Chromotropic Acid and Its Zirconyl and Thorium Complexes

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(Received November 26, 1962)

Chromotropic acid reacts with some metal ions to form its colored complexes[1], and many kinds of the azo-derivatives are especially sensitive to various metal ions; they are therefore used widely as colorimetric reagents and as metal indicators in chelatometry.

Chromotropic acid has two naphtholic hydroxyl groups, and the first dissociation constant was measured spectrophotometrically.

The composition of zirconyl and thorium chromotropate was determined by the continuous-variation and the mole-ratio methods, while the stability constants of the zirconyl and thorium complexes were measured from their absorbances.

Calculations

The Dissociation Constant of Chromotropic Acid.—Disodium chromotropate (abbr. H_2Ch-Na_2) is dissociated in water as follows:

$$H_2Ch^{2-} \rightleftarrows HCh^{3-} + H^+$$

The first dissociation constant, K_1, is

$$K_1 = [HCh]\,[H]\,/\,[H_2Ch]$$

Therefore,

$$pK_1 = pH - \log\,[HCh]\,/\,[H_2Ch]$$

When [HCh] is equal to $[H_2Ch]$, the pH is pK_1. As the concentrations are proportional to the absorbances, pK_1 is obtained by the following equation:

$$pK_1 = pH - \log\,(E_1 - E)/(E - E_2) \tag{1}$$

in which E_1 and E_2 are the characteristic absorbances of H_2Ch and HCh respectively at a constant wavelength, and E is an absorbance of their mixed solution at an arbitrary pH value.

The second dissociation constant, however, can not be obtained, because the dissociation occurs above pH 14, and it is too hard to get it under ordinary experimental conditions.

The Stability Constants of the Zirconyl and Thorium Complexes. — K_1 and K_2 are the first and the second dissociation constants of chromotropic acid, and K_{MCh} is the stability constant of the zirconyl or thorium complex.

$$K_1 = [H]\,[HCh]\,/\,[H_2Ch] \tag{2}$$

$$K_2 = [H]\,[Ch]\,/\,[HCh] \tag{3}$$

$$K_{MCh} = [MCh]\,/\,[M]\,[Ch] \tag{4}$$

The total concentration of chromotropic acid C_{Ch}, and the total zirconyl or thorium concentration, C_M, are

$$C_{Ch} = [H_2Ch] + [HCh] + [Ch] + [MCh] \tag{5}$$

$$C_M = [M] + [MCh] \tag{6}$$

On the basis of Eqs. 2—6, the stability constant, K_{MCh}, is:

$$K_{MCh} = \frac{[MCh]\{[H]^2/K_1K_2 + [H]/K_2 + 1\}}{\{C_{Ch} - [MCh]\}\{C_M - [MCh]\}} \tag{7}$$

The apparent stability constant, K'_{MCh}, is:

$$K'_{MCh} = [MCh]/\{C_{Ch} - [MCh]\}\{C_M - [MCh]\} \tag{8}$$

[MCh] can be obtained from the absorbance of the zirconyl or thorium complex solution.

$$E = \varepsilon_{H_2Ch}[H_2CH] + \varepsilon_{HCh}[HCh] + \varepsilon_{Ch}[Ch] + \varepsilon_{MCh}[MCh]$$

ε_{H_2Ch}, ε_{HCh}, ε_{Ch} and ε_{MCh} are the absorption coefficients of H_2Ch, HCh, Ch and MCh respectively. [Ch] may be neglected below pH 4.

$$E = \varepsilon_{H_2Ch}[H_2Ch] + \varepsilon_{HCh}[HCh] + \varepsilon_{MCh}[MCh] \tag{9}$$

Therefore, the concentration of [MCh] is

$$[MCh] = \frac{E\{1 + K_1/[H]\} - \varepsilon_{H_2Ch}C_{Ch} - \varepsilon_{HCh}C_{Ch}K_1/[H]}{\varepsilon_{MCh}\{1 + K_1/[H]\} - \varepsilon_{H_2Ch} - \varepsilon_{HCh}K_1/[H]} \tag{10}$$

By substituting Eq. 10 into Eqs. 7 and 8, K_{MCh} and K'_{MCh} can be calculated.

Experimental and Results

Reagents.—*Disodium Chromotropate.*—The purification of chromotropate is carried out in a dark room. Disodium chromotropate dihydrate (Dôjindo Pharaceutical Co.) is dissolved in water, acidified by concentrated hydrochloric acid, and treated with active carbon by heating. The filtrate is evaporated so as to deposit crystals by a rotary evaporator and

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[1] K. C. Mathur and A. K. Dey, *Z. anal. Chem.*, **154**, 347 (1957).

then cooled. The crystals are recrystallized again by the same manner, and then dried over phosphorus pentoxide to obtain the anhydrous compound. The sodium content is found to be quantitative by the use of a flame photometer.

Zirconyl Chloride[2]. — When a saturated solution of zirconyl chloride octahydrate (c. p. grade) is added to an acetone-hydrochloric acid mixture, the flocky octahydrate is precipitated and filtered. After the procedure is repeated twice, the precipitate is washed with acetone and dried in air. Cubic colorless crystals were obtained. The zirconyl content is analyzed gravimetrically by the use of cupferron[3].

Found: ZrO_2, 38.23, 38.26. Calcd. for $ZrOCl_2$-$8H_2O$: ZrO_2, 38.24%.

A 5×10^{-4} M zirconyl chloride solution is prepared by dissolving 16.11 mg. of a zirconyl chloride octahydrate with a 0.1 M potassium chloride solution in a 100 ml.-measuring flask, and it should be used within 20 min.

Thorium Perchlorate.—Thorium nitrate is purified through thorium hydroxy peroxide five or six times[5]. Thorium hydroxide prepared from the purified thorium nitrate is disssolved in perchloric acid, and the concentration is measured gravimetrically by oxalate[4].

Procedure.—All experiments are carried out in a dark room, because chromotropate tends to decompose in daylight, especially at higher pH values.

The Dissociation Constant of Chromotropic Acid. — Five milliliters of a 5×10^{-4} M chromotropate solution and a suitable buffer solution are poured into a 50 ml.-measuring flask, which is then filled up to the mark with 0.2 M sodium perchlorate and water to keep the ionic strength (μ) at 0.1. The spectra are measured with a Hitachi EPS-2 automatic recording spectrophotometer (Fig. 1). The pH values are measured with a Horiba Model M-4 glass electrode pH meter. With an increasing pH, a new absorption maximum appears at 361.5 mμ, and the absorbance is determined by a Shimadzu Model QR-50 spectrophotometer with 1 cm. quartz cell. pK_1 is calculated from Eq. 1, and the average value of six runs is shown in Table I.

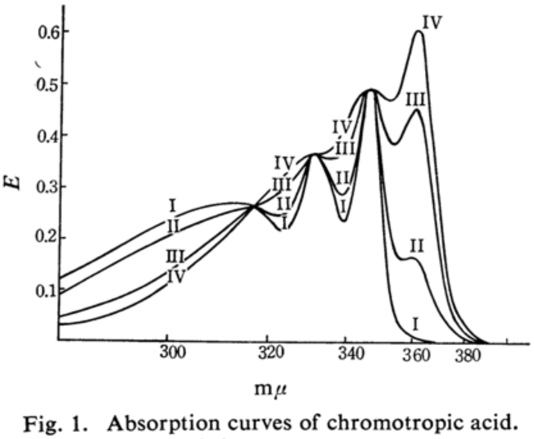

Fig. 1. Absorption curves of chromotropic acid. 5×10^{-5} M, $\mu=0.1$

	I	II	III	IV
pH	1∼3	5.0	5.8	10∼12

TABLE I. pK_1 OF CHROMOTROPIC ACID

The authors	5.44±0.03	(μ=0.1, 16∼23°C)
Schwarzenbach et al.[6]	5.36	(μ=0.1, ∼20°C)
Zollinger et al.[7]	5.53	(20°C)

Zirconyl Complex. — Each 5 ml. of a 5×10^{-4} M solution of zirconyl and chromotropate is mixed in a 50 ml.-measuring flask containing a suitable amount of hydrochloric acid; the flask is then filled up to the mark with a potassium chloride solution and water to maintain the ionic strength at 0.1.

A new absorption maximum appears at 356.5 mμ. The absorbance reaches its maximum at pH 2 after standing for one hour.

The composition was determined by the continuous variation method (Fig. 2). The composition should be 1 : 1, but the stability of the complex is not very good.

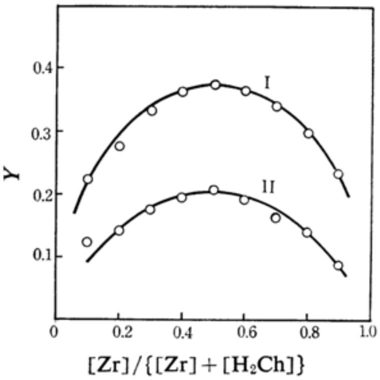

Fig. 2. Continuous variations.

I $[Zr]+[H_2Ch]=2\times10^{-4}$ mol./l.
II $[Zr]+[H_2Ch]=1\times10^{-4}$ mol./l.
pH=2, μ=0.1, at 357.5 mμ

From Eq. 8, the following equation can be obtained.

$$\log K'_{\mathrm{MCh}}=\log[\mathrm{MCh}]/\{C_{\mathrm{Ch}}-[\mathrm{MCh}]\}$$
$$-\log\{C_{\mathrm{M}}-[\mathrm{MCh}]\}$$

The values of the first term were plotted against the second term at a constant pH (Fig. 3).

In Fig. 3, straight lines are obtained, and the slope indicates that the ratio of zirconyl to chromotropic acid is 1 to 1; log K'_{MCh} is 3.6_3 at pH 2.0, and 29 at pH 1.2.

Thorium Complex.—Five milliliters of a 5×10^{-4} M chromotropate solution and 5 ml. of a 2.5×10^{-3} M thorium perchlorate solution are poured into a 50 ml.-measuring flask containing a suitable amount

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[2] A. W. Henderson and K. B. Higbie, *J. Am. Chem. Soc.*, **76**, 5857 (1954).

[3] W. W. Scott, "Standard Methods of Chemical Analysis", D. van Nostrand Co. Inc., New York (1939), p. 1099.

[4] Ibid., p. 953.

[5] R. L. Swan, *J. Chem. Soc.*, **125**, 781 (1924).

[6] J. Heller and G. Schwarzenbach, *Helv. Chim. Acta*, **34**, 1876 (1951).

[7] H. Zollinger and W. Büchler, ibid., **34**, 591 (1951).

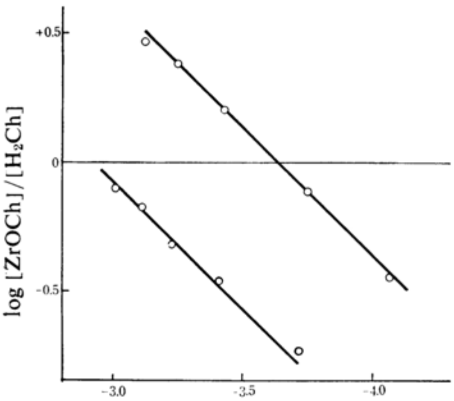


Fig. 3. Plots of log [ZrOCh]/[H$_2$Ch] against −log [Zr].

$C_{H_2Ch}=5\times10^{-5}$ M/l. $\mu=0.1$ at 357.5 mμ

of perchloric acid and then diluted to the mark by a sodium perchlorate solution and water so that the ionic strength is kept at 0.1. The absorption curve has a maximum at 361 mμ. The absorbance at 361 mμ reached its maximum after standing for 90 min., when it was measured. The absorbance is plotted against pH in Fig. 4. As the absorbance decreased above pH 3.6, the following experiment was carried out at pH 3.3∼3.5.

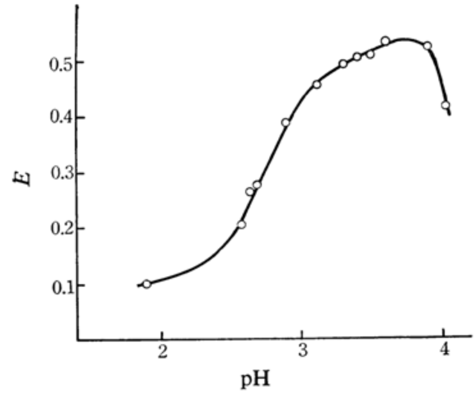


Fig. 4. Effect of pH on the absorbance of the complex.

$\mu=0.1$ at 361 mμ

The Mole-ratio Method.—A plot of the moles of chromotropic acid against the absorbance is given in Fig. 5. The 1 : 1 complex is indicated, being considerably dissociated under the conditions of this experiment.

The Continuous-variation Method.—At pH 3.5, equimolecular solutions of chromotropic acid and thorium perchlorate were mixed in varying proportions, the total number of moles remaining constant. The absorbances of each solution were measured at 361 mμ after they had been left standing for 2.5∼3 hr. in a dark room. The values of the absorbances calculated on the assumption of "no reaction" were then substracted from the measured absorbances to give what are commonly referred to as Y values (Fig. 6). The ratio of chromotropic acid to thorium was 1 to 1.

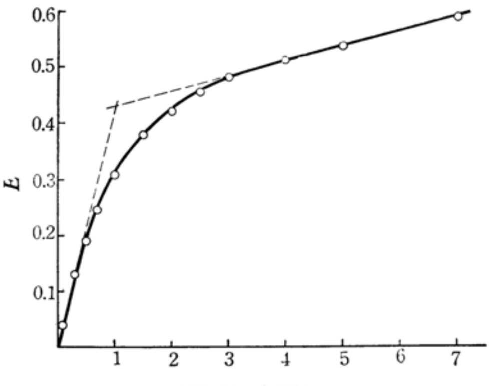


Fig. 5. Mole ratio method.
$C_{Th}=5\times10^{-5}$ M/l. $\mu=0.1$ at 361 mμ

Stability Constant.—ε_{H_2Ch}, ε_{HCh} and ε_{MCh} were calculated from the absorbances at 361 mμ; the values were 1.89×10^2, 1.16×10^4 and 1.17×10^4 respectively. The stability constant, K_{MCh}, was calculated from Eqs. 9 and 10 by using $pK_2=15.6$[6]

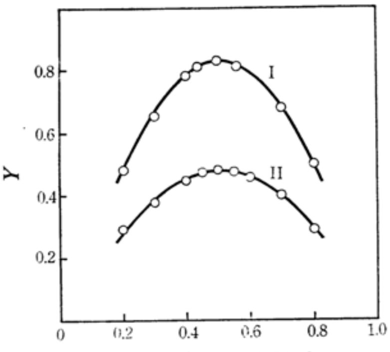


Fig. 6. Continuous variations.
I [Th]+[H$_2$Ch]$=2.5\times10^{-4}$ M/l.
II [Th]+[H$_2$Ch]$=1.5\times10^{-4}$ M/l.
$\mu=0.1$, pH=3.5, at 361 mμ

TABLE II. STABILITY CONSTANTS OF THORIUM CHROMOTROPATE

C_{Ch} $\times10^{-5}$	C_{Th} $\times10^{-5}$	pH	E	[ThCh] $\times10^{-5}$	K_{ThCh} $\times10^{18}$
2	2	3.42	0.0774	0.59	4.80
3	3	3.41	0.1334	1.09	5.05
4	4	3.41	0.2060	1.71	5.44
5	5	3.42	0.2775	2.31	5.11
6	6	3.42	0.3469	2.89	4.80
7	7	3.41	0.4125	3.44	4.56
8	8	3.42	0.4994	4.18	4.59
9	9	3.40	0.5629	4.72	4.51
10	10	3.42	0.6508	5.46	4.24
			The average value		4.79

(Table II). The apparent stability constants (Eq. 8) are shown in Table III. A plot of the apparent stability constants against pH is indicated in Fig. 7.

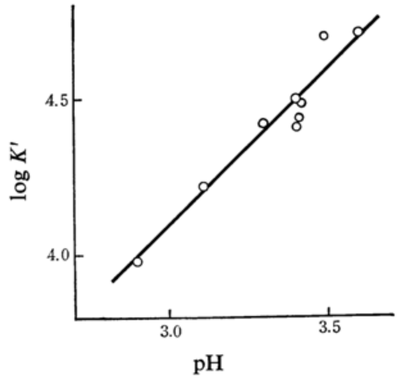


Fig. 7. Relationship between log K'_{ThCh} and pH.

TABLE III. APPARENT STABILITY CONSTANTS OF THORIUM CHROMOTROPATE

C_{Ch} $\times 10^{-5}$	C_{Th} $\times 10^{-4}$	pH	E	[ThCh] $\times 10^{-5}$	K'_{ThCh} $\times 10^{4}$
5	2.5	2.90	0.3969	3.37	0.955
5	2.5	3.11	0.4559	3.88	1.65
5	2.5	3.30	0.4976	4.25	2.71
5	2.5	3.40	0.5072	4.33	3.15
9	0.9	3.40	0.5629	4.71	2.57
7	0.7	3.41	0.4125	3.44	2.72
6	0.6	3.42	0.3469	2.89	3.00
5	2.5	3.49	0.5331	4.56	5.02
5	2.5	3.60	0.5346	4.57	5.18

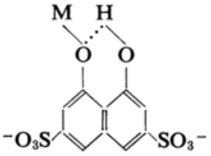
Discussion

The first dissociation constant of chromotrophic acid (pK_1) is 5.4_4, and so, below pH 3.5, chromotropic acid exists predominantly in the form of $\mathrm{H_2Ch}$. It reacts with zirconyl or thorium ions to form its complex. Figures 3 and 8 show that the metal ions react with the acid to replace only one hydrogen ion. There are two possibilities:

$$\mathrm{M} + \mathrm{H_2Ch} \rightleftarrows \mathrm{MHCh} + \mathrm{H^+}$$

$$\mathrm{M(OH)}_n + \mathrm{H_2Ch} \rightleftarrows \mathrm{MCh} + \mathrm{H^+} + \mathrm{H_2O}$$

In the former case, the following structures of the complex are possible:



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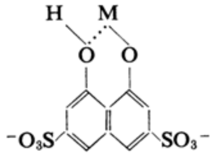

II

Form I is not a chelate but a salt, and by preliminary experiments, 1-naphthol-4-sulfonic acid does not react with the ions under the conditions of this experiment. Therefore, the complex is unlikely to be of Form I.

The second dissociation constant of acid (pK_2) is 15.6[6], because the second hydrogen atom is bridged between two oxygen atoms. The first hydrogen atom is far more exchangeable by the metal ions than the second one. Therefore, it is difficult to consider Form II.

In the latter case, the reaction species of zirconyl or thorium ion can not be detected directly from the absorbance because they have no absorbance at any wavelength.

Zirconium would exist in the form of $\mathrm{Zr(OH)_2^{2+}}$ in acidic solutions, but the species has not yet been exactly confirmed[7].

Kraus and Holmberg[8] stated that the hydrolysis of $2.5\times10^{-4}\sim1.5\times10^{-2}$ M thorium ions was negligible below pH 3 and was influenced by the concentration, but that at about pH 3.5 the number of moles of hydroxide attached to thorium was several tenths of the total and that the equilibrium was rapidly established.

In our experiments, the concentration of zirconyl or thorium ions less than 2.5×10^{-4} M and the pH is about 1~2 in zirconyl and about 2~3.5 in thorium. Although the state of the ions has not been studied under the conditions of our experiments and although the reaction species have not been confirmed, zirconyl or thorium ions should have some $\mathrm{M(OH)}_n{}^{4-n}$ ions in acidic solutions. Therefore, the latter equation seems to hold.

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8) B. A. J. Lister and L. A. McDonald, *J. Chem. Soc.*, **1952**, 4315.

9) K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).