

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## A Spectrophotometric Study of the Thallium(III) Nitrate Complex

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Spectrophotometric studies have been made at 22° of acid thallium(III) perchlorate solutions containing nitrate. The data have been interpreted in terms of a mononitratothallium(III) complex,  $K_1 = (\text{TlNO}_3^{++})/(\text{Tl}^{+++})(\text{NO}_3^-) = 8.3$  at  $\mu = 0.567$ ,  $(\text{H}^+) = 0.44$ ; 4.7 at  $\mu = 1.15$ ,  $(\text{H}^+) = 1.0$ ; 2.8 at  $\mu = 2.00$ ,  $(\text{H}^+) = 1.0$ ; 2.0 at  $\mu = 3.00$ ,  $(\text{H}^+) = 1.0$ . The molar absorptivities for  $\text{Tl}^{+++}$ ,  $\text{TlOH}^{++}$  and  $\text{TlNO}_3^{++}$  have been determined. A method has been developed for interpreting spectrophotometric data when significant hydrolysis as well as complex formation occurs. Data on the affinity of nitrate for various cations are tabulated.

The existence of a complex between thallium(III) and nitrate ions has been suggested several times in the literature. A postulated mechanism for the isotopic exchange between thallium(III) and thallium(I) ions in nitrate media includes a path through a mononitratothallium(III) complex.<sup>1</sup> The formal potential of the thallium(I)–thallium(III) couple at 25° is  $-1.260$  volt in 1 *F*  $\text{HClO}_4$ <sup>2</sup> and  $-1.230$  volt in 1 *F*  $\text{HNO}_3$ ,<sup>3</sup> indicating weak complexing in the latter medium.

Recently Peschanski<sup>4</sup> has observed a thallic nitrate complex spectrophotometrically. The data were analyzed by the method of continuous variations.<sup>5</sup> The combining ratio was determined to be 1 to 1, and the mass action formation constant,  $(\text{TlNO}_3^{++})/(\text{Tl}^{+++})(\text{NO}_3^-)$ , was evaluated to be 1.5 liter/mole at 18° and an ionic strength of 3.5 *M* in 2.5 *F*  $\text{HClO}_4$ .

The present study was undertaken to obtain further information about the stability and the absorption spectrum of the thallium(III) nitrate complex species by a spectrophotometric method.

### Experimental

Reagent-grade chemicals were used at all times.

Stock thallic perchlorate solutions were prepared by oxidation of thallos acetate solutions made alkaline with sodium hydroxide. A 30% solution of hydrogen peroxide was added slowly until further addition of peroxide produced no vigorous reaction. The resultant hydrous thallic oxide was washed by decantation, filtered, washed, dried at 115° for 2 hours and then dissolved in a large excess of perchloric acid. Stock solutions were stored in dark bottles as suggested by Biedermann<sup>6</sup> to prevent reduction of thallium(III) by sunlight.

The stock thallic perchlorate solutions were standardized iodometrically: sodium iodide was added and the liberated iodine was titrated with sodium thiosulfate to a starch endpoint. From the standardization data and the weight of thallic oxide used, the prepared oxide was calculated to have an empirical formula of  $\text{Tl}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .

The perchloric acid concentration of a stock thallic perchlorate solution was determined by a difference method. The solution was titrated with standard sodium hydroxide using a glass and modified calomel (saturated with sodium chloride instead of potassium chloride) electrode-pair in conjunction with a Leeds and Northrup line-operated, direct-reading pH meter. The perchloric acid concentration was evaluated by subtracting the known equivalents of thallic perchlorate from the equivalents of hydrogen ion determined in this way.

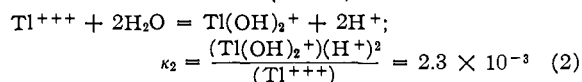
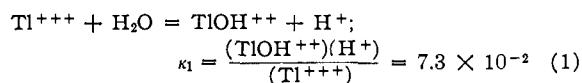
A standard sodium nitrate solution was prepared by dis-

solving a dried, weighed amount of sodium nitrate in water. A stock sodium perchlorate solution was standardized gravimetrically by precipitation of potassium perchlorate with potassium nitrate.

Absorbance measurements were made with a Beckman model DU quartz photoelectric spectrophotometer with an ultraviolet attachment using matched 1,000-cm. silica cells. Measurements were made in an air-conditioned room whose temperature was controlled at  $21.7 \pm 0.6^\circ$ .

### Results

**Hydrolysis of Thallium(III).**—The observation of McConnell and Davidson<sup>7</sup> that the absorbance of thallic perchlorate solutions increased with decreasing perchloric acid concentration led them to suggest that hydrolyzed species such as  $\text{TlOH}^{++}$  or  $\text{Tl}(\text{OH})_2^+$  might be absorbing. Quantitative data regarding hydrolysis of thallium(III) has been obtained by Biedermann<sup>6</sup> by potential measurements. The following mass-action hydrolysis constants were obtained at an ionic strength of 3.00 *M* and at 25°



There was no evidence for polynuclear complexes even though in some solutions the hydrogen ion concentration was as low as 0.020 *M*. It is evident from the magnitude of the hydrolysis constants that for moderate acid concentrations a spectrophotometric study involving thallium(III) solutions must consider at least the first hydrolysis equilibrium.

Using Biedermann's constants, assuming that they do not vary much with temperature, it was possible to estimate the molar absorptivities (molar extinction coefficients) for the thallium species present in acid thallic perchlorate solutions.

The absorption spectra of solutions, approximately  $5 \times 10^{-3}$  *F* in  $\text{Tl}(\text{ClO}_4)_3$ , containing amounts of  $\text{HClO}_4$  varying from 0.44 to 3.0 *F*, and maintained at an ionic strength of 3.00 *M* with sodium perchlorate were determined over the wave length region, 250 to 270  $\text{m}\mu$ . It was found that the absorbance could best be explained in terms of  $\text{Tl}^{+++}$  and  $\text{TlOH}^{++}$  absorbing, as no other species present absorbs appreciably in this region. In this case, the absorbance *A* is given by

$$A = \epsilon_{\text{Tl}}(\text{Tl}^{+++}) + \epsilon_{\text{OH}}(\text{TlOH}^{++}) \quad (3)$$

(7) H. McConnell and N. Davidson, *THIS JOURNAL*, **71**, 3845 (1949).

(1) R. J. Prestwood and A. C. Wahl, *THIS JOURNAL*, **71**, 3137 (1949).

(2) M. S. Sherrill and A. J. Haas, Jr., *ibid.*, **58**, 952 (1936).

(3) A. A. Noyes and C. S. Garner, *ibid.*, **58**, 1268 (1936).

(4) D. Peschanski, *Compt. rend.*, **238**, 2077 (1954).

(5) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(6) C. Biedermann, *Arkiv Kemi*, **5**, 441 (1953).

where  $\epsilon_{Tl}$  and  $\epsilon_{OH}$  are the molar absorptivities of  $Tl^{+++}$  and  $TlOH^{++}$ , respectively. From Biedermann's values for the hydrolysis constants, the equilibrium concentrations ( $Tl^{+++}$ ) and ( $TlOH^{++}$ ) could be calculated. If eq. 3 is divided by ( $Tl^{+++}$ ), the function  $A/(Tl^{+++})$  results.

$$\frac{A}{(Tl^{+++})} = \epsilon_{Tl} + \epsilon_{OH} \frac{(TlOH^{++})}{(Tl^{+++})} \quad (4)$$

A plot of this function *versus*  $(TlOH^{++})/(Tl^{+++})$  at a given wave length should yield a straight line whose intercept and slope are, respectively, equal to the molar absorptivities of the thallium(III) and monohydroxythallium(III) ions at this wave length. Good straight lines resulted from these plots, and values of  $\epsilon_{Tl}$  and  $\epsilon_{OH}$  obtained in this manner are given in columns 2 and 3 of Table I.

TABLE I  
MOLAR ABSORPTIVITIES OF VARIOUS IONIC SPECIES

Wave length, m $\mu$	$\epsilon_{Tl^{+++}}$	$\epsilon_{TlOH^{++}}$	$\epsilon_{NO_3^-}$	$\epsilon_{TlNO_3^{++}}$
270.0	4.3	159	2.4	216
267.5	4.9	182	2.1 <sup>a</sup>	252
265.0	5.6	207	1.9	333
262.5	6.3	239	1.8 <sup>a</sup>	381
260.0	7.5	270	1.8	478
257.5	8.3	331	1.9 <sup>a</sup>	626
255.0	8.9	387	2.9	..
252.5	10.8	445	..	..
250.0	12.2	513	8.0	..

<sup>a</sup> Interpolated value.

**The Mononitratothallium(III) Ion.**—The analysis of spectrophotometric data to yield formation constants and molar absorptivities may be made in a number of ways. The method of continuous variations as used by Peschanski<sup>4</sup> cannot be considered to be very precise. The familiar method of McConnell and Davidson<sup>8</sup> cannot be used as such unless hydrolysis is neglected. It is not valid to neglect the hydrolysis of thallium(III), as even in solutions with a hydrogen ion concentration of unity, the monohydrolysis product contains approximately 7% of the thallium(III) in the solution. The contribution of the dihydroxythallium(III) ion is, however, negligible. By a rigorous derivation which includes the contribution due to the first hydrolysis product, an expression similar to that of McConnell and Davidson has been derived which is useful for the analysis of spectrophotometric data.

Let  $A$  be the absorbance measured at a given wave length for a solution containing thallium(III) perchlorate, perchloric acid, sodium nitrate and sodium perchlorate against a solution containing the same formal (total) concentrations of sodium nitrate and perchloric acid at the same ionic strength.

$$A = \epsilon_{Tl}(Tl^{+++}) + \epsilon_1(TlNO_3^{++}) + \epsilon_{OH}(TlOH^{++}) + \epsilon_N(NO_3^-) - \epsilon_N x \quad (5)$$

where  $\epsilon_{Tl}$ ,  $\epsilon_1$ ,  $\epsilon_{OH}$  and  $\epsilon_N$  are the molar absorptivities of  $Tl^{+++}$ ,  $TlNO_3^{++}$ ,  $TlOH^{++}$  and  $NO_3^-$ , respectively, and  $x$  is the formal concentration of sodium nitrate.

$$x = (NO_3^-) + (TlNO_3^{++}) \quad (6)$$

Let  $m$  be the formal concentration of thallium(III) perchlorate; then

$$m = (Tl^{+++}) + (TlNO_3^{++}) + (TlOH^{++}) \quad (7)$$

By introducing equations 6 and 7 into equation 5, the absorbancy becomes

$$A = \epsilon_{Tl}m + \epsilon'(TlNO_3^{++}) + \epsilon''(TlOH^{++}) \quad (8)$$

where

$$\epsilon' = \epsilon_1 - \epsilon_{Tl} - \epsilon_N \text{ and } \epsilon'' = \epsilon_{OH} - \epsilon_{Tl}$$

Let  $A_0$  be the absorbance of a solution without nitrate but otherwise having the same formal concentrations of thallium(III) perchlorate and perchloric acid and the same ionic strength as that for which  $A$  was measured.

$$A_0 = \epsilon_{Tl}(Tl^{+++})_0 + \epsilon_{OH}(TlOH^{++})_0 \quad (9)$$

$$m = (Tl^{+++})_0 + (TlOH^{++})_0 \quad (10)$$

where the subscript "0" refers to the equilibrium concentration of the particular species in this solution. Combining equations 8, 9 and 10

$$A - A_0 = \epsilon'(TlNO_3^{++}) + \epsilon''[(TlOH^{++}) - (TlOH^{++})_0] \quad (11)$$

The equilibrium concentration of  $TlNO_3^{++}$  may be obtained from equation 7 and the mass-action formation constant for this complex,  $K_1 = (TlNO_3^{++})/(Tl^{+++})(NO_3^-)$ .

$$(TlNO_3^{++}) = \frac{K_1(NO_3^-)[m - (TlOH^{++})]}{1 + K_1(NO_3^-)} \quad (12)$$

If two experimental restrictions are imposed, then equation 11 can be obtained in a useful form. With sufficient excess nitrate,  $(TlNO_3^{++}) \ll x$  and  $(NO_3^-) \sim x$ . If the perchloric acid concentration of the solution is sufficiently high, then the contribution to the acidity due to the hydrolysis of thallium(III) may be neglected; *i.e.*,  $(TlOH^{++}) \ll H$ , and  $(H^+) \sim H$ , where  $H$  is the formal concentration of perchloric acid.

Expressions for the equilibrium concentrations,  $(TlOH^{++})$  and  $(TlOH^{++})_0$ , may be obtained from equation 7 or 10, 1 and the definition of  $K_1$ .

$$(TlOH^{++})_0 = \frac{m\kappa_1/H}{(1 + \kappa_1/H)} \quad (13)$$

$$(TlOH^{++}) = \frac{m\kappa_1/H}{(1 + \kappa_1/H + K_1x)} = \frac{(1 + \kappa_1/H)}{(1 + \kappa_1/H + K_1x)} (TlOH^{++})_0 \quad (14)$$

The desired equation may now be obtained by dividing equation 11 into  $x$  and substituting for the concentrations of  $TlNO_3^{++}$  and  $TlOH^{++}$  those given by equations 12 and 14.

$$\frac{x}{A - A_0} = \frac{(1 + \kappa_1/H)}{K_1[\epsilon'm - \epsilon''(TlOH^{++})_0]} + \frac{x}{[\epsilon'm - \epsilon''(TlOH^{++})_0]} \quad (15)$$

A plot of the function  $x/(A - A_0)$  vs.  $x$  should be a straight line with a slope-to-intercept ratio of  $K_1/(1 + \kappa_1/H)$ . This ratio is constant for a given hydrogen ion concentration and a given ionic strength, and is independent of wave length. It varies with ionic strength since  $\kappa_1$  is a function of ionic strength. Equation 15 reduces to the familiar McConnell-Davidson equation if hydrolysis is neglected.

(8) H. McConnell and N. Davidson, *THIS JOURNAL*, **72**, 3164 (1950).

The formation constant  $K_1$  can be obtained from plots of equation 15, provided some measure of  $(1 + \kappa_1/H)$  is available. It can easily be shown that  $(1 + \kappa_1/H)$  can be estimated from the molar absorptivities of  $\text{Tl}^{+++}$  and  $\text{TlOH}^{++}$  and the absorbance  $A_0$  of solutions without nitrate. If an expression for  $\kappa_1/H$  is obtained by eliminating  $(\text{Tl}^{+++})_0$  and  $(\text{TlOH}^{++})$  from equations 9, 10 and 13, then

$$\left(1 + \frac{\kappa_1}{H}\right) = \frac{\epsilon_{\text{OH}} - \epsilon_{\text{Tl}}}{\epsilon_{\text{OH}} - A_0/m} \quad (16)$$

The absorbance  $A$  for four series of solutions was measured at intervals over the wave length region 256 to 270  $\mu$ . Each series of six solutions had a different ionic strength and contained  $\text{Tl}(\text{ClO}_4)_3$ ,  $\text{HClO}_4$ ,  $\text{NaClO}_4$  and varying amounts of  $\text{NaNO}_3$ . The compositions of these four series of solutions are given in Table II. The absorbance  $A_0$  for similar solutions but *sans* nitrate also was measured.

From the appropriate value of  $A_0$  and the values of  $\epsilon_{\text{Tl}}$  and  $\epsilon_{\text{OH}}$  previously obtained, the function  $(1 + \kappa_1/H)$  has been calculated at several wave lengths for each of the four series of solutions investigated. These data, together with the standard deviation for each series, are given in Table III.

Two examples of plots of equation 15 are given in Fig. 1 for Series D ( $\mu = 3.00$ ) at  $\lambda = 256 \mu$

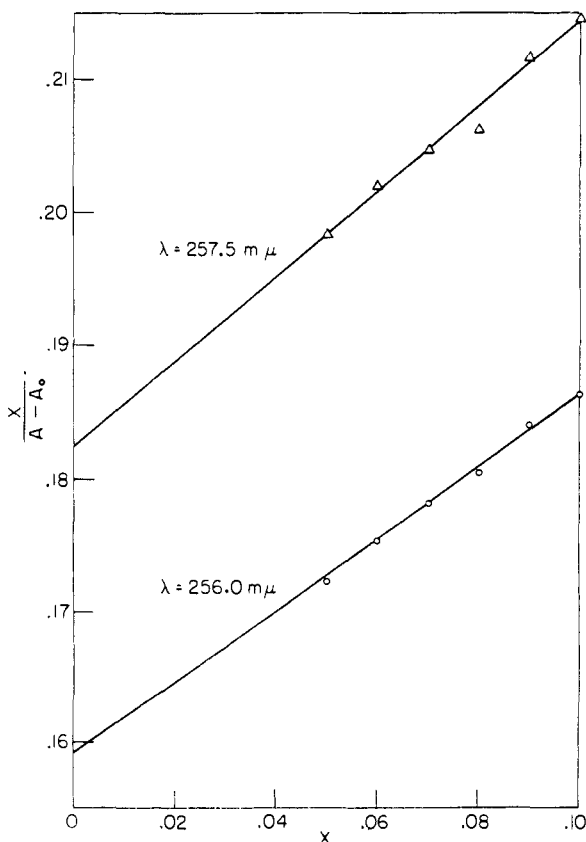


Fig. 1.—Plots of  $x/(A - A_0)$  vs.  $x$  for  $\lambda = 256.0 \mu$  and  $\lambda = 257.5 \mu$  for solutions at  $\mu = 3.00$ ,  $(\text{H}^+) = 1.022 M$ .

and  $\lambda = 257.5 \mu$ . These and all other plots gave very good straight lines indicating that  $\text{TlNO}_3^{++}$  is the principal nitrate complex species present in

the solutions used in this study. It was felt that this was sufficient confirmation of the combining ratio as determined by Peschanski,<sup>4</sup> so that no additional study was required to establish the identity of the complex species present.

TABLE II

FORMATION CONSTANTS FOR THE MONONITRATOTHALLIUM-(III) COMPLEX AT 22° AND AT VARIOUS IONIC STRENGTHS

Wave length, $\mu$	Series A <sup>a</sup>		Series B <sup>b</sup>		Series C <sup>c</sup>		Series D <sup>d</sup>	
	Slope <sup>e</sup>	$K_1$	Slope <sup>e</sup>	$K_1$	Slope <sup>e</sup>	$K_1$	Slope <sup>e</sup>	$K_1$
256.0	...	..	0.286	4.75	0.293	2.76	0.280	1.90
257.5	...	..	.320	4.72	.325	2.75	.321	1.89
260.0	0.442	8.57	.423	4.86	.413	2.90	.450	2.11
262.5	.543	8.78	.552	4.46	.519	2.99	.558	2.07
265.0	.642	7.98	.603	4.57	.610	2.81	.638	1.84
267.5	.793	8.82	.85	5.02	.79	3.00	.91	2.23
270.0	1.01	8.31	.97	4.62	.91	2.68	1.03	2.19
275.0	1.35	7.62	...	..	...	..	...	..
280.0	1.76	7.86	...	..	...	..	...	..
Av.	8.28 ± 0.47		4.72 ± 0.19		2.84 ± 0.12		2.03 ± 0.16	

<sup>a</sup>  $\text{Tl}(\text{ClO}_4)_3 = 0.00511 F$ ;  $\text{HClO}_4 = 0.436 F$ ;  $\text{NaNO}_3, 0.050$  to  $0.100 F$ ;  $\mu = 0.567$ . <sup>b</sup>  $\text{Tl}(\text{ClO}_4)_3 = 0.00524 F$ ;  $\text{HClO}_4 = 1.022 F$ ;  $\text{NaNO}_3, 0.050$  to  $0.100 F$ ;  $\mu = 1.15$ . <sup>c</sup>  $\text{Tl}(\text{ClO}_4)_3 = 0.00524 F$ ;  $\text{HClO}_4 = 1.022 F$ ;  $\text{NaNO}_3, 0.050$  to  $0.100 F$ ;  $\mu = 2.00$ . <sup>d</sup>  $\text{Tl}(\text{ClO}_4)_3 = 0.00524 F$ ;  $\text{HClO}_4 = 1.022 F$ ;  $\text{NaNO}_3, 0.050$  to  $0.100 F$ ;  $\mu = 3.00$ . <sup>e</sup> Slope of plots of equation 15.

TABLE III

ESTIMATES OF THE FUNCTION  $(1 + \kappa_1/H)$  AND OF THE HYDROLYSIS CONSTANT  $\kappa_1$  AT 22° AND AT VARIOUS IONIC STRENGTHS

$\mu$	( $\text{HClO}_4$ ) wt./l.	No. of measurements	$(1 + \kappa_1/H)$	Stand. dev.	$\kappa_1$ , mole/l.
0.567	0.436	5	1.153	0.002	0.067
1.15	1.022	6	1.083	.004	.085
2.00	1.022	6	1.074	.003	.076
3.00	1.022	6	1.073	.002	.075

From plots like Fig. 1 and the average values of  $(1 + \kappa_1/H)$ ,  $K_1$  was calculated at each of several wave lengths for the four series of solutions. These data together with the average values of  $K_1$  and their standard deviations are given in Table II.

Values for the molar absorptivity of  $\text{TlNO}_3^{++}$  were obtained from slopes of the plots of equation 15 (tabulated in Table II) and other data according to equation 17.

$$\epsilon_1 = \frac{1}{m(\text{slope})} + \frac{(\epsilon_{\text{OH}} - \epsilon_{\text{Tl}}) \kappa_1/H}{(1 + \kappa_1/H)} + \epsilon_{\text{Tl}} + \epsilon_{\text{N}} \quad (17)$$

Of the terms in equation 17 only values for the molar absorptivity of nitrate ion,  $\epsilon_{\text{N}}$ , have not been obtained previously. These were calculated from

TABLE IV

COMPARISON OF VALUES OF  $K$  FROM PLOTS OF THE EXTENDED DEBYE-HÜCKEL EQUATION USING VARIOUS VALUES OF  $A$

$\mu$	$\log K_1$	$F_{A=1}$	$K_{A=1}^a$	$F_{A=1.2}$	$F_{A=1.5}$	$F_{A=2}$
0.567	0.918	2.218	165	2.118	1.988	1.827
1.15	.673	2.243	175	2.094	1.921	1.706
2.00	.453	2.229	169	2.044	1.826	1.571
3.00	.308	2.229	169	2.011	1.768	1.484
		$K$	$170 \pm 4$	$\sim 150^b$	$\sim 115^b$	$\sim 100^b$

<sup>a</sup> Values obtained as antilog  $(F_{A=1})$ . <sup>b</sup> Values obtained by extrapolation of curves to  $\mu = 0$ .

TABLE V  
 ASSOCIATION CONSTANTS OF SOME COMPLEX NITRATES

Ion	$K_1$ , l./mole	Temp., °C.	$\mu$	(H <sup>+</sup> ), mole/l.	Method
Ag <sup>+10</sup>	0.67	25	0		Conductivity
Ba <sup>++11</sup>	8.3	18	0		Conductivity
Bi <sup>+3 12</sup>	18	25	0		Solubility
Ca <sup>++11</sup>	1.9	18	0		Conductivity
Cd <sup>++11</sup>	2.5	18	0		Conductivity
Cd <sup>++13</sup>	1.3	25	3		Potentiometric titr.
Ce <sup>+3 14</sup>	1.4	25	0.89	0.89	Ion exchange
Fe <sup>+3 15</sup>	0.3	26	1.0	0.10	Spectrophotometry
Fe <sup>+3 16</sup>	6.8-0.6	20	0.066-0.43		Kinetics
K <sup>+10</sup>	0.63	25	0		Conductivity
Hg <sub>2</sub> <sup>++17</sup>	1.2-1.05 <sup>a</sup>	25	0.50-3.0	0.010	Potentiometry
Hg <sup>++17</sup>	1.28 <sup>b</sup>	25	3.0	0.010	Potentiometry
Pb <sup>++11</sup>	15	18	0		Conductivity
Pb <sup>++18</sup>	2.8 <sup>c</sup>	25	2.0	0.001	Polarography
	3.3	25	2.0	0.01	Potentiometry
	1.6	25	2.0		Spectrophotometry
Pb <sup>++19</sup>	14	25	0		Spectrophotometry
Pb <sup>++20</sup>	15.1	25	0		Conductivity
Pu <sup>+4 21</sup>	2.9	25	2.0	2.0	Spectrophotometry
Pu <sup>+4 22</sup>	3.5	25	1.0	1.0	Potentiometry
Sr <sup>++11</sup>	6.7	18	0		Conductivity
Tl <sup>+10</sup>	2.2	18	0		Conductivity
Tl <sup>+3 4</sup>	1.5	18	3.5	2.5	Spectrophotometry
Tl <sup>+3</sup>	8.3-2.0	22	0.57-3.0	0.44-1.0	Spectrophotometry
Th <sup>+4 23</sup>	2.8 <sup>d</sup>	25	6	0.09	Distribution
Th <sup>+4 24</sup>	4.7	25	0.5	0.5	Distribution
UO <sub>2</sub> <sup>++25</sup>	0.21	25	5.4	2.0	Spectrophotometry
UO <sub>2</sub> <sup>++26</sup>	0.5	25	1.0	0.01	Potentiometry

<sup>a</sup>  $K_2 = (M(\text{NO}_3)_2)/(M)(\text{NO}_3^-)^2 = 0.5$  at  $\mu = 3.0$ .  $K_2 = 1.0$ . <sup>c</sup>  $K_2 \sim 0.8$ ; calculated from  $K_1 = 3.4$ . <sup>d</sup>  $K_2 = 1.9$ .

absorption measurements made during the course of this work or interpolated from the experimental values. A tabulation of all the molar absorptivities obtained in this study is given in Table I.

The magnitude of complexing in acid thallium(III) perchlorate solutions containing nitrate is illustrated in Fig. 2 which shows the fraction of thallium(III) in the various species at an ionic

strength of 3.00  $M$ ,  $(\text{H}^+) = 1.00 M$ , as a function of the free nitrate concentration. The curves were calculated from Biedermann's value of  $\kappa_1$  and the value which we have obtained for  $K_1$  at  $\mu = 3.00$ .

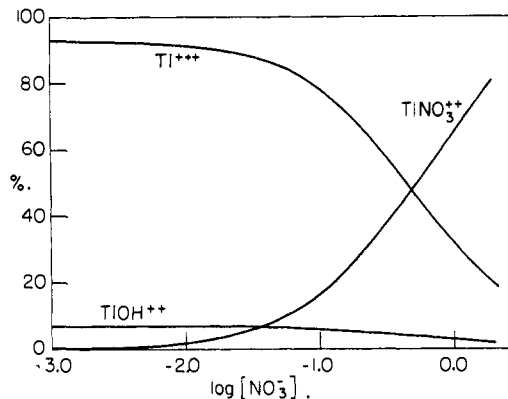


Fig. 2.—Fraction of thallium(III) in its various forms at  $\mu = 3.00$ ,  $(\text{H}^+) = 1.00 M$ , as a function of the free nitrate concentration.

### Discussion

In conclusion, the association constant,  $K_1 = (\text{TlNO}_3^{++})/(\text{Tl}^{+++})(\text{NO}_3^-)$ , has been measured spectrophotometrically at 22° at four values of ionic strength:  $K_1 = 8.3 \pm 0.5$  (standard deviation) at  $\mu = 0.567$ ;  $K_1 = 4.7 \pm 0.2$  at  $\mu = 1.15$ ;  $K_1 = 2.8 \pm 0.1$  at  $\mu = 2.00$ ;  $K_1 = 2.0 \pm 0.2$  at  $\mu = 3.00$ . These values are in good agreement with

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$K_1 = 1.5$  at  $18^\circ$  and  $\mu = 3.5$  obtained by Peschanski.<sup>4</sup>

The thermodynamic formation constant for the mononitratothallium(III) complex  $K$  was estimated using the extended form of the Debye-Hückel equation as an estimate of the activity coefficients.

$$F = \log K_1 - 0.505 \left( \Delta \sum_i z_i^2 \right) \frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} = \log K + B\mu \quad (18)$$

where  $\Delta \sum_i z_i^2 = (2)^2 - (3)^2 - (1)^2 = -6$ .

Following the suggestion of Guggenheim and Schindler,<sup>9</sup>  $A$  was first assumed to be unity and the function,  $F = \log K_1 + (3.03\sqrt{\mu})/(1 + \sqrt{\mu})$  was plotted vs.  $\mu$ . This resulted in a straight horizontal line; i.e.,  $B = 0$ , and led to an estimate of 170 l./mole for  $K$ . Additional values of  $A$  up to 2 were assumed and  $F$  plotted as before. The results obtained from these plots are given in Table IV. The only plot resulting in a straight line was that for  $A = 1$ ; all others were concave upwards. The value of  $K$ ,  $170 \pm 4$  (standard deviation) given for  $A = 1$  is the average value for antilog ( $F_A = 1$ ). All other values of  $K$  were obtained by extrapolating plots of equation 18 to  $\mu = 0$ . It seems reasonable to suspect that  $K$  lies between 100 and 200,

and because of the good agreement for  $A = 1$ , 170 is probably a rather good estimate.

Since values had been obtained for  $(1 + \kappa_1/H)$  at the various ionic strengths, estimates were made for  $\kappa_1$  as a function of  $\mu$ . These estimates are included in Table III. It should be pointed out that Biedermann's work, from which  $(1 + \kappa_1/H)$  was estimated, was done at  $25^\circ$  whereas our study was at  $22^\circ$  and these estimates do not include any correction for this discrepancy.

Table V displays some of the measured values of the association constants of complexes of nitrate with various cations. This table is not intended to be an exhaustive survey or a critical evaluation of nitrate association constants but rather only to indicate certain complexes which have been investigated and how the stability of the thallium(III) complex compares with the others. An extensive discussion of Table V does not appear to be justified since the data are too incomplete and their reliability is too uncertain. It seems evident, however, that a number of nitrate complexes do exist although as a general rule their stability is not very great. It appears that the mononitratothallium(III) ion possesses rather unusual stability.

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## Polarography in Acetonitrile.<sup>1</sup> I. Metal Ions which Have Comparable Polarographic Properties in Acetonitrile and in Water

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Acetonitrile is a much weaker base than water. Consequently inorganic cations generally have lower solvation energies in acetonitrile than in water, except in those cases where there is specific interaction between the cation and acetonitrile. The half-wave potentials of cations which are reversibly reduced should, therefore, be less negative in acetonitrile than in water, and this is indeed the case. The polarography of the alkali and alkaline earth metal ions and ammonium ion in anhydrous acetonitrile has been studied, and the following half-wave potentials (vs. S.C.E.) were determined: Li  $-1.95$ , Na  $-1.85$ , K  $-1.94$ , Rb  $-1.95$ ,  $\text{NH}_4$   $-1.83$ , Ca  $-1.82$ , Sr  $-1.76$  and Ba  $-1.63$  v. The alkali metal ions are reversibly reduced, with the exception of lithium, which shows a slight deviation. The half-wave potentials of cadmium (as the perchlorate) and zinc (as the nitrate) are about 0.3 v. less negative in acetonitrile than in water, the reduction of zinc being reversible. Zinc forms very stable complexes with halide ions in acetonitrile.

Acetonitrile is an interesting solvent for polarographic studies. It is a weaker base<sup>2-8</sup> and a much weaker acid<sup>9,10</sup> than water. Quite generally,

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therefore, cations and especially anions have lower solvation energies in acetonitrile than in water, except in those cases where there is specific interaction with the solvent (as with silver and cuprous copper ions). Thus most cations are reduced at considerably more positive<sup>11</sup> potentials in acetonitrile than in water, and anions which depolarize the dropping mercury electrode anodically do so at more negative potentials in acetonitrile than in water. Moreover, in water as solvent the most negative potential which can be attained at the dropping mercury electrode is approximately  $-2.3$  v. vs. the saturated calomel electrode, whereas in the less acidic solvent acetonitrile the useful potential range can be extended to  $-2.8$  v. (ignoring

(11) The sign convention used is the same as that in Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952.