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# Ionic and Molecular Transport in Hydrophobized Montmorillonite Films: An Electrochemical Survey

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Clay-modified electrodes are used to investigate the swelling properties of quaternary ammonium cation-modified Wyoming montmorillonite. Disruption of the structure of the clay was observed at modification rates exceeding 37% of the available exchange sites. Signals for the transport of an anionic pore sampler were attenuated in the presence of the QAC-modified clays. The electrochemistry of nitrobenzene proved the presence of hydrophobic locations within the clay film. Nitrobenzene transport was attenuated by the presence of the clay film but to a lesser extent than the anion, suggesting sorption of the aromatic to the modified clay.

## Introduction

Clay liner modification can be beneficial by reducing diffusion of solutes due to increased sorption (1-9). Batch studies of modified clays indicate that sorption can be enhanced by adding quaternary ammonium head-terminated hydrophobic chains to clays, thus creating more hydrophobic residues within the clay (10-18). Since the overall structure of the clay bed depends upon the shrink/swell behavior of the clay in the presence of water, such modification may also result in pore structure changes, which could increase pressure-driven fluid flow through the bed. There are then two competing trends in tailoring of the clays: enhanced sorption vs increased disruption of the clay structure.

In this study, very thin clay films normally behaving as single particles are prepared with three different quaternary ammonium cations (QAC) at several different coverage levels, none exceeding the cation exchange capacity (CEC) of the clay. The effect of the QAC on the structure of the film and subsequent transport of an anionic (pore sampling) probe molecule is investigated using clay-modified electrodes (19-27) and compared to the effect of the QAC loading on the transport of a hydrophobic probe molecule (nitrobenzene).

## Materials and Methods

Nitrobenzene, NaCl, cetyltrimethylammonium chloride (CTAC), octadecyltrimethylammonium bromide (OTAB), phenyltrimethylammonium chloride (PTAC) (all from Aldrich), and  $\text{Na}_3\text{Fe}(\text{CN})_6$  (City Chemical Corp., New York, NY) were used as received. SWy-1 montmorillonite, purified by Jackson's method (28) (Source Clay Repository, University of Missouri, Columbia, MO) was sodium exchanged (29). Amended montmorillonites containing quaternary ammonium cations were prepared by re-suspending 0.035 g of purified clay in 1 mL of aqueous solution containing  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$ , and  $10^{-2}$  QAC.

The largest concentration of OTAB was  $10^{-3}$  M due to its lower solubility. The cation exchange capacity (CEC) of SWy-1 is 76.4 mequiv/100 g, or a total of 26.7  $\mu\text{mol}$  per solution. The largest total amount of added QAC is 10  $\mu\text{mol}$  (1 mL of  $10^{-2}$  M), producing maximum adsorption of 37% of the exchange capacity of the clay. Loading was limited to no more than 37% because flocculation of the clay suspension was observed at 33% loading, and precipitation was observed at 50% loading. At the maximum of 37% loading, samples were white, soap-like, opaque suspensions.

Scanning electron microscopy was performed on a Stereoscan 240 Scanning electron microscope (Cambridge Instruments, Inc.). Clay films for the SEM were prepared by spin coating onto a thin glass slide.

## Clay-Modified Electrodes and Electrochemistry

A clay gel is prepared as described above, and 1  $\mu\text{L}$  was spin coated onto clean Pt ( $A = 7.5 \times 10^{-3} \text{ cm}^2$ ) or pyrolytic graphite (PG;  $A = 1.8 \times 10^{-2} \text{ cm}^2$ ) encased in glass. Cleaning was accomplished by polishing with 0.05  $\mu\text{m}$  of alumina and sonicating to remove any remaining polishing material. Spin coating creates a lateral arrangement of clay sheets parallel to the electrode surface (Figure 1) (22). Spin coating was accomplished by up-ending the electrode on a PINE Instrument analytical rotator at 1000 rpm for 20 min. The film is checked optically for any cracks, and those with visible cracks are discarded. The dry clay film is 5-7  $\mu\text{m}$  thick as determined by SEM (24). The clay-coated electrode is soaked for 5 min in a supporting electrolyte used to control the interlayer dimensions of the montmorillonite.

SWy-1 clays exposed to  $>0.7$  M NaCl have interlayer dimensions of 5.5-9.5 Å while clays exposed to  $<0.5$  M NaCl have interlayer dimensions of 30-60 Å (30, 31).

The wetted clay-coated electrode is transferred to a solution containing the same electrolyte with the probe molecule ( $2 \times 10^{-3}$  M  $\text{Na}_3\text{Fe}(\text{CN})_6$ ) or 50-250 ppm nitrobenzene (Aldrich) and potential scans are initiated. Cyclic voltammetric measurements were done with a computer-controlled VersaStat potentiostat (EG&G Princeton Applied Research) in a standard three-electrode compartment with a nitrogen purge using a Pt counter-electrode and a saturated calomel electrode (SCE) as a reference. For  $\text{Fe}(\text{CN})_6^{3-}$ , the potential was swept between +0.6 and -0.2 V vs SCE at a scan rate 50 mV/s. This scan rate has been shown to result in a sampling depth less than the width of the clay film (24). Solutions containing nitrobenzene were potentially swept between -0.4 and -1.2 V vs SCE at a scan rate of 50 mV/s.

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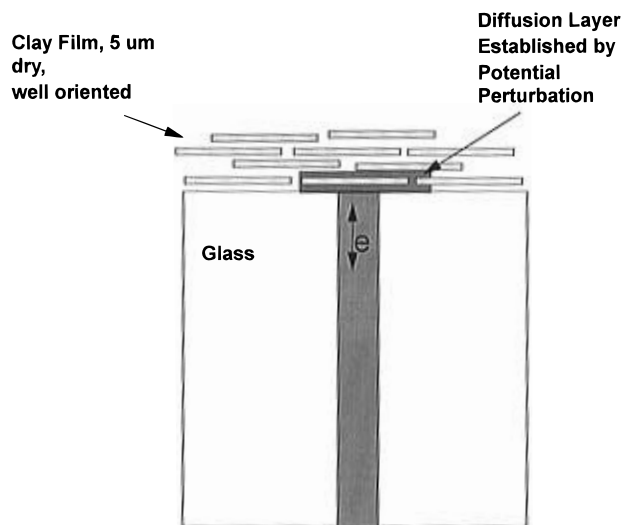


FIGURE 1. Schematic of the clay-modified electrode. Platelets are oriented laterally over the surface. The probe molecule diffuses from the bathing solution through the clay to the sampling volume, which is controlled by the rate of the potential perturbation applied to the electrode surface.

The potential perturbation at the Pt surface reduces the arriving probe molecule and sets up a diffusion layer within the clay film (Figure 1). The sampling volume within the clay film is set by the rate at which the potential is perturbed. The faster the scan rate, the smaller the sampling depth. The current associated with the reduction of the probe molecule as it arrives within the sampling depth is described by the Randles–Sevcik equation:

$$I_p = \text{const } n^{3/2} A D_{\text{soln}}^{1/2} \nu^{1/2} C_{\text{cme}} \quad (1)$$

where  $n$  is the number of electrons transferred,  $A$  is the electrode area ( $\text{cm}^2$ ),  $\nu$  is the rate at which the potential is scanned ( $\text{V/s}$ ),  $D_{\text{cme}}$  is the effective diffusion coefficient within the clay film ( $\text{cm}^2/\text{s}$ ), and  $C_{\text{cme}}$  is the concentration of the probe molecule at that time within that portion of the clay film ( $\text{mol}/\text{cm}^3$ ). The concentration will grow with time as the probe diffuses through the clay film until it reaches a steady-state concentration. The concentration within the clay film is determined by the partitioning of the probe molecule into the clay film:

$$C_{\text{cme}} = \kappa C_{\text{soln}} \quad (2)$$

where  $\kappa$  is the partition coefficient.

The data are reported as the normalized currents. This allows a cross comparison of results obtained at a variety of Pt electrodes and also adjusts for differences in the solution activity coefficients as the electrolyte concentration is varied. The normalized current becomes a function of the partition coefficient and the ratio of the diffusion coefficient within the clay to the diffusion coefficient in solution:

$$R = I_{\text{cme}}/I_{\text{bare}} = (D_{\text{cme}}/D_{\text{soln}})^{1/2} \kappa \quad (3)$$

For the anion  $\text{Fe}(\text{CN})_6^{3-}$ , the normalized current is  $<0.04$  when the clay film is soaked in high NaCl concentrations, suggesting that the only mechanism for transport across the film requires transport at some point through the 5-Å channels. When the film is more fully swollen, the normalized currents for  $\text{Fe}(\text{CN})_6^{3-}$  rise, the jump in the

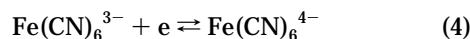
currents coinciding with what Norrish (30, 31) terms the “jumping off” point in the interlayer dimension of the clay film (20, 24, 22, 32). If films are deliberately formed with cracks and pinholes or with nonswelling clays, the observed normalized currents are independent of time and of the salt concentration of the bathing solution (32). Each data point shown is the average of three separate measurements.

These results suggest that the current associated with the anionic probe molecule is affected by the interlayer pore dimension. Since classical double-layer theory predicts a substantial electric field at the edges of the interlayer pore and a diminished electric field at the center (33), it would be expected that the current of the anionic probe molecule will depend upon the negative charge, unless ion pairing is significant in its transport. Recent results indicate that trivalent anions have a larger measured steady-state current as compared to quaternary anions, consistent with a model of ionic transport within the interlayer pores (34).

Cationic and neutral probe behavior is more complicated (Figure 1). In addition to the channel width effects, the electrostatic field can enhance the concentration of the probe molecule (and signal) and shift the potential at which reduction is observed negative. Furthermore, the cation can if sufficiently hydrophobic adsorb to the surface, again with a diagnostic shift in the reduction potential, positive (35–37). The current associated with strongly adsorbed species tends to be much smaller than for that associated with the channel-filling species due to the large reduction in the diffusion coefficient.

## Results and Discussion

The signal for  $\text{Fe}(\text{CN})_6^{3-}$  is generated by its reversible reduction within the diffusion layer near the electrode surface (Figure 1):



The presence of both a reduction peak and an oxidation peak within 60–100 mV apart signals a reversible electron transfer process (Figure 2). The normalized signal magnitude depends upon  $\kappa$ , the partition coefficient, and  $D_{\text{cme}}$ , the diffusion coefficient for the complex within the clay film (eq 3). The small physical pore size due to poor swelling will show up in the  $D_{\text{cme}}$  term while the electric field effects will show up in both  $\kappa$  and  $D_{\text{cme}}$ . For both these terms, one expects exclusion of  $\text{Fe}(\text{CN})_6^{3-}$ . At high bathing salt concentrations, the channel dimensions are low, and little space exists within the center of the channel where the anion may travel in a low electric field. At low bathing salt concentrations, the channel dimensions are large, and the signal for the probe molecule increases between 0.7 and 0.5 M NaCl.

The addition of QAC to the films changes this behavior. Figure 3 shows the change in the probe signal as a function of both the bathing electrolyte and the addition of PTAC, the “chainless” QAC. The swelling behavior of the lower amended clays (0%, 0.037%, and 0.37% of the CEC) is identical. At amendment rates of 3.7%, the increase in the probe signal is still noted at the jumping off point between 0.7 and 0.5 M NaCl, but the magnitude of the signal in the fully swollen regime is 75% of the original signal. The reduction in the signal is either the result of less swelling due to a reduction in the charge of the clay or due to physical impediments from the phenyl side group. A survey of

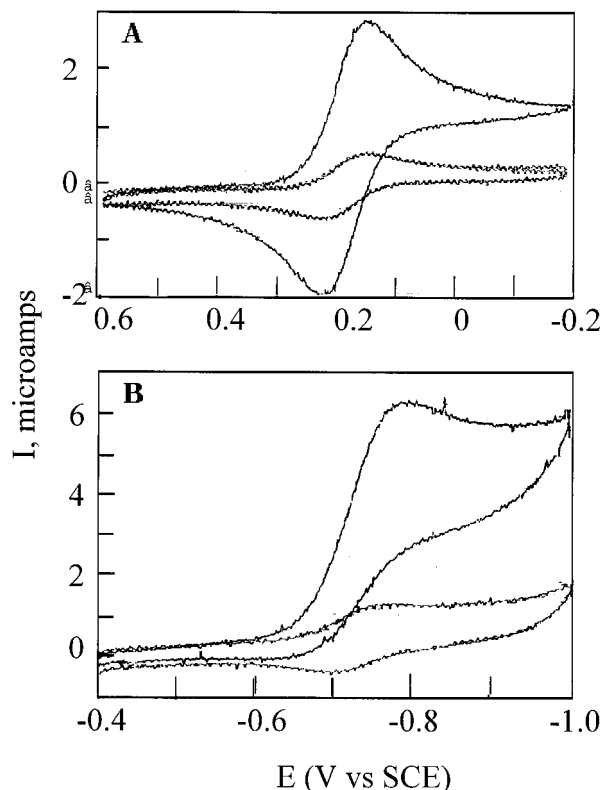


FIGURE 2. Typical cyclic voltammograms obtained for the probes at the bare electrode and a clay-modified electrode. The magnitude of the current is diminished due to the presence of the clay. (A) 3 mM  $\text{Fe}(\text{CN})_6^{3-}$  at a bare and a clay-modified electrode. The smaller signal is at the clay-modified electrode. There are two peaks: one related to the reduction of the probe and one related to its oxidation, indicating a reversible electrode process. (B) 100 ppm nitrobenzene at a bare and at a clay-modified electrode with 37% of the exchange sites occupied by CTAC. The larger signal is at the bare electrode, and the lack of a return or oxidation peak is the result of solvent attack on the anion radical produced during reduction. The smaller signal is at a CTAC-amended clay-modified electrode. Note the return signal.

variably charged clays indicates that very large charge differences are required to change the signal due to swelling (4) so we rule out this possibility.

An estimate of the effect on the volume by the phenyl groups is made by considering the geometry of the carbon bonds and the C–C and C–H bond lengths in the phenyl group. The length of the phenyl group is approximately 5.1 Å. Assuming that the maximum change in the pore dimension occurs with a perpendicular arrangement of the phenyl group, the relative volumes (with and without phenyl group) can be calculated:

$$\left[ \frac{\text{Vol}_{\text{with phenyl}}}{\text{Vol}_{\text{no phenyl}}} \right] = \left[ \frac{l \times w \times (d - 10.2 \text{ Å})}{l \times w \times d} \right] = \left[ \frac{d - 10.8 \text{ Å}}{d} \right] \quad (5)$$

where  $l$  and  $w$  are the lateral dimensions of the platelet, and  $d$  is the distance between plates. An estimate of  $d$  of 60–90 Å can be obtained either from X-ray diffraction (30) or classical double-layer calculations (33). For this estimate of  $d$ , we find that the volume fraction of the original fraction after addition of PTAC to be 0.83, which is in the ballpark of the value obtained.

At an amendment rate of 37.5%, there is no jump in signal between 0.7 and 0.5 M NaCl, and the signal in the presence of dilute NaCl (where the clay is expected to be

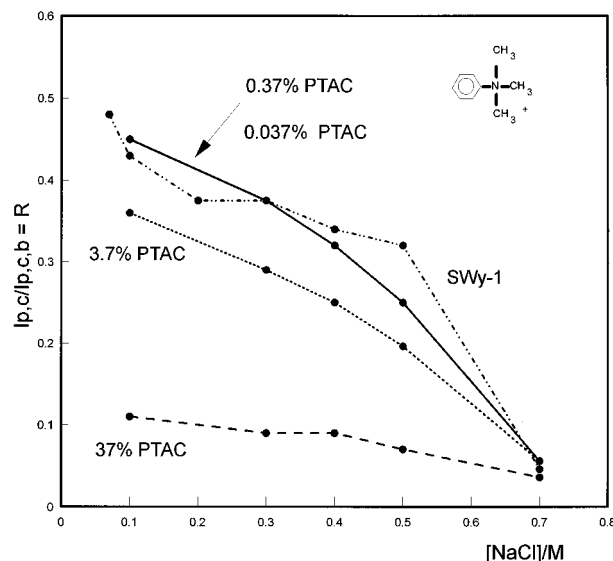


FIGURE 3. Normalized current (clay-modified to bare electrode) for the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  as a function of bathing salt concentration and as a function of PTAC amendment rate as a percent of the available exchange sites.

swollen) is 20% of the signal of the unamended clay. There are three possible explanations for this data. One explanation is that the film does not swell when the charge is reduced to 30% of the native amount. This is consistent with studies showing that the swelling increases with clay charge (up to a point) (32). A second explanation might be that swelling is inhibited by cross linking (38–43). A final and less likely explanation is that the clay does indeed swell to its full extent (60–90 Å) but that the transport of the probe molecule is physically impeded by blockage of the pores by the phenyl groups. Since the maximum extension of the phenyl group was just computed above to be 5.1 Å, the additional exclusion of the probe molecule would be far less than would result in a 80% reduction of the signal. We suggest that at this amendment rate that the reduction in the signal is driven by a reduction in swelling of the clay film. This would imply that PTAC-amended clays would have to have less than 37.5% of the charge sites of the clay in order to avoid structural disruptions in the clay film.

Figure 4 shows the same type of data for the cetyl-treated clays. As for PTAC, no signal for the probe anion is observed in the high salt solution (where no swelling is expected). At lower salt concentrations where the clay is expected to be swollen, there is no change in the probe signal for the slightly amended clays (0.037 and 0.37%) as compared to the untreated clay. As was noted with PTAC, there is a reduction in the signal for the 3.7% amended clay in 0.1 M NaCl. Both the PTAC- and CTAC-treated clays show the same jumping off point for the clay (between 0.7 and 0.5 M NaCl). Amendment of the clay with 37% CTAC resulted in very large signals and was accompanied by noticeable morphological changes as observed by SEM (Figure 5). Since the critical micelle concentration for CTAC is at  $10^{-3}$  M (our 3.7% clay treatment), it is likely that intact micellar adsorption of CTAC occurred on the clay, giving rise to the increased signal.

Data for the longer chain amendment (OTAB) is very similar (Figure 6). The 0.037% and 0.37% treated clays are insulating with respect to the probe molecule at high salt exposure while in dilute salt the film has transport

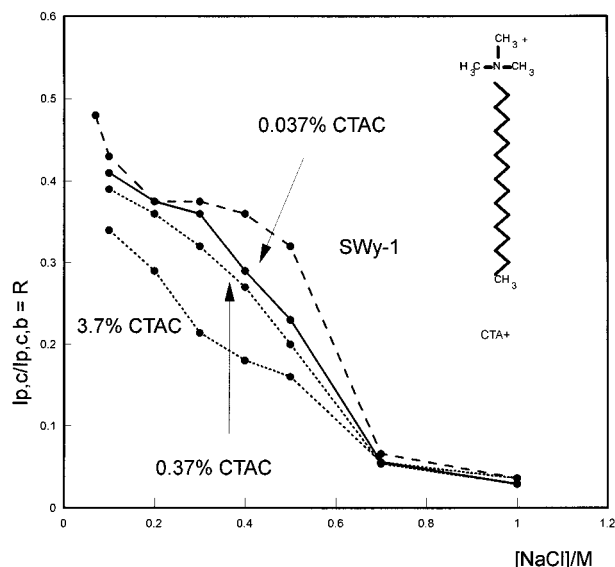


FIGURE 4. Normalized current (clay-modified to bare electrode) for the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  as a function of the bathing salt concentration and as a function of the CTAC amendment rate as a percent of the available exchange sites.

characteristics similar to the untreated clay. The 3.7% treated clay shows the same reduction in the signal already noted for the chainless PTAC and shorter chained CTAC. What is noteworthy about the OTAB is that the jumping off point has been shifted to a region between 0.5 and 0.4 M NaCl, suggesting that the long chain of the OTAB inhibits the expansion of the clay film. This point is illustrated by comparing the normalized currents (ratios) at 0.5 M NaCl as a function of increasing amendment rates (Figure 7). Note that the normalized current for OTAB is much lower than for CTAC and PTAC and is independent of the percent of exchange sites occupied.

The data for the anion probe experiments suggest that the expansion of the clay film is inhibited by increasing amounts of the QAC. When the amendment rate for PTAC reaches 37% of the CEC, little expansion of the film in response to water is noted. However, when the clay is amended with 37% of CTAC, disruption of the film occurs, possibly due to adsorption of intact CTAC micelles. The longer chain length amendments (OTAB) affect the facility with which the swelling of the clay is achieved with the effect most noticeable at the jumping off point (0.5 M NaCl).

Having ascertained the effects of the QAC on the swelling behavior of the clay using the anionic probe, we next address the issue of the ability of the QAC amendments to retain a hydrophobic probe molecule, nitrobenzene. For this molecule, the electrochemistry can provide supporting evidence as to the degree of hydrophobicity. The nitrobenzene reduction follows the following sequence where R is the benzene portion of the molecule (44, 45):



In an aqueous solution, the first step of this reaction normally is observed as an irreversible electron transfer event in which the electron is inserted and followed by the addition of a proton before the re-oxidation can be observed. The anion radical produced on reduction is attacked by water. In a nonaqueous environment, it is possible to

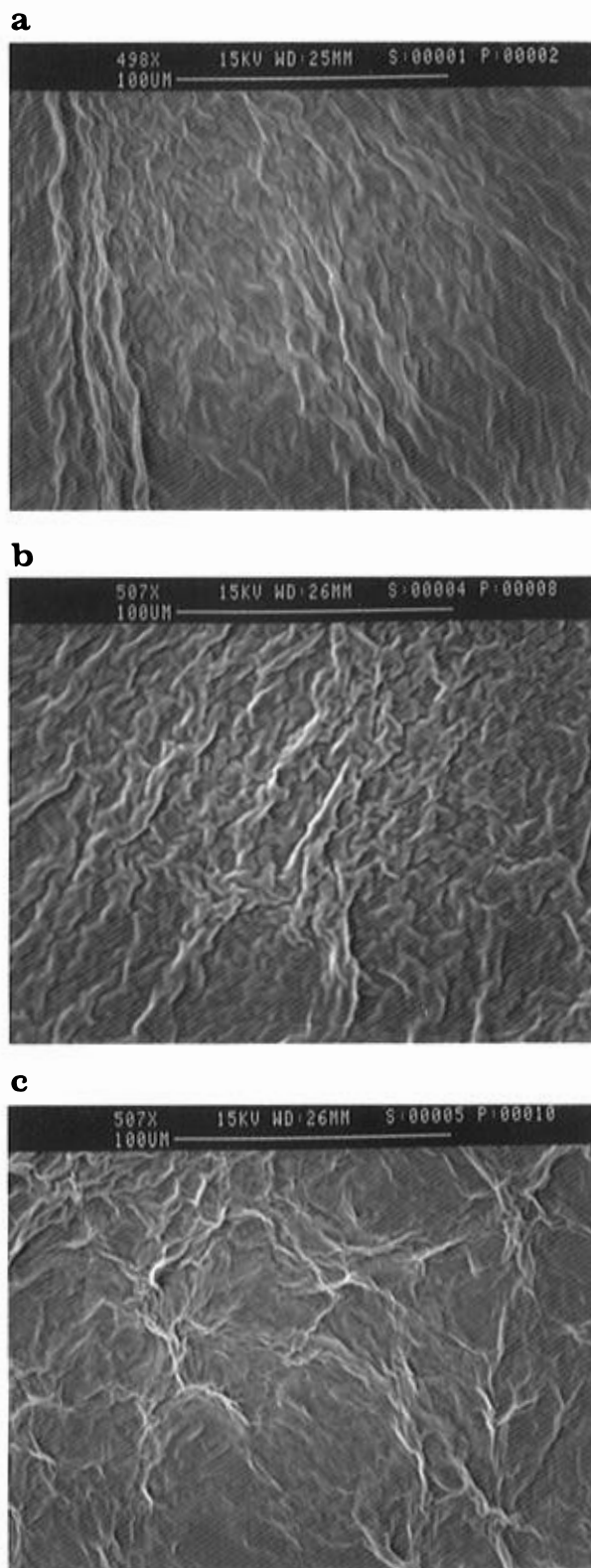
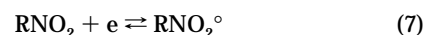


FIGURE 5. Scanning electromicrographs of the surface of SWy-1 amended with (a) 0%, (b) 3.75%, and (c) 37.5% CTAC.

observe the anion radical formed on reduction:



The observation of the re-oxidation of the nitrobenzene thus becomes a measure of the water content present. Cyclic voltammograms obtained at the bare electrode (Figure 2B) and at the untreated clay, fully swollen in dilute NaCl, both lack a well-defined return oxidation peak. The loss of the

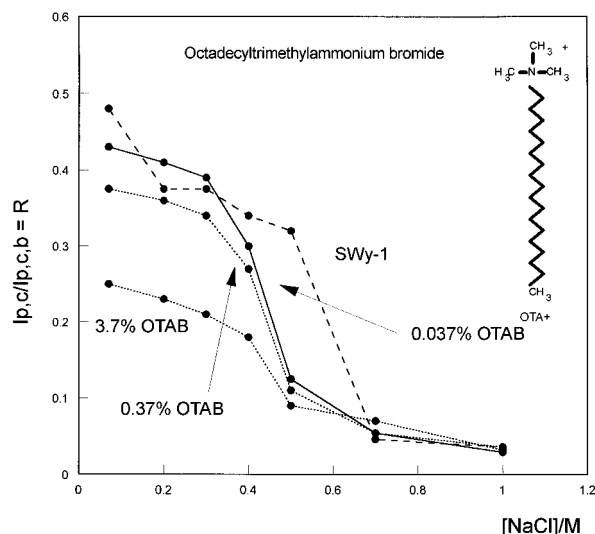


FIGURE 6. Normalized current (clay-modified to bare electrode) for the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  as a function of the bathing salt concentration and as a function of the OTAB amendment rate as a percent of the available exchange sites.

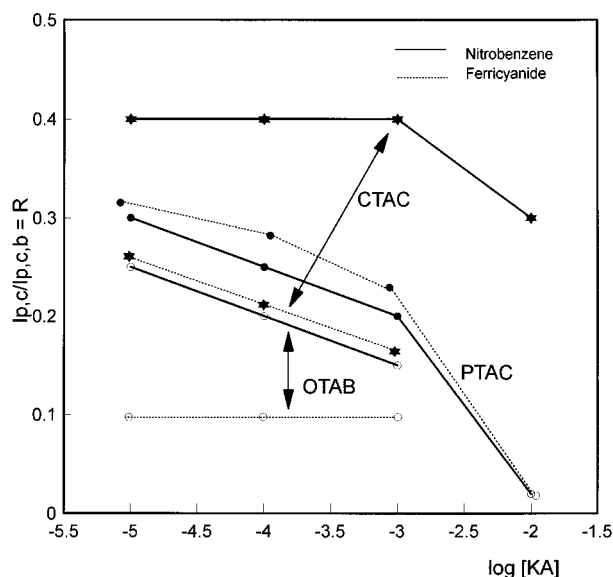


FIGURE 7. Normalized currents for  $\text{Fe}(\text{CN})_6^{3-}$  and nitrobenzene in clay-modified electrodes exposed to 0.5 M NaCl as a function of amendment rate and amendment type.

return peak is particularly noticeable at the unamended clay electrode. In a CTAC film (37% available exchange sites occupied), the signal observed is much smaller, consistent with impeded diffusion; however, more importantly, the symmetry of the reversible electrochemistry is observed, consistent with the change in the film to a fully hydrophobized system. It is possible that indication of hydrophobicity simply reflects the possibility of adsorption of intact CTAC micelles.

As noted above, the effects of the surfactant are manifested most greatly in the regime of 0.5 M NaCl. In Figure 7, the effect of increasing surfactant on the normalized current ratios for 100 ppm nitrobenzene are shown. The results are similar for  $\text{Fe}(\text{CN})_6^{3-}$  and nitrobenzene when the clay is amended with PTAC, suggesting that any reduction in the signal as compared to the unamended clay is due to changes in pore volume. However, when the clay is amended with CTAC or OTAB, the signal for nitrobenzene is larger than that for  $\text{Fe}(\text{CN})_6^{3-}$ . The

normalized current depends upon the relative clay diffusion coefficient to bulk solution diffusion coefficient (which is volume dependent) and upon the partition coefficient (eq 3). Unless pinholes have developed at these low amendment rates, the accessible pore volumes can only decrease, not increase. Consequently, the most likely explanation for the increase in the nitrobenzene signals is an increase in concentration of nitrobenzene within the clay film (sorption), which would be reflected in an increase in the partition coefficient. These results are in agreement with other observations of interlamellar adsorption of nitrobenzene in hexadecylammonium-modified layer silicates (46).

## Acknowledgments

This work was supported by U.S. EPA Grant R819598-01-0.

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*Received for review September 29, 1995. Revised manuscript received April 26, 1996. Accepted May 20, 1996.*<sup>®</sup>

ES950728T

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, July 15, 1996.