

# Effect of anions on the underpotential deposition of thallium(I) on polycrystalline silver

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## Abstract

Underpotential deposition (upd) of thallium(I) on a polycrystalline silver surface in solutions containing specifically adsorbing anions (sulphate and chloride) has been studied by voltammetry and the electrochemical quartz crystal microbalance (EQCM). The specific adsorption of thallium cations on the silver surface at potentials positive with respect to the pzc appears to be enhanced by the specific adsorption of anions. This leads to ion pair formation between the specifically adsorbed thallium cation and anion even at potentials positive with respect to the upd region. The decrease in the upd shift is explained by the fact that additional energy is required to break the bond between the formed pair. The electrode mass change measured by EQCM is smaller due to the discharge of thallium cations from the adsorbed ion pairs. The agreement between voltammetric and EQCM data is observed in the potential region close to the bulk thallium deposition where the adsorption of anions is weak and, consequently, there is little formation of ion pairs. The effect of sulphate and chloride anions on the thallium upd process is in accordance with their adsorbing strength. It seems very likely that this scheme can be applied when other upd processes in strongly adsorbing anions containing solutions are considered. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Thallium upd; Silver electrode; Anion effect

## 1. Introduction

In this paper we describe our results for an anion effect on the underpotential deposition (upd) of thallium(I) on polycrystalline silver obtained by using the electrochemical quartz crystal microbalance (EQCM). Reinvestigation of this system was motivated by several mismatches between the results reported in the electrochemical literature. By using voltammetry and EQCM Yang and Furtak [1] observed an anomaly in the upd of thallium(I) on polycrystalline silver. According to their results, while the measured mass change is consistent with the expected value, each thallium ion seems to contribute approximately two charges upon adsorption before the completion of the first upd layer instead of

one. In the second upd layer the effective charge transfer corresponds to 1 electron. Klimmeck and Jüttner [2] reported the difficulties in the interpretation of the impedance behaviour of thallium adsorption on Ag(100) and Ag(110) single crystal surfaces. Assuming a simple reaction model for the interpretation of the electrode impedance, namely a sorption reaction connected with a metal ion transfer accompanied by diffusion, they found a double layer capacity ranging up to 270  $\mu\text{F cm}^{-2}$ , which is much higher than normally found for the double layer capacity. In addition, the exchange current density values found are much lower than given in the literature.

In the experiments discussed above, the supporting electrolyte solutions were mainly acidified sodium sulphate solutions. Although an ideal charge stoichiometry of thallium monolayer adsorbate, indicating the absence of anion adsorption, has been reported [3], it

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seems worthwhile to study the anion effect in more detail by EQCM.

## 2. Experimental

Voltammograms and electrode frequency changes were measured simultaneously by using a quartz supported silver electrode. The quartz crystals used here were 5 MHz AT-cut of 15 mm diameter and 0.3 mm thickness from the Institute of Mineral Substances Synthesis, Aleksandrovo City (Russia). Silver electrodes were vacuum deposited onto both sides of the quartz crystal. The circular silver region in the centre of the crystal has a diameter of 6 mm. The quartz supported working electrode was placed into a holder between two silicone rubber packing rings and fixed vertically to the hole at the side of a water-jacketed ( $25 \pm 0.1^\circ\text{C}$ ) three-electrode electrochemical cell. A platinum plate was used as a counter electrode. A  $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$  reference electrode was placed in an isolated compartment to avoid contamination by chloride ions. All potentials were measured relative to this electrode. The separate thallium electrode made of platinum wire electroplated by thallium was used to measure  $\text{Tl}/\text{Tl}^+$  equilibrium potentials. The instrumentation used for voltammetric and frequency measurements is described previously [4,5]. Depending on the potential sweep rate, the current and frequency sampling rate was from 5 to  $89 \text{ s}^{-1}$ . The accuracy of the frequency sampling was greater than 0.1 Hz.

To display the correlation between the mass change ( $\Delta m$ ) and the measured voltammograms, a predicted current intensity ( $I_m$ ) can be calculated from the observed mass change which is obtained from the measured frequency changes ( $\Delta f$ ) [1,6]:

$$\Delta m = -\Delta f [2f_0^2 A^{-1} (\mu_q \rho_q)^{-1/2}]^{-1} \quad (1)$$

$$I_m = -lFM^{-1} d(\Delta m)/dt \quad (2)$$

where  $f_0$  is the fundamental frequency of the quartz crystal,  $A$  is the piezoelectrically active area,  $r_q$  and  $m_q$  are the density and the shear modulus of quartz respectively;  $F$  is the Faraday constant,  $M$  is the molar mass of the electrodeposited material and  $l$  is the formal (or macroscopic) partial charge number (for a full discharge this number is equal to the valence number  $z$ ). The term ‘electrosorption valency’ and a different symbol ( $\gamma$ ) have also been suggested for the quantity denoted by  $l$ . The concept of electrosorption valency is widely used now but in our work we follow the IUPAC recommendations [7]. We reserve the term ‘electrosorption valency’ for the actual microscopic partial charge number which can be obtained only on the basis of some model assumptions. As a first approach,  $l$  is assumed to be equal to 1 for upd of thallium(I) on

silver. Assuming that the piezoelectrically active area is equal to the electrochemically active geometric area ( $0.25 \text{ cm}^2$ ) the sensitivity of the EQCM (the value in the square brackets of Eq. (1)) was calculated to be equal to  $4.6 \times 10^{-9} \text{ g Hz}^{-1}$ . The sensitivity was also measured by electrodepositing silver from silver perchlorate solution. The latter value, equal to  $5.6 \times 10^{-9} \text{ g Hz}^{-1}$ , has been used in all calculations.

The measured voltammograms shown in the figures of this paper are background corrected, i.e. in parallel the voltammograms were measured in blank solutions and these current values are subtracted from those presented in figures. In further consideration, the current from the voltammogram is denoted by  $I_e$ .

Solutions were prepared in triply-distilled water using the reagents: doubly-distilled  $\text{HClO}_4$  (72%) and  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  (ultrahigh purity),  $\text{Tl}_2\text{SO}_4$  (four times re-crystallized from reagent grade) and  $\text{TlClO}_4$  (prepared by reducing  $\text{Tl}_2\text{O}_3$  with  $\text{H}_2\text{O}_2$  in perchloric acid medium, then four times re-crystallized). Prepurified nitrogen was bubbled through the cell prior to each experiment.

## 3. Results

### 3.1. Adsorption of thallium on silver from acidic sulphate media

By changing the bulk concentration of thallium ions in the range from 0.18 mM to 0.1 M a series of voltammograms and the corresponding frequency responses of the quartz supported silver electrode were obtained from a solution of  $X \text{ M Tl}_2\text{SO}_4 + 0.1 \text{ M Na}_2\text{SO}_4 + 1 \text{ mM H}_2\text{SO}_4$ . The measurements in each solution were performed using eight different potential scan rates from 5 to  $100 \text{ mV s}^{-1}$  in order to check the scan rates when the thallium upd process can be assumed to be in equilibrium. The potential scan rates of 5 and  $10 \text{ mV s}^{-1}$  were found to satisfy this condition. These data agree with those earlier reported [1,3]. Therefore, the data obtained in this work are presented only for the potential scan rate of  $10 \text{ mV s}^{-1}$ .

The data displayed in Fig. 1 exemplify the two most important phenomena observed in the above series of measurements. First, the curves from Fig. 1a exactly reproduce the results obtained by Tang and Furtak [1], such that in the potential region of the first thallium monolayer formation (adsorption/desorption peaks  $A_1$ ,  $A_2/D_1$ ,  $D_2$ )  $I_e$  is twice (and more) as large as  $I_m$  although both of them reveal the same variation with the potential. Second, at higher bulk concentrations of thallium cations even this similarity disappears. At some potentials  $I_m$  drops to zero (Fig. 1b) whereas the voltammograms ( $I_e$ ) in Fig. 1a and b do not demonstrate any significant changes except the shift of the potentials. The results obtained are not in contradiction

with those obtained by Tang and Furtak [1] who have used 10 mM concentration of thallium cations and lower. In this range our results are the same as reported by them. It should be emphasized that at the end of the first monolayer formation (adsorption/desorption peaks  $A_3$ ,  $A_4/D_3$ ,  $D_4$ ) and at more negative potentials (second monolayer formation) a full coincidence of  $I_m$  with  $I_c$  has been observed independently of the concentration of thallium cations.

From the voltammograms measured, the so-called formal partial charge numbers for thallium adsorption on silver can be calculated assuming, as a first approach, that the  $I_c$  variation with the potential represents the thallium adsorption. Another assumption has been that the surface coverage is constant at the potentials of adsorption/desorption peaks. This assumption is related to the first one and at the same time is better supported. The charge-potential relations, which have been obtained by integration of voltammograms measured for different thallium concentrations and which represent the coverage-potential relations if the first assumption is valid, are only shifted in underpotential. Then the charge numbers were calculated according to the relationship [8]

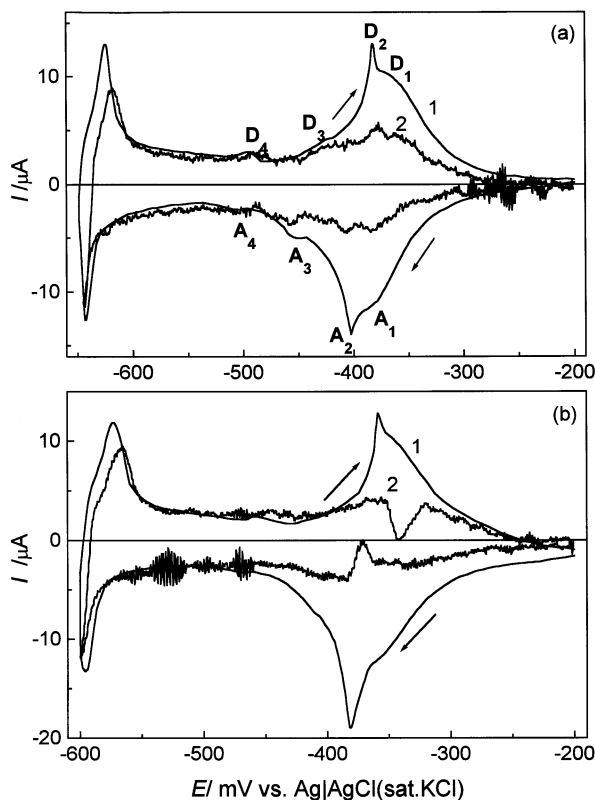


Fig. 1. Stabilized cyclic voltammograms, background corrected, (1) and cyclic voltammograms calculated from the derivatives of the frequency responses, assuming  $l = 1$ , (2) for a quartz supported silver electrode recorded at  $10 \text{ mV s}^{-1}$ ,  $X \text{ M Ti}_2\text{SO}_4 + 0.1 \text{ M Na}_2\text{SO}_4 + 1 \text{ mM H}_2\text{SO}_4$ . (a)  $X = 6.25 \text{ mM}$ ; (b)  $X = 50 \text{ mM}$ .

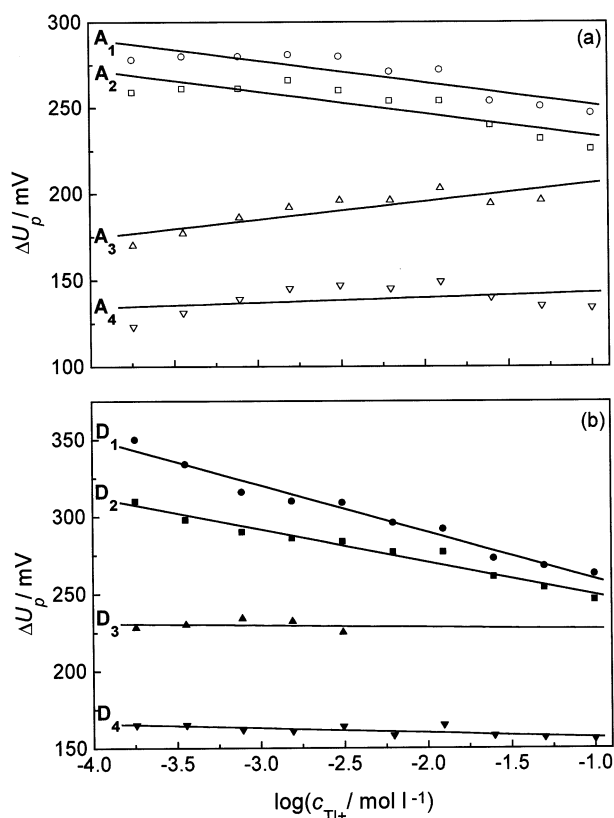


Fig. 2. Plots of the differences between the upd adsorption (A) and desorption (D) peak potentials (voltammograms were recorded at  $10 \text{ mV s}^{-1}$ ) and the reversible Nernst potentials vs. the logarithm of thallium(I) concentration,  $X \text{ M Ti}_2\text{SO}_4 + 0.1 \text{ M Na}_2\text{SO}_4 + 1 \text{ mM H}_2\text{SO}_4$ . A and D definitions are shown in Fig. 1.

$$\Delta U_p = K + \frac{RT}{F} \left( \frac{1}{l} - \frac{1}{z} \right) \ln a_{\text{Tl}^+} \quad (3)$$

where  $\Delta U_p$  is the difference between the upd peak potential and the reversible Nernst potential in the solution with activity  $a_{\text{Tl}^+}$ ,  $K$  is a constant. Instead of the activity, concentration  $c_{\text{Tl}^+}$  was used in calculations because the relation  $E_{\text{Tl}^+/\text{Tl}} - \log c_{\text{Tl}^+}$  was found to be linear with a slope equal to  $58 \text{ mV}$ . For all observed adsorption/desorption peaks, relations  $\Delta U_p - c_{\text{Tl}^+}$  are presented in Fig. 2. For adsorption peaks  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$ , the slopes give partial charge numbers equal to  $1.28 \pm 0.07$ ,  $1.28 \pm 0.08$ ,  $0.85 \pm 0.03$  and  $0.95 \pm 0.05$ , respectively. Correspondingly, for desorption peaks  $D_1$ ,  $D_2$ ,  $D_3$  and  $D_4$  these numbers are  $2.06 \pm 0.13$ ,  $1.55 \pm 0.07$ ,  $1.02 \pm 0.08$  and  $1.05 \pm 0.02$ , respectively.

From the results presented above, it can be seen clearly that in the region of adsorption/desorption peaks  $A_3$ ,  $A_4/D_3$ ,  $D_4$  and of more negative potentials (the end of the first thallium monolayer and the beginning of the second monolayer formation) there is a good agreement between voltammetric and EQCM measurements,  $l$  is equal to 1. As far as the formation of the first monolayer is considered, a more detailed study is required. It seems that the influence of sulphate anions cannot be excluded.

### 3.2. Adsorption of thallium on silver from acidic perchlorate and chloride media

Chloride anions are known as ions adsorbing more strongly than sulphate, therefore, in this work their effect on the upd of thallium on silver was studied in order to compare this effect with that of sulphate ions. First, the voltammetric and EQCM measurements were made in the acidic perchlorate solutions without the addition of chloride. Fig. 3a shows that there is a good agreement between  $I_e$  and  $I_m$  in the whole potential region, the first and the second thallium monolayer formation. An addition of a small amount of chloride anions has a drastic effect on the upd of thallium (Fig. 3b). Again, as in the case of sulphate anions,  $I_e$  is different from  $I_m$  in the first monolayer formation region. This difference is more pronounced than in the case of sulphate ions. In addition, there is no such correlation between the variation of  $I_e$  and  $I_m$  with potential which has been observed for sulphate ions (Fig. 1a). The increase in the concentration of chloride

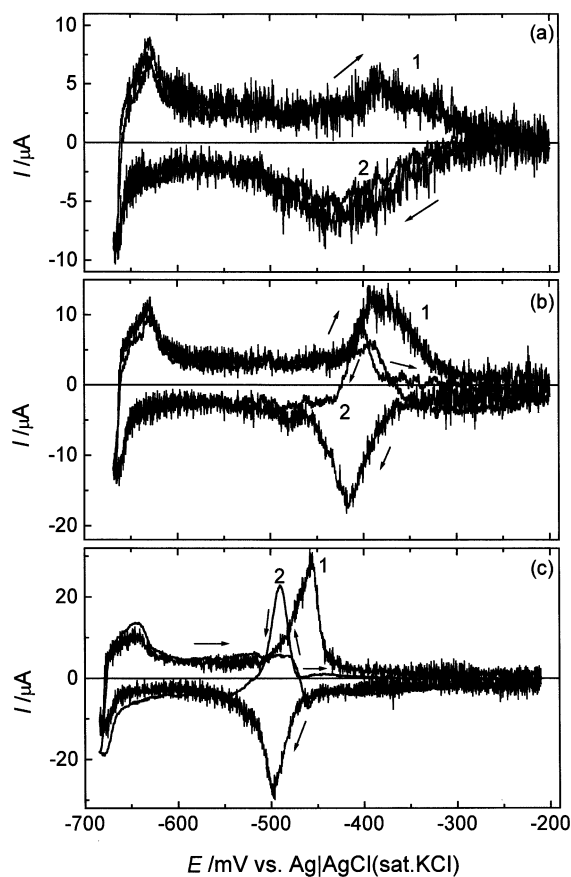


Fig. 3. Measured stabilized cyclic voltammograms, background corrected, (1) and cyclic voltammograms calculated from the derivatives of the frequency responses, assuming  $l = 1$ , (2) for a quartz supported silver electrode recorded at  $10 \text{ mV s}^{-1}$ ,  $6 \text{ mM TiClO}_4 + 0.1 \text{ M HClO}_4 + X \text{ mM KCl}$ . (a)  $X = 0 \text{ mM}$ ; (b)  $X = 0.2 \text{ mM}$ ; (c)  $X = 20 \text{ mM}$ .

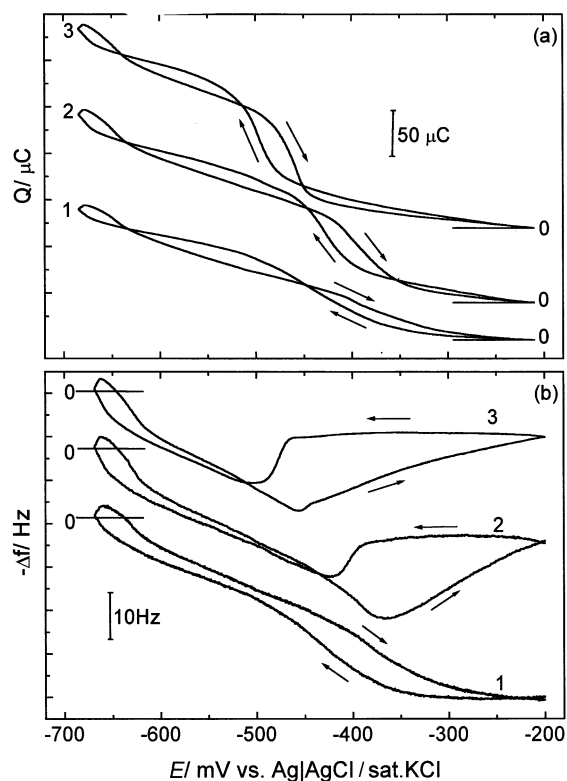


Fig. 4.  $Q_c(E)$ -isotherms, obtained by integrating the corresponding cyclic voltammograms, (a) and full cycles of frequency responses for a quartz supported silver electrode (b) recorded at  $10 \text{ mV s}^{-1}$ ,  $6 \text{ mM TiClO}_4 + 0.1 \text{ M HClO}_4 + X \text{ mM KCl}$ .  $X = 0 \text{ mM}$ , curves 1;  $X = 0.2 \text{ mM}$ , curves 2;  $X = 20 \text{ mM}$ , curves 3.

anions changes this variation to such an extent that  $I_m$  changes its sign from negative to positive in the first monolayer formation region (Fig. 3c).

The above results lead to the conclusion that the statement made by Tang and Furtak, that the EQCM gives a correct estimate of the mass transferred during the upd process of  $\text{Tl}/\text{Ag}$  [1], is not valid for the first monolayer formation region. Sulphate anions seem to exhibit specificity in adsorbing when in the first monolayer formation region, thus influencing the EQCM data. As was mentioned above, this influence is not so pronounced as in case of chloride ions. EQCM measurements were made in the perchlorate solution containing a small amount of sulphate anions ( $10 \text{ mM}$ ) and the results obtained were very close to those depicted in Fig. 3a. The influence of sulphate is more clearly observed only at a higher concentration reaching  $0.1 \text{ M}$ .

At the same time the voltammetric behaviour of the upd of thallium on silver is classical. In the monolayer adsorption, two general anion effects are noted when measuring in strongly adsorbing anion-containing solutions [9,10]. First, the underpotential shift is observed, second, the area under the monolayer peak is enlarged. Curves 1–3 from Fig. 4a demonstrate well such a behaviour. However, the explanation of these phenom-

ena given by Kolb et al. [9,10] does not appear to be correct. Discussion on this matter is reserved for the next section.

The integral adsorption isotherms of thallium adsorption on silver,  $Q_c(E)$ , in the presence of chloride ions (curves 1–3 from Fig. 4a) were obtained by integrating the corresponding full cycles of voltammograms. They are given for a comparison with the EQCM data,  $\Delta f(E)$ , shown in Fig. 4b. In this figure, the data are presented as received, i.e. full cycles measured in frequency units, but in a reversed order. This makes comparisons easier as the change of mass is of opposite sign with respect to the change of frequency. The reason for presenting them without converting frequency units into charge or mass units is that the frequency changes can be due to simultaneous adsorption of thallium and chloride.

It seems worth comparing our results of EQCM measurements of chloride adsorption with those obtained by other methods. Usually, different methods show the same variation of chloride adsorption with potential but the difference in measured adsorption values can reach several tens of a percent [11]. The potential behaviour of chloride adsorption shown in Fig. 5 coincides with that reported earlier [11]. For quantitative comparison, the reference points must be chosen. At potential values near  $-100$  mV versus the silver wire reference electrode, an ordered hexagonal structure of chloride ad-layer on Ag(111) was observed by STM while at more positive potentials STM images are blurred [12]. The observed full surface coverage confirms the earlier results obtained by XPS, Auger, SERS, radiotracer and voltammetric methods [11]. In order to evaluate whether our EQCM measurements give reasonable values for chloride anion adsorption, the surface roughness factor must be known. From previous voltammetric investigations [3], the voltammetric adsorption/desorption peaks  $A_1/D_1$ ,  $A_2/D_2$  and

$A_3/D_3$  observed at relatively large underpotentials have been assigned to the formation of the first thallium monolayer on Ag(111) and on Ag(100). This is fully confirmed by STM and GIXS investigations [13,14]: at potentials between  $-475$  and  $-680$  mV versus Ag|AgCl|3 M KCl, the thallium deposit forms an incommensurate, hexagonal two-dimensional monolayer in which the adatoms are closely packed together. For Ag(111) and Ag(100), Siegenthaler et al. [3] have found that the full charge consumed during formation of the complete thallium monolayer is close to  $200 \mu\text{C cm}^{-2}$ . Despite the fact that in our work the polycrystalline silver electrode is used and the adsorption/desorption peaks are not very distinct, the main features of the measured voltammogram (curve 1 in Fig. 1a) are similar to those obtained for single crystal silver electrodes [3,13,14]. In addition, STM investigation [13] has shown that the most anodic peak,  $A_1/D_1$ , is associated with the imperfection of single crystals, i.e. with the deposition of thallium atoms at the terrace edges. Therefore, it is reasonable to assign the same value ( $\sim 200 \mu\text{C cm}^{-2}$ ) to the charge consumed within the potential range of peaks  $(A_1-A_4)/(D_1-D_4)$ . The full charge consumed during a negative potential scan from  $-200$  to  $-670$  mV is equal to  $140 \mu\text{C}$  (curve 1 in Fig. 4a). The geometric area of the electrode surface is equal to  $0.25 \text{ cm}^2$  then the real area is obtained equal to  $0.7 \text{ cm}^2$ .

The overall frequency change for chloride adsorption is approximately equal to 10 Hz when the bulk concentration of chloride anions is equal to  $2 \times 10^{-2} \text{ M}$  (curve 3 in Fig. 5). This frequency change, multiplied by the sensitivity of the EQCM ( $5.6 \times 10^{-9} \text{ g Hz}^{-1}$ ) and by the Faraday constant and then divided by the molar mass of chloride and by the real area of the electrode surface, gives the surface coverage by chloride anions equivalent to  $220 \mu\text{C cm}^{-2}$ . This value should correspond to the potential approximately equal to 0 mV because frequency change was measured from  $-670$  mV (reference point for frequency measurement, Fig. 5) to 0 mV versus Ag|AgCl|KCl<sub>sat</sub>. However, according to the reported data [11] the occupied surface fraction varies from 0.1 to 0.2 at  $-670$  mV. When this fraction is accounted for, the surface coverage is equivalent to  $250\text{--}280 \mu\text{C cm}^{-2}$  at 0 mV versus Ag|AgCl|KCl<sub>sat</sub>. In comparison with typical values for monolayer formation, this value is too large. Assuming that the monolayer is formed of only partially dehydrated chloride anions or of specifically adsorbed cation–chloride pairs, reasonable coverage values can be obtained. Although some data in favour of the adsorption of cation–chloride pairs are reported [15], an additional analysis is needed. This study will be the subject of the next paper.

Comparative analysis of all data reported above leads to several important conclusions. That is discussed in the next section.

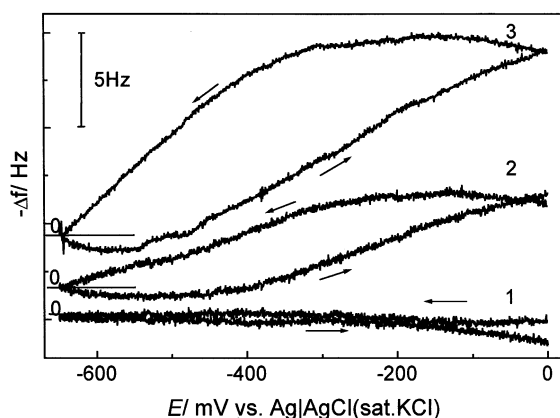


Fig. 5. Full cycles of frequency responses for a quartz supported silver electrode (b) recorded at  $10 \text{ mV s}^{-1}$ ,  $0.1 \text{ M HClO}_4 + X \text{ mM KCl}$ .  $X = 0 \text{ mM}$ , curve 1;  $X = 0.2 \text{ mM}$ , curve 2;  $X = 20 \text{ mM}$ , curve 3.

#### 4. Discussion

In the absence of chloride anions, there is almost a full coincidence of  $Q_c(E)$  with  $\Delta f(E)$ , curves 1 from Fig. 4a and b. This coincidence is clearly demonstrated by their differential forms,  $I_c(E)$  and  $I_m(E)$  from Fig. 3a. When the chloride anions are added, the curves remain unchanged in the more negative potential region and this region decreases with an increase in the concentration of chloride anions. In the remaining potential region, one can observe a decrease in frequency change (positive going in a potential direction) which corresponds to the increase in electrode mass. In addition, this potential region is characterized by a large hysteresis of frequency change. Now, it seems appropriate to add an analysis of the dependences from Fig. 5. The frequency change due to the presence of chloride ions is also characterized by a pronounced hysteresis, though smaller than in the previous case. This hysteresis should be related to the specific adsorption of chloride anions that reveals itself in some irreversibility of adsorption/desorption at non-zero potential scan rates. Comparison of  $\Delta f(E)$  curves from Fig. 4b with those from Fig. 5 shows that the upd process comprises adsorption/desorption of thallium and chloride ions.

From now, a new interpretation will be included into the analysis. First, at the potentials close to the reversible  $Tl/Tl^+$  potential both voltammetric and EQCM data agree independently of the absence or the presence of specifically adsorbing ions. This follows from all the data presented above (see Figs. 1–5), especially from the data presented in differential form, as in this the curvatures of integral forms are well represented (Figs. 1 and 3). This leads to the first conclusion that for EQCM measurements, where only frequency changes but not their absolute values are meaningful, the reference point (an absolute frequency value with respect to which the frequency change is measured) must be chosen with care. In the presence of specifically adsorbing anions, such a reference potential (correspondingly, reference frequency value) must be the potential of the maximum surface coverage by upd monolayer because this potential is the most negative and, therefore, the influence of anions should be as small as possible.

Another conclusion follows immediately from this consideration and the experimental data presented above but first the classical interpretation of the upd process in strongly adsorbing anions containing solutions should be outlined [9]. First, the underpotential shift is decreased and this change must be caused by the interaction of the anion with substrate, which is obviously stronger than that with adsorbate. Second, the area under the monolayer peak is enlarged and this is because the metal atom adsorption is now accompanied by anion desorption, both processes contributing to the current in the same direction.

Now we are going to show that thallium adsorption on silver cannot be described in these classical terms. It was shown above that the  $I_c(E)$  and  $I_m(E)$  dependences coincide in the potential region of monolayer formation close to the bulk thallium deposition even in the presence of strongly adsorbing chloride anions. That means that the anion desorption cannot contribute to the overall current. Otherwise,  $I_m(E)$  should be smaller than  $I_c(E)$  due to desorption of these ions. In addition, the variation of these currents with potential should be different. Other evidence for our statement comes from the fact that a negligible current increase is observed in the voltammogram when the chloride ions are added in perchloric acid solution whereas the quantitative analysis of frequency responses (Fig. 5) according to Eq. (2) shows that this current should be clearly observed. Actually, when chloride anions are being desorbed, other solution species (perchlorate ions, water dipoles, cations) participate in the rearrangement of the electrical double layer and in part compensate charge change effects. The enlargement of the area under the monolayer peak can be explained by the formation of monolayers of higher density in the presence of strongly adsorbing anions. More detailed analysis of the mechanism of this enlargement is beyond the scope of the present work.

None of the data obtained in this work support the earlier explanation for the decrease in the underpotential shift in the presence of strongly adsorbing ions, i.e. that this shift is caused by the interaction of the anion with substrate, which is stronger than that with adsorbate [9,10]. A more reasonable explanation lies in terms of enhanced adsorption. The specific adsorption of thallium cations on the silver surface at potentials positive with respect to the pzc should be enhanced by the specific adsorption of sulphate ions, and thus there is a probability of ion pair formation between specifically adsorbed thallium and sulphate ions. Such adsorption was observed, for example, for thallium adsorption on a positively charged mercury surface in the presence of nitrate ions [16]. Assuming this type of enhancement of adsorption allows an explanation of the decrease in the underpotential shift and the disagreement of  $I_c(E)$  and  $I_m(E)$  in the potential region of the first monolayer formation ( $-450$  to  $-200$  mV versus  $Ag|AgCl|KCl_{sat}$ ). When there are no specifically adsorbing anions in the solution, there is a good agreement between  $I_c(E)$  and  $I_m(E)$  in the whole upd region (Fig. 3a). Sulphate anions enhance adsorption of thallium at the potentials before the first monolayer formation, i.e. an ion pair between specifically adsorbed thallium and sulphate ions is formed. When the potential is scanned into the negative direction, two effects should be observed. First, the discharge of thallium cations and the monolayer formation should start at more negative potentials because the bond in the ion

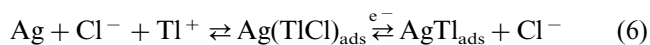
pair must be broken. Such a phenomenon (decrease in the underpotential shift) is always observed in the voltammograms, curves 1 from Fig. 1a and b. In the case of chloride ions, which are more strongly adsorbing anions, this effect is more pronounced, curves 1 from Fig. 3b and c. Second, in the presence of specifically adsorbing anions the change of electrode mass measured by EQCM should be smaller than that calculated from the voltammetric data according to Faraday's law because thallium cations are already adsorbed before they are discharged. Analysis of the data presented in Fig. 4a and b supports this conclusion (the mass change can be calculated simply by multiplying the frequency change value by  $5.6 \text{ ng Hz}^{-1}$ ). Correspondingly,  $I_m(E)$  should be smaller than  $I_c(E)$ . That is also confirmed by experimental data (Fig. 1a and b, Fig. 3b and c). Even more, the enhanced adsorption of thallium ions can explain the anomalous behaviour of  $I_m(E)$  most clearly observed in Fig. 3b and c, i.e. the reversal of the  $I_m(E)$  sign during the negative potential scan. During this scan the desorption of chloride anions occurs. The desorption rate increases starting from the potential approximately equal to  $-350 \text{ mV}$ , when the concentration of chloride ions is equal to  $2 \times 10^{-4} \text{ M}$ , and to  $-450 \text{ mV}$ , when this concentration is equal to  $2 \times 10^{-2} \text{ M}$  (curves 2 and 3 from Fig. 5). These potentials are close to those from which the reversal of the  $I_m(E)$  sign begins. Two effects can contribute to this anomaly: first, desorption of chloride ions that decreases the change of electrode mass and, correspondingly,  $I_m(E)$ ; second, the rapid decrease in chloride surface concentration can cause the desorption of thallium cations, which have been paired with chloride anions and which have not been discharged yet. A semiquantitative analysis of the data shows that the second effect should play the major role. This consideration also explains why the anomalies in the variation of  $I_m$  with potential in sulphate media occur at higher concentration of thallium cations (curves 2 in Fig. 1a and b) than in case of chloride anions. Anomalies are due to occurrence of adsorbed ion pairs. Sulphate anions are less strongly adsorbing ions than chlorides. Therefore, a higher concentration of thallium cations is necessary to form the amount of ion pairs comparable with the amount of pairs formed in the case of chloride anions.

## 5. Conclusions

The reactions for the upd model discussed above can be written as



for the potentials more positive than the region of the first monolayer formation,



for the potentials of the first monolayer formation region, reactions (6) and (7), and for the second monolayer formation region, reaction (7). The anomalies observed in the variation of  $I_m$  with potential are mainly due to reactions (5) and (6).

In the case of other specifically adsorbing anions, for example, sulphate ions, a similar reaction route can be written. It seems very likely that the above scheme can be applied when other upd systems are considered.

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