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EFFECT OF CLAY CHARGE ON SWELLING: A CLAY-MODIFIED ELECTRODE STUDY

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Abstract—The uniformity of clay films affects the transport of an anionic electroactive probe through the film. When cations other than Na+ are present in the initial swelling of the film (such as native K+ and Ca^{2+}), or when the native clay is highly charged, internal dislocations of the film, caused by variable stacking domains, enhance the diffusive transport of $Fe(CN)_6^{3-}$ across the film. This effect is investigated using clay-modified electrodes in which the clays are of variable exchange forms (Na+, Ca^{2+}, or K+) and variable charge. The charge on the clay is determined both by the native form of the clay and by reduction of structural Fe^{3+}. The results suggest that swelling of clays increases in a linear fashion with CEC, at least for minimally charged clays.

Key Words—Charged clays, Diffusive transport, Iron reduction.

INTRODUCTION

The swelling of clays has many implications for use of clays as capping materials, for construction sites, and for industrial uses (drilling). Classically, swelling has been suggested to depend upon the cation exchange capacity (CEC) of the clay. Alternatively, swelling is thought to depend upon surface adsorption of water.

We examined the role of native clay charge as well as induced changes in clay charge on swelling in this study. We studied well-oriented clay films (5 μ thick dry) coated over Pt electrodes. When the films (Figure 1a) were well swollen in a NaCl bath (30 to 60 Å interlayer dimension) rapid transport of the small anion $Fe(CN)_3^{3-}$, 8.32 Å diameter ($r_{Fe(CN)62-} = 2\ l_{CN} + r_{Fe3+}$, where l is the bond length of C≡N (Schreemeyer *et al* 1985) and r_{Fe3+} is the Fe^{3+} (Huheey 1978) radii), was facilitated. When the films were collapsed (3 to 10 Å interlayer dimension) the films became insulating with respect to the $Fe(CN)_6^{3-}$ (Figure 1b). The transport of the anion was monitored by its reduction at the underlying Pt electrode upon arrival across the film. Prior work detailed the preparation of the clay film (Lee and Fitch 1990), the electrochemical scan rates necessary to keep the electrochemical perturbation near the electrode surface (Fitch and Du 1992), and the relationship between the observed currents and film swelling (Lee and Fitch 1990, Fitch and Fausto 1988).

In this work we found that these small films are extraordinarily sensitive to the presence of mixed salts in the swelling bath or native to the clay, that swelling is linear with CEC, and that reduction of Fe within the crystal lattice increases the transport of the probe anion.

MATERIALS, METHODS, AND THEORY

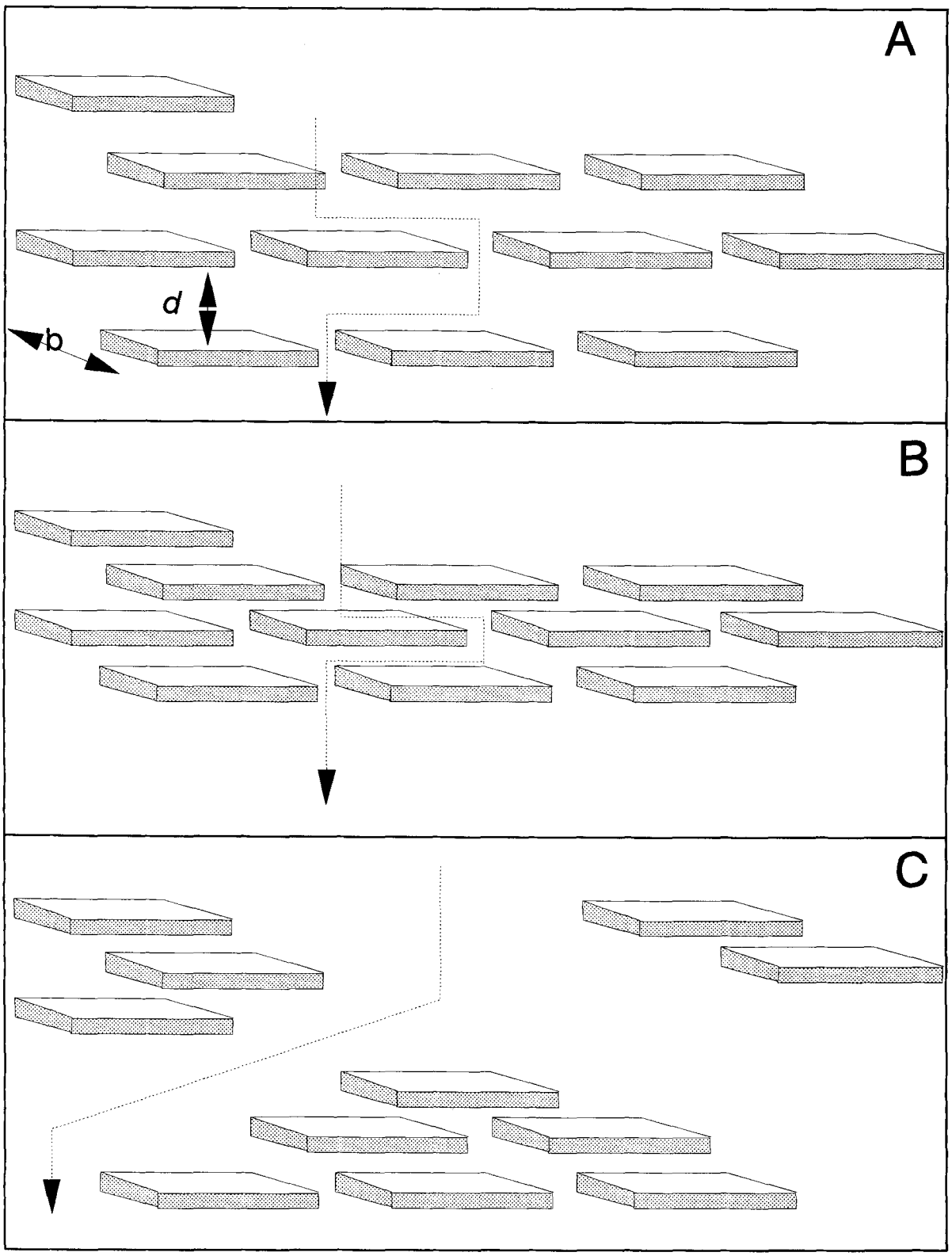
$Na_3Fe(CN)_6$ (City Chem. Corp), $K_3Fe(CN)_6$ (Pfaltz and Bauer, Inc.), NaCl, KCl, and $CaCl_2$ (Aldrich) were used as received.

Clays (SAz-1, SWy-1, SHCa, SWa-1, and STx-1) were obtained from the Source Clays Repository of the Clay Minerals Society. The composition of the clays is given in Table 1. The clays were purified and freeze dried as previously described (Lee and Fitch 1990). Na^+ exchanged clays were prepared by dissolving 30 g of as received clay in 100 ml of 2 M NaCl and stirring for 48 hours. The supernatant was decanted and replaced with fresh 2 M NaCl three times. The Na-exchanged clay was washed and decanted 10 times checking each time for the presence of Cl^- with $AgNO_3$. After exchange the clays were freeze dried.

Freeze dried clay suspensions (35 g/liter) were prepared for use. A one μl droplet of the clay suspension was placed on a glass sheathed Pt (1 mm diameter) electrode upended in a Pine Instrument MSR Analytical Rotor, which was rotated for 15 minutes at 800 rpm. Drying of the clay in this fashion resulted in a well oriented film (Lee and Fitch 1990) about 3–7.5 μm thick (Subramanian and Fitch 1992). The clay film was next placed for 5 minutes in a N_2-purged solution of NaCl, where the potential of the electrode surface was cycled between +0.8 and −0.2 V vs a saturated calomel reference electrode, SCE. The amount of NaCl in the solution controls the final dimensions of the interlayer domain (Norrish 1954, Slade *et al* 1991). The swollen film thickness has previously been estimated to be more than twice that of the dry state. After swelling in this O_2 free environment the clay-modified

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Table 1. Composition and formula of clays[1].

Clay	Name	Formula	CEC meg/100g	Native cation	%Fe_2O_3	%FeO
SHCa-1	California Hectorite	$(Mg_{2.65}Li_{0.33}Al_{0.02})Si_4O_{10}(OH)_{1.35}Fe_{0.65}$	44	Na^+, K^+, Ca^{2+}	0.02	0.25
SWy-1, ox	Wyoming Montmorillonite	$(Si_{8.0})(Al_{2.94}Fe^{3+}{}_{0.32}Fe^{2+}{}_{0.03}Mg_{0.58})^2$	76.4	Na^+, Ca^{2+}	3.35	0.32
SWa-1, ox	Washington Nontronite	$(Si_{7.3}Al_{0.7})(Al_{1.06}Fe_{2.73}Mg_{0.26})^3$	76[4]		32.53	
SAz-1	Cheto Montmorillonite	$(Si_{7.6}Al_{0.24})(Al_{2.8}Fe_{0.34}Mg_{0.86})^3$	120	Ca^{2+}	1.42	0.08
STx-1	Texas Montmorillonite		84.4	Ca^{2+}	0.65	0.15

[1] Unless otherwise specified all information is from Van Olphen (1979).
[2] Calculated from van Olphen (1979).
[3] Lear and Stucki (1985).
[4] Khaled and Stucki (1991).

electrode (CME) was transferred to a second N_2-purged solution containing both the salt and 3 mM $Na_3Fe(CN)_6$ where the electrochemical experiment was performed. This entire procedure was repeated in triplicate for each data point.

Cyclic voltammetry was performed in a conventional three electrode cell using an E.G.&G. PAR VersaStat Potentiostat with an HP 7371 plotter. The potential was scanned between +0.8 and −0.2 V vs SCE at 50 mV/s. This sweep rate has been shown to be sufficiently fast to confine the electrochemically generated diffusion layer within the clay film (Fitch and Du 1992). After a steady state signal was achieved, the clay was wiped clean from the surface and a signal obtained at the bare electrode.

The peak current for a reversible electron transfer event, I_p, at the bare electrode is (Bard and Faulkner 1980):

$$I_p = 2.69 \times 10^5 n^{3/2} F A D_{soln}{}^{1/2} C_{bulk} \nu^{1/2} \quad (1)$$

where n is the number of electrons involved in the reduction, F is Faraday's constant, A is the area accessible for transport of charge, defined by the electrode surface area in cm^2, D_{soln} is the solution diffusion coefficient, 7×10^{-6} cm^2/s (Oesterling and Olson 1967), C_{bulk} is the concentration of the electroactive species in the bulk solution in mol/cm^3, and ν is the scan rate of the experiment in V/s.

At negatively charged clay-modified electrodes the area available for transport is defined by the summed cross-sectional area of the pores, defined by the interlayer spacing, ∂, and the platelet edge, b:

$$A_{CME} = \partial \Sigma b \quad (2)$$

Equation (2) assumes a uniform film with a single interlayer spacing. The diffusion coefficient in the clay, D_{CME}, is the scaled distance of the actual path to the path as the crow flies and for drag along the particle surface. This term is the tortuosity, τ, of the film (Meredith and Tobias 1962, Nye and Tinker 1977, Baver *et al* 1972, Millington and Quirk 1961):

$$D_{CME} = \tau D_{soln} \quad (3)$$

The concentration of the electroactive molecule in the film is the bulk concentration scaled by the partition coefficient, κ:

$$C_{CME} = \kappa C_{bulk} \quad (4)$$

Combining equations (1) through (4) we obtain the normalized current, R (peak current at CME/peak current at bare electrode):

$$R = \partial \Sigma b \tau^{1/2} \kappa / A \quad (5)$$

The magnitude of κ is 1 for an un-retained solute and varies in charge for an excluded anion, equation (5) becomes:

$$R = \kappa \partial \Sigma b \tau^{1/2} / A = \kappa \theta \tau^{1/2} \quad (6)$$

where θ is the porosity of the film. In summary, the parameter τ carries information about the path length, κ relates to the partition coefficient, and θ is related to the spacing of the channels formed by the clay.

The ratio current was plotted vs $[Na^+]^{-1/2}$. In the classical formulation a direct relationship between the distance between platelets, ∂, and $[Na]^{-1/2}$ is predicted (Sposito 1984):

$$\partial = 2(\beta C)^{-1/2} - V_{ex}/S_E \quad (7)$$

←

Figure 1. a. Schematic of a well ordered thin (5 μ) clay film. The gallery dimension, ∂, is well swollen by dilute NaCl. The transport of anionic probe to the underlying Pt electrode must occur via gallery pores. Transport is monitored by the reduction of the electrochemically anionic probe as it arrives at the electrode surface. The current is less than that observed at the bare electrode since the area for diffusion is less. b. Clay film is less swollen when pre-treated with concentrated NaCl. The available transport area, proportional to the gallery dimension, ∂, decreases. c. Variable swelling domains cause dislocations within the film, resulting in contiguous large pores creating a pathway to the underlying electrode surface.

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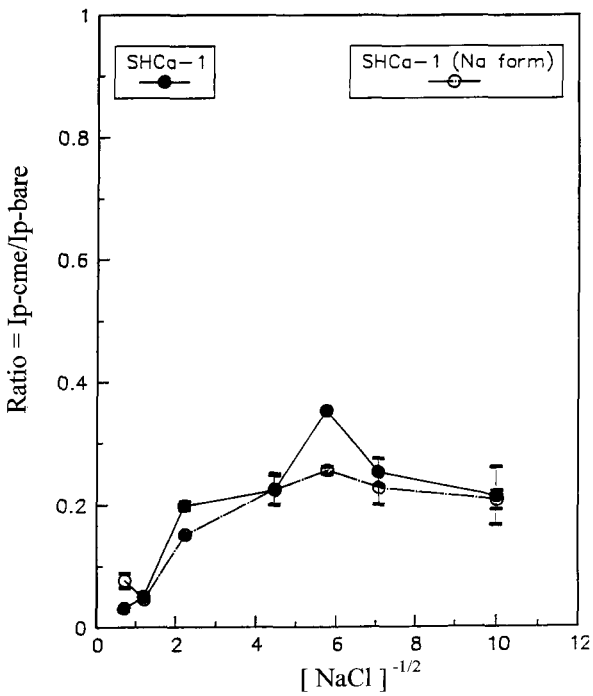


Figure 2. The ratio currents ($R = I_{p,CME}/I_{p,bare}$) for reduction of $K_3Fe(CN)_6$ at Ca-exchanged and Na-exchanged SHCa-1 modified electrodes as a function of the concentration of NaCl in the swelling solution.

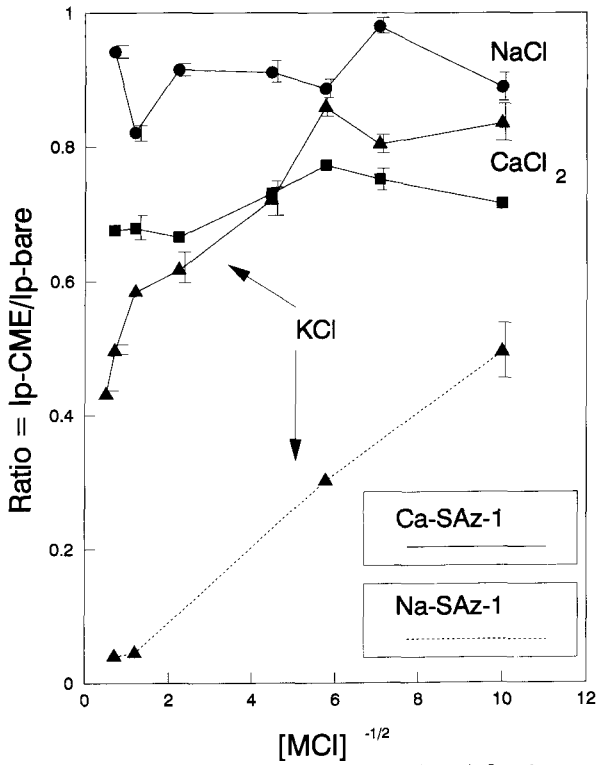


Figure 3. The ratio currents ($R = I_{p,CME}/I_{p,bare}$) for the reduction of $K_3Fe(CN)_6$ at Ca-exchanged and Na-exchanged SAz-1 clay-modified electrodes as a function of the concentration of the cation in swelling solution (NaCl, KCl, or $CaCl_2$).

where S_E is the exclusion specific surface area, m^2/g, C is the concentration of the 1:1 electrolyte in mol/dm^3, and V_{ex} is the exclusion volume (dm^3/kg). The term β (m/mol) is:

$$\beta = 2F^2/\epsilon_o DRT \quad (8)$$

where F is Faraday's constant, ϵ_o is the permittivity of free space, D is the dielectric constant of water, R is the gas constant, and T is the temperature in K. From equations (6) and (7) we note that the ratio value should be directly proportional to $[Na^+]^{1/2}$ if swelling is osmotically controlled and if $\tau^{1/2}$ is independent of ∂.

Dithionite-reduced SWy-1 and SWa-1 were prepared as previously described (Lear and Stucki 1985, Stucki *et al* 1984, Lear and Stucki 1989). In the dithionite preparation, an extensive washing step is performed (Khaled and Stucki 1991), in addition the dithionite itself is unstable, consequently no excess dithionite remains. The clays were shipped by overnight express and used in electrochemical experiments the following day. In these experiments the entire procedure (spin coating + electrochemistry) was performed in an Argon filled glove bag, in addition to the usual N_2 purging of solutions. The full set of electrochemical triplicate experiments consumed 1 week. The unused portion of the clay was returned by overnight express and analyzed for change in the oxidation/reduction state via the 1,10 phenanthroline photochemical method (Komadel *et al* 1990). This handling of the clay did allow for some re-oxidation of the sample. Transport between labs and experimentation resulted in a de-

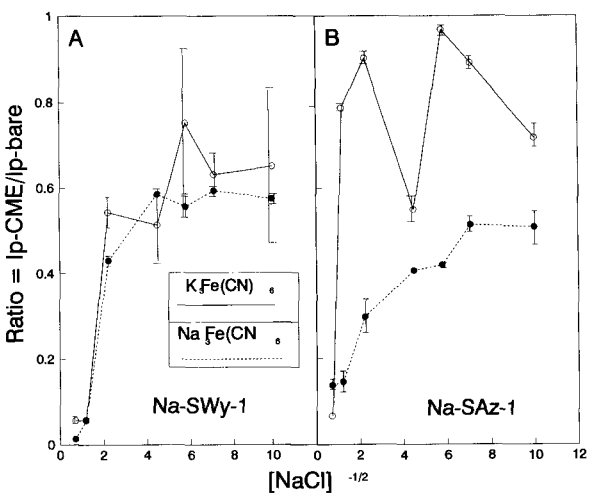


Figure 4. The ratio currents ($R = I_{p,CME}/I_{p,bare}$) for the reduction of $Fe(CN)_3^{3-}$ at A) Na-SWy-1 and B) Na-SAz-1 as a function of NaCl in the swelling solution. Upper curve is $K_3Fe(CN)_6$. Lower curve is $Na_3Fe(CN)_6$.

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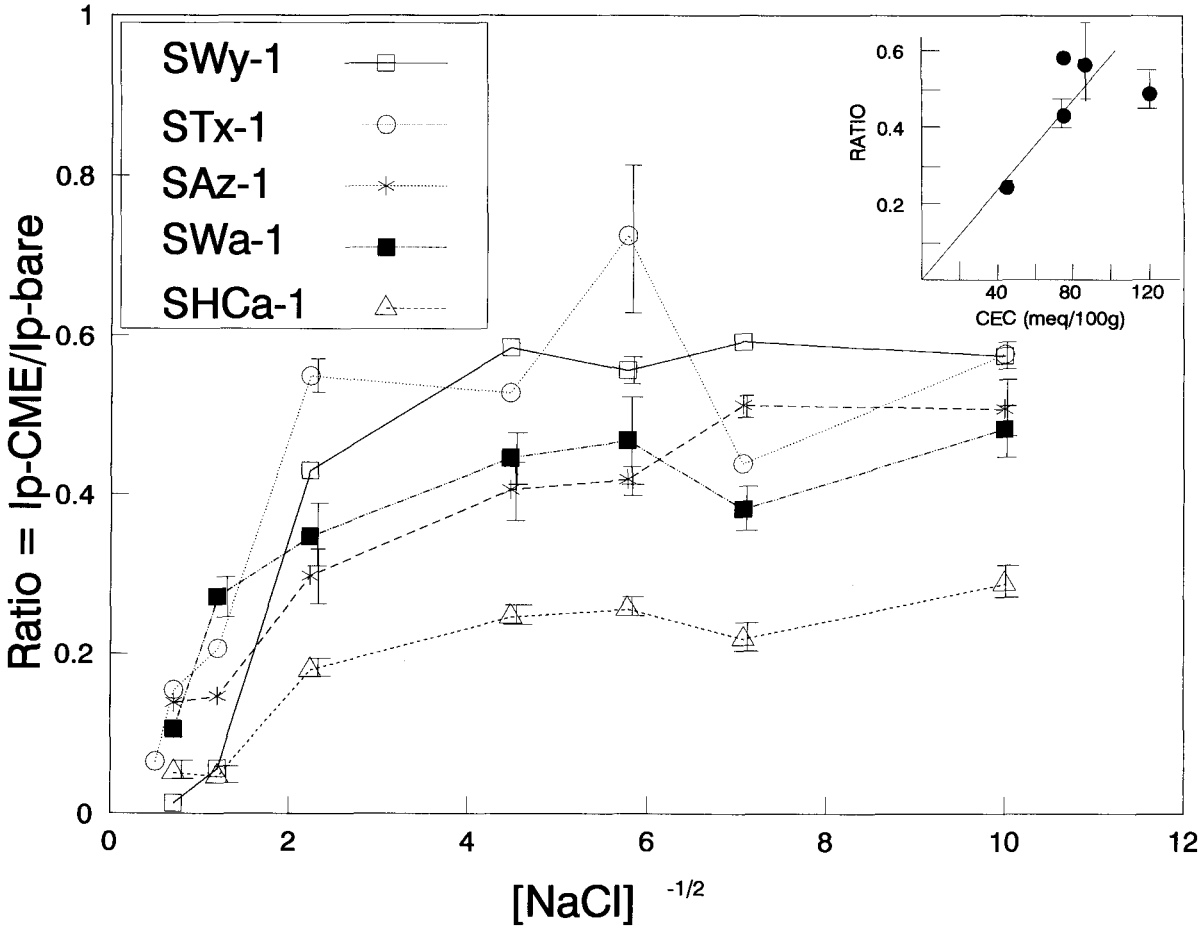


Figure 5. The ratio currents ($R = I_{p,CME}/I_{p,bare}$) for the reduction of $Na_3Fe(CN)_6$ at variable clay-modified electrodes as a function of NaCl in the swelling solution. Inset shows R at 0.02 M NaCl as a function of the cation exchange capacity (CEC) of the clay.

crease in the Fe^{2+} content from 39% to 28%. Therefore, the extent of reduction of SWa-1 during experimentation was assumed to be approximately 34%.

RESULTS

Prior work with clay-modified electrodes showed a good correlation of the normalized peak current ($R = I_{p,CME}/I_{p,bare}$) for reduction of $K_3Fe(CN)_6$ with the interlayer dimension, ∂, for SWy-1 (Lee and Fitch 1990, Fitch and Fausto 1988). ∂ was controlled by swelling in NaCl (Norrish 1954, Slade *et al* 1991). In prior results, swelling solutions containing >0.5 M NaCl resulted in collapsed (insulating) SWy-1 films. For concentrations less than 0.25 M NaCl, there was a rapid rise in the observed currents consistent with reported changes in ∂ (Norrish 1954, Fitch and Fausto 1988, Lee and Fitch 1990, Slade *et al* 1991, Fitch and Du 1992).

A similar change from an insulating to a conducting film was found for Ca-exchanged hectorite, SHCa-1 (Figure 2), but not with native Cheto montmorillonite, SAz-1 (Figure 3). No salt pre-treatment produced an insulating film with native Ca-exchanged SAz-1 clay. This included treatment with KCl and $CaCl_2$. The cations, K^+ and Ca^{2+}, are easily dehydrated. This prevents hydration driven swelling of clay (Suquet *et al* 1975, Norrish 1954). These cations have been found to cause insulating or near-insulating SWy-1 films over all concentration ranges (Lee and Fitch 1990). The presence of Ca^{2+} as the native exchange cation has been shown to affect aggregate structure with Cheto clay forming polycrystalline, turbostratic (6 nm thick) aggregates with curled edges. The Wyoming montmorillonite, however, forms thick (500 nm) non-turbostratic aggregates (Guven 1974). These differences can affect the film structure.

Forming a Na-exchanged SAz-1 clay prior to formation of the clay-modified electrode and swelling in KCl resulted in an insulating film at the highest KCl concentrations (Figure 3). Unlike Na-SWy-1, however,

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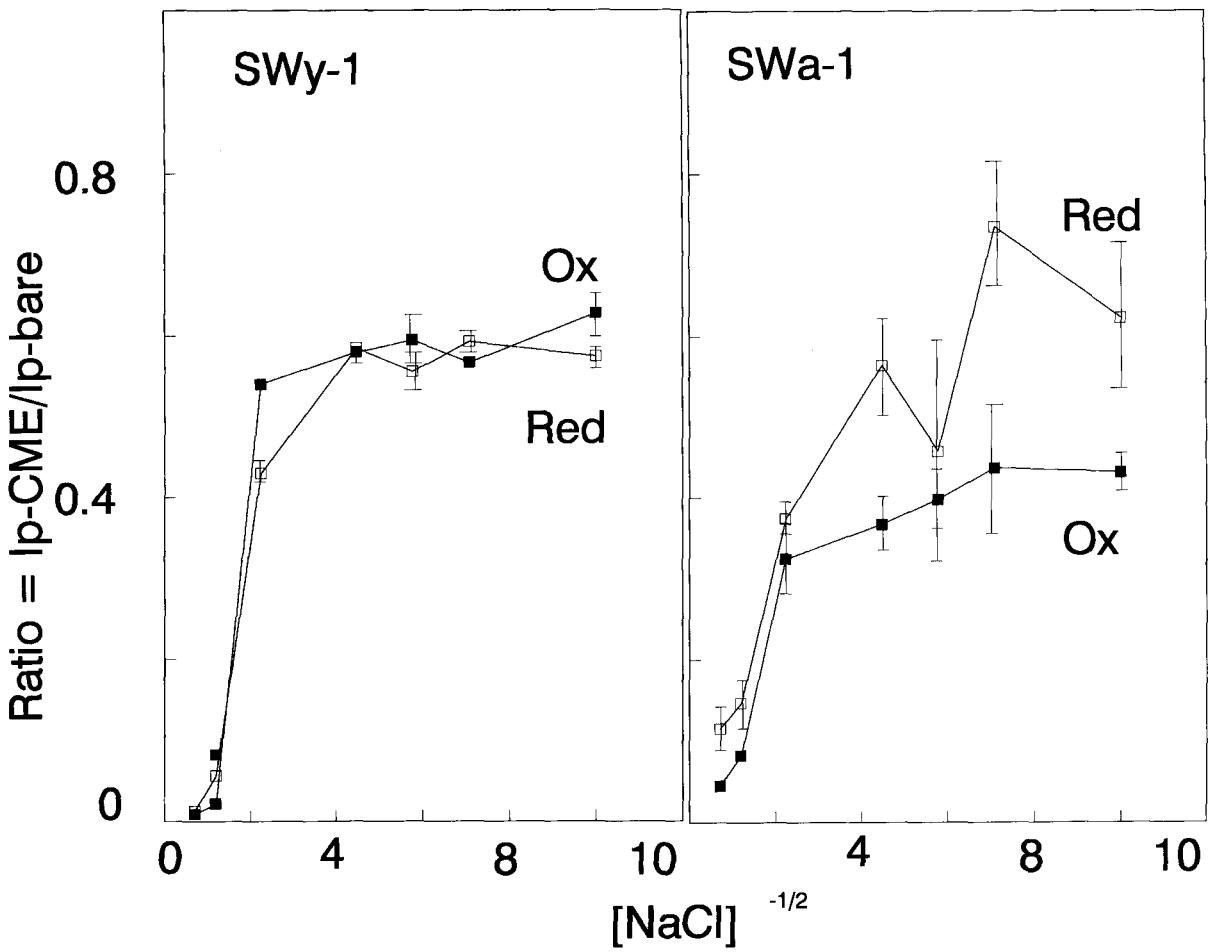


Figure 6. The ratio currents ($R = I_{p,CME}/I_{p,bare}$) for the reduction of $Na_3Fe(CN)_6$ at SWy-1 and SAz-1 clay-modified electrodes as a function of the NaCl in the swelling solution. ●, native and O, dithionite reduced, clays.

Na-SAz-1, did not remain insulating over all KCl concentrations. The extreme sensitivity of SAz-1 to the presence of the exchange cation (Na^+ or K^+) suggested that the cation associated with the probe ion ($K_3Fe(CN)_6$ vs $Na_3Fe(CN)_6$) could play a major role. Figure 4b shows that the swelling curve for Na-SAz-1 in NaCl varies dramatically in extent depending on the co-ion of the probe molecule. These results were also found for SWy-1 (Figure 4a). For both SAz-1 and SWy-1 the swelling curve is more erratic when using $K_3Fe(CN)_6$ vs $Na_3Fe(CN)_6$. Our interpretation of these results is that variable swelling domains result when the system is not rigorously mono-cationic (Figure 1c). Domains associated with collapsed layers served to dislocate the layering of the film, ultimately resulting in larger pin hole formation throughout the film. This interpretation also nicely provides an explanation of the results in Figure 2 for SHCa-1 in which slightly more erratic results were obtained for Ca-SHCa-1 vs Na-SHCa-1.

The implications of these results are not startling and conform to the theory that at least the initial portion of swelling is driven by the type of intercalated cation, suggesting that adsorbed water plays a role in the initial phase of swelling. In order to investigate the role of charge on more extensive swelling in the presence of Na^+, these results suggest that we need Na-exchanged clays, as well as Na^+ as the co-ion of the probe anion.

Figure 5 shows the results obtained in swelling five Na-exchanged clays. In all cases, an insulating layer with respect to $Fe(CN)_6^{3-}$ is obtained in >0.25 M NaCl, with swelling of the clay taking place generally between 0.7 and 0.3 M NaCl. The rise of the swelling curve is rapid, except for Na-SHCa. In all cases, there appears to be a plateau in swelling.

A classical (Derjaguin, Landau, Verwey and Overbeek, DLVO theory; Parker 1986, Adamson 1982) interpretation of swelling predicts unlimited swelling with decreasing amount of salt present. Such swelling is linear with $[Na^+]^{1/2}$ according to equations (6) and (7).

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The plateau observed suggests that DLVO theory fails to explain swelling. Another test of DLVO theory is whether the extent of clay swelling depends on the amount of charge on the clay as measured by the cation exchange capacity (CEC) of the clay. Low (1980) found an empirical equation:

$$\ln(P + 1) = \ln\beta + (A + bS + c(CEC))/(m_w/m_c) \quad (9)$$

where P is the swelling pressure in atm, β, a, b, and c are empirical constants, S is the surface area (cm^2/g), CEC is the cation exchange capacity (meq/g) of the clay, and m_w and m_c are the masses of water and clay (g). If m_w and m_c are constants, as they are in CME studies, then swelling should increase exponentially with the charge on the clay. The inset in Figure 6 indicates that swelling does increase with CEC, but in a linear fashion. It is not clear if linearity would continue with more highly charged clays or if a maximum would be observed. These results suggest that long range swelling is in part controlled by CEC, but not in a fashion predicted by DLVO theory.

The smectitic clays in Figure 5 all have charge originating in the octahedral layer but of different origin. The nontronite, SWa-1, has charge originating from Fe^{2+} substitution for Al^{3+} in the crystal lattice, the montmorillonites have charge originating from Mg^{2+} and Fe^{2+} substitution for Al^{3+} in the crystal lattice, while the hectorite (SHCa-1) has charge originating from Li^+ substitution for Mg^{2+} in the crystal lattice. This variability in the atom composition may affect the comparison based on charge. A better test of the effect of charge is to hold clay type constant and vary charge.

Variable charge was accomplished by dithionite reduction of octahedral Fe^{3+} to Fe^{2+} (Lear and Stucki 1985, Stucki *et al* 1984, Lear and Stucki 1989, Khaled and Stucki 1991, Wu *et al* 1989) resulting in a higher 2:1 layer charge (Table 1). Figure 6 shows a comparison of the native and reduced SWy-1 and SWa-1. Little change is observed for SWy-1 while an increase in $Fe(CN)_6^{3-}$ transport is observed on reduction of SWa-1. The differential change in pore structure between clays can be attributed to the total Fe content (SWy-1, 3.35%, vs SWa-1, 35.53%). Reduction of SWa-1 results in a larger change in the layer charge (see estimated values, Table 1).

Our results indicate a larger ratio value for reduced SWa-1 as might be predicted from a charge driven swelling process. However, the data also shows greater variability both in the shape of the swelling curves and in the error bars associated with any given experimental point for both clays. This is consistent with the effects we noted earlier for multi-cationic systems ($K^+ + Na^+$ or $K^+ + Na^+ + Ca^{2+}$). We suggested that such variability was the consequence of multiple swelling domains causing dislocations within the film. A similar effect may be operative here, with variable swelling domains resulting from different domains of Fe reduction. It has previously been shown that reduction of iron results in structural changes (platelet stacks increasing from 4 or 5 in number to 20 to 40 (Shen *et al* 1992)) and in variable stacking domains (as in Figure 1c) which changes the macroporosity of the film (Stucki *et al* 1984, Wu *et al* 1989).

SUMMARY

The uniformity of clay films affects the transport of an anionic electroactive probe. When K^+ or Ca^{2+} or high layer charge is present, internal dislocations in the film, caused by variable stacking domains, enhance the diffusive transport of $Fe(CN)_6^{3-}$ across the clay film.

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