Reaction of Radical Cations of Tetramethylbenzidene with Colloidal Clays

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Pulsed laser photolysis studies have been used to investigate the nature of the interaction of the cation of tetramethylbenzidene, TMB^+, with colloidal montmorillonite. TMB^+ reacts rapidly at a diffusion-controlled rate with the clay particles with a rate constant $k = 3 \times 10^{12}$ M^{-1} s^{-1}. A further rapid reaction on the clay surface of TMB^+ produces the dimer cation of the TMB. All events were identified by rapid spectrophotometry, which shows significant differences in the absorption spectra of the cations when absorbed onto the clay particles. In homogeneous solution the TMB^+ shows a spectrum with a pronounced maximum at $\lambda = 470$ nm. This maximum disappears when TMB^+ is absorbed on clays, and the spectrum contains a maximum in the 400-nm region. The presence of other anionic assemblies, e.g., micelles in the system, bind TMB^+ and decrease the rate of cation exchange on the clay. The kinetics are identified by laser photolysis and discussed in terms of established reactions.

Introduction

Numerous studies over the past several years have documented the influence of interfacial phenomena on photochemical reactions.[1-3] Colloidal systems, e.g., micelles, microemulsions, vesicles, and semiconductors are of great interest because of their ability to promote specific photochemical reactions and inhibit others.[4-6] Recently work has been published that described the photochemistry occurring on surfaces of colloidal clay minerals.[7-9] As an adjunct to this work results are presented for the reaction of aromatic amines with colloidal clay minerals.

The clay mineral used in this work is montmorillonite. Montmorillonite is best described as a 2:1 expanding layer clay. This indicates that a planar sheet of aluminum atoms in octahedral configuration with oxygen shares some of the oxygen atoms with two sheets of silica atoms in tetrahedral configuration, one on each side. These three sheets make up a layer of montmorillonite clay.

Clay minerals do not consist solely of Al, Si, and O atoms in an organized array. Tetravalent silicon in the tetrahedral sheets may be replaced by trivalent species such as aluminum or ferric ion. Aluminum in the octahedral sheet may be replaced by manganous ion or ferrous ion. The small size of these atoms/ions permits them to replace Si or Al atoms in the crystal lattice via isomorphous substitution.[10,11] Isomorphous substitution results in a net negative charge on a clay particle due to the substitution of atoms in higher positive valence states by atoms of lower valence. The negative charge is balanced by the adsorption of cations, such as Na^+ or Ca^{2+}, on the particle (layer) surface. In aqueous suspension these counterions exhibit kinetic action between the clay surface and the bulk phase and may be exchanged by other cations available in solution.[12] The ability of clay minerals to exchange counterions for other cations is known as the cation-exchange capacity or CEC, which is a measure of the amount of substitution of the mineral cation, and is usually expressed in milliequivalents per 100 g of dry clay.

Montmorillonite particles in aqueous solution are constructed from stacks of layerlike clay fragments and are known as tactoids (platelike). The number of layers composing a clay particle is determined by a number of factors, including the chemical composition of the clay and the nature of the exchangeable cations. Montmorillonite possesses unique adsorptive properties due to the ability of its layers to expand thus accommodating guest molecules.

The reaction of aromatic amines, such as benzidine and its tetramethyl derivative, TMB, with clay minerals has been studied in the past.[13-15] Benzidine is known to transfer electrons to reactive sites on the clay mineral surface. These sites may be aluminum atoms at the crystal edges which act as Lewis acids or Fe^{3+} in crystal lattice which can be reduced to Fe^{2+}.[16]

The result of the reaction of benzidine or TMB with montmorillonite is a green amine/clay complex, the green color arising from the monovalent radical cation of the amine. However, electronic absorption spectra of the amine/clay complex are not consistent with the spectrum of the cations in simple solution.[17] It has been demonstrated that photochemical probes will colonize or sequester on the surface of colloidal montmorillonite particles and the spectrum of the TMB/colloidal clay complex is consistent with these results. Work is reported here to confirm that organic radical cations colonize on colloidal montmorillonite particles. Data are reported for the reaction of *N,N,N′,N′*-tetramethyl-*p*-phenylaminediamine (TMPD), also known as Wurster's Blue, and *N′,N′*-dimethyl-4,4′-bipyridinium, known as methyl viologen (MV), with colloidal montmorillonite.

The adsorption of organic radical cations on clay surfaces is primarily, though not simply, a cation-exchange process.[12] The ability of montmorillonite to form a colloid in solution presents a unique opportunity to measure and quantify the kinetics of the cation-exchange process. The knowledge that the spectroscopic properties of organic radical cations change upon their adsorption to the clay surface permits observation of their decay processes in colloidal clay solution following laser photoionization. This technique permits conclusions to be drawn concerning the effect of solvent and clay particle size on the cation-exchange process.

Experimental Section

Instrumentation. Absorption spectra were obtained on a Perkin-Elmer Model 552 UV–visible spectrophotometer. Electron paramagnetic resonance (EPR) spectroscopy experiments were conducted on a Varian E-line series EPR spectrometer. Colloidal particle sizes were measured on a Nicomp HN5-90 dynamic light

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scatter spectrometer. Centrifugations were conducted on a Sorvall SS-3 superspeed centrifuge.

Laser flash photolysis studies were conducted with a Lambda Physik X100 excimer laser, filled with a xenon/chlorine gas mixture capable of delivering a 308-nm pulse. The duration of the pulse is 12 ns (fwhm) and is delivered with an energy of 80–100 mJ. The signal emanating from the photomultiplier tube was captured by a Tektronix 7912 AD programmable digitizer transient waveform unit. This unit was interfaced with a Tektronix 4052A computer for data processing and display.

Chemicals. *N,N,N′,N′*-Tetramethylbenzidine (Aldrich), *N,N,N′,N′*-tetramethyl-*p*-phenylaminediamine dihydrochloride (Eastman), sodium chloride (Fisher), sodium dodecyl sulfate (B.D.H. Chemicals Ltd.), and sodium hydrosulfite (Fisher) were used as supplied. *N,N′*-Dimethyl-4,4′-bipyridinium dichloride (Aldrich) was recrystallized from methanol three times. The primary solvent used for this work, ethanol and water (1:1 v/v), was prepared with reagent quality absolute ethanol (AAPER Alcohol Co.) and distilled/deionized water.

Colloidal Montmorillonite Preparation. The montmorillonite used in this work was obtained from the Georgia Kaolin Co. as the pure mineral. The Na^+-exchanged form was prepared by stirring the clay sample for several days with 1 N NaCl. This was followed by several washings with distilled water and centrifugation cycles to remove the excess sodium chloride and other exchangeable cations from the clay. The clay was then resuspended and dialyzed until a negative chloride test was obtained with 0.1 M $AgNO_3$.

The clay colloids were made by dispersing the mineral with a high-shear Waring blender for approximately 5 min. This was normally followed by 5 min of sonication. The particles had an average hydrodynamic radius of 1500–2000 Å and consisted of 3–4 layers (Na^+-exchanged form).[11]

Technical data supplied by Georgia Kaolin Co. indicated the CEC of montmorillonite is 100 mequiv/100 g. This convenient CEC provided an easy measure of the amount of clay dispersed in solution. One gram of montmorillonite suspended in 1 L of water gives a concentration of cation exchange sites of 1×10^{-3} equiv/L normally expressed as 1 mequiv/L.

Calculation of the Effective Concentration of Molecules Adsorbed on the Montmorillonite Particles. Due to the adsorption of the organic radical cations on the colloidal montmorillonite particle, the effective concentration of cations is much greater than in bulk solution.

The montmorillonite particles are known to exist as platelike sheets in solutions. Calculations based on the surface area, concentration, and charge of the particles yield a surface area of approximately 92 Å^2 or about 9.6 Å between each negative charge. Based on the CEC and surface area of the mineral this value is in reasonable agreement with other estimates[16] of the surface area per unit charge for montmorillonite.

The surface and internal volume of the montmorillonite colloid were calculated from an assumed width of the Stern layer on the outside of the particle surface (10 Å), the interlayer spacing of the silicate sheets in an aqueous solution (20 Å), the length of the particles (4000 Å), the thickness of an aluminosilicate sheet in montmorillonite (11 Å), and the number of montmorillonite particles in solution (5.7×10^{14} particle/g) for a colloid concentration of 1 g/L. In this instance, the total volume for intercalation of organic radical cations by the colloid is calculated to be 0.55 cm^3 for the clay–water sample quoted above.

Results and Discussion

TMB Adsorbed on Montmorillonite. Absorption Spectra. Figure 1a shows the absorption spectrum of an ethanol/water solution (1:1 v/v) of TMB^+ obtained by oxidizing 1×10^{-4} M TMB with dilute bromine water. This spectrum, with an absorption maximum at 470 nm and two smaller peaks at 460 and 440 nm, agrees well with literature references for TMB^+ in homogeneous solution and SDS micelles.[17,18] The peak at 300 nm is due to nonoxidized TMB.[14,19] Also depicted at Figure 1a is the absorption spectrum of TMB adsorbed on colloidal montmorillonite. This spectrum was obtained by mixing an ethanol/water solution containing 1×10^{-4} M TMB with 1 mequiv/L of montmorillonite prepared by the method described previously. The solution was allowed to mix in ordinary room light for approximately 12 h to ensure complete thermal reaction of TMB. The color of the solution was dark green, agreeing well with literature values indicating a strong or complete reaction of TMB.[20] A confirmation of this was obtained following centrifugation of the clay. After centrifugation the clay was green and the supernatant liquid clear. An absorption spectrum of the supernatant gave no indication of the presence of any TMB species indicating complete reaction of TMB with montmorillonite.

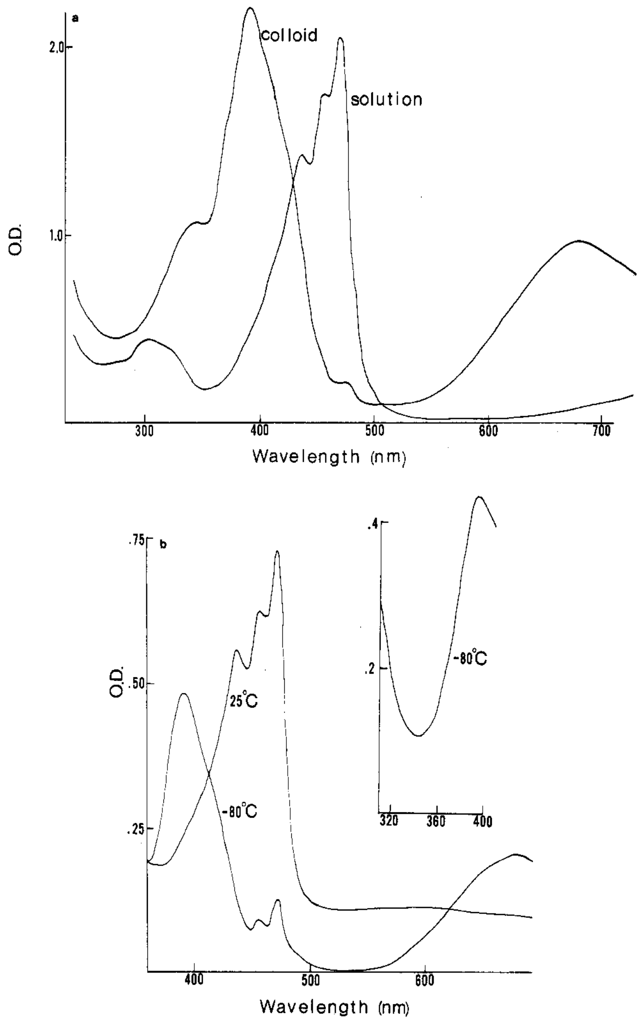

Figure 1. (a) Absorption spectrum of TMB^+ in ethanol/water solution produced by oxidizing 1×10^{-4} M TMB with dilute Br_2/H_2O and 1×10^{-4} M TMB adsorbed on colloidal montmorillonite (1 g/l) with a montmorillonite colloid (1 g/L) in reference cell. (b) Absorption spectrum of TMB^+ at 25 and −80 °C.

Figure 1b demonstrates the effect of temperature on the absorption spectrum of TMB^+ in solution. Takemoto[17] was the first to investigate the change in the absorption spectrum of TMB^+ with decreasing temperature and concluded upon examining intensity data than an *n* value equal to 2.0–2.3 for the equilibrium

$$nR^+ \rightarrow R_n^{\,n+}$$

indicated that TMB^+ dimerized at lower temperatures. A comparison of parts a and b of Figure 1 indicates that the 680- and 390-nm absorption peaks of the TMB/clay complex are due to the presence of $(TMB^+)_2$ on the clay surface. The smaller ab-

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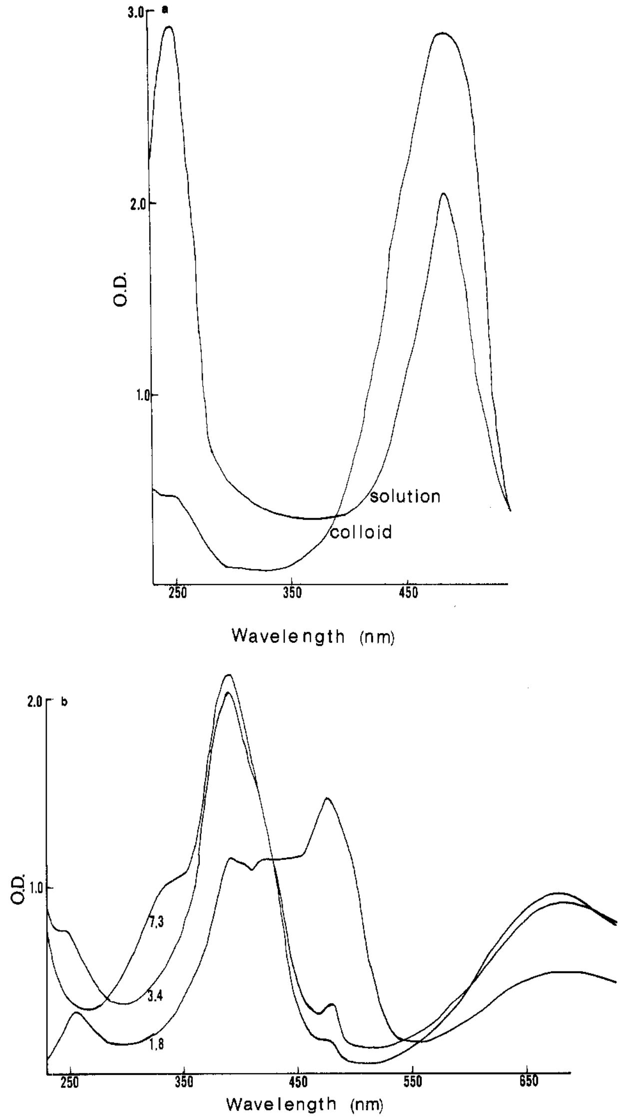

Figure 2. (a) Absorption spectrum of TMB^{2+} in ethanol/water solution obtained by lowering to pH 1.8 a 1×10^{-4} M TMB solution oxidized by dilute Br_2/H_2O and 1×10^{-4} M TMB a pH 1.8 adsorbed on colloidal montmorillonite (1 g/L) with a montmorillonite colloid (1 g/L) in reference cell. (b) Absorption spectra demonstrating the effect of lowering pH on a standard TMB/montmorillonite colloid.

sorption peaks (shoulders) of the TMB/clay complex at 480 and 340 nm cannot be attributed to dimerization. In solution at extremely low temperatures (−117 °C) all absorption peaks near 470 nm disappear, indicating complete transformation of TMB^+ monomer to dimer, while there is never any evidence of TMB in solution (or SDS) producing an absorption shoulder at 340 nm.

In addition to temperature effects, varying pH also has significant effects on the absorption spectra of TMB in solution and when adsorbed on colloidal montmorillonite. Figure 2a shows the absorption spectrum of the divalent cation, TMB^{2+}, obtained by lowering the pH to 1.8 of an ethanol/water solution of 1×10^{-4} M TMB which was oxidized by dilute bromine water. The TMB^{2+} moiety is yellow-orange and has an absorption maximum at 480 nm, while the peak at 250 nm is consistent with the absorption maximum for $TMBH_2^{2+}$.[14,19] These results are consistent with the observation of Beck and Brus[19] for the net disproportionation reaction of TMB^+ in acidic media:

$$TMB^+ + TMB^+ + 2H^+ \rightarrow TMB^{2+} + TMBH_2^{2+}$$

Dilute bromine water oxidizes $TMBH_2^{2+}$ to TMB^{2+} directly

$$TMBH_2^{2+} + Br_2 \rightarrow TMB^{2+} + 2HBr$$

giving an absorption spectrum identical with that depicted in Figure 2a. Also depicted in Figure 2a is the absorption spectrum obtained following the addition of montmorillonite (1 mequiv/L) to an ethanol/water solution of 1×10^{-4} M TMB at pH 1.8. The resulting colloidal solution is yellow and the spectrum is that of the TMB^{2+} moiety adsorbed on the clay surface.

On the basis of the preceeding information it is appropriate to assign the 480-nm absorption shoulder of the green colored, $(TMB^+)_2$, colloid shown in Figure 1a to the presence of a small amount of TMB^{2+} on the montmorillonite surface. This is not an unreasonable assignment as montmorillonite is known to have both Lewis and Bronsted acidic character, and the acidity of the particle surface is often greater than of bulk solution.[12]

So that this could be investigated further, a TMB/montmorillonite colloid was prepared by the method described previously, and the change in its absorption spectrum was monitored with changing pH as noted on Figure 2b. At pH 7.3 the colloid is green and gives the same absorption spectrum as indicated on Figure 1a. At pH 3.4 the colloid is still green, and the absorption spectrum indicates that primary species on the clay is still $(TMB^+)_2$. It is pertinent to note that the 340-nm absorption shoulder has disappeared while the peak at 480 nm, attributed to the presence of TMB^{2+}, starts to grow in. At pH 1.8 the colloid starts to turn yellow and its spectrum indicates that $(TMB^+)_2$ is undergoing a disproportionation reaction:

$$\underset{\text{green}}{(TMB^+)_2} + 2H^+ \rightarrow \underset{\text{yellow}}{TMB^{2+}} + TMBH_2^{2+}$$

If allowed to react for a sufficient period of time, the absorption spectrum of the colloid at pH 1.8 is identical with that depicted on Figure 2a, indicating that all dimer disproportionates, and that the $TMBH_2^{2+}$ moiety is further oxidized to TMB^{2+}.

Previous literature references to the reaction of TMB and montmorillonite often attributes the yellow coloring of this clay at low pH to the protonated monovalent radical cation, $TMBH^{2+}$.[21] However, EPR studies on the yellow colloid indicate that the TMB species responsible for yellow coloring has no free-radical character. The presence of TMB^{2+} has been further confirmed by Brus[22] using Raman spectroscopy.

$TMPD^+$ and MV^+ Adsorbed on Montmorillonite. Absorption Spectra. Figure 3a shows the absorption spectra of $TMPD^+$ in solution and on colloidal montmorillonite. These solutions were prepared as indicated for TMB.

TMPD has been widely studied, and spectra of $TMPD^+$ in solution and in the solid state are well characterized.[23,24] These studies have shown that in solution a monomer–dimer equilibrium exists for TMPD radical cations, the dimer taking precedence at lower temperatures or higher concentrations. The absorption spectrum of $TMPD^+$ in solution agrees well with literature references for the $TMPD^+$ monomer while the absorption spectrum of the $TMPD^+$/clay colloid complex agrees well with references to the dimer of $TMPD^+$. It is interesting to note that the TMPD/clay complex very closely resembles reported spectra for the $TMPD^+$ dimer in low-temperature solution.[24] This is in contrast to the TMB/clay complex, which has features not recorded in reference spectra of the TMB^+ dimer in low-temperature solution.

Another aromatic organic cation which has a well characterized dimer is methyl viologen. Figure 3b shows the absorption spectrum of a 1×10^{-4} M deoxygenated solution of methyl viologen reduced with sodium hydrosulfite. The solution is deep blue and the absorption spectrum is characteristic of MV^+ monomer. Also depicted on Figure 3b is the spectrum of a MV^+/clay complex formed by adding 1 mequiv/L of montmorillonite to a reduced, deoxygenated solution of 1×10^{-4} M methyl viologen. The MV^+/clay colloid solution was purple and the spectrum agrees well with literature references to the MV^+ dimer.[25,26]

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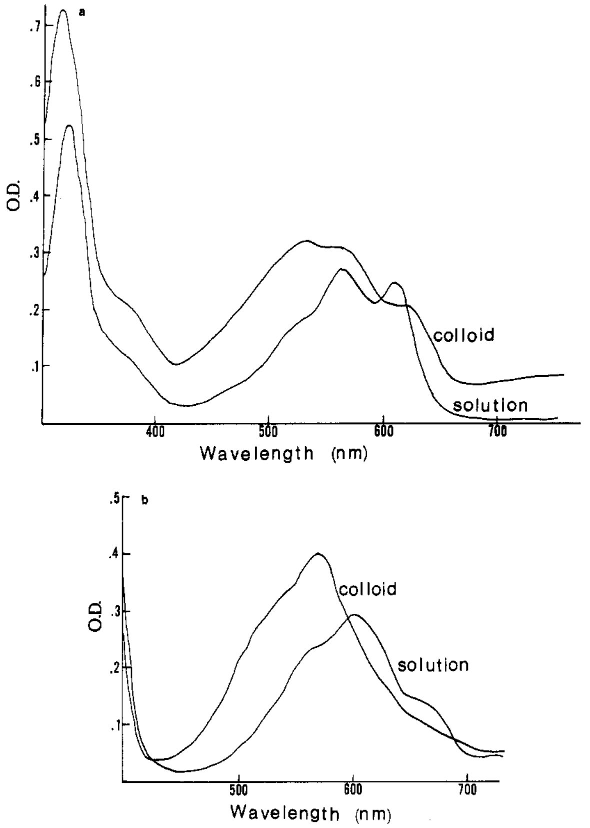

Figure 3. (a) Absorption spectrum of $TMPD^+$ in ethanol/water solution produced by oxidizing 1×10^{-4} M TMPD with dilute Br_2/H_2O and 1×10^{-4} M TMPD adsorbed on colloidal montmorillonite (1 g/L) in reference cell. (b) Absorption spectrum of MV^+ in water obtained by reducing deoxygenated 1×10^{-4} M MV^{2+} with sodium hydrosulfite and MV^+ adsorbed on colloidal montmorillonite (1 g/L)e with a montmorillonite colloid in reference cell.

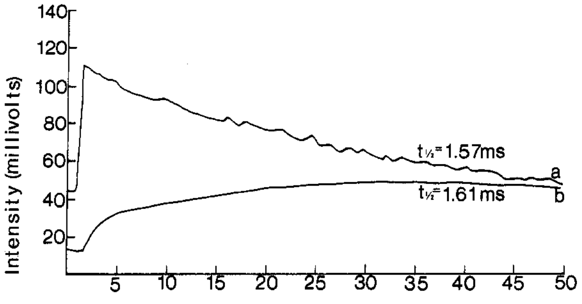

Figure 4. (a) Transient decay curve of TMB^+ (λ = 470 nm) produced by laser photoionization of 1×10^{-4} M TMB in ethanol/water solution containing 0.25 mequiv/L (0.25 g/L) of montmorillonite. (b) Transient growth curve of $(TMB^+)_2$ (λ = 390 nm) on montmorillonite surface.

Pulsed-Laser Kinetic Study of the TMB Reaction with Colloidal Montmorillonite. The adsorption of TMB^+ by montmorillonite is primarily (though not simply) a cation-exchange process. Pulsed-laser techniques present an ideal method of studying and quantifying the kinetics of this cation-exchange process.

Initial studies showed that TMB^+ was irreversibly adsorbed by clay colloids, and its kinetics were monitored by observing in its absorption spectrum at λ_{max} = 470. To ensure that only a cation-exchange process was being monitored we made a comparison between the transient decay at λ = 470 nm and the transient growth at λ = 390 nm since absorption data indicate that TMB^+ molecules dimerize on the clay surface. Figure 4 shows the transient decay of TMB^+ produced by low-intensity laser photoionization of 1×10^{-4} M TMB in ethanol and water containing 0.25 mequiv/L of montmorillonite. Also depicted is the growth of TMB^+ dimer (390 nm) on the same colloidal solution. The fact that the half-life of monomer decay is very close to the half-life of dimer growth indicates that the lifetime of the TMB^+ monomer on the clay surface is very short, and that movement of TMB^+ on the clay particle surface is rapid leading to the TMB^+ dimer. Direct observation of TMB^+ (λ = 470 nm) thus monitors the initial interaction of TMB^+ with clay particles.

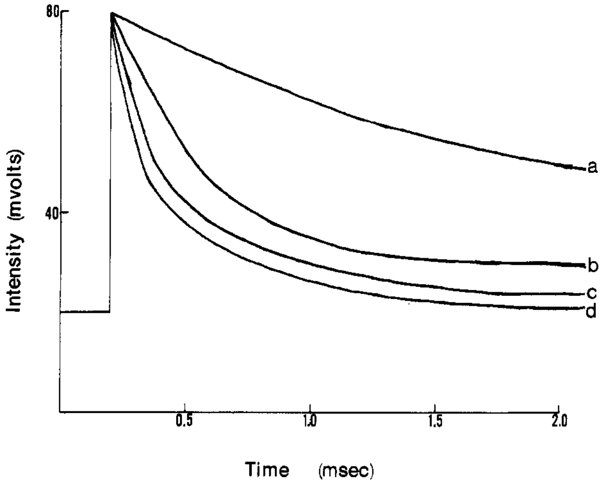

Figure 5. Transient decay curves of TMB^+ (λ = 470 nm) demonstrating the effect of increasing montmorillonite concentration: (a) no clay, (b) 0.5 mequiv/L, (c) 1 mequiv/L, (d) 2 mequiv/L.

Figure 5 depicts the transient decay of TMB^+ (λ = 470 nm, produced by laser photoionization of 1×10^{-4} M TMB in ethanol/water solution, with varying concentration of montmorillonite. The decay of TMB^+ follows pseudo-first-order kinetics. The rate constant for cation exchange can be determined from the relationship

$$k = k_0 + k_c[\text{clay}]$$

where k and k_0 are the observed rate constants for TMB^+ decay in the presence and absence of clay, respectively, k_c is the cation exchange rate constant, and [clay] is the concentration of clay expressed in mequiv/L.

Figure 6a shows a plot of various first-order rate constants, k, determined by the laser and computer assembly described previously, vs. concentration of colloidal montmorillonite in ethanol/water solution; the plot is linear. In terms of equivalents of exchangeable cations the method yields a rate constant

$$k_c = 3.25 \times 10^6 \text{ L equiv}^{-1} \text{ s}^{-1}$$

By considering the number of exchangeable cations and the number of clay particles in a standard colloidal solution (1 g/L) a more conventional second-order rate constant can be derived

$$k_c = 3.43 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$$

A diffusion-controlled rate constant k_c for the reaction of cations with clay particles can be calculated from the Smoluckowski equation

$$k_c = 4\pi\gamma D(6 \times 10^{20}) \text{ M}^{-1} \text{ s}^{-1}$$

where γ is the interaction distance, taken as the particle radius of ~4000 Å, and D is the sum of the diffusion constants of the reactants, taken as the diffusion of the small cation only, i.e., 10^{-5} cm^2/s. The calculated rate constant for $\sim 3 \times 10^{12}$ M^{-1} s^{-1} agrees well with the measured value. No correction was made for the effect of electrostatic attraction of the cation and the anionic clay, which would increase the calculated rate constant. However, it can be stated that the capture of organo cations by anionic montmorillonite particles is a very efficient reaction and ap-

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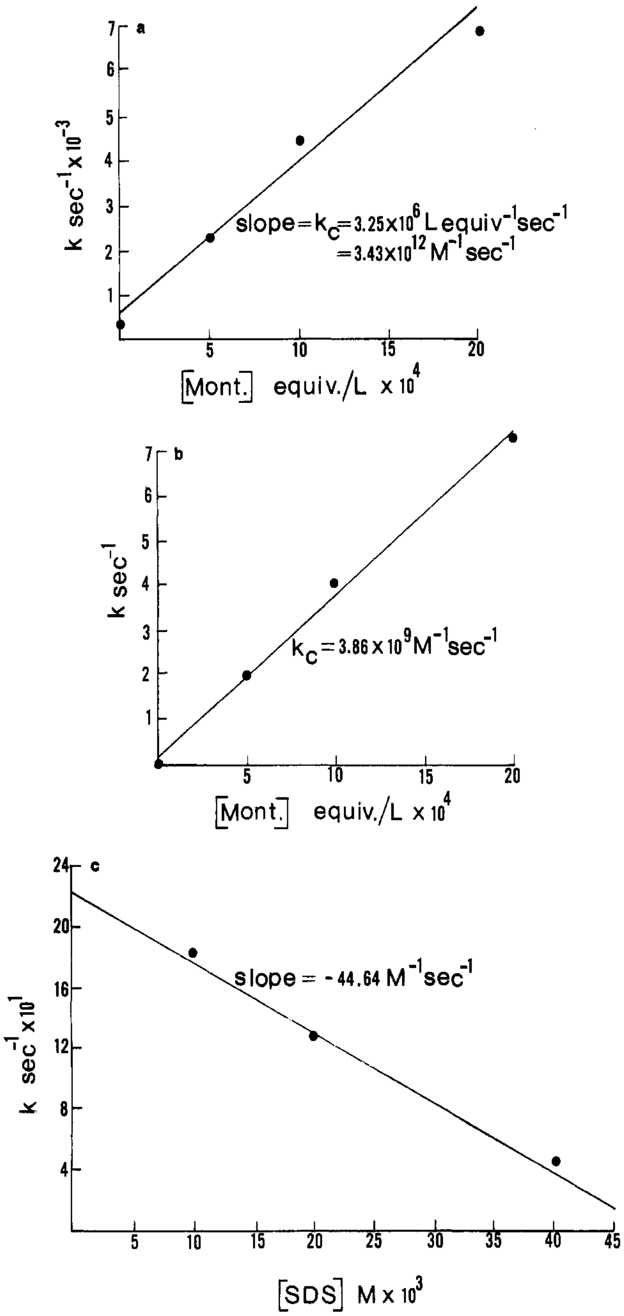

Figure 6. (a) Plot of rate constants for the decay of TMB$^+$ in ethanol-/water solution vs. increasing montmorillonite concentration. (b) Plot of rate constant for the decay of TMB$^+$ in 0.01 M SDS solution vs. increasing montmorillonite concentration. (c) Plot of rate constants for the decay of TMB$^+$ at increasing SDS concentration and a standard montmorillonite concentration of 1 g/L.

proaches the diffusion-controlled limit for the process.

In order to investigate the exchange of TMB$^+$ between NaLS micelles and clay particles, we conducted a kinetic study with colloidal montmorillonite in SDS micellar solution. Figure 6b shows the plot of rate constants, k, for the decay of TMB$^+$ in 1 $\times$ 10^{-2} M SDS at various concentrations of montmorillonite. The data show that TMB$^+$ is stabilized in NaLS solution compared to homogeneous solution. The plot of k vs. [clay] yields a straight line of slope $k_c = 3.86 \times 10^9$ M^{-1} s^{-1}. The rate constant for cation exchange is three orders of magnitude smaller than that measured on ethanol/water solvent. This is not unexpected because Alkaitis and Grätzel[27] have shown that TMB$^+$ is stabilized by SDS micelles by interaction of the cation with the negative surface. This lowers the effective [TMB$^+$] in solution and also lowers the rate of cation exchange

$$\mathrm{TMB^+ + micelle} \underset{k_{-1}}{\overset{k_1}{\rightarrow}} \mathrm{(TMB^+)micelle} \qquad (1)$$

This mechanism predicts that the rate of cation exchange should decrease with increasing SDS concentration. Figure 6c shows the plot of rate constants, k, for the decay of TMB$^+$ with clay colloid solution with varying concentrations of SDS; the concentration of montmorillonite was kept constant at 1 mequiv/L. The negative slope of the linear plot is in agreement with the suggestion mechanism for TMB$^+$ exchange from NaLS micelles to clay particles.

Attempts to measure the rate of TMB$^+$ decay in 0.1 M SDS with varying concentrations of clay proved unsuccessful since the lifetime of the TMB$^+$ transient in the micelle was so long it was beyond the capacity of the instruments to measure it.

Since the plot in Figure 6c is a linear relationship it is useful in determining the retention of TMB$^+$ by SDS micelles. The earlier equilibrium suggests that the TMB$^+$ in solution (TMB$^+$)$_s$, compared to that on the micelle (TMB$^+$)$_m$, is given by

$$\frac{(\mathrm{TMB^+})_m}{(\mathrm{TMB^+})_s} = \frac{k_1}{k_{-1}}[\mathrm{micelle}]$$

The concentration of NaLS is 8.1 $\times$ 10^{-3} mol/L and the aggregation number is 61, thus giving a [micelle] of 3.1 $\times$ 10^{-4} mol/L, at 10^{-2} M NaLS. The ratio of $k_{\mathrm{TMB^+ + C_{lay}}}$ in the absence and presence of 10^{-2} M NaLS is 2.45 $\times$ 10^3, which is also the ratio

$$\frac{(\mathrm{TMB^+})_s + (\mathrm{TMB^+})_m}{(\mathrm{TMB^+})_s} \simeq \frac{(\mathrm{TMB^+})_m}{(\mathrm{TMB^+})_s}$$

Hence, the rate constant ratio k_1/k_{-1} is 8 $\times$ 10^6. The rates of attachment of solutes (e.g., TMB$^+$) to NaLS micelles is close to diffusion control, i.e., $\sim$10^{10} L mol s^{-1}. This value taken in conjunction with the ratio $k_1/k_{-1} = 8 \times 10^6$, gives k_{-1} as 1.25 $\times$ 10^3 s^{-1}, the measured rate of exit of TMB$^+$ from an NaLS micelle into the aqueous bulk.

Conclusion

The reactions of organic cations with colloidal clay systems exhibit selected features that are unique to clay surfaces, the most important feature being clusters or organization of the adsorbed cations on the surfaces. The homogeneous kinetics of the system are readily explained in the light of experience already gained in simpler systems.

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Registry No. TMB, 366-29-0; TMB$^+$, 21296-82-2; TMB^{2+}, 2655-65-4; TMPD$^+$, 34527-55-4; TMPD, 100-22-1; MV$^+$, 25239-55-8; MV^{2+}, 4685-14-7; SDS, 151-21-3.

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