Use of EQCM in a study of thallium(I) electrosorption on mercury

Vytautas Daujotis* and Aušra Teišerskienė

Department of General and Inorganic Chemistry, Vilnius University, LT-2734 Vilnius, Lithuania

EQCM and cyclic voltammetry data present additional evidence for a full, not partial, charge transfer during electrochemical adsorption/desorption of thallium(I) ions onto/from the surface of mercury electrode. In the potential region, where the mercury surface is positively charged, thallium(I) ions are reduced directly from the solution. Thallium(I) ions that are adsorbed in the region of the positive surface charge, most probably in the form of the ionic pairs, are not reduced. At more negative potentials the previously adsorbed stable ionic pairs slowly undergo transition into a less stable form. From this form, thallium(I) ions can be reduced or desorbed into the solution.

Key words: thallium ions, mercury, adsorption, EQCM

INTRODUCTION

The one-electron redox couple thallium(I)/thallium (mercury) is considered as simple as possible. Actually, the analysis of this system is complicated by adsorption of the reactant – thallium ions. Frumkin and Titievskaya [1] established the specific adsorption of thallium ions from the potential shift of the maximum of the electrocapillary curve of mercury in the positive direction. There is still a disagreement whether thallium is adsorbed prior to charge transfer (or full charge transfer occurs during adsorption) [2–4] or its adsorption is followed by the partial charge transfer [5–9]. Lorenz [8, 9], who introduced the model of microscopic partial charge transfer into the theory of electrode reactions, stressed that this reaction was the first example which allowed a complete evaluation of partial charge transfer.

It has been shown by Frumkin et al. [2] that the Gibbs adsorption of thallium ions, Γ, with the partial charge transfer number λ is, from the thermodynamic viewpoint, equivalent to co-adsorption of $(1-\lambda)$ Γ thallium(I) ions and $\lambda\Gamma$ neutral thallium atoms with a concomitant increase of the free charge of electrode surface by the quantity $\lambda\Gamma$. This approach was used to calculate Lorenz's coefficients λ_1 and λ_2 from thermodynamic data [3]. The values obtained were close to those obtained by Lorenz from impedance measurements. However, according to Frumkin they are just formal charge transfer coefficients, whereas according to Lorenz these values are actual (microscopic) charge transfer coefficients. Frumkin et al. [2] interpreted the experimental data of the surface tension of thallium amalgams on the basis of Lippman's equation for reversible redox systems. According to this interpretation, both the surface excess of thallium(I) ions in the solution and of thallium atoms in the metal phase are of essential importance. When the chemical potential of thallium atoms is increased, the surface excess of thallium atoms passes through a maximum, then decreases and becomes negative. Due to the resulting dipole moment in the surface layer of the metal phase, the change of the surface free charge is not monotonous when the potential shifts in the negative direction. This results in three separate potentials of the zero free charge [2]. Later, a similar change of the surface excess of thallium atoms in metal phase was confirmed by Koene et al. [10]. Blankenborg et al. [4] also started with the idea that not only the thallium(I), but also thallium in the amalgam adsorbs to a significant extent. It was found that ignoring the existence of reactant adsorption in analysing admittance data the finite charge transfer rate is easily overlooked, whereas in analysing demodulation voltammetry data this will generally lead to incorrect charge transfer parameters [4].

In the microscopic treatment of amalgam forming electrode reactions, Koper and Schmickler [12] did not include this kind of treatment for metal amalgamation process, as its physics is very poorly

understood. Instead, they suggest using the appropriate Born–Haber cycle at the equilibrium potential in order to decide whether the amalgamation step is rate-limiting or not. The potential energy surface calculated predicts partial charge transfer. However, this prediction is based on a theory that is rather empirical. A lot of assumptions are made when the Anderson model is applied [12].

Actually, to differentiate between the partial charge transfer across the interface and the formation of image charges in metal is still not feasible in general. The purpose of the present work was to use electrochemical quartz microbalance for measurement of the formal charge transfer coefficient, to examine the assumptions and results obtained in the studies of thallium(I)/mercury system.

EXPERIMENTAL

To the best of our knowledge, the EQCM with a working liquid mercury electrode has not been used for quantitative studies of monolayer adsorption. The method of preparation of mercury-coated EQCM, suitable for quantitative measurement of adsorbed mass, and the technique used are described in detail by us elsewhere [12]. Mercury was electrodeposited on platinum, the geometric area of which was 0.385 cm². The sensitivity of the mercury-coated EQCM was equal to $9.25 \pm 0.05 \ 10^{-9}$ g Hz^{-1} [11]. The Ag|AgCl|KCl$_{sat}$ reference electrode was placed into an isolated compartment to avoid contamination by chloride ions. More details are presented in ref. 12.

Ten measurements of frequency per second were made with an accuracy of 0.1 Hz. Every EQCM and voltammetric measurement was repeated four times. The time interval between the repeated measurements was no less than 5 min. During this time the potential applied to the working electrode (+100 mV $vs.$ Ag|AgCl|KCl$_{sat}$) was positive enough to remove the traces of dissolved thallium from the mercury film. The averaged and background-corrected data are presented without additional smoothing. For background correction, blank solution current and frequency responses were simply subtracted from those measured in the presence of thallium(I).

Solutions were prepared in triply-quartz-distilled water using the reagents: doubly-distilled HClO$_4$ (72%), KClO$_4$ (three times re-crystallized from reagent grade), TlClO$_4$ (prepared by dissolving metallic thallium (99.99%) in perchloric acid medium, then four times re-crystallized), Pb(ClO$_4$)$_2$ (prepared by dissolving PbO (pure for analysis) in perchloric acid and then twice re-crystallized). Argon (99.99%) was passed through the cell prior to each experiment.

RESULTS

From the background-corrected current (curve 1 in Fig. 1a) and frequency response (curve 2 in Fig. 1a) the charges Q_e and Q_m were calculated and plotted against each other (Fig. 1b). Q_e was calculated from the current by numerical integration. When calculating Q_m the change of electrode mass was calculated from frequency change via the Sauerbrey equation and then the charge via Faraday's law. In the later calculation, the number of electrons participating in charge transfer was assumed to equal unity, and that gave the total surface coverage measured in charge units. Linear dependence of Q_e on Q_m with a slope equal to unity is observed at the charges higher than ~–50 µC (Fig. 1b). This value corresponds to –0.5 … –0.55 V $vs.$ Ag|AgCl|KCl$_{sat}$. In the potential region more negative than –0.55 V, for all polarographic waves, both cathodic and anodic, the formal number of charge transfer is equal to one. Such a coincidence shows that the number of electrons participating in charge transfer is equal to one. The current and frequency changes are linear with the bulk concentration of thallium ions.
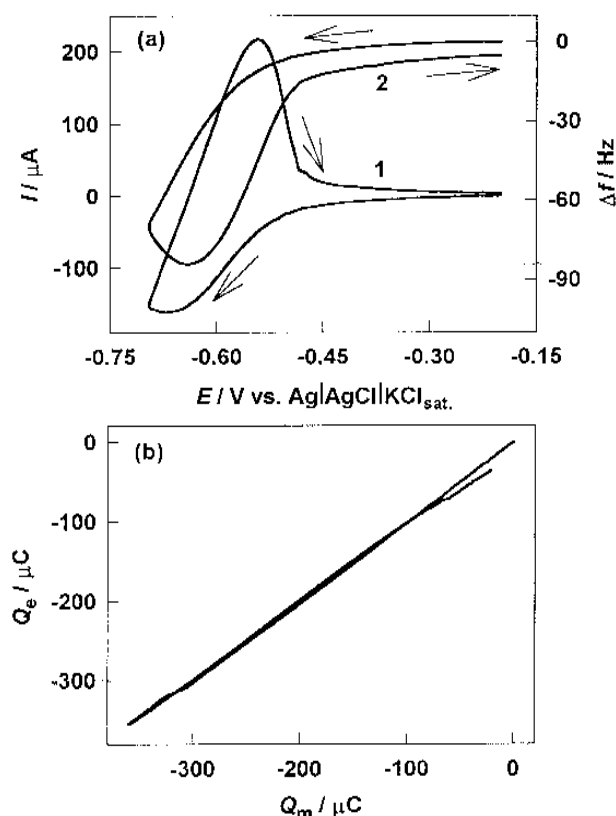

Fig. 1. (*a*): Cyclic voltammogram (*1*) and frequency response (*2*) for a mercury electrode recorded at 80 mV s^{-1} in 1 mM TlClO$_4$ + 0.1 M KClO$_4$; (*b*): plot of the charge calculated from the cyclic voltammogram, Q_e, $vs.$ the total surface coverage calculated from the full cycle of frequency response, Q_m
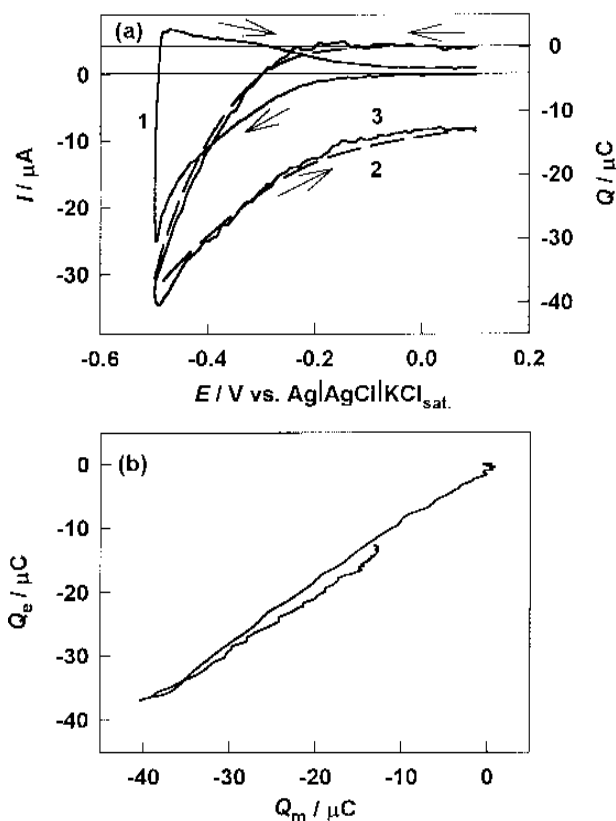
Fig. 2. (*a*): Cyclic voltammogram (*1*), $Q_e(E)$ (*2*, dashed line) and $Q_m(E)$ (*3*) isotherms, obtained from the cyclic voltammograms and from the full cycle of frequency response for a mercury electrode recorded at 80 mV s^{-1} in 1 mM TlClO$_4$ + 0.1 M KClO$_4$; (*b*) plot of Q_e, *vs.* Q_m (both from (*a*))

The cyclic voltammogram obtained at potentials less negative than –0.5 V is rather asymmetrical with respect to the potential axis, curve 1 in Fig. 2a. The symmetry does not depend on the potential scan rate (20, 40, 80 and 160 mVs^{-1}). There is only a negligible dependence of the charge consumed and the change of the mass of electrode on thallium(I) bulk concentration (1, 2.8, and 5 mM). This is typical for an adsorption-limited **reaction where adsorption occurs onto the unoccupied sites of the surface**.

A common feature observed in Figs. 2–4 is an almost full coincidence of the charge consumed, Q_e, and the charge calculated from the change of the mass of electrode, Q_m, when the potential is scanned in the negative direction. It gives the formal charge transfer number, $l_{Tl} = (dQ_e/dQ_m)_E$, close to unity.

A different behaviour is observed when the potential scan is reversed in the positive direction. The coincidence of Q_e and Q_m is still observed for the potential scan rate 80 mV s^{-1} (Fig. 2a), but the derivative $(dQ_e/dQ_m)_E$ calculated from the data pre-

sented in Fig. 2b is slightly less than one (approximately 0.89). Decreasing the potential scan rate (Figs. 3 and 4) results in more drastic changes. Scanning the potential from –500 mV to –250 mV results in formal charge transfer numbers equal to 0.72 and 0.65 (slopes of curves in Figs. 3b and 4b) for scan rates 40 and 20 mV s^{-1}, respectively.

After a full potential scan cycle is completed, the final values of Q_e and Q_m do not coincide with their values at the start of scan. This shows that after anodic scan the system is not yet at equilibrium. Experimental observations support the latter statement. At the stop potential both Q_e and Q_m vary in time by several minutes until they reach the initial values. It should be emphasized that the voltammograms are not stabilized, because only one potential scan cycle is performed. The diffusion gradients of electroactive species appear not only in the solution, but also in the amalgam (thallium atoms). When several potential scan cycles are per-
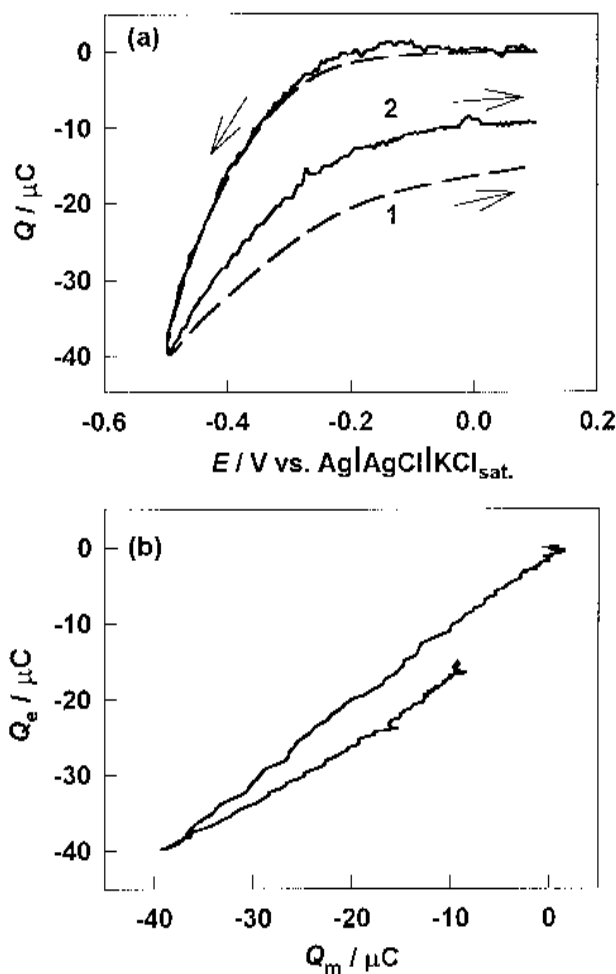

Fig. 3. (*a*): $Q_e(E)$ (*1*, dashed line) and $Q_m(E)$ (*2*) isotherms for a mercury electrode recorded at 40 mV s^{-1} in 1 mM TlClO$_4$ + 0.1 M KClO$_4$; (*b*) plot of Q_e, *vs.* Q_m (both from (*a*))

Fig. 4. (a): $Q_e(E)$ (*1*, dashed line) and $Q_m(E)$ (*2*) isotherms for a mercury electrode recorded at 20 mV s^{-1} in 1 mM TlClO$_4$ + 0.1 M KClO$_4$; (*b*) plot of Q_e, *vs.* Q_m (both from (*a*))
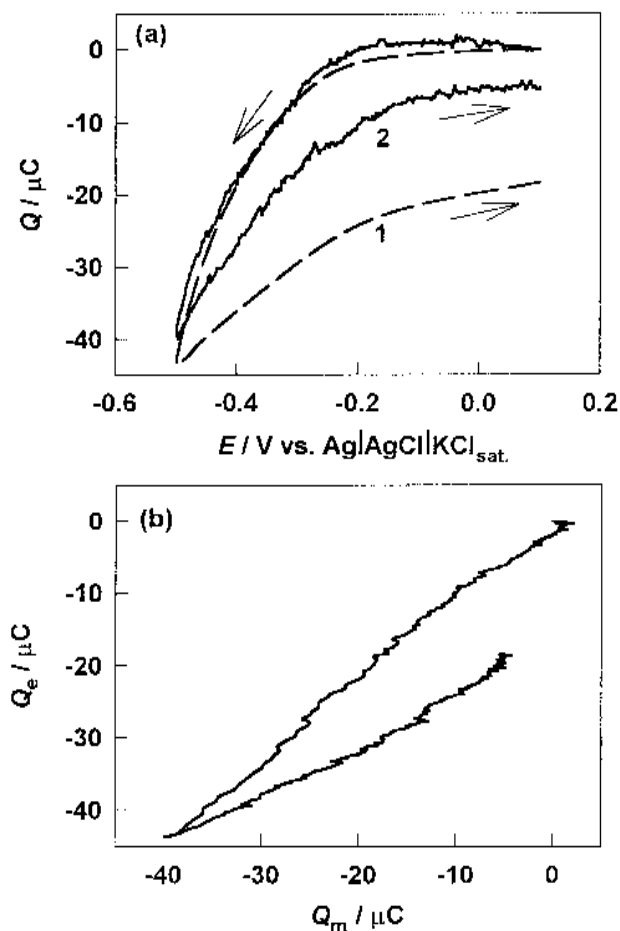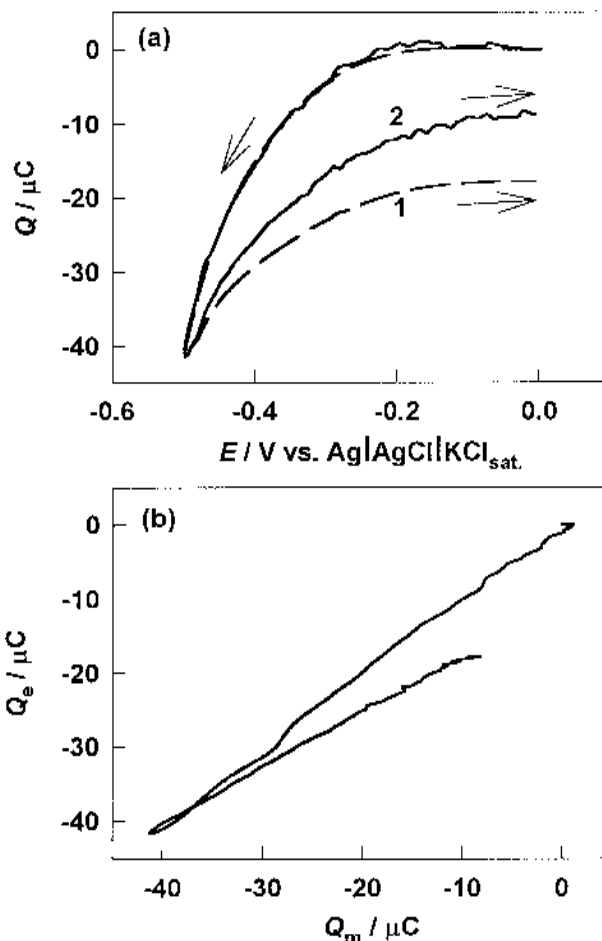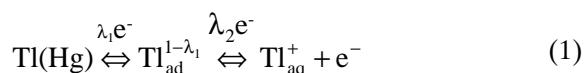
Fig. 5. (*a*): $Q_e(E)$ (*1*, dashed line) and $Q_m(E)$ (*2*) isotherms for a mercury electrode recorded at 80 mV s^{-1} in 2.8 mM TlClO$_4$ + 0.1 M KClO$_4$; (*b*) plot of Q_e, *vs.* Q_m (both from (*a*))

formed, these gradients are stabilized and the stabilized voltammogram is obtained. Increasing thallium(I) bulk concentration results in the appearance of a difference between Q_e and Q_m during positive potential scans even at 80 mV s^{-1} (Fig. 5a). This difference becomes smaller when the scan rate is increased. Thus, the effect due to an increase of thallium(I) bulk concentration is similar to that appearing during the decrease of the potential scan rate.

DISCUSSION

According to Lorenz and Salié [5–9], the process in the system thallium(I)/mercury can be written as

$$\text{Tl(Hg)} \overset{\lambda_1 e^-}{\Longleftrightarrow} \text{Tl}_{ad}^{1-\lambda_1} \overset{\lambda_2 e^-}{\Longleftrightarrow} \text{Tl}_{aq}^+ + e^- \tag{1}$$

where $\lambda_1 \approx 0.6$ and $\lambda_2 \approx 0.4$ from impedance and chronoamperometric analysis. The change of the mass of electrode occurs only due to the second

part of the equation (1). The formal charge transfer number measured by EQCM can be of unity value when the rates of both consecutive steps are equal (the surface concentration of $\text{Tl}_{ad}^{1-\lambda_1}$ is constant). This is hardly possible when the potential is changed. The unity value of the formal charge transfer coefficient, obtained during the negative potential scan (Figs. 2–5), is in contradiction with the reaction (1). One can argue that some other processes distort EQCM measurements, but then the unity value obtained must be considered accidental. This is hardly possible, either.

Our EQCM data presented above provide some additional evidence for the model which does not include partial charge transfer. The main seems to be the unity value during the negative potential scan. Our measurements were performed in perchlorate solution. A comparison of our data with those obtained in nitrate solution [2] is reasonable, because the electrocapillary properties of the mercury elec-

trode surface are close in both solutions. For example, the pzc of the mercury electrode is close to –470 mV *vs*. Ag|AgCl|KCl$_{sat}$ both in perchlorate and in nitrate solution. Similarly to the nitrate solution [2], in the potential range corresponding to the region of the positive free charge of the surface the adsorbed thallium(I) ions should be bound with adsorbed perchlorate, forming ionic pairs Tl$^+$–ClO$_4^-$ or polar TlClO$_4$ molecules.

The data obtained in this work fit the model presented by Frumkin et al. [2, 3]. In this model, the explanation of the regularities of the absorption of thallium(I) ions was based: first, on the possibility of the formation of ionic pairs in the potential region of the positive free charge of mercury surface and, second, on the non-monotonic change of the surface free charge due to a change of the surface excess of thallium atoms in the metal phase. The formation of ionic pairs thalium(I)–nitrate in the potential region of the positive free charge of mercury surface was already proved by Delahay et al. [13]. Later other authors also reported an increase of the double layer capacitance caused by adsorption of thallium(I) ions on mercury in the presence of various anions; this is mainly determined by the interaction between thallium(I) ions and the anions adsorbed on the mercury surface [14].

As follows from the data presented in Figs. 2–5, during the negative potential scan the previously adsorbed thallium(I) ions are rather stable in these ionic pairs. There is no other explanation for the coincidence between the change of electrode mass, Q_m, and the charge consumed, Q_e, except that the reduction of thallium(I) ions occurs only directly from the solution.

Analysis of the electrocapillary curves presented in ref. 6 shows that for the system investigated in this work the maximum of the electrocapillary curve should be positioned at approximately –370 mV *vs*. Ag|AgCl|KCl$_{sat}$. When the potential passes through the pzc during the potential scan in the negative direction, the previously adsorbed and stable ionic pairs probably undergo transition into a less stable form. Further corroboration is needed in order to assume the model of this form.

When the scan rate is lower and reversed to the positive direction, it should be assumed that the backward re-orientation of adsorbed thallium(I) ions into the stable form does not take place in the time scale of the potential scan to the positive direction. The more rapid change of Q_m, when compared with Q_e, can be explained by the desorption of thallium(I) ions from the less stable form of adsorbed thallium(I).

The above consideration is supported by the measurements performed in the solutions with a higher content of thallium ions. An increase of thallium(I) bulk concentration results in the shift of the potential of the electrocapillary curve maximum to the positive direction [2]. Consequently, the potential region of the negative free charge of the surface is extended. Then the higher potential scan rates are needed to avoid the transition of the previously adsorbed stable form of thallium(I) into a less stable form and, consequently, to avoid the desorption of thallium(I) ions from mercury surface. Thus, for 1 mM thallium(I) concentration, a potential scan rate of 80 mV s^{-1} is sufficient to sustain the coincidence between Q_m and Q_e (Fig. 2), but this rate is not sufficient enough to sustain such a coincidence in the case of increased thallium(I) bulk concentration, 2.8 mM (Fig. 5).

The Sluyters group confirms that the adsorption of thallium(I) ions on mercury surface takes place. Also, they have shown that no distinction can be made as to whether the reaction proceeds via the adsorbed or via the non-adsorbed Tl$^+$ species; at the present level of understanding we must consider the two processes, charge transfer and reactant adsorption, as occurring independently, although they are coupled, because they share the mass-transfer flux to and from the electrode-solution interface [15]. It should be emphasized that such a distinction cannot be made when classical electrochemical (voltammetric) means are used. The use of EQCM can help in making such a distinction, because it is possible to evaluate from the simultaneously measured electrode mass change and the charge consumed whether the adsorbed species are discharged or the species are discharged directly from the solution. The data presented in this paper confirm the assumption that under the conditions specified in this work charge transfer and reactant adsorption can occur independently.

CONCLUSIONS

The stable form of adsorbed thallium ions, evidently in the form of ionic pairs between thallium(I) and perchlorate ions, is slowly formed at the potentials corresponding to the potential region of the positive surface free charge. In this potential region, thallium(I) ions are reduced directly from the solution with a transfer of one electron. In the potential region of the negative surface charge, the adsorbed stable ionic pairs slowly undergo transition into a less stable form. From this form, thallium(I) ions can be reduced during the further negative potential scan or desorbed into the solution during the positive potential scan.

References

1. A. Frumkin and A. Titievskaya, *Zh. Fiz. Khim*. **31,** 485 (1957).
2. A. N. Frumkin, N. S. Polianovskaya and B. B. Damaskin, *J. Electroanal. Chem*., **39**, 123 (1972).
3. N. Polianovskaya, B. Damaskin and A. Frumkin, *J. Electroanal. Chem.*, **73**, 267 (1976).
4. S. G. J. Blankenborg, M. Sluyters-Rechbach and J. H. Sluyters, *J. Electroanal. Chem.*, **401**, 3 (1996).
5. G. Salié and W. Lorenz, *Z. Phys. Chem. N.F.* **29**, 408 (1961).
6. G. Salié, *J. Electroanal. Chem*. **447**, 211 (1998).
7. G. Salié, *ACH-Models in Chemistry*, **137**, 165 (2000).
8. W. Lorenz, *J. Electroanal. Chem*., **80**, 1 (1977).
9. W. Lorenz, *J. Phys. Chem*., **95**, 10575 (1991).
10. L. Koene, M. Sluyters-Rechbach. and J. H. Sluyters, *Russ. J. Electrochem*., **31**, 736 (1995).
11. M. T. M. Koper and W. Schmickler, J. Electroanal. Chem., **450**, 83 (1998).
12. V. Daujotis, C. Klingenberg and A. Teišerskienė, *Anal. Chim. Acta*, **419**, 243 (2000).
13. G. Susbielles, P. Delahay and E. Solon, *J. Phys. Chem*., **70**, 2601 (1966).
14. M. I. Bellavance and B. Miller, in *Encyclopedia of Electrochemistry of Elements: Thallium*, vol. 4 (ed. A. J. Bard), New York 1972, p. 179.
15. S. G. J. Blankenborg, M. Sluyters-Rechbach and J. H. Sluyters, *J. Electroanal. Chem*., **349**, 255 (1993).

V. Daujotis, A. Teišerskienė

EKKM NAUDOJIMAS TIRIANT TALIO(I) JONŲ ELEKTROLITINĘ SORBCIJĄ ANT GYVSIDABRIO

S a n t r a u k a

Taikant EKKM ir ciklinės voltamperometrijos metodus parodyta, kad talio(I) jonų elektrocheminė adsorbcija/desorbcija ant/nuo gyvsidabrio elektrodo paviršiaus vyksta esant visam (ne daliniam) krūvio pernešimui. Potencialų srityje, kurioje gyvsidabrio paviršiaus krūvis yra teigiamas, talio(I) jonai redukuojami tiesiogiai iš tirpalo. Talio(I) jonai, adsorbuoti jonų porų pavidalo teigiamų paviršiaus krūvių srityje, neredukuojami. Esant neigiamesniems potencialams, anksčiau adsorbuotos stabilios jonų poros lėtai transformuojasi į mažiau stabilią formą. Iš šios formos talio(I) jonai gali redukuotis arba desorbuotis į tirpalą.