

# Study of Growth and the Electrochemical Behavior of Prussian Blue Films Using Electrochemical Quartz Crystal Microbalance

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Using cyclic voltammetry and chronoamperometry combined with electrochemical quartz crystal microbalance, the deposition of Prussian blue (PB) on a gold electrode from solutions containing Fe<sup>3+</sup> and Fe(CN)<sub>6</sub><sup>3-</sup> ions was studied. The change of mass in cyclic voltammetry experiments in the first cycles points to fast deposition of PB. In longer cycling the exit and entrance of cations (K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) is observed in the anodic and cathodic run, respectively. In potentiostatic deposition four types of behaviors of the mass (and charge) change in time as functions of potential were found. The results point to the electrodeposition of a mixture of the "insoluble" and "soluble" form of PB in the range 0.55–0.25 V. Energy-dispersive X-ray (EDX) analysis indicates that at 0.35 V both soluble and insoluble PB is formed. Prolonged cycling of such electrodes in KCl solutions does not change the K:Fe ratio. At 0.10 V K<sub>2</sub>Fe[Fe(CN)<sub>6</sub>] is obtained. The solubility products of KFe[Fe(CN)<sub>6</sub>] and Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> were estimated based on the potentiostatic deposition experiments. The process of the dissolution of the PB deposits under potentiostatic conditions at positive potentials was also studied and the rate of dissolution was calculated. When the PB layers on the electrode are very thin, the change of mass shows that, as a net result, nonhydrated potassium ions exit or enter the layer in the redox reactions. Similar behavior is observed for ammonium ions. Smaller values of apparent molar mass are found when thicker PB layers are used.  
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Prussian blue (PB = [iron(III)-hexacyanoferrate(II)]) exists in the solid state in two forms. At large excess of Fe(III) in the solution with respect to Fe(CN)<sub>6</sub><sup>4-</sup>, "insoluble" PB (Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>) is formed.<sup>1</sup> When the excess Fe(CN)<sub>6</sub><sup>4-</sup> is used, the formation of so-called soluble PB (KFe[Fe(CN)<sub>6</sub>]) is observed.<sup>1</sup> 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)].<sup>1,2</sup> These compounds may be attached to the 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,<sup>1–26</sup> there are some problems, such as the lattice reconstruction, the combined role of various counterions and solvent, and the role of anions and hydrogen ions in the course of the electroreduction or oxidation, which call for further attention.

We hope that further progress in the understanding of these and other related phenomena can be reached when the investigation of the rate of formation of PB deposits and of the mechanism of PB transformation in a wide range of potentials is carried out on the Au/quartz electrode using the microgravimetry combined with parallel electrochemical experiments. The comparison of the charge and mass of the electrode appeared to be fruitful in the study of metal hexacyanoferrates<sup>25–29</sup> and the conducting polymers.<sup>30–34</sup>

This work further explores the possibilities of this method in such studies and brings new information about the nature of PB films on electrodes and their reactions. Such information may be useful in the application of ferri–ferrocyanide-based materials for construction of supercapacitors.

## Experimental

**Reagents.**—The solution used for PB deposition was prepared from acidified solutions of K<sub>3</sub>Fe(CN)<sub>6</sub> (2 mM), FeCl<sub>3</sub> (2 mM), and KCl (0.5 M) mixed in proportion 1:1:2. Salts used in experiments were of p.a. quality and were not additionally purified. Double-distilled water, additionally purified in a Milli-Q ultrapure water system, was used in all experiments.

**Apparatus.**—Quartz microbalance was produced at the Institute of Physical Chemistry of the Polish Academy of Sciences. Its construction was described by Kutner et al.<sup>35</sup> Crystals with two fundamental frequencies: 5 and 10 MHz were used. Frequency of crystals was monitored by a PM 6680B high-resolution programmable

timer/counter (Fluke). The dependence of the frequency on the mass of the electrode was determined in 0.22 M HClO<sub>4</sub> 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 metallic silver. The dependence of the mass ( $\Delta m$ ) on the frequency ( $\Delta f$ ) for a crystal is described by the Sauerbray equation

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

where  $\mu_q$  is the shear modulus of the quartz,  $\rho_q$  denotes the density of quartz, and  $A$  is the area of the oscillating gold electrode. Combination of Eq. 1 with the Faraday law gives the equation, which also simply relates the change of frequency with charge

$$\Delta f = -2 \frac{M}{nFA} \Delta q f_0^2 \mu_q^{-1/2} \rho_q^{-1/2} \quad [2]$$

Theoretically Eq. 2 enables the determination of the molar mass ( $M$ ) of species, which changes the mass of the electrode in the course of the electrochemical reaction.

In the case of silver reduction we found the following  $\Delta m$  (in ng) vs.  $\Delta f$  (in Hz) dependencies for both crystals

$$5 \text{ MHz: } \Delta m = (52.5 \pm 17.5) - (4.874 \pm 0.066) \Delta f \\ r = 0.998, n = 22 \quad [3]$$

$$10 \text{ MHz: } \Delta m = (31.3 \pm 16.1) - (1.274 \pm 0.014) \Delta f \\ r = 0.998, n = 36 \quad [4]$$

Measurements of quartz-crystal impedance were carried out using a Hewlett-Packard HP 8753A network analyzer in reflectance mode. The quartz crystal was connected to a network analyzer with 50  $\Omega$  coaxial cable, and position of the quartz crystal remained unchanged during measurements. Electrochemical experiments were performed using an EG&G Princeton Applied Research potentiostat (model 273) controlled by a personal computer

Scanning electron microscopy (SEM) was carried out using the LEO 435 VP apparatus (Germany) equipped with the X-ray spectrometry module (Röntec M1) working in the energy-dispersive X-ray (EDX) mode.

**Electrodes.**—The Au/quartz oscillators (supplied by the Tele and Radio Research Institute, Warsaw, Poland) covered by layers of PB were used as working electrodes, while Au wire and Ag/AgCl/1 M KCl served as a counter and reference electrode, respectively.

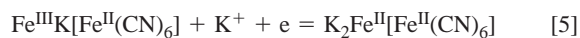
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**Methodology of a typical experiment.**—In the cyclic voltammetric (CV) experiment a clean electrode was placed in solution and the potential of the electrode was scanned at 20 mV/s in the potential range +0.70 to –0.20 V.

In a routine potentiostatic experiment a magnetic stirrer mixed the solution. In a nonstirred solution the electrode process occurred during the first 3–4 min and later ceased. In such a solution we observed the formation of spatial structures between the working and the counter electrodes, which were stable from several to several tens of minutes even after the disconnection of the potentiostat. Such structures were not strongly attached to the working electrode, and though their presence led to a decay of the electrochemical process, it did not change the quartz frequency. Since in a stirred solution we did not observe such a phenomenon, the magnetic stirrer with constant velocity stirred the solution ~200 rev/min and a constant current was recorded. In Fig. 1 we show the dependence of the current and the mass of the electrode on time at a constant potential in a typical PB deposition experiment.

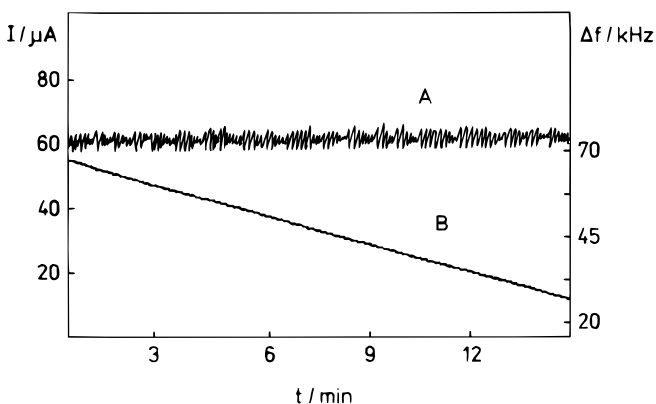
### Results

**Formation of the PB layers via cyclic polarization.**—Several CV curves recorded during deposition of PB are shown in Fig. 2. In the cathodic scan the current corresponds to the electroreduction of PB to Berlin white, and in the anodic one the reverse process occurs. Assuming the participation in the reaction of both the soluble and insoluble forms of PB, their processes may be described by the following equations<sup>1,2</sup>

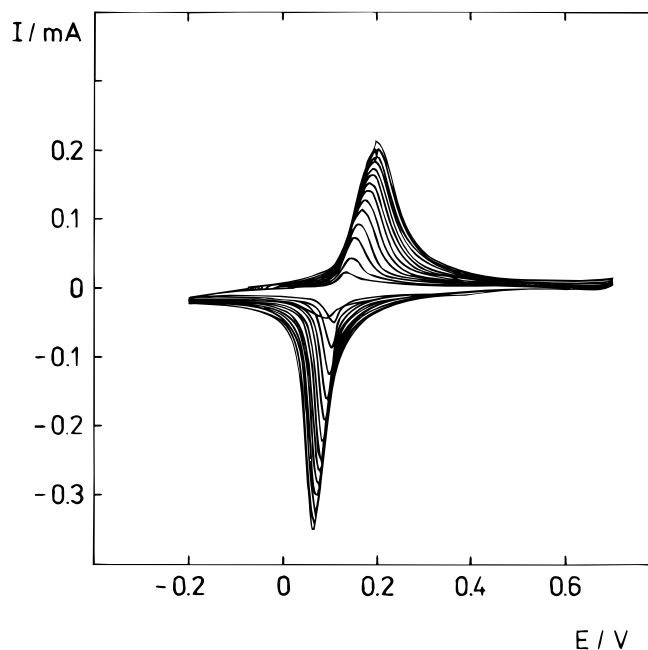


Changes in the frequency of the microbalance recorded during cyclic polarization of the Au/quartz electrode in the working solution are presented in Fig. 3. The formation of the PB deposit on the Au/quartz electrode is manifested in three ways by the following changes: (i) changes of the frequency measured (at the same potential) as a difference of frequency corresponding to successive cycles; (ii) the increase of the charge, calculated from the current–potential curve, corresponding to the oxidation of Berlin white to PB; and (iii) changes of the frequency in anodic runs, measured as a difference of frequency corresponding to the most negative and the most positive potential.

The time dependence of these effects, represented as a function of a number of cycles (*n*), is given in Fig. 4. According to the results presented in this figure, we observed a linear increase of frequency with time [phenomenon (i)], regardless of the fact that the frequency was measured at the most negative or at the most positive potential. Effect (iii) was not linear with time, as was also effect (ii), not



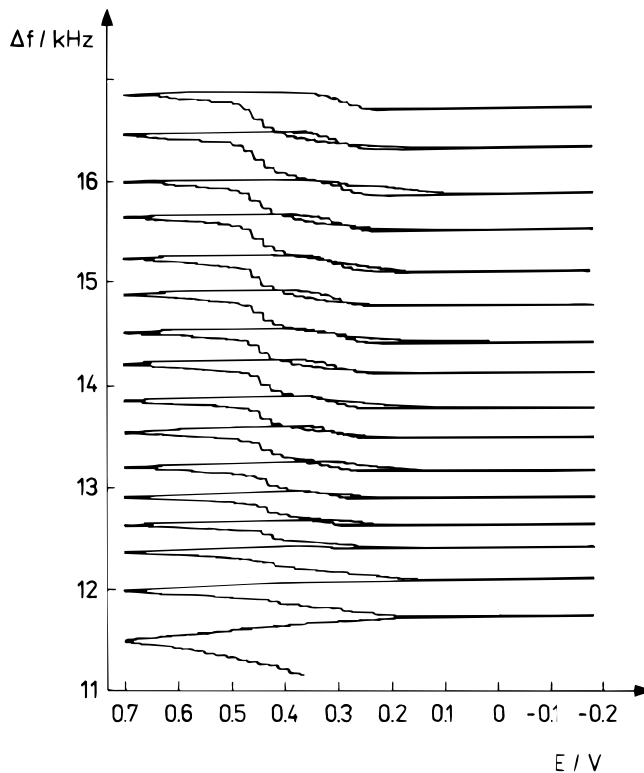
**Figure 1.** Time dependence of the current (A) and the mass of the electrode (B) recorded during potentiostatic formation of the PB deposit at 0.10 V. Solution was prepared by mixing the solution of 2 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with 0.5 M KCl and 2 mM  $\text{FeCl}_3$  in 1:2:1 proportion. pH 3.5.



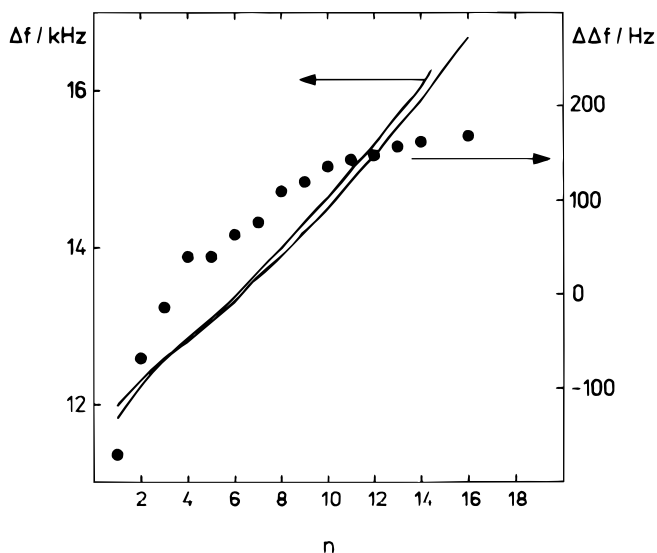
**Figure 2.** CV curves (scan rate 20 mV/s) recorded during deposition of PB from the solution with the same composition as in Fig. 1.

shown in Fig. 4 but discussed later. At longer time of the experiment, the frequency changes within one cycle became smaller with prolonged cycling, reaching a limiting value.

The same behavior was also observed when the changes of the charge of the electrode with the time of cycling were measured. After approximately ten cycles the charge at a given scan rate was practically constant.



**Figure 3.** Changes of the microbalance frequency during cyclic polarization recorded simultaneously with CV curves presented in Fig. 2.

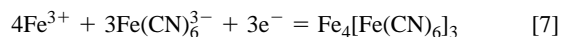


**Figure 4.** Changes of the microbalance frequency (Fig. 3) in successive cycles (lines). Difference of frequency corresponding to the most negative and the most positive potential in each anodic half-cycle (points).

In order to understand this behavior more clearly, the experiments were performed in a different way. The formation of the PB layer was carried out at  $E = 0.15$  V. Every 3 min the experiment was interrupted and the electrode removed from the working solution. Then it was transferred to 0.5 M KCl solution where the CV curve was recorded. After that the PB deposition was continued for 3 min. Each set of experiments lasted 24 min. The results presented in Fig. 5, show that the mass of the electrode increased linearly with time. No tendency of the total process to slow down is observed. On the other hand, both the charge corresponding to the reduction of PB and the change of mass corresponding to one cycle exhibits a tendency to saturation. Thus, these results are in full agreement with those presented previously (Fig. 2–4). They could suggest that in the case of CV when the charge between successive cycles stops to change, there is no further deposition of PB. However, such a conclusion cannot be true, since as shown earlier, the deposition of PB is a linear function of time.

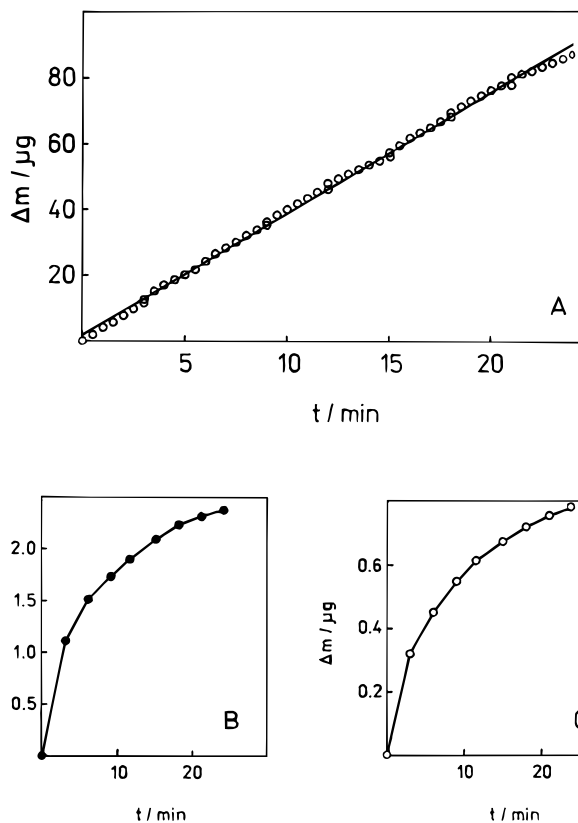
As follows from the results presented in Fig. 3, the formation of the PB deposits practically occurred only when the electrode is polarized toward negative potentials. When the potential scan direction was reversed toward more positive values, the cations were removed from the layer and the mass of the electrode changed very slightly.

*Formation of the PB deposits at constant potential.*—Deposition of PB on electrodes was also carried out under potentiostatic conditions in a range of potentials from 0.60 to 0.10 V. Every experiment lasted 15 min. During these experiments both the current and the change of mass corresponding to the formation of the PB deposits were measured. Assuming that the insoluble form of PB is formed, the following reaction should occur

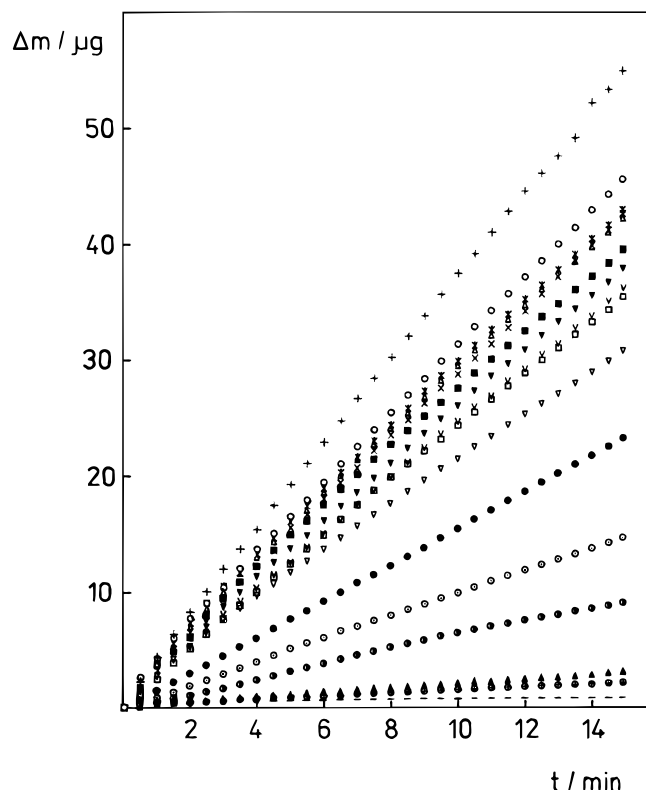


The typical change of mass presented in Fig. 1 shows that the frequency, and consequently, the mass of the PB deposit, increases linearly with time, while the average current flowing through the system remains practically constant.

The values of the frequency of the microbalance were recalculated into the mass using Eq. 1 or 2. Changes of the deposited mass as a function of time are presented in Fig. 6. For all potentials the changes of mass were linear in time with high correlation coefficients ( $R = 0.999$ ). The slopes  $dm/dt$ , calculated from these dependencies, are presented in Table I. These results showed that the reproducibility of the  $dm/dt$  slopes was better than 0.4%.



**Figure 5.** Mass changes recorded during deposition of PB at 0.15 V (A). Charge changes (B) and mass changes obtained during one anodic cycle (C) calculated from CV curves recorded in 0.5 M solution of KCl for the electrode modified with PB.



**Figure 6.** Time dependencies of the microbalance mass changes recorded during deposition of PB at constant potentials in the range from 0.60 to 0.10 V. Acidified solution of 2 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with 0.5 M KCl and 2 mM  $\text{FeCl}_3$  in 1:2:1 proportion.

**Table I. Velocity of the formation of PB layers (in ng per min) and charges (mC) measured at various deposition potentials.**

Potential (V)	$\Delta m/\Delta t + SD$ (ng min <sup>-1</sup> )	Charge (mC)	Potential (V)	$\Delta m/\Delta t + SD$ (ng min <sup>-1</sup> )	Charge (mC)
0.60	0	0	0.25	2362 ± 12 2372 ± 9	10 9.4
0.55	136 ± 2	0.68	0.24	2488 ± 13	9.3
0.50	198 ± 2	0.9	0.22	2586 ± 21	6.1
0.45	627 ± 6	1.89	0.21	2770 ± 21	5.4
0.40	992 ± 4	3.9	0.20	2788 ± 21 2795 ± 21	2.21 2.58
0.35	1562 ± 3	6.9	0.15	2971 ± 14	2.74
0.30	1997 ± 18	8.9	0.10	3628 ± 14	3.03

The dependence of the deposition rate on the potential ( $E$ ) reflects the change of the surface concentration of hexacyanoferrate(II) with potential, according to the modified Nernst equation

$$C_{\text{Fe(CN)}_6^{4-}} = \frac{C^0}{1 + a} \quad [8]$$

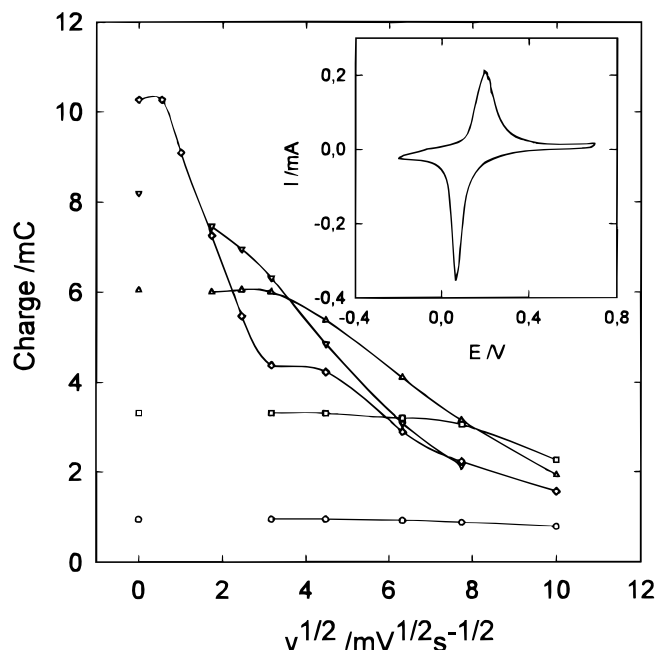
where  $C^0$  is the initial concentration of  $\text{Fe(CN)}_6^{3-}$  and  $a = \exp[(E - E^0)nF/RT]$ .  $E^0$  denotes the formal potential and the other symbols have their usual meaning. At the most positive potential (0.60 V),  $dm/dt \approx 0$ , since the concentration of  $\text{Fe(CN)}_6^{4-}$  is then near 0.

To determine the efficiency of the PB deposition, in the separate experiment we compared the mass changes measured by the microbalance with charges recorded during potentiostatic experiments. In the range of potentials from 0.45–0.25 V, the ratio ( $k$ ) of the mass to the charge was equal to  $k = m/q = (2.0 \pm 0.3) \times 10^{-3}$  g/C. Thus, the ratio of the molecular weight to the number of electrons ( $M/n$ ) equals to  $191 \times 29$  g. Assuming that the deposit was the insoluble PB, with  $M = 859.2$ , the average efficiency of the reduction process equals 67%. Taking into account very low solubility of PB, this is a rather unexpected result. The real efficiency is probably even lower, since in the calculation of the molecular weight, water molecules should be taken into account.

Also, the charge corresponding to the electrode reaction of the deposited film was determined. After the deposition of PB at a constant potential the electrode was transferred to 0.5 M KCl solution and the CV curves were recorded at 20 mV/s in the potential range -0.20–0.70 V starting from -0.20 V (inset to Fig. 7). The dependence of the cathodic charge on the potential is presented in Table I. As follows from the results presented in this table, in a range of potentials from 0.60 to 0.25, a gradual increase of the charge occurs which reaches a maximum at 0.25 V. At less positive potentials in the narrow potential window 0.25–0.20 V, the charge suddenly drops to much lower values. The charge at  $E = 0.20$  V was only about 25% of that measured at  $E = 0.25$  V. At still less positive potentials one observes some increase of the charge. However, at  $E = 0.10$  V its value amounts to only 30% of that at  $E = 0.25$  V.

The results presented in Table I should be considered as approximate data, since both the cathodic and anodic charges are dependent on the scan rate. The dependencies of the cathodic charges on a square root of a scan rate, recorded after transferring the modified electrodes (obtained at various potentials in the range 0.25–0.45 V) to 0.5 M KCl solution, are presented in Fig. 7. Under these conditions, stable  $I$ - $E$  curves were obtained starting from the third cycle. For the scan rates lower than 10 mV/s, the cathodic charges were independent of  $\nu$ . However, the scan rate at which the stabilization of the charges occurred was shifted toward shorter times as the deposition potential became more negative. The results presented in Fig. 7 illustrate a transfer from infinite to finite diffusion space behavior.

The deposits obtained at potentials less positive than 0.25 V were unstable in experiments with the scan rate lower than 0.5 mV/s,



**Figure 7.** Dependence of the apparent cathodic charge of the PB electroreduction on the square root of the scan rate for the PB deposits at the potentials: (○) 0.45, (●) 0.40, (▽) 0.35, (▼) 0.30, and (□) 0.25 V. Inset shows a typical CV curve (scan rate 20 mV/s) recorded after transfer of the electrode with deposited PB layer from the working solution to 0.5 M KCl solution.

since the charges corresponding to the reduction (or oxidation) process decreased from cycle to cycle.

In order to study the changes which accompany the transformation of the deposit formed at more negative potential into the form stable at more positive values (lattice reconstruction), deposition was carried out at  $E = 0.10$  V. Next the electrode was transferred to freshly prepared working solution (the same as that described in the section on Reagents) and conditioned for 4 min at  $E = 0.30$  V. The electrode was again transferred to the fresh working solution and kept at  $E = 0.10$  V for next 4 min. The whole experiment was then repeated, but between successive formations of the deposit, the electrode was conditioned for 1 h in 0.5 M KCl solution.

The changes of mass and the cathodic charges recorded during such experiments are presented in Table II. As follows from these data, the cathodic charge (2.98 mC) corresponding to deposition potential  $E = 0.10$  V increased to 8.35 mC when the electrode was transferred to working solution and kept at  $E = 0.30$  V. The latter value was similar to that measured after 15 min potentiostatic conditioning of the electrode at 0.30 V in a single-step experiment (8.9 mC). When the deposit was again conditioned at 0.10 V, in practice no change of the cathodic charge was observed. On the basis

**Table II. Gold/quartz electrode parameters obtained during deposition of PB layers at 0.10 V, next at 0.30 V and finally at 0.10 V. <sup>a</sup>**

$E$ (V)	$t$ (min)	$\Delta f$ (Hz)	$\Delta m$ (ng)	$\Delta m/\Delta t + SD$ (ng min <sup>-1</sup> )	$Q$ (mC)	$I$ ( $\mu\text{A}$ )
0.10	15	45 660	58 170	3 878 ± 19	2.98 (2.82)	65
0.30	4	6 920	8 815	2 204 ± 11	8.35 (6.96)	30
0.10	4	11 350	14 460	3 615 ± 18	8.30 (8.17)	65

<sup>a</sup>  $\Delta f$  is the change in frequency;  $\Delta m$  the change in mass,  $\Delta m/\Delta t$  velocity of the deposition process,  $Q$  charge measured (cathodic process) after transferring the electrode from the working solution to 0.5 M solution of KCl, and  $I$  is the deposition current.

of these charge values one could draw a conclusion that PB deposit formed at 0.30 V and later again kept at 0.10 V is rather stable, and at still less positive potential (0.10 V) does not undergo any deep structural modification. It follows from the changes of the mass that at 0.10 V the deposit was still formed at a rate comparable to that observed earlier (Table I). During such experiments a slight destruction of the PB deposits was observed.

When the PB-modified electrode was conditioned in 0.5 M KCl solution during 60 min (cycling in the range from  $-0.20$  to  $0.50$  V), one observed a slow dissolution or reconstruction of the deposit manifested by a small decrease of the cathodic charge. This process was faster in the case of the deposit formed at  $E = 0.30$  V. The cathodic charge, after cycling in the supporting electrolyte, dropped in this case by 17%.

These results show that the deposits formed at 0.10 V and conditioned at 0.30 V exhibit the electrochemical properties identical with those of films obtained at 0.30 V.

In conclusion, one may distinguish four regions of potentials for the formation of the PB deposits on the electrode

(i) At potentials more positive than 0.60 V the formation of the deposits in our working solution is not observed. The changes of the frequency observed during potentiostatic experiments carried out at 0.60 V are in the order of 1–2 Hz/min and should not be accepted as an analytical signal. Also, no electrochemical response is observed when the electrode, conditioned at 0.60 V, is transferred to 0.5 M KCl solution and the CV curve recorded.

(ii) In the range of potentials from 0.55 to 0.25 V, both the mass of the electrode and the charge measured from the CV experiments change approximately linearly with the potential and the formation of the PB deposit is fast.

(iii) In a narrow range of potentials from 0.25 to 0.20 V, a sudden decrease of the cathodic charges is observed, whereas on the basis of the changes of the mass we can conclude that the deposit is still formed.

(iv) At even less positive potentials ( $<0.20$  V) the frequency changes during the deposition of PB are faster than at more positive potentials, whereas changes of the electrode charges are almost constant. The deposit formed in this potential range can be rather quickly transformed into PB deposit obtained at more positive potentials.

**SEM of PB layers.**—SEM was used in order to measure the ratio of potassium to iron ions in the PB layers deposited at various potentials (0.10 and 0.35 V). During the preparation of the samples, both mass and charge of layers were monitored. Before the SEM experiments, freshly prepared layers were washed carefully with water and next dried at room temperature under vacuum for 24 h. The example of the SEM image is shown in the inset to Fig. 8. The surface of the obtained layers is cracked but relatively smooth and is covered by a large amount of small clots.

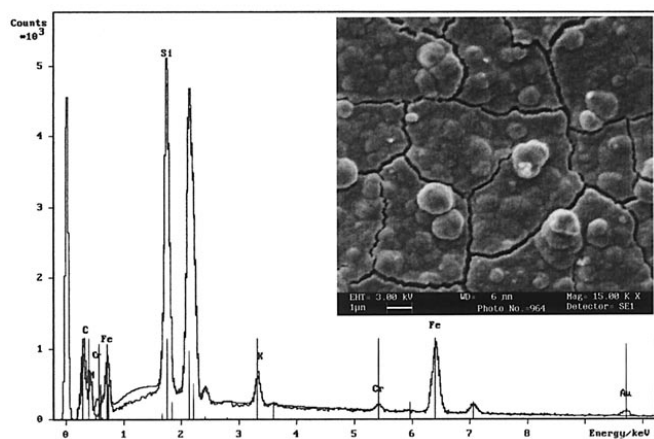


Figure 8. EDX analysis of PB layer obtained at 0.1 V and cycled in 0.5 M solution KCl. Inset shows the SEM image of the dried layer.

An example of the results obtained by EDX analysis of these layers is shown in Fig. 8. Surprisingly, not only K, Fe, C, N, and O are detected, but also Au, Si, and Cr are found. Thus, the energy of electrons must have been so high that it penetrated across the PB layer to the gold and quartz support.

The ratio of K to Fe depends on the potential at which the layers were prepared. When the deposition occurred at 0.10 V, the K:Fe ratio, determined in two regions ( $0.2 \times 0.2$  mm) of the sample, was equal to  $(1.00 \pm 0.08):(1.13 \pm 0.12)$  and  $(1.00 \pm 0.08):(1.21 \pm 0.13)$ , respectively. At 0.35 V this ratio was equal to  $(1.00 \pm 0.17):(6.10 \pm 0.59)$  and  $(1.00 \pm 0.19):(6.85 \pm 0.66)$ . Thus, the layers formed at 0.10 V had almost exactly the K:Fe ratio equal to that which exists in  $K_2Fe[Fe(CN)_6]$ . The layers formed at more positive potentials were probably composed of insoluble PB with an admixture of the soluble form. The proportion of insoluble to soluble forms was approximately 1:1.5.

The prolonged cycling in the region of potentials corresponding to the  $K_2Fe_2[Fe(CN)_6] = KFe[Fe(CN)_6] + e + K^+$  electrode reaction and stopping the potential in the region corresponding to the oxidized form had no influence on the K:Fe ratio in practice. It was equal to  $(1.00 \pm 0.15):(6.71 \pm 0.64)$ .

The obtained K:Fe ratios should be very close to the real values, since the K:Fe ratio obtained for the  $K_3[Fe(CN)_6]$  crystal was equal to  $(2.69 \pm 0.16):(1.00 \pm 0.08)$ .

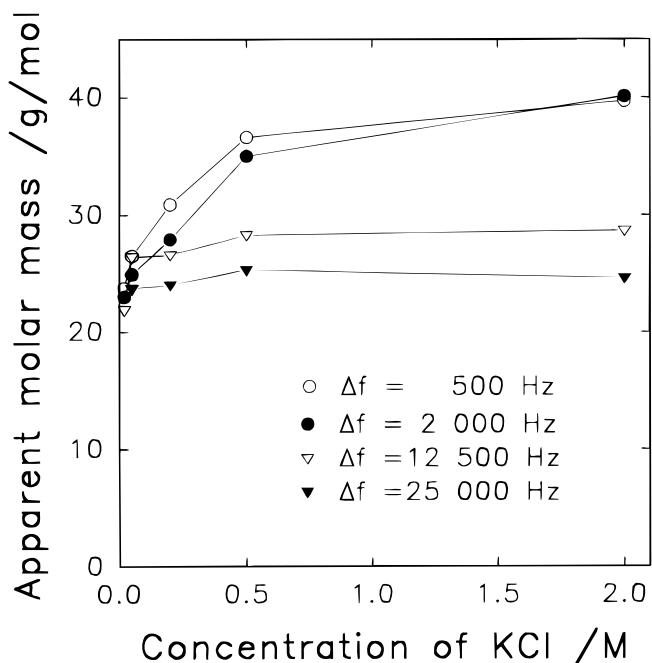
**The change of the mass during electro-oxidation and electroreduction of the film.**—In order to explore the mechanism of the electrochemical reactions of the PB-film, we prepared several PB modified electrodes by maintaining the gold/quartz electrode in modifying solution at  $E = 0.35$  V for different times corresponding to the following frequency changes: 500, 2000, 12,500, and 25,000 Hz. In the case of the first electrode the obtained PB layer was very thin (roughly 13 monolayers), while in the fourth case the layer was the thickest (approximately 650 monolayers). Such modified electrodes were next transferred into solutions with various concentrations of KCl (0.02–2 M) and conditioned for 120 s at  $E = 0.35$  V. At the end of each conditioning the CV curves and change of mass of the electrode were recorded, in a range 0.30 to  $-0.20$  V at scan rate  $v = 20$  mV/s.

During the experiments described the charge corresponding to the cathodic part of the CV curve slowly decreased with time, pointing probably to a slight destruction of the PB layer. After 6–8 cycles the charge was stable and did not exhibit any changes in solutions containing various concentrations of KCl.

The dependence of the apparent molar mass of the cation, which compensates the negative charge transferred through the layer during the cathodic sweep, on the concentration of KCl is presented in Fig. 9. It can be calculated from these results that in the case of two thinner layers ( $\Delta f = 500$  and 2000 Hz), the molar mass in 2 M KCl solution is very close to the value expected for the nonhydrated potassium ion, i.e., 39 g/mol. However, in the case of the thickest layer at a scan rate of 2–200 mV/s, the obtained apparent molar masses are lower and equal to 23–24 g/mol, similar to those reported earlier.<sup>25,26</sup>

It should also be noted that when the electrode covered with the thin layer of PB is used in 2 M  $NH_4NO_3$  solution, during its oxidation and reduction the molar mass equals 18 g/mol,<sup>36</sup> equal to the molar mass of unhydrated  $NH_4^+$  ion.

In order to estimate the influence of the PB formation on parameters of the quartz crystals, we measured the crystal impedance in air and in 0.05 and 2 M solutions of KCl. We then compared them with the results obtained for “thin” and “thick” PB layers. The results of the quartz crystal impedance measurements are presented in Table III. When going from bare crystal in aqueous solutions to crystal coated with PB layer, the frequency change was 2.8 and 23 kHz for thin and thick layers, respectively. In order to measure the reproducibility of the measurements we repeated the experiments in the case of thin PB layer. The changes in resistivity ( $R$ ) were of the order of 2–5%, and the changes in the quality factor ( $Q$ ) were of the order of 5–20%. As follows from the results presented in this table, when



**Figure 9.** Dependence of the apparent molar mass of the counterion on concentration of KCl solution in the process of electroreduction of the PB layers.

quartz crystals were immersed in aqueous solution, the resistivity of the crystals increased approximately three times and further changes of the resistivity were small. On the other hand, the quality factors of crystals ( $Q$ ) were much higher. The immersion of the crystal into aqueous solution results in the lowering of the  $Q$  parameter by two orders of magnitude. Thus, the comparison of this parameter for thin and thick PB layers is difficult.

#### Discussion

**Chemical formula of the deposit.**—In Fig. 10 (part A) the dependencies of the mass of the deposit on the potential as determined from the quartz microbalance and calculated from the cathodic charges measured in the KCl solution are shown. In the calculation we assumed two chemical formulas for the deposits, one corresponding to the soluble PB,  $\text{KFe}[\text{Fe}(\text{CN})_6]$ , and the second corresponding to the PB insoluble form,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , not taking into account the hydration of both forms. As it follows from the results presented in this figure, at potentials ranging from 0.25 to 0.60 V, the data corresponding to the soluble PB almost match the data from the microbalance, whereas those corresponding to the insoluble form were approximately 40% lower at all potentials. However, both sets of data

**Table III.** The gold/quartz electrode parameters measured in air and in various supporting electrolytes.<sup>a</sup>

Measurement	$f_0$ (MHz)	$\Delta f_0$ (kHz)	$R$ ( $\Omega$ )	$Q$
Air	9.923554	0	171	59754
0.05 M KCl	9.920008	3.546	511	453
2 M KCl	9.919670	3.884	450	706
PB <sup>b</sup> 0.05 M KCl	9.917252	6.302	448	930
PB <sup>b</sup> 0.5 M KCl	9.917252	6.302	445	960
PB <sup>b</sup> 2 M KCl	9.917102	6.452	441	949
PB <sup>c</sup> 0.05 M KCl	9.897981	25.573	452	824
PB <sup>c</sup> 0.5 M KCl	9.896237	27.317	455	887
PB <sup>c</sup> 2 M KCl	9.895620	27.934	439	917

<sup>a</sup>  $f_0$  is the fundamental frequency,  $R$  resistance, and  $Q$  the quality factor.

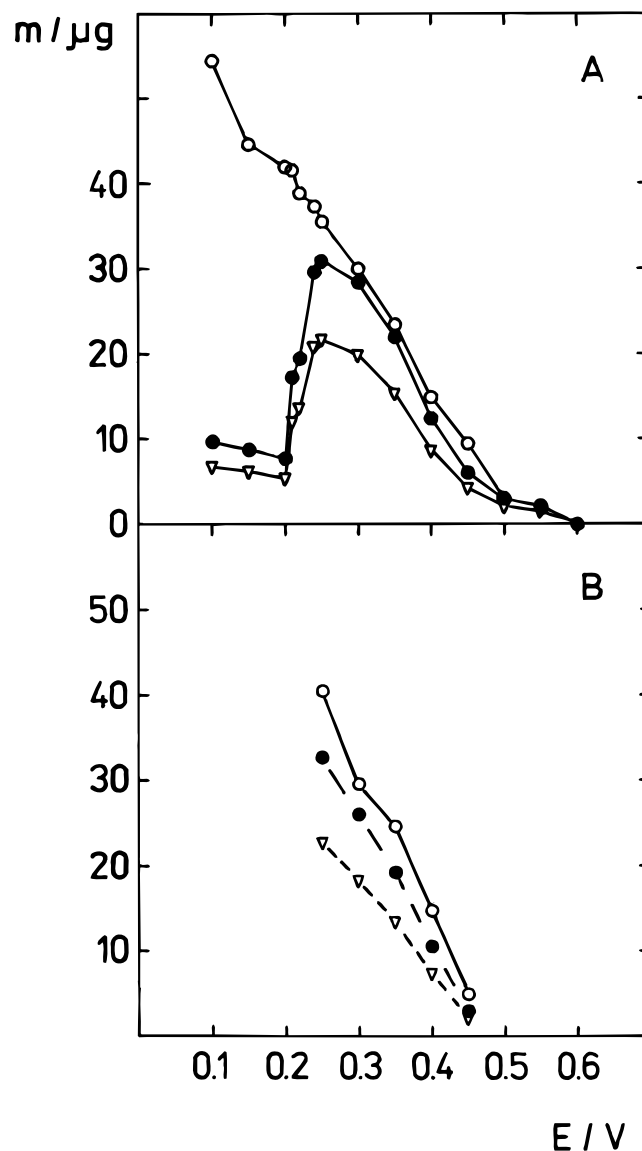
<sup>b</sup> Thin PB layer.

<sup>c</sup> Thick PB layer.

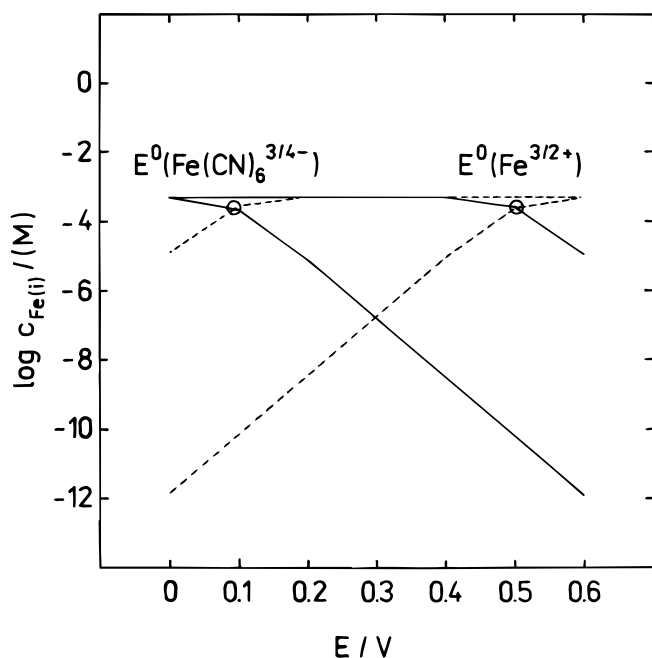
match if in calculation of the chemical formula water molecules are taken into account. In the case of the soluble PB one should assume the formula  $\text{KFe}[\text{Fe}(\text{CN})_6] \times 1-3 \text{H}_2\text{O}$ , and in the case of the insoluble form the formula should be  $\text{Fe}_4[\text{Fe}(\text{CN})_6] \times 15-30 \text{H}_2\text{O}$ .

It is known that PB is strongly hydrated. An  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  cell unit has<sup>14-16</sup> structural water molecules.<sup>22</sup> Even more extensive hydration of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  was reported.<sup>13,23,25</sup> Taking into account this strong hydration of PB, these results point rather to the formation of the insoluble form during potentiostatic deposition of this compound on the gold/quartz support. However, our EDX analysis indicates that the layers formed at 0.35 V are composed of a mixture of the soluble and insoluble PB. This conclusion is in agreement with the earlier results obtained by EDX spectroscopy where it was shown<sup>17</sup> that the cycled film may be a mixture of two forms.

Our experiments did not confirm the earlier report<sup>12</sup> that cyclic polarization changes the original composition of deposited films. We found that the K:Fe ratio remains almost unchanged after prolonged cyclic polarization of the electrode.



**Figure 10.** Dependence of the mass changes of the microbalance on potential: (○) values obtained after 15 min PB deposition at constant potential; (●, ▲) soluble and insoluble PB, respectively, obtained from CV curves recorded in 0.5 M KCl solution. (A) Charges obtained for  $\nu = 20 \text{ mV/s}$ , (B) charges obtained from extrapolation to  $\nu = 0$ .

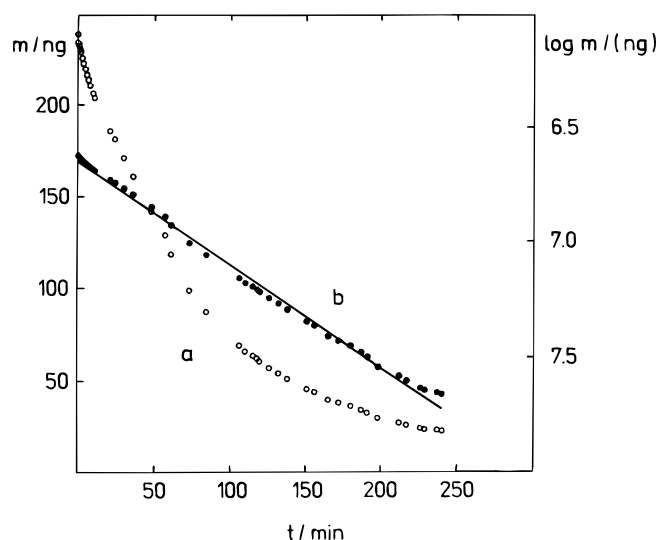


**Figure 11.** Dependencies of the  $\text{Fe}^{2/3+}$  and  $\text{Fe}(\text{CN})_6^{3/4-}$  concentrations on potential calculated from Eq. 8.

In Fig. 11 the concentration profiles for the oxidized and reduced species calculated from the standard potentials of the  $\text{Fe}^{3/2+}$  and  $\text{Fe}(\text{CN})_6^{3/4-}$  electrode reactions are shown. The comparison of the data from Fig. 6 and 10 (part A) shows that at  $E = 0.60$  V, no deposit is formed. Thus, from the potential dependence of the mass measured by microbalance we can calculate the potential ( $E_{\text{sp}}$ ) at which the PB starts to grow on the electrode surface. Such a calculation leads to  $E_{\text{sp}} = 0.52$  V. The concentrations of  $\text{Fe}(\text{III})$  and  $\text{Fe}(\text{CN})_6^{3/4-}$  at this potential may be calculated from the Nernst equation. Thus, the solubility products of  $\text{KFe}[\text{Fe}(\text{CN})_6]$  and  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  could be estimated. They are equal to  $1.2 \times 10^{-15} \text{ M}^3$ , and  $2.8 \times 10^{-46} \text{ M}^7$ , respectively. In the literature there are no reliable solubility data which could be compared to the first of these two values. The second value obtained ( $\text{p}K_{\text{sp}} = 45.6$ ) may be compared with that given by Tananayev et al.<sup>37</sup> ( $\text{p}K_{\text{sp}} = 40.5$ ). Taking into account all assumptions made in such calculations, in our opinion this method may lead to the estimation of the solubility products of other insoluble compounds.

*Properties of deposits formed at different potentials.*—In the calculations of the solubility products of deposits, on the basis of the apparent reversibility of the system we assumed that the Nernst equation could be applied. Since at  $E = 0.60$  V no deposit formation was observed, after formation of the deposit at less positive potential, when the PB-modified electrode is polarized to 0.60 V, one should observe its dissolution. In order to verify this conclusion, we formed the deposits on the electrodes at two potentials, 0.30 and 0.10 V. Next the electrodes were transferred to the KCl solution, kept at 0.60 V, and their mass was monitored for 4 h. The film produced at 0.30 V was dissolved completely. However, the film formed at 0.10 V remained on the electrode, though large oscillations of the frequency were observed and the average frequency remained almost unchanged. Cyclic voltammetric experiments conducted with this electrode support this finding. The charges transferred during oxidation and reduction of the PB layer remained almost unchanged.

The time dependence of the mass of the electrode during such dissolution is shown in Fig. 12 (curve a). From the results presented in this figure it follows that the nature of the  $m$ - $t$  dependence is different than that observed during the PB formation, where linear  $m$ - $t$  dependence exhibited diffusional limitations. Assuming that the dissolution of the deposit is the first-order reaction, from the log  $m$ - $t$



**Figure 12.** (a) Time dependence of the mass changes of the deposit ( $m$ ) formed at 0.35 V and kept at constant potential 0.60 V in 0.5 M KCl solution. (b) Such dependence in log  $m$  on  $t$  coordinates.

dependence we could calculate the rate constant of this reaction, which most probably is potential dependent. Such an analysis is shown in Fig. 12 (curve b). The rate constant calculated from this dependence equals  $4.5 \times 10^{-3} \text{ min}^{-1}$  and shows that the dissolution process is slow.

*Formal molar mass of species which compensate charge.*—From the dependence of the frequency (mass) of the electrode on the charge passed across the electrode, we have determined formally the molar mass of the counterions which enter or exit the film in order to maintain its neutrality during electrode reaction. In the case of the electrode covered by thin layers of PB in the solutions containing high concentrations of potassium and ammonium salts, the net mass balance indicates that nonhydrated  $\text{K}^+$  and  $\text{NH}_4^+$  ions enter or exit the layer in the course of the redox process. Evidently the cations which enter the layer at the phase boundary move from weak interaction with bulk water to weak interaction with molecules of water present in the layer. At present it is unclear how these cations are accommodated without removal of water from the layer and why such results may be obtained only with quite thin PB layers.

These results also indicate that the determined molar mass strongly depends on thickness of the PB layer, and when the thickness increases, the apparent molar mass of the cation is lower than that corresponding to the potassium cation, as reported in the literature.<sup>20,24</sup> Apparently for thicker PB films the microbalance responds only to the part of the reacting layer. We tried to solve this problem by measuring the resistivity and quality factor ( $Q$ ) of the electrodes (see Table III). The results obtained in the case of the PB layer suggest that the quality factor remains almost unchanged, while for thick layers some increase of the  $Q$  values is observed. However, these results should be taken with caution since the observed changes were small as compared with the experimental error. We intend to discuss the problem of these molar mass changes in the near future on the basis of work which is in progress.<sup>36</sup>

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#### References

1. K. Itaya, I. Uchida, and V. D. Neff, *Acc. Chem. Res.*, **19**, 162 (1986).
2. D. Ellis, M. Eckhoff, and V. D. Neff, *J. Phys. Chem.*, **85**, 1225 (1981).
3. K. P. Rajan and V. D. Neff, *J. Phys. Chem.*, **86**, 4361 (1982).
4. V. D. Neff, *J. Electrochem. Soc.*, **125**, 886 (1978).

5. K. Itaya, H. Akahoshi, and S. Toshima, *J. Electrochem. Soc.*, **129**, 1498 (1982).
6. K. Itaya, T. Ataka, S. Toshima, and T. Shinohara, *J. Phys. Chem.*, **86**, 2415 (1982).
7. K. Itaya, I. Uchida, and S. Toshima, *J. Phys. Chem.*, **87**, 105 (1983).
8. K. Itaya, I. Uchida, S. Toshima, and R. M. De La Rue, *J. Electrochem. Soc.*, **131**, 2086 (1984).
9. K. Itaya, N. Shoji, and I. Uchida, *J. Am. Chem. Soc.*, **106**, 3423 (1984).
10. H. Kellawi and D. R. Rosseinsky, *J. Electroanal. Chem.*, **131**, 373 (1982).
11. R. J. Mortimer and D. R. Rosseinsky, *J. Electroanal. Chem.*, **151**, 133 (1983).
12. R. J. Mortimer and D. R. Rosseinsky, *J. Chem. Soc., Dalton Trans.*, 2059 (1984).
13. A. Hamnett, S. J. Higgins, R. J. Mortimer, and D. R. Rosseinsky, *J. Electroanal. Chem.*, **255**, 315 (1988).
14. V. D. Neff, *J. Electrochem. Soc.*, **132**, 1382 (1985).
15. D. R. Rosseinsky, J. S. Tonge, J. Berthold, and J. F. Cassidy, *J. Chem. Soc., Faraday Trans.*, **83**, 231 (1987).
16. A. Xidis and C. D. Neff, *J. Electrochem. Soc.*, **138**, 3637 (1991).
17. C. A. Lundgren and R. W. Murray, *Inorg. Chem.*, **27**, 933 (1988).
18. P. J. Kulesza, *Inorg. Chem.*, **29**, 2395 (1990).
19. B. J. Feldman, and R. W. Murray, *Inorg. Chem.*, **26**, 1702 (1987).
20. K. Itaya, T. Ataka, and S. Toshima, *J. Am. Chem. Soc.*, **104**, 4767 (1982).
21. K. Itaya and I. Uchida, *Inorg. Chem.*, **25**, 389 (1986).
22. H. J. Buser, D. Schwarzenbach, W. Petter, and A. Lundi, *Inorg. Chem.*, **26**, 2704 (1977).
23. A. Hamnett, P. A. Christensen, and S. J. Higgins, *Analyst*, **119**, 735 (1994).
24. D. A. Buttry in *Electroanalytical Chemistry*, A. J. Bard, Editor, Vol. 17, Dekker, New York (1992).
25. B. J. Feldman and O. M. Melroy, *J. Electroanal. Chem.*, **234**, 213 (1987).
26. A. Dostal, B. Meyer, F. Scholz, U. Schröder, A. M. Bond, F. Marken, and S. J. Shaw, *J. Phys. Chem.*, **99**, 2096 (1995).
27. J. Bacskai, K. Martinusz, E. Czirok, G. Inzelt, P. J. Kulesza, and M. A. Malik, *J. Electroanal. Chem.*, **385**, 241 (1995).
28. E. Czirok, J. Bacskai, P. J. Kulesza, G. Inzelt, A. Wolkiewicz, K. Miecznikowski, and M. A. Malik, *J. Electroanal. Chem.*, **405**, 205 (1996).
29. Y. Wang, G. Zhu, and E. Wang, *J. Electroanal. Chem.*, **430**, 127 (1997).
30. R. Borjas and D. A. Buttry, *J. Electroanal. Chem.*, **280**, 73 (1990).
31. M. Skompska and A. R. Hillman, *J. Chem. Soc., Faraday Trans.*, **92**, 4101 (1996).
32. M. Skompska and A. R. Hillman, *J. Electroanal. Chem.*, **433**, 127 (1997).
33. G. Inzelt, *J. Electroanal. Chem.*, **287**, 171 (1990).
34. G. Inzelt and J. Bacskai, *Electrochim. Acta*, **37**, 647 (1992).
35. W. Koh, W. Kutner, M. T. Jones, and K. M. Kadish, *Electroanalysis*, **5**, 209 (1993).
36. M. Zadroncki, P. K. Wrona, and Z. Galus, To be published.
37. I. W. Tananayev, M. A. Gluskowa, and G. B. Seifer, *Zh. Nieorg. Khim.*, **1**, 66 (1956).