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Speciation and Solubility of Thallium in Low Temperature Systems, Part Two: Additional Aqueous and Solid Thallium Species Potentially Important in Soil Environments

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Introduction

Thallium has numerous applications in industry. It is also of great environmental concern because of its high toxicity. Therefore, stabilities of its aqueous and solid species under low temperature environments are fundamentally important to its impact on environments. In previous publications (Xiong 2007, 2009), a number of aqueous and solid thallium species and their stabilities have been addressed. However, several thallium species that are potentially important to soil environments, especially saline soil environments, have not been covered.

In this study, additional aqueous and solid thallium species that are potentially important to solubility of thallium in soil environments are presented. These species include TlBr(cr), $TlIO_3$(cr), TlI(cr), TlI_3(cr), and TlI(aq). In addition, solubility product constants for TlCl(cr) at 0 °C and 50 °C are also evaluated in this study. The solubility product constants or stability constants for these species are evaluated by using the Specific Interaction Theory (SIT) model. Relevant solubility data in NH_4I, $MgSO_4$, KCl, KI, KNO_3, and Na_2SO_4 solutions from the literature compiled by Silcock (1979) are utilized for all evaluations. In combination with the relevant SIT coefficients obtained in previous work (Xiong 2007, 2009), the SIT coefficients evaluated in this study would enable us to model thallium chemistry/geochemistry in moderate to high ionic strength environments such as saline soil environments. Unless otherwise noted, uncertainties presented in this study are two standard deviations (2σ).

Solubility Product Constant of $TlIO_3$(cr) at 25 °C

In the previous studies (Xiong 2007, 2009), thermodynamic solubility product constants potentially important in soil environments at 25 °C for some solid phases including lanmuchangite ($TlAl(SO_4)_2 \cdot 12H_2O$), dorallcharite ($TlFe_3(SO_4)_2(OH)_6$), lorandite ($TlAsS_2$), and TlCl (cr), have been provided.

In this study, the thermodynamic solubility product constants of $TlIO_3(cr)$ at 25 °C are evaluated by using the SIT model. The evaluation procedure is similar to that described in Grenthe et al. (1992).

The solubility reaction of $TlIO_3(cr)$ can be expressed as follows,

$$TlIO_3(cr) \leftrightarrow Tl^+ + IO_3^- \tag{1}$$

According to the SIT model, the solubility product constant of $TlIO_3(cr)$ at infinite dilution is evaluated in the following form,

$$\log K_{sp} = \log Q_{sp} - 2D + \Delta\varepsilon(\text{Eq. 1}) \times I_m \tag{2}$$

In Eq. (2), $\log K_{sp}$ is a solubility product constant at infinite dilution, whereas $\log Q_{sp}$ is a solubility product quotient at a constant ionic strength (e.g., conditional solubility product constant). The D in Eq. (2) is the Debye-Hückel term, and $\Delta\varepsilon$ is the stoichiometric summation of specific interaction coefficients regarding Eq. (1) in a respective medium. The Debye-Hückel term is given by the following equation,

$$D = \frac{A_\gamma \sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \tag{3}$$

In Eq. (3), A_γ is Debye-Hückel slope for activity coefficient, which is 0.5092 at 25 °C (Helgeson and Kirkham, 1974); and I_m ionic strength on molal scale.

In Figure 1, a plot showing [log Q_{SP} – 2D] as a function of molality of KNO_3 is presented. In this plot, the intercept is log K_{sp}, which is –5.48 ± 0.02 (Table 1), and the slope is -Δε(Eq. 1), which is -0.48 ± 0.06. The Δε(Eq. 1) in a KNO_3 medium is given by

$$\Delta\varepsilon(\text{Eq. 1}) = \varepsilon(\text{Tl}^+, \text{NO}_3^-) + \varepsilon(\text{K}^+, \text{IO}_3^-) \qquad (4)$$

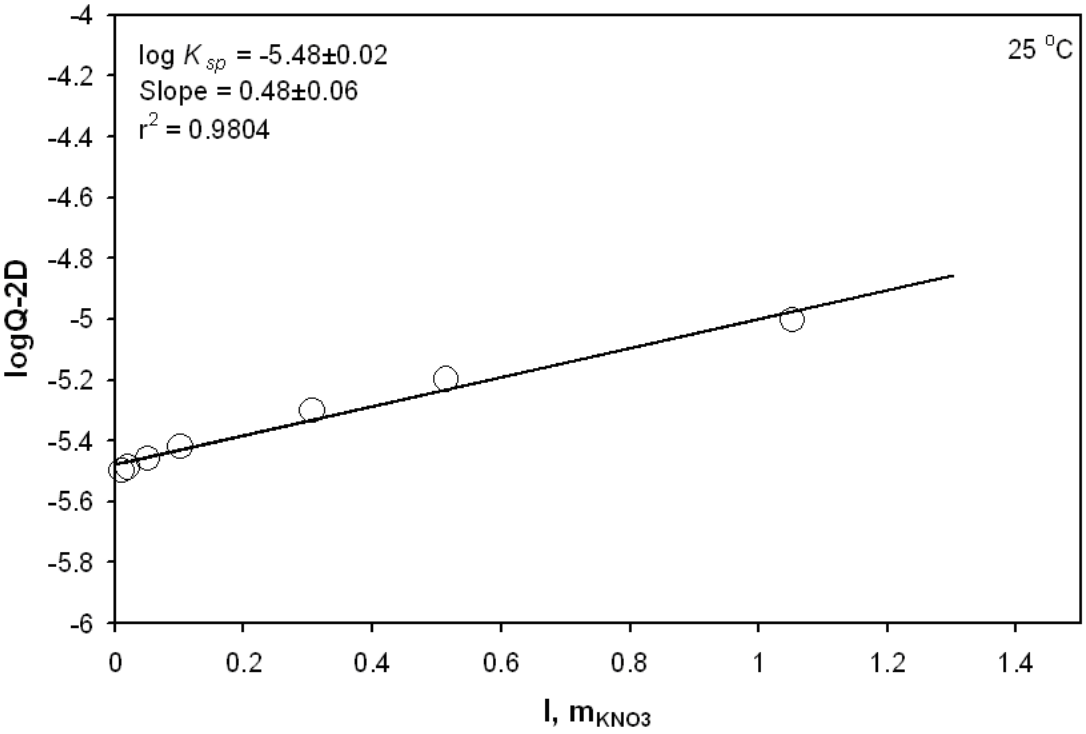

Figure 1. A plot showing [log Q_{SP} – 2D] as a function of molality of KNO_3 at 25 °C. The log Q_{SP} is conditional solubility product of $TlIO_3$(cr) in a KNO_3 medium.

Based on Δε(Eq. 1) = –0.48 ± 0.06, and ε(Tl^+, NO_3^-) = –0.24 ± 0.02 (Xiong 2009), ε(K^+, IO_3^-) is derived as –0.24 ± 0.06 (Table 2).

The log K_{sp} for $TlIO_3(cr)$ is also evaluated from solubilities of $TlIO_3(cr)$ in a $MgSO_4$ medium (Figure 2). The log K_{sp} obtained is –5.49 ± 0.01, which is in excellent agreement with that evaluated from a KNO_3 medium (Table 1). The Δε(Eq. 1) in a $MgSO_4$ medium is given by

$$\Delta\varepsilon(\text{Eq. 1}) = \varepsilon(\text{Tl}^{+}, \text{SO}_4^{2-}) + \varepsilon(\text{Mg}^{2+}, \text{IO}_3^{-}) \qquad (5)$$

Table 1. Thermodynamic solubility product constants and complex formation constant obtained in this study

Species	Reactions	T, °C	log K_{sp} ± 2σ or log β_1 ± 2σ	Remarks*
$TlIO_3(cr)$	$TlIO_3(cr) = Tl^{+} + IO_3^{-}$	25	–5.48 ± 0.02	Evaluated from solubility data of $TlIO_3(cr)$ in KNO_3 and $MgSO_4$ solutions.
TlCl(cr)	$TlCl(cr) = Tl^{+} + Cl^{-}$	0	–4.37 ± 0.03	Evaluated from solubility data of TlCl(cr) in KNO_3 solutions.
		25	–3.62 ± 0.03	Evaluated from solubility data of TlCl(cr) in $MgSO_4$ and KCl solutions.
		50	–3.06 ± 0.01	Evaluated from solubility data of TlCl(cr) in KNO_3 solutions.
TlBr(cr)	$TlBr(cr) = Tl^{+} + Br^{-}$	20	–5.60 ± 0.01	Evaluated from solubility data of TlBr(cr) in $MgSO_4$ solutions.
		20	–5.60 ± 0.01	Evaluated from solubility data of TlBr(cr) in Na_2SO_4 solutions.
TlI(cr)	$TlI(cr) = Tl^{+} + I^{-}$	20	–7.46 ± 0.01	Evaluated from solubility data of TlI(cr) in $MgSO_4$ solutions.
		20	–7.46 ± 0.02	Evaluated from solubility data of TlI(cr) in Na_2SO_4 solutions.
TlI(aq)	$Tl^{+} + I^{-} = TlI(aq)$	20	1.86 ± 0.02	Evaluated from solubility data of TlI(cr) in KI solutions.
$TlI_3(cr)$	$TlI_3(cr) = Tl^{3+} + 3I^{-}$	25	–24.40 ± 0.24	Evaluated from solubility data of $TlI_3(cr)$ in NH_4I solutions.

*Solubility data used for evaluation of log K_{sp} or log β_1 were compiled from Silcock (1979).

Table 2. SIT interaction coefficients derived in this study

SIT Coefficient	Value ± 2σ	Reference
$\varepsilon(Tl^+, NO_3^-)$	–0.24 ± 0.02	Xiong (2009)
$\varepsilon(Tl^+, SO_4^{2-})$	–0.29 ± 0.03	This work
$\varepsilon(Tl^+, Cl^-)$	–0.63 ± 0.12	This work
$\varepsilon(Tl^+, I^-)$	–0.24 ± 0.14	This work
$\varepsilon(TlI(aq), K^+, I^-)$	–0.29 ± 0.20	This work
$\varepsilon(K^+, IO_3^-)$	–0.24 ± 0.06	This work
$\varepsilon(Mg^{2+}, IO_3^-)$	–0.05 ± 0.04	This work
$\varepsilon(Na^+, Br^-)$	–0.28 ± 0.14	This work
$\varepsilon(Mg^{2+}, Br^-)$	0.10 ± 0.03	This work
$\varepsilon(Na^+, I^-)$	–0.18 ± 0.14	This work
$\varepsilon(Mg^{2+}, I^-)$	0.12 ± 0.03	This work
$\varepsilon(Tl^{3+}, I^-)$	–0.77 ± 0.16	This work

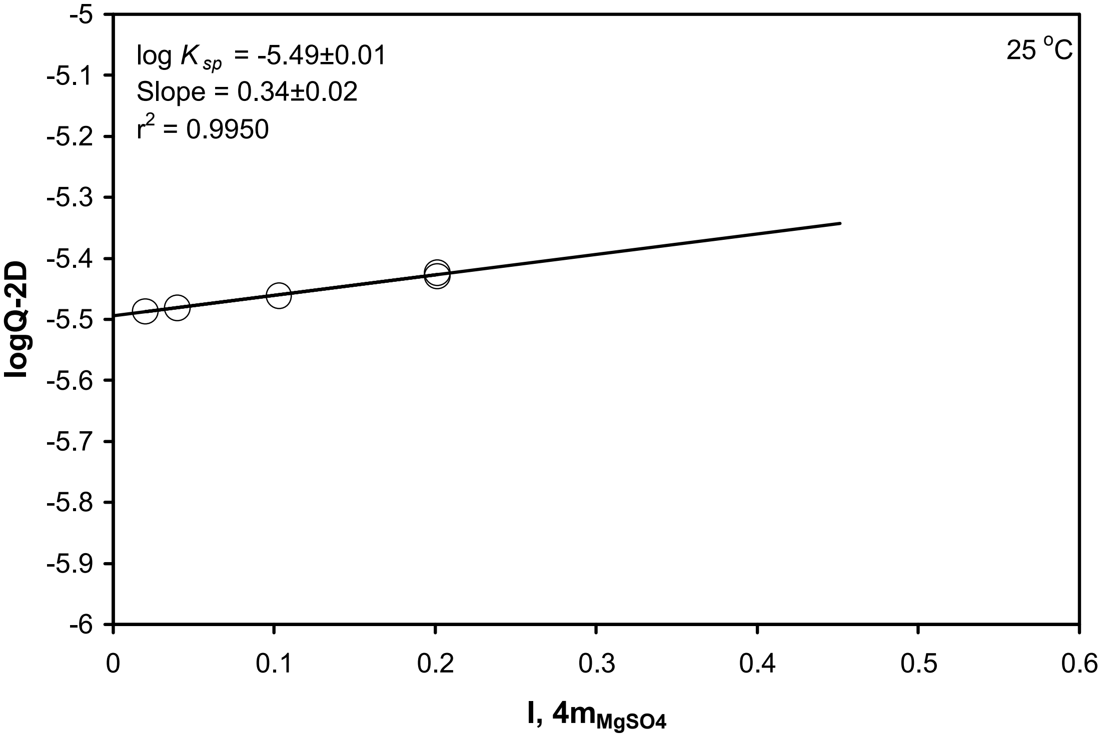

Figure 2. A plot showing [log Q_{SP} – 2D] as a function of molality of $MgSO_4$ at 25 °C.

The log Q_{SP} is conditional solubility product of $TlIO_3$(cr) in a $MgSO_4$ medium.

Solubility Product Constant of TlCl(cr) at 0 °C–50 °C

In the work of Xiong (2009), the log K_{sp} for TlCl(cr) at 25 °C was evaluated from solubility data of TlCl(cr) in KNO_3 solutions. In order to obtain $\varepsilon(Mg^{2+}, IO_3^-)$ in Eq. (5), $\varepsilon(Tl^+, SO_4^{2-})$ is evaluated from solubility data of TlCl(cr) at 25 °C in $MgSO_4$ solutions.

In Figure 3, a plot showing [log Q_{SP} – 2D] for solubility of TlCl(cr) as a function of ionic strengths in $MgSO_4$ solutions is displayed. The conditional solubility product constant, log Q_{SP}, refers to the following reaction,

$$TlCl(cr) = Tl^+ + Cl^- \qquad (6)$$

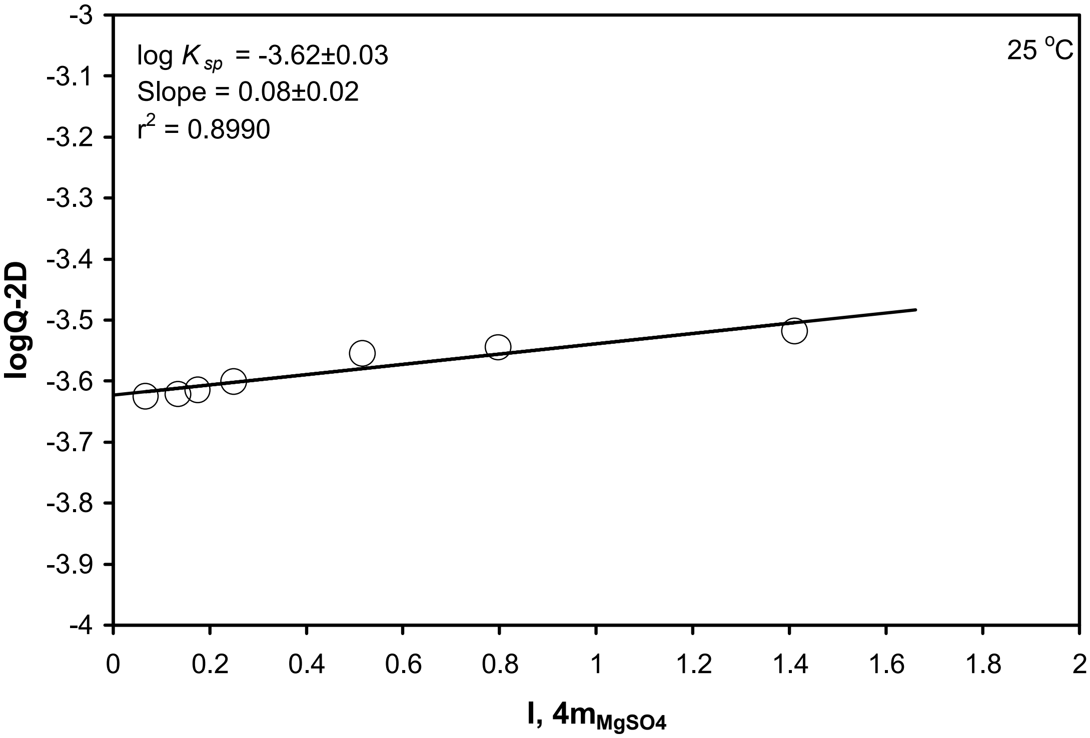

Figure 3. A plot showing [log Q_{SP} – 2D] as a function of molality of $MgSO_4$ at 25 °C. The log Q_{SP} is conditional solubility product of TlCl(cr) in a $MgSO_4$ medium.

According to the SIT model, the solubility product constant of TlCl(cr) at infinite dilution is evaluated in the following form,

$$\log K_{sp} = \log Q_{sp} - 2D + \Delta\varepsilon(\text{Eq. } 6) \times I_m \qquad (7)$$

The Δε(Eq. 6) in a $MgSO_4$ medium is given by

$$\Delta\varepsilon(\text{Eq. } 6) = \varepsilon(Tl^+, SO_4^{2-}) + \varepsilon(Mg^{2+}, Cl^-) \qquad (8)$$

According to Δε(Eq. 6) = –0.08 ± 0.02, and $\varepsilon(Mg^{2+}, Cl^-)$ = 0.209 ± 0.022 from Xiong (2006), $\varepsilon(Tl^+, SO_4^{2-})$ is derived as –0.29 ± 0.03 (Table 2). In addition, the log K_{sp} (–3.62 ± 0.03) of TlCl(cr) at 25 °C evaluated from solubility data in $MgSO_4$ solutions are in excellent agreement with that evaluated from a KNO_3 medium (Xiong 2009), which is -3.65 ± 0.01.

Substituting Δε(Eq. 1) = –0.34 ± 0.02 and $\varepsilon(Tl^+, SO_4^{2-})$ = –0.29 ± 0.03 into Eq. (5), $\varepsilon(Mg^{2+}, IO_3^-)$ is derived as –0.05 ± 0.04 (Table 2).

As TlCl(cr) could be important in saline soil solutions, the solubility product constants of TlCl(cr) at 0 °C and 50 °C are also evaluated from solubilities of TlCl(cr) in a KNO_3 medium (Figures 4 and 5, Table 1). The log K_{sp} for TlCl(cr) at 0 °C and 50 °C obtained in this study are -4.37 ± 0.03 and –3.07 ± 0.01, respectively.

Additionally, in order to enable researchers to model speciation and solubility of thallium in solutions with high ionic strengths such as saline soil solutions, the interaction coefficient, $\varepsilon(Tl^+, Cl^-)$ is required. This interaction coefficient is important because Cl^- is expected to be a major ion in such high ionic strength solutions. However, this interaction coefficient is not available in the existing literature and should be derived. To remedy this situation, solubility data of TlCl(cr) in KCl solutions are evaluated to derive this interaction coefficient.

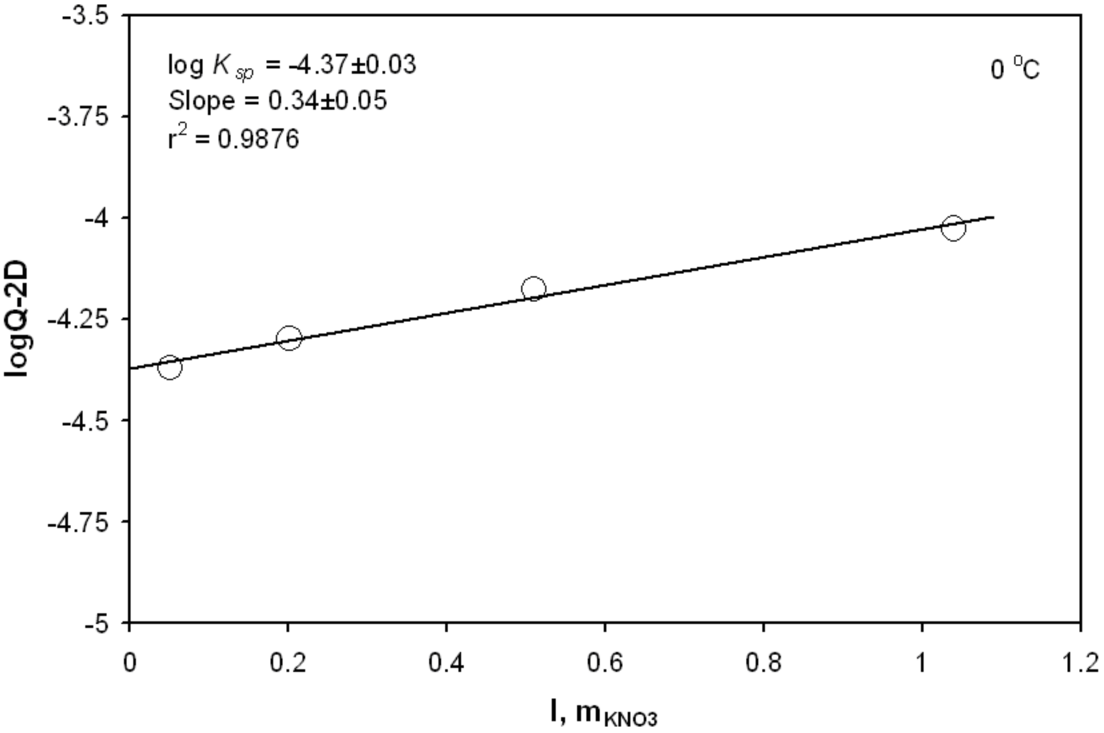

Figure 4. A plot showing [log Q_{SP} – 2D] as a function of molality of KNO_3 at 0 °C. The log Q_{SP} is conditional solubility product of TlCl(cr) in a KNO_3 medium.

The Δε(Eq. 6) in a KCl medium is given by

$$\Delta\varepsilon(\text{Eq. 6}) = \varepsilon(\text{Tl}^+, \text{Cl}^-) + \varepsilon(\text{K}^+, \text{Cl}^-) \qquad (9)$$

According to Δε(Eq. 6) = –0.63 ± 0.12 (the negative slope) in Figure 6 and $\varepsilon(K^+, Cl^-)$ = 0.00 ± 0.01 from Ciavatta (1980), $\varepsilon(Tl^+, Cl^-)$ is derived as –0.63 ± 0.12 (Table 2).

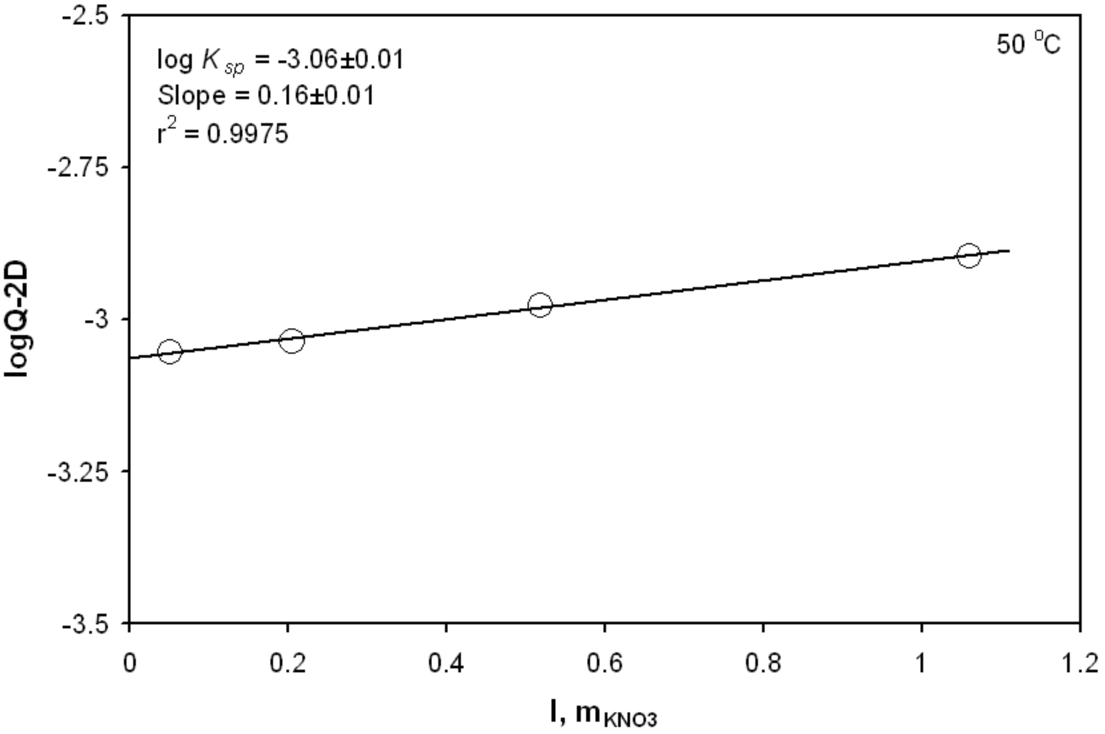

Figure 5. A plot showing [log Q_{SP} – 2D] as a function of molality of KNO_3 at 50 °C. The log Q_{SP} is conditional solubility product of TlCl(cr) in a KNO_3 medium.

Solubility Product Constant of TlBr(cr) at 20 °C

In Figures 7 and 8, log K_{sp}'s for TlBr(cr) at 20 °C are evaluated from solubility data of TlBr(cr) in $MgSO_4$ and Na_2SO_4 solutions, respectively. The dissolution reaction of TlBr(cr) is expressed as,

$$\mathrm{TlBr(cr)} = \mathrm{Tl}^{+} + \mathrm{Br}^{-} \tag{10}$$

Based on the SIT model, its solubility product constant at infinite dilution is evaluated in the following form,

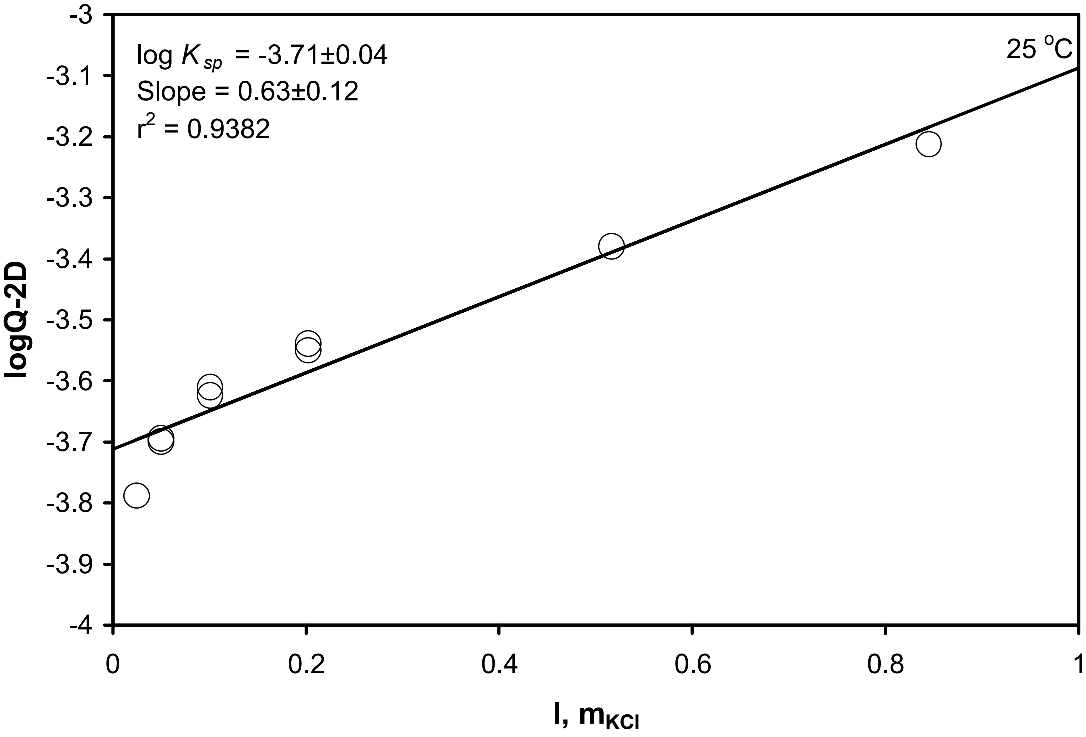

Figure 6. A plot showing [log Q_{SP} – 2D] as a function of molality of KCl at 25 °C. The log Q_{SP} is conditional solubility product of TlCl(cr) in a KCl medium.

$$\log K_{\mathrm{sp}} = \log Q_{\mathrm{sp}} - 2\mathrm{D} + \Delta\varepsilon(\text{Eq. } 10) \times \mathrm{I_m} \qquad (11)$$

The $\Delta\varepsilon$(Eq. 10) in a $MgSO_4$ medium is given by

$$\Delta\varepsilon(\text{Eq. } 10) = \varepsilon(\mathrm{Tl}^{+}, \mathrm{SO_4}^{2-}) + \varepsilon(\mathrm{Mg}^{2+}, \mathrm{Br}^{-}) \qquad (12)$$

and the $\Delta\varepsilon$(Eq. 10) in a Na_2SO_4 medium is given by

$$\Delta\varepsilon(\text{Eq. } 10) = \varepsilon(\mathrm{Tl}^{+}, \mathrm{SO_4}^{2-}) + \varepsilon(\mathrm{Na}^{+}, \mathrm{Br}^{-}) \qquad (13)$$

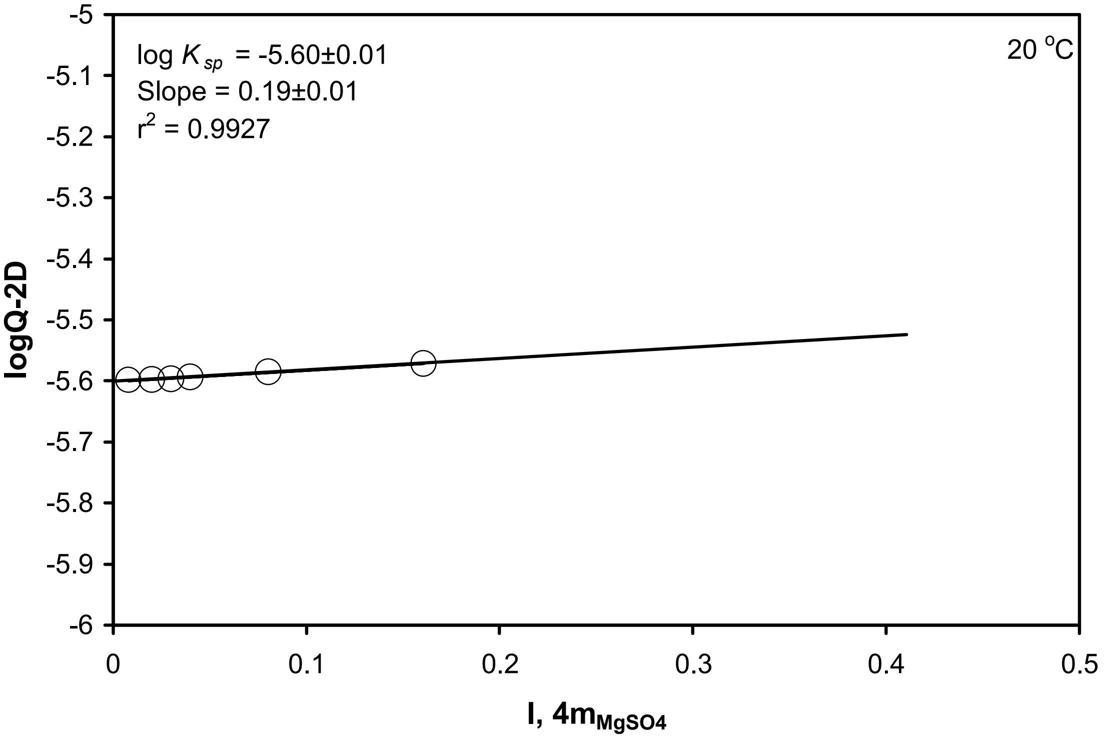

Figure 7. A plot showing [log Q_{SP} – 2D] as a function of ionic strengths in $MgSO_4$ solutions at 20 °C. The log Q_{SP} is conditional solubility product of TlBr(cr) in a $MgSO_4$ medium.

The log K_{sp} at 20 °C evaluated from solubility data of TlBr(cr) in $MgSO_4$ and Na_2SO_4 media are –5.60 ± 0.01 and –5.60 ± 0.01 (Table 1), respectively, which are in excellent agreement. Based on Δε(Eq. 10) = –0.19 ± 0.01 for Eq. (12) at 20 °C and ε(Tl^+, SO_4^{2-}) = –0.29 ± 0.03 derived above, ε(Mg^{2+}, Br^-) is calculated to be 0.10 ± 0.03 (Table 2). Similarly, based on Δε(Eq. 10) = –0.57 ± 0.14 for Eq. (13) at 20 °C, ε(Na^+, Br^-) is calculated to be –0.28 ± 0.14 (Table 2).

Solubility Product Constants of TlI(cr) at 20 °C

In Figures 9 and 10, log K_{sp}'s for TlI(cr) at 20 °C are evaluated from solubilities of TlI(cr) in $MgSO_4$ and Na_2SO_4 solutions, respectively. The dissolution reaction for TlI(cr) can be cast as,

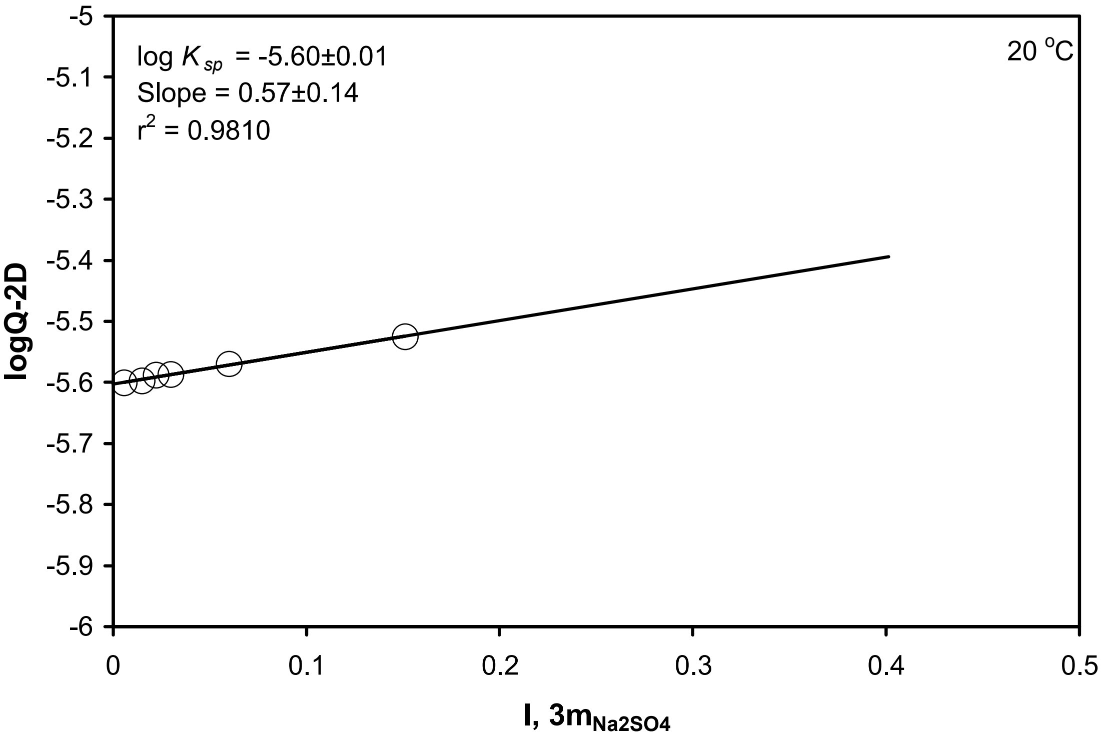

Figure 8. A plot showing [log Q_{SP} – 2D] as a function of ionic strengths in Na_2SO_4 solutions at 20 °C. The log Q_{SP} is conditional solubility product of TlBr(cr) in a Na_2SO_4 medium.

$$\mathrm{TlI(cr)} = \mathrm{Tl}^{+} + \mathrm{I}^{-} \qquad (14)$$

According to the SIT model, the solubility product constant of TlI(cr) at infinite dilution can be evaluated in the following form,

$$\log K_{\mathrm{sp}} = \log Q_{\mathrm{sp}} - 2\mathrm{D} + \Delta\varepsilon(\mathrm{Eq.\ 14}) \times \mathrm{I_m} \qquad (15)$$

The Δε(Eq. 14) in a $MgSO_4$ medium is governed by the following equation,

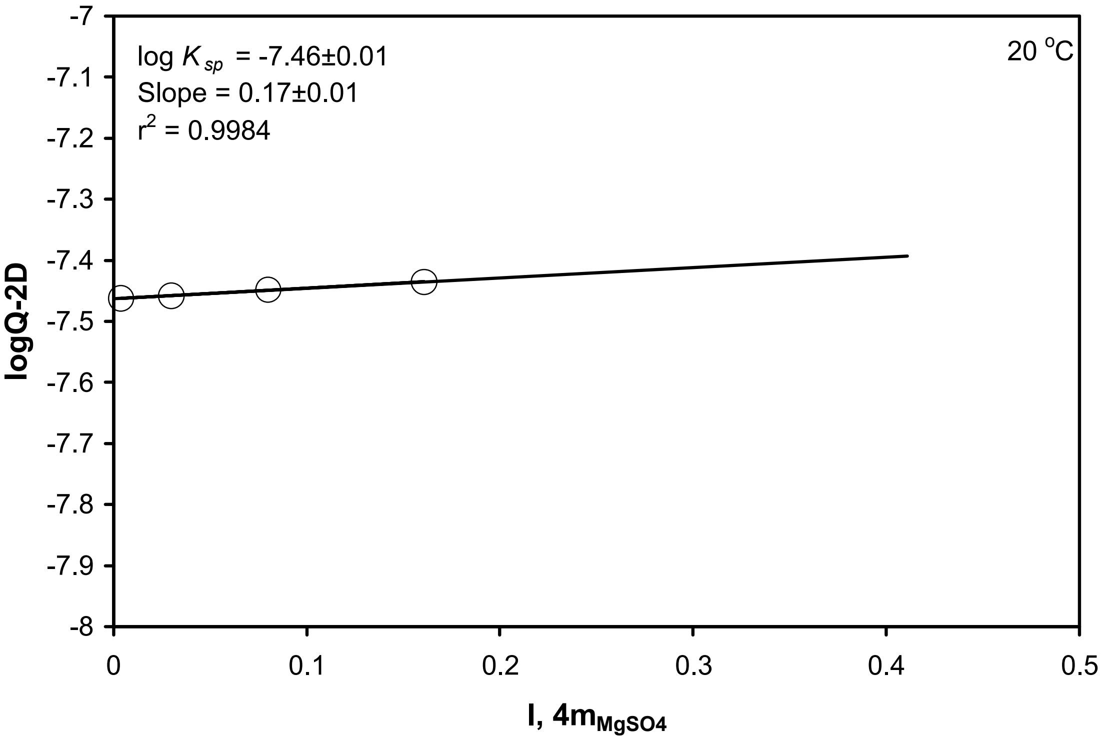

Figure 9. A plot showing [log Q_{SP} – 2D] as a function of ionic strengths in $MgSO_4$ solutions at 20 °C. The log Q_{SP} is conditional solubility product of TlI(cr) in a $MgSO_4$ medium.

$$\Delta\varepsilon(\text{Eq. } 14) = \varepsilon(\text{Tl}^+, \text{SO}_4^{2-}) + \varepsilon(\text{Mg}^{2+}, \text{I}^-) \qquad (16)$$

Similarly, the Δε(Eq. 14) in a Na_2SO_4 medium is related to the following equation,

$$\Delta\varepsilon(\text{Eq. } 14) = \varepsilon(\text{Tl}^+, \text{SO}_4^{2-}) + \varepsilon(\text{Na}^+, \text{I}^-) \qquad (17)$$

Figures 9 and 10 indicate that the log K_{sp} for TlI(cr) at 20 °C evaluated from solubilities of TlI(cr) in $MgSO_4$ and Na_2SO_4 media are –7.46 ± 0.01 and –7.46 ± 0.02 (Table 1), respectively. These two values are in excellent agreement. According to Δε(Eq. 14) = –0.17 ± 0.01 for Eq. (16)

at 20 °C and ε(Tl^+, SO_4^{2-}) = –0.29 ± 0.03 derived above, ε(Mg^{2+}, I^-) is derived as 0.12 ± 0.03 (Table 2). Similarly, based on Δε(Eq. 14) = -0.47 ± 0.14 for Eq. (17) at 20 °C, ε(Na^+, I^-) is computed as –0.18 ± 0.14 (Table 2).

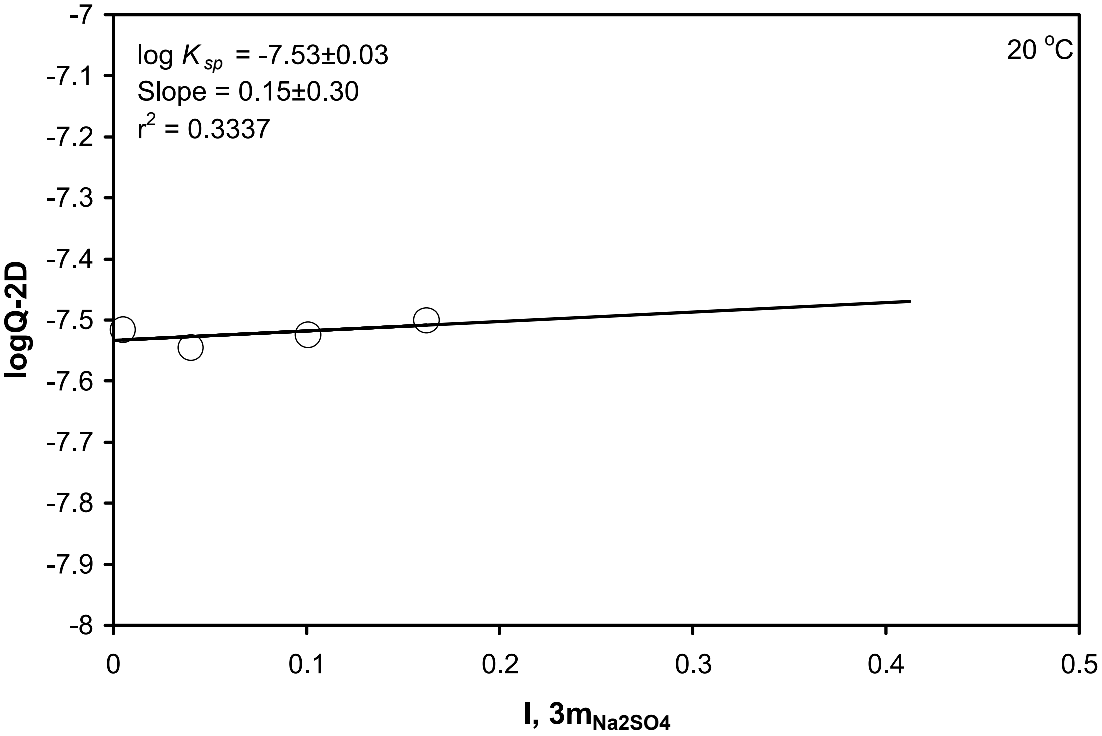

Figure 10. A plot showing [log Q_{SP} – 2D] as a function of ionic strengths in Na_2SO_4 solutions at 20 °C. The log Q_{SP} is conditional solubility product of TlI(cr) in a Na_2SO_4 medium.

Solubility Product Constants of TlI_3(cr) at 25 °C

In Figure 11, log K_{sp} for TlI_3(cr) at 25 °C are evaluated from solubilities of TlI_3(cr) in NH_4I solutions. The dissolution reaction for TlI_3(cr) can be written as,

$$TlI_3(cr) = Tl^{3+} + 3I^- \qquad (18)$$

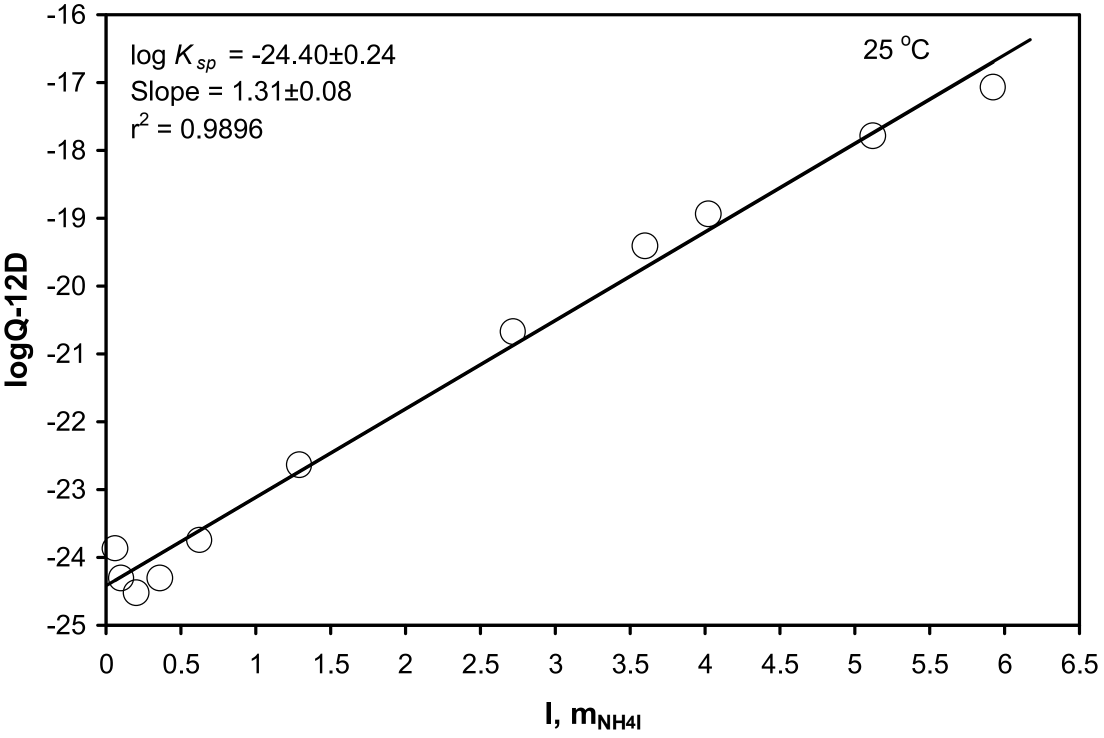

Figure 11. A plot showing [log Q_{SP} – 12D] as a function of ionic strengths in NH_4I solutions at 20 °C. The log Q_{SP} is conditional solubility product of TlI_3(cr) in an NH_4I medium.

According to the SIT model, the solubility product constant of TlI_3(cr) at infinite dilution can be evaluated in the following form,

$$\log K_{sp} = \log Q_{sp} - 12D + \Delta\varepsilon(\text{Eq. } 18) \times I_m \quad (19)$$

The Δε(Eq. 18) in an NH_4I medium is governed by the following equation,

$$\Delta\varepsilon(\text{Eq. } 18) = \varepsilon(Tl^{3+}, I^-) + 3 \times \varepsilon(NH_4^+, I^-) \quad (20)$$

Figure 11 shows that the log K_{sp} for TlI_3(cr) at 25 °C is –24.40 ± 0.24. According to $\Delta\varepsilon$(Eq. 18) = –1.31 ± 0.08, and using $\varepsilon(Na^+, I^-)$ = –0.18 ± 0.14 derived in this study, $\varepsilon(Tl^{3+}, I^-)$ is derived as –0.77 ± 0.16 (Table 2).

Formation Constant of TlI(aq) at 25 °C

Figure 12 demonstrates that if total thallium concentrations are not corrected for TlI(aq) regarding solubilities of TlI(cr) in KI solutions, the log K_{sp} (i.e., –6.08, the intercept in Figure 12) evaluated would be orders of magnitude higher than that evaluated from $MgSO_4$ and Na_2SO_4 (log K_{sp} = –7.46 ± 0.02, Table 1). The log K_{sp} evaluated from $MgSO_4$ and Na_2SO_4 is much lower and reliable, as there is no contribution from TlI(aq) because of very low concentrations of I^-. Therefore, the solubility data of TlI(cr) in KI solutions imply that Tl^+ forms a relatively strong complex with I^-, and TlI(aq) substantially increases solubilities of TlI(cr) in KI solutions.

In this study, the conditional formation constant of TlI(aq) are calculated based on the log K_{sp} determined in $MgSO_4$ and Na_2SO_4 media. First, log Q_{sp}, conditional solubility product quotient in KI solutions, are calculated utilizing a re-arranged version of Eq. (15),

$$\log Q_{\mathrm{sp}} = \log K_{\mathrm{sp}} + 2D - \Delta\varepsilon(\text{Eq. 14}) \times I_m \tag{21}$$

where $\Delta\varepsilon$(Eq. 14) in a KI medium should be

$$\Delta\varepsilon(\text{Eq. 14}) = \varepsilon(Tl^+, I^-) + \varepsilon(K^+, I^-) \tag{22}$$

As the corrections for TlI(aq) are expected to be proportional to concentrations of I^-, the negative slope in Figure 12 should be the same as $\Delta\varepsilon$(Eq. 14) for Eq. (22). Using $\Delta\varepsilon$(Eq. 14) = –0.42 ± 0.02, log Q_{sp} at different concentrations of KI are calculated (Table 3). Based on $\Delta\varepsilon$(Eq.

14) = –0.42 ± 0.02, and assuming $\varepsilon(K^+, I^-) \approx \varepsilon(Na^+, I^-)$, which is –0.18 ± 0.14 derived in this study, $\varepsilon(Tl^+, I^-)$ is calculated to be –0.24 ± 0.14 (Table 2).

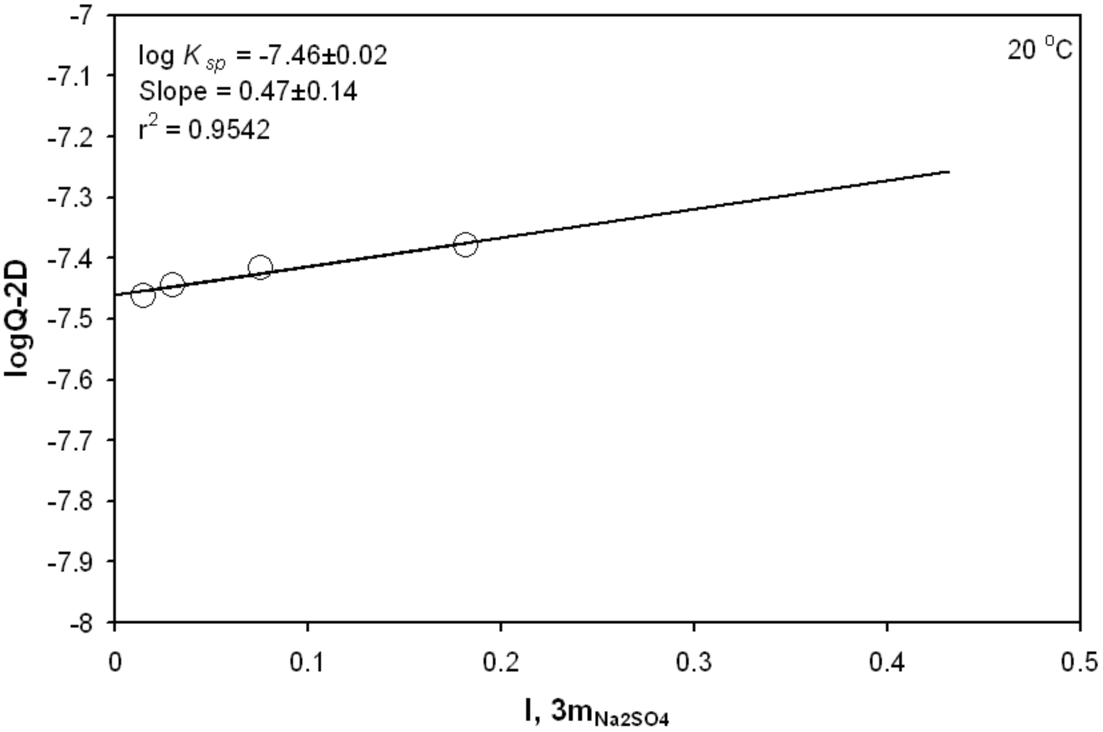

Figure 12. A plot showing [log Q_{SP} – 2D] as a function of ionic strengths in Na_2SO_4 solutions at 20 °C. The log Q_{SP} is conditional solubility product of TlI(cr) without corrections for TlI(aq) in a KI medium.

Second, the total concentrations of thallium can be expressed as,

$$m_{\Sigma Tl} = m_{Tl^+} + m_{TlI(aq)} \tag{23}$$

Rearranging Eq. (23),

$$m_{TlI(aq)} = m_{\Sigma Tl} - m_{Tl^+} \qquad (24)$$

As the equation for Q_{SP} is,

$$Q_{SP} = m_{Tl^+} \times m_{I^-} \qquad (25)$$

Substituting Eq. (25) into Eq. (24),

$$m_{TlI(aq)} = m_{\Sigma Tl} - \frac{Q_{SP}}{m_{I^-}} \qquad (26)$$

Therefore, based on log Q_{sp} calculated above, and solubility data for total thallium concentrations and I^-, $m_{TlI(aq)}$ can be calculated. According to known concentrations of m_{Tl^+}, m_{I^-} and $m_{TlI(aq)}$, conditional formation constant for TlI(aq) can be computed following the reaction below,

$$Tl^+ + I^- = TlI(aq) \qquad (27)$$

$$\beta_1^I = \frac{m_{TlI(aq)}}{m_{Tl^+} \times m_{I^-}} \qquad (28)$$

The conditional formation constants calculated in this way are listed in Table 3. It should be mentioned that the log β_1^I = 0.72 ± 0.06 at I = 4.38 m and 20 °C evaluated by this study is consistent with the log β_1^I = 0.74 ± 0.02 at I = 4 M and 25 °C in the literature (Kulba and

Mironov, 1960; cited in Smith et al. 2004). For these calculations, it is assumed that total iodide concentrations are equal to free iodide concentrations without corrections for concentrations of TlI(aq), as concentrations of the latter species are negligible in comparison with high concentrations of total iodide. Based on those conditional formation constants listed in Table 3, the thermodynamic formation constant is evaluated in accordance with the following equation (Figure 13),

Table 3. Conditional solubility product quotients of TlI(cr) and formation constants of TlI(aq) at 20 °C obtained in this study

KI, m*	Solubility of TlI(cr), m*	log Q_{sp}	log β_1^I
1.84	9.14E-06	–6.15 ± 0.04	1.09±0.04
2.48	1.35E-05	–5.86 ± 0.05	0.98±0.05
3.14	2.18E-05	–5.57 ± 0.05	0.90±0.05
3.78	3.38E-05	–5.30 ± 0.06	0.81±0.06
4.38	4.96E-05	–5.04 ± 0.06	0.72±0.06

*Solubility data were from compilations of Silcock (1979).

$$\log \beta_1 = \log \beta_1^I + 2D + \Delta\varepsilon(\text{Eq. 27}) \times I_m \qquad (29)$$

The log β_1 obtained is 1.86 ± 0.02, which is a relatively strong complex. According to $\Delta\varepsilon$(Eq. 27) = 0.13 ± 0.01, $\varepsilon(\text{Tl}^+, \text{I}^-)$ = –0.24 ± 0.14, and $\varepsilon(\text{K}^+, \text{I}^-) \approx \varepsilon(\text{Na}^+, \text{I}^-)$ = -0.18 ± 0.14 derived in this study, $\varepsilon(\text{TlI(aq)}, \text{K}^+, \text{I}^-)$ is calculated to be –0.29 ± 0.20 (Table 2).

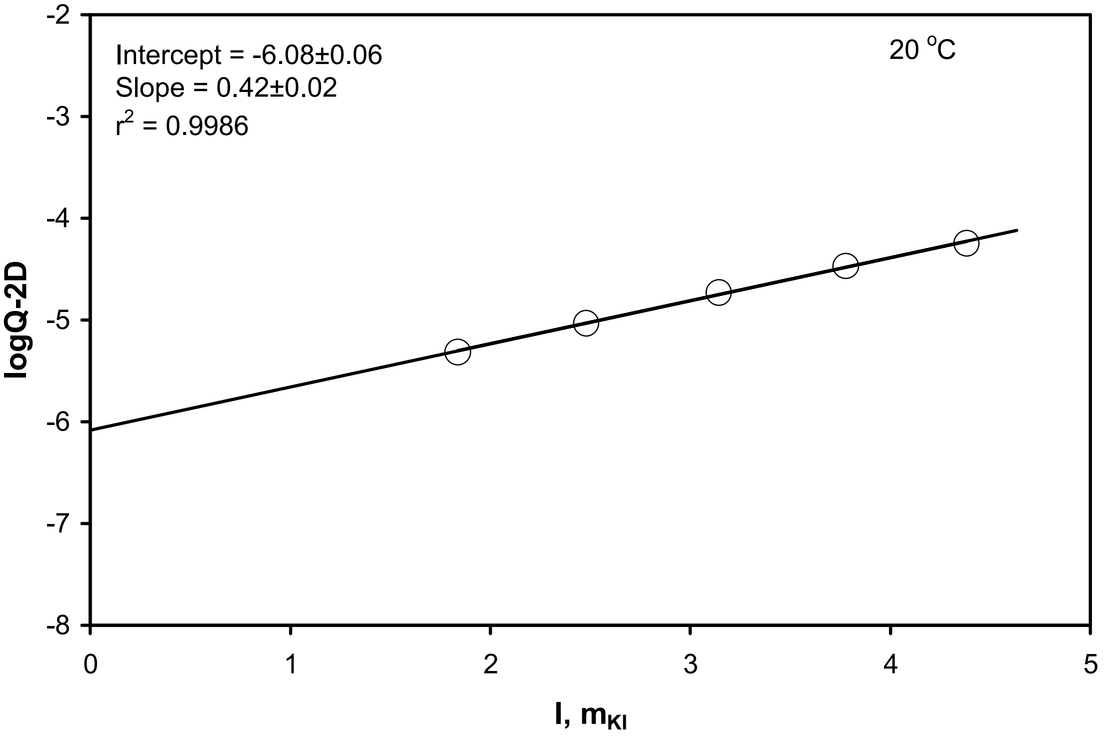

Figure 13. A plot showing [log β_1^I + 2D] as a function of ionic strengths in KI solutions at 20 °C. The log β_1^I is conditional formation constant of TlI(aq) in a KI medium.

Discussions and Summary

The above results indicate that, in the order of increasing solubility for thallium(I), thallium iodide has the lowest solubilities, followed by thallium bromide, thallium iodate, and thallium chloride. Under very oxidizing conditions, thallium could form TlI_3(cr), which has very low solubilities. Therefore, in the soil environments where there are relatively high concentrations of iodide or bromide, TlI(cr) or TlBr(cr) could become solubility-limiting phase(s) for thallium. As the aqueous complex, TlI(aq), is relatively strong, it would become a dominant species in soil solutions where iodide concentrations are sufficiently high.

In conjunction with the SIT coefficients related to thallium aqueous species derived before (Xiong, 2007, 2009), the relevant SIT coefficients provided by this study would make it feasible to model the speciation and solubility of thallium in natural waters with moderate and high ionic strengths. For instance, seawater contains relatively high concentrations of Cl^-, Na^+, Mg^{2+}, SO_4^{2-}, Ca^{2+}, and K^+ with an ionic strength of about 0.7 m. In saline soil solutions, the major components are Na^+ and Cl^-. In strongly saline soil solutions, salinities may be higher than 16 ds/m in terms of electric conductivity, which would be higher than ~10 g/L in terms of total dissolved salts (or higher than ~0.2 m in terms of molality for NaCl equivalent). To model speciation and solubility of thallium under those conditions, the SIT model with the relevant SIT coefficients for thallium aqueous species would be appropriate.

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