system, since it is bigger[13] than the free Zn(II), which has $n\alpha_c \approx 1.5$[10] and $m \approx 8$ in the same experimental conditions.

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THE EFFECT OF ADATOMS ON THE REVERSIBILITY OF SOME REDOX COUPLES

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Abstract

Cyclic voltammetric studies were performed for six redox couples at a Pt electrode, in the absence and in the presence of Bi, Pb and Cd adatoms. Standard rate constants were evaluated for all the systems in the absence and in the presence of adatoms.

Whenever a catalytic effect was obtained the effect of coverage was studied in a quantitative way. It was found that the rate constant increases initially rapidly and then passes through a maximum or reaches a constant value, at coverages of the order of a monolayer. For all the systems the influence of the adatoms decreases in the order Bi > Pb > Cd.

Introduction

Heavy metals electrodeposited at an under potential (UPD) onto a Pt surface have shown to catalyse a number of electrochemical reactions. The subject has been reviewed by Adzic [1]. One somewhat surprising observation is that such adatom modified surfaces catalyse "simple" electron transfer reactions, as it has been demonstrated earlier by Adzic et al. [2] and recently by Kokkinidis [3].

Adzic and Despic [2] have found that the heterogeneous rate constants for the reactions of Ti^{3+}/Ti^{4+} and Fe^{2+}/Fe^{3+} couples at Au/Cu_{ads} and Au/Ag_{ads} electrodes were increased by almost an order of magnitude. Recently Schultze et al. [4] have studied the kinetics of the $Ru(NH_3)_6^{2+} / Ru(NH_3)_6^{3+}$ couple at Pt/Tl_{ads} and Pt/Pb_{ads}. They found no effect on the exchange current densities due to the presence

of adatoms.

Kokkinidis has reported the influence of UPD adatoms on the kinetics of a series of redox couples in aqueous and non aqueous media [5-8]. From such studies catalysis but also inhibition has been detected.

Catalysis has been clearly demonstrated by Kokkinidis for the electrochemical oxidation of p-hydroquinone and of o-hydroquinone in aqueous medium at Pt/Tl_{ads}, Pt/Bi_{ads} and Pt/Pb_{ads} electrodes [3]. We have sought to characterize such effects in a more quantitative way.

In this paper we report the influence of Bi, Pb and Cd adatoms on the kinetics of the following redox couples: p-hydroquinone/p-benzoquinone, o-hydroquinone/o-benzoquinone, 3-methoxy-o-hydroquinone 3-methoxy-o-benzoquinone, Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and $Ir\ Cl_6^{3-}/Ir\ Cl_6^{2-}$, in aqueous medium.

Whenever a significant catalytic effect was obtained the effect of coverage, Θ_M, was studied in a quantitative way.

Experimental

Solutions were prepared from triply distilled water. $K\ Mn\ O_4$ was used in order to remove all the organic impurities that have been shown to affect the electrochemical behaviour of the Pt electrode. Chemicals of high purity were used for all the solutions. Quinones were used without further purification.

The glassware was carefully cleaned following published procedure [9]. Pt electrodes were chemically cleaned by dipping them in a mixture of H_2SO_4 and HNO_3 1:1, rising them with water and then immersing them for a few minutes in boiling distilled water. Then, the electrochemical activation following an established procedure [10] was

applied until the standard cyclic voltammetric response was obtained. The electrochemical cleaning was carried out whenever it was found necessary.

The real surface area of the electrode was calculated by graphic integration of the charge of the area under the hydrogen desorption peaks. The roughness factor was determined by dividing the hydrogen desorption charge by 210 $\mu C\ cm^{-2}$. A roughness factor of the order of two was always obtained.

Solutions were freshly prepared and deoxygenated with O_2 free nitrogen for about 30 minutes. The reversibility of the redox couples have been shown to be affected by the presence of O_2 in the solution.

Typical 3-compartment 3-electrode cells were used. The reference electrode was for most experiments a standard hydrogen electrode prepared in situ. Sometimes a saturated calomel electrode was also used. The potentials are referred to the normal hydrogen electrode (NHE).

Pt/M_{ads} electrodes were prepared by holding the Pt electrode, at 0.2V, in the aqueous solution containing both the cation M^{n+} and the redox couple under study.

Preliminary experiments were performed, in the absence of the redox couple, in order to calculate the degree of coverage, Θ_M, as a function of concentration and holding time for deposition. Θ_M was calculated by integrating the charge Q_M due to the oxidation of the corresponding deposited layers and the charge Q_H^S, due to the desorption of hydrogen, in the absence of cations. Θ_M is then

calculated by dividing the number of metal adatoms Q_M/n, by the number of Pt atoms Q_H^S.

Standard rate constant, K_s, were evaluated from ΔE_p values obtained at various sweep-rates (10-250 mV s^{-1}). When $n\Delta E_p$ values were in a convenient range (70-200 mV) Nicholson dimensionless plots were used to evaluated K_s through the equation |11|

$$K_s = \left(\frac{nF \Pi D}{RT}\right)^{1/2} . v^{1/2} . \psi \tag{1}$$

Whenever $n\Delta E_p$ values were greater than 200, therein other methods given by Nicholson and Shain |12|, for an irreversible electron transfer process were used.

Results and Discussion

Cyclic voltammetric studies were performed with the following systems: o-hydroquinone, p-hydroquinone and 3-methoxy-o-hydroquinone in aqueous perchloric medium, iron(II) in aqueous sulphuric medium, hexaciano ferrate in an aqueous solution of potassium nitrate and hexacloroiridate in perchloric aqueous medium, in the absence and in the presence of Bi^{3+}, Pb^{2+} and Cd^{2+} at low concentrations (10^{-4}-10^{-5}M). Sweep-rates ranging from 2 to 250 mV s^{-1} were used according to the potential profile shown in fig. 1.

The plot of peak currents as a function of the square-root of sweep rate, both in the absence and in the presence of cations, gave good straigh lines, for all the systems studied, suggesting that oxidation currents are under diffusion control. From the slopes of the

I_p vs. $v^{1/2}$ plots, diffusion coefficients were calculated. The values obtained were (6.0 ± 0.4) x 10^{-6}, (7.0 ± 0.4) x 10^{-6}, (6.0 ± 0.2) x 10^{-6}, (5.0 ± 0.5) x 10^{-6}, (6.0 ± 0.3) x 10^{-6} and (1.0 ± 0.4) x 10^{-5} cm^2 s^{-1}, respectively for the o-hydroquinone, p-hydroquinone, 3-methoxy-o-hydroquinone, Fe^{2+}, $Fe(CN)_6^{4-}$ and $Ir Cl_6^{4-}$ species. Identical values were obtained for the diffusion coefficients of the reduced species, in the presence of cations whenever peak currents were corrected from desorption currents due to metal adatoms desorption.

In all cases analysis of peak currents, peak potential, and other features on the cyclic voltammograms seem to indicate that the systems behave as simple electron transfer processes witout any influence, of coupled chemical reactions, e.g. protonation steps.

The effects obtained by adding for example, Bi^{3+}, and by holding the potential at 0.2V, in order to allow a certain degree of coverage to be reached, are demonstrated by the cyclic voltammograms displayed on fig. 1., for all the systems studied.

It is evident from the peak separation, ΔE_p, and also other features presented by the CV's that the reversibility of the quinones has been increased by the presence of Bi adatoms on the Pt electrode surface. However, the best catalytic effect is obtained with the o-hydroquinone/o-benzoquinone redox couple, for which ΔE_p values have decreased from 300 to 30 mV, which is the value expected for a reversible two electron transfer process. The effect obtained for the inorganic couples is much smaller, but, then, the kinetics of those systems are already very fast at clean Pt electrodes.

CV's for the o-hydroquinone/o-benzoquinone and also for the p-hydroquinone/p-benzoquinone in the presence of Bi^{3+} are similar to those reported by Kokkinidis |3|.
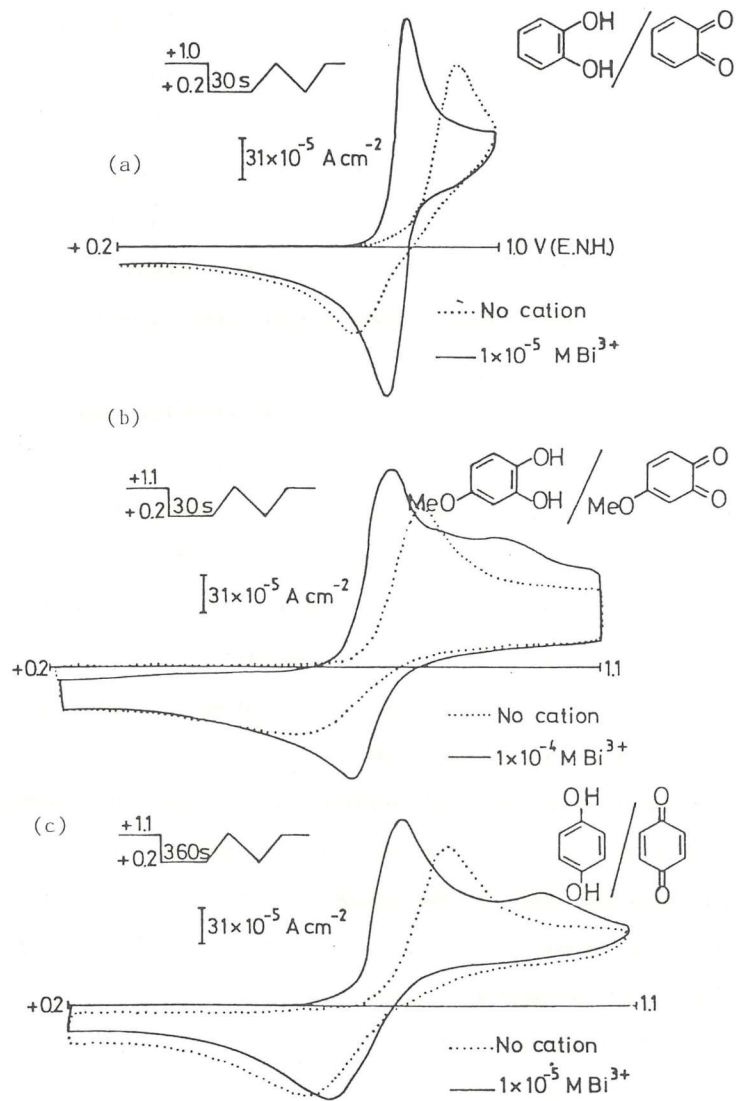
Fig. 1. Cyclic voltammograms at 0.1 V/s in the absence (...) and in the presence (——) of Bi^{3+}, for the following systems:

(a) $2.5 \times 10^{-3}M$ o-hydroquinone + 0.5M $HClO_4$

(b) $3.0 \times 10^{-3}M$ 3-methoxy-o-hydroquinone + 0.5M $HClO_4$

(c) $2.5 \times 10^{-3}M$ p-hydroquinone + 0.5M $HClO_4$

Fig. 1. (Cont.)
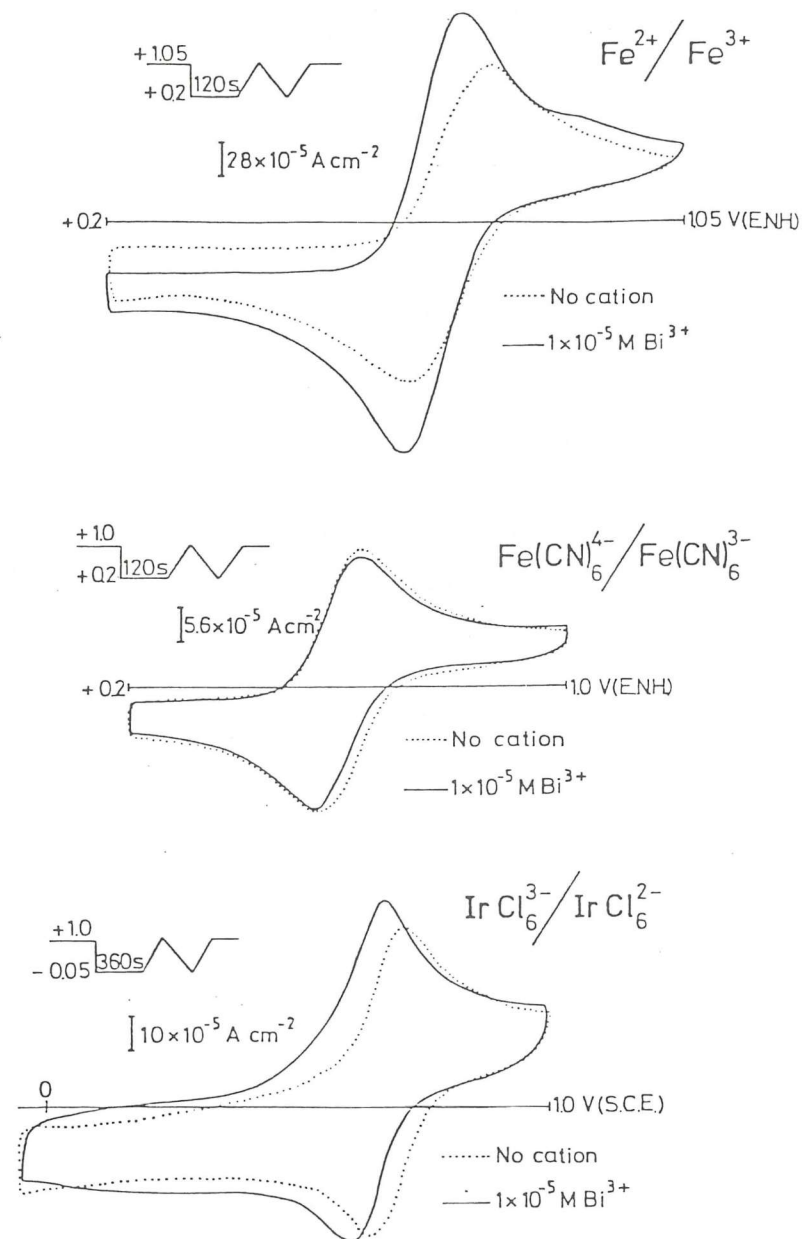
(d) $1 \times 10^{-2}M$ $Fe(NO_3)_2 \cdot 9H_2O$ + 0.5M H_2SO_4

(e) $1 \times 10^{-3}M$ $Fe(CN)_6^{4-}$ + 0.5M KNO_3

(f) $2 \times 10^{-3}M$ $Na_2 Ir Cl_6$ + 0.5M $HClO_4$

Figure 2 shows the effects due either to Bi^{3+} or to Pb^{2+} adsorbed on a Pt electrode at 0.2V for 30s to allow controlled coverage of the Pt electrode by the corresponding metal adatoms.
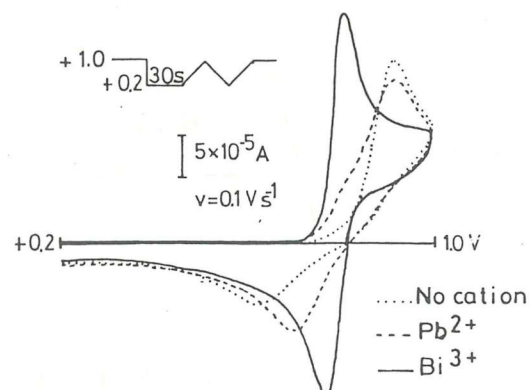
FIG. 2. CV's for 2.5×10^{-3} M o-hydroquinone + 0.5M $HClO_4$ in the absence (...) and in the presence of 1×10^{-5}M of Bi^{3+} (——) and Pb^{2+} (- - -).
Geometric area of the Pt electrode 0,161 cm^2.

Bi adatoms clearly demonstrate a better catalytic effect, however the degree of coverage when oxidation begins is different for both metals.

CV's on fig. 2 are reported for the o-hydroquinone/o-benzoquinone couple, but similar experiments were performed for all the systems studied and it has been found that the catalytic activity induced on a clean Pt surface by the different adatoms studied, decreases in the order Bi > Pb > Cd.

The effect of coverage by adatoms is demonstrated on figure 3, which shows a set of CV's for the oxidation of o-hydroquinone at Pt/Bi_{ads} electrodes with different coverages, due to different holding times at 0.2V, according to the potential profile shown.
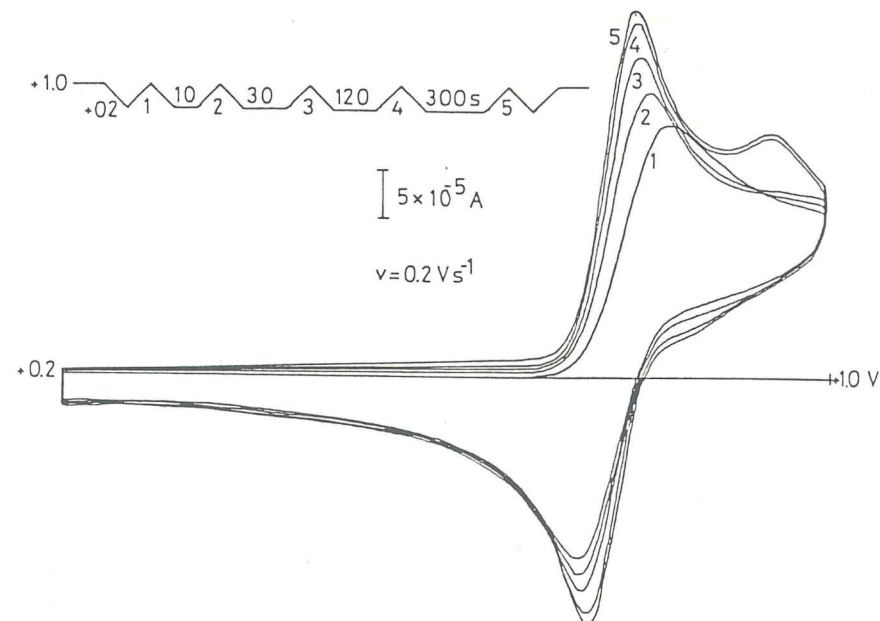
FIG. 3. Effect of coverage by Bi adatoms for the oxidation of 2.5×10^{-3} M o-hydroquinone + + 0.5M $HClO_4$ aqueous solution on a Pt electrode with 0.161 cm^2 of geometric area $[Bi^{3+}] = 1 \times 10^{-5}$M.

It is clear that the reversibility of the o-hydroquinone is a function of the coverage of the Pt electrode by Bi adatoms.

For each coverage various sweep-rates were used and CV's recorded until $n\Delta E_p$ values were in a convenient range (70-200 mV). From ΔE_p values measured with an accuracy of $\pm$ 5 mV, standard rate constants Ks, were evaluated by using Nicholson's working curve. An averaged K_s value was obtained for each coverage.

Whenever $n\Delta E_p$ values were greater than 200 mV, such as, in the case of the oxidation of the quinones at a clean Pt electrodes, than the equations given by Nicholson and Shain |12| for an irreversible electron transfer process were used to evaluate K_s. Therein values of $K_s < 10^{-4}$ cm s^{-1} were obtained by this means.

Studies similar to those reported in fig. 2 and fig. 3 were performed for all the systems. Table 1 summarises the results of such studies.

TABLE 1. Standard rate constants at a Pt/M$_{ads}$ electrode as a function of metal adatoms.

$$\Theta_M^{0.2\ V} = 0.5$$

Couple	Medium	$E°/V$ (NHE)	$10^2\ K_s/cm\ s^{-1}$ Pt	Pt/Bi$_{ads}$	Pt/Cd$_{ads}$	Pt/Pb$_{ads}$
para-benzoquinone (OH/O)	HClO$_4$	0.70	0.001 ± 0.0002	0.09± 0.005	0.001 ± 0.0002	0.03 ± 0.001
o-benzoquinone (OH OH/O O)	HClO$_4$	0.76	0.004 ± 0.0007	1.6 ± 0.3	0.004 ± 0.0006	0.5 ± 0.005
MeO quinone (OH MeO/O O)	HClO$_4$	0.77	0.07 ± 0.001	0.9 ± 0.1	0.07 ± 0.001	0.50 ± 0.04
Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$	KNO$_3$	0.69	0.07 ± 0.001	2.3 ± 0.5	2.0 ± 0.3	2.0 ± 0.6
Fe^{2+}/Fe^{3+}	H$_2$SO$_4$	0.68	0.2 ± 0.02	3.1 ± 0.2	0.2 ± 0.01	3.0 ± 0.2
IrCl$_6^{3-}$/IrCl$_6^{2-}$	HClO$_4$	1.02	2.8 ± 0.5	2.9 ± 0.8	3.0 ± 0.7	3.0 ± 0.5

Values obtained for the standard rate constants for all the quinones in the absence of metal adatoms are characteristic of irreversible electron transfer processes. K_s values for the **orto** and **para**-hydroquinone were not significantly different, however the K_s value obtained for the methoxy-quinone, is ten times greater probably due to the presence of the MeO group.

K_s values for the Fe^{2+}/Fe^{3+} in 0.5M H$_2$SO$_4$ and Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ in 0.5M KNO$_3$ in the absence of adatoms are in good agreement with values given by Agarwal [13] and by Gerischer et al. [14], respectively.
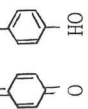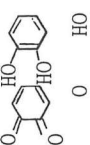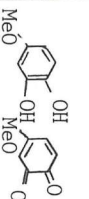
From K_s values in table 1. it is remarkable the enhancement induced by Bi adatoms on the kinetics of the o-hydroquinone/o-benzo-quinone redox couple. For the other quinones the effect still exists, although to a less extent; in fact a factor of about 100 is obtained for the p-hydroquinone and a factor of 10 for the methoxy-quinone.

For the Fe^{2+}/Fe^{3+} redox couple an enhancement in K_s of about 10 is achieved, at Pt/Bi$_{ads}$ and Pt/Pb$_{ads}$ electrodes. Similar effects have been observed by Adzic et al [2] at Au/Cu$_{ads}$ and Au/Ag$_{ads}$ electrodes.

The kinetics of Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ and IrCl$_6^{3-}$/IrCl$_6^{2-}$ redox couples don't show any significant enhancement due to the presence of adatoms, either because they are already fast processes or else because they are electron transfer processes occuring through an outersphere mechanism without further complications.

On table 1 differences due to the different adatoms are evident, however, we believe that such differences are probably due to the potentials where underpotential monolayers are dissolved and not due to the specific adatoms (see fig. 4 and table 2.).
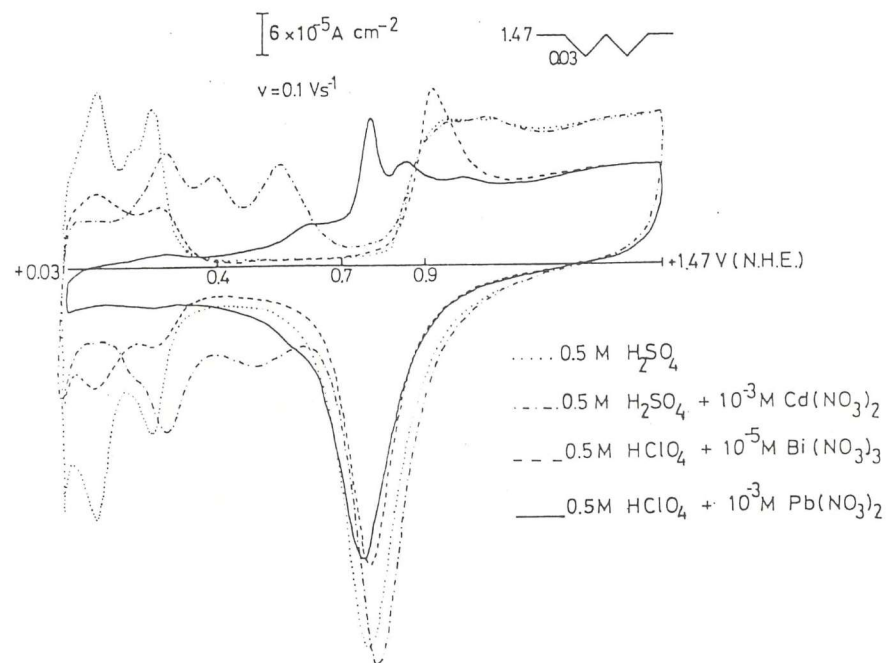
Figure 4. Cyclic voltammograms showing the upd region where Bi, Cd and Pb adatoms are deposited and removed.

Table 2. Changes in coverage when the potential changes from 0.2 to 0.7 V.

Metal	coverage Θ_M at 0.2 V	coverage when E reaches 0.7V
Bi	0.3	0.3
	0.5	0.4
Cd	0.3	0
	0.6	0
Pb	0.3	0.2
	0.5	0.3

A systematic study of the effect of coverage by metal adatoms was performed, by holding the electrode at 0.2 V, during different time intervals. For each coverage CV's at various sweep-rates were recorded and K_s values were evaluated following the procedure already described. The process was repeated for several coverages with Bi and also Pb. K_s values evaluated as a function of coverage by Bi, Θ_{Bi}, and Pb, Θ_{Pb}, are plotted in fig. 5.
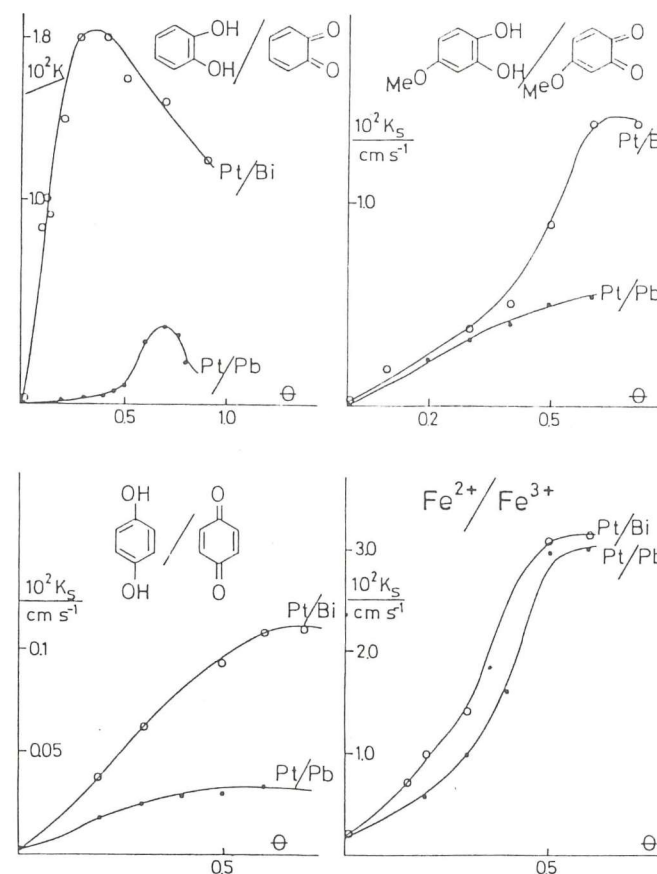

FIGURE 5. Plots of the standard rate constants as a function of coverage at 0.2 V.

Plots of K_s vs Θ (fig. 5) demonstrate very well that the rate constants initially increase rapidly and then pass through a maximum. Once again, the couple o-hydroquinone/o-benzoquinone shows the most remarkable catalytic effects the maximum rate being obtained at Θ_{Bi} = 0.3 and Θ_{Pb} = 0.7, where Θ means the percentage of metal adatoms relatively to the total number of Pt atoms on the Pt surface.

In general, for all the redox processes that have shown to be influenced by the metal adatoms studied, the catalytic activity of the Pt/M_{ads} electrodes depends on the value of the coverage, the best catalytic activity being achieved when the oxidation process occurs on a Pt electrode covered by a monolayer of Bi or Pb adatoms. Such condition could never be reached with Cd adatoms for the redox systems studied, with an E_o > 0.7 V. In such circumstances, the oxidation takes place on a clean Pt surface instead of o Pt/Cd_{ads} surface (Cd adatoms has been completely removed at 0.7 V).

It is also noticeable that while with the quinones the two curves corresponding respectively to Pt/Bi_{ads} and Pt/Pb_{ads} surfaces are quite apart from each other, in the case of Fe^{2+}/Fe^{3+} such curves are almost coincidents.

Conclusions and Discussion

Our studies have revealed, once more, that metal adatoms can affect significantly the reversibility of simple electron transfer processes, as it has been also well demonstrated by other authors.

Two groups of redox couple were investigated, namely (i) organic redox couples–quinones – and (ii) inorganic redox couples, which were traditionally regarded as redox processes occuring respectively through an "inner-sphere" and an "outer-sphere" mechanisms. However, recently spectroscopic and radiotracer[16] measurements have demonstrated the adsorption of hexacyanoferrate on platinum.

Significant catalysis was obtained for the quinones, following the order o-hydroquinone > 3-methoxy-o-hydroquinone > p-hydroquinone. For the Fe^{2+}/Fe^{3+} redox couple an increase in K_s values by a factor of the order of ten was also obtained due to the presence of Bi and Pb adatoms.

No catalysis was detected for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and $IrCl_6^{3-}/IrCl_6^{4-}$ couples at the Pt/M_{ads} electrodes, probably due to the high rates of these reactions even in the absence of adatoms.

According to Schultze [17] the general effects expected from the surface layers, e.g. adatoms, on the kinetics of the electrochemical processes arise from the following phenomena:

(i) chemical interactions between the reactant or an intermediate and a covalent bound adsorbate;

(ii) geometrical blocking effects of the metal adsorbate especially at active sites of the substrate;

(iii) electrostatic interactions between the reactants and a charged adsorbate;

and/or

(iv) electronic effects in the case of thicker layers of low conductivity.

Due to its physical properties [18] Bi and Pb adatoms adsorbed on a Pt surface might be considered as covalent bound catalysts or inhibitors ($\Delta \chi$ < 0.5 and γ/z = 1). The same can not be expect for Cd, for which $\Delta \chi$ = 0.5 and γ/z = 0.15), then according to Pauling [19] some percentage of ionicity shall persist on the adsorbed Cd species. In general it is expected that the kinetics of outer-sphere electron transfer reactions which take place at the outer-Helmholtz plane should not be influenced by the metal adatoms, while the electron transfer processes occuring through an inner-sphere

reaction involving formation and breaking of chemical bonds should be influenced by the metal adatoms.

For the quinones it is well established that the oxidation process occurs through a mechanism which involves strong interaction between adsorbed intermediates and the electrode surface, even on a carefully pretreated electrode. Then the observed behaviour due to the presence of Bi and Pb adatoms agrees with the expectations. The same is not true for the Fe^{2+}/Fe^{3+} redox couple, for which changes due to adatoms were not in principle predicted. However, Adzic et al. [2] have observed effects similar to ours for Fe^{2+}/Fe^{3+} redox couple, in aqueous H_2SO_4 solutions due to Bi, Pb and Tl adatoms on Au substrate.

According to Adzic at al. [2] once that effects of adatoms on the ϕ_2 potential can be neglected due to the presence of supporting electrolyte, then a possible explanation for the catalytic effects obtained might be a decrease in the activation energy due to changes of electron density at the Fermi level on the substrate brought by the presence of adatoms.

Quite recently Schultze et al. [4] have found that the redox couple Fe^{2+}/Fe^{3+} in the presence of SO_4^{2-}, i.e., in aqueous sulphuric medium can not be considered anymore as a model outer-sphere reaction since SO_4^{2-} may be specifically adsorbed [20]. Evidence of so has also been obtained from spectroscopic and radiotracer experiments [21,22].

It seems to us also important to mention here that kinetic parameters for the Fe^{2+}/Fe^{3+} measured by different authors have shown some discrepancies which have been attributed either to impurities in the solution or else to different procedures in the activation of the electrode. The value of K_s for the Fe^{2+}/Fe^{3+} redox couple has even been used to infere about electrode cleaning and anions effects [23]. We believe that it might also be possible, that the

underpotential adsorption of adatoms on the Pt surface avoids adsorption of impurities then, the oxidation of Fe^{2+}/Fe^{3+} occurs on a well cleaned electrode due to adsorption and desadsorption of adatoms on a convenient range of potential.

We agree that the explanations advanced for all the effects observed need more experimental evidence, possible from other type of measurements.

Acknowledgements

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ELÉCTRODO SENSÍVEL AO ANIÃO 5,5-DIETILBARBITURATO COM MEMBRANA DE PVC, SEM SOLUÇÃO DE REFERÊNCIA INTERNA COM SENSOR DE TETRAOCTILAMÓNIO EM 2-NITROFENILOCTILÉTER.

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RESUMO: Descreve-se a construção e as características gerais de funcionamento de um eléctrodo sensível a 5,5 - dietilbarbiturato, sem solução de referência interna em que o sistema sensor 5,5 - dietilbarbiturato de tetra-octilamónio /2-nitrofeniloctiléter disperso em PVC é usado como membrana aplicada num suporte condutor.

ABSTRACT: **5,5 - Diethylbarbiturate ion - selective electrode with a PVC membrane without inner reference solution with tetraoctylammonium sensor in 2 - nitrophenyloctylether**. We describe the construction and general performance characteristics of an ion-selective membrane electrode sensitive to 5,5 - diethylbarbiturate ion without inner reference solution, in which tetraoctylammonium 5,5 - diethylbarbiturate /2- nitrophenyloctylether dispersed in PVC is used as sensor membrane applied on a conductive support.

KEYWORDS : 5,5 - Diethylbarbiturate, selective electrode, PVC membrane.

INTRODUÇÃO

Nos últimos anos tem sido feito um esforço de investigação significativo no campo específico da aplicação da potenciometria com eléctrodos selectivos de iões ao controlo analítico de produtos farmacêuticos [1, 4] já que a técnica constitui uma boa alternativa às metodologias sugeridas na maioria das farma-