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Electrochemical and Electrogravimetric Investigations of Prussian Blue on the Gold Electrode in the Presence of Thallium(I) Ions*

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Electrode processes of Prussian Blue (PB), deposited on the gold electrode, have been investigated in potassium and thallium salts solutions, using electrogravimetric and cyclic voltammetric methods. It is shown, that both electrode processes of PB (reduction of PB to Everitt's salt and its oxidation to Berlin Yellow) undergo changes, when potassium ions are replaced by thallium(I) ones. In the presence of thallium, the formation of new redox system is observed, and Tl(I) acts as a counter-ion. The equilibrium constant of the reaction: K(I)PB + Tl(I) = Tl(I)PB + K(I) was estimated to be equal to $K = (1.7 \pm 0.6) \times 10^4$. At the same time almost 50% of the PB layer looses its electrochemical activity, whereas the remaining PB phase is electrochemically active. After transfer of the electrode to KNO_3 solution, majority of inactivated layer recovers its previous activity. These findings are tentatively interpreted as a result of formation of two phases of PB with Tl(I): electrochemically active and inactive. Both phases are in equilibrium, and thallium ions could be replaced by potassium one. In the case of the $Fe(CN)_6^{3-/4-}$ electrode process (at more positive potentials), in the presence of Tl(I) irreversible deactivation occurs, since in KNO_3 solution, no reactivation of the electrode process is observed.

Key words: Prussian Blue, thallium ions, cyclic voltammetry, quartz microbalance

Prussian Blue (PB = [iron(III)-hexacyanoferrate(II)]) exists in two forms. At large excess of Fe(III) in the solution with respect to $Fe(CN)_6^{4-}$ "insoluble" PB ($Fe_4(Fe(CN)_6)_3$ is formed. When the excess of $Fe(CN)_6^{3-}$ is used, the formation of so-called "soluble" PB ($KFe(Fe(CN)_6)$ is observed [1]. Both forms of PB are electroactive. PB may be oxidized *via* intermediate Berlin Green to Prussian Yellow [PY-Fe(III)Fe(III)], and reduced to Prussian White [PW-Fe(II)Fe(II)].

These compounds may be deposited on the support electrodes by electrochemical and chemical methods. Although rather extensive work on the electrochemistry of PB, both in aqueous and in solid state has been carried out [1–28], there are some problems such as the lattice reconstruction, the combined role of various counter-ions and solvent, and the role of anions and hydrogen ions in the course of the electroreduction or oxidation, which call for further attention.

In the present work we are going to discuss peculiar electrochemical behaviour of the PB layers in the presence of thallium(I) ions. Such behaviour of PB in the presence

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* Dedicated to Professor B.B. Damaskin on the occasion of his 70th birthday.

of various cations has been of interest since the earliest investigations, both from the point of view of the ability of cations to penetrate the PB lattice and the stability and diversity of produced forms [3,7,29,30], and synthesis of PB layers in the presence of various cations [30].

Electrochemical behaviour of hexacyanoferrates (HCF) in the presence of Tl(I) was a subject of limited number of papers [29,31]. Although radius and real energy of solvation [32,33] for the Tl(I) ion are to some extent similar to alkali metal ions (especially to K^+), chemical properties of Tl(I) point to its greater softness than that of K^+. The behaviour of PB in Tl^+ solutions has been already studied by electrochemical methods [29]. In the present work we used electrogravimetry in addition to electrochemistry in a hope that combination of these two methods will be useful in further understanding of the behaviour of that complex system.

In our previous paper [31], we observed a shift of the current – potential curves of Cu-HCF in the presence of Tl(I), towards more positive potentials, which was attributed to specific chemical interactions between Tl(I) ions and the CN groups. Results obtained in the present paper suggest that interaction of Tl(I) with PB is similar to that observed previously.

EXPERIMENTAL

Solutions. Majority of experiments were carried out in 0.1 M solutions of KNO_3 (analytical grade, POCh, Gliwice, Poland). $K_3[Fe(CN)_6]$, $TlNO_3$, $FeCl_3$ and HNO_3 (*pro analysi*) were used without additional purification. The solutions were prepared using carefully purified water. Initially, the tap water was purified by passage through the carbon filters. Next it was twice distilled and then passed throughout a system of Millipore® filters.

Electrodes and cell. In the experiments, the Au/quartz oscillators (crystals with 5 MHz fundamental frequency (f_0), supplied by the Tele and Radio Research Institute, Warsaw, Poland), described in our previous papers [28,31], were used as working electrodes. The oscillators were prepared using the standard procedure. A thick (1000 Å) gold layer was evaporated on a thin (50 Å) chromium layer, which served as a support to improve adherence of gold to quartz. Geometric working area of the electrodes was 0.3 cm^2.

At the beginning of each experiment the working electrode was cleaned by cyclic polarization in potential range from 0.0 to 0.95 V in 0.5 M H_2SO_4 solution, and next rinsed with water. The Prussian Blue films were removed from the electrode in KOH solution, and next the electrode was placed in 0.5 M H_2SO_4 solution and cleaned by cyclic polarization in the same potential range.

The counter electrode was a gold wire ($A = \sim 1$ cm^2) and Ag/AgCl/1 M KCl served as a reference electrode.

The dependence of the frequency of the Au/quartz electrode was determined in 0.22 M $HClO_4$ solutions containing various concentrations of silver ions (from 0.05 to 2.4 mM). The mass of the electrode was calculated from the oxidation charge of deposited metallic silver. The dependence of the mass (Δm) on the frequency (Δf) of a crystal is described by the Sauerbray equation:

$$\Delta f = -2\,\Delta m\, f_0^2\, (\mu_q \rho_q)^{-1/2} A^{-1} \qquad (1)$$

where μ_q stands for the shear modulus of the quartz, ρ_q for the density of quartz, and A determines – the surface area of the oscillating gold electrode.

For the silver reduction process we found the following Δm (in ng) vs. Δf (in Hz) dependence:

$$\Delta m = (13.0 \pm 10.3) + (5.91 \pm 0.11) \times \Delta f, \ r = 0.994, \ n = 17 \qquad (2)$$

The slope of this dependence is very close to that calculated from the Sauerbray equation.

Methods and equipment. Electrochemical and microgravimetric experiments were simultaneously carried out using an AUTOLAB potentiostat (PGSTAT 20, Eco Chimie, The Netherlands) which allows to detect the second signal. Autolab instrument was used in additional electrochemical experiments.

Experiments were conducted at ambient temperature (23±1°C).

RESULTS AND DISCUSSION

Procedure for the PB film deposition. The PB films were obtained by cyclic voltammetric method in KNO_3 (0.5 M) solution, acidified with HNO_3 to pH = 2. Concentrations of $FeCl_3$ and $K_3Fe(CN)_6$ were the same and equal to 1.25 mM. The gold electrode was cyclically polarized between 0.95 and 0.0 V with the scan rate 10 mV/s. The film deposition experiment was stopped, usually, after 20 scans. Typical current – potential and frequency – potential curves recorded during the PB film deposition are presented in Fig. 1. These curves are similar to those presented previously [28]. The electrode process observed in the range of potentials close to 0.2 V, corresponds, in the cathodic scan, to reduction of PB to Berlin White, while in the anodic scan, the reverse process occurs:

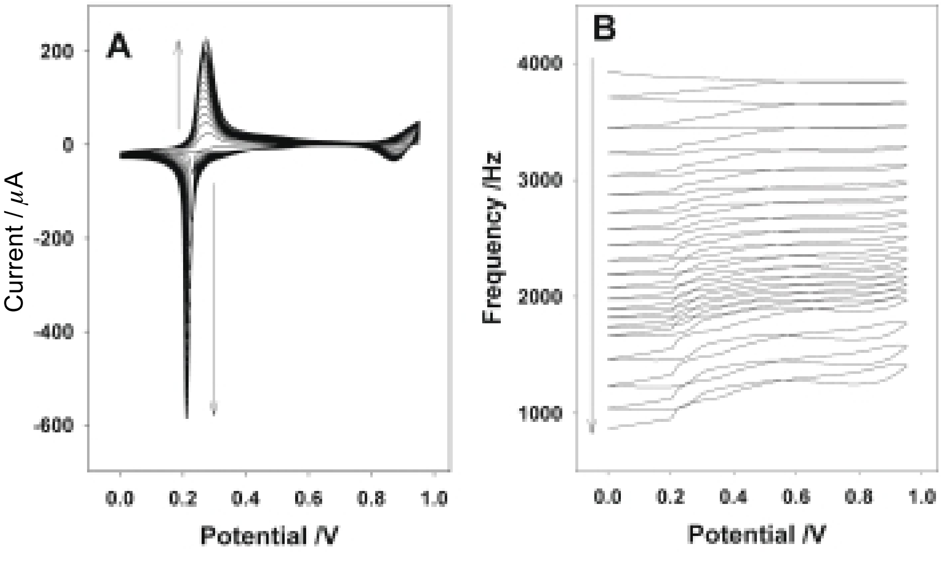

Figure 1. (A) CV curves recorded during deposition of the Prussian Blue film on the gold electrode in 0.5 M KNO_3 solution acidified with HNO_3 to pH = 2, containing 1.25 mM of $K_3[Fe(CN)_6]$ and $FeCl_3$, at $\nu = 10$ mV s^{-1}. (B) The respective gravimetric responses.

$$KFe^{III}[Fe^{II}(CN)_6] + K^+ + e = K_2Fe^{II}[Fe^{II}(CN)_6] \qquad (3)$$

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4K^+ + 4e = K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 \qquad (4)$$

Eq. (3) describes the processes of the "soluble" form, and the reaction of the "insoluble" form of the PB is represented by eq. (4).

After 20-th scans, the frequency of the oscillating circuit is lowered by 3000 Hz due to deposition of the PB film, which in the redox processes exhibited charge equal to 2.5 mC (the electrode process close to 0.2 V), *i.e.* equivalent to 25.9 nM of the compound on the electrode. A simple calculation shows, that the average molar mass of the PB which is formed at the electrode surface is close to 685 g/mole of electrons. Since the masses of the soluble ($K_2Fe[Fe(CN)_6]$) and insoluble Berlin White ($K_4Fe_4[Fe(CN)_6]_3$) are equal to 346.0 and 253.9 g/mole of electrons, respectively, these calculations show that either (i) the deposits are highly hydrated, or (ii) simultaneously with the electrochemically active form, some other substance, which is electrochemically inactive is also deposited. In the first case (i), 19 (soluble) or 24 (insoluble form) water molecules should participate in the deposition process. It seems, that this hydration level is typical for the Berlin White (or Prussian Blue) which show the zeolitic character. Thus, we assumed that the second hypothesis (coprecipitation of electrochemically inactive substance) is less probable.

One may estimate from the mass-charge dependence, recorded during the film formation process, the average molar mass of the counter ions, which participate in the electrode process. In this case both the charge and the mass changes accompanying the electrode processes of both systems Fe(III)/Fe(II) and $Fe(CN)_6^{3-/4-}$ are small in comparison with those due to the film deposition. This tendency grows with successive scans. The results obtained are presented in Fig. 2. In part 2A the f – Q dependence, while in 2B – the average molar masses for all 20 scans are given. For the more negative redox system (Fe(III)/Fe(II)), the molar masses were calculated from the cathodic half-cycles, in the potential range from 0.6 to 0.0 V. For the more anodic system, the molar masses were calculated from the cathodic – anodic scans, in the range of potentials 0.8 – 0.95 – 0.8 V. The results presented in this Figure convincingly suggest, that for the redox system at more negative potentials, the charge transfer process is accompanied by the exchange of the potassium ion, since the average molar mass is, for the most of recorded curves, close to 40 g/mole. Interference by other processes should be rather small.

In the case of the redox system observed at more positive potentials, the average molar masses are in the range of 100–150 g/mole, and for the last three scans they are even larger. This result indicates, that the electrode processes for the soluble PB form, described usually by the following equation:

$$Fe^{III}[Fe^{III}(CN)_6] + K^+ + e = KFe^{III}[Fe^{II}(CN)_6] \qquad (5)$$

is accompanied by some additional process of the mass exchange which is not directly associated with the transfer of charge. Such a behaviour could be tentatively

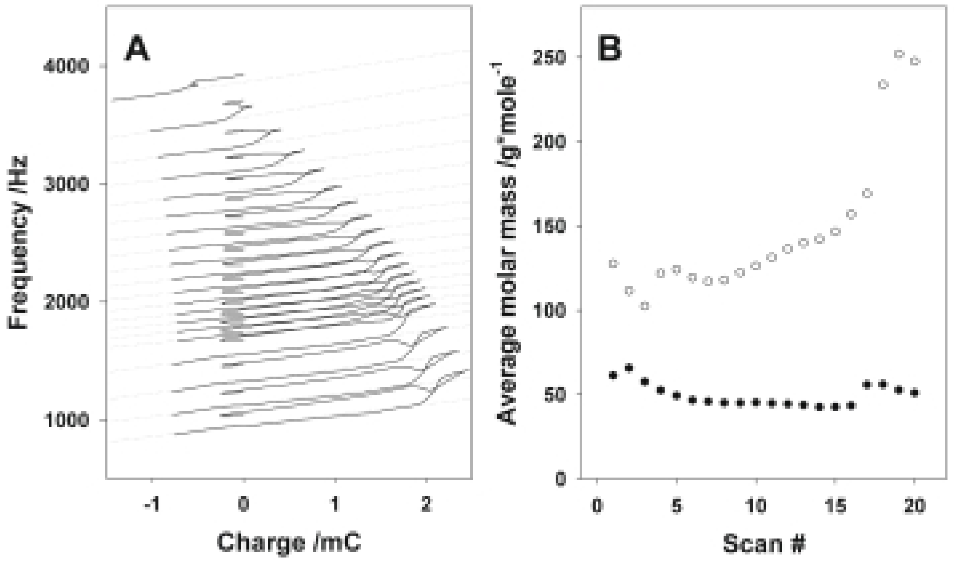

Figure 2. (A) The frequency – charge dependencies for all scans from Fig. 1; (B) The average molar masses calculated for all scans for both redox systems: filled circles – the Fe(III)/Fe(II) and open circles – the $Fe(CN))_6^{3-/4-}$ system.

explained by the anions adsorption/desorption processes (either $Fe(CN)_6^{3-}$ or Cl^-) occurring in this positive potentials regions, with adsorption on oxidized form of PB – Prussian Yellow smaller than on the PB layers.

In the case of the insoluble form of PB, it is not clear how the electrode process at more positive potentials (around 0.85 V) should be described. If this form is oxidized in this region of potentials, it should be rather accompanied by uptake of the anion of the supporting electrolyte:

$$Fe_4^{III}[Fe^{III}(CN)_6]_3X_3 + 3e = Fe_4^{III}[Fe^{II}(CN)_6]_3 + 3X^- \qquad (6)$$

Results presented in Fig. 1 indicate however, that in this region of potentials the frequency increases. Thus one may conclude that the reaction (5) prevails over the reaction (6).

Chemical modification of the PB with Tl(I). The cyclic voltammetric and gravimetric experiments were conducted in three regions of potentials: (i) from 0.0 to 0.95 V where both reactions may occur, (ii) from 0.0 to 0.5 V, corresponding to the first redox system, and (iii) from 0.5 V to 0.95 V, corresponding to the redox system which reacts at more positive potentials. Concentration of Tl(I) was changed from 0 to 0.1 M.

The current – potential curves recorded in the presence of thallium(I) are shown in Fig. 3. The general conclusion is, that addition of Tl(I) ions influences both electrode processes. Earlier Scholz and co-workers found [29], that in the presence of Tl$^+$ (and also Rb$^+$), the hexacyanoferrate system (*i.e.* the redox system which reacts at more positive potentials) disappeared, and the iron(III/II) system (*i.e.* the redox system which reacts at less positive potentials) remained unchanged. The difference may result from other way of the preparation of the PB modified electrode.

In the case of the electrode process occurring at more negative potentials, we observe the formation of new redox system with different voltammetric characteristics. This system is formally more irreversible than that observed in the presence of potassium ions. In the latter case (K$^+$), the difference between the E_{pc}^{1} and E_{pa}^{1} equals to 0.075 V, and a slight increase of this difference is observed in the presence of higher concentrations of Tl(I) (to about 0.090 V), which could be, at least partly, attributed to uncertainties in determination of the anodic peak potential. In the former case (Tl$^+$), the difference between E_{pc}^{2} and E_{pa}^{2} equals to about 0.145 V, and both peaks are shifted towards more positive potentials by 0.06 V at the ten-fold increase of Tl(I) ions concentration. Such a behaviour is very similar to that observed [31] previously by us in the case of the copper hexacyanoferrate in the presence of Tl(I) ions. From the potential extrapolated to 1 M Tl(I) concentration, equal to 0.452 V, we estimated the equilibrium constant of the reaction:

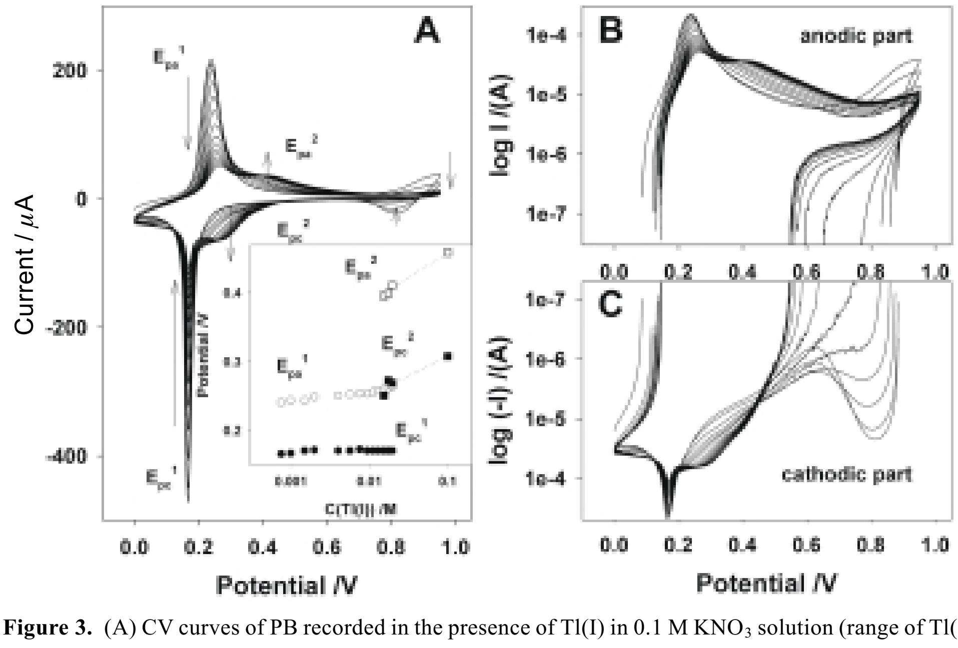

Figure 3. (A) CV curves of PB recorded in the presence of Tl(I) in 0.1 M KNO$_3$ solution (range of Tl(I) concentration given in the inset). In the inset, the changes in the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials as a function of Tl(I) concentration are shown. Scan rate $\nu = 10$ mV s^{-1}. (B) and (C) The logarithmic version of CV curves.

$$K(I)PB + Tl(I) = Tl(I)PB + K(I) \quad (7)$$

as equal to $K = (1.7\pm0.6)\times10^4$. This equilibrium constant is almost one order of magnitude greater than that calculated [31] for the CuHCF ($(2.5\pm0.6)\times10^3$). Thus, one may conclude, that interaction of PB with Tl(I) is stronger than that with CuHCF.

In the case of the redox system which occurs at more positive potentials, we observed significant decrease of current with increase of Tl(I) concentration. This behaviour is better visible on the right hand side of Fig. 3, where the current axes are in the logarithmic scale.

The gravimetric data are presented in Figure 4. Two important facts should be noted. First of all in the case of the redox system observed at potentials near to 0 V, the difference between the frequency at the potential 0.6 V and at 0.0 V in the cathodic scan grows from 180 Hz in 0.1 M solution of KNO_3 to 900 Hz in 0.01 M Tl(I) solution. Thus, the observed increase of the difference in frequencies corresponds approximately to ratio of molar masses of Tl(I) (204) and K(I) (39).

Similar results are observed in the case of polarization in a more narrow potential range (Fig. 4B). In this case the difference in frequency increases from 147 (KNO_3) to 780 Hz, *i.e.* 5.3 times.

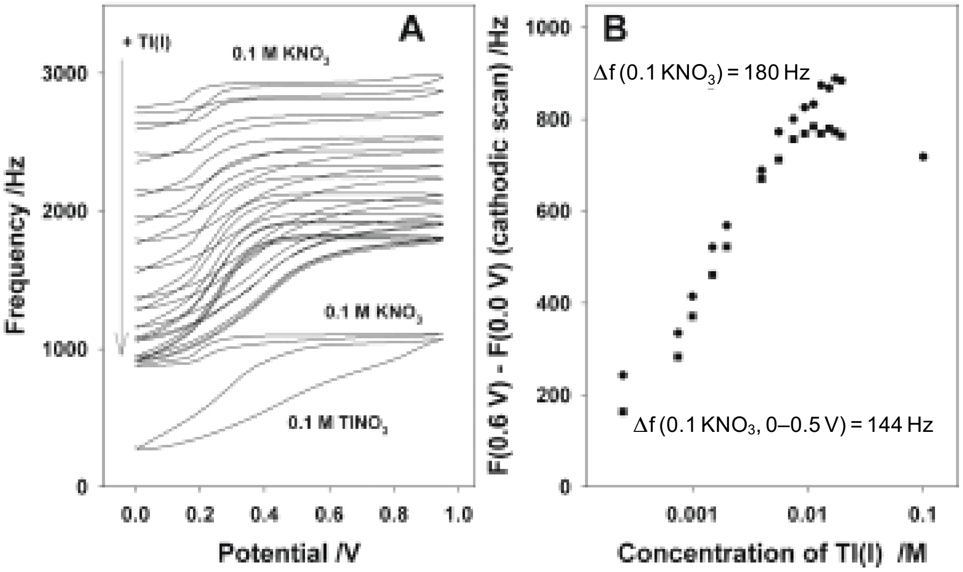

Figure 4. (A) The frequency changes recorded in 0.1 M KNO_3 solution with increasing Tl(I) concentration (range of Tl(I) concentration given in part B). An arrow shows changes in the initial frequency. Scan rate $\nu = 10$ mV s^{-1}. (B) Difference between the frequency at the potential 0.6 V (or 0.5 V) and 0.0 V in the cathodic scan as a function of Tl(I) concentration. Circles – polarization in the range 0÷0.95 V, squares – polarization range 0÷0.5 V.

The second observation is related to the initial frequency of all gravimetric curves. As it follows from Fig. 4A, with transfer from 0.1 M KNO_3 to 0.01 M solution of Tl(I) (with 0.1 M KNO_3), the initial frequency decreases by 1800 Hz, which indicates, that in the PB layer potassium ions are replaced by thallium ones. From this initial frequency change, equal to 1800 Hz (which corresponds to 10.6μg), one may calculate the number of Tl(I) ions, which replaced K(I) ions. The calculated number is equal to 65 nM of Tl(I). Since on the electrode surface only 26 nM of $K_2Fe[Fe(CN)_6]$ or $K_4Fe_4[Fe(CN)_6]_3$ is deposited (from the charge measurements), one can conclude, that not only all potassium ions (~52 nM) are replaced by thallium ones, but even additional Tl(I) ions may be introduced to PB layers. Such a hypothesis seems rather not much probable. In our opinion, this higher than expected mass increase, corresponds rather to an increase in hydration of the Tl(I) modified PB layers.

The gravimetric frequency *vs* potential dependencies also show, that the mass exchange process is accompanied by a hysteresis. In the anodic cycle, the Tl(I) ions are removed from the layer in a broad potential region, whereas in the cathodic cycle, the Tl(I) uptake process is much faster and is observed in a narrower (~300 mV) potential range, at the same scan rate. This suggests that dynamics of the thallium(I) ions exchange in the anodic and the cathodic processes is different.

In Fig. 5 (left panel) there are shown the frequency – charge dependencies obtained during cycling the potential of the electrode from 0 to 0.95 V for increasing concentrations of Tl(I) in the solution. From the results presented in this Figure one

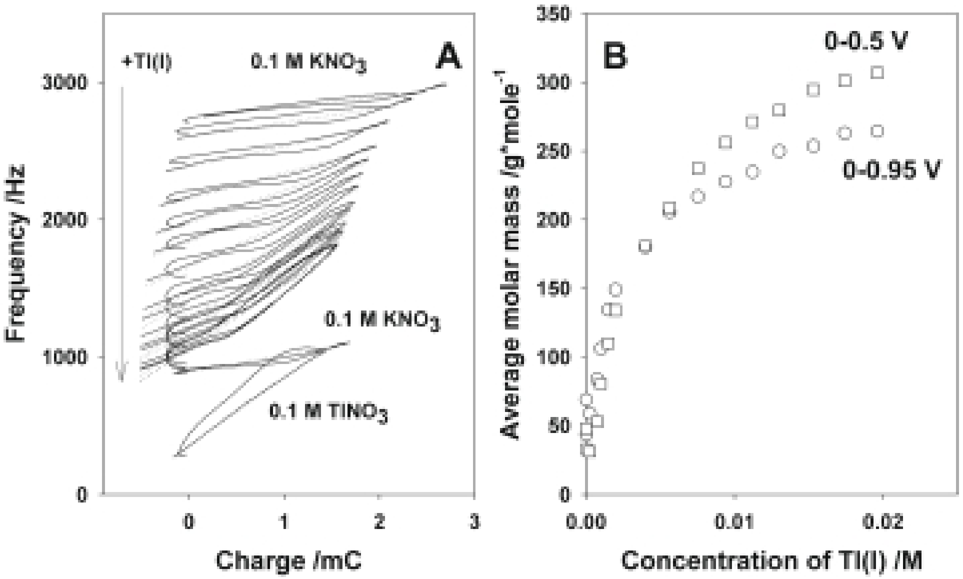

Figure 5. (A) The frequency – charge dependencies recorded in 0.1 M KNO_3 solution with increasing Tl(I) concentration (range of Tl(I) concentration given in part B). (B) The average molar masses calculated from the dependencies shown in part (A) for two polarization ranges: circles – 0 ÷ 0.95 V, and squares – 0 ÷ 0.5 V.

may draw a conclusion that the dynamics of the gravimetric response changes as grows concentration of Tl(I) ions. For lower Tl(I) concentrations and lower charges, the changes of the frequency are relatively small. On the other hand for higher charges, the slope of the frequency – charge dependence increases, and finally is similar to that observed in 0.1 M solution of $TlNO_3$.

On the right panel of this Figure 5, there are shown the average molar masses obtained for increasing concentration of Tl(I). Although the general tendency of these changes is acceptable, the final molar masses are higher than that expected for Tl(I) ion (204 g/mole). This result may suggest also, that probably occurs an increase in the deposit hydration level, when potassium ion is replaced by thallium one.

In Fig. 6 (left panel) there are given the charges, measured during cycling in all three regions of potentials, as a function of Tl(I) concentration. As it follows from the results presented in this Figure, in all cases an increase in Tl(I) concentrations leads to a decrease of electrochemical activity of the deposits. For 0.02 M Tl(I) concentration, only 55% of PB layer is electrochemically active. Similar conclusion could be drawn from the gravimetric experiments. However, after transferring the electrode to 0.1 M KNO_3 solution, an increase of the charge is observed during successive scans (Fig. 6, right panel). The details of the reactivation process are presented in Fig. 7. From the electrochemical and gravimetric experiments we could finally conclude, that at the end of such experiments, 80% of initial PB layer is electrochemically active.

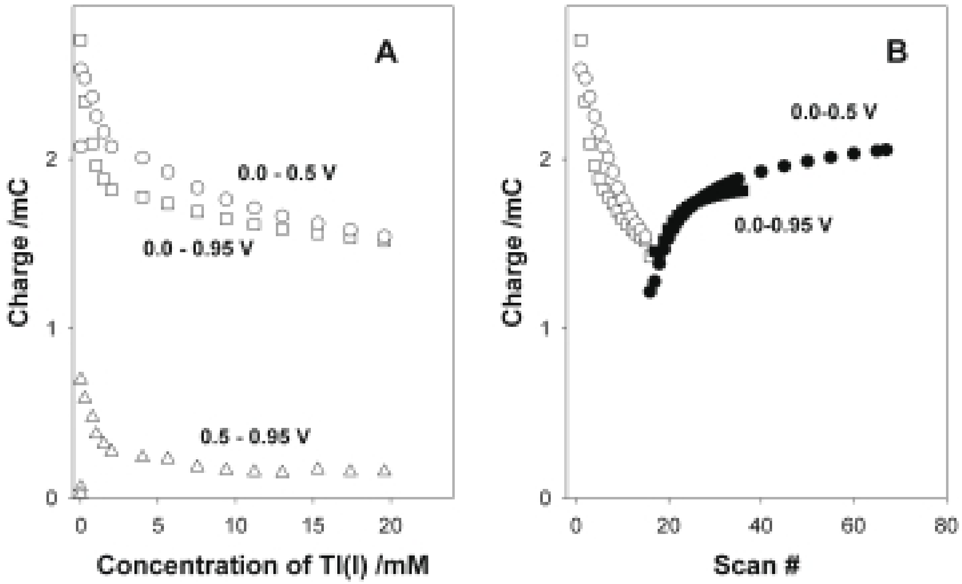

Figure 6. (A) Changes in the charges of CV curves under influence of Tl(I), measured during cycling in all three regions of polarization. (B) Open symbols – the charges from part (A) of this Figure, filled symbols – changes in the charges measured after transferring the electrode to 0.1 M KNO_3 solution.

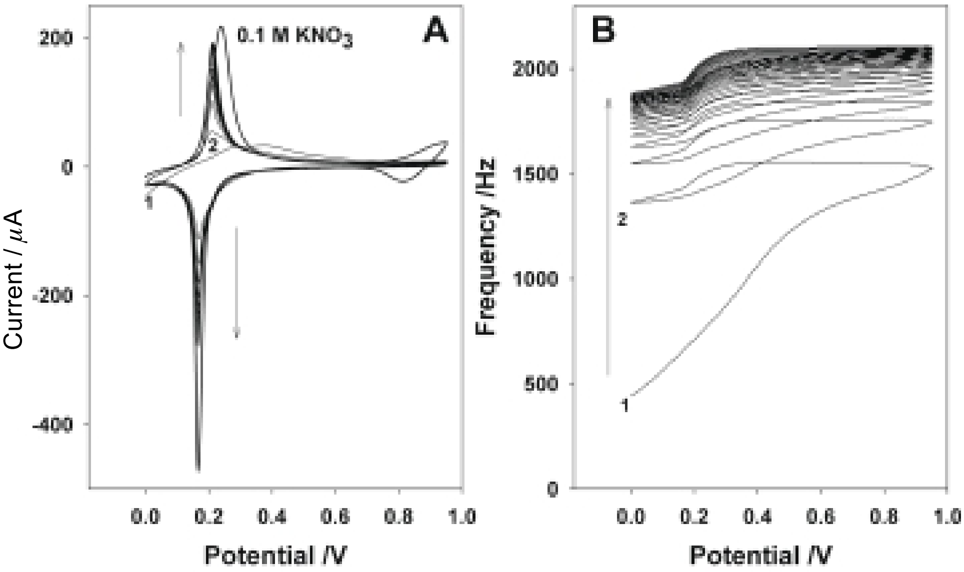

Figure 7. (A) CV curves of the PB system recorded after transferring the Tl(I) modified electrode to 0.1 M KNO_3 solution. The numbers denote the first and second scan. Thick line – CV curve recorded for freshly prepared PB film. Scan rate $\nu = 10$ mV s^{-1}. (B) The respective gravimetric responses.

CONCLUSIONS

The results obtained may suggest that the PB layer on the electrode is composed of two phases (compounds) – one phase is electrochemically active with respect to thallium ions, and the second, which most probably is also the thallium modifed PB, is not electrochemically active with respect to thallium ion in the investigated region of potentials. Basing on both coulometric and gravimetric data, we could conclude that approximately 45% of the total PB layer is composed of the phase, which in the presence of Tl(I) ions is electrochemically inactive. The mechanism of transformation of the inactive thallium(I) modified PB into active PB phase, in the presence of potassium ions, is not clear.

Since after experiments with thallium, and transfer of the modified electrode to KNO_3 solution the PB layer recovers most of the electrochemical activity, active and inactive thallium phases of PB, should remain in equilibrium. When thallium ion bounded to inactive PB phase is replaced with potassium ion bounded to active PB phase, both phases become electrochemically active. This process could be schematically described in the following way:

$$\text{PB-Tl}_{\text{active}} + \text{K}^+ = \text{PB-K}_{\text{active}} + \text{Tl}^+ \quad (8)$$

$$\text{PB-Tl}_{\text{inactive}} + \text{PB-K}_{\text{active}} = \text{PB-K}_{\text{active}} + \text{PB-Tl}_{\text{active}} \qquad (9)$$

In the case of the redox system which appears at more positive potentials, we could conclude, that in the presence of thallium(I) ions, this system disappears, and even after prolonged cycling in KNO_3 solutions, it has never been observed again. These suggestions extend the ideas of Scholz and co-workers [29] who focused on the role of size of the exchanged cations.

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