Electrochemical studies of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ on gold ultramicroelectrodes varying the concentrations of KF as supporting electrolyte

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Abstract

Gold disk ultramicroelectrodes of 10 µm diameter were fabricated using gold wires. These ultramicroelectrodes were characterized by electrochemical measurements and scanning electron microscopy (SEM). Electrochemical behavior of the hexacyano ferrate couple using gold ultramicroelectrodes (10 µm diameter) was investigated in a range of different concentrations of KF as supporting electrolyte. The steady state response at a gold ultramicrodisc at different concentrations of hexacyanoferrate couple with high concentrations of electrolyte was utilised to determine the diffusion coefficients of both electroactive species. Voltammetric experiments shown, that the oxidation and reduction of this couple is affected by the concentration of the supporting electrolyte. Theoretical Tafel plots were calculated considering double layer effects and comparisons with the experimental results indicated that determination of the heterogeneous rate constants for the free (unpaired) anions species seems to be imposible. Even at lower concentrations and after correction for double layer effects, the reaction is still dominated by ion pair effects.

Key word: Gold ultramicroelectrodes; scanning electron microscopy; Tafel plots.

Estudios electroquímicos del sistema $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ sobre ultramicroelectrodos de oro variando la concentración de KF como electrolito de soporte

Resumen

Ultramicroelectrodos de oro de 10 µm de diámetro fueron fabricados utilizando alambres de oro. Estos ultramicroelectrodos fueron caracterizados electroquimicamente y utilizando microscopía de barrido electrónico para determinar la forma real de la superficie y obtener información acerca de la calidad del sello entre la interface del metal y el material aislante utilizado en la construcción del electrodo. El comportamiento electroquímico de la pareja redox $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ fue investigado a diferentes concentraciones del electrolito de soporte KF. Los experimentos realizados por Voltamperometría mostraron que la oxidación y reducción de estas especies son afectadas por la concentración del electrolito de soporte. La velocidad de transferencia electrónica es favorecida al aumentar la concentración del electrolito de soporte. Cálculos teóricos de curvas Tafel tomando en cuenta los efectos de la doble capa fueron realizados y comparados con los resultados experimentales. Estos estudios mostraron que no se puede determinar las constantes de velocidad heterogénea para las especies iónicas no apareadas, debida a que aún a concentraciones muy bajas del electrolito de soporte, la reacción sigue siendo controlada por efectos de par iónico.

Palabras clave: Ultramicroelectrodos; microscopía de barrido electrónico; curvas Tafel.

Introduction

Electrochemical studies of the hexacyanoferrate couple in absence of supporting electrolyte KCl using carbon ultramicroelectrodes have shown that the reduction of $Fe(CN)_6^{3-}$ is suppressed completely [1]. This suppression was attributed to a "dynamic diffuse layer effect" in which the transport of charged reactants across the diffuse part of the double layer limits the rate of their electroreduction. However, other factors such as the kinetics of electron transfer at the surface could be involved. The influence of ion pair formation between the hexacyanoferrate couple and the alkali metal cations of the electrolyte on the rate and mechanism of the charge transfer has been established [2, 3]. First order dependence of the rate constant on cation concentration of the electrolyte was found by Peter et.al. [3] for this couple over a wide range of electrolyte concentrations. Other authors have suggested that the hexacyanoferrate electrode transfer process can also be governed by other factors besides the processes of charge transfer and diffusion [4, 5]. Adsorption of ferrocyanide and ferricyanide on the electrode surface has been reported. Fleischman *et al.* [4] studied this redox system in alkali chloride solutions using enhanced Raman spectroscopy (SERS) on gold surface. Beriet and Pletcher [5] have reported that the reduction of ferricyanide as well as the oxidation of ferrocyanide could be affected by surface poisoning on the platinum surface. However it is necessary to point out that the experiments carried out by Fleischmann et.al and Beriet and Pletcher were made using KCl as supporting electrolyte and it is known that chloride ions can be adsorbed at Pt and Au electrodes [6]. The adsorption of this anion can change the kinetic behaviour of the hexacyanoferrate redox system in solutions of low concentrations of supporting electrolyte. Although some authors have verified the presence of adsorbed species [4, 5] on Pt and Au electrodes, other authors have not found any evidence of specific adsorption [3] on gold electrodes when KF was used as supporting electrolyte. On the other hands, the hexacyanoferrate system is often considered as a 'model' redox system [7, 8].

All the research carried out on this system so far has shown that many problems related to the charge transfer mechanism still require investigation. In the present work the hexacyanoferrate couple was studied in a range of different concentrations of KF as supporting electrolyte. The aim was to obtain information that will allow an understanding of the relative importance of the effects produced when much, little or no supporting electrolyte was used, as well as to obtain more information about the charge transfer kinetics of this system.

Experimental

Reagent grade concentrated 70% $HClO_4$, KF, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, were obtained from Fluka; All these chemicals were used as received. Supporting electrolyte solutions of KF were treated with purified active charcoal for gas adsorption (particle size 0.85-1.70 mm) from BDH to eliminate organic impurities. The fabrication of gold ultramicroelectrodes proved to be a difficult task. The main difficulty for reproducing a good seal stems from the relatively large difference between the thermal expansion coefficients of the gold and glass, which produces a large gap at the gold-glass interface. It was found that using a composite of AralditeTM CY1301 + Hardener HY 1300 from Ciba-Geigy Plastic, very good seals between the gold and the composite could be obtained. Gold discs were then fabricated using gold wires of 10 and 20 μm diameter, 99.99% (Goodfellow Metal). The gold ultramicroelectrodes were polished with different grades of alumina (Buehler) and using ultrapure water as lubricant.

The gold ultramicroelectrodes were treated electrochemically by cycling between 0 and 1.45 V vs. SCE in 0.2 mol dm^{-3} $HClO_4$.

Electrochemical experiments were carried out using a single compartment cell with a two electrode configuration using a saturated calomel electrode (SCE) as reference electrode. Cyclic voltammetry experiments were carried out using a waveform generator (Hitek Instruments) coupled to a current amplifier with a low pass filter (sensitivity of 0.01 $\mu A\ V^1$), built in house. The amplifier and the cell were placed in an earthed metal Faraday box.

Results and Discussion

The electrochemical characterization was performed using $HClO_4$ as supporting electrolyte

because the range of potential where oxygen electrosoption occur can be reduced, hence increased surface roughening avoided. Figure 1 show the voltammogram obtained at a gold ultramicroelectrode in $HClO_4$ aqueous solution. In the double layer region, an electrode process is observed around 0.65 V. This shoulder is attributed to the adsorption of the ClO_4^- anion [9]. In the oxide formation region, replacement of the adsorbed anions by OH^- occurs and two peaks are observed. The first peak at 1.25 V is attributed to the formation of the first sublattice of OH^- deposited in between adsorbed anions [9]:

$$\lfloor M_x A^- \rfloor M + H_2O \rightarrow \lfloor M_x A^- \rfloor MOH + H^+ + e^- \quad (1)$$

where $[M_x A^-]M$ represent the adsorbed anions on metal. The second peak at 1.35 V has been attributed to the deposition of OH^- accompanied by desorption of the anions [10]:

$$M_x A^- + H_2O \Leftrightarrow M_{x-1} + MOH + A^- + H^+ + e^- \quad (2)$$
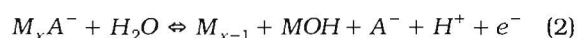
A peak is observed on the cathodic side of the voltammogram between 0.85 and 0.9 V, which corresponds to the reduction of adsorbed oxygen. The shape of the voltammogram is similar to that reported for polycrystalline gold [11]. The effective area of the gold ultramicroelectrode was calculated taking into account that the cathodic charge in aqueous solutions of $HClO_4$ increases almost linearly with the applied potential above 1.2 V and that this charge is independent of pH [12].

The charge value (Q_B) used was taken from the curve cathodic charge vs anodization potential reported by Brummer et.al. [12]. This value and the charge obtained experimentally by integration of the oxide stripping peak (Figure 3) were used to calculate the real area of the microdisc from the ratio: $A_{real} = \dfrac{Q_{exp}}{Q_B}$ (3). For a series of experiments carried out at 60 mV/s, using gold wires of 10 μm diameter, the real area calculated was 77.38 ± 2.21 μm². The quality of the seal between the electrode material and the insulating material as well as the shape of the microdisk were investigated by scanning electron microscopy (Figures 2A and 2B).

Steady state voltammetric studies to different concentrations of the hexacyanoferrate couple were performed keeping the concentrations of
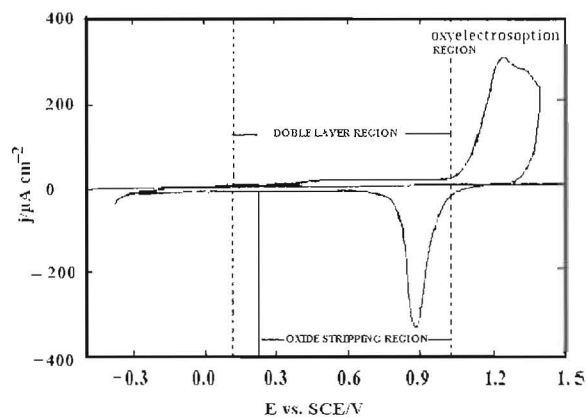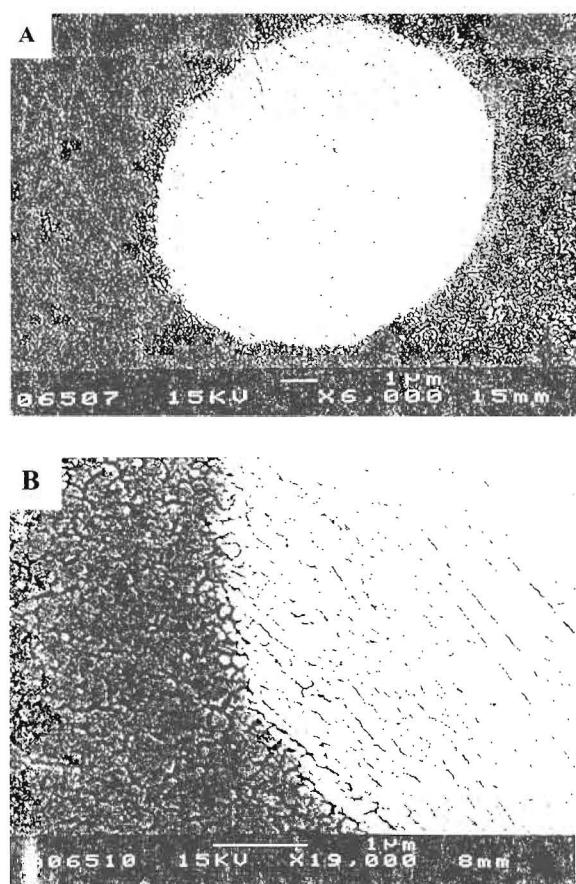
Figure 1. Cyclic voltammogram at a gold ultramicroelectrode of 5 μm radius (sealed in epoxy composite), in 0.2 mol dm^{-3} $HClO_4$; v= 70 mV s^{-1}.

Figures 2A and 2B. SEM photograph of a gold ultramicroelectrode fabricated with gold wire (10 μm diameter) sealed with epoxy.
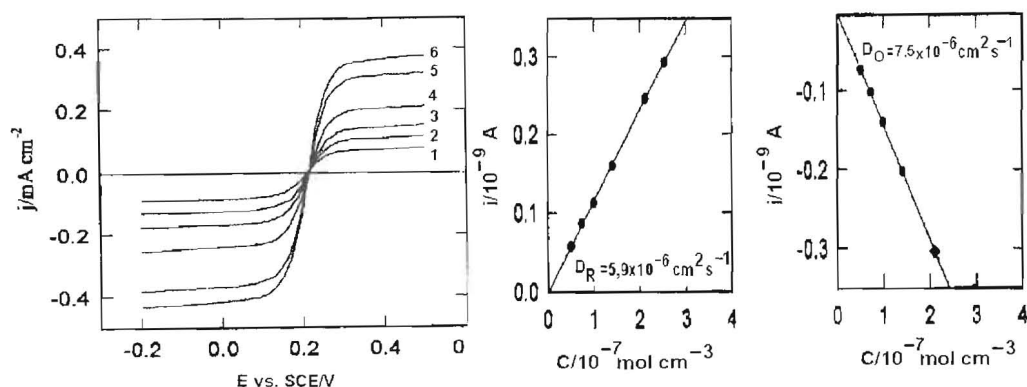
Figure 3. A) Steady state voltammograms at a gold ultramicroelectrode (10 μm diameter) sealed in glass for different concentrations of hexacyanoferrate couple: 1) 5×10^{-5}; 2) $7,3 \times 10^{-5}$; 3) 1×10^{-4}; 4) 1.4×10^{-4}, 5) 2.1×10^{-4}, 6) 2.5×10^{-4} mol dm^{-3} in 0.5 mol dm^{-3} KF; $v = 20$ mV s. B) Current vs. concentration plots from data in Figure 3a.

ferrocyanide equal to the concentration of ferricyanide to determine the diffusion coefficient of the oxidised and reduced forms (Figure 3a). In these experiments it was observed that the diffusion limited current was proportional to the concentration (Figure 3b). The diffusion coefficients of the oxidised and reduced species were determined from the slope of plots of diffusion current vs. concentration applying the equation:

$$D^{\circ} = \frac{s}{4n\,Fr} \qquad (4)$$

The value obtained for the oxidised species was $5.74 \times 10^{-6} \pm 0.2 \times 10^{-6}$ cm^2 s^{-1} and the value for the reduced species was $7.25 \times 10^{-6} \pm 0.2 \times 10^{-6}$ cm^2 s^{-1}. These values agree with the values reported in the literature [13].

Supporting electrolyte dependence

A very large number of experiments were carried out using different [electrolyte]/ [hexacyanoferrate couple] ratios. All the experiments were initiated at the equilibrium potential. In solutions where the concentration of supporting electrolyte was > 0.1 mol dm^{-3}, well defined steady-state behaviour was observed using a gold ultramicroelectrode (Figure 4A). The equilibrium potential of the hexacyanoferrate couple shifted to more positive potential as the concentration of supporting electrolyte was increased beyond 0.1 mol.dm^{-3}. Although the equilibrium potential had an unknown contribution from the

liquid junction potential of the reference electrode (SCE), the changes observed seemed too large to be attributed to changes of liquid junction potential. The potential shift was attributed to the association of the K$^+$ cations and the hexacyanoferrate ions. When the concentration of supporting electrolyte was < 0.1 mol dm^{-3} and the hexacyanoferrate couple concentration $\leq 1 \times 10^{-3}$ mol dm^{-3}, steady state limiting currents were not observed (Figure 4B).

According to Wightman et al. [14], electrochemical measurements performed when the electrolyte/analyte ratio is > 1 can give information which is not affected due to scavanging electrolyte in the diffuse layer. In a series of experiments the [electrolyte]/ [hexacyanoferrate couple] ratio was changed from 0 to 100, using a constant concentration of hexacyanoferrate. However no steady-state behaviour was observed. On the other hands, if migration effects are considered, the ratio i_i / i_d (where i_i is the limiting current when supporting electrolyte is absent from solution and i_d is the diffusion controlled limiting current in the presence of excess supporting electrolyte) must be > 1 for the anion oxidation, according the equations developed by Amatore et al. [15] for the oxidation or reduction of multiply charged ions in the absence of supporting electrolyte. For this reason comparisons with this model can not be made. Moreover, this model has been developed by making several assumptions such as similar diffusion coefficients for pro-
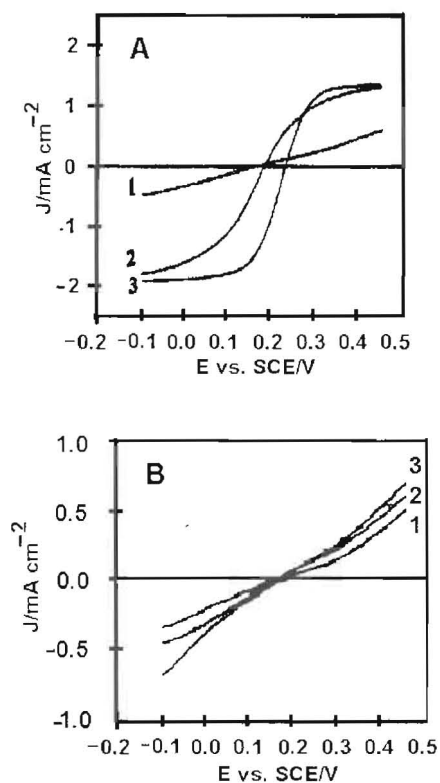
Figures 4A and 4B. Voltammograms obtained at a gold ultramicroelectrode (10 μm diameter) sealed in epoxy for the system hexacyanoferrate couple 1 x 10^{-3} mol dm^{-3} in different concentrations of KF to ν = 5 mV s^{-1}, A: 1) 1 x 10^{-2}; 2) 1 x 10^{-1}, 3) 1 mol dm^{-3}; B: 1) 0; 2) 1 x 10^{-3}, 3) 1 x 10^{-2} mol dm^{-3}.

ducts and reactant, no double layer effects, and no ion pairing.

According to the results obtained by Campbell and Peter [16] for the system $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ on gold electrodes using impedance measurements and KF as supporting electrolyte, a minimum in the apparent rate constant is observed when the total concentration of K^+ cations is increased over the range 4×10^{-4} to 1 mol dm^{-3}. Experiments with different concentration of supporting electrolyte in the range where the total concentration of K^+ increase from 7×10^{-4} to 0.01 mol dm^{-3} were carried out. Figure 5 shows Tafel plots under the experimental conditions mentioned above. From these plots, the apparent exchange current i^o_{app} and the electron transfer coefficients were determined for both processes.

It was found that the sum of the electron transfer coefficients for the anodic and cathodic processes is less than one. These results agree with the values obtained by Peter et al. [3] using a coulostatic method. Figure 6 shows log k^o_{app} vs. log $[K^+]_{total}$ plots for the oxidation and reduction processes. The k^o_{app} was determined using the equation:

$$k^o_{app} = \frac{j^o_{app}}{nFC^\infty} \quad (5)$$

Where j^o_{app} is the exchange current density and C^∞ is the concentration of the hexacyanoferrate couple in the bulk solution. A minimum in the apparent rate constant k^o_{app} is found when the total concentration of K^+ is between 1×10^{-3} to 3×10^{-2} mol dm^{-3}.

Effects of association of the K^+ cation with the hexacyanoferrate couple or double layer effects on the rate of electron transfer could be responsible for the behaviour observed in this range. According to Eaton et al. [17] the association constant K_1 and K_2 for the equilibrium reactions:

$$K^+ + Fe(CN)_6^{4-} \xrightarrow{K_1} KFe(CN)_6^{3-} \quad (6)$$

$$K^+ + Fe(CN)_6^{3-} \xrightarrow{K_2} KFe(CN)_6^{2-} \quad (7)$$
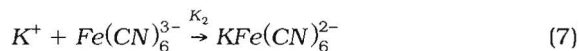
are related to the thermodynamic association constant, K^o, by the following equation:

$$\log K = \log K^o - \frac{NI^{\frac{1}{2}}}{1+1.5I^{\frac{1}{2}}} \quad (8)$$

based on the extended Debye-Hückel theory; where $K=K_1$ or K_2, are the equilibrium constants depending on the equilibrium studied, and they are defined in terms of the molar concentration of the species present in the reaction; where N is a constant; N=4.08 for reaction (6), and N=3.06 for the reaction (7); I is the ionic strength. From this equation, values of K were determined for a constant concentration of the hexacyanoferrate couple and different concentrations of supporting electrolyte. From these values, the concentrations of $KFe(CN)_6^{3-}$ and $KFe(CN)_6^{2-}$ were determined.

Figure 7 shows the behavior of ion-pair association with the total concentration of K^+ present in the system. Not surprisingly, it is observed that the ion association of the ferrocyanide anion occurs more appreciable than the association of
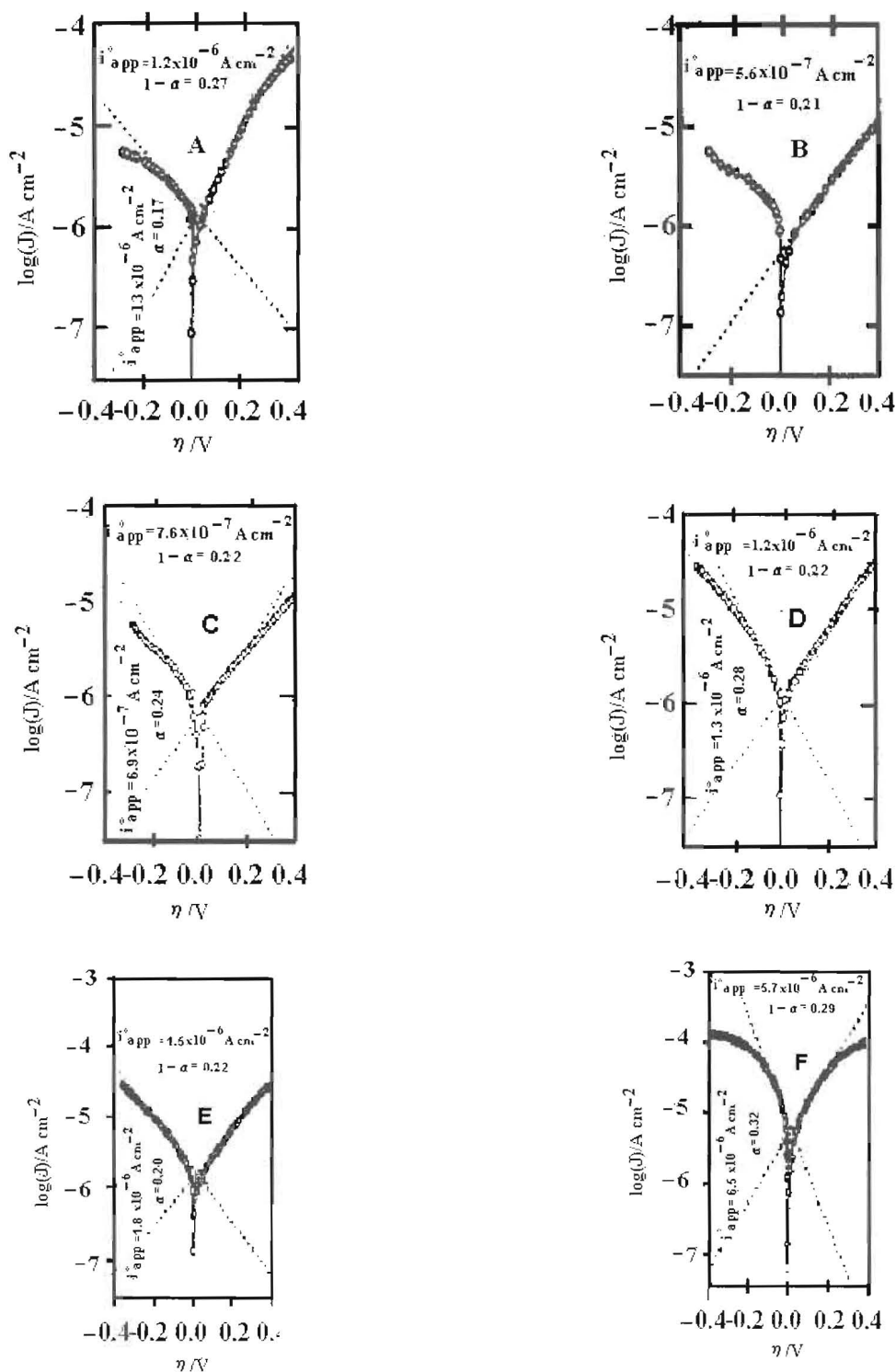
Figure 5. Tafel plots at a gold ultramicroelectrode (10 μm diameter) sealed in epoxy for the system hexacyanoferrate couple 1 x 10^{-4} mol dm^{-3} in different concentrations of KF: A)₃Without supporting electrolyte; B) 4 x 10^{-4}; C) 1.5 x 10^{-3}; D) 6.9 x 10^{-3}; E) 0.01; F) 0.05 mol dm   ; v = 25 mV s^{-1}.
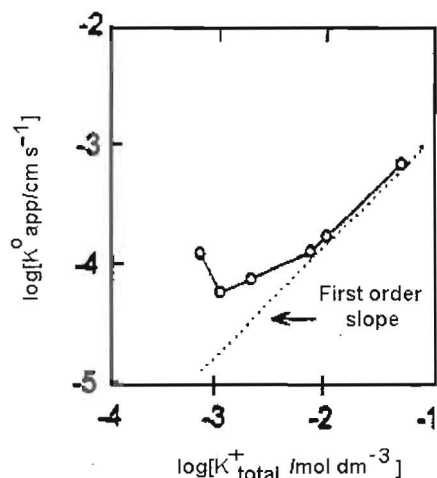
Figure 6. Log [k$^o_{app}$] vs. log ([K$^+$]$_{total}$) plot for the oxidation and reduction of the hexacyanoferrate couple at a gold ultramicroelectrode (10 μm diameter); v = 25 mV s^{-1}.

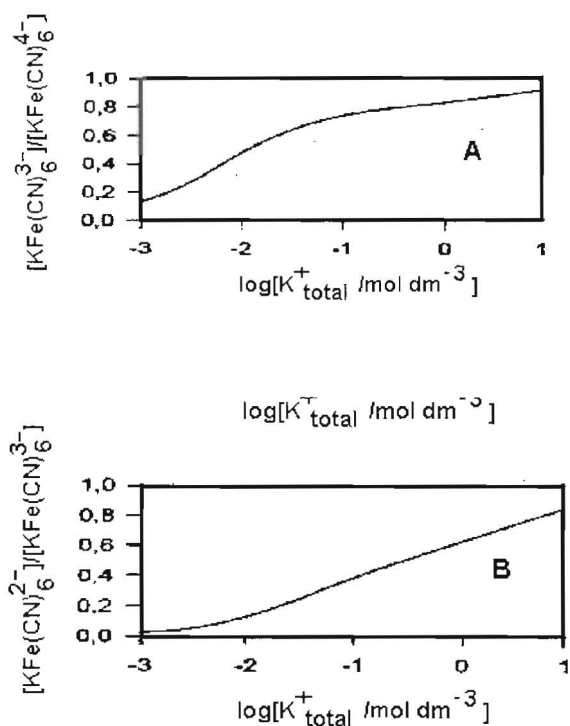Figure 7. Ion-association behavior calculated from equation (9) for the system Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ 1x10^{-4} mol dm^{-3} when the total concentration of K$^+$ is increased.

the ferricyanide anion. When the total concentration of K$^+$ is 2.2x10^{-3} mol dm^{-3}, the extent of the association is 24% for the ferrocyanide anion, while it is only 4% for the ferricyanide anion (Figure 7).

From Figure 5 the Tafel plot for the electrochemical process in absence of supporting electrolyte shows the anodic and cathodic branches are not symmetrical. The anodic branch is higher than the cathodic branch. This behavior may be attributed to double layer effects.

For gold polycristalline surfaces the potential of zero charge is ~ -0.05 ± 0.1V vs. SCE [18]. This means the charge on the metal surface (q^M) near the equilibrium potential is positive. This excess of positive charge on the metal will result in the concentration of ferrocyanide anions near to the electrode surface being higher than in a bulk solution and higher than the concentration of ferricyanide anions at the microelectrode surface. This difference in concentration produces that the current density at potentials positive of the equilibrium potential will be enhanced. The plots in Figures 8a and 8b were obtained using the following equation:

$$q^M = \pm\left[2RT\varepsilon\varepsilon_o \sum C_i^s\left(e^{-Z_i F\phi_2/RT} - 1\right)\right]^{\frac{1}{2}} \qquad (9)$$

which is derived from the Gouy - Chapman theory of the diffuse double layer. The plots were calculated considering no association of the anion with the K$^+$ cations (Figure 8a) and considering this association effects (Figure 8b). In this equation, c$_i^s$ is the concentration of ions in bulk solution, and ϕ_2 is the potential in the outer-Helmholtz layer [19]. From these plots it is seen that when the electrode is charged positively, a high concentration of anions must be near to the electrode surface, which is reflected in the small values of ø$_2$. If association of these electroactive species with the cations from the supporting electrolyte is considered, the concentration of these species near to the electrode surface is less with respect to the situation where no association is considered. This behaviour is also observed in the values of ø$_2$ in Figure 8b.

The charge on the metal electrode can be related to the potential by the equation:
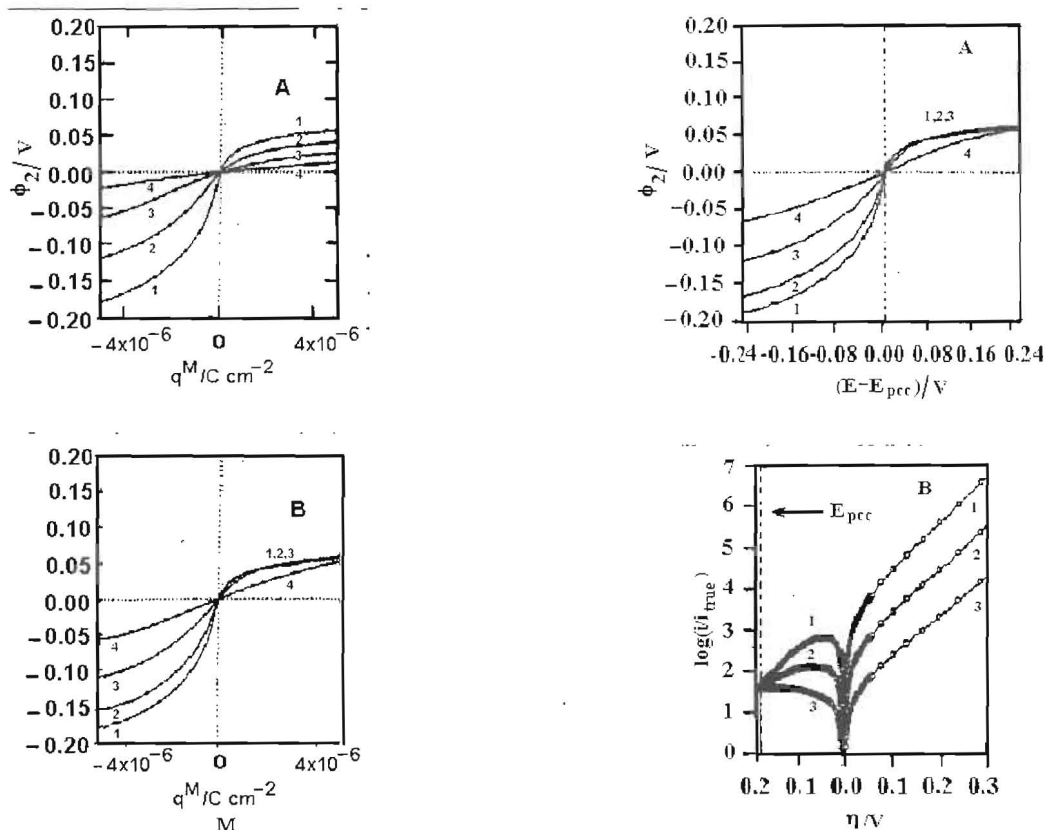
Figure 8. Potential Φ_2 vs. q^M plots calculated from equation (10): A) without considering specific adsorption and association of the electroactive species with K^+ cations and B) without considering specific adsorption and taking into account association of the electroactive species with K^+ cations ; concentration of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{4-}$: 1) $1x10^{-4}$; 2) $1x10^{-3}$; 3) $1x10^{-2}$; 4) $1x10^{-1}$ mol dm^{-3} KF.

$$q^M = \int_{Epcc}^{E} C_{dl} dE \tag{10}$$

if C_{dl} is considered constant in the potential range studied, the potential diference $E-E_{pzc}$ is given by:

$$E - E_{pcc} = \frac{q^M}{C_{dl}} \tag{11}$$

Figure 9A shows the behaviour of ϕ_2 vs. $E-E_{pzc}$ calculated using this aproximation and C_{dl} equal to 25 µF cm^{-2}.

According to Figure 4A the equilibrium potential of the hexacyanoferrate couple shifted to

Figures 9A y 9B. A) Potential$\Phi_2$vs. (E - E_{pcc})plots from data in figure 8B, assuming C_{dl} = 25 µF cm^{-2}; B) Log(j/j$_{true}$) vs. overpotential (η) calculated from equation (14) taking data in (figure 9); considering $\eta=(E - E_{formal})$; assuming the effective charge is: 1) -3; 2) -2; 3) -1 and $\alpha= 0.5$; $[Fe(CN)_6^{4-}/Fe(CN)_6^{3-}]=1x10^{-4}$ mol dm^{-3} and $[KF]=1$ x10^{-2}mol dm^{-3}.

more positive potential as the concentration of supporting electrolyte was increased. This mean that for building Tafel plots, the overpotential must be calculated taking into account the formal potential (E°'), which is dependent on the medium since it includes the logarithmic activity coefficient terms (γ_i) as well as the standard electrode potential (E°), according to the following relationship:

$$E^{o'} = E^o - \frac{RT}{nF} \sum v_i \ln \gamma_i \tag{12}$$

If the overpotential (η) is calculated as (E - E°') and this data and ϕ_2 are taken from Figure 9A, the behavior of the ratio between the current

density and the true exchange current density can be evaluated for the hexacyanoferrate couple at conditions where supporting electrolyte is present or absent using the equation:

$$\frac{j}{j_t^o} = e^{(\alpha n - z)f\,\phi_2}\left[e^{(1-\alpha)nf\eta} - e^{\alpha nf\eta}\right] \quad (13)$$

where j_t^o is the true exchange current density, α is the cathodic transfer coefficient, z is the ionic valence of the oxidised species, $f = F/RT$, n is the number of electrons transfered. Figure 9B shows this behavior. It is seen that the theory predict that the cathodic current should be considerably hindered by double layer effects even taking into account the formation of ion-pair. Experimentally this effect was not as large as predicted in Figure 9B. The ion - pair species may be reacting faster than the free ferricyanide anions present near to the electrode- solution interface. The association constant of formation of ion - pair species may be different in the double layer from the association constant of these species in the bulk solution. The concentration of the ion - pairs species in equilibrium with the free association species may be affected in the double layer region due to the potential difference developed in the electrode - solution interface.

Electrochemical and chemical reactions could be also occurring in parallel during the oxidation and reduction of the hexacyanoferrate couple, influencing the electrochemical response observed experimentally.

Conclusión

Microelectrode studies of the oxidation and reduction of hexacyanoferrate couple have shown that the electrochemical process is affected by the concentration of KF the supporting electrolyte. The experimental results show that a low concentration of potassium ion and overall ionic strength, the electrode kinetics become dominated by double layer effects. At higher concentration of potassium ion, the apparent rate constant increases approximately linearly with [K$^+$] as has been reported previosly [6]. Attempts to model the double layer effects on assuming that the reaction involves the free hexacyanoferrate ions showed that the predicted influence of the potential was larger than that

observed experimentally. This provides evidence that the main reacting species are ion pairs, even at these low ionic strengths. The reason for this apparent anomaly is that the rate constants for the ion pair species are considerably higher than those for the free ions. Therefore the electrode reaction proceeds via the ion pairs, even when they are minority species. The experimental Tafel plots gave α and (α -1) values that do not sum to unity. This effect has been reported previously for measurements made by the coulostatic metods at much higher concentrations of KF [6]. The reason for this anomalous behaviour remains obscure. It is certainly not due to a preceding rate limiting chemical step involving ion pair formation, since this is expected to occur with a second order rate constant in excess of the diffusion controlled limit of 10^{10} dm^3 mol s^{-1}. Tafel plots predicted for taking into account the double layer effect show a large effect only on the cathodic branch. By contrast the anodic branch is largely unaffected because ϕ_2 is small. It therefore seems unlikely that double layer effects are responsables for the observed values of α. The hexacyanoferrate system is often considered as a 'model' redox system. However this study has revealed that the system is extremely complex. Comparison of experimental rate constant with values predicted by Marcus theory [20] are clearly not justified because the reacting species are ion pairs and the apparent rate constant is sensitive to the total potassium ion concentration.

In conclusion, this study has shown that it appears impossible to determine the rate constants for the hexacyanoferrate couple for the free (unpaired) anionic species. Even at the lower concentrations and after correction for double layer effects, the reaction is still dominated by ion pair effects.

Acknowledgements

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