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# Electromigration of Carrier-Free Radionuclides. 7. 201Tl-Thallium(I) Sulphate Complexes in Aqueous Solutions

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Dedicated to Academician *G. N. Flerov* on the Occasion of his 75th Birthday

*Stoichiometric stability constants of the thallium (I) sulphate complex [Tl(SO_4)]^- have been determined by measurements of the 201Tl-Tl(I) ion mobility at 298.1 (1) K in solutions of $Na_2SO_4/Na(H)ClO_4$, $\mu = 0.1$, pH $\leq 4$, and $Na_2SO_4/H_2SO_4$, $0.1 \leq \mu \leq 0.48$, pH 2—2.5. The thermodynamic stability constant of this complex anion of $K_1^0 = 15.7(1.0)$ l · mol^{-1} has been calculated on the basis of experimental data.*

*Durch Messungen der 201Tl-Tl(I)-Ionenbeweglichkeit in Lösungen des Typs $Na_2SO_4/Na(H)ClO_4$, $\mu = 0,1$, pH $\leq 4$, bzw. $Na_2SO_4/H_2SO_4$, $0,1 \leq \mu \leq 0,48$, pH 2—2,5, sind stöchiometrische Stabilitätskonstanten des Thallium(I)-Sulfat-Komplexes [Tl(SO_4)]^- bestimmt worden. Aus den experimentellen Daten sind thermodynamische Stabilitätskonstanten des Komplexanions zu $K_1^0 = 15,7$ (1,0) l · mol^{-1}, T = 298,1 (1) K, berechnet worden.*

## Keywords

ion mobility; stability; thallium 201; thallium complexes; thallium sulfates; thermodynamic properties

## 1. Introduction

In our previous communication [1] one could find values of stoichiometric stability constants for bromide and iodide complexes of thallium(I) cation in dilute halide/perchlorate solutions with varying halide concentration and constant overall ionic strength $\mu$. The constants were calculated on the basis of electromigration measurements of carrier-free radiothallium(I) 201Tl in Na(H)ClO_4 inert electrolytes. The electrophoretic method employed allowed well-reproducible experimental data exactly under those low overall ionic strength conditions when other methods yield relatively large errors for values of thallium(I) complex stability constants.

This paper continues investigations of monovalent thallium complexes. We have studied Tl(I) overall ion mobility $\bar{u}_{Tl(I)}$ in sulphate containing solutions with overall ionic strengthes $\mu$ less than 0.5. According to literature data, a thallium(I) sulphate anion [Tl(SO_4)]^- is formed in these solutions [2—11]. The value of its thermodynamic stability constant $K_1^0$ is in the interval from 10 to 100 l · mol^{-1}, according to the recent measurements [9]. Such a noticeable spread makes it desirable to carry out additional determinations of thermodynamic and stoichiometric stability constants of the thallium(I) sulphate complex, respectively.

## 2. Experimental

201Tl: The carrier-free radionuclide 201Tl acquired through the firm "Isotope" has been used for investigations. Prepa-

ration of the radiothallium sample for the experiments is described in ref. [1]. Radiothallium in stock solutions of $10^{-2}$ mol · l^{-1} HClO_4/$10^{-4}$ mol · l^{-1} N_2H_4 was injected into the migration cell. The injected volume was of about 1 to 3 μl.

*Electrolytes:* The overall ion mobility of radiothallium 201Tl-Tl(I) (migration rate at the voltage gradient 1 V · cm^{-1}) was determined at the temperature 298.1(1) K in solutions of background electrolytes Na(H)ClO_4 with constant or varying overall ionic strength $\mu$: $Na_2SO_4$/Na(H)ClO_4, $\mu = 0.1$, pH $\simeq 4$, and $Na_2SO_4/H_2SO_4$, $0.1 \leq \mu \leq 0.48$, pH 2 ... 2.5. In all electrolytes the presence of $10^{-4}$ mol · l^{-1} N_2H_4 stabilised radiothallium in the monovalent oxidation state.

Concentrations of sulphate ions at the given acidities were calculated with allowance for variation of dissociation constant $K = [SO_4^{2-}] \cdot [H^+] \cdot [HSO_4^-]^{-1}$, inversely proportional to the overall ionic strength of the solutions [12, 13].

All electrolytes are prepared with chemically pure agents and bidestilled water immediately before the experiments.

*Electromigration method:* Direct measurements of radiothallium ion mobilities were performed by means of a set-up developed in our laboratory. It allows carrying out on line electrophoresis in electrolytes free of finely devided inert fillers, at constant voltage gradients, temperature and chemical composition of background solutions [14, 15].

## 3. Results and discussion

The experimental results of overall ion mobilities $\bar{u}_{\mathrm{Tl(I)}}$ of radiothallium(I) in solutions of Na(H)ClO$_4$ background electrolytes with $\mu = 0.1$ and sulphate concentrations $\leq 3.33 \cdot 10^{-2}$ mol $\cdot$ l$^{-1}$ are shown in Fig. 1.

The $\bar{u}_{\mathrm{Tl(I)}}$ data decreased by approximately one third in the investigated interval of ligand concentrations, but it preserved its positive value, wich indicated formation of relatively weak thallium(I) sulphate complex.

When processing the experimental results we assumed, firstly, that in our case no thallium(I) disulphate complexes [Tl(SO$_4$)$_2$]$^{3-}$ exist. The assumption is based on the character of the function $\bar{u}_{\mathrm{Tl(I)}} = f([\mathrm{SO_4^{2-}}])$. Secondly, variation of perchlorate ion concentration in the electrolyte systems did not affect the ion mobilities of the Tl$^+$ cation, since neutral associates with ClO$_4^-$ are not very stable [16—18].
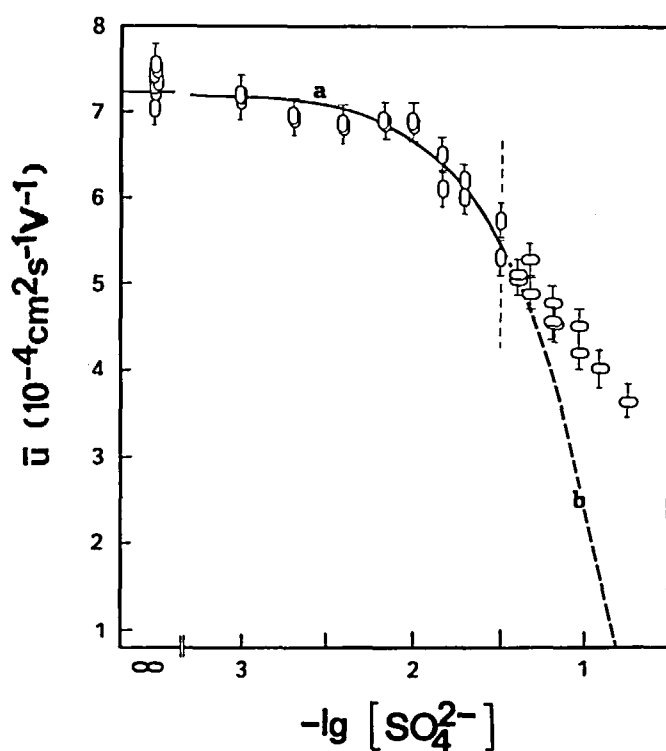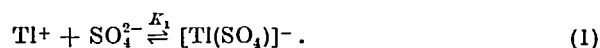


Fig. 1. Overall ion mobility of $^{201}$Tl-Tl(I) in solutions Na$_2$SO$_4$/Na(H)ClO$_4$, $\mu = 0.1$, pH $\simeq 4$ (a); Na$_2$SO$_4$/H$_2$SO$_4$, $\mu = 0.1 ... 0.48$, pH 2 ... 2.5 (b), $T = 298.1$ (1) K, $10^{-4}$ mol $\cdot$ l$^{-1}$ N$_2$H$_4$

So changes in the Tl(I) overall ion mobility are only due to the complex formation

$$\mathrm{Tl^+ + SO_4^{2-} \overset{K_1}{\rightleftharpoons} [Tl(SO_4)]^-} . \tag{1}$$

On the basis of reaction (1) one can formulate the function $\bar{u}_{\mathrm{Tl(I)}} = f([\mathrm{SO_4^{2-}}])$ in the following form:

$$\bar{u}_{\mathrm{Tl(I)}} = \frac{u_{\mathrm{Tl^+}}^0 + u_{[\mathrm{Tl(SO_4)}]^-}^0 \cdot K_1 \cdot [\mathrm{SO_4^{2-}}]}{1 + K_1[\mathrm{SO_4^{2-}}]} \tag{2}$$

where $u_{\mathrm{Tl^+}}^0$ is the individual ion mobility of the $^{201}$Tl-thallium(I) cation equal to $+7.3(3) \cdot 10^{-4}$ cm$^2$ s$^{-1}$ V$^{-1}$ in Na(H)ClO$_4$ electrolytes with $1.5 \cdot 10^{-3} \leq \mu \leq 0.5$ [1]; and $u_{[\mathrm{Tl(SO_4)}]^-}^0$ is the individual ion mobility of the complex anion of an unknown value. We took it equal to $-7(1) \cdot 10^{-4}$ cm$^2$ s$^{-1}$ V$^{-1}$, because similare experiments [19—21] showed that there are close absolute values for individual ion mobilities of charge $z = +1$ and $z = -1$ complex ions of one and the same central cation.

The stoichiometric stability constant $K_1^{0,1} = [[\mathrm{Tl(SO_4)}]^-] \cdot [\mathrm{Tl^+}]^{-1} \cdot [\mathrm{SO_4^{2-}}]^{-1} = 5.4(1)$ l $\cdot$ mol$^{-1}$ is calculated by Eq. (2) with the use of the least squares method in the MINUIT [22] program. The solid curve in Fig. 1 is calculated on the basis of the fitted parameter $K_1^\mu$ and $u_{\mathrm{Tl^+}}^0 = +7.2(1) \cdot 10^{-4}$ cm$^2$ s$^{-1}$ V$^{-1}$. Its good agreement with the experimental points can be considered as confirmation of our assumption on close absolute values of Tl$^+$ and [Tl(SO$_4$)]$^-$ individual ion mobilities. The thermodynamic stability constant of the thallium(I) sulphate complex $K_1^0$ was calculated by the Eq. (3)

$$K_1^0 = K_1^\mu \frac{\gamma_{[\mathrm{Tl(SO_4)}]^-}^\mu}{\gamma_{\mathrm{Tl^+}}^\mu \cdot \gamma_{\mathrm{SO_4^{2-}}}^\mu} . \tag{3}$$

Since activity coefficients $\gamma^\mu$ of the single-charged Tl(I) ions have close values at the same overall ionic strength in dilute electrolyte solutions, $\gamma_{[\mathrm{Tl(SO_4)}]^-}^\mu \simeq \gamma_{\mathrm{Tl^+}}^\mu$ is assumed. The activity coefficient of the sulphate ion for $\mu = 0.1$ is known: $\gamma_{\mathrm{SO_4^{2-}}}^{0.1} = 0.355$ [23]; then

$$K_1^0 = K_1^{0,1} \cdot [\gamma_{\mathrm{SO_4^{2-}}}^{0.1}]^{-1} = 15.2(3) \text{ l} \cdot \text{mol}^{-1} . \tag{4}$$

When processing the experimental overall ion mobility data of $^{201}$Tl-thallium(I) in sulphate containing solutions with $0.1 \leq \mu \leq 0.48$, Eq. (2) in the form of

$$K_1^\mu = \left\{ \frac{\bar{u}_{\mathrm{Tl(I)}} - u_{\mathrm{Tl^+}}^0}{u_{[\mathrm{Tl(SO_4)}]^-}^0 - \bar{u}_{\mathrm{Tl(I)}}} \right\} \cdot [\mathrm{SO_4^{2-}}]^{-1} \tag{5}$$

was applied.

Tab. 1. Stoichiometric ($K_1^\mu$) and thermodynamic ($K_1^0$) stability constants of the thallium (I) sulphate complex [Tl(SO$_4$)]$^-$; $T = 298.1$ (1) K

| [SO$_4^{2-}$] [mol $\cdot$ l$^{-1}$] | $\bar{u}_{\mathrm{Tl(I)}}$ [$10^{-4}$ cm$^2$ s$^{-1}$ V$^{-1}$] | $\mu$ | $a_{\mathrm{SO_4^{2-}}}$ [mol $\cdot$ l$^{-1}$] | $K_1^\mu(*)$ [l $\cdot$ mol$^{-1}$] | $K_1^0(**)$ [l $\cdot$ mol$^{-1}$] | $K_1^0(*)$ [l $\cdot$ mol$^{-1}$] |
|---|---|---|---|---|---|---|
| $\leq 3.33 \cdot 10^{-2}$ | — | 0.10 | — | 5.1 (1) (†) | 15.2 (3) | 16.7 |
| $3.0 \cdot 10^{-2}$ | +5.04 (16) | 0.10 | $1.1 \cdot 10^{-2}$ | 6.0 | 16.9 | 18.3 |
| $3.0 \cdot 10^{-2}$ | +5.10 (16) | 0.10 | $1.1 \cdot 10^{-2}$ | 5.8 | 16.4 | 17.8 |
| $3.9 \cdot 10^{-2}$ | +4.86 (16)$\cdot$ | 0.13 | $1.2 \cdot 10^{-2}$ | 5.1 | 16.0 | 17.4 |
| $3.9 \cdot 10^{-2}$ | +5.26 (17) | 0.13 | $1.2 \cdot 10^{-2}$ | 4.1 | 12.9 | 14.0 |
| $5.7 \cdot 10^{-2}$ | +4.76 (16) | 0.18 | $1.5 \cdot 10^{-2}$ | 3.6 | 13.9 | 15.1 |
| $5.7 \cdot 10^{-2}$ | +4.53 (16) | 0.18 | $1.5 \cdot 10^{-2}$ | 4.0 | 15.5 | 16.8 |
| $8.6 \cdot 10^{-2}$ | +4.50 (15) | 0.27 | $1.7 \cdot 10^{-2}$ | 2.7 | 14.1 | 14.6 |
| $8.6 \cdot 10^{-2}$ | +4.18 (15) | 0.27 | $1.7 \cdot 10^{-2}$ | 3.1 | 16.0 | 16.6 |
| $1.35 \cdot 10^{-1}$ | +4.00 (15) | 0.42 | $2.0 \cdot 10^{-2}$ | 2.1 | 14.3 | 16.0 |
| $1.57 \cdot 10^{-1}$ | +3.63(15) | 0.48 | $2.2 \cdot 10^{-2}$ | 2.1 | 15.7 | 18.0 |

symbols: (*) according to Eq. (5)
(**) according to Eq. (5) containing sulphate ion activities; means value $K_1^0 = 15.2$ (1.0) l $\cdot$ mol$^{-1}$
(*) according to Eq. (7); mean value $K_1^0 = 16.5$ (1.5) l $\cdot$ mol$^{-1}$
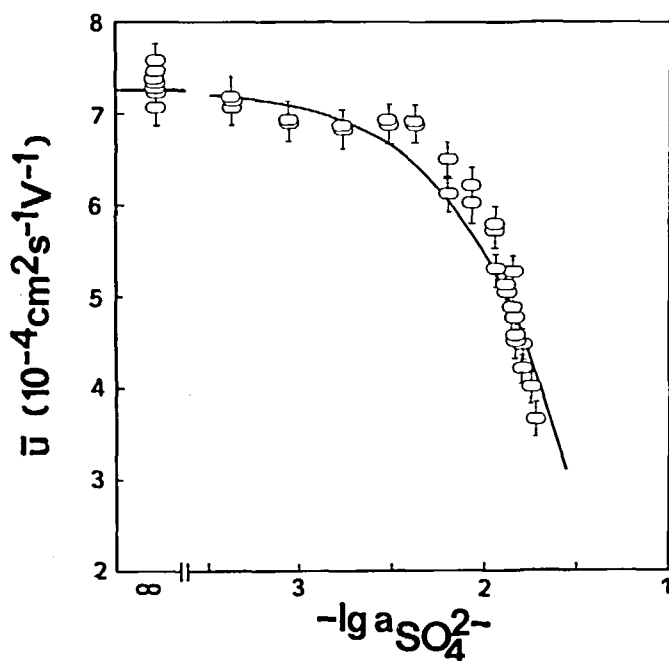(†) according to Eq. (2)

Fig. 2. Overall ion mobility of $^{201}$Tl-Tl(I) in sulphate containing solutions as a function of sulphate ion activity

$\mu = 0.1 \ldots 0.48$, $p$H $2 \ldots 4$, $T = 298.1$ (1) K, $10^{-4}$ mol·l$^{-1}$ N$_3$H$_4$

Value of $K_1^\mu$ inversely proportional to $\mu$ were obtained (Tab. 1).

This effect is evidently due to changing activities of sulphate ions ($a_{SO_4^{2-}}$) in the electrolytes. To determine $a_{SO_4^{2-}}$ in the solutions with known sulphate concentrations and overall ionic strengthes, sulphate activity coefficientes were approximated by Eq. (6) [24]:

$$\gamma_{SO_4^{2-}}^\mu = (\gamma_{Na_2SO_4}^\mu)^3 \cdot (\gamma_{Na^+}^\mu)^{-2} . \tag{6}$$

The values of $\gamma_{Na_2SO_4}^\mu$ and $\gamma_{Na^+}^\mu$ were obtained on the basis of known data [25] by their interpolation to the given values of $\mu$. Dependence of the $^{201}$Tl-Tl(I) overall ion mobility on the sulphate ion activity is shown in Fig. 2.

When sulphate ion concentrations are replaced by their activities in Eq. (5), the values of the thermodynamic stability constant become close to $K_1^0$ calculated by Eq. (4) (Tab. 1).

Final, the thermodynamic stability constant of the thallium(I) sulphate complex can be evaluated in a way different from the above one if one uses empiric equation (7) [26], extrapolating ($\mu$; $K_1^\mu$) data to hypothetical $\mu = 0$ solutions:

$$\lg K_1^0 = \lg K_1^\mu - \Delta z^2 A \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - D\mu \right) . \tag{7}$$

Here $\Delta z^2$ equals $-4$ for the complex formation considered, $A$ is the constant in the Debye-Hückel equation equal to 0.511, and the quantity $D$ calculated by us is equal to 0.26. The values of $K_1^0$ calculated by Eq. (7) are listed in Tab. 1. They are in satisfactory agreement with $K_1^0$ obtained from Eq. (4) and using sulphate activities in Eq. (5).

Thus, closeness of values of thermodynamic stability constants of thallium(I) sulphate complex obtained by three different methods of data processing allows, to our mind, a conclusion that mean value $K_1^0 = 15.7(1.0)$ l·mol$^{-1}$ calculated on the basis of electromigration measurements of the $^{201}$Tl-Tl(I) overall ion mobility in sulphate containing electrolytes is reliable.

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