



Review

Leashed ferrocenes at clay surfaces: potential applications for environmental catalysis

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Abstract

The surfaces of clays are highly reactive and are known to catalyze a range of reactions. Clay surface catalysis has been implicated in the in situ remediation of many organic compounds in the environment. The exact mechanism for catalysis is not yet well understood but crystal lattice iron redox reactions have been implicated. Understanding the reduction of clay crystal lattice iron depends upon the ability to reproducibly and reversibly deliver charge to the interlayer sites of the clay. This study uses ferrocene surfactants as a means to deliver charge to the interlayer of well ordered clay films. Ferrocenyl surfactants are shown to deliver charge to crystal lattice iron dependent upon the chain length of the surfactant. Nanocomposites formed from ferrocenyl surfactants and clay exhibit increased capacitance, also dependent upon the chain length of the surfactant.

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1. Introduction

Catalytic reactions can occur at both industrially important surfaces and in nature. In this paper, we attempt to intrigue a variety of experts in the field of catalysis with an important reaction involving clays in environmental settings.

Interesting (and catalytic) nanocomposites can be formed by controlled mixing of clay and organic reagents. Environmental applications demand use in a larger and less controlled environment. Clays are known to be the active mineral component of soil and subsequently influence greatly the movement of cations, anions, metals, and organics in the environ-

ment [1]. The environmental movement and sorption of cations are greatly influenced by smectite clays [2].

Natural and synthetic clays have been widely employed both as inert matrices and as active participants in reactions. The unique ability of clay to provide a useful matrix and to participate in reactions has been exploited in industrial domains. Specifically, modified clays have been used as catalysts for various synthetic processes including Diels-Alder reactions [3], polymerization of olefins [4], and reactions of hydroxymethylferrocenes with acids [5]. Several patents have outlined Fe-exchanged silicate matrices as catalysts to reduce NO_x car emissions [6,7]. In another application, sensors for trace detection have found increased sensitivity following preconcentration of analytes within a clay film [8,9]. Choy et al. recently outlined a novel process utilizing synthetic clays as carriers for gene therapy in leukemia cells with dramatic decreases in subsequent tumor growth [10].

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Because of the high natural occurrence of clays in soils, environmental applications of clay technology are especially attractive and provide results at relatively low cost. Modified silicates have been shown to be effective sorbents for organic pollutants such as chlorophenol and benzene [11,12], toluene and aniline [13], trichloroethylene [14], and hydrophobic herbicides [15]. These organoclays can be utilized in landfills, which are often lined with clay composites, to retard the breakthrough of organic contaminants into groundwater [16,17]. Traditional unmodified clay liners have been shown to have leakage problems in a matter of years [18]. In some cases, in situ remediation of polluted soils takes place by injecting surfactants to intercept toxins [19]. Heavy metals such as Pb, Hg, Zn, [20] and Cu [21] can also be trapped within a modified clay structure and removed from water. For a useful review of the use of organoclays in the environment, see Xu et al. [22].

Utilizing the ability of clay itself to be electrochemically active, toxic substances like nitrobenzene [23], carbon tetrachloride [24], trichloroethane [25], pentachloroethane [26], and chromium [27] can be reduced to a less toxic state via electron donation from metal sites within the clay matrix. However,

understanding of the specific conditions under which these types of electron transfer reactions take place is murky at best and additional basic research is needed. We, here particularly call the attention of physical chemists working in the area of aqueous interfacial reactions to this important area of research.

The structure of clay is important in determining the electrochemical activity of the iron within the crystal lattice. A layer is composed of one or two tetrahedral sheet(s) and one octahedral sheet bonded together by the sharing of lateral oxygen atoms (Fig. 1). Clays with one silicate and one aluminate sheet are termed 1:1 clays. Likewise, clays with one aluminate sheet sandwiched by two silicate sheets are 2:1 layer clays. Native clays are generally anionic due to isomorphous substitution of Si^{4+} and Al^{3+} with lower valence ions of similar size due to chemical alterations caused by weathering of the parent silicate material [1]. Because of the negative charge, cations are attracted to the surface of the layers and sit in the hexagonal cavities created by the shared oxygens. These cations may be exchanged for new ones, leading to a distinguishing feature of clays termed “cation exchange capacity” (CEC, in milliequivalents (meq) of charge/100 g).

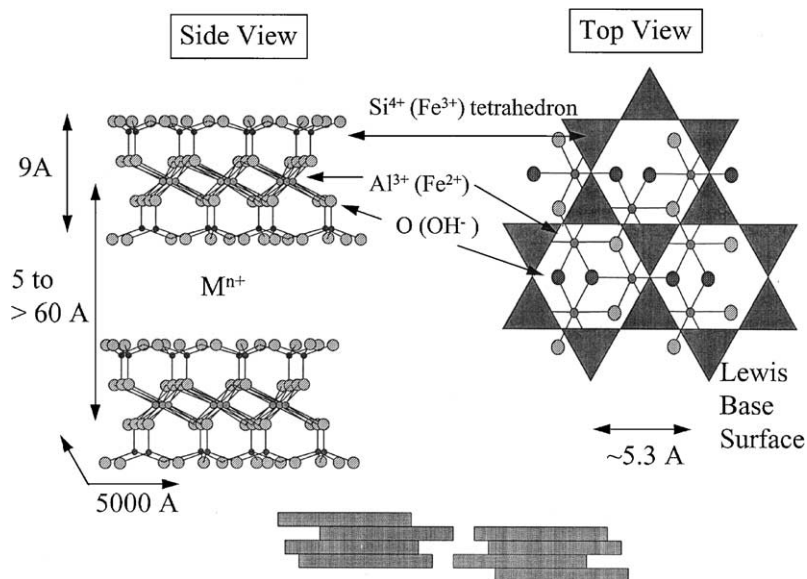


Fig. 1. Diagram of 2:1 layer clay minerals. The side view illustrates the two layers of silicon tetrahedron sandwiching the aluminum octahedron. The top view illustrates ditrigonal holes on clay surface.

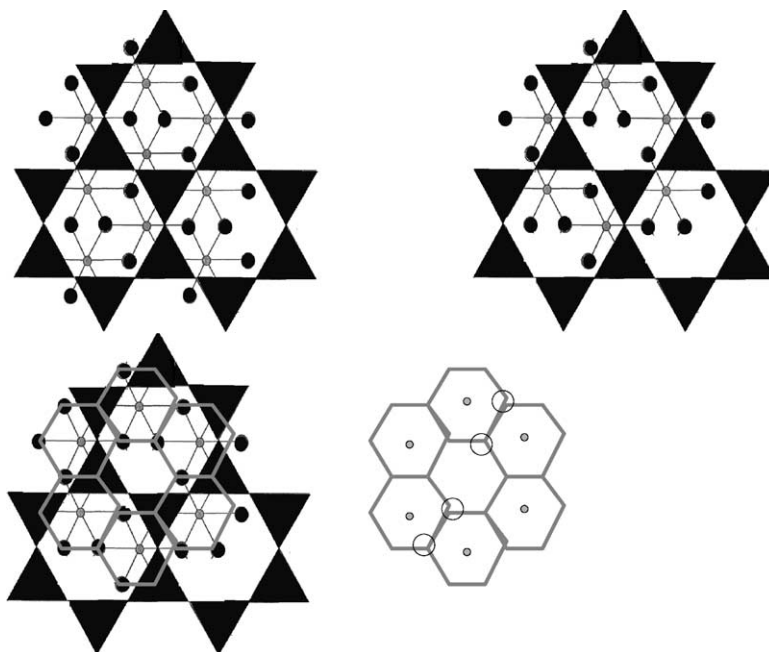


Fig. 2. (Upper left) Trioctahedral clay; (upper right) dioctahedral clay. (Lower left) Hexagonal structure of oxygen and hydroxyl ligands of the octahedral layer. (Lower right) Arrangement of filled and vacant octahedral site in the octahedral layer of the clay sheet.

Clays are characterized as dioctahedral, with two of the possible three octahedral sites filled or trioctahedral, with all three sites filled (Fig. 2). Standard Wyoming (SWy-1) montmorillonite, the clay used in this study, is a 2:1 dioctahedral clay. Substitution of iron and magnesium for aluminum in the octahedral layer results in net negative charge of the clay crystal. SWy-1 has the formula $(\text{Al}_{1.94}\text{Fe}_{0.35}\text{Mg}_{0.58})\text{Si}_8$ and a CEC of 76.4 meq/100 g [28]. The net negative charge of the clay is compensated by counter ions. Depending upon the hydration energy of the counter ion, its concentration, and the clay charge, clay will swell during the intercalation process.

Intercalation of water into the interlayer region of montmorillonite results in swelling of the clay layers, a phenomenon measured by X-ray diffraction as early as 1954 by Norrish [29]. The initial swelling, which includes the first four monolayers of water, results from the hydration sphere of the ions present. This swelling expands the interlayer from 5 to ~ 20 Å. After this initial swelling, more water can enter via osmotic forces driven by the concentration gradient, and the distance between layers can expand to 30–60 Å [30].

Montmorillonite is one of the most highly swelling clays known and has recently been suggested for use as thermal energy storage by Sadek and Mekhamer based on this unique ability [31].

The high swelling capacity of Wyoming montmorillonite may be related to its relative ease of reduction of crystal lattice iron by chemical reagents. Iron substitution within smectites affects the charge of clays and their ability to retain environmental pollutants. Generally, the intercalant is oxidized while the structural Fe(III) is reduced. These spontaneous electrochemical reactions are often accompanied by vibrant color changes [32]. Various other physical and chemical properties are, in part, determined by iron concentration and oxidation state. For example, iron oxidation state influences swelling behavior and specific surface area. Reduction of Fe(III) to Fe(II) decreases swelling [33]. Swelling behavior has obvious effects on transport of nutrients and pollutants in the environment [2,34].

Since iron is electrochemically active, it can be tuned to a specific oxidation state. For environmentally realistic applications, the process of reducing

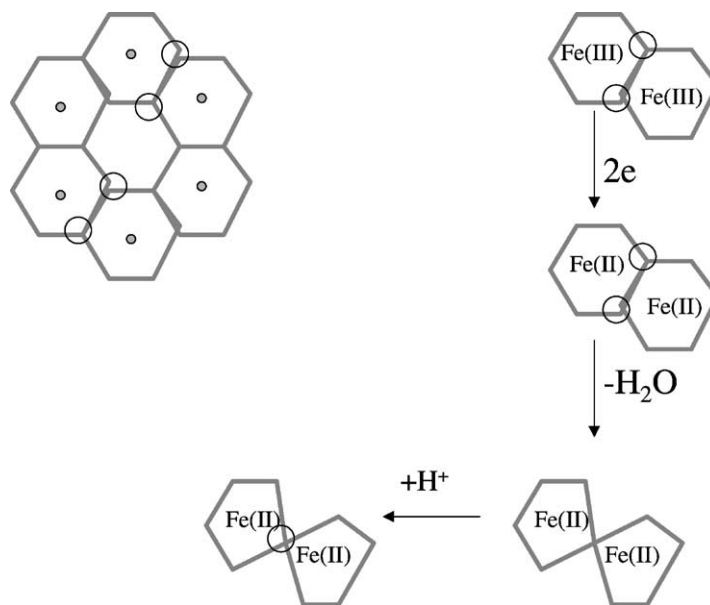


Fig. 3. Reaction mechanism proposed by Stucki for the reduction of octahedral Fe(III) to Fe(II). Electron transfer to the iron is followed by loss of water from two adjacent hydroxyls followed by protonation of the remaining oxygen.

and oxidizing iron must be an understandable and reversible process, and structural changes that take place in the clay lattice upon oxidation–reduction elucidated.

Two general theories have been proposed for the reduction of high iron containing nontronite clay by simple chemical reagents. The early theory put forth by Stucki and co-workers [35] suggested that two iron sites in the dioctahedral clay were reduced and two associated hydroxyl groups were lost as water to form two five coordinate sites as opposed to two six coordinate sites within the octahedral lattice (Fig. 3). More recent work suggests that Fe(II) in the crystal lattice of clay maintains a six coordinate number, suggesting a more complex reaction for the reduction of iron which involves migration of iron to the vacant sites in the dioctahedral lattice [36]. Both theories suggest that there will be a structural barrier to reduction of the lattice iron.

In the natural environment, montmorillonite clay is ubiquitous and serves as the surface for a wide variety of reactions. Although the body of literature on oxidation–reduction reactions of structural Fe in the clay is growing, little has been done with lower charged smectites, i.e. montmorillonites. As the amount of iron

in montmorillonites is low, many of the conventional means to study oxidation state, namely UV-Vis and Mössbauer spectroscopy, must be adjusted or scrapped altogether. The oxidation state of the iron must then become an indirect measurement, and attention shifts to the oxidation state of the intercalant.

The study of oxidation–reduction of clays requires a charge delivery method. The reagent dithionite is used to reduce iron containing clays so that these materials, in turn, can serve as electron source for environmental reactions in contaminate degradation. Dithionite, however, is destroyed in the reaction and can neither be used to reversibly cycle charge to the active iron sites nor to fully interrogate the reaction mechanism. An alternative delivery mechanism of charge to the crystal lattice iron is desirable. We have chosen ferrocene based both on its potential and size. The approximate size of the clay ditrigonal hole is 5 Å. The ferrocene C–C bond is ~1.44 Å and the Fe–ring bond distance is 2.06 Å [37] suggesting that ferrocene should be able to penetrate the ditrigonal hole in the octahedral lattice. Such penetration may allow ferrocene to access the iron sites lying beneath the ditrigonal hole in the octahedral lattice. A problem with ferrocene alone as a charge delivery reagent is the fact that it is sparingly water soluble and

unlikely to adsorb to clays. Attaching the ferrocene to a cationic functional group should aid in delivering the electroactive group into the clay. Such attachment is also designed to overcome an additional problem.

One problem that must be addressed is the potential electrochemical activity of the intercalated ferrocene group. Unfortunately, previous studies have shown that electroactive compounds are either weakly held and easily washed out or are adsorbed to the surface of the clay in a way which precludes their participation in electroactive processes [38–40]. In order to tether electroactive groups in the clay matrix and yet avoid their deactivation, we propose the use of an electroactive surfactant. It is anticipated that distancing the electroactive group from the surface will enhance its freedom to participate in electroactive processes by imparting translational and rotational mobility to the complex and by lifting the complex away from the charged clay surface (Fig. 4). In order for this strategy to be successful, the electroactive group should be anchored to the clay surface, but this anchoring process should not alter clay swelling. Clay swelling can be disrupted in several ways, including alteration of the water content affecting the interlayer distance, changes of charge on the clay surface, and the physical disruption of the clay interlayer space by the presence of a polymer chain, resulting in a hydrophobic environment between the clay sheets. One further criterion for the surfactants is careful choice of aliphatic spacer length (Fig. 5). Spacer length controls whether or not

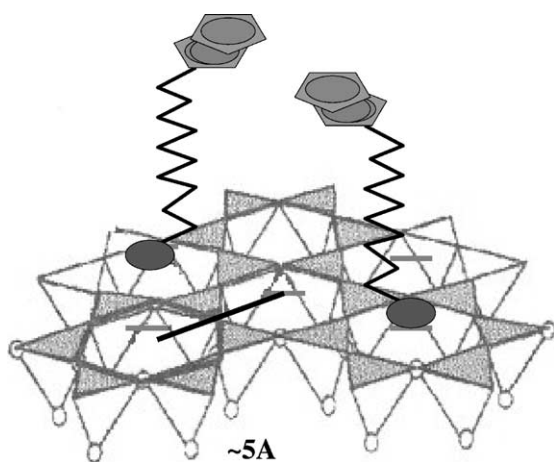


Fig. 4. Ammonium head group attachment to ditrigonal holes of clay surfaces.

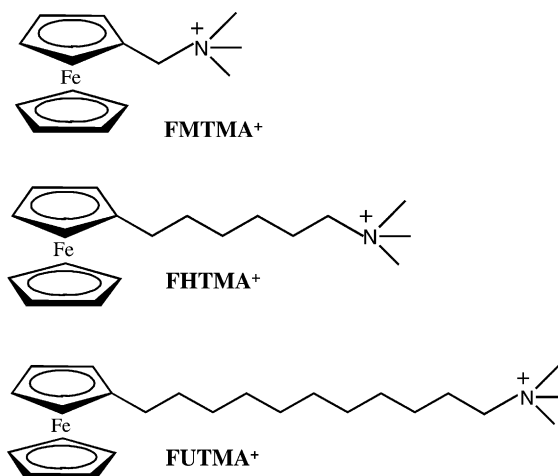


Fig. 5. The compounds studied include ferrocene; (ferrocenylmethyl)trimethylammonium (FMTMA⁺) chloride; (ferrocenylhexyl)trimethylammonium (FHTMA⁺) bromide; and (ferrocenylundecyl)trimethylammonium (FUTMA⁺) bromide.

the electroactive group will interact with neighboring groups or lie flat on the surface of the clay, thereby altering electron transfer to clay octahedral Fe(III) in bulk suspension.

Fig. 5 illustrates three different compounds used to modify the interlayer environment in this study. They consist of (ferrocenylmethyl)trimethylammonium (FMTMA⁺) chloride, (ferrocenylhexyl)trimethylammonium (FHTMA⁺) bromide, and (ferrocenylundecyl)trimethylammonium (FUTMA⁺) bromide. The chemistry of FMTMA⁺ [41] and FUTMA⁺ [42–49] have been reviewed extensively in the literature. Within each compound, an ammonium head group acts as an anchor and ferrocene as the electroactive tail group. The ammonium head group was chosen because it has been previously demonstrated that ammonium head groups are fixed within the ditrigonal hole of the clay surface, resulting in irreversible anchoring of the head group [30,50]. Ferrocene was selected because it is a well-understood electroactive group that undergoes a facile one-electron transfer [51–53]. In addition, the oxidation–reduction potential of the ferrocene group can be modulated via attached substituents until electron transfer reactions with Fe(III) in the clay lattice are thermodynamically viable.

The main variable in this study is the chain length of the compound. Not only will the length affect

where the electroactive group resides in relation to the clay, but it will also affect the rate of penetration of the compound within the clay. It has been demonstrated that length of the aliphatic chain affects the hydrophobicity–hydrophilicity of the clay interlayer. Furthermore, the length of the chain affects the orientation of the compound at the clay surface group [30,54,55] and positioning of the ferrocene. Gallardo et al. work indicates that the orientation of the ferrocene group at the air–water interface is strongly directed by the aliphatic chain length [44]. It is anticipated that such chain length dependent orientation effects may be operative at the clay–water interface.

For the goal of electron transfer between ferrocene groups and clay structural Fe(III) in bulk suspension, the ferrocene group must sit inside the hexagonal cavity of the clay, thus allowing direct access to the underlying Fe(III) in the octahedral layer.

2. Methods

All chemicals were used as received from Aldrich without further purification unless otherwise specified. Water used was purified and deionized to 18 M Ω cm resistance (Barnstead Nanopure II). Clays were obtained from the source Clay Repository (University of Missouri, Columbia, MO), purified, and Na⁺-exchanged as described elsewhere [56]. Suspensions were prepared by diluting 10 g purified clay with 1 l deionized water.

The surfactants were synthesized by a modification of the methods of Saji et al. [48] and Macha [57]. Modification is described elsewhere Swearingen et al. [58]. The compounds were identified by use of UV-Vis, NMR, and mass analysis.

2.1. (Ferrocenylundecyl)trimethylammonium (FUTMA⁺) bromide

The product was confirmed by ¹H NMR and UV-Vis. ¹H NMR [ppm (peak splitting, number of protons, assignment)]: 4.07 (singlet, 5H, unsubstituted ferrocene ring), 4.02 (doublet, 4H, substituted ferrocene ring), 3.52 (triplet, 2H, CH₂- α -N), 3.42 (singlet, 9H, CH₃- α -N), 2.59 (singlet, solvent impurity), 2.28 (triplet, 2H, CH₂-ferrocene), 1.73 (singlet, water impurity) 1.46 (triplet, 2H, CH₂- β -N), 1.30

(multiplet, 16H, CH₂-alkyl chain). UV-Vis (region 400–900): λ_{\max} = 439 nm.

2.2. (Ferrocenylhexyl)trimethylammonium bromide (FHTMA⁺)

¹H NMR and UV-Vis confirmed the product. ¹H NMR [ppm (peak splitting, number of protons, assignment)]: 4.15 (singlet, 5H, unsubstituted ferrocene ring), 4.10 (singlet, 4H, substituted ferrocene ring), 3.55 (triplet, 2H, CH₂- α -N), 3.43 (singlet, 9H, CH₃- α -N), 2.28 (triplet, 2H, CH₂- α -ferrocene), 1.80 (singlet, water impurity), 1.71 (multiplet, 2H, CH₂- β -N), 1.41 (multiplet, 6H, CH₂-alkyl chain). UV-Vis (region 400–900): λ_{\max} = 437 nm.

Standard electrochemical methods were used as described by Swearingen et al. [58].

Bulk aqueous composites of ferrocenyl surfactants and clay were prepared by weighing out appropriate amounts of surfactant and clay and diluting with deionized water. Amount of surfactant was determined as percentage of CEC of the clay, ranging from 5 to 100%. Clay was prepared as 10 g/l suspensions.

In order to perform DRIFT analysis, an FUTMA⁺–SWy-1 slurry was dried down until only a solid remained and placed into the sample holder of a Nicolet Nexus 870 FT-IR. Spectra were run with gold as the background under N_{2(g)}-purge. For reference, spectra were also taken for SWy-1 and FUTMA⁺. The spectrum for SWy-1 was subtracted from the FUTMA⁺–SWy-1 spectra in order to obtain the shifts for FUTMA⁺. DRIFT work performed at Argonne National Labs.

3. Results

Preliminary visual studies of ferrocene with clay gels suggests that ferrocene and FHTMA⁺ do not react with SWy-1 clay, while the longer chain surfactants ferrocene do react with the clay (Fig. 6). The color produced by the reaction can be due to either the ferrocene or ferrocenium conversion or Fe(III) to Fe(II) conversion of the clay. Spectroelectrochemistry shows that ferrocene has an absorption band at 630 nm which disappears upon reduction (Fig. 7). Nontronite clay (similar dioctahedral structure as SWy-1, but with a large increase in Fe content (2.73 atoms per unit cell

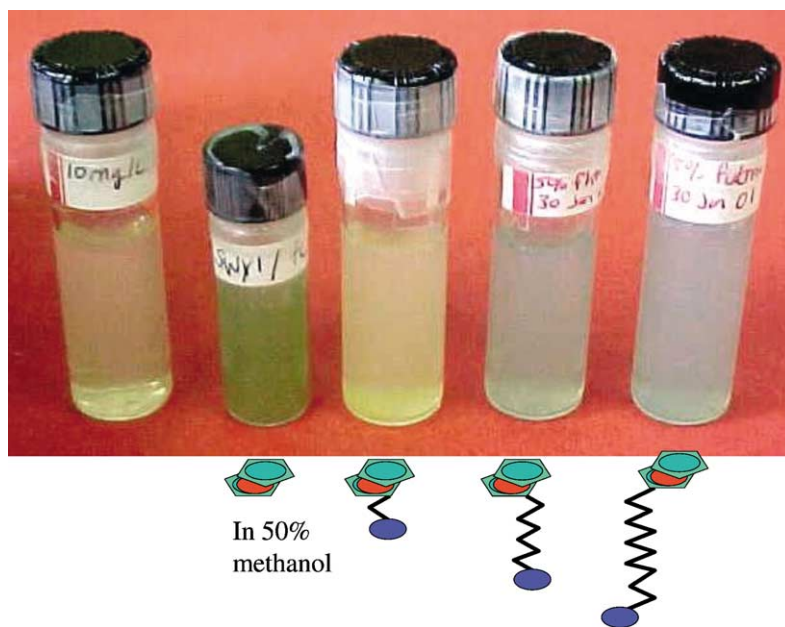


Fig. 6. Reaction of clay suspensions with the four reagents causes some, but not all, of the compounds to react as can be determined from the color of the resulting suspensions.

versus 0.35 atoms per unit cell for SWy-1 [28]) has an intervalence charge transfer at 730–750 nm causing a yellow green to blue green color of nontronite clay. This band is so weak in Wyoming montmorillonite that its absorbance change can not be monitored. To determine the source of the color conversion Mössbauer, DRIFT, and UV-Vis experiments were performed. Reliable Mössbauer spectra could not be obtained because of the weak absorption due to the low number of active sites within the SWy-1 clay. DRIFT data suggest that the ferrocene tail group in FUTMA⁺ has under-

gone oxidation, as can be particularly noted from the 478 cm⁻¹ band tracking the Fe–C_p stretch (Table 1). UV-Vis data also confirms that the 630 nm band associated with ferrocene disappears when clay reacts with the surfactant FUTMA⁺.

Two hypotheses present themselves for the mechanism of the reaction of the ferrocenyl surfactants with the clay. The first reaction mechanism [59] is based on the fact that the rate of ferrocene to ferrocenium conversion can be altered by solution conditions. In a high acid environment, a proton attaches itself to

Table 1
Major IR bands in cm⁻¹

Ferrocene [65]	FUTMA ⁺	Ferrocenium ([65], p. 150)	FUTMA ⁺ /SWy-1	Assignment
3077	3096	3108	3118	C–H stretch
1410	1408	1421	1418	C–C stretch
1100	1103	1116	1112	C–C stretch
1005	998	1017	–	C–H deform.
855	856	860	–	C–H
820	819	805	–	C–H
492	–	501	493	Ring tilt
478	485	423	419	Fe–C _p stretch

When not listed, bands are obscured and could not be determined. FUTMA⁺ present at 33% CEC of 10 g/L SWy-1.

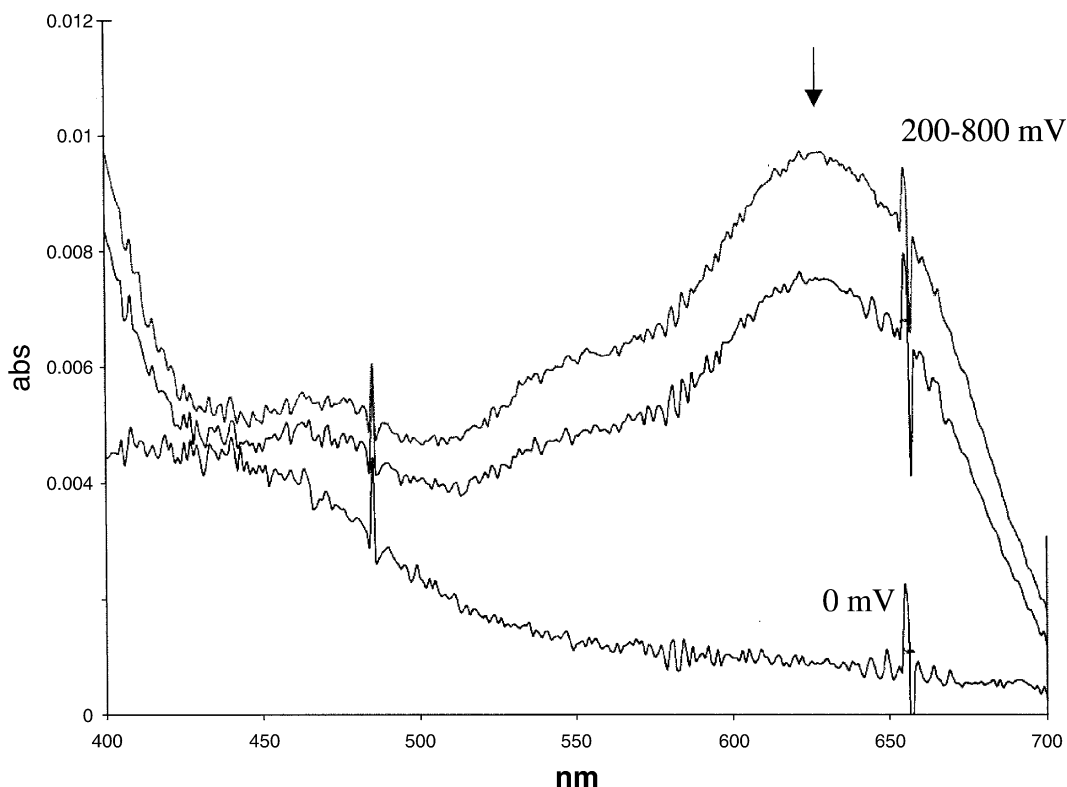


Fig. 7. Spectroelectrochemistry of ferrocene indicates that when ferrocene is oxidized as ferrocenium there is an absorption band at 630 nm. Reduction of the ferrocene causes removal of the 630 nm band and development of a broad peak at around 450 nm.

Fe(II) of ferrocene causing the rings to distort. This allows access of oxygen and the formation of the hydroperoxyl reactive intermediate. As the surface acidity of sodium exchanged Wyoming montmorillonite is quite high (pH 1.5–3.0) [60,61], it is possible that the reaction of ferrocene with the clay is not driven by the iron centers in the octahedral lattice but by the local proton concentration.

In order to ascertain which mechanism is correct we measured the potentials associated for the oxidation of the ferrocenyl surfactants and compared these potentials to the two different possible electron acceptors (oxygen and clay). The four different ferrocene materials have very different potentials due to the competing electron withdrawing effects of the ammonium head group and the electron donating effects of the aliphatic chain. FMTMA⁺ has a single carbon spacer between the ferrocene ring and the ammonium head group and, consequently, has a potential shifted posi-

tive (harder to oxidize) from ferrocene. The long chain surfactants each have potentials shifted negative (easier to oxidize) due to the electron donating effect of the chain. These electrochemically derived potentials are accompanied by shifts in peaks in the NMR (Figs. 8 and 9) and in UV-Vis spectra of the compounds.

If we examine the various potentials involved in the formation of the hydroperoxyl radical for the four different ferrocene compounds, it is clear that all of the reactions are uphill, suggesting that none should proceed. FMTMA⁺ ($E^{\circ} = 0.39 \pm 0.001$ V), FUTMA⁺ ($E^{\circ} = 0.15 \pm 0.005$ V) and FHTMA⁺ ($E^{\circ} = 0.05 \pm 0.001$ V) are all negative with respect to the reaction forming the hydroperoxyl species (-0.29 V). However, since the hydroperoxyl radical is an unstable intermediate in H₂O₂ production [62], the net reaction of oxygen to water is thermodynamically feasible for all four compounds. This indicates that this mechanism, by itself, is not capable of explaining

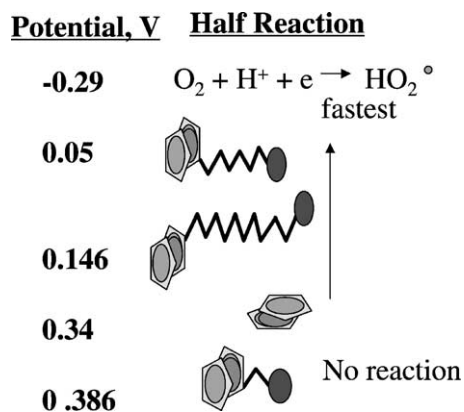


Fig. 8. A potential diagram of the four possible electron donors with respect to the half reaction of oxygen to the radical HO_2° . FHTMA does not react. The reaction is fastest for FHTMA.

why ferrocene and $FMTMA^+$ fail to react with the clay while $FHTMA^+$ and $FUTMA^+$ do react.

The alternative model for compound–clay reaction is that the ferrocene is donating electrons to the octahedral iron of the clay. The estimated potential of the octahedral Fe(III) in clay is 0.2 V versus SCE [63]. This potential is shifted negatively from that of Fe(III) in solution (0.53 V) because of the electron withdrawing effects of the oxygen ligands, causing Fe(III) in the clay crystal lattice to be easier to reduce than Fe(III) in solution. Assuming that the ferrocene species are

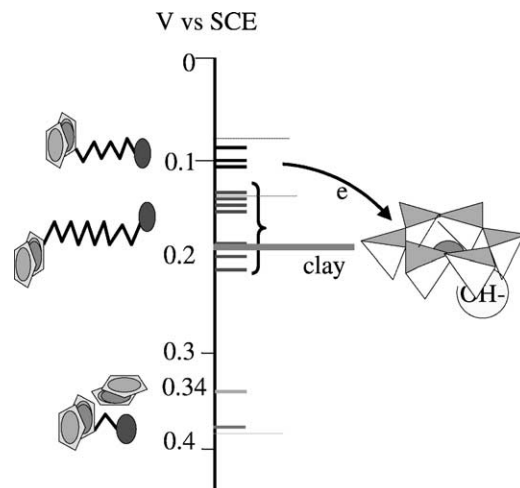


Fig. 10. Redox potentials of surfactants in the clay; the clay and surfactants in solution (dashed lines).

electron donors and the iron in the clay crystal lattice is the electron acceptor, the reactions should be thermodynamically feasible for $FHTMA^+$ and $FUTMA^+$ but not for ferrocene or $FMTMA^+$, consistent with the observed results (Fig. 10).

The potentials of the compounds determined at the bare electrode, however, may not accurately describe the potential of the compound that has been stabilized within the negatively charged clay film. It has been

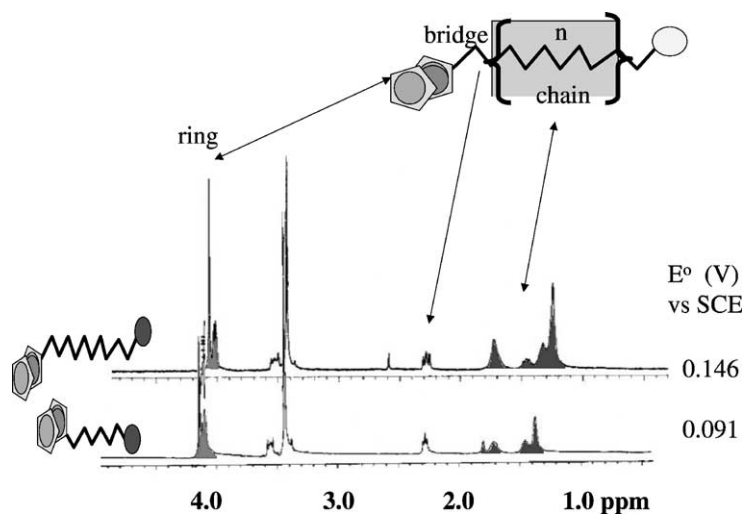


Fig. 9. The measured redox potentials of the compounds are accompanied by characteristic shifts in the NMR structure indicating greater electron donation into the ring by the $FUTMA$ compound.

shown elsewhere that when a cationic compound is stabilized within a negatively charged film by purely long range electrostatic effects the potential of the intercalated compound should shift negative.

$$\Delta E = E_{\text{clay}}^{\circ} - E_{\text{soln}}^{\circ} = \frac{RT}{nF} \ln \frac{K_{\text{I}}}{K_{\text{II}}} - \frac{RT}{nF} \ln [X\text{Na}] - \frac{RT}{nF} \ln \frac{1}{[\text{Na}^+]} \quad (1)$$

In Eq. (1), R is the natural gas constant, F the Faraday constant, T the temperature, n the number of electrons involved in the oxidation–reduction process, $X\text{Na}$ represents the clay exchange (X) sites occupied by sodium. ΔE° is the difference in the formal potentials for the compound of interest measured from solution (bare electrode) and at the clay-modified electrode. K_{I} and K_{II} are the exchange constants for the oxidized and reduced forms of the complex. The magnitude of K_{I} and K_{II} depend upon the charge of the intercalant and the charge associated with the clay surface. Eq. (1) indicates that the potential difference observed is a function of the relative stabilization of the oxidized versus the reduced forms of the compound within the clay, the extent of the ion exchange reaction, and the concentration of sodium in the bathing solution.

In order for this equation to be applicable the oxidizable group should reside within the Debye length of the clay. This would ensure that the electroactive group oxidation state would be influenced by the clay surface potential. Assuming that the surfactant chains were fully extended the distance of the electroactive tail group from the clay can be estimated as shown in Table 2. The potential experienced by the electroactive tail group was then calculated from the charge on the clay and the surface area of the clay using standard equations for the double layer:

$$\frac{\text{meq}}{\text{g}} = 1.0365 \times 10^{-2} \sigma S_{\text{m}} \quad (2)$$

Table 2
Estimated chain lengths and clay surface potential for SWy-1 in 0.1 M NaCl

Compound	# Carbons	Fc–clay distance (Å)	Potential (mV)
–	–	0	–84
FMTMA ⁺	1	1.5	–41
FHTMA ⁺	6	6.4	–6
FUTMA ⁺	11	12.7	–0.6

The Debye length would occur at 2.5 Å.

where meq/g is the cation exchange capacity of the clay (CEC), σ the resulting surface charge of the clay (C/m²), and S_{m} the surface area of the clay (m²/g). Typical values for Wyoming montmorillonite are 76.4 meq/100 g [28] and 800 m²/g [64], giving a surface charge of 0.09213 C/m².

The surface potential, Ψ_{o} , is calculated from:

$$\Psi_{\text{o}} = \left[\frac{2kT}{ze} \right] \sinh^{-1} \left[\frac{\sigma}{\sqrt{8n_{\text{o}}\epsilon\epsilon_{\text{o}}kT}} \right] \quad (3)$$

where n_{o} is the number of ions/m³ of the bathing solution, ϵ the unitless dielectric constant for water at 25 °C of 80, $\epsilon_{\text{o}} = 8.45 \times 10^{-12}$ C²/(J m), $k = 1.3805 \times 10^{-23}$ (J/molecule K), T the temperature (K), z the charge on the bathing ion, e the charge of the ion of 1.021×10^{-19} C/ion, and Ψ_{o} the surface voltage (V). The decay of the surface potential is calculated by Eq. (4):

$$\Psi = \Psi_{\text{o}} e^{-\kappa x} \quad (4)$$

where κ is the inverse Debye length related to the number of ions in solution and takes the same units as the distance x . For a singly charged solution, κ is calculated in the following manner:

$$\kappa = 3.29 \times 10^7 \sqrt{C_{\text{o}}} \quad (5)$$

where C_{o} is the electrolyte concentration (mol/l) and κ in units of cm^{–1}.

The potential near the clay surface as a function of distance was calculated and compared to the distance of the ferrocene group sites if the aliphatic chain were fully extended. This calculation indicates the length of the aliphatic chain greatly changes the clay surface potential experienced by the ferrocene group (Table 2).

To test this hypothesis clay-modified electrodes were constructed. The surfactants were allowed to load into the films from the bulk solution, and the oxidation–reduction potentials of the various compounds measured via cyclic voltammetry at steady state. A range of potentials for each compound was noted, consistent with the heterogeneous nature of loading of the compound (Fig. 10) [58]. The average potential shift did not change the earlier conclusion regarding the acid promoted oxidation. Nor does the data change the conclusion that the variation in potentials correlates with the lack of reaction of ferrocene and FMTMA⁺ in the clay. We, therefore, at this point

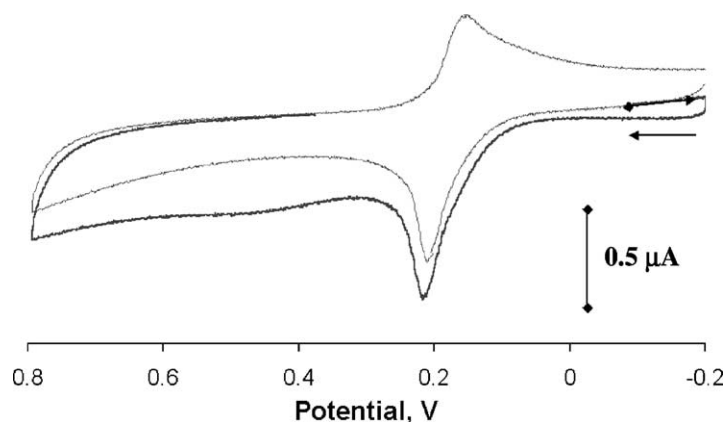


Fig. 11. Cyclic voltammograms of clay-modified electrode, and surfactant intercalated clay-modified electrode (Swearingen et al., 2002 [58]). Bar is $0.5 \mu\text{A}$; V vs. SCE. Surfactant is present in 0.4 mM in 0.1 M NaCl , clay film weight is 0.01 mg , and scan rate is 500 mV/s .

in time, conclude that the most probable reaction is that ferrocene serves as an electron donor to the iron in the clay. Further work is ongoing to verify this conclusion.

An interesting outcome of this research derives from the range of potentials observed for the compounds within the clay. The range of potentials observed for the FHTMA^+ and FUTMA^+ surfactants in the clay suggest that a multitude of sites exist within the clay which implies that a band structure could be obtained for ferrocene in the clay. Such a band structure may lead to large capacitance clay nanocomposite materials. Data obtained for the FHTMA^+ and FUTMA^+ at SWy-1 clay-modified electrodes indicates that such a proposition is, indeed, correct (Fig. 11) [58]. Fig. 11 shows that ferrocenyl surfactant loaded clays have a larger capacitance than clay-modified electrodes without ferrocenyl surfactant. It is important to note that the capacitance increase occurs only after the ferrocene group is oxidized suggesting that the capacitance is related to charge conduction through the ferrocenyl groups. This behavior mimics that of electroactive polymers which become electronically conductive when oxidized or reduced [58].

Results indicate that the most successful high capacitance trials were those with the most positive potential shifts. Since the most positive potential shifts are correlated with the largest ion exchange reaction (Eq. (1)), it is hypothesized that the most extensively loaded clays have the largest probability of containing

surfactant tail groups in adjacent (5 \AA distant) ditrigonal holes and, therefore, the largest probability of having ferrocene tail groups in proximity to deliver charge.

Further experiments will involve change of the oxidation–reduction state of the clay and variation of the clay net charge.

In summary, a catalytic aqueous surface reaction of major environmental importance has been presented. It is hoped that researchers wielding the tools of modern surface science will find the reactions interesting and amenable to study. The mechanism of Fe(III) to Fe(II) reduction in montmorillonite clays in nature, while ubiquitous, is sufficiently poorly understood that attempts to modulate the rate of the reaction are based on guesswork as to the underlying mechanisms determining rate of the reaction (access versus potential).

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