83. Electrochemical Properties of Hydroxyphenazine-Coated Electrodes

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Summary

Glassy carbon and gold electrodes were coated with 1-hydroxyphenazine, and the electrochemical properties of these electrodes were tested using them as a rotating disc electrode to reduce $Ru(bipy)_3^{3+}$, Fe^{3+}, quinoxaline, O_2, and to oxidize Eu^{2+}. The fixed redox couple can be reversibly reduced and oxidized, and acts as an intermediate medium for the electron transfer. For example the $Ru(bipy)_3^{3+}$ ($E_{1/2} = 1010$ mV *vs.* SCE. (saturated calomel electrode) on a glassy carbon electrode in 1 M H_2SO_4) is only reduced at 50 mV, whereas the oxidation of Eu^{2+} ($E_{1/2} = -460$ mV *vs.* SCE. on a Hg-electrode in 1 M HCl) takes place at -100 mV. The heterogeneous rate constant depends on the second order reaction between the attached coating and the redox couple in solution. Depending on this rate constant, selectivity of the electrode is observed.

Introduction. - Recently, there has been an increasing interest in electrochemistry of so-called chemically modified electrodes. These electrodes are prepared by attaching irreversibly an electroactive substance to a conducting material (*e.g.* on Pt, graphite, glassy carbon). The attachment may be obtained by coating with a polymer [1-8], chemical binding [9-18], or irreversible adsorption [18-26]. Possible application fields of modified electrodes are: asymmetric synthesis [13] [14], electrocatalysis [1] [8] [15] [17] [22-26], or photogalvanic cells [25] [26]. Chemical modification may also be used to protect photoanodes from photocorrosion [2] [12]. A survey of chemically modified electrodes has been given in some review articles [27-29].

Attaching organic redox systems to electrodes can be realized by adsorption or polymerisation [25] [26]. During some photogalvanic experiments with phenazine [30], we recognised an adsorption at the electrodes, which altered the electrode behaviour markedly.

This report describes some electrochemical properties of these electrodes.

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Experimental Part

Chemicals. All chemicals used were of analytical quality *(Fluka)*, except Ru(bipy)$_3^{3+}$, Eu^{2+} and 1-hydroxyphenazine. The complexe Ru(bipy$_3$$^{3+}$ was obtained by oxidation of Ru(bipy)$_3$Cl$_2$ by PbO_2, the complexe Ru(bipy)$_3$Cl$_2$ was prepared by the method of *Palmer & Piper* [31]. By reduction of Eu^{3+} with a *Jones*-reductor [32] Eu^{2+} was obtained.

Photochemical preparation of 1-hydroxyphenazine. This compound was prepared by irradiating a 10^{-3}M phenazine solution in 1M H_2SO_4 with a 500 W Projector-lamp for 7 h [33] [34]. Green dihydrophenazine precipitated, and the solution turned from pale yellow to red, while producing 1-hydroxyphenazine as a secondary product. Dihydrophenazine was removed by filtration, the solution was neutralized with Na_2CO_3, and extracted with ether. The ether solution was extracted with 10% solution of NaOH. The aq. extract was acidified slightly with dil. HCl-solution and extracted with ether again. The ether layer was dried over Na_2SO_4. Distillation of the ether gave 1-hydroxyphenazine, which was recrystallized from ethanol. The mass spectrum obtained corresponded to that published [35], and the elemental analyses were in agreement with the theoretical values.

$C_{12}H_8N_2O$ Calc. C 73.46 H 4.11 N 14.28% Found C 73.21 H 4.10 N 14.15%

Apparatus. The electrochemical investigations were performed on a *Metrohm Polarecord* E 506, a *Metrohm* VA-Scanner E 612, a *Hewlett-Packard* 7044A X-Y recorder, and a *Tacusell* EDI rotating disc electrode. All the experiments were carried out at room temperature, 22±2°, and all potentials were reported with respect to the saturated calomel electrode (SCE).

Electrode preparation. Glassy carbon and gold electrodes (⌀2 mm) were polished with 3μ diamond *(Buehler-Met Ltd.)* and washed with distilled water and ethanol. The electrodes were coated by holding them in a solution containing 10^{-3}M 1-hydroxyphenazine and 1M H_2SO_4, and by scanning their potential between −0.3 and 1.3 V *vs.* SCE, for 90 minutes. About $2.5 \cdot 10^{-8}$ mol cm^{-2} ¹) of 1-hydroxyphenazine were adsorbed onto the electrode in this time. Instead of using a 1-hydroxyphenazine solution, an irradiated phenazine solution could be used.

Results and discussion. – In 1M sulfuric acid, the cyclic voltammogram (CV. *Fig. 1A*) of 1-hydroxyphenazine shows two separate one-electron steps. The first step appears at 105 mV, the second at − 190 mV *vs.* SCE. An increase in signal is obtained if the potential is scanned to more positive values. *Figure 1B* shows the first twenty cycles of such an experiment. The reason for the enhancement of the CV. curves is probably due to an anodic polymerisation at the electrode. Similar polymerisations have been found by *Albery et al.* [25] [26] with thionine. If the electrode is removed from this solution, washed, and placed in background electrolyte (1M H_2SO_4), the CV. in *Figure 1C* is obtained. The signal is rather asymmetric, having a sharp cathodic peak at 0 mV and a broad anodic peak at 45 mV *vs.* SCE. This CV. clearly demonstrates that a redox couple is fixed at the electrode surface. *Figure 2A* shows the scan rate dependency of the surface signal. As expected for fixed species, the intensity increases proportionally to the scan rate. The preparation of the electrode surface is quite reproducible. The amount of electroactive species adsorbed depends mainly on the preparation time. The integrated current shows that the amount of surface bound material after 200 cycles is about $2.5 \cdot 10^{-8}$ mol cm^{-2}. Extended treating time gave up to $4 \cdot 10^{-7}$ mol of surface bound material per cm^2. The chemically modified electrodes are quite durable. In one experiment, over 5000 cyclic voltammograms were run at 100 mV s^{-1}, with less than 50% loss of electroactive material and maintenance of the electrochemical

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¹) Determined by measuring the area under the peaks of the cyclic voltammograms.

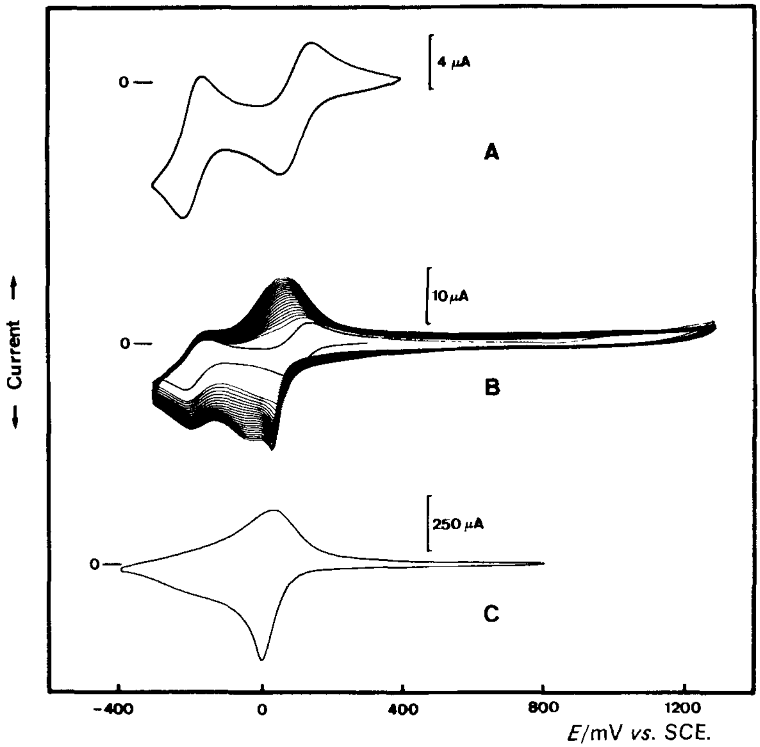

Fig. 1. (A) *Cyclic voltammogram of* 10^{-3}M *hydroxyphenazine in* 1M H_2SO_4 *recorded at a clean glassy carbon electrode.* (B) *First 20 cycles of a continuously recorded cyclic voltammogram of the same solution as* (A), *but scanned to more positive potentials.* (C) *Cyclic voltammogram of a hydroxyphenazine-coated glassy carbon electrode in* 1M H_2SO_4 (scan rate: 100 mV s^{-1})

properties. Studies with different background electrolytes show that there is almost no anion influence, but that there is a strong pH-dependence *(Fig. 2B)*. With increasing pH, the peak-to-peak separation grows from 45 mV at pH 0 to 175 mV at pH 2, and the signal is shifted toward more negative potentials. At pH 3 a signal is no longer detected.

The electrochemical behaviour of the hydroxyphenazine-coated electrode was investigated using different redox couples in solution. *Figure 3* shows the current-potential curves for a 10^{-3}M $Ru(bipy)_3^{3+}$ solution in 1M H_2SO_4, using an uncoated (A), and a coated (B), rotating disc glassy carbon electrode. Both curves show the same limiting current. The curve obtained from the coated electrode, however, is steeper and its halfwave-potential changed from 1010 mV to 50 mV *vs.* SCE. Obviously, the $Ru(bipy)_3^{3+}$ is only reduced at a potential where the attached hydroxyphenazine is reduced to dihydrohydroxyphenazine. This mediated electron transfer, schematically depicted in *Figure 4*, was demonstrated for the reduction of $Ru(bipy)_3^{3+}$, Ce^{4+}, O_2, Fe^{3+}_{aq}, $Fe(CN)_6^{3-}$, I_2, phenazine, and quinoxaline, as well as for the oxidation of Eu^{2+}.

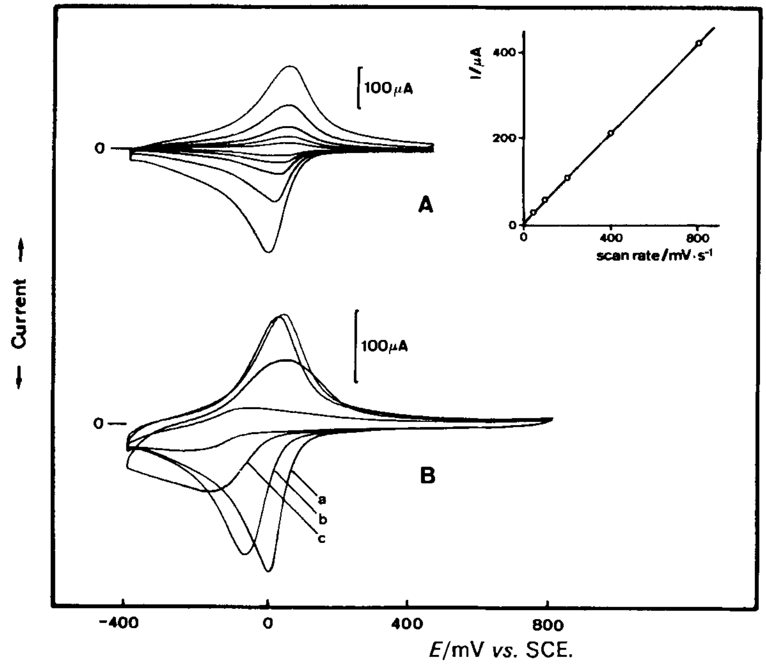

Fig. 2. (A) *Scan rate dependency of the cyclic voltammogram of a hydroxyphenazine-coated gold electrode in 1* M *H_2SO_4.* (B) *pH dependency of the same electrode recorded at a scan rate of 500 mV s^{-1}* (pH: 0 (a), 1.0 (b) and 2.0 (c))

In preceding papers about coated electrodes [8] [25] [37], it was shown that the heterogeneous rate constant on such electrodes are connected to the second order reaction between the attached redox couple and the redox couple in solution.

$$R_F + O_S \underset{k_{-H}}{\overset{k_H}{\rightleftarrows}} O_F + R_S \qquad (1)$$

R_F/O_F redox couple fixed at the electrode
R_S/O_S redox couple in solution

If we assume that the thickness of the coating is small compared to the diffusion layer at the rotating electrode, then the three-dimensional film is reduced physically to a two-dimensional surface coverage (mol cm^{-2}), which corresponds to the number of active sites on the surface. The heterogeneous rate constant might then be expressed as follows:

$$k'_1 = k_H \Gamma_R \qquad (2)$$

$$k'_{-1} = k_{-H} \Gamma_O \qquad (3)$$

Γ_R surface coverage of R_F
Γ_O surface coverage of O_F

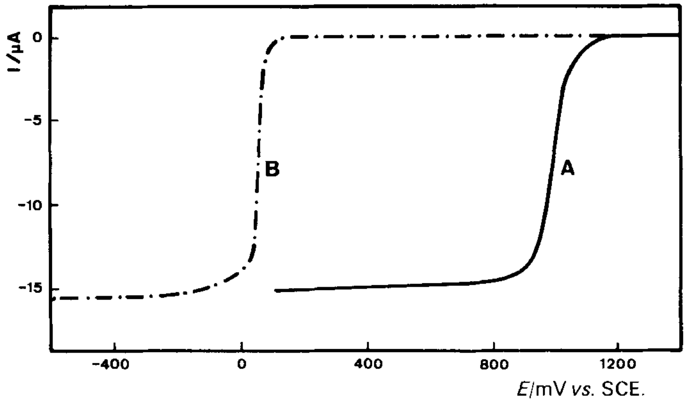

Fig. 3. *Current-potential curves for the reduction of* 10^{-3}M *Ru(bipy)*$_3^{3+}$ *at a clean* (A), *and a coated* (B), *rotating disc glassy carbon electrode* (supporting electrolyte: 1M H_2SO_4, rotation rate: 50 Hz)

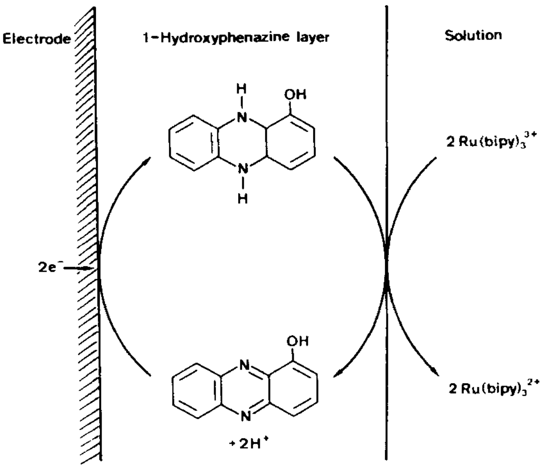

Fig. 4. *Schematic depiction of the reduction of Ru(bipy)*$_3^{3+}$ *on a hydroxyphenazine-coated electrode*

Γ_R and Γ_O depend on the electrode potential[2]), but cannot exceed the total surface coverage. This means that k_1' and k_{-1}' have limiting values and the current-potential curves of such electrodes do not necessarily lead to diffusion-limiting current (see *Fig. 8*). If ln $(I_0/I-1)$ is plotted against F*E*/RT slopes equal to *n* are obtained [37], and not *a* as expected with normal *Tafel*-law behaviour.

In the case of hydroxyphenazine-coated electrodes, the situation is more complicated, since the fixed redox system has three different redox states in acidic solutions:

$$\begin{matrix}\text{phenazinium}\\ \text{monocation }(PH^+)\end{matrix} \rightleftarrows \begin{matrix}\text{dihydrophenazine}\\ \text{cation radical }(PH_2{}^{+})\end{matrix} \rightleftarrows \text{dihydrophenazine }(PH_2)$$

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[2]) *Nernst*-equation gives $E-E_0=\frac{RT}{nF}\ln\frac{\Gamma_O}{\Gamma_R}$.

All of these states might have a certain reactivity. We therefore suggest that the hetereogenous rate constant is equal to:

$$k'_1 = k_{H_1}\Gamma_{PH_2^+} + k_{H_2}\Gamma_{PH_2} \tag{4}$$

k_{H_1} second order rate constant for the reaction between the fixed PH_2^+ and O_S
k_{H_2} second order rate constant for the reaction between the fixed PH_2 and O_S
$\Gamma_{PH_2^+}$ coverage of the cation radical
Γ_{PH_2} coverage of the dihydrophenazine

and analogously,

$$k'_{-1} = k_{-H_1}\Gamma_{PH^+} + k_{-H_2}\Gamma_{PH_2^+} \tag{5}$$

Since the second order rate constant is different for reactions with different redox couples, such an electrode might be selective. This is demonstrated with *Figures 5* and *6*. Since the ΔG for the reduction of Fe^{3+} by the dihydrohydroxyphenazine is negative, but that for the oxidation of Fe^{2+} by the hydroxyphenazine is

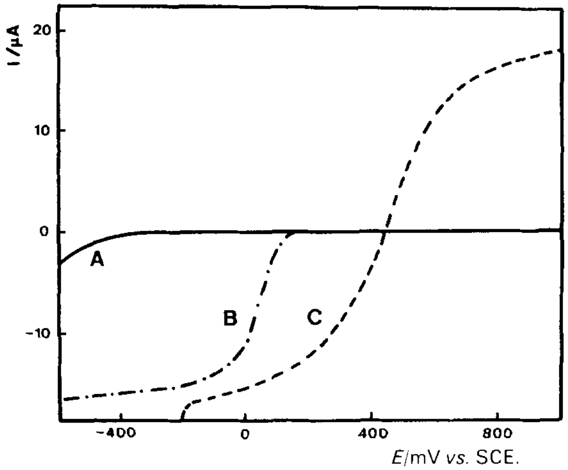

Fig. 5. (A) *Current-potential curve of a solution containing 10^{-3}M Fe^{2+} and 10^{-3}M Fe^{3+}, measured with a clean rotating disc glassy carbon electrode* (supporting electrolyte: 1M H_2SO_4, rotation rate: 50 Hz), (B) *as* (A) *but with a hydroxyphenazine-coated GC-electrode,* (C) *as* (A) *but with a clean Pt-electrode*

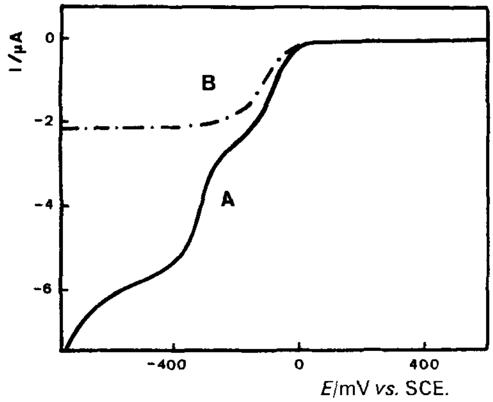

Fig. 6. *Current-potential curves for the reduction of 10^{-4}M quinoxaline at a clean* (A), *and a coated* (B), *rotating disc glassy carbon electrode* (supporting electrolyte: 1M H_2SO_4, rotation rate: 50 Hz)

positive, k_{H_1} and k_{H_2} are much bigger than k_{-H_1} and k_{-H_2}. Therefore, the current-potential curves obtained with a rotating hydroxyphenazine-coated electrode show only a wave for the reduction of Fe^{3+}, but not for the oxidation of Fe^{2+} *(Fig. 5)*. *Figure 6* shows that at an uncoated electrode (curve A), quinoxaline is reduced in two steps. At the coated electrode (curve B), however, only the reaction to the quinoxaline radical is fast enough to get a noticeable current step. We believe that *Albery's* results obtained with a thionine-coated electrode and *Wurster's* blue[3]) has similar explanation [26].

The reduction of oxygen to hydrogen peroxide *(Fig. 7)* is very fast at hydroxyphenazine-coated electrodes; even at 50 Hz we obtained a diffusion-controlled reduction. Unfortunately, the potential of the fixed hydroxyphenazine is practically too low for fuel cells. The potential would be negative enough to reduce H_2O_2 to H_2O, however, for kinetic reasons this reaction does not take place at this electrode.

In *Figure 8* the oxidation of Eu^{2+} is shown. At medium to high rotation rates the diffusion-limiting current is not reached with this reaction. The current-potential curve is controlled by the reaction occurring at the electrode surface. For further investigations, the rotation rate and the concentration dependency of this reaction has been studied with two different coatings. The results are presented in *Figure 9* with *Koutecky-Levich* plots [8] [36] [37], where i_L^{-1} is is plotted against $\omega^{-1/2}$. As

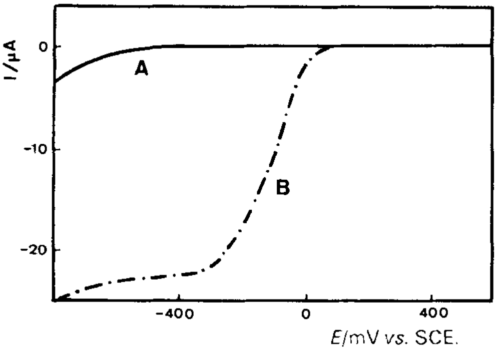

Fig. 7. *Current-potential curves for the reduction of a saturated solution of oxygen at a clean* (A), *and a coated* (B), *rotating disc glassy carbon electrode* (supporting electrolyte: 1M H_2SO_4, rotation rate: 50 Hz)

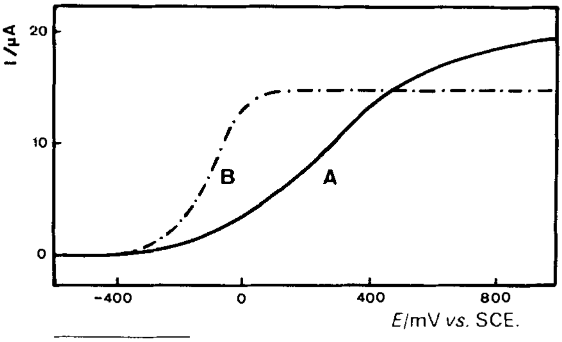

Fig. 8. *Current-potential curves for the oxidation of* 10^{-3}M Eu^{2+} *at a clean* (A), *and a coated* (B), *rotating disc glassy carbon electrode* (supporting electrolyte: 1M HCl, rotation rate: 50 Hz)

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[3]) N,N,N',N'-tetramethyl-p-phenylenediamine.

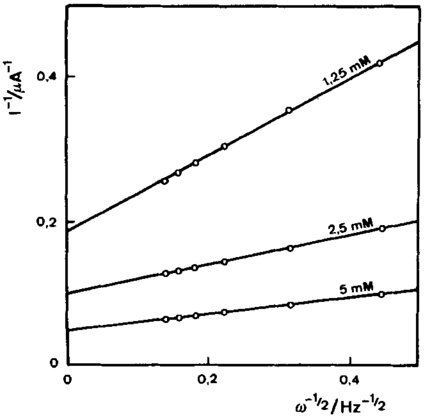

Fig. 9. Koutecky-Levich *plots, (limiting current)$^{-1}$* vs. *(rotation rate)$^{-1/2}$, for the oxidation of Eu^{2+} at a GC-electrode coated with 3 · 10^{-9} mol cm^{-2} hydroxyphenazine*

expected, both slopes and intercepts of the lines are, within experimental errors, inversely proportional to the bulk concentration of Eu^{2+}. Since i_L is measured at positive potentials where only phenazine is stable at the electrode, the term $k_{-H_2}\Gamma_{PH_2^+}$ in equ. 5 vanishes and the obtained values k'_{-1} correspond to $k_{-H_1}\Gamma_{PH^+}$. From the intercepts k'_{-1} might be evaluated [8]. This data in the *Table* shows that the heterogeneous rate constants depend on the coverage (number of fixed redox centers), but are not directly proportional to it. Probably, for higher coverage, the surface-attached layer is too thick to be treated as a two-dimensional surface coverage. Therefore a more elaborate model is needed to describe this system. The concentration ratio R_F/O_F follows the *Nernst* relation only directly at the electrode surface. Due to the reaction with the redox species in solution, the concentration of active species decreases further out in the layer. This means that the concentration profiles for the fixed and the penetrating redox species is not constant throughout the film in the direction (x) toward the solution. Therefore, the second order reaction constant should be evaluated by integrating the reaction over the whole layer (Δx). Assuming that only one active species at the electrode is responsible for the oxidation, i is given by:

$$i = nFAk_{-H}\int_0^{\Delta x} O_F(x, E)\ R_S(x, E)dx \qquad (6)$$

$O_F(x, E)$ and $R_S(x, E)$ are the functions of the concentration profiles for a given potential E.

Table. *Values of* k'_{-1} *[cm s^{-1}] for the oxidation of Eu^{2+}in 1* M *HCl*

	Coverage Γ [mol cm^{-2}]	
	$3\cdot10^{-9}$	$5\cdot10^{-8}$
Concentration of Eu^{2+} [mM]		
1.25	$1.42\cdot10^{-3}$	$6.45\cdot10^{-3}$
2.5	$1.31\cdot10^{-3}$	$7.50\cdot10^{-3}$
5.0	$1.30\cdot10^{-3}$	$5.30\cdot10^{-3}$

Unfortunately $O_F(x, E)$ and $Eu^{2+}(x, E)$ are very difficult to evaluate. Therefore, to get reasonable information about k_{-H} only very thin layers should be used.

Conclusions. - Electrochemical processes on hydroxyphenazine-coated electrodes occur indirectly *via* the attached coating. This implies that for a reduction reaction the hydroxyphenazine must first be reduced before electrons are able to leave the electrode. On the other hand, oxidation reactions take place only if the hydroxyphenazine coating is in its unreduced state. The electron transfer rate depends on the kinetics of the fixed redox couple and the redox couple in solution. Thermodynamically unfavourable reactions with $\Delta G > 0$ have little chance to be fast enough for an efficient electron transfer at such an electrode. For reactions with $\Delta G \leqq 0$, however, catalytic effects may occur which is demonstrated by the reduction of O_2 and the oxidation of Eu^{2+}. The electrode-potential, however, can only control the heterogeneous rate constant in a rather small region around the potential of the fixed redox couple. If all the fixed redox centers are in their active forms, the heterogeneous rate constant does not increase any more, disregarding the applied overvoltage. Therefore, the observed limiting-current does not always reach the diffusion limit (oxidation of Eu^{2+}), which might be a disadvantage. On the other hand, due to the discussed properties the electrode shows some interesting selectivity. For example, Fe(III) can be reduced, but Fe(II) is not oxidized at this electrode. Quinoxaline is only reduced to the radical, but not to the dihydroquinoxaline. Due to kinetic effects, H_2O_2 is not reduced at this electrode even though ΔG for the reaction between dihydroxyphenazine and H_2O_2 is negative. The heterogeneous rate constant was found to depend on the number of fixed redox centers. For thicker films, however, it was not directly proportional to this number.

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