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Self-Assembly of Ion-Paired Electron-Transfer Centers in a Clay-Modified Electrode

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Electrochemical properties are reported for a montmorillonite-modified graphite electrode intersalated by the complex salt $[Fe(bpy)_3]_2[Fe(CN)_6]$ at loadings in excess of the cation-exchange capacity of the clay. The presence of a multilayer $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ assembler in the clay galleries was indicated by a basal spacing of ~27 Å, as compared to 17 Å for homoionic $Fe(bpy)_3^{2+}$–montmorillonite. Mössbauer and infrared spectra were consistent with the presence of intercalated $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ assemblies. Analogous intersalation was observed for $[Fe(phen)_3]_2[Fe(CN)_6]$. Cyclic voltammograms for the clay interlayered by $[Fe(bpy)_3]_2[Fe(CN)_6]$ exhibited two well-defined waves corresponding to $Fe(bpy)_3^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ interconversion. The electrochemical response for the anionic $Fe(CN)_6^{3-/4-}$ couple indicated that an ion-pairing mechanism was responsible for the observed electroactivity. Enhanced peak currents were observed for the $Fe(bpy)_3^{2+}$ oxidation and also for the $Fe(CN)_6^{3-}$ reduction. The current enhancements have been attributed to electron transfer between $Fe(bpy)_3^{3+}$ and $Fe(CN)_6^{4-}$ centers within the clay films. Analogous behavior was observed for a montmorillonite film intersalated by $[MV]_3[Fe(CN)_6]_2$. In the latter case a current enhancement was observed for $Fe(CN)_6^{4-}$ oxidation, in accord with electron transfer between $Fe(CN)_6^{3-}$ and dimeric $[MV^{\bullet +}]_2$ formed by the electrochemical MV^{2+} reduction.

Introduction

Previous studies in clay-modified electrodes have shown that smectite clays can function as thin coatings to modify the electrochemical properties of electrode surfaces.[1–15] Enhanced chemical stability, special structural features, unusual intercalation properties, and potential use as catalyst or catalyst supports are among the principal advantages of clays as electrode modifiers. Clay films deposited on electrode surfaces can exchange their sodium cation and imbibe redox-active species such as several cationic polypyridyl–metal complexes, $M(bpy)_3^{2+}$ ($M = Fe^{2+}$, Ru^{2+}, Os^{2+}) and $Cr(bpy)_3^{3+}$, and methyl viologen (*N,N′*-dimethyl-4,4′-bipyridinium or MV^{2+}). The cyclic voltammograms obtained from the incorporation of these ions in clay films have wave shapes that are characteristic of a diffusion-controlled process. In addition, anions such as $Fe(CN)_6^{3-}$, $Mo(CN)_8^{4-}$, and $C_2O_4^{2-}$, although normally repelled by the negative charge of the clay layers, readily penetrate montmorillonite films and undergo electron transfer at the electrodes.[2,9,14] This finding implies the presence of electroactive channels between the clay particles comprising the film.

In understanding the electrochemical behavior of clay-modified electrodes, it is essential to know the nature of the electroactive centers present in the interlayer region of the clay films and the mechanism responsible for their electroactivity. Equally important is the transfer of charge compensating ions necessary to maintain electroneutrality during the electrolytic processes on clay surfaces. In the direction of such objectives, recent work has demonstrated[8,16] that for clay-modified electrodes intercalated with $M(bpy)_3^{2+}$ or MV^{2+} ions, the electroactive sites originate mainly from cations that are physically absorbed on the clay surfaces as ion pairs in excess of the cation-exchange capacity of the mineral. The same cations electrostatically bound to ion-exchange sites on the clay surfaces are inactive.

In the present work the concept of ion pair formation is used for introducing into clay films pairs of electroactive species with different redox potentials. We show that metal complex salts of the type $[M(bpy)_3]_n^{2+}(X^{n-})_2$ and $(MV^{2+})_n(X^{n-})_2$, where X^{n-} is an electroactive anion, interact with smectite clays to form intersalated products which exhibit activity arising from the presence of these electroactive cations and anions within the coating. [The term intersalation is used in this work to indicate the presence of an intercalated salt in smectite clay interfaces.] In this study we describe the electrochemical behavior of sodium montmorillonite intersalated with $[Fe(bpy)_3]_2Fe(CN)_6$ and $(MV)_3[Fe(CN)_6]_2$. The former system features both iron ions in the reduced divalent state, whereas the latter contains methyl viologen and iron in their respective oxidized states.

Experimental Section

Materials. Sodium montmorillonite was purchased from the source Clay Minerals Repository (University of Missouri, Columbia, MO). The clay was purified using standard methods.[16]

All chemicals were of reagent grade quality and were obtained from

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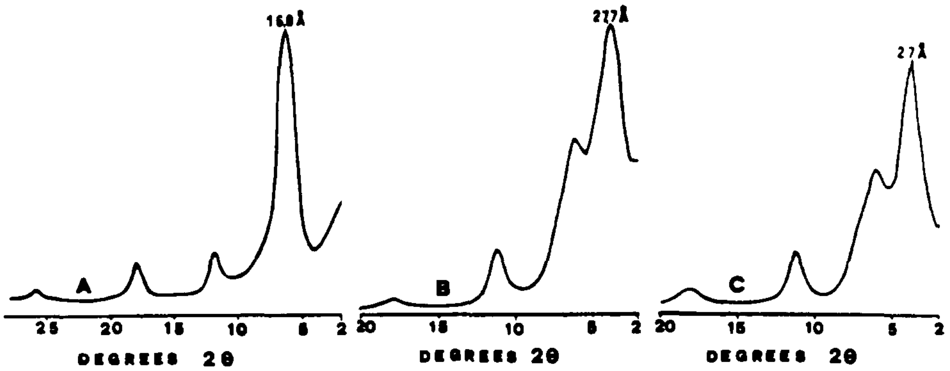

Figure 1. X-ray diffraction patterns of clay complexes obtained from the reaction of sodium montmorillonite with $[Fe(chel)_3]_2Fe(CN)_6$: (A) Homoionic $Fe(bpy)_3{}^{2+}$; (B) $Fe(bpy)_3{}^{2+}/Fe(CN)_6{}^{4-}$ intersalate; (C) $Fe(phen)_3{}^{2+}/Fe(CN)_6{}^{4-}$ intersalate. The *d*-spacings are in angstrom units.

commercial sources. Hydrated $Fe(bpy)_3SO_4$ was prepared according to a published procedure.[17]

$[Fe(bpy)_3]_2Fe(CN)_6$. A solution containing 1 mM of $Fe(bpy)_3Cl_2$ was prepared by adding 2,2′-bipyridine (0.47 g, 3.0 mmol) in 20 mL of ethanol to 20 mL of an aqueous solution containing the corresponding amount of $FeCl_2{\cdot}4H_2O$ (0.20 g, 1.0 mmol). To the resulting mixture was added the stoichiometric amount of $K_4Fe(CN_6){\cdot}3H_2O$ (0.21 g, 0.50 mmol) in 20 mL of H_2O. The red crystals formed on standing were collected, rinsed with some water and ethanol, and air-dried. The IR spectrum, in addition to absorptions due to the bipyridine ligands, showed a single strong cyanide stretching vibration at 2130 cm^{-1}. The corresponding $[Fe(phen)_3]_2Fe(CN)_6$ salt was prepared analogously using 1,10-phenanthroline instead of 2,2′-bipyridine.

$(MV)_3[Fe(CN)_6]_2$. A solution of 1,1-dimethyl-4,4′-bipyridinium dichloride (0.31 g, 1.0 mmol) in 5 mL of H_2O was added to a solution of $K_3Fe(CN)_6$ (0.22 g, 0.66 mmol) in 5 mL of H_2O. After the addition of 5 mL of ethanol, the yellow crystals were collected, washed with some ethanol, and air-dried. The IR spectrum showed, apart from the vibrations of methyl viologen, a strong cyanide stretching vibration at 2125 cm^{-1}.

Metal Complex Exchange Forms of Montmorillonite. Owing to the limited solubilities of the $[Fe(bpy)_3]_2Fe(CN)_6$ and $[Fe(phen)_3]_2Fe(CN)_6$ salts in H_2O, the exchange reactions with montmorillonite were conducted at 80 °C. A homoionic $Fe(bpy)_3$-exchange form of montmorillonite was prepared from the metal complex salt in the following way. A solution of 0.08 g of $[Fe(phen)_3]_2Fe(CN)_6$ in 10 mL of H_2O was heated to 80 °C. To this solution was added a dilute dispersion of sodium montmorillonite, 25 mg in 25 mL of H_2O. Heating was continued for 10 min, and then the mixture was centrifuged, washed with three aliquots of 10 mL of H_2O, and air-dried. The quantity of the metal salt utilized in this exchange reaction was equal to the exchange capacity of the clay, expressed as a CEC-equivalent (CEC = cation-exchange capacity). Homoionic $Fe(phen)_3$–montmorillonite was prepared similarly. $Fe(bpy)_3{}^{2+}$ or $Fe(phen)_3{}^{2+}$–montmorillonites containing intersalated $[Fe(bpy)_3]_2Fe(CN)_6$ or $[Fe(phen)_3]Fe(CN)_6$ were prepared similarly by treating 25 mg of sodium montmorillonite in 25 mL of H_2O with amounts of the complex salt corresponding to three times the CEC of the clay. The intersalated samples obtained in this way were centrifuged to remove as much supernatant liquid as possible before being air-dried. Oriented samples of the clay complexes for XRD measurements were obtained by placing aliquots of the centrifuged pastes onto glass plates and drying them in air at 60 °C.

Apparatus and Procedures. A Philips X-ray diffractometer with Co Kα radiation was used for determining the 001 basal spacings in the intercalated clay structures. ^{57}Fe Mössbauer spectra of powder samples were obtained with a constant-acceleration spectrometer. Electrochemical instrumentation consisted of a PAR Model 174A polarographic analyzer operated in conjunction with a Model 175 universal programmer and a Hewlett-Packard 7045A x-y recorder. All electrochemical experiments were carried out in a conventional three-electrode, single-compartment cell containing a pyrolytic graphite working electrode, a saturated calomel reference electrode, and a platinum-gauze counter electrode. The supporting electrolyte was 0.1 M Na_2SO_4. Basal plane pyrolytic graphite electrodes were constructed by following published procedures.[18] Clay films were cast on electrode surfaces by slow evaporation at room temperature of a drop of clay suspension (2g/L). Ions were incorporated into the film by soaking the electrodes for about 10 min in a 1 mM solution of these ions. The films developed the intense red color characteristic of the $Fe(bpy)_3{}^{2+}$ complexes. The films were rinsed with water before use.

Results and Discussion

Intersalation of $[Fe(chel)_3]_2Fe(CN)_6$ (chel = bpy, phen). The interaction of these complex salts with sodium montmorillonite afforded two distinct types of interlamellar assemblies depending upon the relative amounts of the reactants used in the reaction. Homoionic $Fe(chel)_3{}^{2+}$ intercalates containing only electrostatically bound complex cations on the gallery surfaces were obtained when dilute dispersions of sodium montmorillonite were treated with metal complex solutions containing amounts of salt corresponding to the cation-exchange capacity (CEC) of the clay. Thus, these stoichiometric ion-exchange reactions produced homoionic intercalates exhibiting 17-Å basal spacings and several rational orders of 001 X-ray reflections. The diffraction pattern for $Fe(bpy)_3{}^{2+}$–montmorillonite is illustrated in Figure 1A. The value of 17.0 Å is similar to the value previously reported for homoionic $Fe(chel)_3{}^{2+}$–smectite complexes[6,8] and is consistent with a monolayer coverage of the clay surface with $Fe(chel)_3{}^{2+}$ ions.

A second type of intercalation complex was obtained from the reaction of sodium montmorillonite with an excess of metal salt. In this case the amount of the complex salt exceeded the CEC of the clay. Under these conditions excess $Fe(chel)_3{}^{2+}$ cations and $Fe(CN)_6{}^{4-}$ counterions penetrate the interlayer region and bind to the clay surface in the form of $Fe(chel)_3{}^{2+}/Fe(CN)_6{}^{4-}$ assemblies. The interactions lead to the construction of ordered planes of metal salt in the gallery region of the mineral. The presence of such ordered assemblies has been verified in previous studies describing the intersalation of smectite clays with the sulfate salts of various $M(chel)_3{}^{2+}$ complexes.[19,20] The X-ray diffractograms of $M(chel)_3{}^{2+}/SO_4{}^{2-}$ intersalated phases reveal basal spacings of approximately 29 Å, which indicates two molecular layers of metal complex cation in the clay interlayers.

Figure 1B,C illustrates the 001 X-ray reflections obtained from oriented film samples of intersalated $Fe(bpy)_3{}^{2+}/Fe(CN)_6{}^{4-}$ and $Fe(phen)_3{}^{2+}/Fe(CN)_6{}^{4-}$–montmorillonites. The observed 001 spacings of about 28 Å indicate clearly the presence of $Fe(chel)_3{}^{2+}/Fe(CN)_6{}^{4-}$ ion pairs in the clay galleries. Additional evidence for the presence of $Fe(CN)_6{}^{4-}$ anions in the galleries was obtained from the Mössbauer spectrum of an $Fe(bpy)_3{}^{2+}/Fe(CN)_6{}^{4-}$–montmorillonite sample. The spectrum shown in Figure 2 clearly shows three different sites. Site A arises from the $Fe(CN)_6{}^{4-}$ ions, site B from $Fe(bpy)_3{}^{2+}$, and site C from iron in the clay structure.

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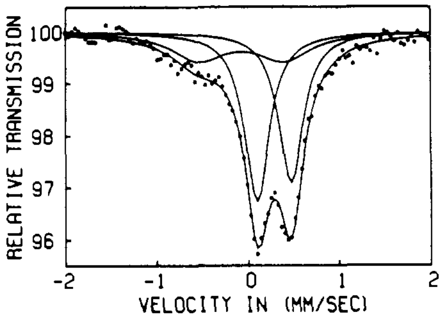

Figure 2. Mössbauer spectrum of $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ intersalate obtained at 78 K. Site A is due to $Fe(CN)_6^{4-}$, site B to $Fe(bpy)_3^{2+}$, and site C to structural iron in the clay.

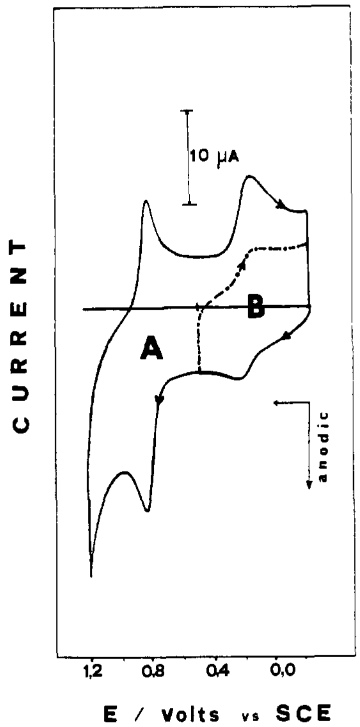

Figure 3. Cyclic voltammograms for an $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ intersalated montmorillonite electrode: (A) potential scanned over both waves (from −0.25 to +1.25 V vs SCE); (B) potential restricted from −0.25 to +0.50 V vs SCE. Scan rate = 100 mV/s^{-1} (0.1 M Na_2SO_4).

Electrochemistry. Stable graphite electrodes modified by clays were readily obtained by evaporating an aqueous suspension of the Na^+-exchange form of the clay. Electrodes prepared in this way, when soaked in a 1 mM solution of $Fe(bpy)_3SO_4$, rinsed with water, and allowed to dry in air, gave cyclic voltammograms in 0.1 M Na_2SO_4 exhibiting well-defined waves with an anodic peak at +0.90 V vs SCE, in agreement with previously observed cyclic voltammograms for physisorbed $Fe(bpy)_2^{3+}/SO_4^{2-}$ ion pairs on clay interfaces.[2,16] Similarly prepared sodium montmorillonite electrodes immersed in 1 mM $K_4Fe(CN)_6$ solution also yielded well-defined waves with an anodic peak potential at +0.23 V vs SCE, in accord with previous observations.[2,9,14]

Figure 3A shows the cyclic voltammogram for a clay-modified electrode that had been presoaked in a 1 mM solution of $[Fe(bpy)_3]_2Fe(CN)_6$. Two well-developed oxidation–reduction waves were observed. The first wave, which had an anodic peak potential at +0.23 V vs SCE, was attributed to the $Fe(CN)_6^{3-/4-}$ couple. The second wave had an anodic peak potential at 0.90 V vs SCE, which coincides with the value obtained for $Fe(bpy)_3^{2+}$ incorporated into a sodium montmorillonite modified electrode. Earlier work[16] has shown that $M(bpy)_3^{2+}$ cations bound electrostatically at ion-exchange sites within the gallaries and at external surfaces of clays are rigorously electroinactive. The electroactivity of the $M(chel)_3^{2+}$ cations in clay-modified electrodes was attributed to intercalated cations that are bound at the clay surface in excess of the cation-exchange capacity of the mineral through ion pair formation with the corresponding anion. In line with this interpretation, we attribute the two waves shown in Figure 3A to the presence of intercalated $Fe(bpy)_3^{2+}$ and $Fe(CN)_6^{4-}$ ions pairs in the clay film. In fact, we observed a continuous decrease in the heights of the anodic/cathodic currents due to the $Fe(CN)_6^{3-/4-}$ couple upon cycling the electrode several times, indicating that the electroactive anion is displaced from the clay film by the sulfate anions of the supporting electrolyte.

An interesting feature of the cyclic voltammogram for the $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ assembly in montmorillonite film is the enhanced anodic wave for the $Fe(bpy)_3^{2+}$ oxidation and the cathodic wave enhancement for the $Fe(CN)_6^{3-}$ reduction. Measurements of the peak current ratio i_{pa}/i_{pc} for the bpy complex yielded a value of 1.42, while the corresponding value for the cyanide couple was 0.71. These results can be explained in the following way: When the potential is swept anodically, the first wave corresponds to the oxidation of $Fe(CN)_6^{4-}$. With further scan, oxidation of $Fe(bpy)_3^{2+}$ to $Fe(bpy)_3^{3+}$ occurs. The electrogenerated $Fe(bpy)_3^{3+}$ ions are thermodynamically capable of oxidizing an excess of $Fe(CN)_6^{4-}$ ions present in the clay film according to the homogeneous chemical reaction 1.

$$Fe(bpy)_3^{3+} + Fe(CN)_6^{4-} \rightarrow Fe(bpy)_3^{2+} + Fe(CN)_6^{3-} \qquad (1)$$

In this case the $Fe(bpy)_3^{3+}$ ions serve as an electron-transfer mediator shuttling electrons between the electrode surface and the $Fe(CN)_6^{4-}$ ions located in the interior of the film. The net result is a significant current enhancement for the oxidation of $Fe(bpy)_3^{2+}$. The sequence of these events does not affect the total concentration of the $Fe(bpy)_3^{3+}$ ions which are reduced in the reverse scan, because the $Fe(bpy)_3^{2+}$ ions produced in reaction 1 are reoxidized at the electrode surface yielding back the same amount of $Fe(bpy)_3^{3+}$. However, the concentration of $Fe(CN)_6^{3-}$ in the double layer is increased by the same amount as the $Fe(bpy)_3^{2+}$ concentration in accord with eq 1. As a result, the cathodic peak current due to the $Fe(CN)_6^{3-}$ reduction is analogously enhanced. In line with this interpretation the ratio i_{pa}/i_{pc} for the $Fe(bpy)_3^{2+/3+}$ couple would be equal to the ratio i_{pc}/i_{pa} for the $Fe(CN)_6^{3-/4-}$ couple. In fact, the experimental results show that

$$(i_{pa}/i_{pc})_{[Fe(bpy)_3^{2+/3+}]} = (i_{pc}/i_{pa})_{[Fe(CN)_6^{3-/4-}]}$$

The effect of the above reaction 1 on the electrochemistry of the $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ pairs is better illustrated in Figure 3, curve B, where the scan region is limited to a range in which only the cyanide couple is electroactive (from −0.25 to +0.50 V vs SCE). Under these conditions the i_{pa}/i_{pc} ratio is very close to 1, because direct oxidation of $Fe(bpy)_3^{2+}$ is not now possible and therefore the necessary $Fe(bpy)_3^{3+}$ ions for producing an excess of $Fe(CN)_6^{3-}$ via reaction 1 are not available. Similar potential scan-dependent currents have been observed by Anson and co-workers in their studies of pairs of electroactive cations incorporated either in Nafion films[21] or in clay coatings,[9] as well as by Mallouk and co-workers, who described the electrochemical behavior of simple, self-assembled vectorial transport chains in zeolite Y modified SnO_2 electrodes[22,23] and at pillared-clay-modified electrodes containing $Os(bpy)_3^{2+}/Fe(CN)_6^{4-}$ pairs.[24]

In order to obtain additional evidence for the ability of clays to assemble several redox-active components at their surfaces in the form of ion pairs, we have examined the electrochemical behavior of another intercalated complex salt consisting of the

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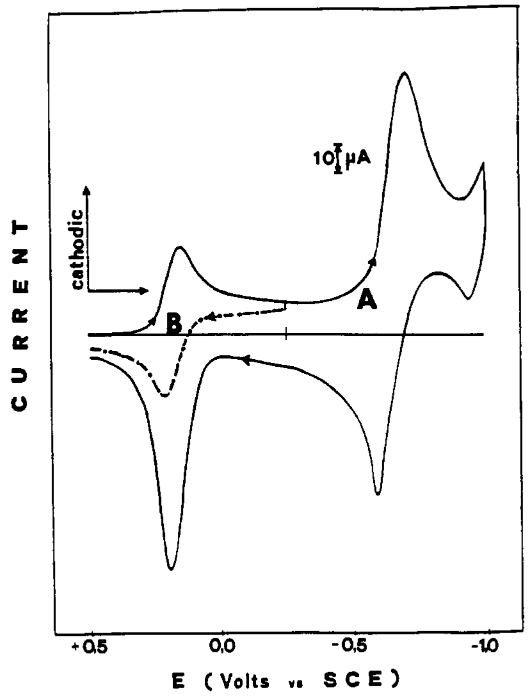

Figure 4. Cyclic voltammograms for a montmorillonite-modified electrode intersalated by $MV^{2+}/Fe(CN)_6^{3-}$: (A) potential scanned over both waves (from +0.50 to −1.00 V vs SCE); (B) potential restricted from +0.50 to −0.25 V vs SCE. Scan rate = 100 mV/s^{-1} (0.1 M Na_2SO_4).

ferricyanide anion and methyl viologen as the countercation. Figure 4 shows cyclic voltammetry for clay electrodes that have been presoaked in a 2 mM solution of $(MV)_3[Fe(CN)_6]_2$. The electrochemical response is similar to that observed for the $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ system. Two well-defined waves corresponding to both $MV^{2+/\bullet+}$ and $Fe(CN)_6^{3-/4-}$ interconversions are seen again. The cathodic wave that peaked at 0.15 V vs SCE arises from direct reduction of $Fe(CN)_6^{3-}$, while that at −0.69 V vs SCE arised from the reduction of methyl viologen to the corresponding radical cation.

The electrochemistry of methyl viologen incorporated into montmorillonite films was first studied by Bard and co-workers.[5,8] They observed that the cathodic wave in the $MV^{2+/\bullet+}$ interconversion was much larger than the corresponding anodic wave and attributed this difference to a chemical reaction which inhibits the reoxidation of the electrogenerated $MV^{\bullet+}$ radical upon scan reversal. They found that only about 20% of the reduction product could be reoxidized at the electrode surface. Spectroelectrochemical and ESR evidence indicated that the radical cation undergoes dimerization in the clay matrix. The formed dimer is strongly adsorbed onto planar surfaces of the clay, becoming immobile and, hence, electroinactive. However, the dimer could be oxidized by anionic mediators, such as $Fe(CN)_6^{3-}$, which were electrogenerated by direct oxidation of $Fe(CN)_6^{4-}$ ions penetrating the clay film from the solution.

Our system is very similar to that of White and Bard[5] with the only difference that in our case a large reservoir of $Fe(CN)_6^{3-}$ preexists in the clay film in the form of $MV^{2+}/Fe(CN)_6^{3-}$ ion pairs. Accordingly, we also attribute the depressed anodic wave of the $MV^{2+/\bullet+}$ couple to the partial dimerization of the electrogenerated $MV^{\bullet+}$ radical and the much larger anodic wave at +0.22 V vs SCE to the direct $Fe(CN)_6^{4-}$ oxidation and, in addition, to the mediating action of excess $Fe(CN)_6^{3-}$ present in the clay film. These $Fe(CN)_6^{3-}$ ions are capable of delivering charges between the electrode surface and the dimeric $(MV^{\bullet+})_2$ species strongly adsorbed on the clay surfaces according to reaction 2.

$$Fe(CN)_6^{3-} + {}^1/_2(MV^{\bullet+})_2 \rightarrow Fe(CN)_6^{4-} + MV^{2+} \quad (2)$$

Here again, as with the $Fe(bpy)_3^{2+}/Fe(CN)_6^{4-}$ system, when the potential scan was limited to a range where only the $Fe(CN)_6^{4-/3-}$ couple was active (from +0.50 to −0.25 V vs SCE), the i_{pc}/i_{pa} ratio was found close to 1 (Figure 4B). This is an expected result, because any contribution to the anodic current from reaction 2 is now absent.

In this work we have demonstrated that the surfaces of montmorillonite films are capable of assembling electroactive cationic and anionic pairs, such as $[Fe(chel)_3]^{2+}/Fe(CN)_6^{4-}$ and $MV^{2+}/Fe(CN)_6^{4-}$, through ion-exchange and intersalation mechanisms. Intersalation endows a clay film with two electroactive sites, a cationic $Fe(chel)_3^{2+}$ or MV^{2+} center and an anionic $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}$ center. These intersalated ions are relatively free to move in the interlayer region and participate in electron-transfer processes. They can also act as charge mediators shuttling electrons between the electrode and other molecules in the clay film. The incorporation of more than one electroactive species in clay-modified electrodes and their mediating action widen the use of these electrodes for electrocatalytic applications.

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