

The Complex Formation of Thallium(III) with Iodide in Aqueous Solution

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The complex formation of Tl^{3+} with I^- has been studied in a medium of acidity 3 M and ionic strength 4 M by emf and solubility measurements.

The measurements show that Tl^{3+} is reduced to Tl^+ by I^- in a wide range of iodide concentration. For high iodide concentrations the complex TlI_4^- is formed, the stability constant being $\beta_4 = (4.6 \pm 1) \times 10^{38} M^{-4}$. Thus, the complex formation is even stronger than that of the chloride and bromide systems.^{1,2}

As early as 1906, Maitland and Abegg³ found that the thallium(III) iodide system performs a number of interesting and unusual reactions. Kul'ba and Mironov have studied the same system more recently.⁴ Both these teams worked with solutions of varying ionic strengths. The present investigation studies the thallium(III) iodide system at a constant temperature, 25°C, and in the medium that has been used before,² the acidity being 3 M and the ionic strength 4 M. A direct comparison, with the thallium(III) chloride and bromide systems, is then possible. The iodide system is so complicated that all the stability constants cannot be determined by known methods. A more detailed discussion of this point is considered important and is given later.

SURVEY OF REACTIONS

In addition to the strong complex formation that occurs when ions of thallium(III) and iodide meet, there is also a redox reaction in which thallium(I) and iodine are formed. The prevailing conditions determine which of these two reactions predominate. Also, there is usually a precipitation of one or more solid phases. The formation of poly-iodide ions, from I^- and I_2 , must also be taken into consideration.

Notation and definitions

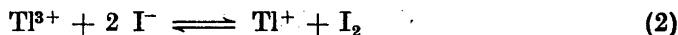
C_M'	Total concentration of Tl(III) originally added.
C_A'	» » » I ⁻ » »
C_M	» » » Tl(III) at equilibrium.
$[M], [P], [A]$	Concentrations of free Tl ³⁺ , Tl ⁺ , and I ⁻ , respectively, at equilibrium.
\bar{n}_M	Complex formation function of the thallium(III) iodide system, defined as

$$\bar{n}_M = \frac{\sum_1^N n\beta_n[A]^n}{1 + \sum_1^N \beta_n[A]^n} \quad (1)$$

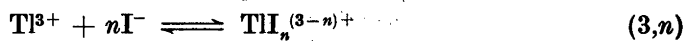
Definitions of the various constants are collected in Table 6, p. 2167.

The redox reaction / complex formation competition

The reactions to be compared are the redox reaction



and the formation of N mononuclear complexes



$n = 1, 2, \dots, N$.

If the iodine concentration is kept constant, the relative preponderance of these reactions is dependent upon the iodide ion concentration, $[A]$, in a rather complex manner. Conversely, for any constant value of $[A]$, the relative preponderance is related to the iodine concentration through the simple relationship: a low iodine concentration promotes the redox reaction and a high iodine concentration promotes the complex formation. In order to study the complex formation, it is clearly necessary to suppress the redox reaction as much as possible. Thus, the situation is now considered in which the iodine concentration is maximum, *i.e.* a saturated iodine solution. The calculations, however, are valid for any constant iodine concentration. The assumption is made that precipitates other than iodine are not formed.

Consider a solution of C_M' M Tl(III) and C_A' M iodide, that is saturated with iodine. The iodide ions may react to form I_3^- , or react according to reactions (2) and (3,1)–(3,N). The formation of Tl(I) complexes is negligible to this investigation.⁵ Hence,

$$C_A' = [A] + [I_3^-] + 2 [P] + \bar{n}_M \cdot C_M \quad (4)$$

$$C_M' = [P] + C_M \quad (5)$$

The constants, K_{tri} and K_{redox} (defined in Table 6), the iodine concentration, $[I_2]_{sat}$, and the varying iodide concentration, $[A]$, are assumed to be known. $[I_3^-]$ and the ratio $[P]/[M]$ may then be calculated:

$$\begin{aligned} [\text{I}_3^-] &= K_{\text{tri}}[\text{I}]_{\text{sat}}[\text{A}] \\ [\text{P}]/[\text{M}] &= K'[\text{A}]^2 \end{aligned} \quad (6)$$

where $K' = K_{\text{redox}}/[\text{I}_2]_{\text{sat}}$.

The following function is now calculated

$$\bar{n}' = \frac{C_{\text{A}'} - [\text{A}] - [\text{I}_3^-]}{C_{\text{M}'}} \quad (7)$$

Eqns. (4) and (5) yield

$$\bar{n}' = \frac{2[\text{P}] + \bar{n}_{\text{M}} C_{\text{M}}}{[\text{P}] + C_{\text{M}}} \quad (8)$$

Finally, eqns. (1) and (6) are introduced

$$\bar{n}' = \frac{\beta_1[\text{A}] + 2\beta_2^*[\text{A}]^2 + \dots + N\beta_N[\text{A}]^N}{1 + \beta_1[\text{A}] + \beta_2^*[\text{A}]^2 + \dots + \beta_N[\text{A}]^N} \quad (9)$$

where $\beta_2^* = K' + \beta_2$.

Referring to eqn. (8), if a value of $[\text{A}]$ is found such that the redox reaction, is suppressed, *i.e.* if $[\text{P}] \ll C_{\text{M}}$, then $\bar{n}' \approx \bar{n}_{\text{M}}$. Alternatively, if $[\text{P}] \gg C_{\text{M}}$, then $\bar{n}' \approx 2$.

From eqn. (9) it may be seen that the function \bar{n}' is mathematically similar to a common complex formation function, \bar{n} , although having a "false" second stability constant, β_2^* . Thus, knowing the behaviour of a common complex formation function, it is possible to outline that of \bar{n}' : For some intermediate value of $[\text{A}]$ the relative abundance of the second complex is at a maximum, *i.e.*, the predominance of the redox reaction is at maximum. For other values of $[\text{A}]$, lower or higher, the other "true" complexes may be dominating; the redox reaction being suppressed by the complex formation.

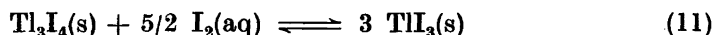
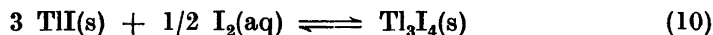
The significance of the iodine concentration is shown by the value of the "false" constant,

$$\beta_2^* = K' + \beta_2 = K_{\text{redox}}/[\text{I}_2]_{\text{sat}} + \beta_2$$

A lower value of $[\text{I}_2]$ causes a higher value of β_2^* and thus a greater predominance of the redox reaction.

Solid phases

Thallium forms three solid iodides,³ *viz.* TlI , Tl_3I_4 , and TlI_3 . Whether or not any precipitate is formed from an aqueous solution is, naturally, dependent upon the total concentrations and upon the solubility products. However, the iodides, when in contact with an aqueous solution, may be transformed into each other according to the reactions



Obviously, this system is governed by the iodine concentration: TII and Tl_3I_4 co-exist at the constant iodine concentration $[\text{I}_2]_1$, which may be regarded as the equilibrium constant of reaction (10). Similarly, Tl_3I_4 and TII_3 co-exist at $[\text{I}_2]_2$, the equilibrium constant of (11). Finally, TII_3 and $\text{I}_2(\text{s})$ co-exist at the iodine concentration $[\text{I}_2]_{\text{sat}}$. Between these limits, only one precipitate is present, TII for iodine concentrations lower than $[\text{I}_2]_1$, Tl_3I_4 between $[\text{I}_2]_1$ and $[\text{I}_2]_2$, and TII_3 between $[\text{I}_2]_2$ and $[\text{I}_2]_{\text{sat}}$. The necessary condition for this pattern is that $[\text{I}_2]_1 < [\text{I}_2]_2 < [\text{I}_2]_{\text{sat}}$.

For the solubility products of the different solid iodides, the following definitions are used: *

$$\text{TII: } K_{s1} = [\text{P}][\text{A}] \quad (12)$$

$$\text{Tl}_3\text{I}_4: K_{s2} = [\text{P}][\text{A}]^{3/4}[\text{I}_3^-]^{1/4} \quad (13)$$

$$\text{TII}_3: K_{s3} = [\text{P}][\text{I}_3^-] \quad (14)$$

From these equations and the definition of the constant K_{tri} , expressions may be derived for the connexions between the solubility products and the equilibrium iodine concentrations, $[\text{I}_2]_1$ and $[\text{I}_2]_2$. Consider a solution having TII and Tl_3I_4 at equilibrium, *i.e.* eqns. (12) and (13) are valid. Then

$$K_{s2} = K_{s1} \cdot K_{\text{tri}}^{1/4} \cdot [\text{I}_2]_1^{1/4} \quad (15)$$

When Tl_3I_4 and TII_3 are at equilibrium, it follows that

$$K_{s2} = \frac{K_{s3}}{K_{\text{tri}}^{1/4} \cdot [\text{I}_2]_2^{1/4}} \quad (16)$$

Eqns. (15) and (16) may be combined to give

$$K_{s1} = \frac{K_{s3}}{K_{\text{tri}} \cdot [\text{I}_2]_2^{1/4} \cdot [\text{I}_2]_1^{1/4}} \quad (17)$$

Eqns. (15) and (16) show that $[\text{I}_2]_1$ and $[\text{I}_2]_2$ are constants, as was stated previously. It is also clear, that if $[\text{I}_2]_1$, $[\text{I}_2]_2$ and one of the solubility products are known, it is possible to calculate the other two solubility products.

MEASUREMENTS

The following constants have been determined experimentally: K_D (distribution coefficient of iodine between carbon tetrachloride and the acid perchlorate medium), K_{tri} , $[\text{I}_2]_{\text{sat}}$, K_{redox} , K_{s3} , and β_4 .

* TII_3 has been subject to much interest because of its tautomerism: it may be regarded as $\text{Tl}^{3+}(\text{I}^-)_3$ but also as $\text{Tl}^+\cdot\text{I}_3^-$. In fact, chrystallographic studies⁶ show it to be isomorphous with $\text{Cs}^+\cdot\text{I}_3^-$, thus favouring the latter formula.

It should be stressed, however, that when studying the solution only, it is unnecessary and actually impossible to judge which formula is the correct one. Thus, the alternative solubility products $K_{s3}' = [\text{M}][\text{A}]^3$ and $K_{s3} = [\text{P}][\text{I}_3^-]$ are connected by the relationship

$$K_{s3}' = K_{s3}/(K_{\text{redox}} \cdot K_{\text{tri}})$$

Evidently, K_{s3}' is a constant as soon as K_{s3} is.

In principle, the same remarks are valid for Tl_3I_4 .

Experimental, general

The iodine used was of analytical grade and resublimed. The hydrogen iodide available contained iodine, which was reduced cathodically in the absence of air. The electrode compartments were separated with a porous plate. The iodine content was reduced considerably, but not completely. For the treatment of other chemicals, see Refs. 1, 2.

All measurement solutions, containing iodide had to be prepared, shaken and analysed with very careful exclusion of oxygen in order to prevent the rapid oxidation of iodide ion to iodine in acid solution. The oxygen was expelled by bubbling carbon dioxide through the solutions. Thence, all operations were performed under a CO_2 atmosphere. The iodide solutions were self-indicative since even traces of iodine gave a yellow colour to the otherwise colourless solutions.

Heterogeneous equilibria were established by shaking the solutions in a thermostat for not less than 20 h. Most equilibria were reached within a few hours.

Determination of K_D , K_{tri} and $[\text{I}_2]_{\text{sat}}$

Method. Small amounts of iodine were dissolved and distributed between carbon tetrachloride and aqueous solutions originally containing C_A' M I^- . The total concentrations of iodine in the organic (C_{org}) and the aqueous (C_{aq}) phases were then determined by thiosulphate titration.

Assuming that I_3^- is the only poly-iodide species formed, the following equation applies:

$$\frac{C_{\text{aq}}}{C_{\text{org}}} = \frac{1}{K_D} + \frac{C_A'}{(K_D/K_{\text{tri}}) + C_{\text{org}}}$$

From a series of measurements, the constants K_D and K_{tri} may be easily calculated.

For the determination of $[\text{I}_2]_{\text{sat}}$, carbon tetrachloride and solutions having $C_A' = 0$ were equilibrated with an excess of solid iodine. C_{org} and C_{aq} were determined as above. In this situation it is clear that $C_{\text{aq}} = [\text{I}_2]_{\text{sat}}$.

Results. The experimental data are given in Table 1. The average values of the constants that were obtained were $K_D = 130.4$, $K_{\text{tri}} = 932 \text{ M}^{-1}$ and $[\text{I}_2]_{\text{sat}} = 0.894 \times 10^{-3} \text{ M}$.

Table 1. Determination of K_D , K_{tri} , and $[\text{I}_2]_{\text{sat}}$.

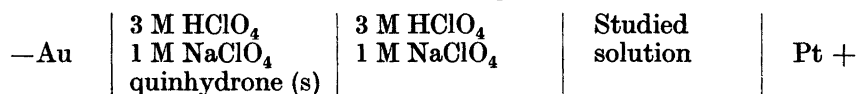
$C_A' \times 10^3$ M	$C_{\text{org}} \times 10^3$ M	$C_{\text{aq}} \times 10^3$ M
0	35.15	0.270
0.974	38.07	0.500
1.948	38.06	0.700
2.922	42.27	0.998
3.896	36.17	1.080
4.87	39.59	1.378
0 ^a	116.2	0.894
0 ^a	116.3	0.894

^a Saturated with iodine.

Note. The solubility of iodine in this medium is lower than that in water and consequently the value of the distribution coefficient is higher. The measured solubility of iodine in CCl_4 , however, is not different from that obtained by other workers.^{4,7}

Emf measurements. Determination of K_{redox} and K_{s3}

Calculations. The emf, E , of the following cell was measured



For the determination of K_{redox} (Table 6), the solution studied first, contained Tl^{3+} and Tl^+ of known concentrations. Using the following eqn.

$$E = E' + \frac{RT}{2F} \ln \frac{[\text{M}]}{[\text{P}]} \quad (18)$$

(*cf.* Ref. 1) the measured values of E are inserted and E' is readily obtained.

Next, C_A' M iodide solutions, saturated with iodine, were studied. The expression for E is now

$$E = E'' + \frac{RT}{2F} \ln \frac{[\text{I}_2]}{[\text{A}]^2} \quad (19)$$

Further,

$$[\text{I}_2] = [\text{I}_2]_{\text{sat}}$$

and $C_A' = [\text{A}] + [\text{I}_3^-] = [\text{A}] (1 + K_{\text{tri}} \cdot [\text{I}_2]_{\text{sat}})$. $[\text{I}_2]$ and $[\text{A}]$ are thus obtainable and the value of E'' is calculated from eqn. (19).

If the two redox systems are at equilibrium with each other, *i.e.* if

$$\frac{[\text{P}] \cdot [\text{I}_2]}{[\text{M}] \cdot [\text{A}]^2} = K_{\text{redox}}$$

the value of E will be the same in eqns. (18) and (19). Thus,

$$E' - E'' = \frac{RT}{2F} \ln K_{\text{redox}} \quad (20)$$

and K_{redox} may be calculated.

From emf measurements of saturated iodine solutions, that contained thallium and iodide, the solubility product K_{s3} of TlI_3 was determined. As has just been noted, a number of reactions may occur in this kind of solutions. However, if $10^{-6} < [\text{A}] < 10^{-4}$ M, the following reaction predominates. (This may be estimated from the values of the constants obtained later; *cf.* p. 2167)



No soluble Tl(III) species are present in appreciable concentrations, and the following equations hold

$$[P] [A] [I_2]_{\text{sat}} = K_{s3}/K_{\text{tri}} \quad (22)$$

$$C_A' = [A] + [I_3^-] + 2[P] + 3 a_{\text{TlI}_3(s)} \quad (23)$$

$$C_M' = [P] + a_{\text{TlI}_3(s)} \quad (24)$$

$a_{\text{TlI}_3(s)}$ is the number of moles of $\text{TlI}_3(s)$ formed per litre of solution.

Now, the function \bar{n}'' , which is similar to \bar{n}' , though valid only for the conditions in this section, is introduced:

$$\bar{n}'' = \frac{C_A' - [A] - [I_3^-]}{C_M'} \quad (25)$$

$[A]$ and $[I_3^-]$ are calculated from the measured value of E , and thus the value of \bar{n}'' is obtained. From eqns. (22)–(25), it may be seen

$$\bar{n}'' = 3 - \frac{K_{s3}}{K_{\text{tri}} \cdot [I_2]_{\text{sat}} \cdot C_M'} \times \frac{1}{[A]} \quad (26)$$

Thus, straight lines are found, when \bar{n}'' is plotted against $1/[A]$ for a number of constant values of C_M' . From the slopes of the lines, K_{s3} is calculated, K_{tri} and $[I_2]_{\text{sat}}$ being known.

Experimental. In the right-hand half-cell of the element, two platinized platinum foils served as electrodes. The air was excluded from the electrode vessel by carbon dioxide, which, when saturated iodine solutions were being studied, was also saturated with iodine vapor. Bottles containing the solutions that had been equilibrated by shaking, were connected to the system, whereupon the gas stream was used as a convenient means to transfer the solution into the electrode vessel. The volume of the solution was usually 20 ml. During the measurements, stirring was performed magnetically. The quinhydrone reference electrode was of the type described previously.¹ The half-cells, and the iodine saturator, were thermostatted at 25°C.

With only thallium present, the electrode behaved as was found before at 20°C.¹ The different electrode foils gave the same potential. The emfs were reproducible to within 1 mV.

Within the range of $[A]$ studied, the iodine/iodide electrode behaved very well, the emf reaching a constant value almost instantaneously, and then remaining constant for hours. The different electrode foils gave the same potential. These emfs were reproducible to within 0.3 mV.

Table 2. The Tl(III)/Tl(I) electrode.

$[P] \times 10^3$ M	$[M] \times 10^3$ M	E mV	E' mV
0.313	2.06	630.0	605.8
0.313	5.15	641.3	605.3
0.313	10.30	649.2	604.3
1.044	2.06	615.2	606.5
1.044	5.15	626.8	606.3
1.044	10.30	635.3	605.9

Results. The result of the study of the Tl(III)/Tl(I) electrode is given in Table 2. As before,¹ there is a slight difference in E' between the series with different $[P]$ (0.3×10^{-3} and 1.0×10^{-3} M), E' being constant, however for each $[P]$.

Table 3. The I_2/I^- electrode in solutions saturated with iodine ($[I_2]_{\text{sat}} = 0.894 \times 10^{-3}$ M).

$C_A' \times 10^3$ M	$[A] \times 10^3$ M	$-E$ mV	$-E''$ mV
0.974	0.531	40.7	144.2
1.948	1.063	58.3	144.0
4.87	2.655	82.0	144.1
9.74	5.31	99.5	143.8
19.48	10.63	117.3	143.8
48.7	26.55	141.2	144.2

Table 3 shows the result of the measurements using the iodine/iodide electrode. The value of E'' is constant within the range of $[A]$ studied, $(0.5-25) \times 10^{-3}$ M. It was found later, however, that when $[A] < 10^{-6}$ M, the concentrations of iodine and iodide were too low to give a proper function of the electrode. Also, when $[A] > 50 \times 10^{-3}$ M, an unusual behaviour of the electrode was observed, as the obtained value of E'' increased more and more rapidly with increasing $[A]$. The explanation probably lies in an incorrect estimation of $[A]$ due to the formation of poly-iodides other than I_3^- .

From the average values, $E' = 606$ mV and $E'' = -144$ mV, the value of the constant $K_{\text{redox}} = 2.2 \times 10^{25}$ was calculated (eqn. 20).

For the determination of K_{s3} , three values of C_M' were chosen, *viz.* 0.003, 0.006, and 0.025 M. C_A' was then chosen in order to give values of $[A]$ in the required range. The result is shown in Table 4. The values obtained for \bar{n}'' are plotted against $1/[A]$ for the three constant values of C_M' (Fig. 1). The values of K_{s3} , calculated from the slopes of these straight lines, are also given

Table 4. Determination of K_{s3} .

$C_M' \times 10^3$ M	$C_A' \times 10^3$ M	E mV	$[A]$ M	\bar{n}''	$K_{s3} \times 10^8$ M ²
3.00	6.97	63.0	9.47×10^{-6}	2.32	1.8
3.00	7.79	45.0	1.91×10^{-5}	2.58	
3.00	8.77	13.5	6.50×10^{-5}	2.88	
3.00	9.74	-34.1	4.14×10^{-4}	2.99	
6.00	15.58	63.5	9.29×10^{-6}	2.59	1.9
6.00	17.53	27.6	3.76×10^{-5}	2.91	
6.00	19.48	-52.6	8.52×10^{-4}	2.99	
25.00	73.05	63.5	9.29×10^{-6}	2.92	1.6
25.00	75.00	-16.5	2.091×10^{-4}	2.98	
25.00	77.72	-64.6	1.359×10^{-3}	3.01	

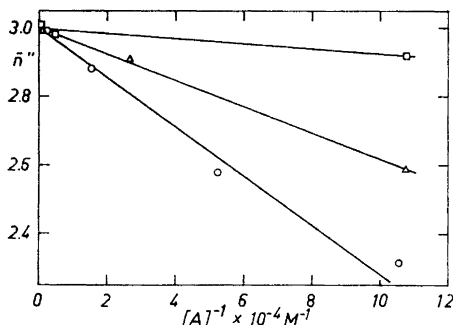


Fig. 1. Determination of K_{s3} . \bar{n}'' as a function of $1/[A]$ for $C_M' = 0.003$ (circles), 0.006 (triangles), and 0.025 M (squares).

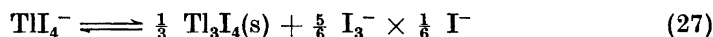
in Table 4. The average value $K_{s3} = 1.8 \times 10^{-8}$, was assumed. The constancy of K_{s3} in conjunction with the fact that the lines meet at a value of 3 (cf. eqn. (26)), confirms that the precipitate formed was TlI_3 .

Using eqns. (16) and (17), it is now possible to calculate K_{s1} and K_{s2} . As proper values of $[I_2]_1$ and $[I_2]_2$, the corresponding concentrations in carbon tetrachloride, (as determined by Kul'ba-Mironov⁴), divided by our value of K_D were used, i.e. $[I_2]_1 = 5.0 \times 10^{-6}$ M and $[I_2]_2 = 2.2 \times 10^{-4}$ M. The calculated solubility products are $K_{s1} = 1.7 \times 10^{-7}$ and $K_{s2} = 6.9 \times 10^{-7}$; the former is in good agreement with the value $K_{s1} = 1.9 \times 10^{-7}$ obtained by Nilsson⁵ using a similar medium.

Determination of β_4

As was mentioned in the previous section, the iodine/iodide electrode was unsuitable at high iodide and iodine concentrations. Therefore, another method for studying solutions having a high iodide concentration was chosen, viz. solubility measurements of Tl_3I_4 as the solid phase. This proved to be a convenient method for the determination of the stability constant β_4 of the final (fourth) thallium(III) iodide complex.

Calculations. It is assumed that TlI_4^- is the final complex and that practically all Tl(III) is present in this form for the high values of $[A]$ considered here. When C_M' M Tl(III) is mixed with C_A' M iodide, a part of the Tl(III) is reduced, however, and, under the proper conditions (see below) $Tl_3I_4(s)$ and I_3^- are formed:



The amount of soluble Tl(I) species present is negligible,⁵ and so is the concentration of free iodine. The total thallium concentration at equilibrium, C_M , is measured and is put equal to $[MA_4]$. Then, according to reaction (27)

$$[I_3^-] = \frac{5}{6}(C_M' - C_M) \quad (28)$$

and

$$[A] = C_A' - 4 C_M' + \frac{1}{6} (C_M' - C_M) \quad (29)$$

Thus it is possible to determine the value of the expression

$$K'' = \frac{[MA_4]}{[I_3^-]^{1/6} \cdot [A]^{1/6}}$$

From the definitions of the constants, the connexion between β_4 and K'' may be derived

$$\beta_4 = K'' \frac{K_{\text{tri}} \cdot K_{\text{redox}}}{K_{s_2}} \quad (30)$$

which also shows that K'' is a constant.

Experimental. The total thallium content in the solutions studied was determined by adding an excess of sodium sulphite, taking the thallium (I) iodide thereby formed on a glass filter crucible, washing the precipitate with dilute sodium iodide and a small portion of water, drying to constant weight and weighing as TII. The volume of solutions used was such that about 0.1 g of precipitate resulted. Before analysis, the solutions were separated from the Tl_3I_4 precipitates by filtering through glass filters. Analysis of this precipitate by weighing before and after heating showed a composition close to Tl_3I_4 .

The method of analysis using reduction by sulphite was tested, with known amounts of Tl(III), to which sulphite and about 1 M iodide were added to make the conditions similar to those of the solutions studied. The obtained amounts of TII agreed with the expected amounts to better than 1 %.

Table 5. Determination of β_4 .

$C_M' \times 10^3$ M	C_A' M	$[I_3^-]_0 \times 10^3$ M	$C_M \times 10^3$ M	$[I_3^-] \times 10^3$ M	$[A]$ M	K''
25.00	0.486	0.29	18.10	6.04	0.387	1.50
25.00	0.728	0.44	18.55	5.82	0.629	1.46
25.00	0.972	0.58	19.39	5.26	0.873	1.57
25.00	1.215	0.73	19.58	5.25	1.116	1.53
50.00	0.728	0.78	36.15	12.32	0.530	1.57
50.00	0.971	1.04	37.13	11.77	0.773	1.57
50.00	1.213	1.30	38.01	11.29	1.015	1.59

Results. Two series of measurements, having $C_M' = 0.025$ and 0.050 M, were performed. C_A' ranged from 0.5 to 1.2 M. The obtained values of C_M are given in Table 5 alongside the values of $[I_3^-]$ and $[A]$ calculated using eqns. (28) and (29). A correction, $[I_3^-]_0$ of the tri-iodide concentration had to be introduced, since the iodide stock solutions, made from hydrogen iodide, were not completely free from I_3^- . Table 5 also shows the values obtained for K'' . The constancy is good, thus confirming that the assumption of TlI_4^- as the prevailing complex was correct: If there were more than four iodides per thallium, K'' would vary with $[A]$, if the complexes were polynuclear, K'' would vary with C_M' . From the average value $K'' = 1.54$, $\beta_4 = 4.6 \times 10^{35}$ is calculated.

From the value of K_{tri} it is now possible to calculate the iodine concentrations of the solutions, $[A]$ and $[I_3^-]$ being known. The values of $[I_2]$ range from

5.1×10^{-6} M to 18×10^{-6} M, *i.e.* between $[I_2]_1$ and $[I_2]_2$, and thus in the range of existence of $Tl_3I_4(s)$. Moreover, the iodine concentrations are low enough to be neglected in eqns. (28) and (29).

CONCLUSIONS

The investigation of systems, having several species in dynamic equilibrium with each other, are subject to certain limitations. It is a general rule of practical complex chemistry that the stability of a complex cannot be determined unless there exists a range of ligand concentration, where the complex is present in a concentration that is not negligible compared to the total concentration of central ion. This lower limit of concentration depends upon the method used for the study of the system.

With particular reference to thallium(III) iodides, the amounts of complexes ought to be compared to the total amount of thallium. This is clear, since we have no means of determining a small amount of thallium (III) in equilibrium with a much larger amount of thallium(I).

For the methods employed in this investigation, the lower limit of complex concentration would be approximately 10 %. The complexes to be considered are the three lower ones, β_4 alone having been determined. Since β_2^* and β_4 are known, it is possible to estimate, using eqn. (9), the values of $\beta_1 - \beta_3$ that would render these complexes detectable, *i.e.* give a maximum relative abundance of each complex ≥ 10 %. The values are $\beta_1 \geq 10^{13.5}$, $\beta_2 \geq 10^{27.5}$ and $\beta_3 \geq 10^{31.5}$.

It is hazardous to make any estimation of the true values of these constants. However, from the values of β_4 it may be judged that the strength of the fourth halide complex increases by approximately the same factor during the change from bromide to iodide as from chloride to bromide. It is reasonable to assume that this also applies to the lower complexes. Thus, the following approximate probable values are suggested: $\beta_1 \approx 10^{11.5}$, $\beta_2 \approx 10^{21}$ and $\beta_3 \approx 10^{29.5}$ (*cf.* also the values estimated by Kul'ba-Mironov,⁴ discussed below). The conclusion is thus reached that the experimental determination of these constants is impossible, without remarkable refinements of the available methods.

From eqn. (9), the function \bar{n}' is now calculated, $\beta_1 - \beta_3$ being neglected (Fig. 2 a). A rough estimation of the true complex formation function, \bar{n}_M

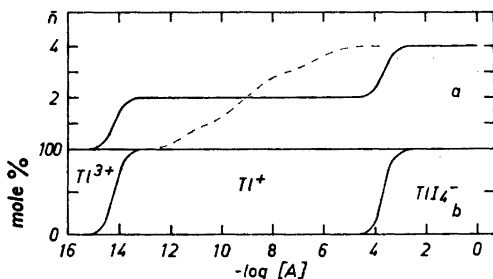


Fig. 2 (a). Fulldrawn curve: \bar{n}' (p. 2158) as a function of $\log [A]$, calculated from the experimentally determined values of K_{redox} and β_4 . Dashed curve: Probable course of \bar{n}_M for the thallium(III) iodide system. (b). The distribution of thallium between different species in a saturated iodine solution.

(calculated from the probable constant values given above), is also shown. The disastrous effect of the redox reaction is evident. Fig. 2 b shows the distribution of thallium between the three possible species, Tl^{3+} , Tl^+ , and TlI_4^- , in a saturated iodine solution.

Reaction (21) on p. 2161 deserves some consideration. The approximations used are valid, except for the highest values of $[A]$, where the concentration of TlI_4^- amounts to a few percent of C_M' . However, the errors caused are smaller than the experimental errors, and no corrections have been applied. As was concluded previously, no other thallium species are present in the solutions.

The comparison with the chloride and bromide systems cannot be very detailed, since β_4 alone has been determined. The high value of β_4 , however, lends further support to the opinion, that the heavier halide ions have a very strong affinity to Tl^{3+} , that increases in the order $Cl^- < Br^- < I^-$. It may also be concluded that no more than four complexes are formed in any of the systems. No polynuclear tendencies have been detected.

The values of β_4 and the other constants obtained by Maitland-Abegg³ and Kul'ba-Mironov⁴ differ a little from those reported in this paper presumably due mainly to the differences of medium. The values of K_{redox} , in particular, obtained by these authors from literature data on standard potentials at the ionic strength zero, are definitely lower than the value given here from direct measurements in the medium used. Consequently (*cf.* eqn. 30) lower values of β_4 are obtained (Table 6). The values of $\beta_1 - \beta_3$ reported by Kul'ba-Mironov are not determined experimentally but based on a theory concerning the ratios between the stability constants. Thus, these values have a reliability comparable to that of the roughly estimated values discussed on p. 2166.

Table 6. Summary of experimental data (with estimated maximum errors).

Quantity	Definition	Experimental value	Remarks
K_D	$[I_2]_{org}/[I_2]$	130.4	
K_{tri}	$[I_3^-]/([I_2][A])$	$932 \pm 5 M^{-1}$	
$[I_2]_{sat}$	Soln. saturated with I_2	$(0.894 \pm 0.005) \times 10^{-3} M$	
$[I_2]_1$	Equil. $TlI(s) - Tl_3I_4(s)$	$5.0 \times 10^{-6} M$	Cf. p. 2164 →
$[I_2]_2$	Equil. $Tl_3I_4(s) - TlI_3(s)$	$2.2 \times 10^{-4} M$	
K_{redox}	$([P][I_2])/([M][A]^2)$	$(2.2 \pm 0.2) \times 10^{25} M^{-1}$	
K_{s1}	$[P][A]$	$1.7 \times 10^{-7} M^2$	
K_{s2}	$[P][A]^2/[I_3^-]^{1/2}$	$6.9 \times 10^{-7} M^2$	
K_{s3}	$[P][I_3^-]$	$(1.8 \pm 0.2) \times 10^{-8} M^2$	
β_n	$[MA_n]/([M][A]^n)$		
β_4		$(4.6 \pm 1) \times 10^{35} M^{-4}$	Present work Ref. 3. Ref. 4.
β_4		$10^{30,3}$	
β_4		$10^{32,15}$	

In general, however, the three investigations give the same picture of the system: a strong complex formation subjected to severe interference from the redox reaction.

In addition to the investigations mentioned, Busev and Tiptsova⁸ give a more qualitative description of the system, which is in accord with the results in this paper.

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