Calculation of Equilibrium Constants for Some Thallium(III) Species in Aqueous Solutions Containing Different Ionic Media

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Using the specific interaction theory, the equilibrium constants for the species $\text{TiCl}_{4}^{n-} (n = 1, 2, 3, 4)$, $\text{TiOH}^{2-}$ and $\text{TiO}_{2} (s)$ in aqueous solutions containing different ionic media have been calculated. The calculated constants have been compared to the appropriate experimental values. On this basis, it is possible to predict which of the constants published in the literature are correct and which are erroneous.

In solution chemistry, a knowledge of the stability constants for the species formed is often of crucial importance. The majority of the known stability constants have been determined using the so-called ionic medium method, where the pure solvent is replaced by an electrolyte solution at a concentration far exceeding that of all the other solutes. The high electrolyte concentration (e.g., 3 M $\text{NaClO}_{4}$) is employed mainly in order to decrease the variation of the activity coefficients of the reacting species. The natural consequence is that the values of the stability constants are often strongly influenced by the type and concentration of the chosen ionic medium. Fortunately, the stability constants can in many cases be recalculated from one ionic medium to another using the specific interaction theory of Brønsted. According to this theory, the activity coefficient, $\gamma_i$, of an ion of charge $z_i$ in a solution of ionic strength, $I$, (in terms of the molality, $m$) can be expressed by the equation:

$$\log \gamma_i = -z_i^2 \cdot D + \sum_k \varepsilon(i,k,I) \cdot m_k$$  \hspace{1cm} (1)

where $D = \frac{0.5107 \cdot \sqrt{T}}{1+1.5\sqrt{T}}$

†Deceased.

Thallium(III) chloride complexes

Using the measurements of the oxidation potentials of mixtures of thalic and thallous perchlorate in perchloric acid solutions with varying ionic strength, the interaction coefficient $\varepsilon(\text{Ti}^{3+}, \text{ClO}_{4}^{-}) = 0.65(6)$ was obtained in a manner similar to that for Fe$^{3+}$. This result is quite reason-
able, since $\epsilon(\text{Fe}^{3+}, \text{ClO}_4^-)$ has been estimated to be 0.56 and $\epsilon(\text{Ga}^{3+}, \text{ClO}_4^-)$ is equal to approximately 0.65. Next, the coefficients $\epsilon(\text{TICl}_2^{1-}, \text{ClO}_4^-)$ were calculated from the equilibrium constants of Woods et al. for the formation of the TICl$_2^{-n}$ complexes in 0.5 M HClO$_4$ and in 3 M HClO$_4$ at 25°C in the following way. For the reaction Ti$^{3+} + \text{Cl}^- \leftrightarrow \text{TICl}^2{+}$, the thermodynamic equilibrium constant $x_i$ can be expressed as

$$x_i = K_i \cdot \frac{\gamma(\text{TICl}^2{+})}{\gamma(\text{Ti}^{3+}) \cdot \gamma(\text{Cl}^-)}$$

where $K_i$ represents the stability constant based on concentrations. According to eqn. (1), the activity coefficients are:

$$\log \gamma(\text{TICl}^2{+}) = -2D + \epsilon(\text{TICl}^2{+}, \text{ClO}_4^-) \cdot \frac{[\text{ClO}_4^-]}{[\text{Cl}^-]}; \quad (3a)$$

$$\log \gamma(\text{Ti}^{3+}) = -3D + \epsilon(\text{Ti}^{3+}, \text{ClO}_4^-) \cdot \frac{[\text{ClO}_4^-]}{[\text{Cl}^-]}; \quad (3b)$$

$$\log \gamma(\text{Cl}^-) = -1D + \epsilon(\text{Cl}^-, \text{H}^+) \cdot [\text{H}^+]; \quad (3c)$$

where $D = 0.2509$ for $I = 3.47$ m and $D = 0.1752$ for $I = 0.51$ m; $\epsilon(\text{Ti}^{3+}, \text{ClO}_4^-) = 0.65$, as stated above and $\epsilon(\text{Cl}^-, \text{H}^+) = 0.12$ calculated from the activity factor of HCl $\gamma_{\text{H}^+, \text{Cl}^-}$ in 2 M HCl according to eqn. (1). Now log $x_i$ for the 3 M (= 3.47 m) solution of HClO$_4$ can be written as

$$\log x_i = 7.10 + 6 \cdot 0.2509 + \epsilon(\text{TICl}^2{+}, \text{ClO}_4^-) \cdot \frac{3.47 - 0.656 \cdot 3.47 - 0.12 \cdot 3.47}{3.47} \cdot \epsilon(\text{TICl}^2{+}, \text{ClO}_4^-) + 5.98,$$

where log $K_i = 7.10 \text{ mol} \cdot \text{kg}^{-1}$ was taken from Ref. 5. Similarly, for the 0.5 M HClO$_4$

$$\log x_i = 0.51 \cdot \epsilon(\text{TICl}^2{+}, \text{ClO}_4^-) + 7.36. \quad (5)$$

Subtraction of eqn. (5) from eqn. (4) gives

$$\epsilon(\text{TICl}^2{+}, \text{ClO}_4^-) = 0.486.$$

The remaining coefficients were calculated in the same way giving the following results:

$$\epsilon(\text{TICl}_2^{1-}, \text{ClO}_4^-) = 0.38 \quad (9)$$

$$\epsilon(\text{TICl}_2^{1-}, \text{H}^+) = 0.22 \quad (4).$$

The stability constants for the TICl$_2^{1-}$ complexes in three different ionic media were now obtained according to eqn. (2) and are presented in Table 1 together with the experimental results. The additional assumptions required in order to obtain the values of some residual coefficients, were:

(a) $\epsilon(\text{Na}^+, \text{TICl}_2^{1-}) - \epsilon(\text{H}^+, \text{TICl}_2^{1-}) = \epsilon(\text{Na}^+, \text{Cl}^-) - \epsilon(\text{H}^+, \text{Cl}^-)$ leading to $\epsilon(\text{Na}^+, \text{TICl}_2^{1-}) = 0.13 \quad (4)$;

(b) $\epsilon(\text{Li}^+, \text{TICl}_2^{1-}) = \epsilon(\text{H}^+, \text{TICl}_2^{1-}) = 0.22$;

(c) $\epsilon(\text{Li}^+, \text{Cl}^-) = \epsilon(\text{H}^+, \text{Cl}^-) = 0.12$.

The activity coefficient for the uncharged species, TICl$_2$, was assumed to be

$$\log \gamma(\text{TICl}) = \epsilon(\text{TICl}) \cdot I$$

**Table 1.** Calculated and experimental stability constants in different ionic media at 25°C for the TICl$_2^{1-}$ complexes, given as:

$$\beta_n = [\text{TICl}_2^{1-}] / [\text{Ti}^{3+}] \cdot [\text{Cl}^-]^{-n}$$

<table>
<thead>
<tr>
<th></th>
<th>0.5 M HClO$_4$ (Woods$^5$)</th>
<th>3 M HClO$_4$ (Woods$^5$)</th>
<th>3 M HClO$_4$ (Kulba$^7$)</th>
<th>3 M HClO$_4$ + 1 M NaClO$_4$ (Ahland$^8$)</th>
<th>3 M NaClO$_4$ (Glaser$^9$)</th>
<th>calc. (Biedermann$^{10}$)</th>
<th>calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $\beta_1$</td>
<td>6.72</td>
<td>7.16</td>
<td>7.13</td>
<td>7.48(±0.05)</td>
<td>7.4</td>
<td>7.04(±0.01)</td>
<td>6.9</td>
</tr>
<tr>
<td>log $\beta_2$</td>
<td>11.82</td>
<td>12.60</td>
<td>12.55</td>
<td>13.26(±0.05)</td>
<td>13.28(±0.13)</td>
<td>13.1</td>
<td>12.32(±0.01)</td>
</tr>
<tr>
<td>log $\beta_3$</td>
<td>14.50</td>
<td>16.15</td>
<td>16.0</td>
<td>16.65(±0.05)</td>
<td>16.56(±0.07)</td>
<td>16.9</td>
<td>15.30(±0.02)</td>
</tr>
<tr>
<td>log $\beta_4$</td>
<td>16.31</td>
<td>18.32</td>
<td>18.4</td>
<td>19.45(±0.06)</td>
<td>19.49(±0.02)</td>
<td>19.2</td>
<td>17.36(±0.01)</td>
</tr>
</tbody>
</table>

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Table 2. Calculated and experimental stability constants in different ionic media at 25°C for the TiOH⁻⁺ species given as:

\[ K_i = \frac{[\text{TiOH}^\text{H}^\text{+}][\text{H}^\text{+}]}{[\text{Ti}^\text{II}^\text{+}]} \quad \text{(mole} \cdot \text{L}^{-1} \text{)} \]

<table>
<thead>
<tr>
<th>Ionic medium</th>
<th>Experimental method</th>
<th>Reference</th>
<th>Log ( K_{\text{exp}} )</th>
<th>Log ( K_{\text{calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 M NaClO₄</td>
<td>kinetics</td>
<td>Harbottle¹²</td>
<td>0.51</td>
<td>-1.28</td>
</tr>
<tr>
<td>3.68 M NaClO₄</td>
<td>kinetics</td>
<td>Prestwood¹³</td>
<td>0.81</td>
<td>-1.13</td>
</tr>
<tr>
<td>3 M NaClO₄</td>
<td>potentiometry</td>
<td>Biedermann¹⁴</td>
<td>-1.14</td>
<td>-0.99</td>
</tr>
<tr>
<td>3 M NaClO₄</td>
<td>spectrophotometry</td>
<td>Rogers¹¹</td>
<td>-1.16</td>
<td>-0.99</td>
</tr>
<tr>
<td>1.5 M NaClO₄</td>
<td>spectrophotometry</td>
<td>Rogers¹¹</td>
<td>-1.07</td>
<td>-1.04</td>
</tr>
<tr>
<td>1.0 M NaClO₄</td>
<td>spectrophotometry</td>
<td>Biryuk¹⁵</td>
<td>-0.48</td>
<td>-0.99</td>
</tr>
<tr>
<td>0.5 M NaClO₄</td>
<td>spectrophotometry</td>
<td>Biryuk¹⁶</td>
<td>-0.90</td>
<td>-0.86</td>
</tr>
<tr>
<td>0.3 M NaClO₄</td>
<td>spectrophotometry</td>
<td>Biryuk¹⁶</td>
<td>-1.04</td>
<td>-0.78</td>
</tr>
<tr>
<td>0.1 M NaClO₄</td>
<td>spectrophotometry</td>
<td>Biryuk¹⁶</td>
<td>-1.18</td>
<td>-0.61</td>
</tr>
<tr>
<td>3 M LiClO₄</td>
<td>calorimetry</td>
<td>Kulba¹⁶</td>
<td>-1.41</td>
<td>-0.99</td>
</tr>
<tr>
<td>3 M LiClO₄</td>
<td>potentiometry</td>
<td>Kulba¹⁷</td>
<td>-1.18</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

As can be seen in Table 1, the stability constants in 3 M HClO₄ have, within the experimental uncertainty, the same values as those in 3 M LiClO₄ in agreement with assumptions (b) and (c) above. The constants calculated for 3 M HClO₄ + 1 M NaClO₄ and for 3 M NaClO₄ are in reasonable agreement (±0.3 logarithmic units) with those measured by Ahrland et al., Glaser and Hendrickson, and by Biedermann and Spiro. It is interesting that the surprisingly different values of \( \beta_4 \) determined in the various ionic media are satisfactorily predicted by the theory.

**Thallium(III) hydrolysis**

In a similar way, using the data of Rogers and Waind for the reaction \( \text{Ti}^\text{III} = \text{H}_2\text{O} \leftrightarrow \text{TiOH}^\text{II} + \text{H}^\text{+} \) at varying ionic strength with NaClO₄ as the inert salt, the value of the interaction coefficient \( \varepsilon(\text{TiOH}^\text{II}, \text{ClO}_4^-) \) can be calculated as equal to 0.50.* This value is, as expected, quite close to the value of \( \varepsilon(\text{TiCl}^\text{III}, \text{ClO}_4^-) = 0.49. \) From the data of Rogers and Waind, the thermodynamic stability constant for the reaction above can also be determined and is found to be -0.18. Now we can recalculate the stability constant for different ionic media and, hopefully, predict which experimental determinations published in the literature are correct and which are not. The results, together with the (experimental) literature values, are given in Table 2. Within the error limits of the calculations (±0.2) and allowing for not more than ±0.05 logarithmic units uncertainty in the experimental values, we can predict that the stability constants determined using potentiometry are correct, whereas the constants determined, for example, from kinetic evidence are probably erroneous. Also, as has already been pointed out by Baes and Mesmer, the constants of Biryuk et al. do not change, as would be expected, with the ionic strength and are probably not reliable. On the contrary, (as can be verified in Table 2), the calculated values do follow the expected trend.

**Solubility product of Ti₂O₃**

From the data of Schindler for the solubility product for Ti₂O₃, \( K_s = [\text{Ti}^\text{III}]^2[\text{H}^\text{+}]^{-3} = 10^{-2.35} \), in 3.5 molal NaClO₄, we can calculate the thermodynamic solubility product, \( K_s \), in the following way:

\[
\log K_s = \log K_i + \log \gamma_{\text{Ti}^\text{III}} - 3 \log \gamma_{\text{H}^\text{+}} = \\
\log K_i - 9D + 3D + \{ \varepsilon(\text{Ti}^\text{III}, \text{ClO}_4^-) - 3\varepsilon(\text{H}^\text{+}, \text{ClO}_4^-) \} \{\text{ClO}_4^-\} = -2.95.
\]

This value represents the solubility product at

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*The coefficient \( \varepsilon(\text{H}^\text{+}, \text{ClO}_4^-) \) calculated from the activity coefficient of HClO₄ using eqn. (1) = 0.12. (1)) to be equal to 0.12.
zero ionic strength and can be compared to the appropriate values listed in Ref.20. The solubility products determined by Vanleugenhaghe et al.\textsuperscript{21} (−2.60) and Suzuki\textsuperscript{22} (−3.20) are relatively close to the calculated one, whereas the values determined by Kovalenko and Lindorf\textsuperscript{23} (+7.8) and Benoit\textsuperscript{24} (−1.6) differ significantly from the calculated solubility product and accordingly are erroneous.

In the light of the present results and considering the growing number of successful applications of the specific interaction theory in combination with the ionic medium method,\textsuperscript{2,25} it is less worthwhile to determine experimentally the stability constants for a chemical system if the values in other ionic media are known. The same is true of standard electrode potentials and enthalpy values. However, if the interaction coefficients cannot be estimated, if it is probable that new species appear, or if very accurate parameter values are required, experiment is the only accessible way.

All the calculations of the stability constants presented in this paper are valid only when the concentrations of the reacting species are negligibly small compared with the concentration of the ionic medium, i.e., the interaction coefficients of the type \( e(TlCl^2+; Cl^-) \) can be set equal to zero.

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References

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   (b) Johnson, C. E. Jr. J. Am. Chem. Soc. 74 (1952) 959.
   (b) Sillén, L. G. and Martell, A. E. Stability constants of metal ion complexes. Supplement no. 1, Special publication no. 25. The Chemical Society, London 1971;

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