Potential step chronoamperometry at hemispherical mercury electrodes: The formation of thallium amalgams and the measurement of the diffusion coefficient of thallium in mercury

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Abstract
Results for the measurement of the diffusion coefficients of Tl0 in a Tl/Hg amalgam (D_Hg), and Tl+ in 1.0 M KF aqueous solution (D_aq) are presented. The values of \( D_{Hg} = (1.2 \pm 0.1) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) and \( D_{aq} = (2.4 \pm 0.2) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) at 22 ± 1 °C are obtained by means of comparison of experimental deposition and stripping chronoamperometric transients with theoretical simulations for a 12.5 μm radius hemispherical mercury drop in which Tl is first deposited and then stripped.

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1. Introduction
In recent years, microelectrodes have become widely used due to their advantageous properties [1,2], and now play a significant role in electrochemical measurements [3]. In particular, these properties include: lower interfacial capacitance, smaller time constant, fast time responses and reduced ohmic drop. Consequently the experimental time scale is sufficiently short to measure many physico-chemical processes (notably kinetics and mass transport [2]), than was previously possible.

The thallium–mercury amalgam was first studied by von Wogau [4] in order to estimate the diffusion coefficients of thallium in mercury and in aqueous solution. Since then various studies have been carried out in order to obtain the diffusivities of thallium in both of these phases [5,6] using polarographic [5–8], chronoamperometric [9–12] and radiochemical methods [13,14]. The amalgam has been studied by several authors in order to study diverse physical and chemical properties such as adsorption effects [15,16], amalgam solidification [17], and bioelectrochemical applications [18]. The Tl/Hg system has been usually selected due to its simplicity, because thallium is highly soluble in mercury [19], and because Tl/Tl+ is a simple single electron transfer reaction.

In the experiments presented here a hemisphere was formed initially on the top of a platinum microdisk electrode by electrodepositing mercury. Two potential steps were then applied as shown schematically in Fig. 1. In the first step (from \( t_0 \) to \( t_a \)) an amalgam of Tl/Hg was formed by means of electrodepositing Tl into the mercury hemisphere, and in the second (from \( t_a \) to \( t_b \)) the thallium was stripped from the amalgam and the resulting chronoamperogram analysed by reference to computer simulation. For this work a hemisphere was the chosen geometry for the Hg electrode in order to simplify the simulation, since only one spherical coordinate is required to simulate this system (vide infra). The theory of this experiment is developed and it is shown how the diffusion coefficients for Tl+ in aqueous solution and Tl in mercury can be simultaneously determined by fitting theory to experiment.

2. Experimental section
All the solutions were prepared with ultra-pure water with a resistivity not less than 18.2 MΩ cm (at 25 °C) and degassed for 30 min with N2 (BOC, High purity oxygen free) before starting each experiment. All reagents were obtained commercially and were used without further purification.
2.1. Electrodes

The working electrode was fabricated in-house by sealing a 25 \( \mu \)m diameter Pt wire (Goodfellow, Cambridge, UK) into a Pyrex glass capillary [20]. Before each experiment the working electrode was polished with diamond spray of particle sizes of 3, 1 and 0.1 \( \mu \)m (Kemet, Maidstone Kent, UK). A silver wire was used as a pseudo-reference electrode for the Hg deposition experiments and a saturated calomel electrode (SCE) was the reference electrode for the thallium experiments. A platinum wire was used as a counter electrode (CE).

2.2. Mercury deposition

The hemispherical mercury drop on the Pt surface was deposited from a solution of 10 mM Hg2(NO3)2 (>97%, Aldrich) with 0.1 M KNO3 (99+%, Aldrich) as supporting electrolyte (acidified with 0.5% of HNO3), using a AutoLab Type III potentiostat (Eco Chemie, Netherlands) [21]. The mercury hemisphere was deposited at –0.25 V vs. Ag wire, and its size was controlled by the amount of charge deposited in the electrode in order to form a hemisphere (for a 25 \( \mu \)m diameter electrode the required amount of charge is 26.6 \( \mu \)C corresponding to 27.6 nmol). This was confirmed experimentally by measuring the limiting currents for the reduction of hexaammineruthenium (III), both before and after Hg deposition (i.e. at a microdisc and microhemisphere, respectively) and verifying that the ratio of these limiting currents was \( \pi/2 \) according to theory [2, 22].

2.3. Thallium deposition-stripping

After the Hg hemisphere deposition step, the electrode was washed in ultra-pure water. The electrode was placed in a solution of 0.02 M TlNO3 (99.999%, Aldrich), with 1 M KF (99%, Aldrich) supporting electrolyte [9] and two potential steps were applied. The first step to effect thallium deposition, was carried out at –0.75 V (vs. SCE), varying the time (from 0.05 s to 0.5 s) in each experiment (see Table 1), and a second potential step to eliminate (strip) thallium at –0.40 V (vs. SCE) for 0.4 s. The length of time in the TI stripping step exceeds the time that is required for the full elimination of TI in the amalgam by at least a factor of 5 (see experimental results). Due to the speed of the elimination process it was necessary to record each data point at the minimum instrumental acquisition time possible (in this case 0.5 ms).

![Fig. 1. Schematic diagram of the experiment showing the two potential steps: first for deposition of thallium of duration \( t_a \) second for the elimination of the thallium from the amalgam of duration \( t_b \).](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>TI Amounts deposited in the Hg hemisphere for the experiments performed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposited Ti (0.0 s)</td>
<td>Deposition time (( t_a )) (s)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>0.10</td>
<td>0.26</td>
</tr>
<tr>
<td>0.50</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Previous studies into the TI/Hg system have shown there are several distinct phases at ambient temperatures and pressures depending on the amalgam composition. At 40.5% (molar percentage) of TI, the amalgam becomes solid [17,19,23,24], and at 28.6% of TI a phase composition of TI2Hg5 has also been reported with solidification at 14.3 °C [19]. For this reason, care was taken to ensure that liquid amalgam contained <25% of TI at the temperature for our experiments (22 ± 1 °C), to ensure a fully liquid hemisphere.

3. Numerical simulation

This section describes the finite difference methods that are used to simulate the thallium deposition and stripping in the double potential step experiment. It is assumed that the mercury drop is hemispherical in shape with a constant radius \( r_e \). Two different species are modeled in these simulations: TI\(_{aq}\) in aqueous solution and TI\(_{o}\) which is only found within the mercury droplet. The diffusion of each species within their respective phases is described by Fick’s second law of diffusion in spherical polar coordinates:

\[
\frac{\partial [\text{TI}_{o}]}{\partial t} = D_{\text{Hg}} \frac{\partial^2 [\text{TI}_{o}]}{\partial r^2} - \frac{2 \partial [\text{TI}_{o}]}{\partial r},
\]

\[
\frac{\partial [\text{TI}_{aq}]}{\partial t} = D_{\text{aq}} \frac{\partial^2 [\text{TI}_{aq}]}{\partial r^2} + \frac{2 \partial [\text{TI}_{aq}]}{\partial r},
\]

where \( D_{\text{Hg}} \) is the diffusion coefficient of TI\(_o\) inside the mercury drop, and \( D_{\text{aq}} \) is the diffusion coefficient of TI\(_a\) in aqueous solution.

Before the potential step is applied, the concentration of aqueous TI\(_a\) is set equal to its bulk solution value at all points in solution, and the concentration of TI\(_o\) is set equal to zero throughout the mercury droplet.

In the first step of the experiment, TI\(_a\) is reduced to TI\(_o\) at the surface of the mercury drop. It is assumed that this happens at such a rate that the aqueous concentration of TI\(_a\) at the mercury surface is equal to zero. The following two boundary conditions are used to describe this process at \( r = r_e \):

\[
[\text{TI}_{aq}] = 0; \quad D_{\text{aq}} \frac{\partial [\text{TI}_{aq}]}{\partial r} = D_{\text{Hg}} \frac{\partial [\text{TI}_{o}]}{\partial r}.
\]

In the second step of the experiment, an oxidative potential converts TI\(_o\) in the mercury droplet back into aqueous TI\(_a\). This is described by the following boundary conditions at \( r = r_e \):

\[
[\text{TI}_{Hg}] = 0; \quad D_{\text{Hg}} \frac{\partial [\text{TI}_{Hg}]}{\partial r} = D_{\text{Hg}} \frac{\partial [\text{TI}_{o}]}{\partial r}.
\]

A boundary condition of zero flux is imposed at the center of the mercury droplet, \( r = 0 \):

\[
\frac{\partial [\text{TI}_{Hg}]}{\partial r} |_{r=0} = 0.
\]

The mass transport equations and the corresponding boundary conditions are solved using a Crank-Nicolson discretisation in conjunction with the Thomas algorithm to generate concentration profiles of the two species. The faradaic current, \( i \), is then found by the concentration gradient of TI\(_a\) at the mercury drop surface:
This calculated current is negative during the deposition phase and positive during the stripping phase. The simulation grid uses a high mesh density in the region of the mercury drop surface to achieve greater accuracy, and a lower mesh density at greater distances from the surface for greater efficiency. The simulation programme is tested for both spatial and temporal convergence by ensuring that an increase in the number of spatial or temporal nodes leads to a negligible change in the simulated current.

We note that the above problem has been solved analytically but approximately [25]. In the following section we compare simulation and approximate analytical theory with the experiment.

4. Results

The platinum microdisk electrode was immersed in the mercury solution, and sufficient current was passed in order to deposit a mercury hemisphere on the Pt. Then the electrode was cleaned and transferred to the Tl solution in which thallium was deposited by a potential step (vide supra) forming an amalgam. Once the desired amalgam concentration was reached (controlled by the deposition time), a second potential step was applied in order to strip the thallium from the amalgam (see Fig. 1). The double potential step chronoamperograms were recorded. The first chronoamperogram was integrated in order to obtain the actual Tl concentration and the stripping transient was then analysed in order to determine the mass transfer behaviour in the system, as in the amalgam, and the stripping transient was then analysed in order to determine the mass transfer behaviour in the system, as defined by the aqueous and mercury phase diffusion coefficients. This procedure was performed for deposition times ranging from 0.05 to 0.5 s. A simulation was then run with an initial set of values for the diffusion coefficients of Tl0 in the amalgam (D_Hg) and Tl+ in the solution (D_aq). The resulting chronoamperogram was then compared to experimental data and an absolute deviation given by

$$\text{MSAD} = \sum_{k=1}^{n} \frac{|i_{\text{exp}}(t_k) - i_{\text{theo}}(D_{\text{Hg}}, D_{\text{aq}}, t_k)|}{i_{\text{exp}}(t_k)}.$$ 

MSAD was calculated as the sum of the differences between each simulated point (i_{theo}) and each experimental point (i_{exp}). Here, t_k, k = 1, 2, 3, ..., N are the times of experimental data points under analysis. Each simulated chronoamperogram was therefore gives its own MSAD score, and D_Hg and D_aq were varied until a minimum MSAD was found corresponding to the optimum fit.

From previous literature studies for the diffusion coefficients for Tl0 diffusion in the Hg/Tl (ranging from 0.98 to 1.12 x 10^{-5} cm^2 s^{-1}) amalgam and for Tl+ in different electrolyte solutions (ranging from 1.74 to 2.00 x 10^{-5} cm^2 s^{-1}) are shown in the Table 2.

Fig. 2 shows typical comparisons between simulation, experimental and analytical results for deposition times of (A) 0.05 and (B) 0.1 s. The theoretical results are closely consistent with the experimental data in Fig. 2A; in Fig. 2B the analytical results show a small deviation due to the fact that they have been obtained by using Koutecky's approximation [25] (filled circles). In both cases the comparison between experiment and simulation shows excellent agreement. The best fit was obtained for D_{Hg} = (2.4 ± 0.2) x 10^{-5} cm^2 s^{-1} and D_{Hg} = (1.2 ± 0.1) x 10^{-5} cm^2 s^{-1}. These values of diffusion coefficient were consistent over the full range of deposition times studied. It was also found that the diffusion coefficients were independent of the amalgam concentration which is in good agreement with previous studies performed by Ma and Kao [10].

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Solution} & \textbf{Method} & \textbf{Reference} \\
\hline
0.98 Tl/Hg Amalgam & Polarography & [7] \\
0.99 Tl/Hg Amalgam & Polarography & [26] \\
1.03 Tl/Hg Amalgam & Chronoamperometry & [9] \\
1.05 Tl/Hg Amalgam & Polarography & [4] \\
1.12 Tl/Hg Amalgam & HMDE & [10] \\
\hline
\textbf{D_{Hg}} x 10^5 (cm^2 s^{-1}) & \\
\hline
2.00 0.5 M NaCl 0.01% gelatin & Polarography & [6] \\
1.96 0.1 M KNO_3 & HMDE & [27] \\
1.82 0.1 M KNO_3 & DME successive drops & [8] \\
1.99 0.1 M KNO_3 & DME successive drops & [11] \\
1.94 0.1 M KNO_3 & HMDE & [12] \\
1.74 1.0 M HClO_4 & RD & [13] \\
1.87 0.5 M KNO_3 & HMDE & [28] \\
1.83 0.1 M KCl & Polarography & [29] \\
\hline
\end{tabular}
\caption{Values of diffusion coefficients of Tl0 in the amalgam (D_{Hg}), and Tl+ in aqueous solutions (D_{aq}).}
\end{table}
For thallium in 1.0 M KF we find a value of $D_{aq} = (2.4 \pm 0.2) \times 10^{-5}$ cm$^2$ s$^{-1}$, compared with the value reported by West et al. [6] at 0.5 M NaF with 0.01% of gelatin of $D_{aq} = 2.00 \times 10^{-5}$ cm$^2$ s$^{-1}$. The value of the Tl diffusion coefficient in mercury of $D_{Hg} = (1.2 \pm 0.1) \times 10^{-5}$ cm$^2$ s$^{-1}$ is in excellent agreement with the literature values (Table 2).

Using these values for the diffusion coefficients concentration profiles were simulated for both inside and outside the hemisphere and for both deposition and stripping of the hemisphere in order to understand better the behaviour of the system.

4.1. Concentration profiles for thallium deposition and elimination

The simulated concentration profiles during the deposition are shown in Fig. 3A and B, which shows the concentration profiles for the Tl amalgam of 0.175 M (0.1 s of deposition). Figure A shows how the thallium concentration profile inside the mercury hemisphere develops over time. At very short times the Tl concentration is limited to the surface region of the hemisphere, but rapidly diffuses inwards. Figure B presents the time-evolution of the Tl$^+$ concentration in the aqueous media showing that at distances bigger than 3 radii from the surface of the electrode the concentration remains effectively the same.

The simulated concentration profiles for the Tl stripping are shown in Fig. 3C and reveal the speed of the stripping: in less than 0.03 s more than the 90% of the total Tl amount in the amalgam is stripped and in 0.1 s more than the 99% of the amalgam is stripped from the Hg hemisphere.

Fig. 3D shows the concentration profiles in the aqueous phase for different times. It is observed that at very short times the concentration profile falls sharply from a high thallium concentration to almost zero in less than 0.2 radii. As time increases the decreasing surface concentration of Tl and the increasing solution concentration of Tl$^+$ leads to a lower concentration gradient such that after ca. 0.1 s the Tl$^+$ concentration is almost constant over distances of 3 radii from the hemisphere surface.

5. Conclusions

It has been shown by comparison of the theoretical results with the experimental data that anodic elimination of thallium from the thallium-mercury amalgam in 1.0 M of KF behaves as a purely diffusional mass transport system. The diffusion coefficients $D_{Hg}$ and $D_{aq}$ have been determined simultaneously and are found to be in good agreement with literature values.

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