

# A $^{205}\text{Tl}$ NMR Titration Study of the Complex Formation between $\text{Tl(I)}$ and $\text{Cl}^-$ in Aqueous Solution

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A 1.5 mM aqueous solution of  $\text{Tl(I)}$  in 4 M KF was titrated with  $\text{Cl}^-$  at 28 °C using automatic titration equipment synchronized with an NMR spectrometer. The titration was followed by  $^{205}\text{Tl}$  NMR in order to determine the stability constants for the species formed in the  $\text{Tl(I)}-\text{Cl}^-$  system and to compare the accuracy of the NMR method with that obtained using standard procedures (e.g., potentiometry, polarography or solubility measurements). The number of complexes, the overall formation constants and their accuracy ( $\beta_1 = 1.0 \pm 0.2$ ;  $\beta_2 = 0.25 \pm 0.05$ ) did not differ significantly from that obtained by standard methods, but time saving and elimination of some potential sources of systematic errors were achieved. The individual  $^{205}\text{Tl}$  chemical shifts for the  $\text{TlCl}_n^{1-n}$  species were also determined:  $\delta_{\text{TlCl}} = 350 \pm 35$  ppm and  $\delta_{\text{TlCl}_2^-} = 1200 \pm 50$  ppm to high frequency from  $\text{Tl}^+$  at infinite dilution in water. The assumption of constant activity coefficients for the investigated species during the titration is discussed in the light of the specific interaction theory.

The vast majority of accurately known stability constants for metal ion complexes in solution have been determined by electroanalytical methods using ion – sensitive or redox electrodes in combination with the ionic medium method.<sup>1</sup> In several cases, as for example the formation of weak complexes, these methods have some disadvantages. A very important one is the sensitivity to small amounts of impurities present in the ionic medium. The ionic medium is often present in concentrations several thousand times higher than the species studied. Impurities may participate in electrode processes and seriously influence the measured potentials leading to systematic errors in the determined stability constants. Also, the difficulty in accounting for the liquid junction potential may contribute to systematic errors. Moreover, when using redox electrodes, it is often necessary to take into account the complex formation of species in other oxidation

state(s) than the one under study. This may complicate the evaluation of the data.

In several cases, nuclear magnetic resonance (NMR) spectroscopy can be used in order to determine equilibrium constants. Substantial time saving can be achieved when preparing the samples since the NMR signal is normally not sensitive to small amounts of impurities in the ionic medium unless they are paramagnetic or influence the chemistry of the system. One of the most favourable elements from the NMR point of view is thallium. The high NMR sensitivity (and hence short measuring time), the extremely wide chemical shift range and relatively narrow signals of  $^{205}\text{Tl}$  have been used by several groups to solve problems in  $\text{Tl(I)}$  and  $\text{Tl(III)}$  chemistry.<sup>2</sup> Previously, the stability constants and the  $^{205}\text{Tl}$  chemical shifts for the very strong complexes formed in the system  $\text{Tl(III)}-\text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have been determined using  $^{205}\text{Tl}$  NMR.<sup>3</sup> It was interesting to investigate if this method could also be applied to a system where very weak complexes are formed. As a typical example of weak com-

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plex formation, the Tl(I)-Cl<sup>-</sup> system was chosen as the subject of the present study (no distinction is made between complexes and ion pairs). In order to ensure constancy of the activity coefficients at varying ligand concentrations, an ionic medium was used. Most often, sodium or lithium perchlorate have been employed for this purpose<sup>1</sup> but it has been shown by several authors<sup>3-7</sup> that Tl(I) forms complexes with ClO<sub>4</sub><sup>-</sup>. Since complex formation between Tl(I) and F<sup>-</sup> has not been detected and, if it takes place at all, is significantly weaker than that between Tl(I) and ClO<sub>4</sub><sup>-</sup>,<sup>7b</sup> 4 M KF was chosen as ionic medium. This difference is also reflected by the results shown in Table 1. <sup>205</sup>Tl chemical shift is -182.6 ppm from Tl<sub>aq</sub><sup>+</sup> when measured in 4 M NaClO<sub>4</sub> solution, but only 95.1 ppm in 4 M KF solution. This is a qualitative indication only since several effects may contribute. A similar deshielding by F<sup>-</sup> ions has been found for <sup>109</sup>Ag in aqueous solutions of AgF.<sup>8</sup>

When, as in this case, only one average NMR signal is observed due to fast chemical exchange, the measured chemical shift  $\delta_{\text{obs}}$  for each experimental point  $i$  can be expressed as

$$\delta_{\text{obs}}^i = \sum_0^n p_n^i \delta_n, \quad (1)$$

where  $p_n = [\text{TlCl}_n^{1-n}]/[\text{Tl}]_{\text{tot}}$  and  $\delta_n$  is the <sup>205</sup>Tl chemical shift of the species TlCl<sub>*n*</sub><sup>1-*n*</sup>. Thus, knowing  $\delta_{\text{obs}}$  and [Cl<sup>-</sup>] for several experimental points, the equilibrium constant  $\beta_n = [\text{TlCl}_n^{1-n}]/([\text{Tl}^+][\text{Cl}^-]^n)$  as well as the chemical shifts  $\delta_n$  can be determined by a curve-fitting procedure. In the following, we assumed that  $[\text{Cl}^-] \approx [\text{Cl}^-]_{\text{tot}}$  (even for the lowest  $[\text{Cl}^-]_{\text{tot}} = 190$  mM only a small fraction ( $\approx 0.1\%$ ) of the chloride is bound in TlCl<sub>*n*</sub><sup>1-*n*</sup> complexes).

## Experimental

The chemicals (TlClO<sub>4</sub>, KF, KCl; all Merck reagent grade) were dried at 120 °C and used without further purification. The <sup>205</sup>Tl NMR spectra were recorded at 51.9 MHz and an ambient probe temperature of 28 ± 0.5 °C using a Bruker CXP-100 spectrometer. The field was stabilized with an external field lock. An automatic titration arrangement synchronized with the NMR spectrometer and controlled by the Aspect 2000

Table 1. <sup>205</sup>Tl NMR chemical shifts for some aqueous solutions of Tl(I) at 28 °C<sup>a</sup>

Solution (1.5 mM) $\delta_{\text{obs}}$ (ppm)	
TlClO <sub>4</sub> in 4 M KF	95.1
TlClO <sub>4</sub> in 4 M NaClO <sub>4</sub>	-182.6
TlClO <sub>4</sub> in 4 M KCl	650.2
TlClO <sub>4</sub> in 4 M HCl	656.2
TlClO <sub>4</sub> in conc HCl	776.2

<sup>a</sup>To high frequency from Tl<sup>+</sup> at infinite dilution in water.

computer in the spectrometer was built and used in order to facilitate the data collection. The equipment is described in Figure 1. The sample solution was contained in a 10 mm nonspinning sample tube. A polyethylene tube (2 mm o.d.) was immersed in the sample in order to deliver the equilibrated solution after each addition of the titrant (15 min were allowed for mixing and 15 min for the thermal equilibration). The presence of this tube in the sample had no influence on the frequency of the signal, but caused a broadening from  $\Delta\nu_1 \approx 25$  Hz to approximately 35 Hz for a nonspinning sample. Some typical NMR parameters: flip angle  $\approx 65^\circ$ ; number of scans per point in the titration = 25000; sweep width = 10 kHz; pulse repetition time = 250 ms.

The chemical shifts are reported in ppm towards higher frequency with respect to an aqueous solution of TlClO<sub>4</sub> extrapolated to infinite dilution. Since the chemical shifts for aqueous solutions of different Tl(I) salts extrapolate to the same value at infinite dilution,<sup>9</sup> this value corresponds to the chemical shifts of the "free" hydrated Tl<sup>+</sup> ion. The accuracy of the determined chemical shifts was about 0.2 ppm. However, since the measured shifts are temperature dependent and the sample temperature was controlled to  $\pm 0.5^\circ\text{C}$ , the actual accuracy in the measured shifts was within an estimate  $\leq 0.4$  ppm.

## Results and data treatment

The results from a titration of a 1.5 mM solution of TlClO<sub>4</sub> in 4 M KF with a 1.5 mM solution of TlClO<sub>4</sub> in 4 M KCl are shown in Fig. 2. No detectable changes in the <sup>205</sup>Tl line width were ob-

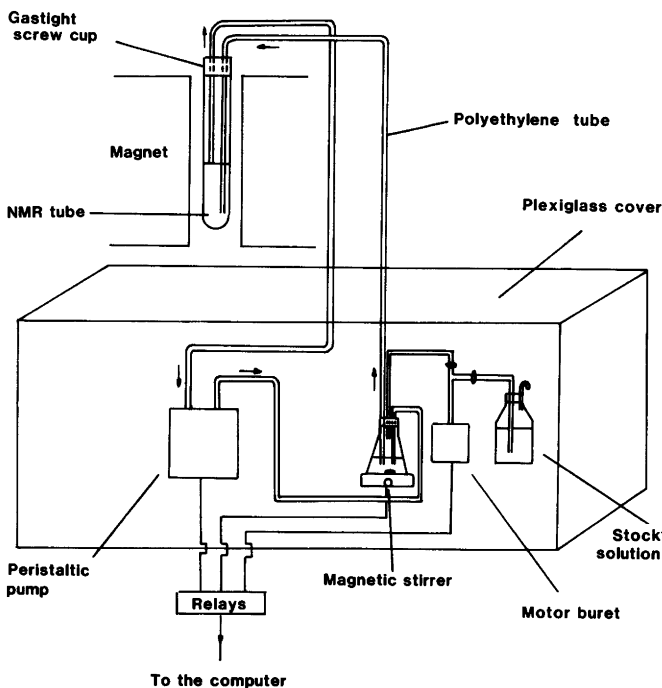


Fig. 1. Automatic arrangement for NMR titrations. Titration and spectra recording completely automatic, controlled by built-in Aspect 2000/ Bruker CXP-100 spectrometer. When sol. spectrum is recorded and stored on disc memory, the motor driven buret activates to add an accurate amount (1.00 ml) of titrant by a preset no. of computer pulses. Peristaltic pump and magnetic stirrer start and sol. is forced through the system. After 6–7 min, the sol. is homogeneous, but is circulated for 15 min. Pump and stirrer are shut off and 15 min delay allowed for thermal equilibration in the NMR tube. The spectrum is recorded and the cycle restarted. Total vol. at start 20.00 ml but can be varied within wide limits. Smallest possible vol. not determined, but 3–4 ml probable for 10 mm tube. Placing flask and pump lower than tube, and pump after tube was seen as satisfactory safety measures to prevent overflow into NMR probe.

served during the titration. Chemical shifts for some other solutions are presented in Table 1. Data from 27 experimental points in the interval  $[\text{Cl}^-] = 0$  to  $[\text{Cl}^-] = 2.3$  M were used in the evaluation. Stability constants and individual chemical shifts for the  $\text{TiCl}_n^{1-n}$  species were calculated using eq. (1) and the least-squares program LETAGROP version SPEFO,<sup>10</sup> which minimized the sum of squares

$$U = \sum_{i=0}^{i_{\max}} (\delta_{\text{obs}}^i - \delta_{\text{calc}}^i)^2, \quad (2)$$

where  $i$  represents an experimental point. In these calculations it was assumed that the activity coefficients of the studied species were constant during the titration (see below).

The refinements showed that, within the experimental accuracy, three  $\text{TiCl}_n^{1-n}$  species have to be taken into account:  $\text{Ti}^+$  ( $n=0$ ),  $\text{TiCl}$  ( $n=1$ ) and  $\text{TiCl}_2$  ( $n=2$ ). Thus five parameters should be determined:  $\delta_0$ ,  $\delta_1$ ,  $\delta_2$ ,  $\beta_1$ , and  $\beta_2$ . However,  $\delta_0 = \delta_{\text{obs}}$  for the solution with  $[\text{Cl}^-] = 0$ , and hence  $\delta_0$  could be measured directly. Accordingly, even if  $\delta_0$  could be calculated and this value was not

significantly different from the experimental value (95.1 ppm), it was assumed to be known and was not refined in the subsequent calculations. This decreased the number of parameters

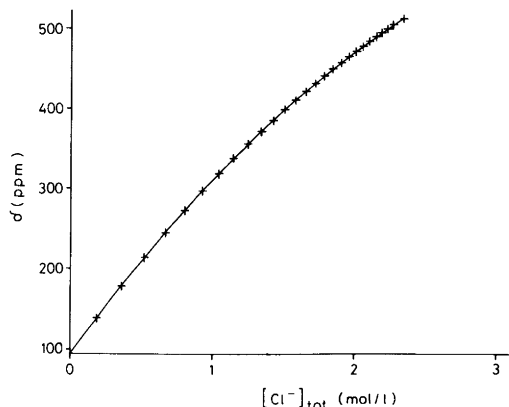


Fig. 2. Measured  $^{205}\text{Ti}$  chemical shifts in a 1.5 mM  $\text{Ti}(\text{I})$  solution in 4 M KF as a function of  $[\text{Cl}]_{\text{tot}}$  at constant ionic strength. The shifts are given to high frequency from  $\text{Ti}^+$  at infinite dilution in water. The full line is calculated using the parameters determined in this work (Table 2).

Table 2. Stability constants and <sup>205</sup>Tl chemical shifts for Tl(I)-Cl<sup>-</sup> complexes

Ionic medium	Method of measurement	Ref. no.	[Cl <sup>-</sup> ] <sub>max</sub> (mol/l)	β <sub>1</sub>	β <sub>2</sub>	β <sub>3</sub>	δ <sub>1</sub> (ppm)	δ <sub>2</sub> (ppm)
4M KF	<sup>205</sup> Tl NMR	<sup>c</sup>	2.3	1.0±0.2	0.25±0.05	—	350±35	1200±50
4M KF	polarography (Tl <sup>+</sup> /Tl electr.)	4	4.0	1.0±0.02	0.36±0.05	—		
1M KF	polarography (Tl <sup>+</sup> /Tl electr.)	4	1.0	2.1±0.1	—	—		
4M NaClO <sub>4</sub>	potentiometry (Tl <sup>+</sup> /Tl electr.)	3	4.0	1.0±0.1	0.16±0.05	—		
4M NaClO <sub>4</sub>	solubility in NaCl	3	4.0	0.8±0.2	0.16±0.05	0.02±0.01		
4M NaClO <sub>4</sub>	solubility in TiClO <sub>4</sub>	3	<sup>a</sup>	0.8±0.2	0.16±0.05	—		
4M LiClO <sub>4</sub>	solubility in LiCl	15	4.0	0.85	0.28	—		
4M LiClO <sub>4</sub>	potentiometry (Tl <sup>+</sup> /Tl electr.)	15	4.0	0.83	0.08	—		
Various	polarography (Tl <sup>+</sup> /Tl electr.)	16	2.0	2.9±0.5 <sup>b</sup>	—	—		
1M NaClO <sub>4</sub>	polarography (Tl <sup>+</sup> /Tl electr.)	16	1.0	4.4 <sup>b</sup>	—	—		
2M NaClO <sub>4</sub>	polarography (Tl <sup>+</sup> /Tl electr.)	17	0.6	1.55	—	—		
3M NaClO <sub>4</sub>	polarography (Tl <sup>+</sup> /Tl electr.)	18	0.15	0.97	—	—		

<sup>a</sup>Varying thallium concentration, [Tl(I)]<sub>max</sub> = 0.1 M.

<sup>b</sup>K<sup>0</sup> (cf. eqn. 5).

<sup>c</sup>Data from this work, collected at 28 °C, but the difference between the stability constants at 25 °C and at 28 °C for these complexes are insignificant.

necessary to explain the experimental data to four. Least-squares refinements were performed using different *i*<sub>max</sub> values and different starting values for the parameters but no systematic variation of the refined parameter values was observed. The calculated equilibrium constants and chemical shifts are presented in Table 2. For comparison, some stability constants reported in the literature are also given. The distribution of thallium among the different complexes is shown in Fig. 3.

Since the Tl(I)-Cl<sup>-</sup> complexes are comparatively weak, it was necessary to extend the titration to quite high chloride concentration. Even if the ionic strength was kept constant during the titration, it is possible that the activity coefficients were affected when fluoride ions in the ionic medium were exchanged for chloride ions and it is important to consider how this influences the determined equilibrium constants. The stepwise equilibrium constants, based on concentrations,

for the formation of TlCl and TlCl<sub>2</sub><sup>-</sup> were written as

$$K_1 = \frac{[\text{TlCl}]}{[\text{Tl}^+][\text{Cl}^-]} \quad \text{and} \quad (3)$$

$$K_2 = \frac{[\text{TlCl}_2^-]}{[\text{TlCl}][\text{Cl}^-]} \quad (4)$$

The corresponding thermodynamic equilibrium constants *K*<sub>1</sub><sup>0</sup> and *K*<sub>2</sub><sup>0</sup> based on activities are

$$K_1^0 = \frac{\gamma_{\text{TlCl}}}{\gamma_{\text{Tl}^+} \cdot \gamma_{\text{Cl}^-}} \cdot K_1 \quad \text{and} \quad (5)$$

$$K_2^0 = \frac{\gamma_{\text{TlCl}_2^-}}{\gamma_{\text{TlCl}} \cdot \gamma_{\text{Cl}^-}} \cdot K_2 \quad (6)$$

Next, the formalism of the semi-empirical specific interaction theory<sup>11-14</sup> was employed in order

to account for possible variations of the activity coefficients during the titration. For an ion,  $j$ , of charge  $z_j$  in a solution of ionic strength  $I$  (in terms of the weight molarity  $m$ ) the activity coefficient  $\gamma_j$  can be expressed by the equation

$$\log \gamma_j = -z_j^2 \cdot D + \sum_k \epsilon(j,k) \cdot m_k, \quad (7)$$

$$\text{where } D = \frac{0.5107 \cdot \sqrt{I}}{1 + 1.5 \cdot \sqrt{I}} \quad (8)$$

represents the Debye-Hückel term. The summation extends over all ions,  $k$ , (present in the solution at weight molarity  $m_k$ ) with charge of opposite sign to that of ion  $j$ . The parameters  $\epsilon(j,k)$  are called interaction coefficients. When applying eqn. (7), we assume that only the ions  $K^+$ ,  $Cl^-$  and  $F^-$  have to be taken into account in the summation. As mentioned above,  $[Cl^-] \approx [Cl^-]_{tot}$  which means that

$$m_{K^+} = m_{F^-} + m_{Cl^-}. \quad (9)$$

This gives for the concentration based equilibrium "constants"

$$\log K_1 = \log K_1^0 - \log \gamma_{TlCl} - 2D + m_{K^+}[\epsilon(Cl^-, K^+) + \epsilon(Tl^+, F^-)] + m_{Cl^-}[\epsilon(Tl^+, Cl^-) - \epsilon(Tl^+, F^-)] \quad (10)$$

and

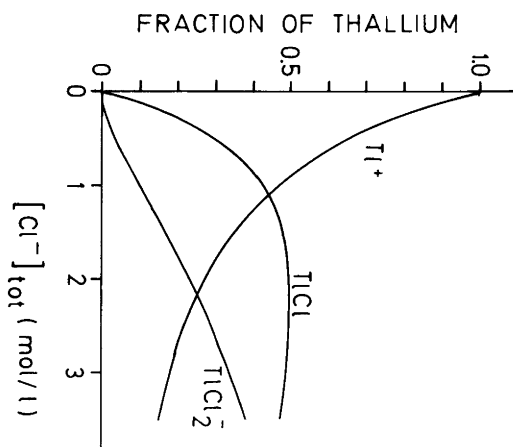


Fig. 3. Fraction of thallium present in different complexes calculated by use of the stability constants determined in this work (Table 2).

$$\log K_2 = \log K_2^0 + \log \gamma_{TlCl} + m_{K^+}[\epsilon(Cl^-, K^+) - \epsilon(TlCl_2^-, K^+)]. \quad (11)$$

At constant  $m_{K^+}$  and constant ionic strength and assuming that the activity coefficient of the uncharged species  $TlCl$  is constant during the titration, we get:

$$K_1 = A \cdot 10^{\Delta\epsilon \cdot m_{Cl^-}} \quad \text{and} \quad (12)$$

$$K_2 = \text{constant}, \quad (13)$$

where  $A$  is a constant and  $\Delta\epsilon$  is the difference

$$\Delta\epsilon = \epsilon(Tl^+, Cl^-) - \epsilon(Tl^+, F^-). \quad (14)$$

Since the differences  $[\epsilon(M^+, Cl^-) - \epsilon(M^+, F^-)]$ , where  $M^+ = Na^+, K^+, Rb^+, Cs^+$  are linear functions of the ionic radii of the alkali metal ions<sup>15</sup> and since  $r_{Na^+} \approx r_{Rb^+} = 1.47 \text{ \AA}$ ,<sup>16</sup> the value of the constant  $\Delta\epsilon$  can be assumed to be equal to  $[\epsilon(Rb^+, Cl^-) - \epsilon(Rb^+, F^-)] = -0.04$  (calculated for  $I = 4.5$  m by use of eqn. (7) and activity coefficients from Ref. 11). This implies that the factor  $10^{\Delta\epsilon \cdot m_{Cl^-}}$  in eqn. (12) varies from 1.0 to 0.80 during the titration. This 20% variation is within the uncertainty in the determined equilibrium constant  $K_1$  (Table 2). We have also included  $\Delta\epsilon$  as a parameter in the least-squares refinements. The calculated value,  $\Delta\epsilon = 0.05 \pm 0.1$ , is consistent with the estimation presented above. However,  $\Delta\epsilon$  is very close to zero and the problem is insensitive to small changes in this parameter. Hence, the error limits are large and a further discussion on this subject is not meaningful.

## Discussion

As can be seen in Table 2, the equilibrium constants determined in this work are not significantly different from the values obtained by Bond<sup>5</sup> who used a polarographic method and the same ionic medium.

The uncertainty in the determination of the equilibrium constants in this work is of the same order of magnitude as in the potentiometric and solubility measurements (v. Table 2). Bond<sup>5</sup> estimated maximum errors in the determined stability constants to be significantly lower although his data base consisted of only six experimental points from  $[Cl^-] = 0$  to  $[Cl^-] = 4.0$  M. Moreover, it has been shown by Nilsson<sup>4</sup> that in 4 M  $NaClO_4$  there is a significant variation in the activity co-

efficients when ClO<sub>4</sub><sup>-</sup> is exchanged for Cl<sup>-</sup> at high chloride concentrations. If this is also the case for 4 M KF, and since the β<sub>n</sub> values determined by Bond have not been corrected for this effect, the maximum errors may be significantly higher.

The individual <sup>205</sup>Tl chemical shifts for the species TlCl and TlCl<sub>2</sub><sup>-</sup> determined in this work are given in Table 2. It would be interesting to compare these values with the shifts for other TlX<sub>n</sub><sup>1-n</sup> complexes. To the best of our knowledge, no such chemical shifts have been reported in the literature. Comparison with corresponding chemical shifts for Tl(III)-halide complexes may be misleading since the latter complex formation is several orders of magnitude stronger and probably includes a higher degree of covalent bonding. Also, the Tl<sup>3+</sup>(aq) ion has been shown to strongly coordinate six water molecules,<sup>17</sup> whereas Tl<sup>+</sup>(aq) shows much weaker and more irregular water coordination.<sup>18</sup> However, when a chloride ion enters the first coordination sphere of a thallium ion, water molecules are probably removed from this sphere both for Tl(I) and Tl(III). Thus, the difference in chemical shift between the free hydrated thallium ion and a chloride complex should, for both oxidation states, include the change in the shielding of the thallium nucleus when a chloride ion replaces water molecules. For Tl(III), (δ<sub>TlCl<sub>2</sub><sup>2+</sup></sub> - δ<sub>Tl<sup>3+</sup></sub>) ≈ (δ<sub>TlCl<sub>2</sub><sup>+</sup></sub> - δ<sub>Tl<sup>3+</sup></sub>) ≈ 115 ppm,<sup>3</sup> whereas for Tl(I), (δ<sub>TlCl</sub> - δ<sub>Tl<sup>+</sup></sub>) is about three times greater and (δ<sub>TlCl<sub>2</sub><sup>-</sup></sub> - δ<sub>Tl<sup>+</sup></sub>) is one order of magnitude greater. However, for both oxidation states the thallium nucleus is deshielded upon the formation of chloride complexes.

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