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Electrooxidation of Poly (p-Aminoazobenzene) Films – Kinetic Studies[*]

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The electrooxidation of poly (p-aminoazobenzene) [poly (p-AAB)] was studied in the presence of H^+ and of $Fe(CN)_6^{4-}$ ions by the means of cyclic voltammetry, chronoamperometry and rotating disc electrode. The diffusion coefficients and heterogeneous rate constants were determined from the analysis of Cottrell and Levich-Koutecky plots. It has been found, that the oxidation of poly (p-AAB) in acidic solution is kinetically controlled and independent of the transport of H^+ ions to the polymer surface. The results obtained in the presence of $Fe(CN)_6^{4-}$ have shown that poly (p-AAB) films are permeable to the ions from electrolyte solution.

Key words: poly(p-aminoazobenzene), electrooxidation, ion permeability

In recent years, aromatic compounds with amine groups have received great attention as the monomers for *in situ* electrochemical preparation of the polymer modified electrodes. The majority of monomers are aromatic compounds with one or two NH_2 substituents and other functional groups (-OH, $-OCH_3$). The resultant polymeric films possess some interesting features, like the electrochromism or sensitivity to H^+ ions. They can act as the ion-exchangers or have catalytic properties and redox activity. Thus, they can be applied in bateries, in electrochromic displays or as the sensors and biosensors [1–7].

Some years ago, Abd El-Rahman *et al.* [8] have reported the electropolymerization of p-aminoazobenzene (p-AAB) by oxidizing the monomer in acetonitrile solution in the presence of pyridine. They have found, that poly (p-aminoazobenzene) [poly (p-AAB)] is electroactive and very stable in the aqueous solutions with pH < 3. In addition, the pH variation induces reversible color changes of poly (p-AAB).

We have investigated the molecular structure and the electrodeposition mechanism of poly (p-AAB) [9]. It has been established, that the polymer film is a mixture of at least two structures. The first structure is linear and created through the head-to-tail (C–N) or head-to-head (N–N) coupling. The second one is acquired through the ortho-substitution. It has also been shown, that the composition of polymer mixture depends on polymerization potential. More positive potentials (1.2 V) induce the linear para-substituted chains to be more predominant.

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In the present paper the evaluation of the kinetic parameters for electrooxidation of poly (p-AAB) and for oxidation of $Fe(CN)_6^{4-}$ at the poly (p-AAB) films is reported.

EXPERIMENTAL

Poly (p-aminoazobenzene) films were obtained either on Au wire or on the Au rotating disc electrode, with 0.1 cm^2, 0.03 cm^2 geometric surface area respectively, from acetonitrile solution containing 0.05 M (p-AAB), 0.05 M pyridine and 0.1 M $LiClO_4$. The electropolymerization was carried out potentiostatically at 1.0 V or 1.2 V *vs*. SSCE (sodium saturated calomel electrode). Before electropolymerization the rotating disc Au electrode (r.d.Au) was polished to a mirror finish with alumina powder, whereas the gold wire was carefully annealed. The synthesis of p-AAB was described elsewhere [10]. The electrochemical properties of the poly (p-AAB) films were studied by using cyclic voltammetry, chronoamperometry and voltammetry at the r.d.e. The electrochemical measurements were carried out on a home-built computer controlled system (Compex). Voltammetry at r.d.e. was performed in the Tacussel setup. All measurements were carried out in a single compartment, three electrode electrochemical cell with respect to SCE (saturated calomel electrode).

The influence of H^+ ions on poly (p-AAB) electroactivity was studied either in aqueous solutions containing 0.1 M $LiClO_4$ and 0.01 M $HClO_4$ or in 0.1 M, 0.5 M, 1 M, 2 M $HClO_4$ solutions.

The kinetic parameters of $Fe(CN)_6^{4-}$ oxidation at the polymer/solution interface were measured at different thickness of poly (p-AAB) in 0.1 M $LiClO_4$ + 0.1 M $HClO_4$ + 2 mM $K_4Fe(CN)_6$ solution. The thickness of the film was determined by the amount of charge passed during electropolymerization.

The solutions were deoxygenated with pure argon before the measurements.

RESULTS AND DISCUSSION

Electrooxidation of poly (p-AAB) in the presence of H^+ ions. Fig. 1 shows the electrochemical response of poly (p-AAB) film in the solutions with different H^+ concentration. The polymer is electroactive in acidic solutions (pH < 3). A formal redox potential E_f was estimated as $E_f = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials. It was found that $E_f = 0.4$ V (vs.SCE) at pH = 1. The E_{pa} shifts to more positive potentials with the decrease of pH and the value of dE_{pa}/dpH is –55 mV/pH. Contrarily, the E_{pc} values only slightly depend on the pH of the solution. The E_f value reported in this work differs from those published by Abd El-Rahman [8] by *c.a.* 60 mV.

Fig. 2 presents the influence of the polymerization charge (film thickness) on CV curves of polymeric films recorded in 0.1 M $HClO_4$. It can clearly be seen, that the increase of the thickness results in the increase of the current. CV curves recorded at very low scan rates were used to estimate the surface concentration of the electroactive groups (Γ). It was found, that the number of groups which participate in films oxidation and reduction is identical and it is not dependent on H^+ concentration (in the range from 0.1 M to 1 M $HClO_4$). However, the Γ values changed with the polymerization charge from 1.7×10^{-9} M cm^{-2} (at Q_p – 7.5 mC) to 2.5×10^{-9} M cm^{-2} (at Q_p – 22.5 mC).

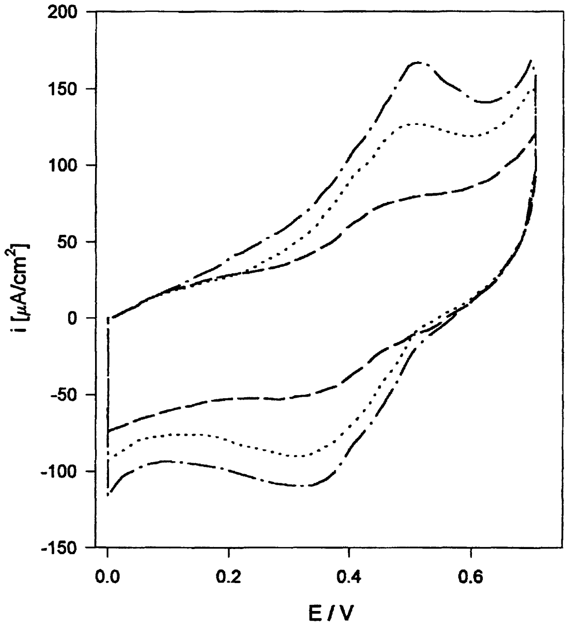

Figure 1. Cyclic voltammograms for poly (p-AAB) recorded at sweep rate 20 mV/s in: 0.1 M (– – –), 0.5 M (· · ·), 1.0 M (– · –) $HClO_4$.

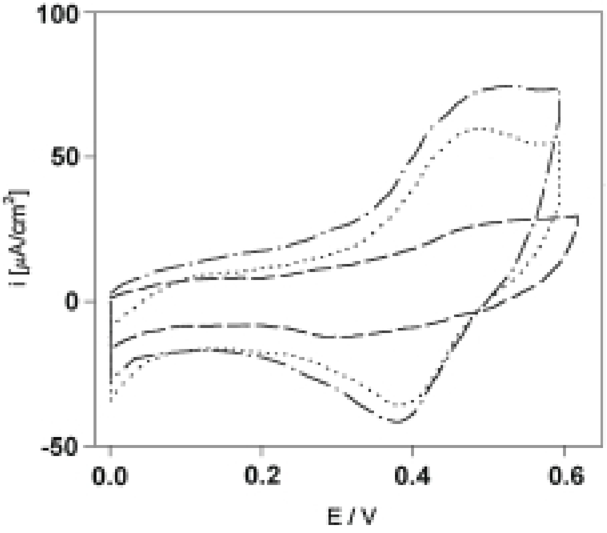

Figure 2. Cyclic voltammograms for poly (p-AAB) films of different thickness; polymerization charge Q_p: 7.5 mC (– – –), 15 mC (· · ·), 33 mC (– · –) recorded in 0.1 M $HClO_4$ at sweep rate 40 mV/s.

The Γ values were used to determine the bulk concentration of electroactive groups $c^0 = \Gamma/d$ (where d is the film thickness) and later to calculate the apparent diffusion coefficient (D_{app}). The following rough assumptions were made to establish the thickness from the polymerization charge: (i) polymerization of a single monomer molecule requires 2 electrons, (ii) the density of the polymer is 1.5 g cm^{-3}, similar to that of polyanilines' [11] and polypyrroles' [12], (iii) the polymerization process proceeds with 100% efficiency. The values of c^0 and D_{app} obtained under these conditions were quite reasonable.

To determine the apparent diffusion coefficient for the charge transport process within the film the single-step chronoamperometric measurements were carried out.

The charge obtained by the integration of i~t curves was later plotted as a function of the square root of time [13,14]. The D_{app} value was estimated from the slope of the linear part of the plots, according to equation (1):

$$Q = Q_{dl} + 2nFAc^0\,(Dt/\pi)^{1/2} \quad (1)$$

where Q_{dl} is the double layer charge, n – number of electrons involved in the process, π and F have their usual meanings. The values of Q_p, d, Γ, c^0 and D_{app} are collected in Table 1.

Table 1. The values of the surface concentration (Γ), the bulk concentration (c^0) of electroactive sites and the apparent diffusion coefficient (D_{app}) for the charge transport within poly (p-AAB) films.

$HClO_4$ [M]	Q_p [mC]	d [μm]	$\Gamma_{ox} = \Gamma_{red}$ [$\times10^{-9}$ M cm^{-2}]	c^0 [$\times10^{-5}$ M cm^{-3}]	D_{app} [10^{-8} cm^2 s^{-1}]
0.1	7.5	1.69	1.70	1.0	0.23
1.0	7.5	1.69	1.81	1.07	0.42
0.1	22.5	5.08	2.40	0.47	1.18
1.0	22.5	5.08	2.46	0.48	1.79

Literature data [8]: $\Gamma = 5.2\times10^{-9}$ M cm^{-2}; $c^0 = 3.4\times10^{-5}$ M cm^{-3}; $D = 1.08\times10^{-8}$ cm^2 s^{-1}; d = 1.5 μm.

Apparently, the values of D_{app} slightly depend on H^+ concentration and they increase with the polymer thickness. When the i/E curves were recorded on the r.d.Au covered with poly (p-AAB) of different thickness, the values of the current did not depend either on H^+ concentration or the rotation speed. However, the current increased very slightly with the thickness of the sample. The latter suggests, that the oxidation of poly (p-AAB) is not affected by the diffusion of H^+ ions to the polymer surface and that the oxidation current is controlled by kinetics of the electron transfer, and can be described by the following equation [13]:

$$i_k = nFAk_{fh}(E)c^0 \quad (2)$$

where i_k is the kinetic current, n, F, A, c^0 were defined above and k_{fh} is the heterogeneous rate constant for poly (p-AAB) oxidation. Equation (2) allows to set up k_{fh} as a function of potential (E). Fig. 3 presents the plot of log k_{fh} *versus* E. As one would expect the dependence is linear.

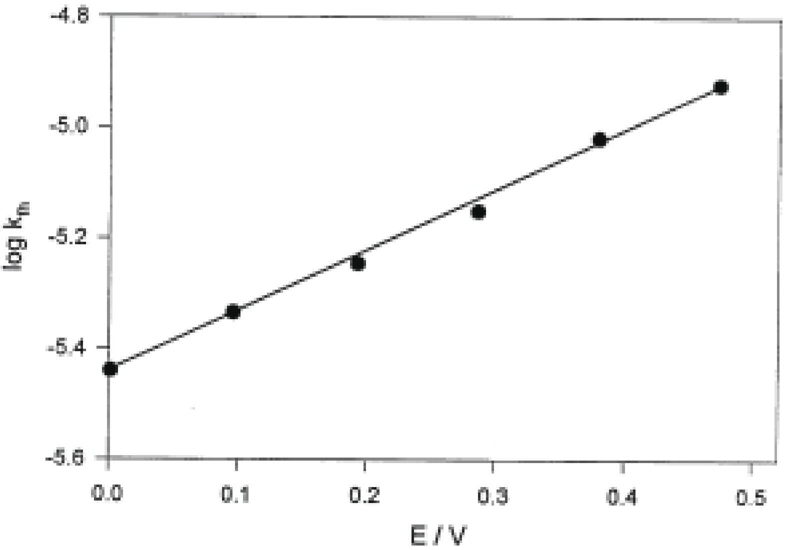

Figure 3. Log k_{fh} *vs* E plot for poly (p-AAB) in 0.1 M $LiClO_4$, k_{fh} values were determined from i/E curves obtained at r.d.Au, $c^0 = 1\times10^{-5}$ M/cm^2 ((Q_p – 7.5 mC) and n = 1 taken for calculation).

Electrooxidation of $Fe(CN)_6^{4-}$ ions at poly (p-AAB)Au electrodes. The electrooxidation of $K_4Fe(CN)_6$ at poly (p-AAB) films of different thickness was investigated in 0.1 M $HClO_4$ solution by the means of cyclic voltammetry and rotating disc electrode voltammetry.

Fig. 4 shows typical CV curves obtained on bare Au and on poly (p-AAB) coated electrodes.

As expected the highest value of the current is recorded on bare Au electrode. The increase of poly (p-AAB) film thickness results in the decrease of the redox current. This outcome is quite opposite to the influence of the film thickness on the current recorded in pure 0.1 M $HClO_4$ solution. Only one pair of redox peaks is observed in CV curves for poly (p-AAB). As the values of E_{pa} and E_{pc} are almost the same as in the case of bare Au electrode, these peaks can be ascribed to the oxidation and reduction of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple. Interestingly, as the thickness of polymer film increases the oxidation/reduction peaks of the redox couple become less pronounced.

The E_f for poly (p-AAB) measured in the presence of $Fe(CN)_6^{4-}$ ions are shifted towards less positive potentials in comparison with the values of E_f evaluated in pure 0.1 M $HClO_4$ solution. The results suggest that the oxidation of $Fe(CN)_6^{4-}$ at Au/poly (p-AAB) electrode accelerates polymer oxidation. However, the results also imply that poly (p-AAB) is permeable to $Fe(CN)_6^{4-}$ ions. In order to validate these postulations the r.d.e. measurements at different rotation rates and for the various thickness of poly (p-AAB) coatings were carried out.

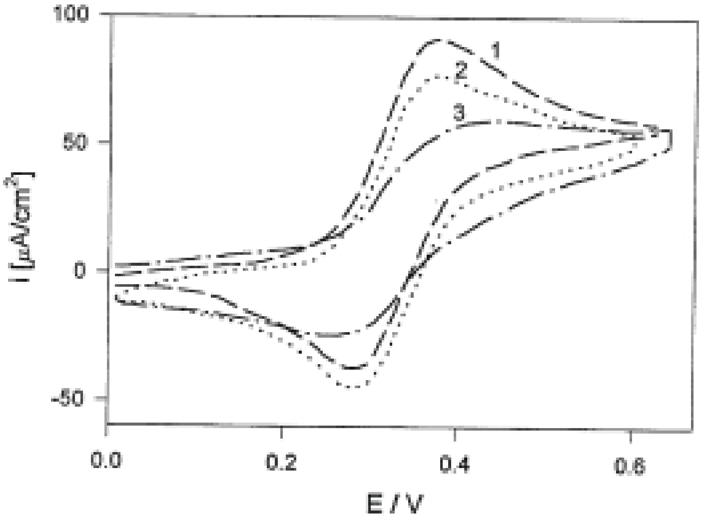

Figure 4. Cyclic voltammograms for oxidation of $Fe(CN)_6^{4-}$ on the bare (curve 1) and poly (p-AAB) coated r.d.Au electrode (curves 2, 3). Solution: 0.1 M $HClO_4$ + 2 mM $Fe(CN)_6^{4-}$, sweep rate 40 mV/s. Polymerization charge: Q_p = 7.5 mC (2), 15 mC (3).

Fig. 5 shows the influence of poly (p-AAB) thickness on the steady state current – potential curves (j/E) obtained for oxidation of $Fe(CN)_6^{4-}$ on bare and on polymer coated r.d.Au electrodes.

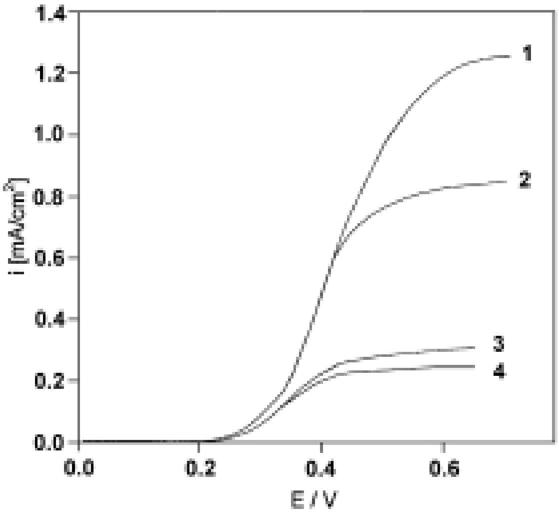

Figure 5. Typical current – potential curves for oxidation of $Fe(CN)_6^{4-}$ on the bare (curve 1) and poly (p-AAB) coated r.d.Au electrodes (curves 2–4). Solution: 0.1 M $HClO_4$ + 2 mM $Fe(CN)_6^{4-}$, rotation rate: 2300 rpm, sweep rate 2 mV/s. Polymerization charge: Q_p = 7.5 mC (2), 15 mC (3), 22.5 mC (4).

Obviously, the increase of the film thickness results in the decrease of the limiting current. Such behavior mostly reflects the difference in diffusion rates of $Fe(CN)_6^{4-}$ ions within the swollen film. The quantitative analysis of the r.d.Au. results can be made on the basis of the Koutecky-Levich equation [13–17]

$$1/i = 1/i_S + 1/i_L \qquad (3)$$

where $i_L = 0.62\ nF\ AD^{2/3}_{sol}\ \upsilon^{-1/6}\ c^b\ \omega^{1/2}$ and $i_S = nF\ A\,\kappa\ D_S\ c^b\ d^{-1}$
where i is the measured limiting current, i_L is the Levich current, i_S is the permeation current of $Fe(CN)_6^{4-}$ through poly (p-AAB) films, D_{sol} is the diffusion coefficient of $Fe(CN)_6^{4-}$ in a bulk of the solution, D_S is the diffusion coefficient of $Fe(CN)_6^{4-}$ inside the film, c^b is the bulk concentration of $Fe(CN)_6^{4-}$, υ is the kinetic viscosity of the solution, κ is the partition coefficient, d is the thickness of polymer film and ω is the rotation rate of the disc electrode.

The Koutecky-Levich plots (i^{-1} vs. $\omega^{-1/2}$) for poly (p-AAB) films of different thickness are presented in Fig. 6.

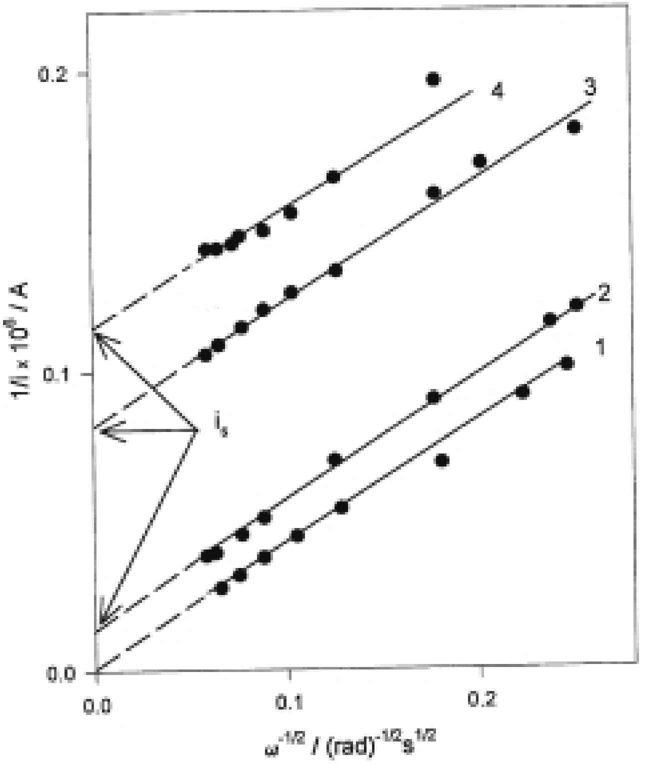

Figure 6. Levich-Koutecky plots for $Fe(CN)_6^{4-}$ oxidation on r.d.Au electrode in 0.1 M $HClO_4$, on bare Au electrode (1) and on poly (p-AAB) films (2–4). Polymerization charge: Q_p = 7.5 mC (2), 15 mC (3), 22.5 mC (4).

As expected the plots are linear with the slopes approaching the value obtained for bare Au electrode. Namely, the estimated values of D_{sol} are 5.6×10^{-6} cm^2s^{-1} (for bare electrode), 5.2×10^{-6} cm^2s^{-1} (for film of 1.69 μm, Q_p – 7.5 mC) and 3.68×10^{-6} cm^2s^{-1} (for film of 5 μm, Q_p – 22.5 mC). The latter means that the diffusion coefficient of $Fe(CN)_6^{4-}$ ions in the film is only a few times smaller than in the solution. Thus, one can conclude that poly (p-AAB) films are permeable and that the oxidation reaction of $Fe(CN)_6^{4-}$ takes place mainly in the polymer pores and at the surface of Au.

If so, it is possible to treat the i_s current as kinetic current i_k described by equation (2). As the redox reaction of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple is reversible, the Koutecky-Levich plots (i^{-1} vs. $\omega^{-1/2}$) can be sketched for different values of the overpotential (η). A typical relation of that kind is shown in Fig. 7, for 1.69μm – thick poly (p-AAB) film (Q_p – 7.5 mC).

The plots in Fig. 7 were used to evaluate the k_{fh}~η relation. The latter allowed the values of $k_{s,fh}$ to be determined according to equation (4):

$$\log k_{fh} = \log k_{s,fh} + (\eta_{\beta}\beta F\eta)/2.3(RT) \qquad (4)$$

The values of the standard rate constant ($k_{s,fh}$) are linearly dependent on the thickness of poly (p-AAB) films (Fig. 8) and on the polymerization charge.

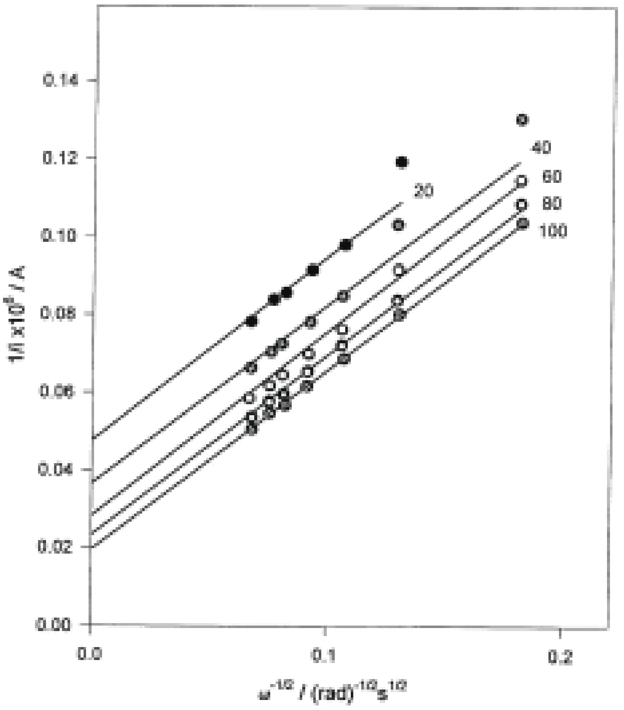

Figure 7. Levich-Koutecky plots for $Fe(CN)_6^{4-}$ oxidation at r.d.Au electrode covered with poly (p-AAB). Polymerization charge Q_p = 7.5 mC. The values of overpotential (η) are ascribed to the curves.

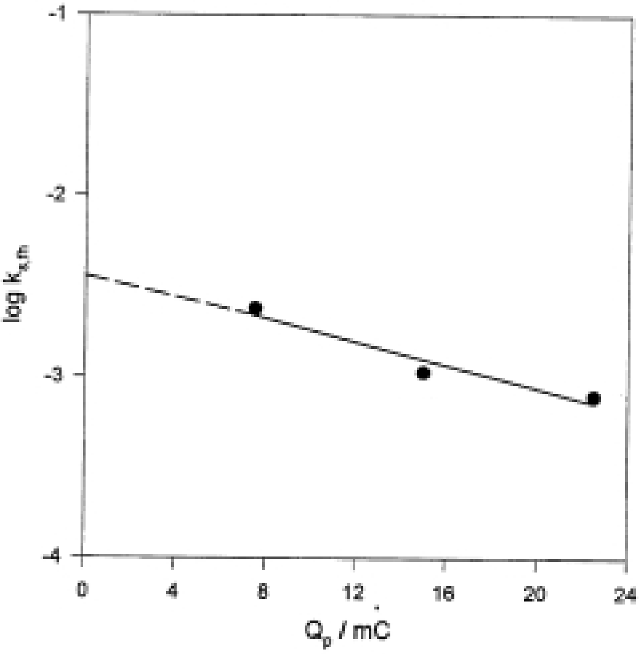

Figure 8. Dependence of $k_{s,fh}$ standard heterogeneous rate constant for oxidation of $Fe(CN)_6^{4-}$ ions on Au electrode covered with poly (p-AAB) films on the polymerization charge.

Extrapolation of the log $k_{s,fh}$~Q_p relation to the zero film thickness gives the value of $k_{s,fh}$ for the redox reaction taking place on bare Au electrode. The $k_{s,fh}$ value found equaled $3.8\times10^{-3}\pm0.4\times10^{-3}$ cm s^{-1}. However, the values of $k_{s,hf}$ obtained in direct measurements on bare r.d.Au depended on the treatment of the electrode during the experiments. Namely, the $k_{s,fh}$ was equal to 1.2×10^{-2} cm s^{-1} when the electrode was cleaned in-between the runs, while the 8×10^{-3} cm s^{-1} $k_{s,fh}$ value was characteristic for electrode cleaned only once – at the beginning of the measurements.

The values of $k_{s,fh}$ for the bare Au electrode are in good agreement with the literature data [18].

CONCLUSIONS

- The oxidation of poly (p-AAB) in the presence of H^+ ions is neither influenced by the mass transport of protons to the surface of the polymer nor by the changes of H^+ bulk concentration.
- The oxidation of $Fe(CN)_6^{4-}$ ions takes place within the film, mostly at the Au\poly (p-AAB) interface. The latter is a result of film permeability.
- The transport rate within the film (characterized by D_{app}) is very slow compared to the diffusion rate of $Fe(CN)_6^{4-}$ ions through the film (characterized by κD_s values).

REFERENCES

1. Osaka T., Ogano S., Naoi K. and Oyama N., *J. Electrochem. Soc*., **136**, 306 (1989).
2. Koura N., Ejiri H. and Takeishi K., *J. Electrochem. Soc*., **140**, 602 (1993).
3. Anderson M.R., Mattes B.B., Reiss H. and Kanner R.B., *Science*, **252**, 1412 (1991).
4. Shaolin M., *J. Electroanal. Chem*., **370,** 135 (1994).
5. Jackowska K., Bukowska J. and Jamkowski M., *J. Electroanal. Chem.*, **388**, 101 (1995).
6. Pałys B., Skompska M. and Jackowska K., *J. Electroanal. Chem*., **428**, 19 (1997).
7. Handbook of conducting polymers. Ed. Skotheim T.A., Marcel Dekker, NY, 1998.
8. Abd El-Rahman H.A., Ohsaka T., Kitamura F. and Tokuda K., *J. Electroanal. Chem*., **315**, 161 (1991).
9. Jackowska K., Bukowska J., Jamkowski M. and Kudelski A., *Synth. Metals*, **72**, 201 (1995).
10. Vogel A.I., A Text Book of Practical Organic Chemistry Including Qualitative Organic Analysis, Longmans, London 1956.
11. Stilwell D.E. and Park S.M., *J. Electrochem. Soc*., **135**, 2491 (1988).
12. Diaz A.F., Castillo J.I., Logan I.A. and Lee W.Y., *J. Electroanal. Chem*., **129**, 115 (1981).
13. Bard A.J. and Faulkner L.R, Electrochemical Methods, Fundamentals and Applications, J. Wiley & Sons, NY, 1980.
14. Ohsaka T., Kunimura S. and Oyama N., *Electrochim. Acta*, **33**, 639 (1988).
15. Maksymiuk K. and Doblehofer K., *Electrochim. Acta*, **39**, 217 (1994).
16. Skompska M. and Peter L.M., *J. Electroanal. Chem*., **383**, 43 (1995).
17. Gough D.A. and Leypoldts J.K., *Anal. Chem*., **51**, 439 (1979).
18. Kawiak J., Jędral T. and Galus Z., *J. Electroanal. Chem*., **145**, 163 (1983).