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

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Biedermann, Georg and Glaser, Julius, 1986. Calculation of Equilibrium Constants for Some Thallium(III) Species in Aqueous Solutions Containing Different Ionic Media. – Acta Chem. Scand. A 40: 331–334.

Using the specific interaction theory, the equilibrium constants for the species $TlCl_n^{3-n}$ ($n = 1,2,3,4$), $TlOH^{2+}$ and $Tl_2O_3(s)$ 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 $NaClO_4$) 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.[1] According to this theory, the activity coefficient, γ_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:

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

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

represents the Debye-Hückel term at 25 °C, and the summation extends over all the ions k present in solution at the molality, m_k. The ε terms, called interaction coefficients, are set equal to zero when the charge of the ion k has the same sign as that of the ion i. The concentration dependence of ε is usually very small, so that an average value covering a wide I range (up to 3 to 4 m) can be used as a first approximation.[1b,2] The interaction coefficients must be calculated from independent measurements. (It has to be kept in mind, when the specific interaction theory is used, that it can only predict changes in the stability constants from one ionic medium and/or concentration to another, but no prognosis as to the appearance of new species can be provided.) In the following, examples are given of calculations of stability constants for some Tl(III) species in aqueous solutions containing different ionic media.

Thallium(III) chloride complexes

Using the measurements of the oxidation potentials of mixtures of thallic and thallous perchlorate in perchloric acid solutions with varying ionic strength,[3] the interaction coefficient $\varepsilon(Tl^{3+}, ClO_4^-) = 0.65(6)$ was obtained in a manner similar to that for Fe^{3+}.[2] This result is quite reason-

[†]Deceased.

able, since $\varepsilon(Fe^{3+}, ClO_4^-)$ has been estimated to be 0.56 [2] and $\varepsilon(Ga^{3+}, ClO_4^-)$ is equal to approximately 0.65.[4] Next, the coefficients $\varepsilon(TlCl_n^{3-n}, ClO_4^-)$ were calculated from the equilibrium constants of Woods et al.[5] for the formation of the $TlCl_n^{3-n}$ complexes in 0.5 M $HClO_4$ and in 3 M $HClO_4$, at 25 °C in the following way. For the reaction $Tl^{3+} + Cl^- \rightleftarrows TlCl^{2+}$, the thermodynamic equilibrium constant $\varkappa_1$ can be expressed as

$$\varkappa_1 = K_1 \cdot \frac{\gamma(TlCl^{2+})}{\gamma(Tl^{3+}) \cdot \gamma(Cl^-)}, \tag{2}$$

where K_1 represents the stability constant based on concentrations. According to eqn. (1), the activity coefficients are:

$$\log \gamma(TlCl^{2+}) = -2^2 \cdot D + \varepsilon(TlCl^{2+}, ClO_4^-) \cdot [ClO_4^-]; \tag{3a}$$

$$\log \gamma(Tl^{3+}) = -3^2 \cdot D + \varepsilon(Tl^{3+}, ClO_4^-) \cdot [ClO_4^-]; \tag{3b}$$

$$\log \gamma(Cl^-) = -1^2 \cdot D + \varepsilon(Cl^-, H^+) \cdot [H^+]; \tag{3c}$$

where $D = 0.2509$ for $I = 3.47$ m and $D = 0.1752$ for $I = 0.51$ m; $\varepsilon(Tl^{3+}, ClO_4^-) = 0.65_6$ as stated above and $\varepsilon(Cl^-, H^+) = 0.12$ calculated from the activity factor of HCl γ_{H^+,Cl^-}^0 in 2 M HCl [6] according to eq. (1). Now $\log \varkappa_1$ for the 3 M (= 3.47 m) solution of $HClO_4$ can be written as

$$\log \varkappa_1 = 7.10 + 6 \cdot 0.2509 + \varepsilon(TlCl^{2+}, ClO_4^-) \cdot 3.47 - 0.656 \cdot 3.47 - 0.12 \cdot 3.47 = 3.47 \cdot \varepsilon(TlCl^{2+}, ClO_4^-) + 5.98, \tag{4}$$

where $\log K_1 = 7.10$ mol·kg^{-1} was taken from Ref. 5. Similarly, for the 0.5 M $HClO_4$

$$\log \varkappa_1 = 0.51 \cdot \varepsilon(TlCl^{2+}, ClO_4^-) + 7.36. \tag{5}$$

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

$$\varepsilon(TlCl^{2+}, ClO_4^-) = 0.48_6. \tag{6}$$

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

$\varepsilon(TlCl_2^+, ClO_4^-) = 0.38$ (9)
$\varepsilon(TlCl_3) = 0.20$ (6)
$\varepsilon(TlCl_4^-, H^+) = 0.22$ (4).

The stability constants for the $TlCl_n^{3-n}$ complexes in three different ionic media were now obtained according to eqn. (2) and are presented in Table 1 together with the experimental results.[5,7-10] The additional assumptions required in order to obtain the values of some residual coefficients, were:

(a) $\varepsilon(Na^+, TlCl_4^-) - \varepsilon(H^+, TlCl_4^-) = \varepsilon(Na^+, Cl^-) - \varepsilon(H^+, Cl^-)$ leading to $\varepsilon(Na^+, TlCl_4^-) = 0.13$ (4);
(b) $\varepsilon(Li^+, TlCl_4^-) = \varepsilon(H^+, TlCl_4^-) = 0.22$;
(c) $\varepsilon(Li^+, Cl^-) = \varepsilon(H^+, Cl^-) = 0.12$.

The activity coefficient for the uncharged species, $TlCl_3$, was assumed to be

$$\log \gamma(TlCl_3) = \varepsilon(TlCl_3) \cdot I$$

Table 1. Calculated and experimental stability constants in different ionic media at 25 °C for the $TlCl_n^{3-n}$ complexes, given as:

$$\beta_n = \frac{[TlCl_n^{3-n}]}{[Tl^{3+}][Cl^-]^n} \quad (mole \cdot l^{-1})^{-n}$$

| | 0.5 M | 3 M | 3 M | 3 M HClO₄ + 1 M NaClO₄ | | | 3 M NaClO₄ | |
	HClO₄ (Woods[5])	HClO₄ (Woods[5])	LiClO₄ (Kulba[7])	(Ahrland[8])	(Glaser[9])	calc.	(Biedermann[10])	calc.
$\log \beta_1$	6.72	7.16	7.13	7.48(±0.05)		7.4	7.04(±0.01)	6.9
$\log \beta_2$	11.82	12.60	12.55	13.26(±0.05)	13.28(±0.13)	13.1	12.32(±0.01)	12.1
$\log \beta_3$	14.50	16.15	16.0	16.65(±0.05)	16.56(±0.07)	16.9	15.30(±0.02)	15.2
$\log \beta_4$	16.31	18.32	18.4	19.45(±0.06)	19.49(±0.02)	19.2	17.36(±0.01)	17.4

Table 2. Calculated and experimental stability constants in different ionic media at 25°C for the $TlOH^{2+}$ species given as:

$$K_1 = \frac{[TlOH^{2+}][H^+]}{[Tl^{3+}]} \quad (mole \cdot l^{-1})$$

Ionic medium	Experimental method	Reference	Log $K_1^{exp.}$	log $K_1^{calc.}$
6 M NaClO$_4$	kinetics	Harbottle[12]	0.51	−1.28
3.68 M NaClO$_4$	kinetics	Prestwood[13]	0.81	−1.13
3 M NaClO$_4$	potentiometry	Biedermann[14]	−1.14	−0.99
3 M NaClO$_4$	spectrophotometry	Rogers[11]	−1.16	−0.99
1.5 M NaClO$_4$	spectrophotometry	Rogers[11]	−1.07	−1.04
1.0 M NaClO$_4$	spectrophotometry	Biryuk[15]	−0.48	−0.99
0.5 M NaClO$_4$	spectrophotometry	Biryuk[15]	−0.90	−0.86
0.3 M NaClO$_4$	spectrophotometry	Biryuk[15]	−1.04	−0.78
0.1 M NaClO$_4$	spectrophotometry	Biryuk[15]	−1.18	−0.61
3 M LiClO$_4$	calorimetry	Kulba[16]	−1.41	−0.99
3 M LiClO$_4$	potentiometry	Kulba[17]	−1.18	−0.99

As can be seen in Table 1, the stability constants in 3 M HClO$_4$ have, within the experimental uncertainty, the same values as those in 3 M LiClO$_4$ in agreement with assumptions (b) and (c) above. The constants calculated for 3 M HClO$_4$ + 1 M NaClO$_4$ and for 3 M NaClO$_4$ are in reasonable agreement (±0.3 logarithmic units) with those measured by Ahrland et al.,[8] Glaser and Henricksson,[9] and by Biedermann and Spiro.[10] It is interesting that the surprisingly different values of β$_4$ 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[11] for the reaction $Tl^{3+} = H_2O \rightleftarrows TlOH^{2+} + H^+$ at varying ionic strength with NaClO$_4$ as the inert salt, the value of the interaction coefficient $\varepsilon(TlOH^{2+}, ClO_4^-)$ can be calculated as equal to 0.50.* This value is, as expected, quite close to the value of $\varepsilon(TlCl^{2+}, ClO_4^-) = 0.49$. From the data of Rogers and Waind,[11] 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,[18] the constants of Biryuk et al.[15] 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 Tl$_2$O$_3$

From the data of Schindler[19] for the solubility product for Tl$_2$O$_3$, $K_s = [Tl^{3+}] \cdot [H^+]^{-3} = 10^{-2.34}$, in 3.5 molal NaClO$_4$, we can calculate the thermodynamic solubility product, K_s, in the following way:

$\log K_s = \log K_s + \log \gamma_{Tl^{3+}} - 3 \log \gamma_{H^+} = \log K_s - 9D + 3D + \{\varepsilon(Tl^{3+}, ClO_4^-) - 3\varepsilon(H^+, ClO_4^-)\}[ClO_4^-] = -2.95$.

This value represents the solubility product at

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*The coefficient $\varepsilon(H^+, ClO_4^-)$ calculated[6] from the activity coefficient of HClO$_4$[6] 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.[21] (-2.60) and Suzuki[22] (-3.20) are relatively close to the calculated one, whereas the values determined by Kovalenko and Lindorf[23] ($+7.8$) and Benoit[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,[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 $\varepsilon(TlCl^{2+}, Cl^-)$ can be set equal to zero.

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