

CLAY MODIFIED ELECTRODES

PART IV. THE ELECTROCHEMISTRY AND ELECTRON SPIN RESONANCE OF METHYL VIOLOGEN INCORPORATED INTO MONTMORILLONITE FILMS

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ABSTRACT

The electrochemical behavior of methyl viologen (N,N'-dimethyl-4,4'-bipyridinium or MV^{2+}) incorporated into montmorillonite modified electrodes was studied. The first reduction to the cation radical ($MV^{\cdot+}$) leads to the formation of a dimer that is not oxidizable within the clay film at potentials near the $MV^{2+}/MV^{\cdot+}$ wave. The presence of the dimer was confirmed by spectroelectrochemistry and electron spin resonance (ESR) spectroscopy. The dimeric viologeh could be reoxidized via a mediation of charge from the electrode surface by $Fe(CN)_6^{4-}$. The equilibrium constant for the dimerization reaction $2 MV^{\cdot+} \rightleftharpoons (MV^{\cdot+})_2$ was estimated as $5 \times 10^4 M^{-1}$ based on the ESR data compared to ca. $380 M^{-1}$ for this reaction in aqueous solution.

INTRODUCTION

The modification of electrode surfaces with thin films of clay minerals has recently been reported [1]. Cations, such as $Ru(bpy)_3^{2+}$ (bpy is 2,2'-bipyridine), $Fe(bpy)_3^{2+}$, or MV^{2+} (methyl viologen), when incorporated into ion exchange sites on the clay surface, were electroactive. Clay modified electrodes have several novel properties, including the recently reported ability to yield an enantiomeric excess of $Co(bpy)_3^{2+}$ during an electrochemical oxidation of a racemic mixture of $Co(bpy)_3^{2+}$ [2]. Clay layers also have the ability to segregate efficiently different cationic species on their surfaces [3] and function as supports for catalysts such as dispersed metals or metal oxides [4] and semiconductors [5].

The electrochemical behavior of MV^{2+} incorporated into montmorillonite modified electrodes is of interest for a number of reasons. Methyl viologen (or paraquat) is a widely-used herbicide and its interaction with soils, including clay minerals, has been studied extensively [6]. Its herbicidal activity decreases significantly when incorporated into clays; this has been attributed to its strong adsorption on the silicate surface, preventing subsequent uptake by plants. The interaction has both electrostatic and Van der Waals components; strong adsorption of neutral aromatic

compounds shows the extent of interaction between the π cloud and the oxygen-rich silicate surface.

In addition, viologen derivatives have been employed extensively in photoelectrochemical (PEC) cells as electron acceptors or mediators [7] with recent application in PEC's containing suspensions of CdS incorporated into clay particles [5]. The reversibility and favorable potential of the $2+ / +$ couple, along with large changes in the optical spectrum accompanying the electrochemical reduction, make these compounds well-suited for applications in PEC cells and electrochromic displays. The electrochemical and spectroelectrochemical behavior of MV^{2+} in solution has been reported by a number of laboratories [8].

The properties of MV^{2+} and $MV^{\cdot+}$ make these species useful probes for studying the structure and properties of modified electrodes [9]. The radical cation ($MV^{\cdot+}$), in addition to being highly colored, is paramagnetic and has a well defined electron spin resonance (ESR) spectrum [10]. However, in concentrated aqueous solutions or viscous media the radical cation forms a diamagnetic dimer $(MV^{\cdot+})_2$ with an associated hypsochromic shift in the optical spectrum [10b,11].

This paper examines the unusual electrochemical behavior of MV^{2+} incorporated into montmorillonite modified electrodes. The irreversible nature found for the electron transfer reaction in clay contrasts with most modified electrodes involving viologen moieties that show reversible reactions, at least for the first reduction. Optical and ESR data are used to explain the observed electrochemical behavior.

EXPERIMENTAL

Materials

Ca-montmorillonite (STx-1) was purchased from the Source Clay Minerals Repository (University of Missouri, Columbia, MO) and had a cation exchange capacity (CEC) of 84 meq/100 g. The Na^+ form of the clay was used in all experiments and was prepared by adding 5 g of clay to 200 ml of a 1.0 M NaCl solution and stirring with a mechanical stirrer for 72 h. Colloids were prepared by centrifuging the above suspensions at 9000 rpm for 30 min. The clear supernatant was discarded and 200 ml of distilled water was added and the mixture was vigorously stirred for 0.5 h. This procedure was repeated 4 times. The final centrifugation was at 5000 rpm for 10 min. The slightly opaque supernatant was decanted and stored; this colloid (2 g/l) was stable against flocculation for several months.

N,N'-dimethyl-4,4'-bipyridinium dichloride (Sigma Chemicals) was recrystallized twice from methanol/acetone. NaCl (Fisher), tetramethylammonium chloride (TMACl, Eastman) and $K_4Fe(CN)_6$ (MCB) were used as received. Na_2SiO_3 (Baker) was used as both supporting electrolyte and an antiflocculant in several experiments and was used as received. Distilled water for all experiments was from a Millipore water reagent system.

Instrumentation for electrochemical experiments consisted of a Princeton Applied

Research (PAR) model 173 potentiostat/galvanostat and a PAR model 179 digital coulometer. Cyclic voltammograms were recorded on a Houston Instruments model 2000 X-Y recorder. All electrochemical experiments were performed in an undivided three electrode cell with a 20 ml volume. Working electrode substrates were conductive SnO₂ glass (1.0 cm²). The counter electrode was Pt gauze and the reference electrode was a saturated calomel electrode (SCE).

Procedure

Clay films were prepared by dropping a known volume (50 μl/cm²) of a clay colloid (2 g/l) onto clean SnO₂. The films were heated in air for 30 min at 80°C and then cooled. They were subsequently soaked in a nitrogen degassed 10.0 mM solution of MV²⁺ for 30 min, rinsed with water and then transferred to the degassed electrochemical cell. The nominal dry thickness of the film, as estimated by profilometry, was about 900 nm.

For the ESR experiments, 3 ml of the degassed clay colloid were placed in a three-compartment electrochemical cell (total volume 5 ml) that was previously fitted with electrodes and evacuated. The working electrode was Pt gauze. Na₂SiO₃ (50 mM) was added as supporting electrolyte and antiflocculant followed by the addition of MV²⁺. The solution was exhaustively reduced at -1.0 V vs. SCE. The resulting purple solution was transferred to an evacuated glass capillary (3 mm i.d.) using Schlenk techniques. The capillaries were sealed with rubber septa; the solution contained in these was stable towards decomposition by oxygen for several weeks.

RESULTS

Electrochemistry

A typical cyclic voltammogram (CV) for MV²⁺ incorporated into an STx-1 modified electrode is shown in Fig. 1. Data pertaining to the position of peak potentials and current ratios (i_{pa}/i_{pc}), as a function of scan rate, are given in Table 1. The formal potential, $E^{\circ'}$, for the 2+/+ couple at this concentration was estimated to be -0.72 V from the position of the peak potentials. This can be compared to a value of -0.69 V reported for the couple in aqueous solution at a bare electrode [8c]. The electrode, which was colorless in the oxidized form, turned deep purple upon reduction. For scan rates of 5 to 500 mV/s, i_{pc} was proportional to $v^{1/2}$ (v is the scan rate). This yields an effective diffusion coefficient, D_{eff} , of about 9×10^{-12} cm²/s, if the concentration of MV²⁺ within the film is taken as 1.2 M. This concentration was estimated from the charge required for exhaustive reduction, the geometric area, and the film thickness in the dry state, as determined by profilometry. No attempt was made to correct for errors introduced by film swelling due to hydration. At these scan rates the diffusion layer was confined within the clay film. Continuous potential cycling at 50 mV/s for several h showed a slow, constant decrease in the peak heights. This was not a result of the loss of MV²⁺ from

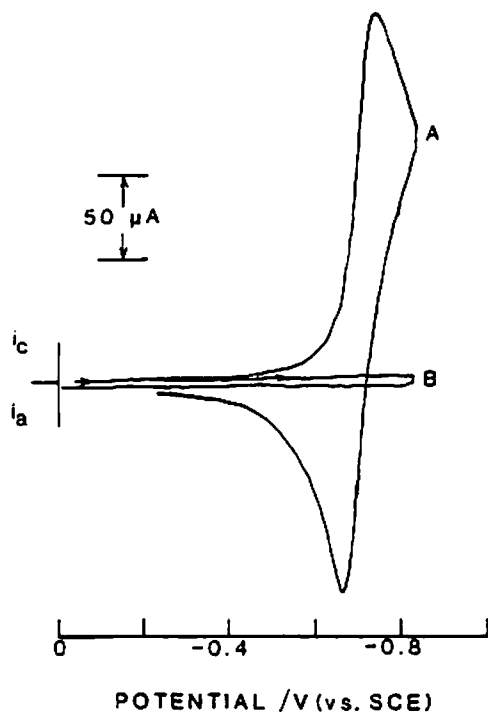


Fig. 1. Cyclic voltammogram of an STx-1 modified electrode in a 50 mM NaCl solution (first scan). Curves A and B are in the presence and absence, respectively, of incorporated MV^{2+} . The working electrode was SnO_2 glass (1 cm^2 , area). Scan rate, 50 mV/s.

the film, but rather from the formation of an electroinactive dimer in the clay matrix. More evidence for this assertion will be given in later sections. The use of 1.0 M TMACl as the supporting electrolyte gave identical electrochemical results and

TABLE I

Electrochemical data for cyclic voltammetry of an STx-1/ MV^{2+} clay modified electrode ^a

$\nu/\text{mV s}^{-1}$	$-E_{pc}/V$ ^a	$-E_{pa}/V$	$\Delta E_p/V$	$\frac{i_{pa}}{i_{pc}}$ ^b	$(E_p - E_{p/2})/V$	$i_{pc}\nu^{-1/2}/\mu\text{A mV}^{-1/2} \text{ s}^{1/2} \text{ e}$
5	0.74	0.71	0.03	0.60	0.044	21.5
50	0.75	0.67	0.08	0.65	0.050	26.2
500	0.82	0.62	0.20	0.80	0.075	19.2

^a 10^{-7} mol/cm^2 of MV^{2+} contained in film ca. 900 nm thick on an SnO_2 substrate. The solution was 50 mM NaCl. All potentials reported in V vs. SCE.

^b Ratio estimated by the method of Adams [12].

^c Experiments with some films taken in order 50, 5, 500 mV/s. Since complete regeneration of MV^{2+} was not possible, the decreasing trend probably represents some loss of MV^{2+} . The initial value obtained at 50 mV/s was used in calculation of D .

did not result in the exchange of the MV^{2+} that was adsorbed on silicate surfaces by TMA^+ in solution (TMA^+ is tetramethylammonium).

The values of $i_{pa}/i_{pc} < 1$ which decrease with decreasing v suggest that the electrogenerated MV^{2+} is involved in a reaction which prevents its reoxidation upon scan reversal. Further evidence of this is obtained by a bulk (coulometric) reduction of the film. The colorless electrode was first held in the oxidized form, at -0.40 V. The potential was then stepped past the first reduction peak to -0.80 V. The decay of the current was completed in ca. 30 min and 10.9 mC of charge were passed, resulting in a deep purple film. The amount of MV^{2+} in the film (ca. 0.8×10^{-7} mol) roughly corresponds to that found for this amount of charge (uncorrected for double layer charging or residual current), ca. 1×10^{-7} mol. When the potential was stepped back to -0.40 V, only 1.9 mC (17% of the cathodic charge) passed, even when the electrode was held at this potential for several hours. The film remained purple for several days, in the absence of oxygen, and could not be reoxidized to the MV^{2+} form at any potential within the solvent limit. To insure that the apparent loss of MV^{2+} was not an artifact of film thickness or preparation method, several electrodes were prepared by spin coating [1b]. The resulting films, which were about 90 nm thick, showed the same electrochemical behavior, i.e., only about 20% of the reduction product could be reoxidized.

Although the reduction product could not be reoxidized directly at the electrode, it could be oxidized by an electrogenerated mediator, such as $Fe(CN)_6^{3-}$, via a thermodynamically favorable electron transfer reaction. The ability of anions to penetrate montmorillonite films and undergo electron transfer has been shown previously [1b]. The following results show that anionic mediators can shuttle charges from the electrode surface to cations that are strongly adsorbed within the clay matrix. Typical CV's for the oxidation of a 1.0 mM solution of $Fe(CN)_6^{4-}$ (E° is 0.12 V) are shown in Fig. 2 for a bare electrode and an STx-1 modified electrode. The response of the modified electrode over this potential range was the same when MV^{2+} was incorporated into the film. The mediating ability of $Fe(CN)_6^{3-}$ was demonstrated by the following experiment. An STx-1/ MV^{2+} modified electrode was immersed in a solution containing 1.0 mM $Fe(CN)_6^{4-}$ and the potential was stepped to -0.8 V until the film was exhaustively reduced; under these conditions $Fe(CN)_6^{4-}$ remained reduced and had no effect on the electrochemistry at these potentials. When the potential was scanned in a positive direction, again only a small peak could be observed for direct oxidation of MV^{2+} (Fig. 3). However, as the potential was swept past 0.12 V where $Fe(CN)_6^{4-}$ oxidation occurs, a large anodic wave was observed (compare to Fig. 2B) with essentially no cathodic wave present on the return scan. We ascribe this wave to the oxidation of $Fe(CN)_6^{4-}$ which penetrates the film to produce $Fe(CN)_6^{3-}$; the latter reacts with MV^{2+} regenerating $Fe(CN)_6^{4-}$ in a "catalytic" reaction sequence. After about 5 potential cycles between -0.2 and 0.6 V the film turned colorless and the behavior observed in Fig. 2B was restored. Subsequent cathodic scans showed peak heights for MV^{2+} reduction the same as those prior to exhaustive reduction, indicating that electroactivity had been restored and that no material had been ejected from the film.

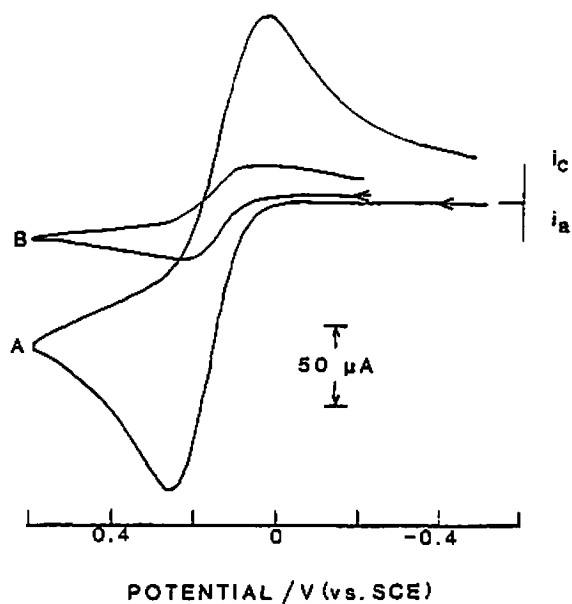


Fig. 2. Cyclic voltammogram of a 1.0 mM solution of $\text{Fe}(\text{CN})_6^{4-}$. Curves A and B are for a bare SnO_2 and an STx-1 modified electrode, respectively. Supporting electrolyte, 50 mM NaCl. Scan rate, 50 mV/s.

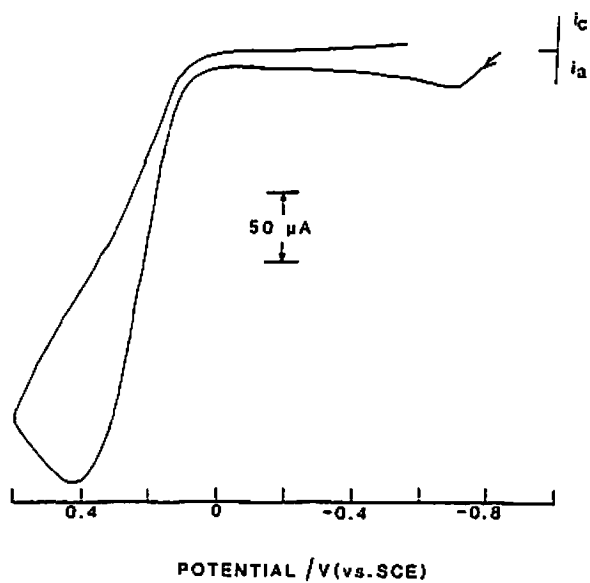


Fig. 3. Cyclic voltammogram of an exhaustively reduced STx-1/ MV^{2+} electrode in a 1.0 mM $\text{Fe}(\text{CN})_6^{4-}$ solution. Supporting electrolyte, 50 mM NaCl. Scan rate, 50 mV/s.

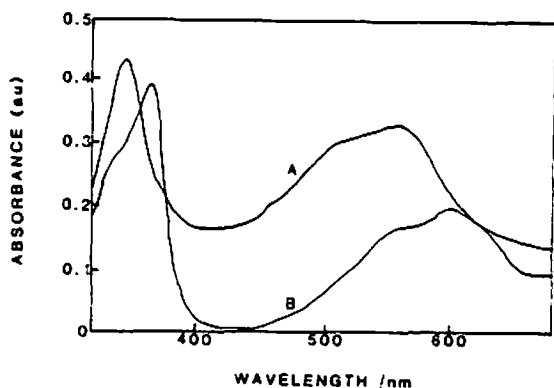


Fig. 4. Absorbance spectra for reduced MV^{2+} . Curve A is an exhaustively reduced STx-1/ MV^{2+} -modified SnO_2 electrode and curve B is a $5.0 \times 10^{-5} M$ solution of MV^{2+} .

Spectroelectrochemistry

The optical spectra for an exhaustively reduced STx-1/ MV^{2+} film and a $5.0 \times 10^{-5} M$ solution of MV^{2+} are shown in Fig. 4. The blue absorption maximum, which is 603 nm for MV^{2+} in solution, was shifted to 550 nm for the film. This blue shift in the absorption bands is typical of the formation of the dimeric species and both spectra are in good agreement with those previously reported for monomeric and dimeric methyl viologen [11].

There was no evidence for a shoulder at 603 nm (corresponding to monomer) even when only small fractions of the total charge were injected. This is contrary to behavior observed for methylene blue (MB) [13] and tetrathiafulvalene (TTF) [14] radical cations, which also have a propensity to dimerize on montmorillonite surfaces. MB and TTF, when incorporated into montmorillonite, show absorbance maxima corresponding to both monomeric and dimeric species with an associated isosbestic point. Thus, for these species there is an equilibrium between the monomer and dimer, with monomer favored at low concentrations. ($A^{+\cdot} = MB^{+\cdot}$, $TTF^{+\cdot}$)



The absence of a peak at 603 nm for MV^{2+} suggests that for this species the equilibrium heavily favors dimer formation. This result was further substantiated by the ESR results.

ESR

Several attempts were made to obtain an ESR signal from MV^{2+} in clay films generated electrochemically in situ [9d]. The electrochemically reduced films, with their usual purple color, were ESR silent even at the highest receiver gains. Since the area of the electrode was relatively small (0.4 cm^2) the possibility of a small

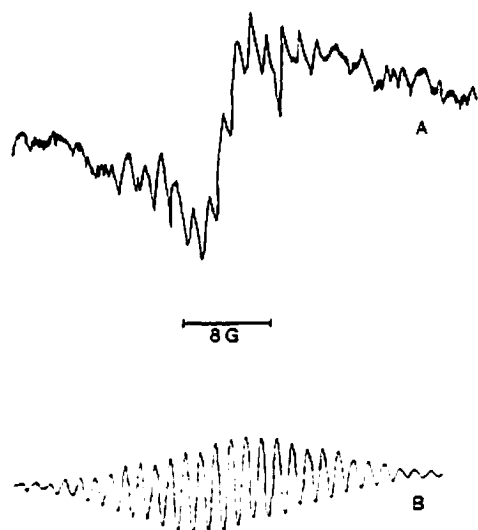


Fig. 5. ESR spectra of an exhaustively reduced $5 \times 10^{-4} M$ MV^{2+} solution. Curves A and B are in the presence and absence, respectively, of colloidal STx-1 (2 g/l). Modulation amplitude was 1.0 G for both. Receiver gain was 1.0×10^5 and 2.4×10^3 for curves A and B, respectively.

undetected signal existed. Therefore attempts were made to observe the spectra of MV^{2+} incorporated into colloidal clay dispersions, so that the total amount of material inside the ESR cavity was increased significantly. The details of the preparation of these samples is given in the experimental section.

A solution containing 2 g/l of clay, $5 \times 10^{-4} M$ MV^{2+} (30% of the cation exchange capacity, CEC) and 50 mM $NaSiO_3$ as supporting electrolyte gave the ESR spectrum shown in Fig. 5A, at maximum receiver gain. When the MV^{2+} concentration was decreased by a factor of five, similar results, with the peak height attenuated by roughly the same factor, were obtained. This can be compared to the spectrum of the same concentration of MV^{2+} in solution in the absence of clay (Fig. 5B), which was easily detectable at intermediate receiver gains. The partial absence of hyperfine structure of the solution spectrum is a result of the large field modulation amplitude which was kept at 1.0 G, necessary to detect the signal in the clay sample. Lowering the modulation amplitude for the solution sample produced the rich hyperfine structure normally associated with MV^{2+} [10].

DISCUSSION

Bipyridinium cations, including methyl viologen, are among the substances most strongly adsorbed by clay minerals. The planar structure of MV^{2+} exhibits a particularly strong interaction with expanded lattice clays such as montmorillonite as reported by Tomlinson et al. [6c]. In this work, based on solution-equilibrium techniques, they identified a quantity, the strong absorption capacity (SAC), which

is a fraction of the CEC. A value of 0.76 was reported for the ratio of SAC/CEC for MV^{2+} adsorbed by montmorillonite. The SAC corresponds to the limiting value of the adsorption capacity below which no MV^{2+} could be detected in solution after equilibration and centrifugation of the clay minerals. Further, the value they obtained for the SAC was not altered even in the presence of up to 2.0 M NH_4^+ ion. The strong adsorption of MV^{2+} by STx-1 layers is supported by the ability to use 1.0 M TMACl as supporting electrolyte without loss of material from the film. Both coulometry and CV indicate that after reduction of MV^{2+} , $MV^{•+}$ cannot be oxidized directly back to MV^{2+} . The decreasing values of i_{pa}/i_{pc} with decreasing scan rate (Table 1) are indicative of an irreversible reaction following a charge transfer as shown by eqns. (2) and (3) [15].



Thus, as $MV^{•+}$ is produced at the electrode surface, it reacts to form the electroinactive product. Electrochemical interpretation of the type of following reaction is somewhat clouded by the quasi-reversibility of the electrode reaction. However, the data at slow scan rates suggest the possibility of a second order following reaction such as dimerization (eqn. 1). Narrowing of CV peaks has been associated with second order following reactions, giving (at 25°C) values for $E_p - E_{p,2}$ of 39 mV rather than 56 mV associated with a reversible charge transfer with no following reaction [16]. At slow scan rates some narrowing is observed (Table 1). The dimerization mechanism is confirmed unambiguously by spectroelectrochemical and ESR results which show the presence of a dimeric species.

The formation of dimer is not complete, however. In all cases 17–20% of the exhaustively reduced viologen could be reoxidized directly. Note that this corresponds to the fraction of the CEC not associated with the SAC (24%) as reported by Tomlinson et al. [6c]. Thus, one might conclude that the fraction of strongly adsorbed $MV^{•+}$ corresponds to the irreversible component of the electron transfer. Additional insight into this assertion comes from inspection of the apparent diffusion coefficient, D_{app} for MV^{2+} in the clay films, which was estimated to be 9×10^{-12} cm²/s from peak heights in the CV data. D_{app} is the sum of contributions from the actual physical diffusion of electroactive material and from electron exchange (hopping) between adjacent sites, as shown by eqn. (4) [17,18].

$$D_{app} = D_0 + (\pi/4)(k_{ex}d^2c) \quad (4)$$

D_0 corresponds to physical diffusion and the second term corresponds to "diffusion" via electron hopping, where k_{ex} is the second order electron transfer rate constant and d is the distance between electroactive centers of concentration c . The low value of D_{app} for MV^{2+} in clay suggests that diffusion occurs mainly via electron hopping. Physical diffusion seems unlikely, at least for the fraction corresponding to the SAC, since the molecules cannot be displaced from the clay binding sites to diffuse. Thus, a large component of D_{app} can probably be associated with a hopping mechanism.

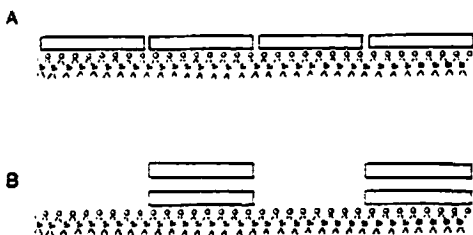


Fig. 6. Schematic representation of the configuration of methyl viologen on the clay silicate surface. The situation prior to and after exhaustive reduction is shown in A and B, respectively. The planar viologen is represented by rectangles.

The planar MV^{2+} ion is known to lie flat on the silicate surface [6e]. Its geometrical area can be estimated as a rectangle of dimensions $0.63 \times 1.34 \text{ nm}^2$ that occupies exchange sites on the silicate surface of approximately 1.19 nm^2 [6e]. With surface sites saturated with MV^{2+} , electron exchange between adjacent sites is possible. The situation changes, however, upon reduction and subsequent dimerization. The methyl viologen cation radical assumes a face-to-face eclipsed configuration upon dimerization [8b,c]. Proposed configurations on the silicate surface are shown schematically in Fig. 6. This arrangement has previously been suggested for dimeric methylene blue in montmorillonite [19]. Thus, in the reduced state, electron hopping between sites is greatly reduced, since the probability of hopping is proportional to the square of the distance between centers, which is now at least 1.3 nm. Therefore, since most of the centers cannot diffuse physically, the electroactivity is substantially reduced.

The dimer can be oxidized via mediation with $Fe(CN)_6^{3-}$ (Fig. 3). This CV behavior is typical for a catalytic mechanism as shown in eqns. (5) and (6) [20].



Notice that MV^{2+} has no influence on the electrochemistry at these potentials. Thus, as $Fe(CN)_6^{4-}$ is oxidized at the electrode surface, it is quickly regenerated by reacting with $(MV^{\cdot+})_2$, resulting in a depletion of $Fe(CN)_6^{3-}$. Therefore i_{pa} is enhanced and there is no or only a small peak observed on the reverse scan. This behavior is observed only for a few scans as the source of $(MV^{\cdot+})_2$ is finite. A return to normal CV behavior (Fig. 2) and the colorless electrode indicate that all of the viologen has been oxidized. This behavior implies that the reduced viologen is still electroactive and the possibility of the formation of an electroinactive reduction product (e.g., via a protonation reaction), can be eliminated. Further, it supports the contention that the formation of the dimeric species hinders diffusion by electron hopping.

The last point to be addressed is the extent of dimerization in the clay layer. The equilibrium constant for reaction (1) has been reported to be 380 M^{-1} for the

dimerization of MV^{2+} in aqueous solution [10b]. Note that the value of K is dependent upon the medium [11b]. An estimate of K can be made from ESR data based on eqns. (7) and (8).

$$M + 2D = c \quad (7)$$

$$K = D/M^2 \quad (8)$$

c is the total concentration of reduced viologen and M and D are concentrations of the monomer and dimer, respectively. The concentration of M in the solution case was $3.9 \times 10^{-4} M$ based on eqns. (7) and (8) (for $c = 5.0 \times 10^{-4} M$ and $K = 380 M^{-1}$). The solution ESR spectrum was then used as a standard to determine a value for M in the clay colloid by integration of the spectra in Fig. 5. Values of 1.0×10^{-4} and $2.4 \times 10^{-4} M$ were determined for M and D , respectively, for the total clay colloid + solution mixture ($c = 5.0 \times 10^{-4} M$). However, adsorption onto the clay surface effectively reduces the volume occupied by the viologen species and greatly increases their concentrations. For a clay density at 2 g/l the volume occupied by the clay is estimated to be 2 cm³/l of solution (density ca. 1 g/cm³). Thus, the corrected values for M and D are 5.0×10^{-3} and 0.12 M , respectively, for a film initially containing MV^{2+} at 30% of the CEC. On the basis of these estimates, K is $5 \times 10^4 M^{-1}$.

A reviewer has suggested as an alternative possibility that the blue shift in the bands of the optical spectrum of the reduced film [21] can be attributed to strong interactions of the reduced form with the silicate surface. In this case the dimerization equilibrium may not be perturbed to the extent proposed above. However, we feel that the attenuated ESR signal for the reduced form together with the known ability of methyl viologen to segregate from other cations on the montmorillonite surface producing locally high concentrations favors the perturbation of the equilibrium and dimerization explanation. Thus, the greatly increased extent of dimerization found with the clay can be attributed not only to the increased local concentrations of the viologen species, but also to an increased equilibrium constant that reflects the ability of the clay to segregate methyl viologen from other cations.

CONCLUSIONS

The electrochemical behavior of methyl viologen adsorbed into montmorillonite modified electrodes was shown to be different from other, less strongly adsorbed, cations. Diffusion through the film probably occurs via electron hopping and is drastically hindered upon electrochemical reduction and subsequent dimerization. The MV^{2+} species is extensively dimerized within the clay structure with an equilibrium constant for dimerization of about $5 \times 10^4 M^{-1}$.

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