reagents and thorium is shown in Figs. 5 and 6. Figure 5 gives the effect of the ionic strength on the absorption spectra of the system containing the *p*-compound and thorium. In Fig. 6, the absorbances of the system containing thorium and the *o*-, *m*-, and *p*-compounds is plotted against log μ.

The effect is more remarkable than in the case of other, similar phenyl-azo-chromotropic acid derivatives for thorium investigated by us in this series. When the value of is increased, the violet color of the solution is gradually changed to pink, the color of the reagents in an acidic medium.

Stability of the Color. The stability of the color of the systems containing the reagents and

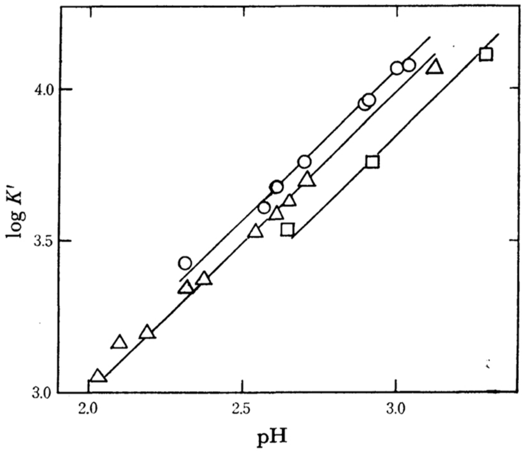

Fig. 10. Relationship between pH and log K' at 25°C, $\mu=0.1$.
-□- *o*-compound -△- *p*-compound
-○- *m*-compound

TABLE 1. APPARENT STABILITY CONSTANTS OF THE THORIUM COMPLEXES

pH	E	C_R	C_{Th}	log K'	ε_{H_2R}	ε_{ThHR}
o-Compound						
2.64	0.089	5×10^{-5} M	5×10^{-5} M	3.54	1.59×10^3	1.29×10^4
2.92	0.095	5×10^{-5} M	5×10^{-5} M	3.76		
3.29	0.112	5×10^{-5} M	5×10^{-5} M	4.11		
m-Compound						
2.61	0.087	2.5×10^{-5} M	2.5×10^{-5} M	3.68	1.54×10^3	2.16×10^4
2.70	0.095	2.5×10^{-5} M	2.5×10^{-5} M	3.76		
2.91	0.119	2.5×10^{-5} M	2.5×10^{-5} M	3.96		
3.04	0.136	2.5×10^{-5} M	2.5×10^{-5} M	4.08		
2.31	0.067	2.5×10^{-5} M	2.5×10^{-5} M	3.43	1.50×10^3	2.15×10^4
2.57	0.081	2.5×10^{-5} M	2.5×10^{-5} M	3.61		
2.89	0.116	2.5×10^{-5} M	2.5×10^{-5} M	3.95		
3.00	0.134	2.5×10^{-5} M	2.5×10^{-5} M	4.07		
p-Compound						
2.19	0.092	2.5×10^{-5} M	2.5×10^{-5} M	3.20	2.77×10^3	2.72×10^4
2.32	0.100	2.5×10^{-5} M	2.5×10^{-5} M	3.35		
2.54	0.114	2.5×10^{-5} M	2.5×10^{-5} M	3.53		
2.61	0.119	2.5×10^{-5} M	2.5×10^{-5} M	3.59		
2.71	0.131	2.5×10^{-5} M	2.5×10^{-5} M	3.70		
2.03	0.101	2.5×10^{-5} M	5×10^{-5} M	3.05		
2.10	0.109	2.5×10^{-5} M	5×10^{-5} M	3.16		
2.37	0.087	2.5×10^{-5} M	2.5×10^{-5} M	3.37	2.16×10^3	2.70×10^4
2.65	0.109	2.5×10^{-5} M	2.5×10^{-5} M	3.63		
3.12	0.174	2.5×10^{-5} M	2.5×10^{-5} M	4.07		

thorium was almost the same as that of phenylazo-chromotropic acid - thorium.1)

Composition of the Complex. In order to confirm the composition of the complexes, two methods were employed, the continuous variation and the mole-ratio methods.

As Figs. 7, 8, and 9, show the results indicate that thorium forms 1 : 1 complexes with the reagents.

The composition of the thorium complex with the *o*-compound is not obtained by the mole-ratio method because the difference of absorbances is too small to give the break point at 1 : 1.

Apparent Stability Constants. The apparent stability constants of the thorium complexes (Table 1) may be obtained by assuming the formation of the complexes to be in accordance with the following equation1):

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

$$K' = [\mathrm{ThHR}]/[\mathrm{Th}][\mathrm{H_2R}]$$
$$= [\mathrm{ThHR}]/(C_{\mathrm{R}} - [\mathrm{ThHR}])(C_{\mathrm{Th}} - [\mathrm{ThHR}])$$

where K' indicates the apparent stability constants of the complexes, C_{R} and C_{Th} are the total concentrations of the reagents and of thorium respectively, and [ThHR] is the concentration of the complexes.

In Fig. 10, the logarithm of the apparent stability constants are plotted against the pH value. The results are seen to be satisfactory: the order of the apparent stability constants of the throrium complexes, *m*->*p*->*o*-compounds, agrees with that of the first acid dissociation constants of the reagents.