Clay modified electrodes

Part 9. Electrochemical studies of the electroactive fraction of adsorbed species in reduced-charge and preadsorbed clay films

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ABSTRACT

Clay modified electrodes (CME) were prepared with natural (untreated) and reduced-charge (prepared by treatment with Li^+) montmorillonite. Both the values of c_t, the total concentration, and c^*, the electroactive concentration of adsorbed $M(bpy)_3^{2+}$ (M = Ru, Os, or Fe), were found to be a factor of 10 smaller in the reduced-charge clay, yielding very similar c^*/c_t ratios, even though the cations were restricted to the external surfaces in the reduced-charge clay. The electrochemical inactivity of the intercalated cations by itself can therefore not account for the low values of the c^*/c_t ratio found in CME. The number of defects in the films appears to be more important than the specific adsorption sites in determining what proportion of the adsorbates will be electroactive. No evidence of mediated electron transport by adsorbed species was seen in films prepared with MV^{2+} pre-exchanged clay. However, at low scan rates, electron transfer from lattice Fe(II) resulted in initial i_{pa}/i_{pc}-values larger than unity for adsorbed $Fe(bpy)_3^{2+}$. This effect was also observed for adsorbed $Ru(bpy)_3^{2+}$, but not for $Os(bpy)_3^{2+}$, in both the natural and reduced-charge montmorillonite films.

INTRODUCTION

A key issue in the behavior of clay modified electrodes (CME) [1–14] is the fraction of the total adsorbed species that can communicate via electron transfer with the substrate and the sites within the clay film that such electroactive species occupy. It has been shown that only a small fraction of the total species contained in a clay layer is electroactive [3,5,8,10,13,14]. Moreover, several studies [5,13,15] suggest that species intercalated into the interlamellar spaces are not electroactive. A recent paper by King et al. [13], concerning CME with films of clay pre-exchanged with the species of interest, suggested that species adsorbed onto platelet surfaces are also not electroactive and that only ion-paired species adsorbed in excess of the cation exchange capacity (CEC) contribute to the observed faradaic current. This

paper deals with this question by comparing the voltammetry of clay films cast with untreated clay with that of reduced-charge and pre-exchanged clay. Reduced-charge clay is prepared by treatment of the clay suspension with an ion, such as Li^+, which can substitute into the octahedral vacancies in the clay sheets (as opposed to behaving as exchangeable cations in the interlamellar spaces) and shows a greatly reduced CEC compared to the untreated clay.

CME are of interest because clay minerals are cheap, widely available naturally occurring materials. Their well-defined layered structures [16–18], flexible adsorption properties [19], and potential as catalysts and/or catalyst supports [20–24] make them interesting materials with which to modify electrode surfaces. They also have higher thermal and chemical stability than many of the other materials that have been used for such modifications, e.g., Nafion and other polyelectrolytes [25].

Clay modified electrodes are prepared by the deposition of clay films on a conductive substrate. The aim is to take advantage of the adsorption and/or catalytic properties of these films to improve the selectivity or the sensitivity of the electrodes toward solution species. The electrochemical behavior of a variety of cations adsorbed in CME have been studied [26]. Enhanced peak currents, in comparison to those found at a bare electrode, were found in the cyclic voltammograms of clay-adsorbed metal–bipyridyl cations, despite their significantly lower diffusion coefficients in clay films with respect to those in solution. This was attributed to the high local concentration of cations in the films. The local concentrations achieved were so much larger than those in solution that enhancements were found, despite the fact that only a small fraction (20% or less) of the adsorbates were electroactive. Clays are heterogeneous materials. Each individual clay has a range of different compositions and particle sizes. Furthermore, the clay films are imperfect stacks of clay layers. They contain many defects such as holes and pores of various sizes. Therefore, there are many different adsorption sites in CME. The question is: at which of these many types of sites are the electroactive cations adsorbed?

In an attempt to answer this question, the concentration of electroactive species in the films, c^*, the total concentration of cations in those films c_t, and the ratio, c^*/c_t, were measured for different cations in natural, reduced-charge, and pre-exchanged montmorillonite films.

Experimental

The clay used was a montmorillonite (STx-1) from Gonzales County, TX, obtained from Clay Source Minerals Repository (University of Missouri, Columbia, MO). The sodium form of the clay was prepared and the < 2.0 μm and < 0.2 μm fractions were separated by literature procedures [27,28]. Briefly, the clay was stirred in 1 M NaCl for 48 h to convert it to the sodium form. After centrifugation and washing with water, it was dialyzed through a Spectrapor membrane until a negative chloride·test was obtained. The fractions were then separated by centrifugation (Beckman, Model J2-21) and freeze-dried. The clay monovalent cation exchange

capacity (CEC) was 0.85 mmol/g. The reduced-charge clay was prepared from the $< 2.0\ \mu$m fraction. The clay was first converted to the lithium form by stirring it in 1 M LiCl overnight. The sediment was then washed, first with water and then four times with EtOH, and heated to $250\,^{\circ}$C for 18 h. This produced a grey powder that was darker than the original clay and much more difficult to disperse in water [29]. Hereafter, material prepared in this manner will be referred to as Li-250.

Ru(bpy)$_3$Cl$_2$ and methyl viologen were obtained from Aldrich (Milwaukee, WI) and were used without further purification. Propyl viologen sulfonate (PVS), Os(bpy)$_3^{2+}$ and Fe(bpy)$_3^{2+}$ were synthesized and purified according to published procedures [30–32]. Clay, pre-exchanged with MV^{2+}, was prepared by stirring a solution of the cation with a suspension of $< 0.2\ \mu$m fraction of the clay (STx-1) for 3 h. The ratio of cation in solution to clay cationic sites was such that if all of the MV^{2+} had been adsorbed, it would occupy 85% of the clay cation exchange capacity. The solid was then separated by centrifugation, washed first with water (5 times), then in 1:1 acetone water and acetone (3 times), and dried at $90\,^{\circ}$C for 1 h. Spectroscopic measurement on the supernatant liquid showed that the clay had adsorbed 83% of its CEC of MV^{2+} or 97% of the MV^{2+} initially present in the solution. Hereafter, this clay will be referred to as MV^{2+}/STx-1.

Preparation of the electrodes

In all cases, the supports were 1×2 cm pieces of indium-doped SnO$_2$ coated glass (ITO) (Delta Technologies, Stillwater, MN). They were cleaned by three cycles of sonication in EtOH. Clay films were deposited by either of two methods. Some were prepared by spin coating. One drop of H$_2$SO$_4$ (10% v/v) was added to a 10 g/l suspension of the clay in distilled water to produce a low viscosity gel. Positive indication of the formation of the gel was that even after several days undisturbed, there was no indication of sedimentation. Without this acid treatment, films could not be made by spin coating. The clay suspension did not wet the hydrophobic supports. Drops of the clay gel were spin-coated at 3000 rpm (Headway Research, Photo-Resist Spinner). This gave films with interference colors ranging from purple to yellow. Most of the electrodes were prepared by evaporation. Small volumes (0.1 to 0.4 ml) of clay suspensions (1 to 3 g/l) were placed on the ITO substrate, and the water was allowed to evaporate. Part of the films were then rubbed off to give 1 cm^2 electrodes. The thickness of the films before and after soaking in Ru(bpy)$_3^{2+}$ were measured on a DEKTAK FLM profilometer (Sloan Technology, Santa Barbara, CA).

Methods and equipment

The clay modified electrodes were soaked in solutions (typically 0.05 to 0.1 mM) of one of the cations or PVS overnight. The amount of solution species adsorbed by the film was determined by measuring the concentration of cation left in the soaking solutions spectrophotometrically. The UV–visible absorption spectra were measured with a Hewlett-Packard Model 8451A spectrophotometer (Palo Alto, CA). Cyclic voltammetry experiments were performed using a Princeton Applied Research

(Princeton, NJ) Model 175 universal programmer and a Model 173 potentiostat. Chronocoulometric measurements were done on a BAS 100 electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). All electrochemical experiments were done in an undivided three-electrode cell. The counter electrode was Pt gauze and the reference electrode was a saturated calomel electrode (SCE). The solutions were degassed by bubbling them with N_2 prior to the measurements.

RESULTS

Spin-coated electrodes

Cyclic voltammograms of spin-coated electrodes, soaked for 24 h in $Ru(bpy)_3^{2+}$, $Os(bpy)_3^{2+}$, $Fe(bpy)_3^{2+}$, MV^{2+} or PVS, were taken at different scan rates. For the metal–bipyridyl cations, quasi-reversible waves were obtained. Approximate values of c^*, the concentrations of electroactive species in the films, were calculated from i_{pc} at low scan rates (1 mV/s) by using the equation for a reversible wave of a surface-confined species. These values are shown in Table 1 along with the values of c_t, the total concentration of cation adsorbed in the film, calculated from the decrease in the concentrations of the soaking solutions. As we have previously reported, this gave more reliable values of c_t than those obtained from measurements of the absorbance of the films themselves [33]. There were wide fluctuations in both c^* and c_t. However, the ratios c^*/c_t were remarkably similar, except for adsorbed $Fe(bpy)_3^{2+}$, which gave a lower value.

A possible explanation for the lower c^*/c_t ratio of $Fe(bpy)_3^{2+}$ is leaching of the adsorbed cations from the film by exchange of ions from the electrolyte. This was a

TABLE 1

Fraction of electroactive cation for electrodes prepared by spin coating suspensions of montmorillonite (STx-1)

Cation adsorbed	$10^8 \times$ Total amount mol [a]	$10^4 c_t/$ mol cm^{-3}	$10^5 c^*/$ mol cm^{-3} [b]	c^*/c_t
$Ru(bpy)_3^{2+}$ [c]	3.16	9.2	6.2	0.067
$Ru(bpy)_3^{2+}$ [d]	6.47	8.6	5.2	0.061
$Ru(bpy)_3^{2+}$ [e]	5.30	22.0	15.4	0.070
$Os(bpy)_3^{2+}$ [e]	7.10	30.0	20.0	0.067
$Fe(bpy)_3^{2+}$ [e]	11.50	48.0	10.0	0.021
MV^{2+} [e]	6.40	25.0	–	–
PVS [e]	0.12	0.5	–	–

[a] From the decrease in concentrations of the soaking solutions.
[b] From the peak current at 1 mV/s.
[c] From Table 3 of ref. 33, for a 300 nm thick film in 0.1 mM Na_2SO_4.
[d] From Table 4 of ref. 33, for a 570 nm thick film in 0.1 mM Na_2SO_4.
[e] The films were 200 nm thick in phosphate buffer, pH 7, electrolyte. The initial concentration of the soaking solutions were 0.1 mM for the bipyridyl cations and 0.05 mM for the viologen species.

problem encountered with all of the cations, causing a decrease in the peak currents with time. For example, i_{pc} of the $Os(bpy)_3^{2+}$-containing film at 50 mV/s decreased from 73 μA in the third scan to 66 μA for the tenth scan and was down to only 24 μA after 2 h in the electrolyte. In the case of adsorbed $Ru(bpy)_3^{2+}$, there was little change between the third and tenth scans, but after 2 h, i_{pc} had decreased from 30 μA to 18 μA. Leaching was most important for the $Fe(bpy)_3^{2+}$ electrode. Its cathodic current decreased from 44 μA to 28 μA from the third to the tenth scans and was down to only 11 μA after 2 h. To get more reliable values of the initial c^*/c_t for the $Fe(bpy)_3^{2+}$ electrode, one might apply a correction to c_t to account for its decrease due to leaching. For example, the value of c_t could be multiplied by the ratio of the peak currents after and before leaching. However, it is not certain that leaching decreases c^* and c_t in the same proportion or that c^*/c_t remains the same after leaching as it was before. However, to minimize this effect on the results, the values of i_{pc} at 1 mV/s that were used in the calculation of c^* were measured at the beginning of each experiment, before any significant leaching took place. Nevertheless, the ratios of Table 1 are probably underestimated, especially in the case of $Fe(bpy)_3^{2+}$, where leaching was particularly rapid.

Because of leaching, precise values of D_{app}, the apparent diffusion coefficient of the cations in the films, could not be obtained from the slopes of i_p vs. $v^{1/2}$. The film concentrations of electroactive adsorbed cations decreased during the time it took to record the cyclic voltammograms at different scan rates. This caused curvature in i_p vs. $v^{1/2}$ plots, giving smaller slopes and resulting in significantly underestimated values of D_{app}. Only a rather crude estimate of D_{app} could be made. Still, the D_{app} obtained from the slopes of i_{pc} vs. $v^{1/2}$, 10^{-11} through 10^{-12} cm^2/s, were of the same order of magnitude as published values for these cations in CME [1,5].

Only the cathodic currents were used in the estimation of D_{app}, because at low scan rates, the peak current ratio, i_{pa}/i_{pc}, was found to be larger than unity for adsorbed $Ru(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$. This effect was most obvious for adsorbed $Fe(bpy)_3^{2+}$. At 1 mV/s, the peak current ratio for this cation was found to be 3.7 for the first, 1.7 for the second, and 1.3 for the third scans. The two first scans are shown in Fig. 1. A small decrease in the cathodic current could be attributed to leaching of the adsorbed cation, but this explanation could not cover the much larger decrease in the anodic current. We attributed this to electron transfer from atoms in the clay lattice. Since this was seen for $Fe(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$, but not for $Os(bpy)_3^{2+}$, the source of electrons was probably structural Fe(II), as proposed in previous studies with CME [3,5]. In subsequent scans, i_{pa}/i_{pc} returned to unity when all of the structural iron was oxidized.

In the case of viologen-soaked electrodes (MV^{2+} and PVS), irreversible waves were obtained, especially with PVS. As shown in Fig. 2, a completely irreversible cathodic wave was seen in the first scan. It decreased rapidly in intensity and all but disappeared after 10 scans. This was attributed to reduction of all of the adsorbed PVS, rather than leaching, since the wave reappeared if the electrode was exposed to air for 15 min. Note also that c_t was very small for this uncharged species. Figure 3
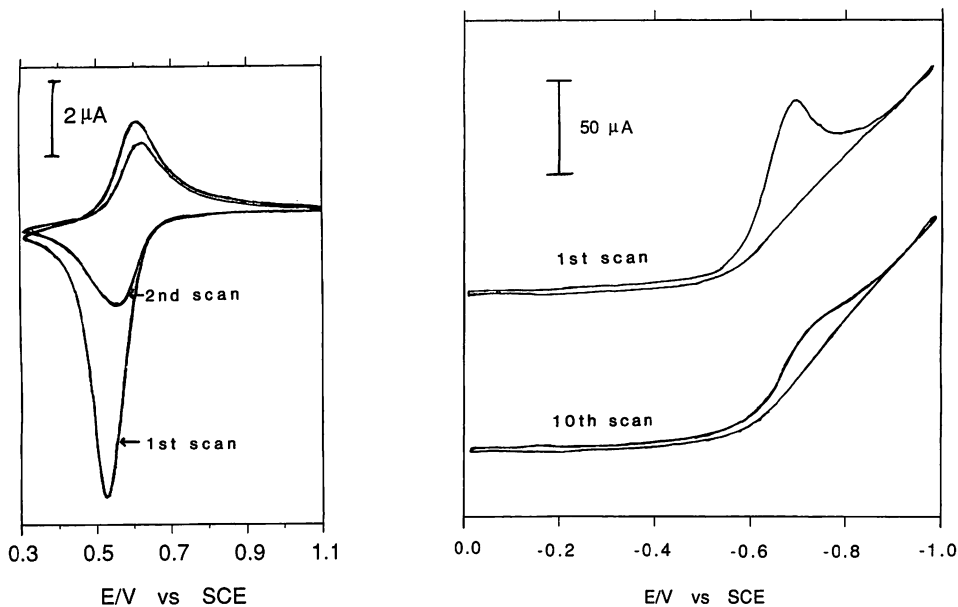
Fig. 1. Cyclic voltammogram of a spin-coated montmorillonite electrode (200 nm thick) soaked 24 h in 0.1 mM Fe(bpy)$_3^{2+}$, at 1 mV/s in phosphate buffer, pH 7.

Fig. 2. Cyclic voltammogram of a spin-coated montmorillonite electrode (200 nm thick) soaked 24 h in 5.0×10^{-5} M propyl viologen sulfonate (PVS), at 50 mV/s in phosphate buffer, pH 7.

shows the wave of a MV^{2+}-soaked electrode at 50 mV/s. More reversible waves could be obtained at faster scan rates. The value of c^*/c_t obtained from the cathodic current at 5 mV/s was 3%. This is only an approximation, since the reduction peak was far from symmetrical, a pre-condition for the evaluation of c^* from i_{pc}. As discussed in an earlier study [6], the irreversibility of viologen species in CME can be attributed to reorganization of the reduced viologen, e.g., dimer formation, to lead to a form in which electron transfer to the substrate is hindered. As noted above, chemical oxidation by air or a dissolved oxidant occurs readily.

Evaporated electrodes

Table 2 contains the values of c^*, c_t and the ratio c^*/c_t for electrodes prepared by evaporation of montmorillonite suspensions on indium–tin oxide supports. They were calculated in the same manner as those of Table 1, except for a complication in the evaluation of c_t. Profilometry showed that part of the clay was washed away from the films during the soaking, so that the thicknesses of the films were smaller after soaking than before. Some solid material was also seen at the bottom of the flasks after the electrodes were removed from the soaking solutions. Therefore, different film volumes were used in the calculation of c_t and c^*, i.e., those given by the initial and final thicknesses, respectively.
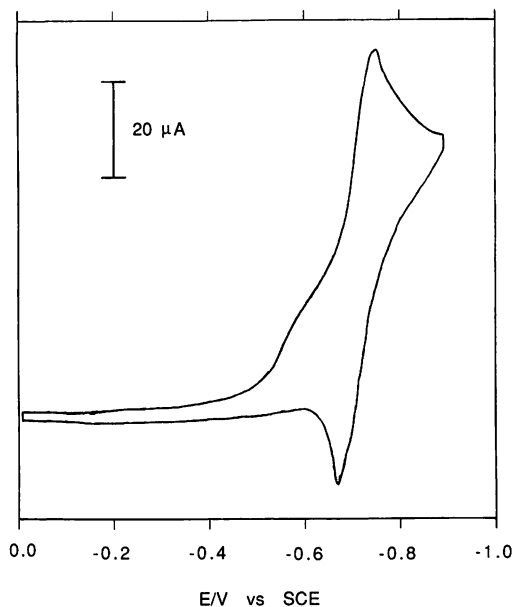
Fig. 3. Cyclic voltammogram of a spin-coated montmorillonite electrode (200 nm thick) soaked 24 h in 5.0×10^{-5} M methyl viologen (MV^{2+}), at 50 mV/s in phosphate buffer, pH 7.

Comparison of Tables 1 and 2 shows much less variation in the values of c_t for the evaporated electrodes than for the spin-coated ones. Also, the values of c^* were smaller, producing a ratio c^*/c_t less than one-half of that found for the spin-coated electrodes. A decrease in currents with time due to leaching was also seen for these electrodes. Once again, it was most rapid for the film containing $Fe(bpy)_3^{2+}$. For this cation, the peak current at 50 mV/s decreased from 26 to 19 μA after only 10 scans. In the same period there was little change in the peak currents of the films containing either $Ru(bpy)_3^{2+}$ or $Os(bpy)_3^{2+}$. For the $Fe(bpy)_3^{2+}$, leaching was probably already complete prior to measurement of the current at 1 mV/s used for the

TABLE 2

Fraction of electroactive cations for electrodes prepared by evaporation of montmorillonite (STx-1) suspensions [a]

Cation adsorbed	10^8 Amount/ mol [b]	$10^4 c_t/$ mol cm^{-3}	$10^5 c^*/$ mol cm^{-3} [c]	c^*/c_t
$Ru(bpy)_3^{2+}$	13.1	6.6	2.10	0.032
$Os(bpy)_3^{2+}$	18.1	9.0	2.20	0.025
$Fe(bpy)_3^{2+}$	15.2	7.6	0.85	0.008

[a] All electrodes soaked 24 h in 0.1 mM solution of the cation.
[b] From the decrease in concentrations of the soaking solutions.
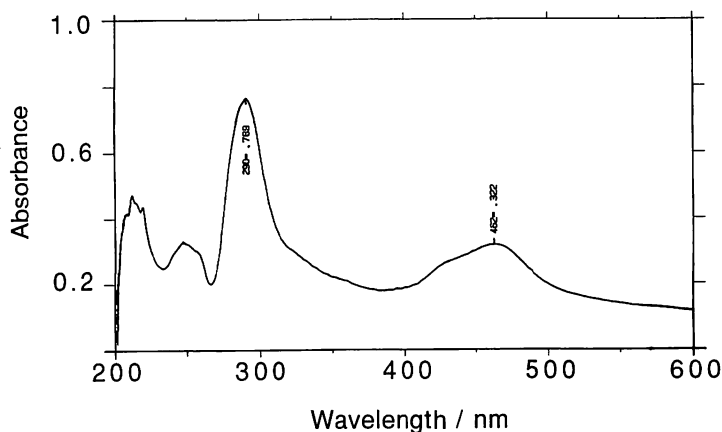[c] From the currents at 1 mV/s, in phosphate buffer, pH 7.

Fig. 4. Absorbance spectrum of a suspension of reduced-charge montmorillonite (Li-250), 0.5 g/l, containing 7.5×10^{-5} mol/g of Ru(bpy)$_3^{2+}$.

evaluation of $c*$, while corresponding values for Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ were obtained prior to any significant leaching. Finally, electron transfer from lattice Fe(II) was also seen here at low scan rates. In the first scan at 1 mV/s, i_{pa} was significantly larger than i_{pc} for the Ru(bpy)$_3^{2+}$, but not for the Os(bpy)$_3^{2+}$ soaked electrodes.

Reduced-charge electrodes

Spectroscopic measurements on a solution of Ru(bpy)$_3^{2+}$ before and after it was stirred overnight in a suspension of reduced-charge montmorillonite (Li-250) showed that the clay adsorbed 7.5×10^{-5} mol/g of this cation, only about 9% of what was adsorbed by the original STx-1 montmorillonite. The absorption spectrum of a suspension of this clay, saturated with Ru(bpy)$_3^{2+}$ (shown in Fig. 4) is characteristic of adsorption of this cation on the external surfaces of clay, as opposed to intercalation [34]. It is more reminiscent of the spectrum seen in kaolin, a non-swell-

TABLE 3

Fraction of electroactive cation for electrodes prepared by evaporation of reduced-charge clay (Li-250) suspensions. The thickness of all films was 5.5 μm; all electrodes were soaked in 0.1 mM solutions of the cation for 24 h

Cation adsorbed	10^8 Amount [a]/ mol	$10^5 c_t$/ mol cm^{-3}	$10^6 c*$ [b]/ mol cm^{-3}	$c*/c_t$
Ru(bpy)$_3^{2+}$	5.3	8.0	4.80	0.060
Os(bpy)$_3^{2+}$	5.0	7.6	4.40	0.057
Fe(bpy)$_3^{2+}$	2.4	3.6	0.80	0.022

[a] From the decrease in concentrations of the soaking solutions.
[b] From the currents at 1 mV/s, in phosphate buffer, pH 7.

ing clay, than in natural montmorillonite [35]. This result is consistent with our expectations about the behavior of charge-reduced clays. Heating of lithium-exchanged montmorillonite causes migration of the lithium cations to the vacant octahedral sites in the clay lattice, reducing the CEC to less than 10% of the original value and destroying the ability of the clay to swell in water [29,36].

A set of electrodes was prepared by allowing 0.2 ml of a 3 g/l suspension of this clay to evaporate on pieces of ITO-coated glass. The thickness of these films given by profilometry was 5.5 μm. Table 3 contains the values of c_t, c^*, and c^*/c_t obtained for these electrodes after soaking in solutions of the metal cation–bipyridyl complexes. As expected, since the CEC of the reduced-charge clay was only about 9% of that of the original clay, the values of c_t were at least an order-of-magnitude smaller than those of Tables 1 and 2. The values of c^* were also an order-of-magnitude smaller than those found for the natural clay, resulting in very similar ratios of c^*/c_t for the two types of clay. This was surprising, since the low value of c^*/c_t found for the natural clay has been attributed to the inactivity of intercalated cations [13]. These constitute the majority of adsorbed species in natural clays [37], but are completely absent in the reduced-charge clay [29,36].

Leaching of the adsorbed cation by the electrolyte was more rapid for these films, reflecting the weaker interaction of cations with reduced-charge clay. Again, it was most pronounced for the $Fe(bpy)_3^{2+}$ electrode. Evidence of transfer of electrons from lattice iron was again seen in the anomalous ratio of i_{pa}/i_{pc} at low scan rates for the ruthenium and iron bipyridyl cations, but not for the osmium cation.

$MV^{2+}/STx-1$ electrodes

King et al. [13] studied electrodes prepared by pre-exchanging the clay suspension with the ions of interest before casting a film on the substrate. They found essentially no electroactivity in such films. In Fig. 5, the cyclic voltammograms of an electrode covered by a film of clay pre-exchanged with MV^{2+} ($MV^{2+}/STx-1$) is compared with that of an $Na^+/STx-1$ film and that of a bare ITO electrode. A small cathodic peak at -0.70 V vs. SCE for the $MV^{2+}/STx-1$ electrode with no back wave was seen. Thus, at least a small portion of the MV^{2+} contained in the pre-exchanged clay could be reduced. This peak disappeared after a few scans, presumably when all the electroactive MV^{2+} was reduced. Note that the blue color characteristic of the reduced cation was not seen, because the concentration of cations that could be reduced was too small to change the color of the film.

In Fig. 6, the cyclic voltammograms of a bare ITO electrode, an electrode covered by a film of $Na^+/STx-1$, and an electrode covered by a film of $MV^{2+}/STx-1$, all immersed in 2 mM MV^{2+}, are compared. A small enhancement in current was seen in going from the bare to the $Na^+/STx-1$ electrode. However, the cyclic voltammogram of the electrode covered with a film of $MV^{2+}/STx-1$ was very similar to that of the bare electrode. Figure 7 contains a similar comparison of the voltammograms of the three different electrodes in 2 mM PVS. Here, the enhancement of the current was clearer for the $Na^+/STx-1$ electrode. However, once again, the $MV^{2+}/STx-1$ electrode showed a cyclic voltammogram very similar to that of

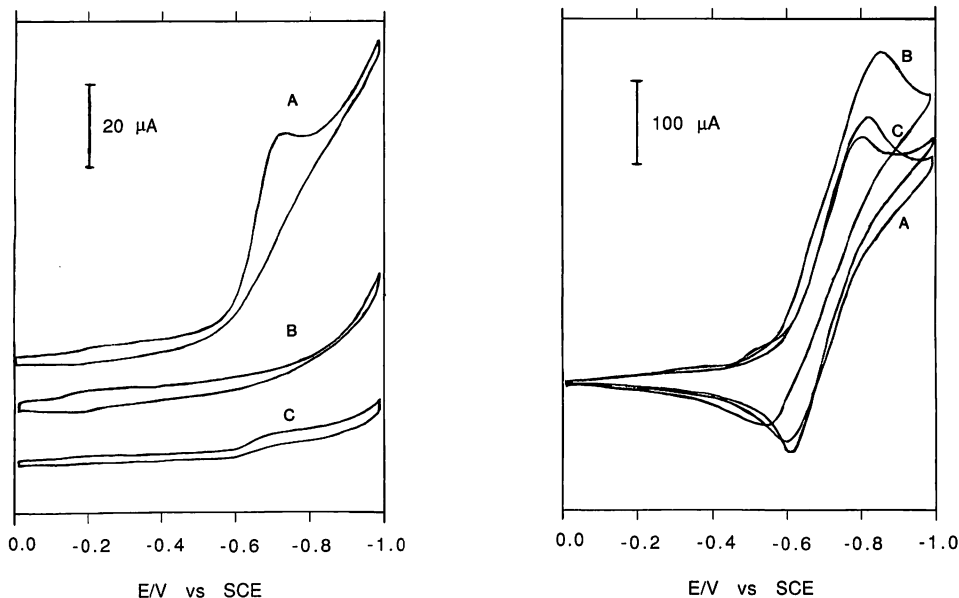Fig. 5. Cyclic voltammograms of electrodes modified with clay films 2.6 μm thick, 1 cm^2 area, at 50 mV/s in phosphate buffer, pH 7. (A) MV^{2+}/STx-1 film; (B) Na$^+$/STx-1 film; (C) bare indium–tin oxide electrode.

Fig. 6. Cyclic voltammograms of electrodes modified with clay films 2.6 μm thick, 1 cm^2 area, immersed in 2 mM MV^{2+} in phosphate buffer, pH 7 at 50 mV/s. (A) MV^{2+}/STx-1 film; (B) Na$^+$/STx-1 film; (C) bare indium–tin oxide electrode.

the bare electrode. No evidence of mediated electron transport between solution PVS and the electrode surface by adsorbed MV^{2+} was seen. The ratio i_{pc}/i_{pa} for PVS obtained for the MV^{2+}/STx-1 electrode was very similar to that of the bare electrode and was actually smaller than for the Na$^+$/STx-1 electrode. Finally, the reductions of the viologens were only partially irreversible. In all cases, the values of i_{pc}/i_{pa} were larger than 1, approaching values of 2 in some cases. The partial reversibility was demonstrated further by the deep blue color appearing in the films during the negative sweep, which is characteristic of the reduced cation. Note that when clay-adsorbed MV$^{\cdot+}$ accumulated, as opposed to solution MV$^{\cdot+}$, the films took on a purple color, indicative of the formation of the dimeric form (MV)$_2^{2+}$ [6].

Chronocoulometry

To obtain more precise values of D_{app} (the apparent diffusion coefficient of Ru(bpy)$_3^{2+}$ in the two types of clay films) chronocoulometric measurements were made. The results are shown in Table 4. To avoid the problem of leaching of the adsorbed cation from the films, the electrodes were equilibrated 3 h in the electrolyte prior to the measurements. Therefore, the values of c_t at the time of the
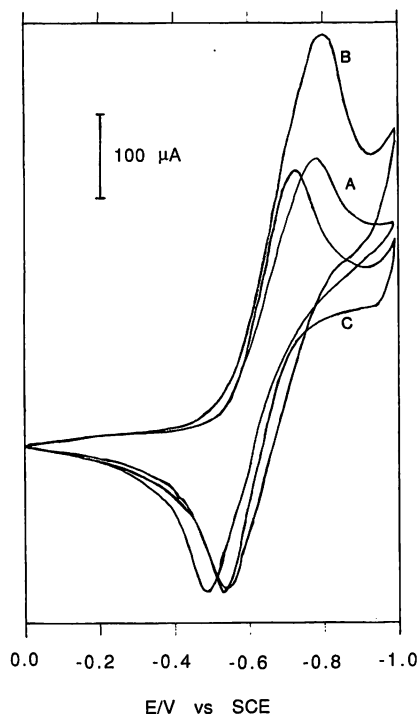
Fig. 7. Cyclic voltammograms of electrodes modified with clay films 2.6 μm thick, 1 cm^2 area, immersed in 2 mM PVS in phosphate buffer, pH 7 at 50 mV/s. (A) MV^{2+}/STx-1 film; (B) Na$^+$/STx-1 film; (C) bare indium–tin oxide electrode.

measurement were not known. The values of c^* obtained from the cathodic peak current at low scan rates (2 mV/s) after this 3 h period were those for the films after leaching was complete. The value of D_{app} for the reduced-charge clay was found to be more than two orders of magnitude larger than that for the usual clay. This

TABLE 4

Apparent diffusion coefficient of Ru(bpy)$_3^{2+}$ determined by chronocoulometry in charged-reduced and untreated clay films. The reduced-charged film (Li-250) was 700 nm thick, the STx-1 film, 250 nm thick. Measurements were taken in 0.1 M Na$_2$SO$_4$ electrolyte

Clay	$10^6\,c^*/$ mol cm^{-3}	10^5 Slope [a]/ C s$^{-1/2}$	$10^{10}\,D_{app}/$ cm^2 s^{-1}
Li-250	2.3 [b]	2.2	77.0
STx-1	32.00 [c]	1.7	0.24

[a] Slope of the charge vs. $t^{1/2}$ plots.

[b] From i_{pc} at 2 mV/s.

[c] From i_{pc} at 1 mV/s.

explains why at higher scan rates, similar currents were found for both types of clay, despite the much lower values of c^* found for the reduced-charge films. Note that the value of D_{app} calculated from the slope of i_{pc} vs. $v^{1/2}$ for the first electrode of Table 1 was 1.2×10^{-11} cm^2/s, less than half of what was found by chronocoulometry. This is caused by leaching.

DISCUSSION

As mentioned in the Introduction, there are many possible adsorption sites in clay films [26]. First, there are intercalation sites, where the cations are adsorbed between two clay layers. Cations can also be adsorbed on the clay external surfaces or at the edges of clay sheets. Further, metal–bipyridyl cations can also be adsorbed as ion pairs, with their counter ions in excess of the clay CEC [13,38]. Finally, imperfections in the stacking of the clay layers result in holes, pores, and other defects in the films where the adsorbed species could be found.

It is generally accepted that intercalated cations are not electroactive. This was first proposed as an explanation for the low values of the ratio c^*/c_t found in CME [1–13]. Intercalated cations account for the majority of the electrostatically bound species. For example, X-ray diffraction studies on oriented clay films show that the interlayer charges account for 80% of the total CEC in montmorillonite [37]. Further support for this comes from studies of films prepared from clays pre-exchanged with metal–bipyridyl cations, which show no activity when only intercalated cations were present [13]. Simple filling of the voids in the swollen clay films by small amounts of the soaking solution cannot account for all of the observed electroactivity. The results in Tables 1 to 3 show that the values of c^* obtained were much larger than those of the soaking solutions (0.1 mM). Even the lowest c^*, that of Fe(bpy)$_3^{2+}$ in reduced-charge clay (Table 3), was 8 times larger than the soaking solution concentration. For the natural (untreated) clays, c^* was several orders of magnitude larger than the soaking solution concentrations. Increased local concentration in the films was even found for the uncharged species PVS (see Table 1). Therefore, if one eliminates space filling of the voids in the films by the soaking solution and intercalated cations, two candidates for the electroactive species remain: those adsorbed by cation exchange on the external surfaces, edges, or in pores, and those adsorbed as ion pairs with their counter ions. It is exclusively the latter that were proposed to be the active ones by King et al. [13].

However, on first inspection the results of Tables 1 and 3 would appear to conflict with the accepted idea of the total inactivity of intercalated cations. As expected, the absorption spectrum shown in Fig. 4 indicates that in the reduced-charge clay, there were no intercalated cations. Reduced-charge clay modified electrodes might, therefore, be expected to have much larger values of c^*/c_t than those modified with the natural montmorillonite. This was not the case. This would seem to suggest that at least some fraction of the intercalated cations are electroactive in the natural clays. This is supported by the small peak found in Fig. 5 for a film of a clay pre-exchanged with MV^{2+}. This film was presumed to contain only

intercalated and surface-adsorbed cations. Moreover, in Table 4, the apparent diffusion coefficient was much larger for the reduced-charge clay. The lower mobility of the electroactive species in the natural clay could be attributed to the smaller contribution to the current from the much more strongly bound intercalated cations.

A possible explanation for this disparity is the effect of leaching. The $c*$ of the reduced-charge clays might be more significantly underestimated than those of the natural clays because of the more rapid leaching in these films. However, it is unlikely that this could result in a difference of a factor of 10. Table 4 also shows that the values of $c*$ for $Ru(bpy)_3^{2+}$ in the two types of clay still differed by a factor of 10, even after leaching could be considered complete. Moreover, the initial currents at 50 mV/s for both types of clays were of the same order of magnitude. If we accept the much larger D_{app} of the reduced-charge clay, $c*$, prior to leaching, must have been significantly larger in the natural clays.

Furthermore, this disparity may not exist at all. One of the important points made by King et al. [13] is that of all of the electrostatically bound cations, those adsorbed on the external surface as well as intercalated ones, were electrochemically inactive. Only the adsorbed "ion pairs" contributed to the currents [13]. Our result can be interpreted as evidence supporting the inactivity of cations adsorbed by ion exchange on the external surface. Despite the fact that in reduced-charge clay most of the cations belong to this group, Table 3 shows that only a very small fraction of the adsorbate was active. Surface adsorbed cations can therefore be eliminated from consideration for the same reason intercalated cations were eliminated in the natural clays. The small $c*/c_t$ implies that the electroactive species do not constitute the majority of the adsorbate. The electroactivity must therefore come from other adsorption sites, i.e., the adsorbed ion pairs. They might be expected to be found in lower concentration in the reduced-charge films. This may also explain the higher D_{app}, since adsorbed ion pairs might be expected to have a higher mobility in the reduced-charge clays than in the more highly charged natural clays.

One final point on this subject. In both their thickness and method of preparation, the reduced-charge films of Table 3 were more similar to the thick evaporated films of Table 2 than to the thin spin-coated films of Table 1. If we compare Tables 3 and 2, the reduced-charge films did indeed have somewhat larger $c*/c_t$ fractions, although it was nowhere near the tenfold increase expected if all nonintercalated cations would have been active. The differences of the results in Tables 1 and 2 suggest the importance of defects in the films. The stacking in the thicker films prepared by slow evaporation (Table 2) is expected to be more ordered than that of the spin-coated films (Table 1). Hence, the larger electroactive fractions of the spin-coated films point to the importance of the number of defects. With more defects, the probability that clay-bound cations have access to the substrate surface is increased. Thus the occurrence of defects in the films may have a greater effect on the $c*/c_t$ ratios than the specific adsorption sites. In other words, small fractions of all types of adsorbed cations may be electroactive, provided that a defect in their vicinity provides access to the electrode surface.

No evidence of mediated electron transport between solution PVS and the electrode surface by adsorbed MV^{2+} was seen (Figs. 6 and 7). However, Fig. 1 clearly shows electron transfer from species in the clay lattice to adsorbed $Fe(bpy)_3^{2+}$. We believe the source of the electrons is Fe(II) in the clay lattice. Montmorillonite has been reported to reduce chemically oxidized $Ru(bpy)_3^{3+}$ [3]. Electron transfer from the lattice has previously been proposed to account for the anomalously larger first anodic wave of adsorbed $Ru(bpy)_3^{2+}$ [5]. $Ru(NH_3)_6^{2+}$ was found to mediate electron transfer between adsorbed $Ru(bpy)_3^{2+}$ and an unknown site in the clay lattice, assumed to be Fe(II) [5,11]. The wave sometimes seen near 0.6 V vs. SCE in CME has been attributed to structural iron. Here, we see that at low scan rates, i_{pa}/i_{pc} ratios close to 4 were found for adsorbed $Fe(bpy)_3^{2+}$. Electron transfer was slow but finite. This may provide an alternative pathway, via lattice species, for the electrons from clay-adsorbed species to the substrate.

CONCLUSIONS

The small values of the electroactive fraction $c*/c_t$ found in reduced-charge montmorillonite suggest that most of the cations adsorbed on the clay external surface are inactive, as are the intercalated cations. In agreement with a previous report [13], this suggests that mainly adsorbed ion pairs are electroactive. However, the importance of the method of preparation and thickness of the films suggests that the presence of defects in the vicinity of the adsorbate may be more important than the specific adsorption site in determining whether such a species will be electroactive. Electron transfer from species in the clay lattice and to the adsorbate may also provide an alternative pathway for the electron through the film to the substrate.

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