MASS CHANGES DURING ADSORPTION OF METAL BIPYRIDYL COMPLEXES BY CLAY FILMS MONITORED WITH AN ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE

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Abstract—The adsorption of $[M(bpy)_3]^{2+}$ ions (M = Ru or Os) by clay films immersed in pure water and in electrolyte solutions was investigated by electrochemical quartz crystal microbalance (EQCM), UV-visible spectroscopy and powder X-ray diffraction. In water, the adsorption of the cations resulted in a decrease in the mass of the films. This decrease in mass is attributed to the expulsion of some 50 water molecules from the clay interlayer spaces for each cation adsorbed. Water is lost to make room for the large metal complex cations in the interlayer spaces, and because of decreases in the volume of the interlayer spaces during adsorption of the cations. In 0.05 M NaCl or 0.05 M Na_2SO_4, UV-visible measurements show a rapid initial adsorption of the cations by ion exchange, followed by a slower additional adsorption of the cations above the clay's CEC, presumably as ion pairs with the electrolyte counter ions. The EQCM show initial reductions in the mass of the films that were two to three times larger in pure water. These initial mass decreases were followed by smaller mass 're-increases' at longer times that were not observed in water. The larger initial mass losses are attributed to the loss of more water from the clay interlayer spaces. In 0.5 M Na_2SO_4 or 1.0 M NaCl, adsorption of the cations never exceeded the clay's CEC. The initial decreases in mass upon addition of the cations all but disappeared, leaving only the smaller positive mass changes at longer times.

Key Words—Clay-modified Electrodes, Clay Films, EQCM, Ion Exchange, Microgravimetry, UV-visible Spectroscopy.

INTRODUCTION

In an electrochemical quartz crystal microbalance (EQCM) system, the working electrode of an electrochemical cell is deposited on a piezoelectric quartz crystal, one side of which is in contact with the electrolyte. By following the changes in the resonance frequency of the quartz crystal, small mass changes (typically of the order of 10^{-9} to 10^{-4} g/cm^2) occurring at the surface of the electrode can be monitored *in situ* during electrochemical experiments (Buttry and Ward, 1992; Buttry, 1991; Oyama and Ohsaka, 1995).

The EQCM measurements have proven very useful in the study of the complex mass transfer phenomena that accompany electron transfer in chemically modified electrodes (Oyama and Ohsaka, 1995; Hillman, 1997). The oxidation or reduction of electroactive centers in films must be accompanied by the motion of charge-compensating counter and/or co-ions in order to maintain electrical neutrality. Charge transfer in films is also often accompanied by the motion of solvent molecules in or out of the films. For example, EQCM measurements on electrodes modified with films of poly(vinylferrocene) show a mass increase upon oxidation. This has been attributed to migration of electrolyte counter anions into the films to compensate for the positive charge created by oxidation of the ferrocene groups (Varineau and Buttry, 1987; Jureviciute *et al.*, 2000),

along with an inflow of water molecules (Hillman *et al.*, 1989). In contrast, in Prussian Blue films, charge neutrality upon oxidation is maintained by the desorption of cations, accompanied by a counter flow of water to fill the voids left in the films by expulsion of the cations (Lasky and Buttry, 1988).

There are few reports on the use of EQCM to study mass changes in clay films. Measurements by EQCM have been used to monitor the electrodeposition of clays on electrode surfaces (Graham *et al.*, 1995; Shirtcliffe, 1999). Hotta *et al.* (1997a, 1997b) used an EQCM to investigate the self-assembly of clay films on gold surfaces. The same group showed that charge neutrality during the electrochemical oxidation of $[Ru(bpy)_3]^{2+}$ in clay-modified electrodes (CMEs) was maintained by leaching of the adsorbed complex out of the clay films (Yao *et al.*, 1995, 1998a, 1998b).

We report here a study of the adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by clay films monitored by EQCM, UV-visible spectroscopy and powder X-ray diffraction (XRD). In water, adsorption of the metal complexes was found to result in decreases in the mass of the films. In 0.05 M Na_2SO_4 or 0.05 M NaCl these reductions in mass were much larger, and they were followed by smaller mass increases at longer times that were not observed in water.

EXPERIMENTAL

The clay used, STx-1 (Gonzales County, Texas) was obtained from the Source Clay Minerals Repository of

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31

The Clay Minerals Society (Purdue University, West Lafayette, IN). It was converted to the Na-form and the <0.2 μm size fraction was separated by following the methods described by Tanner and Jackson (1947) and Jackson *et al.* (1949). [Os(bpy)$_3$]Cl$_2$ was prepared following the procedure outlined by Gaudiello *et al.* (1984). All other chemicals were obtained from Aldrich (Milwaukee, WI) and used without purification.

All the clay films were prepared by the so-called 'solvent evaporation method' in which small volumes of clay suspensions were spread onto the surface of substrates and the water allowed to evaporate overnight in air. 10 g/L suspensions of the clays were prepared by dispersing the STx-1 powder in distilled water. A few drops of 2 M H$_2$SO$_4$ were added to lower the pH to 2, and the suspensions were left standing for 10 days, during which time the pH gradually increased to a final value above 4.

The films used for the EQCM measurements were deposited onto gold-coated 10 MHz AT cut quartz crystals (Elchema Potsdam, New York). The area of the gold electrodes was 0.196 cm^2. An acid-treated 10 g/L clay suspension was diluted to 1.0 g/L. Aliquots of this suspension ranging from 4.0 to 13.5 μL were then spread on the surface of the quartz electrodes and allowed to dry. This gave clay films weighing between 4.0 and 13.5 μg. The EQCM measurements were made using an Elchema EQCN-600 system in a Model EQCN-602 Faraday Cage.

The films used for the UV-visible measurements were prepared by spreading 9.45 μL of an acid-treated 10 g/L clay suspension on pieces of tin-doped indium oxide-coated glass (ITO, Delta Technology, Stillwater MN) and allowing the water to evaporate. The area of the film was 1.2 cm^2. The air-dried films were immersed in pure water, or in one of the electrolyte solutions, and left to equilibrate for several hours. The films were then transferred to UV-visible cells containing 1.5 mL of 0.1 mM solutions of the cations ([Os(bpy)$_3$]$^{2+}$ or [Ru(bpy)$_3$]$^{2+}$) dissolved in the same electrolyte solution as the one in which the films had been equilibrated. Note that the films were carefully placed in the UV-visible cell in such a way that they were not in the path of light. The absorbance of the solutions was monitored as a function of time at the maxima of the cations MLCT bands (ε = 12,000 M^{-1}cm^{-1} at 480 nm for [Os(bpy)$_3$]$^{2+}$ (Creutz *et al.*, 1980), and ε = 14,600 M^{-1}cm^{-1} at 452 nm [Ru(bpy)$_3$]$^{2+}$ (Kalyanasundaram, 1982)). The amounts of the cations adsorbed by the films at different time were calculated from decreases of the concentration of the soaking solutions. UV-visible measurements were taken with a Hewlett-Packard model 8452A diode array spectrophotometer.

The films used for the XRD measurements were 4 cm^2 in size. They were prepared by spreading 40 μL of 10 g/L acid-treated clay suspensions on glass slides and allowing the water to evaporate. The XRD patterns were
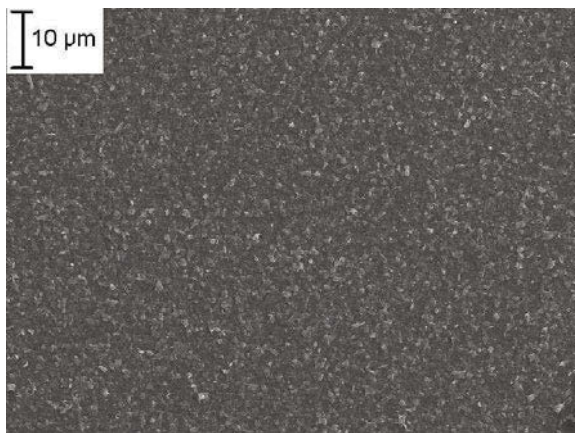

Figure 1. SEM image of the surface of a clay film. The film was prepared by spreading 13.5 μL of an acid-treated 1.0 g/L clay suspension on a 0.2 cm^2 glass substrate and allowing the water to evaporate. The film was sputtered with gold prior to the measurement.

obtained using a Philips X-ray diffractometer equipped with a graphite monochromator and a vertical goniometer, using CuKα radiation at 40 kV and 20 mA and a scanning rate of 0.04°2θ s^{-1}. The scanning electron microscope (SEM) images of some of the films were taken on a JEOL JSM-6400 Scanning Electron Microscope.

RESULTS

EQCM results

The quality of the clay films was found to be very important in getting consistent EQCM results. Initially, the films were prepared by evaporation of neutral suspensions of the clay (pH ≈ 6). However, SEM examination showed that these films were not uniform in thickness. They were much thicker near the edges than in the center. This could also be seen by the deeper color of the edges of the films after ion exchange with the metal bipyridyl complexes. Furthermore, films deposited from neutral clay suspensions did not adhere well to the gold electrode surfaces. They tended to peel off during the measurements.

Treatment of the clay suspensions with dilute H$_2$SO$_4$ prior to deposition was found to greatly improve the quality of the films. Figure 1 shows the SEM image of one such film*. It shows that the coating was continuous and that the clay particles were uniformly distributed on the surface of the electrode. However, it also shows that the surface was rough. In liquid media, surface rough-

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* The term clay coatings may be more appropriate. A reviewer has suggested that these may not be true clay films in the sense that they appear to consist of small clay particles rather than completely delaminated clay.

ness can be a problem in the interpretation of QCM measurements since liquid can be trapped in the surface cavities resulting in an additional mass component (Buttry and Ward, 1992). This is only a major problem however, when the surface roughness of the electrode changes during the measurements. This was not the case here. The SEM images of the surfaces of clay films after exchange with [Os(bpy)$_3$]$^{2+}$ or [Ru(bpy)$_3$]$^{2+}$ were indistinguishable from that shown in Figure 1. With no change in roughness, the contribution from any solution trapped in surface cavities would be approximately the same before and after adsorption of the cations. The QCM measurements are fairly tolerant of non-uniformity in film thicknesses as long as the roughness is randomly distributed. What is important is to have a uniform distribution of the mass at the surface of the resonator. The sensitivity of the EQCM measurements is known to be greater near the center of the quartz crystals, and to fall off toward the edges (Buttry and Ward, 1992).

Exposure to acids is known to affect the structure of clay layers. Acids attack the edge of the clay layers, dissolving some of the Al ions. The dissolved Al cations can then compete with protons for the clay interlayer exchange sites (Van Olphen, 1977). However, the acid treatment conditions used here, ~5 mM H$_2$SO$_4$ at room temperature, were much milder than typical conditions used to prepare acid-activated clays (Breen $et\ al.$, 1997). For example, in a recent report on acid-activated CMEs, the montmorillonite used was heated at 80°C in 2 M H$_2$SO$_4$ (Falaras and Lezou, 1998). Jozefaciuk and Bowanko (2002) reported that an acid concentration of

100 mM at room temperature, 20 times what was used here, had very little effect on clay layers. The XRD patterns of films taken before and after treatment with dilute H$_2$SO$_4$ showed that except for a decrease in the basal spacings from 14.7 to 12.4 Å, the layer structure of the clay was unaffected. The treated clay also retained the ability to swell in water and an extensive cation exchange capacity (CEC) of more than 70 meq/100 g, as estimated from the amount of [Ru(bpy)$_3$]$^{2+}$ adsorbed by the clay. All the measurements reported here were taken from films prepared by evaporation of clay suspensions treated with dilute sulfuric acid.

Figure 2 shows a plot of mass vs. time for a clay film recorded during the adsorption of [Os(bpy)$_3$]$^{2+}$ from pure water. The initial, large, rapid, apparent increase in mass observed upon addition of the water was due mostly to the decrease in the oscillation frequency of the quartz crystal upon its immersion in water. The smaller mass increase that continued for several minutes after immersion is attributed to swelling of the air-dried clay film. This was confirmed by XRD measurements that showed an increase in the basal spacings upon immersion in water (see Figure 5). After 2 h [Os(bpy)$_3$]$^{2+}$ was added. This resulted in a decrease in mass of almost 1.2 µg in <15 min.

The length of time for which the films were allowed to equilibrate in water prior to the addition of [Os(bpy)$_3$]$^{2+}$ had very little effect on the results. Seven films equilibrated in water for periods ranging from 1 h to 240 h were investigated. In all cases, decreases in mass of similar magnitudes were observed upon addition of [Os(bpy)$_3$]$^{2+}$. The average decrease was 1.3 ± 0.15 µg.

The results however, were greatly affected by the presence of electrolytes. For example, Figure 3 shows that in 0.05 M NaCl, the initial drop in mass observed upon addition of [Os(bpy)$_3$]$^{2+}$ was three times larger than in pure water (Table 1). Furthermore, this initial mass decrease was followed by a smaller, sharp 're-increase' in mass at longer times that was not observed in water. This 're-increase' in mass amounted to ~25% of the initial drop. Similar results were obtained for a film immersed in 0.05 M Na$_2$SO$_4$, except that the mass changes took more time. In Na$_2$SO$_4$, it took more than 1000 s after the addition [Os(bpy)$_3$]$^{2+}$ for the mass to reach a minimum, compared to <500 s in NaCl, and >3000 s for the 're-increase' in mass to become perceptible, compared to <1000 s in NaCl. This may be due to the higher concentration of Na cations in 0.05 M Na$_2$SO$_4$ than in 0.05 M NaCl.

The mass changes were also dependent on the concentration of the electrolyte used. Table 1 shows that for films immersed in more concentrated electrolytes, the size of the initial drops in mass upon addition of [Os(bpy)$_3$]$^{2+}$ was greatly reduced. In fact, in 1.0 M NaCl, no initial decrease could be discerned. The mass increases observed at long times were less affected. As a result, net overall mass increases were actually observed
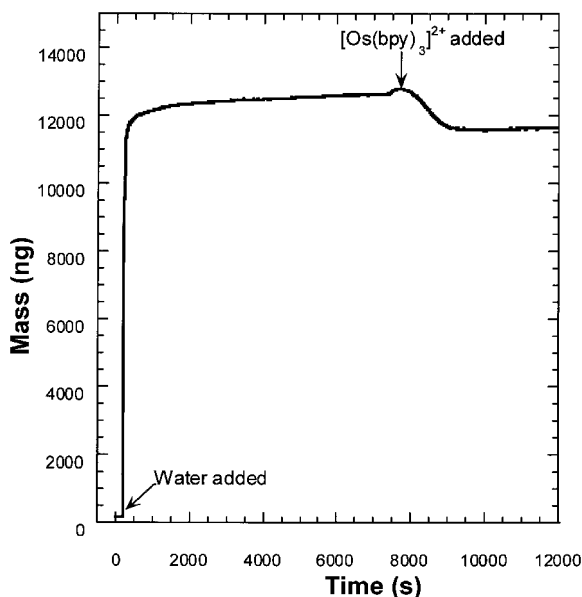

Figure 2. Mass vs. time during the adsorption of [Os(bpy)$_3$]$^{2+}$ by a 13.5 µg film of STx-1. At time 3 min, 4.50 mL of water were added, completely submerging the film. After 2 h, 0.50 mL of 1.0 mM [Os(bpy)$_3$]Cl$_2$ were added to the cell.
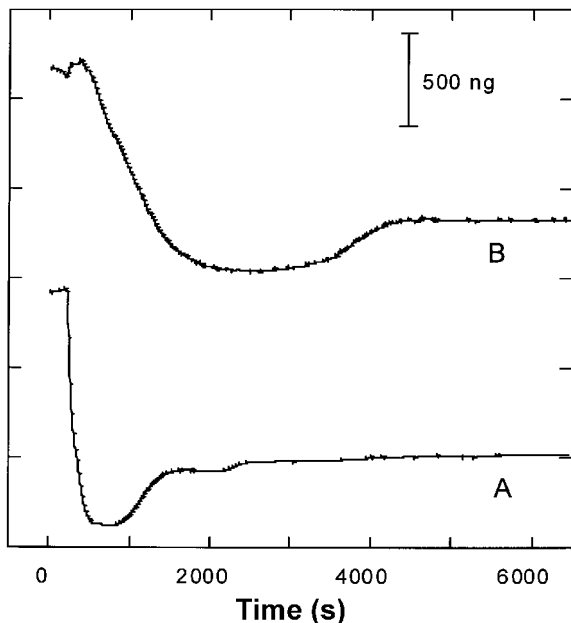
Figure 3. Mass *vs*. time during adsorption of $[Os(bpy)_3]^{2+}$ by clay films from dilute electrolyte solutions. (A) 0.05 M NaCl (B) 0.05 M Na_2SO_4. For 4.0 µg films equilibrated for 1 h in the electrolyte solutions prior to the addition of enough 1.0 mM $[Os(bpy)_3]^{2+}$ to give an initial concentration of the cation in the cell of 0.1 mM.

during the adsorption of $[Os(bpy)_3]^{2+}$ by clay films in both 1.0 M NaCl and 0.5 M Na_2SO_4.

The mass changes observed during adsorption of $[Os(bpy)_3]^{2+}$ by clay films in pure water and in the different electrolyte solutions are summarized in Table 1 which also shows the results of a comparable study of

Table 1. Mass changes during adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by clay films immersed in different electrolyte solutions monitored by EQCM.

Electrolyte	Observed mass change (mg/g of clay)	
	$[Os(bpy)_3]^{2+}$	$[Ru(bpy)_3]^{2+}$
Water	−110	−130
0.05 M NaCl		
I	−330	−270
II	+86	+29
1.0 M NaCl		
I	0	−23
II	+66	+54
0.05 M Na_2SO_4		
I	−300	−280
II	+73	+48
0.5 M Na_2SO_4		
I	−52	−80
II	+86	+60

For 4 µg clay films. I and II refer to the initial mass reductions and the 're-increases' in mass after longer periods of time, respectively, observed in the presence of the electrolytes (see Figure 3).

the adsorption of $[Ru(bpy)_3]^{2+}$ by clay films. The results are very similar. In water, the adsorption of $[Ru(bpy)_3]^{2+}$ resulted in a decrease in the mass of the film of 130 mg/ g. In dilute electrolytes, the initial decreases in mass were much larger. For example, in 0.05 M NaCl, the mass decreased by 270 mg/g. These decreases were followed by smaller 're-increases' in mass at longer times. Increasing the electrolyte concentration reduced the size of the initial mass decreases, but had very little effect on the mass increases observed at longer times.

UV-visible results

Figure 4 shows plots of the absorbance at 480 nm of solutions of $[Os(bpy)_3]^{2+}$ in water, 0.05 M NaCl and 0.05 M Na_2SO_4 following the immersion of clay films. In all three cases, immersion of the clay film caused the absorbance of the solution to decrease. In pure water, most of the decrease occurs in the first 1000 s. From the change in absorbance, the number of moles of the cation adsorbed by the film were calculated for different times after the addition of the films. Table 2 shows that in water the amount of $[Os(bpy)_3]^{2+}$ adsorbed after 1000 s was 0.32 mmol g^{-1} of clay. This corresponded to 0.64 meq/g of cations, a value near the CEC of the clay. From then on this amount increased only slowly with time to 0.39 mmol/g after 5000 s and to 0.41 mmol/g after 10,000 s.

In 0.05 M NaCl and 0.05 M Na_2SO_4, the rapid initial decreases in absorbance observed in the first 1000 s
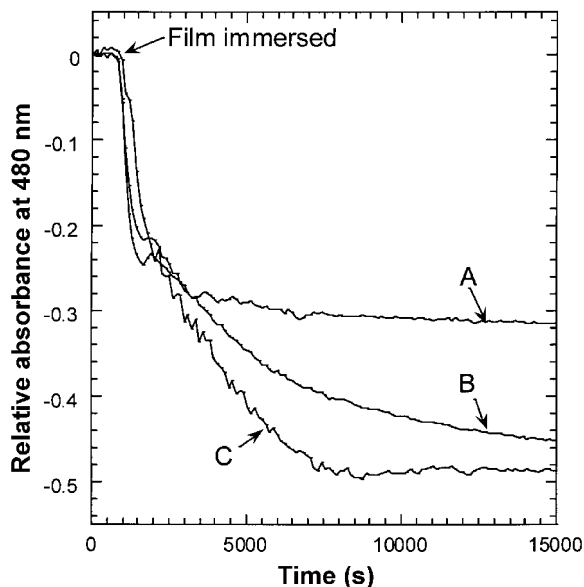

Figure 4. Decrease in absorbance at 480 nm of $[Os(bpy)_3]Cl_2$ solutions in (A) water, (B) 0.05 M NaCl and (C) 0.05 M Na_2SO_4 during adsorption of the cation by clay films. The films (1.2 cm², 94.5 µg) were allowed to equilibrate in water, 0.05 M NaCl or 0.05 M Na_2SO_4 overnight before being transferred to UV cells containing 1.50 mL of 0.1 mM solutions of $[Os(bpy)_3]^{2+}$ in water, 0.05 M NaCl or 0.05 M Na_2SO_4.

Table 2. Amounts of $[Os(bpy)_3]^{2+}$ adsorbed by clay films from the changes in absorbance of the soaking solutions.

Electrolyte	Time (s)*	ΔA**	mmol/g of clay[†]
Water	1000	−0.243	0.32
	5000	−0.297	0.39
	10000	−0.310	0.41
	15000	−0.315	0.42
0.05 M NaCl	1000	−0.218	0.29
	5000	−0.372	0.49
	10000	−0.427	0.56
	15000	−0.456	0.60
1.0 M NaCl	1000	−0.160	0.21
	5000	−0.234	0.31
	10000	−0.260	0.34
0.05 M Na$_2$SO$_4$	1000	−0.212	0.28
	5000	−0.439	0.58
	10000	−0.485	0.64
	15000	−0.488	0.65
0.5 M Na$_2$SO$_4$	1000	−0.134	0.18
	5000	−0.236	0.31
	10000	−0.260	0.34

* Time following immersion of the clay films in the $[Os(bpy)_3]^{2+}$ solutions
** Change in the adsorbance at 480 nm ($\varepsilon = 12,000$ M^{-1} cm^{-1}) of the $[Os(bpy)_3]^{2+}$ solutions following immersion of the clay films
[†] Amount of $[Os(bpy)_3]^{2+}$ adsorbed (mmol/g of clay) determined from ΔA, the volumes of the soaking solutions (1.5 mL) and the weight of the clay films (94.5 µg)

Table 3. Amounts of $[Ru(bpy)_3]^{2+}$ adsorbed by clay films from the changes in absorbance of the soaking solutions.

Electrolyte	Time (s)*	ΔA**	mmol/g of clay[†]
Water	1000	−0.186	0.20
	5000	−0.273	0.30
	10000	−0.284	0.31
	15000	−0.289	0.31
0.05 M NaCl	1000	−0.244	0.26
	5000	−0.422	0.46
	10000	−0.471	0.51
	15000	−0.485	0.53
1.0 M NaCl	1000	−0.175	0.19
	5000	−0.249	0.27
	10000	−0.261	0.28
0.05 M Na$_2$SO$_4$	1000	−0.238	0.26
	5000	−0.438	0.48
	10000	−0.447	0.49
	15000	−0.470	0.51
0.5 M Na$_2$SO$_4$	1000	−0.175	0.19
	5000	−0.286	0.31
	10000	−0.310	0.34

* Time following immersion of the clay films in the $[Ru(bpy)_3]^{2+}$ solutions
** Change in the adsorbance at 452 nm ($\varepsilon = 14,600$ M^{-1} cm^{-1}) of the $[Ru(bpy)_3]^{2+}$ solutions following immersion of the clay films
[†] Amount of $[Ru(bpy)_3]^{2+}$ adsorbed (mmol/g of clay) determined from ΔA, the volumes of the soaking solutions (1.5 mL) and the weight of the clay films (94.5 µg)

were followed by slower more gradual decreases that continued for several hours after immersion of the films. In 0.05 M Na$_2$SO$_4$ for example, the total amount of cation adsorbed after 10,000 s was 0.64 mmol/g (Table 2). This corresponded to 1.3 meq/g, a value well above the clay's CEC. This additional adsorption of $[Os(bpy)_3]^{2+}$ at longer times must therefore occur as ion pairs presumably with electrolyte counter ions.

When higher concentrations of the electrolytes were used, the level of adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by the films was both smaller and slower (Tables 2 and 3). In 0.5 M Na$_2$SO$_4$, for example, the amount of $[Os(bpy)_3]^{2+}$ adsorbed after 10,000 s was only 0.34 mmol/g. In part, this may be due to competition with the electrolyte cations, the concentration of Na$^+$ in the concentrate electrolytes being 1.0 M compared to only 0.1 mM for the metal bipyridyl cations.

XRD results

Figure 5 shows the XRD patterns of several clay films taken in conditions corresponding to some of the key points of the mass *vs.* time plots of Figures 2 and 3. The air-dried films (curve A) gave basal spacings of 12.4 Å. Curve B is the XRD pattern of a film immersed for 1 h in water, recorded immediately after its removal from the water (water-swollen film). The *d* value increased to 18.6 Å. This was unexpected. Sodium-

montmorillonites are well known to display osmotic swelling when immersed in water (Newman, 1987). Much more extensive swelling of the clay had been expected. The limited swelling may be due to the acid treatment of the clay suspension used to cast the film. As mentioned above, acid can attack the edge of the clay layers, dissolving some of the Al ions. The dissolved ions can then compete for the clay interlayer exchange sites (Van Olphen, 1977). Despite the low concentration of acid used (5 mM) perhaps enough Al^{3+} ions were produced during the acid treatment to limit the swelling of the clay film. Support for this explanation is provided by the fact that this measurement could not be repeated with films cast from a Na-STx-1 suspension that had not been treated with dilute H$_2$SO$_4$. Any attempt to remove such films from the water to mount them on the X-ray instrument resulted in the loss of the films. In fact, simply moving the beaker containing the swollen films was enough to cause the re-dispersion of the clay.

After exchange with $[Os(bpy)_3]^{2+}$, the *d* value decreased to 17.5 Å (curve C). This is in agreement with previous reports for smectites intercalated with metal trisbipyridyl cations (Villemure, 1991). Allowing this $[Os(bpy)_3]^{2+}$ exchanged film to dry overnight in air resulted in increases in the intensity of the reflections, but no changes in the *d* value.
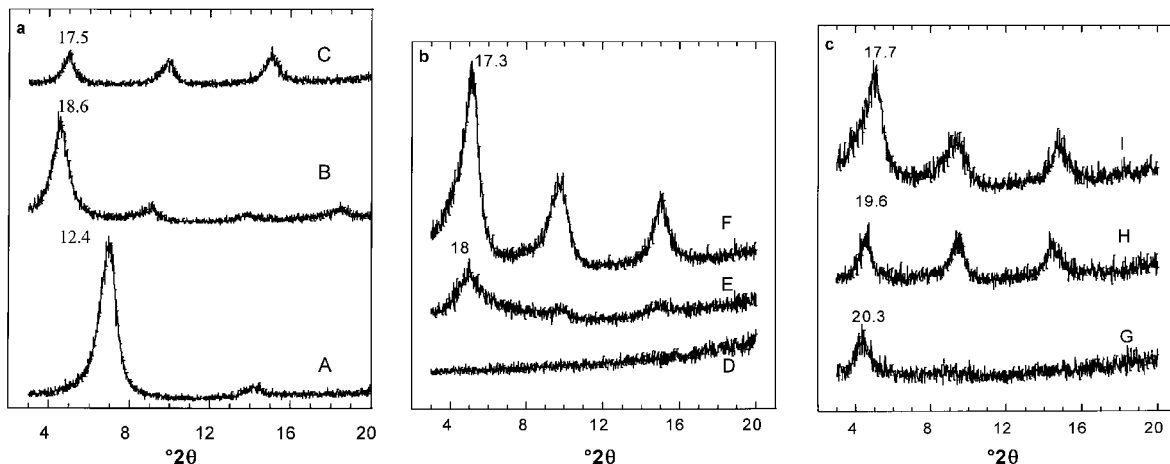
Figure 5. (a) XRD patterns of an air-dried STx-1 film (A) and of wet clay films taken immediately after their removal from solutions. (B) Film soaked for 1 h in water. (C) Film swollen for 1 h in water followed by ion exchange with 0.1 mM $[Os(bpy)_3]^{2+}$. The scans were begun within 1 min of the films being removed from solution. (b) XRD patterns of (D) a film soaked for 1 h in 0.05 M Na_2SO_4, (E) a film swollen for 1 h in 0.05 M Na_2SO_4 followed by 30 min in a mixture of 0.1 mM $[Os(bpy)_3]^{2+}$ and 0.05 M Na_2SO_4 and (F) after allowing the film exchanged with $[Os(bpy)_3]^{2+}$ to dry overnight in air. (c) XRD patterns of (G) a film soaked for 1 h in 0.5 M Na_2SO_4, (H) a film swollen for 1 h in 0.5 M Na_2SO_4 followed by 20 h in a mixture of 0.1 mM $[Os(bpy)_3]^{2+}$ and 0.5 M Na_2SO_4 and (I) after allowing the film exchanged with $[Os(bpy)_3]^{2+}$ to dry in air for 2 h. (All measurements in Å.)

Curve D (Figure 5b) shows the pattern of a clay film soaked in 0.05 M Na_2SO_4 recorded immediately after its removal from the electrolyte. No reflections were seen. This was as expected. The basal spacings of momtmorillonite flakes soaked in 0.05 M Na_2SO_4 have been reported to be more than 50 Å (Norrish, 1954). Curve E shows the pattern of a film soaked in 0.05 M Na_2SO_4 taken 30 min after the addition of $[Os(bpy)_3]^{2+}$. A broad, low-intensity reflection, giving a d value of ~18 Å was observed. The XRD pattern did not change during the period of time corresponding to the 're-increase' in mass observed by EQCM in 0.05 M Na_2SO_4 (see Figure 3). The pattern of a film recorded 90 min after the addition of $[Os(bpy)_3]^{2+}$ was identical to the pattern taken after 30 min. Allowing the film to dry in air resulted in a decrease in the basal spacings to 17.3 Å (Curve F).

Curve G (Figure 5c) shows the XRD pattern of a film recorded immediately after its removal from a 0.5 M Na_2SO_4 solution. A small d_{001} reflection, corresponding to basal spacings of ~20 Å was observed. Again, this was as expected. The swelling of clays is known to be less extensive in more concentrated electrolyte solutions. The swelling of montmorillonite in 0.5 M NaCl has been reported to be limited to 19 Å (Shang *et al.*, 1995). Surprisingly, however, the d value of this film did not decrease very much after exchange with $[Os(bpy)_3]^{2+}$. Curve H shows the XRD pattern of a film taken 20 h after the addition of $[Os(bpy)_3]^{2+}$. The d_{001} reflection decreased to only 19.6 Å, a value significantly larger than the spacings observed for the other films exchanged with $[Os(bpy)_3]^{2+}$ (curves C and F). Furthermore, the d_{002} and d_{003} reflections became more pronounced suggesting an increase in stacking order. Allowing this

film to dry in air resulted in an immediate decrease in the d value to 17.7 Å (curve I).

DISCUSSION

The EQCM measurements indicate that the mass of a clay film immersed in pure water decreased rapidly in the first few minutes following the addition of $[Os(bpy)_3]^{2+}$. The mass change amounted to -0.11 g/g of clay in the film. This decrease in mass was unexpected. In a similar study of the adsorption of $[Ru(bpy)_3]^{2+}$ by saponite, Yao *et al.* (1998a) observed a large mass increase of +0.49 g/g. Simple ion exchange of the Na cations from the clay interlayer spaces by the much heavier $[Os(bpy)_3]^{2+}$ would produce a mass increase of +0.24 g/g (equation 1)*.

$$2\ Na^+\text{-clay} + [Os(bpy)_3]^{2+}_{(aq)} \rightarrow$$
$$[Os(bpy)_3]^{2+}\text{-clay} + 2\ Na^+_{(aq)} \qquad (1)$$
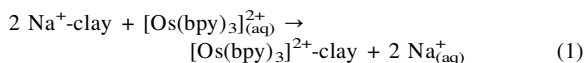
The discrepancy between the observed and expected mass changes, -0.35 g/g, can be attributed to the loss of interlayer water during adsorption of the $[Os(bpy)_3]^{2+}$ ions. The expulsion of water from thin films during ion exchange is commonly invoked to reconcile differences between observed and calculated Δm. For example, Shi and Anson (1997) reported that the ion exchange of

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* For the ion exchange of 0.78 mmol of Na^+ by 0.39 mmol $[Os(bpy)_3]^{2+}$ (see Table 2). If it is assumed that the Na^+ in the interlayer spaces was displaced by H^+ during acid treatment of the clay, the mass change expected for simple ion exchange would increase to +0.26 g/g.

protons by $[Os(bpy)_3]^{2+}$ in Nafion coatings was accompanied by the loss of 26 water molecules for each cation adsorbed. We also note that 0.35 g/g matches the estimated interlayer water content of a film swollen to 18.6 Å, even without including water present on external surfaces of the clay or in defects in the films.

The loss of 0.35 g/g of water corresponds to the loss of 19.4 mmoles of H_2O g^{-1} of clay. Table 4 shows that when this number was compared with the number of moles of $[Os(bpy)_3]^{2+}$ adsorbed by the film determined by UV-Visible spectroscopy, 0.39 mmol/g, it corresponded to the loss of 50 water molecules for each $[Os(bpy)_3]^{2+}$ cation intercalated. The loss of 50 water molecules for each cation adsorbed is realistic. The metal trisbipyridyl cations are much larger than the ions they replace. The volume of one $[Ru(bpy)_3]^{2+}$ ion, estimated from its free rotor radius has been reported to be equivalent to that of ~33 water molecules (Yao *et al.*, 1998). Alternatively, the volume of one $[Ru(bpy)_3]^{2+}$ cation, calculated from the estimated cross section of $[Ru(bpy)_3]^{2+}$ in the clay interlayer spaces, 125 Å^2 (Villemure, 1990) would be equivalent to 37 water molecules. In addition, some of the water loss can be attributed to a decrease in the volume of the clay interlayer spaces during the intercalation of the cations. The XRD measurements showed that the adsorption of $[Os(bpy)_3]^{2+}$ resulted in a decrease in the clay basal spacings from 18.6 to 17.5 Å (Figure 5a). This decrease in basal spacings requires the loss of ~2.5 mmol/g of water from the interlayer spaces, or about seven water molecules for each $[Os(bpy)_3]^{2+}$ adsorbed.

It should be noted here that as in all mass measurements by QCM, it is assumed that the Sauerbrey equation applies to the system under investigation. For changes in frequency to correlate with changes in mass, the film must be rigid or there must be no change in the viscoelastic properties of the films during the measurements (Buttry and Ward, 1992). We are confident that this was the case here. First, Yao *et al.* (1998) measured the impedance of saponite films deposited on the 5 MHz quartz crystal. They reported that the resistance of films equilibrated in 0.01 M

Table 4. Water loss during the adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by clay films immersed in solution of the cations in water.

Δm (g/g)	$[Os(bpy)_3]^{2+}$	$[Ru(bpy)_3]^{2+}$
Observed	−0.11	−0.13
Ion exchange*	0.24	0.16
Water loss**	−0.35	−0.29
$H_2O/[M(bpy)_3]^{2+\dagger}$	50	54

* Mass changes expected for the ion-exchange of Na^+ by the $[M(bpy)_3]^{2+}$ cations (see equation 1), calculated using the amounts of the two ions adsorbed by the films after 5000 s, 0.39 mmol/g and 0.30 mmol/g, for $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$, respectively (see Tables 2 and 3).
** Mass of water that must be lost to make up the difference between the calculated and observed mass changes
† Number of H_2O molecules lost for each $[M(bpy)_3]^{2+}$ adsorbed

Na_2SO_4 for 40 h or more was constant. Although most of the measurements reported here were on films equilibrated for shorter times, in the condition used, the EQCM results were independent of the equilibration time. In water for example, the reduction in mass observed upon addition of $[Os(bpy)_3]^{2+}$ was the same in a film equilibrated for 1 h as in a film equilibrated for 240 h. Second, within experimental error, the relative changes in mass observed for 13.5 μg and 4 μg clay films were the same. According to Buttry and Ward (1992), a linear response over a range of film thicknesses can be taken as evidence of the absence of changes in the viscoelastic properties of the films.

In 0.05 M NaCl or 0.05 M Na_2SO_4 there were two components to the mass changes, an initial drop in mass followed by a smaller mass 're-increase' over a longer period of time. The initial drops in mass were much larger than those seen in pure water (see Table 1). This is attributed to the loss of more water during the intercalation of the cations. Table 5 shows that the number of water molecules that must have been displaced by each cation adsorbed to account for the discrepancies between the observed mass changes and

Table 5. Water loss during the adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by clay films immersed in the dilute electrolyte solutions.

Δm (g/g)	$[Os(bpy)_3]^{2+}$		$[Ru(bpy)_3]^{2+}$	
	0.05 M NaCl	0.05 M Na_2SO_4	0.05 M NaCl	0.05 M Na_2SO_4
Observed*	−0.33	−0.3	−0.27	−0.28
Ion exchange**	0.18	0.17	0.14	0.14
Water loss†	−0.51	−0.47	−0.42	−0.42
$H_2O/[M(bpy)_3]^{2+\ddagger}$	97	93	88	90

* Initial reduction in mass observed during the adsorption of the two cations by clay films (step I in Table 1)
** Mass changes expected for the ion exchange of Na^+ by the $[M(bpy)_3]^{2+}$ cations calculated using the amounts of the two ions adsorbed by the films after 1000 s given in Tables 2 and 3
† Mass of water that must be lost to make up the difference between the calculated and observed mass changes
‡ Number of H_2O molecules lost for each $[M(bpy)_3]^{2+}$ adsorbed

Table 6. Water loss during the adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by clay films immersed in concentrated electrolyte solutions.

Δm (g/g)	$[Os(bpy)_3]^{2+}$		$[Ru(bpy)_3]^{2+}$	
	1.0 M NaCl	0.5 MNa$_2$SO$_4$	1.0 M NaCl	0.5 M Na$_2$SO$_4$
Observed*	0.066	0.034	0.031	−0.02
Ion exchange**	0.21	0.21	0.15	0.18
Water loss†	−0.14	−0.18	−0.12	0.2
$H_2O/[M(bpy)_3]^{2+\ddagger}$	23	29	24	33

* Net mass change observed during adsorption of the $[M(bpy)_3]^{2+}$ by clay films in the concentrated electrolyte solution (sum of steps I and II in Table 1)
** Mass changes expected for the ion exchange of Na^+ by the $[M(bpy)_3]^{2+}$ cations calculated using the amounts of the two ions adsorbed by the films after 10000 s (see Tables 2 and 3)
† Mass of water that must be lost to make up the difference between the calculated and observed mass changes
‡ Number of H_2O molecules lost for each $[M(bpy)_3]^{2+}$ adsorbed

the mass changes expected for adsorption of the $[M(bpy)_3]^{2+}$ cation by ion exchange ranged from 88 and 97, nearly twice as much as in pure water. This probably reflects the larger decreases in the volume of the interlayer spaces during intercalation of the cations. The XRD measurements showed that in the conditions used here, the films equilibrated in the two dilute electrolyte solutions were more swollen (see Figure 5b).

We can also speculate that the 're-increases' in mass observed at longer times in the two dilute electrolytes were due to adsorption of the $[M(bpy)_3]^{2+}$ cations as ion pairs, with the electrolyte counter ions. Figure 4 shows that in the presence of electrolytes, adsorption of the $[M(bpy)_3]^{2+}$ cations by the clay films continued for several hours after the immersion of the films, and proceeded to a level well above the CEC of the clay (Tables 2 and 3). This did not occur in the absence of electrolytes.

In the more concentrated electrolyte solutions, adsorption of the cations never exceeded the CEC (Tables 2 and 3). There is no need to postulate ion-pair adsorption. However, Table 6 shows that once again the mass changes observed were too small for adsorption of the $[M(bpy)_3]^{2+}$ to have occurred by the simple ion-exchange process depicted in equation 1. To reconcile the difference between the observed mass changes and the mass changes calculated for simple ion exchange still required that the adsorption of each cation be accompanied by the loss of between 23 and 33 water molecules.

CONCLUSIONS

The decreases in mass observed upon adsorption of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ by films of STx-1 immersed in pure water solution of the cations are attributed to the expulsion of some 50 water molecules from the clay interlayer spaces for each cation adsorbed. The loss of water is required to make room for these large metal bipyridyl complexes in the clay interlayer spaces and because of the decrease in the volume of clay interlayer spaces that occurred during intercalation of the cations.

In dilute electrolytes, the initial reductions in mass observed during adsorption of the cations were two to three times larger than those found in pure water. This is explained by the loss of more water during intercalation of the cations. UV-visible measurements also showed that in dilute electrolytes, the initial rapid adsorption of the cations by ion exchange was followed by additional adsorption of the cations above the clay's CEC, presumably as ion pairs with the electrolyte counter ions. It is speculated that this ion-pair adsorption accounts for the small 're-increases' in the mass of the films observed over longer periods of time in the electrolyte solutions. In more concentrated electrolytes, the extent of adsorption was greatly reduced. The initial decreases in mass all but disappeared, leaving only the smaller mass increases observed at longer times.

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