of the micelles increases considerably, they certainly are not vesicles; therefore, they are unidimensional and flexible. The main features of the giant CPBr micelles are so unambiguously derived with no requirements for sophisticated fitting procedures. Acknowledgment. I thank J. Appell and P. Pfeuty for interesting discussions. The paper benefitted from the criticisms of O. Parodi.

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Photoprocesses on Colloidal Clay Systems. 2. Quenching Studies and the Effect of Surfactants on the Luminescent Properties of Pyrene and Pyrene Derivatives Adsorbed on Clay Colloids

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The cationic fluorescent probe [4-(1-pyrenyl)butyl]trimethylammonium bromide (PN⁺) is adsorbed by the colloidal particles of the clay minerals montmorillonite and kaolin. The emission spectrum, polarization of fluorescence measurements, and transient fluorescence decay characteristics of PN⁺ are used to study the nature of its adsorbed state. Quaternary ammonium surfactants of varying hydrocarbon chain length cause a rearrangement of the PN⁺ molecules on the surface and decrease its interaction with the mineral surface. Quenching studies with nonionic and cationic molecules indicate that diffusion on the surface of montmorillonite is reduced below that observed in aqueous solution while the apparent rates obtained with kaolin particles are increased. Montmorillonite particles with a surfactant bilayer surrounding their surfaces are formed by the addition of an excess amount of surfactant to the colloid. The emission spectrum and steady-state quenching studies yield information on the location of pyrene on these particles, as well as on the nature of the colloidal particles.

Introduction

There have been numerous studies over the past several years on the influence of interfacial phenomena on photochemical reactions.¹⁻³ One group of systems studied, cationic, anionic, and neutral micelles, has received much attention due to their ability to solubilize hydrophobic molecules in their hydrocarbon-like core. Dramatic increases or decreases in photoinduced electron-transfer reactions have been reported and are a result of the micellar properties such as charge, size, and shape. Indeed, the charge on these assemblies and the resulting potential field are responsible for the charge separation of photochemically produced radicals. Charge separation, i.e., inhibition of back electron transfer, is essential for any practical solar conversion system.

Luminescence quenching techniques have been especially useful in characterizing the nature of many of these systems and explaining their catalytic effects. These ideas and techniques are presently being used in this laboratory to study the photochemistry that occurs on colloidal clay minerals. These colloids have been chosen for study because of their stability in aqueous media and their large cation-exchange capacity (cec). The two minerals used in this work were montmorillonite and kaolin. Both are aluminosilicates containing aluminum in octahedral configuration which shares oxygen atoms with silicon in tetrahedral configuration. Montmorillonite is referred to as a 2:1 layered mineral because its aluminum shares oxygen atoms with silicon on either side of it. Then there occurs an expandable layer into which water, organic molecules, or cations may be intercalated. The aluminosilicate sheet and expandable layer keep repeating throughout the clay structure in a periodic manner. Kaolin, on the other hand, is a nonexpandable 1:1 layer mineral. There is a sharing of oxygen atoms between one silica sheet and one aluminum sheet in a continuous network that cannot be easily disrupted for the intercalation of ions or organic molecules. Hence, only the surface of kaolin particles participates in chemical reactions whereas both the surface and the internal layers are available in montmorillonite particles.

The cation-exchange capacity of these two mineral appears as a periodic negative charge along their structure. It occurs due to the isomorphous replacement of aluminum for ferrous or magnesium ions in the octahedral layer or by the replacement of the silicon in the tetrahedral layer by either aluminum or ferric ions. The replacement of an atom of higher positive valence for one of lower valence results in a net negative charge. This excess of negative charge is balanced by the adsorption of cations on the layer surfaces. In the presence of water, charge-balancing cations may be exchanged with other cations available in solution.

The expandable layer in montmorillonite and cationexchange properties of both minerals have been utilized to adsorb the fluorescent probe [4-(1-pyrenyl)butyl]trimethylammonium bromide (PN⁺). This has enabled a study of the probe's interaction with the clay mineral surface, the effect of the addition of adding cationic surfactants to this surface on the PN⁺-clay binding, and the accessibility of PN⁺ on these colloids by various fluorescence quenching molecules added to the solution.

Experimental Section

Chemicals. Cetylpyridinium chloride (Sigma), nitrobenzene (Eastman), nitromethane (J. T. Baker), sodium iodide (Baker), and thallium(I) sulfate (Fisher) were used

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as received. The cetyltrimethylammonium bromide (Sigma) was recrystallized from an ethanol-water mixture (50:50) and the N,N'-dimethylaniline (Matheson Coleman and Bell) was vacuum distilled prior to use. Pyrene (Sigma) was recrystallized 3 times from ethanol and the cationic pyrene derivative, [4-(1-pyrenyl)butyl]trimethylammonium bromide (PN⁺) was abailable in this laboratory from a synthesis described previously.⁴

Two of the surfactants used in this work, hexyltrimethylammonium bromide and octyltrimethylammonium bromide, were synthesized by refluxing either 1-bromohexane (Sigma) or 1-bromooctane (Sigma) with an excess of trimethylamine (Eastman) for 24 h.

Equipment. A nitrogen laser from Photochemical Research Associates (pulse width, 120 ps; 50 μ J/pulse; $\lambda =$ 337.1 nm) was used to observe the fluorescence decay of pyrene. The fluorescence signals monitored by a RCA 1P28 photomultiplier tube were fed into a Tetronix 7912 AD programmable digitizer and displayed on a Tetronix 546 B storage oscilloscope. All data were analyzed by using a Tetronix 4051 computer which was interfaced to the digitizer for rapid data reduction. The decay curves were fitted to a high degree of precision, i.e., $\sigma \leq 0.0006$ where

$$\sigma = \frac{1}{N} \left(\sum_{i=1}^{n} \left\{ \left(\frac{(*\mathrm{Ru}(\mathrm{II}))_i}{(*\mathrm{Ru}(\mathrm{II}))_{t=0}} \right)_{\mathrm{obsd}} - \left(\frac{(*\mathrm{Ru}(\mathrm{II})_i}{(*\mathrm{Ru}(\mathrm{II}))_{t=0}} \right)_{\mathrm{calcd}} \right\} \right)^{1/2}$$

over the 512 points of the decay curve.

The absorption spectra were obtained with a Perkin-Elmer 552 spectrophotometer. Fluorescence spectra, quenching, and polarization studies were obtained with a Perkin-Elmer MPF-44B fluorescence spectrometer.

Particle size measurements were made on a Nicomp particle analyzer. The centrifugation of clay samples was performed with a Sorvall high-speed centrifuge.

Polarization of Fluorescence Measurements. A convenient method for studying the microviscosity of a particular system⁵ and phase transitions in lipid bilayers,⁶ or simply to observe restrictions in molecular motion, is the measurement of the degree of polarization of fluorescence. This technique was used to observe the reorganization of the fluorescent probe PN⁺ around the surface of the colloidal clay particles. The intensity of the fluorescence emission is measured at crossed $(I_{v,v},I_{h,v})$ and parallel $(I_{v,v},I_{h,h})$ positions of the polarizing filters. The degree of polarization is given by⁵

$$P = \frac{I_{vv} - I_{v,h}(I_{h,v}/I_{h,h})}{I_{vv} + I_{v,h}(I_{h,v}/I_{h,h})}$$
(I)

The subscripts denote the orientation of the electric vector of the light which passes the excitation (first letter) and emission (second letter) slit; v represents a vertical an h a horizontal orientation.

Clay Minerals. The montmorillonite and kaolin primarily used in this work were obtained from the Georgia Kaolin Co. as the pure mineral. The sodium-exchanged form was prepared by mixing the clay sample in a 1 M sodium chloride solution for 1 day. The mineral was centrifuged and resuspended in distilled water several times to remove the gross excess of sodium chloride. The mineral was then resuspended again and dialyzed until a negative chloride test was obtained with 0.1 M AgNO₃.

The colloids used in this work were usually not more than 48 h old. They were made by dispersing a known amount of the dry mineral in distilled and deionized water with a Waring blender for approximately 5 min. The cation-exchange capacity of the montmorillonite colloids was 1 mequiv/(g of mineral). The montmorillonite particles are tactoids, or platelike particles approximately three layers thick (Na⁺-exchanged form⁷) with a measured hydrodynamic radius of 2000 Å. The kaolin particles are similar because they also consist of staked plates. However, the cation-exchange capacity of kaolin was only 0.02 mequiv/g. In addition to the marked difference in the cation-exchange capacity, the minerals also differ in their surface area. Montmorillonite, whose particles contain internal layers available for the intercalation of molecules. has an unusually large surface area of $\sim 750 \text{ m}^2/\text{g}$. Kaolin, with a surface area of $\sim 10 \text{ m}^2/\text{g}$, is nonswelling and has no internal volume available for the intercalation of molecules or cation exchange.

Preparation of Colloids Containing a Fluorescent Probe. The colloid concentration prepared as described above was usually 1 g/L and had a cation-exchange capacity of 1 mequiv/(g of mineral). The fluorescent probe, PN^+ , was added to the colloid while sonicating the mixture in a sonication bath. After a period of approximately 5 min, CTAB was slowly added until the desired concentration was reached. The usual concentration of PN⁺ for this system was 5×10^{-6} M and that of CTAB was 2×10^{-4} M. For PN^+ , the added concentration represented 0.5% of the total cation-exchange capacity (cec) available while the CTAB concentration represented 20%. The ratio of CTAB to PN^+ on a montmorillonite colloid was then 40:1. Centrifugation of several of these colloids with various concentrations of CTAB followed by spectroscopic examination of the supernatant demonstrated that all of the PN⁺ was bound to the colloid up to CTAB concentrations approaching 40% of the cec. Beyond this concentration, the PN^+ was in equilibrium with the aqueous solution.

For kaolin colloids at 1 g/L with an exchange capacity of about 3 mequiv/(g of mineral), the PN⁺ and CTAB concentrations used were 2×10^{-6} M PN⁺ and 2×10^{-5} MCTAB. The ratio of CTAB to PN⁺ in these systems was 10:1.

The excess-CTAB montomorillonite particles were prepared by slowly adding CTAB to a clay colloid (0.2 g of montmorillonite/L) with constant sonication until the final CTAB concentration was 4×10^{-4} M. This concentration of CTAB was twice the cec of the colloid. Pyrene was added from an ethanol solution to an empty 100-mL flask to give a final pyrene concentration of 1×10^{-5} M. The flask was then dried by passing nitrogen through it. The montmorillonite colloid was added to the flask and the suspension was allowed to mix with intermittent periods of sonication for approximately 1 week. The colloid was always diluted by 1/2 for the quenching experiments. Centrifugation of the colloid followed by spectroscopic examination of the supernatant revealed that all of the pyrene was located on the montmorillonite particles.

Calculation of the Effective Concentration of Molecules Adsorbed on Montmorillonite Particles. Due to the adsorption of molecules on the montmorillonite particles, the effective concentration of PN^+ or quencher molecule is much greater than the bulk solution concentration. Use of the bulk concentration of quencher for the calculation

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⁽⁶⁾ Weber, G Annu. Rev. Biophys. Bioeng. 1972, 1, 553.

⁽⁷⁾ van Olphen, H. "An Introduction to Clay Colloid Chemistry"; Wiley: New York, 1977.



Figure 1. Emission spectra of PN⁺ adsorbed on colloidal montmorilionite particles. Note the low concentration at which excimer is formed.

of quenching rate constants will result in values of 10¹¹ M⁻¹ s^{-1} or greater for these systems. The montmorillonite particles are known to exist as platelike sheets in solution. Calculations based on the surface area, concentration, and charge of the particles yield a surface area per charge of approximately 92 Å², or about 9.6 Å between each negative charge. Based on the cec and surface area of this mineral, this value is in reasonable agreement with other estimates of the surface area per charge for montmorillonite.⁸ The surface volume and internal volume of the montmorillonite colloid were calculated from the 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 along the edge (4000 Å), the thickness of an aluminosilicate sheet in montmorillonite (10 Å), and the number of montmorillonite particles in the solution, e.g., 5.7×10^{14} particles/g for a colloid concentration of 1 g/L. In this instance, the total volume rendered by the colloid is calculated to be 0.55 cm³. The value obtained here is in good agreement with other values obtained for bentonite colloids which contain layered particles of similar size and structure.⁹

Results and Discussion

Adsorption of Probe on the Clay Surface. The derivative of pyrene, PN^+ , was used in these studies to gain information about the effect of a positive charge on the binding of a fluorescent probe to the clay particles. It was found that pyrene could not be efficiently adsorbed onto the montmorillonite or kaolin particles by simple mixing in an aqueous solution. However, PN^+ was readily adsorbed. Figure 1 shows the effect of absorbing increasing amounts of PN^+ on a montmorillonite colloid. Since such a large amount of pyrene excimer is formed at low concentrations of PN^+ , excimer formation is taken to indicate a clustering together of the hydrophobic PN^+ molecules on the surface of montmorillonite. Similar results with PN^+ were also obtained for kaolin colloids.

The stacking or clustering together of PN^+ was also indicated by analysis of the time-resolved emission of the pyrene excimer at 475 nm. If the excimer is formed by the migration of two pyrene molecules together, its emission intensity will increase in a period of time that is dependent on factors such as the pyrene concentration and the microviscosity of the medium. However, for those molecules that are stacked or clustered together on a surface, the





Figure 2. (a) Observed decay of the PN⁺ excimer ($\lambda = 470$ nm) on a montmorilionite colloid (1 g/L) with 5 × 10⁻⁶ M PN⁺. (b) Observed decay of the PN⁺ monomer ($\lambda = 400$ nm) in the same system.

emission at 475 nm will be observed immediately after the laser pulse. The monomers which combine to form the excimer will have their emission quenched within the laser pulse if they are stacked. Those that diffuse along the mineral surface to eventually form excimer will have a shortened lifetime. Figure 2a shows the immediate formation and accelerated decay of the pyrene excimer on colloidal montmorillonite.

Figure 2b shows the observed monomer decay ($\lambda = 400$ nm) when PN⁺ is adsorbed on colloidal montmorillonite. Although a rapid decay of the monomer would be expected from the clustering of the molecules as discussed above, there also appears to be a very rapid quenching of the PN⁺ from interaction with the mineral surface. The processes occurring in this system would then be

$$*\mathbf{P} \xrightarrow{\kappa_t} \mathbf{P} + h\nu \tag{1}$$

$$*\mathbf{P} + \mathbf{P} \xrightarrow{k_0} *\mathbf{P}_2 \tag{2}$$

$$*\mathbf{P}_2 \xrightarrow{\kappa_i} 2\mathbf{P} + h\nu \tag{3}$$

*P + clay
$$\xrightarrow{R_q}$$
 P + clay (4)

$$*P_2 + clay \xrightarrow{k_q} 2P + clay$$
(5)

Effect of Surfactant on PN⁺ Fluorescence Emission and Polarization. The emission lifetime of the PN⁺ monomer and, correspondingly, its emission intensity were increased by the addition of a long-chain quaternary ammonium ion surfactant. These surfactants readily bind to the colloidal particles and will cause flocculation at concentrations approaching 50% of the cec of the colloid. The effects of addition of low concentrations of five surfactants on the florescence yield of PN⁺ ($\lambda = 400$ nm) are shown in Figure 3. There is a significant increase in the emission intensity

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Figure 3. Effect of the carbon chain length of the quaternary ammonium ion surfactant on the emission intensity of PN⁺ adsorbed on colloidal montmorillonite. $[PN^+] = 5 \times 10^{-6} \text{ M}$, [clay] = 1 g/L.

upon the addition of surfactants with a chain length of 10 carbon atoms or more. A large fraction of excimer emission disappears upon the first addition of surfactant, indicating that the surfactants disperse the PN^+ molecules into monomer units around the clay surface. The length of the hydrocarbon chain of the surfactant is important because trimethylammonium ions had a negligible effect on the fluorescence yield yet these would be expected to disperse PN^+ in the same manner as the longer chain molecules. Since hexyl- and octyltrimethylammonium ions had only a minimal effect, the critical length of the carbon chain lies between 8 and 10 carbons.

The degree of polarization of the fluorescence of PN⁺ adsorbed on montmorillonite or kaolin colloids with and without CTAB was obtained by using eq I. In the absence of CTAB, the values obtained for the PN⁺ monomer (λ = 378 nm) on montmorillonite and kaolin were 0.286 and 0.283, respectively. These values are abnormally large for room-temperature measurements and close to the maximum of approximately 0.3 obtained at 77 K in a glass matrix. The data indicate that PN^+ is rigidly confined with a limited range of molecular motions available to it. As the emission spectrum (Figure 1) indicates, there is a large amount of pyrene excimer present due to the clustering together of PN⁺ molecules on the surface. When 1×10^{-5} M CTAB is added to either of these systems, the degree of polarization immediately decreases to about 0.06. This effect for PN⁺ adsorbed on a montmorillonite colloid is shown in Figure 4. Concurrently, a decrease in the yield of excimer emission and an increase in the monomer emmission are observed. Continued addition of CTAB leads to further increases in the monomer emission, even beyond the CTAB concentration range where the excimer emission is essentially zero. This last datum indicates that the excited monomer is quenched by the clay surface.

The data depicted in Figures 3 and 4 show that the first addition of CTAB causes the dispersion of PN^+ into monomer units around the clay surface and not into solution since centrifugation of the colloid and examination of the supernatant did not reveal any PN^+ . This dispersion increases the range of molecular motions available to the individual PN^+ molecules and is reflected in the decrease in the degree of polarization of the fluorescence. The continuing increase in the monomer emission intensity and lifetime with increasing CTAB concentration indicates that the long carbon chain of the surfactant decreases the interaction and subsequent quenching of PN^+ by the mineral surface. Since excimer formation has been eliminated (or



Figure 4. Effect of CTAB on the degree of polrization of fluorescence emission from PN⁺ adsorbed on colloidal montmorillonite. [PN⁺] = 5×10^{-6} M, [clay] = 1 g/L.

at least, greatly reduced), the pyrene moiety must be interacting with the mineral surface. It was shown in a previous publication¹⁰ that both montmorillonite and kaolin surfaces are capable of quenching the excited state of tris(2,2'-bipyridine)ruthenium(II). The same quenching mechanism may be involved here, i.e., ferric ion in the crystal lattice of the mineral. The quenching rate constant for ferric ion quenching of caffeine-solubilized pyrene in aqueous solution is 1.1×10^{10} M⁻¹ s^{-1,11} The data show the importance of the length of the carbon chain (Figure 3) in increasing the emission intensity and support the hypothesis that the carbon chain is necessary to inhibit a reaction between the excited PN⁺ and the clay surface.

Quenching Studies. Montmorillonite and kaolin colloids containing PN^+ in the presence and absence of CTAB were used to observe the behavior of these colloidal systems. The excited state of pyrene is quenched by many solute molecules, e.g., dimethylaniline, nitrobenzene, nitromethane, and cetylpyridinium. This property was used in this work to study the interaction of these quenching molecules with PN^+ which is confined to the particle surface and to gain information about the diffusion of molecules on, and to, these surfaces as well as information about the nature of the surfactant-stabilized particles.

Figure 5 shows the time-resolved fluorescence decay of PN^+ adsorbed on a montmorillonite colloid with 20% of its cec occupied by CTAB molecules. The decay curves can be fitted by a double-exponential function

$$I(t) = I(t=0)\{\alpha e^{-k_1 t} + (1-\alpha)e^{-k_2 t}\}$$
 (II)

which is simply the sum of two first-order decay functions.¹² Each first-order decay has an observed rate

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Figure 5. Double-exponential fit of the transient emission decay of PN⁺ coadsorbed on colloidal montmorillonite with CTAB. [PN⁺] = 5×10^{-6} M, [clay] = 1 g/L, [CTAB] = 2×10^{-4} M.

constant, k_1 or k_2 , and each is weighted by the factor α or $1 - \alpha$, respectively. Figure 5 shows the excellent agreement betrween the experimental and calculated data.

If PN⁺ is dynamically quenched while residing on the clay particle, the rate of decay of the excited PN⁺ increases with an increase in the amount of quencher added. Analysis of the transient decay curves in the presence of quencher then yields k_1 and k_2 as a function of quencher concentration. Figure 6 shows the variation of k_1 and k_2 with added concentration of a typical quencher, nitromethane. The linear plots permit a calculation of the second-order quenching rate constants, k_{q1} and k_{q2} , for quenching of PN⁺ by this molecule. It should be noted that α always remained constant in these experiments, indicating that there are two distinct regions of quenching.

A steady-state expression for the fluorescence quenching can be obtained by use of the relationship

$$I = k_{\rm r} \int_0^\infty I(t) \, \mathrm{d}t \tag{III}$$

where k_r = radiative rate constant. Integration of eq II yields

$$I = k_{\rm r} I_0 \left[\frac{\alpha}{k_1} + \frac{1 - \alpha}{k_2} \right] \tag{IV}$$

$$= k_{\rm r} I_0 \left[\frac{\alpha}{k_1^0 + k_{\rm q1}({\rm Q})} + \frac{(1-\alpha)}{k_2^0 + k_{\rm q2}({\rm Q})} \right] \qquad ({\rm V})$$

In the calculation of I_0/I values it is assumed that I_0 in the presence of quencher remains constant and is equal to I_0 in the absence of quencher. This assumption is correct for systems in which only dynamic quenching occurs. This assumption is incorrect, however, when a fraction of the quenching is static because I_0 decreases in the presence of quencher due to the static quenching which occurs within the lifetime of the laser pulse. The calculated I_0/I values will then be less than those measured in steady-state experiments (which reflect the total quenching, dynamic and static) since they only represent the dynamic quenching. This fact has been utilized in this work in order to determine if any, and to what extent, static quenching occurs in these colloidal clay particles.

The steady-state results were graphed by use of the Stern-Volmer equation

$$I_0/I = 1 + K_{sv}[Q] \tag{VI}$$

(12) We thank James Wheeler for writing the computer programs used to fit the experimental data.



Figure 6. Variation of the decay constants k_1 and k_2 with nitromethane concentration added to solution.

where I_0 is the emission intensity in the absence of quencher and I in the presence. $K_{\rm sv}$ is the Stern-Vomer constant and [Q] is the concentration of quencher added to the solution. There was not complete agreement between the calculated I_0/I from the time-resolved emission experiments and I_0/I obtained from the steady-state experiments. The data indicate that about 40% static quenching of PN⁺ by nitromethane occurs on montmorillonite colloids.

The quenching rate constants obtained for this system were 2×10^9 and $1 \times 10^8 \,\mathrm{M^{-1}\ s^{-1}}$ for k_{q1} and k_{q2} , respectively. These values show that 60% ($\alpha = 0.60$) of the quenching of PN⁺ by nitromethane occurs in a region where the rate is close to that observed in water ($k_q = 3.8 \times 10^9 \,\mathrm{M^{-1}\ s^{-1}}$)³ and 40% occurs in an environment where the diffusion of nitromethane to the PN⁺ is restricted. Adsorption experiments have shown that nitromethane is not adsorbed by the montmorillonite particles and therefore the dynamic quenching occurs by the collisional interaction of nitromethane in solution with the particlebound PN⁺. However, the static quenching component may arise from a weak association of nitromethane with the mineral surface in the region of a PN⁺ molecule.

Similar experiments performed using dimethylaniline yielded quenching rate constants of $3 \times 10^{10} (k_{q1})$ and $2 \times 10^9 (k_{q2}) \text{ M}^{-1} \text{ s}^{-1}$. The value of k_{q1} is significantly increased and k_{q2} is in the same range as the value of $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ observed in homogeneous aqueous solution. Adsorption isotherms prepared for this system demonstrated that significant amounts of DMA were adsorbed into and onto the montmorillonite particles. When the fluorescent probe and quenching molecule are adsorbed on the colloidal particle, their effective concentration is actually much higher than that added to the bulk solution and an appropriate correction must be applied in order to

TABLE I: Stern-Volmer Quenching Rate Constants, k_{sv} (M⁻¹), for PN⁺ on Colloidal Montmorillonite and and Kaolin

	montmorillo		kaolin	
quencher	0 M CTAB	$\frac{2\times10^{-4}}{CTAB}M$	0 M CTAB	2 × 10 ⁻⁵ M CTAB
dimethylaniline	4500	1090	7640	8500
nitrobenzene nitromethane	$2470 \\ 250$	1050 125	680	520

obtain an accurate rate constant (see Experimental Section). The corrected values for the quenching rate constants are $1 \times 10^8 (k_{q1})$ and $1 \times 10^7 (k^{q_2}) \text{ M}^{-1} \text{ s}^{-1}$ and are much lower than those observed in homogeneous aqueous solution. These results are in contrast to those obtained in previous work with tris(2,2'-bipyridinium)ruthenium(II) and dimethylaniline which demonstrated that the quenching in the layers and on the surface of the montmorillonite particles occurred almost at a diffusion-controlled rate.¹⁰ The decreased rate constants observed in these systems are a result of the CTAB molecules which. as discussed previously, associate themselves with the PN molecules on the clav surface. Since the ratio of CTAB to PN⁺ is 40:1 and CTAB molecules occupy 20% of the cec, there may be limited accessibility of quenching molecules to the PN⁺ due to the association of CTAB molecules with the PN⁺ and also a reduced mobility of the quencher molecules on the mineral surface. The Stern-Volmer quenching rate constant, K_{sv} , is observed to be dependent on the amount of CTAB adsorbed on the particles as shown in Table I. As demonstrated in the table, the addition of CTAB to the montmorillonite particles causes a decrease in the quenching efficiency of molecules which are adsorbed by the particles, such as dimethylaniline and nitrobenzene, as well as those that are not adsorbed, e.g., nitromethane. In conjunction with the results depicted in Figures 2 and 3, the data in Table I indicate that, in addition to dispersing the PN⁺ around the surface of the particles, the CTAB is adsorbed in close contact with PNa⁺ which not only prevents its interaction and subsequent quenching by the mineral surface but also shields it from the quenching molecules in solution and adsorbed on the colloid.

Complex results were obtained with cetylpyridinium which also yielded a mixture of dynamic and static quenching. At a concentration of 3×10^{-5} M cetylpyridinium, approximately ~50% of the quenched PN⁺ molecules are dynamically quenched with the remaining number statically quenched. This is inferred by a comparison of the quenching curves obtained from steady-state data using eq VI and the time-resolved fluorescence decay using eq IV. The descrepancy between the calculated and steady-state I_0/I values is shown in Figure 7.

The dynamic quenching rate constant (k_{q1}) obtained for this system was 7×10^{11} M⁻¹ s⁻¹. This is, of course, beyond the range of diffusion-conrolled quenching reactions and is a result of using the bulk concentration of cetylpyridinium in the calculation of the quenching rate constant. Spectroscopic measurements of the supernatant liquid after the centrifugation of the montmorillonite colloid indicated that complete adsorption of the CP⁺ occurred at the concentrations used in these experiments. A reevaluation of the data using the effective concentration of cetylpyridinium on the clay particle yielded the quenching rate constants of 3×10^8 (k_{q1}) and 3×10^7 (k_{q2}) M⁻¹ s⁻¹. These values are reduced over that observed in homogeneous aqueous solution and again demonstrate the decreased accessibility of PN⁺ on the clay particle in the presence of CTAB and the low mobility of molecules



Figure 7. Cetylpyridinium quenching of 5×10^{-6} M PN⁺ adsorbed on colloidal montmorillonite (1 g/L): (**II**) calculated from the transient decay data using eq IV; (O) calculated from the steady-state data using eq VI. Colloid contained 2×10^{-4} M CTAB.



Figure 8. Nitromethane quenching of 2×10^{-6} M PN⁺ adsorbed on colloidal kaolin (1 g/L): (**II**) calculated from the transient decay data; (O) calculated from steady-state data. Colloid contained 2×10^{-5} M CTAB.

confined to thee domain of those particles. The $\sim 50\%$ of static quenching observed is probably a result of the adsorption of some cetylpyridinium molecules in cationexchange sites adjacent to the PN⁺ molecules. Since these sites are approximately 10 Å apart, static quenching is understandable. It is interesting, however, that the cationic CP⁺ molecule dynamically quenches PN⁺ in the domain of the montmorillonite particle. Although PN⁺ and CP⁺ are bound to the clay as indicated from the centrifugation experiments, the binding is not strong enough to anchor them to the mineral surface but allows diffusion of these cationic molecules along the mineral surface while they are confined to the clay particle.

Similar quenching experiments were performed by using kaolin colloids. The time-resolved decay of PN^+ coadsorbed with CTAB on these particles was also found to decay by a double-exponential function of the same form as that shown in Figure 5. There are two distinct differences in these PN^+ -CTAB-kaolin colloids. There are no internal layers available for adsorption as there are in the montmorillonite particles and the ratio of CTAB to PN^+ is 10:1 in these systems in contrast to 40:1 on montmorillonite. This lower concentration of CTAB is necessary due to the very low cation-exchange capacity of this mineral. As a result of the lower ratio of CTAB to PN^+ , there is less interaction between the surfactant and probe which, as demonstrated with montmorillonite, inhibits the quenching reactions. The data for steady-state quenching given in Table I show the negligible effect on CTAB used in these systems.

The quenching reactions of nitromethane and dimethylaniline in these kaolin colloids are also a mixture of static dynamic. Typical data are shown in Figure 8 for nitromethane in which $\sim 50\%$ of the quenching is static at a nitromethane concentration of 4×10^{-3} M. The static quenching may be due to a weak association of the quencher with the probe molecule on the kaolin surface. However, centrifugation of the kaolin colloid and spectroscopic examination of the supernatant indicated that neither dimethylaniline nor nitromethane was adsorbed.

Analysis of the dynamic quenching in these systems by the method shown in Figure 6 gave $k_{q1} = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{q2} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for nitromethane and $k_{q1} = 1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, $k_{q2} = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for dimethylaniline in which approximately 74% of the observed quenching was dynamic. As discussed earlier, the double-exponential decay and the two separate quenching rate constants for the same quencher suggest that PN⁺ is located at two distinct sites, where it not only exhibits different rates of radiative decay, but also shows different accessibilities to quenching molecules. The value of k_{q1} for nitromethane is slightly more than a factor of 2 greater than that observed in water. This increased value and the high percentage of static quenching indicate a weak association of nitromethane with the kaolin surface. The association of only a few percent of the added quencher with the kaolin surface would significantly increase its effective local concentration and result in a larger value of the quenching rate constant if it is calculated from bulk concentration. This effect is more dramatically demonstrated by dimethylaniline with $k_{q1} = 1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This value is about 40 times that observed in water and beyond that attainable for a diffusion-controlled quenching reaction. These values are reported here, with an explanation of their calculation, to demonstrate the effects of localizing a probe on a colloidal kaolin particle with the resulting increase in efficiency of quenching by various molecules.

Pyrene Adsorbed on Clay Particles Containing an Excess of CTAB. In order to further investigate the effect of the addition of cationic surfactants to a montmorillonite colloid, a concentration of CTAB was added that was twice the cec of the colloid used. The addition of CTAB in amounts from 50% to 100% of the cec will precipitate the colloidal particles due to the binding of the quaternary ammonium ion to the cation-exchange sites and the subsequent reduction in the ζ potential. However, if more CTAB is added to the mixture, it will associate with the hydrophobic layer now surrounding the particles and form a double layer around the particles which reverses the charge from negative to positive and resuspends the clay.⁷

Although these clay particles are now hydrophobic, PN^+ cannot be exclusively attached to them as centrifugation experiments have shown that a fraction of the PN^+ remains in the solution. Pyrene, however, can be completely solubilized in these systems by allowing it to mix with the colloid for approximately 1 week with periodic sonication (see Experimental Section).

In these colloids a large amount of pyrene excimer is formed at a pyrene concentration of 5×10^{-6} M, significantly below that needed to form an excimer in homogeneous solution or CTAB micelles.³ The CTAB concentration was 2×10^{-4} M and is well below the critical micelle concentration of 10^{-3} M which excludes the possibility that the presence of excimer is attributable to the localization of pyrene in micelles. Hence, pyrene excimer formation



Figure 9. (a) The emission spectrum of pyrene on the excess-CTAB montmorilonite showing the monomer (370-410 nm) and excimer (maximum = 468 nm) emission. (b) Transient growth and decay of pyrene excimer.

 TABLE II:
 Stern-Volmer Constants for Pyrene

 Quenching on Excess-CTAB Clay

quencher	$k_{sv}(clay), M^{-1}$	$\frac{k_{\rm sv}(\rm H_2O)}{\rm M^{-1}},$
I-	300000	200
dimethylaniline	1390	590
cetylpyridinium	80000	300
nitromethane	24	560
nitrobenzene	3000	1220
thallium ion (Tl³+)	18	470

is a result of the localization of pyrene on the surface of the clay particles, which has the effect of dramatically incrasing its local concentration. The emission spectrum of pyrene in these systems is shown in Figure 9. Figure 9 also shows the time-resolved emission decay of pyrene excimer at 470 nm. It is pertinent to note that unlike the formation of the excimer with PN^+ , which was very rapid, the pyrene excimer emission is seen to grow in over a period of approximately 35 ns. This indicates that pyrene molecules adsorbed in the hydrophobic double layer around the clay particles diffuse together in the layer.

Experiments were undertaken to elucidate the nature of the quenching reactions which occur on these colloidal particles. Steady-state Stern-Volmer data are given in Table II for the quenching of the pyrene excimer. It could not be quantitatively determined if the quenching in these systems was static or dynamic because the lifetime of the monomer was very short (<50 ns) and the excimer exhibited complex kinetics that require further analysis. However, the general trend of the quenching behavior and the properties of these colloids can be indicated by a comparison of the relative efficiencies of the quencher molecules used. As expected, molecules such as nitrobenzene and dimethylaniline have a very large efficiency relative to water because they have a greater affinity for the hydrophobic layer surrounding the clay particle than for the aqueous solution. Cetylpyridinium may replace the CTAB on the clay surface and reside in the bilayer surrounding the particle. In other clay systems studied and previously discussed, cetylpyridinium was found to be a very efficient quencher due to its adsorption on the clay and to act by a static and dynamic mechanism. Thallium and nitromethane are more soluble in the polar, aqueous environment and do not readily quench pyrene. Thallium may be repelled from the positive charge around the double layer which also would decrease its ability to quench PN⁺. Correspondingly, iodide ion is attracted to the positive charge on the quaternary ammonium ions which surround the particles and comprise the outer border of the double layer. The very large value of $K_{\rm sv}$ for iodide in these systems in contrast to homogeneous aqueous solution comments on the location of pyrene on these colloidal particles. Evidently, pyrene resides in the region of positive charge close to the double layer surface. In this environment, it is readily quenched by iodide ions associated with the CTAB.

Conclusion

Adsorption of the cationic fluorescent probe PN^+ onto either colloidal montmorillonite or kaolin causes a clustering of probe molecules on the surface. This leads to pyrene excimer formation as evidenced by its characteristic emission spectrum. Fluorescence polarization measurements indicate that the molecule is rigidly bound to the surface. The PN^+ can be dispersed over the surface of the mineral by the addition of quaternary ammonium surfactants which cause the emission from the pyrene monomer to increase and the excimer to decrease. The monomer is quenched by the clay mineral surface but its interaction with the surface can be significantly decreased by coadsorbing a quaternary ammonium surfactant with a hydrocarbon chain length of 10 carbons or more. Excited PN⁺ exhibits a double-exponential decay of its transient fluorescence, suggesting that it is located in two different regions of the particle. Quenching studies demonstrate that the surfactant cetyltrimethylammonium bromide (CTAB) reduces the accessibility of quenchers not adsorbed by the clay to the \mathbf{PN}^{+} on montmorillonite but it has a negligible effect when PN⁺ is located on kaolin. For molecules that are adsorbed by the montmorillonite particles, the quenching rate constants are reduced by at least 1 order of magnitude compared to homogeneous solution due to the limited accessibility of PN⁺ and the reduced diffusion of molecules on the particle surface. All of the quencher molecules used exhibited a mixture of static and dynamic quenching.

The addition of CTAB to a montmorillonite colloid in an amount that is twice the cation-exchange capacity of the colloid reverse the charge on the particles due to the formation of a CTAB bilayer around their surface. The emission spectrum and steady-state quenching studies comment on the location of pyrene in this environment as well as on the nature of these colloidal particles.

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Registry No. CH_3NO_2 , 75-52-5; PN⁺, 81341-11-9; CTAB, 57-09-0; montmorillonite, 1318-93-0; *N*,*N*-dimethylaniline, 121-69-7; nitrobenzene, 98-95-3; cetylpyridinium chloride, 123-03-5; hexyltrimethylammonium bromide, 2650-53-5; octyltrimethylammonium bromide, 2083-68-3; decyltrimethylammonium bromide, 2082-84-0; dodecyltrimethylammonium bromide, 1119-94-4.

Nature of Isotherms for Adsorption on Pair Sites Consisting of Adjacent, Dissimilar Atoms

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Through statistical arguments, approximate isotherms for adsorption on pair sites of a two-component surface (e.g., acid-base pairs of a metal oxide) were derived and compared to Monte Carlo simulations at different concentrations of the two surface constituents (e.g., anions and unsaturated metal cations). These isotherms for both associative and dissociative adsorption are non-Langmuirian. For associative adsorption, the deviation from Langmuirian behavior is caused by a decrease in the number of pair sites blocked per adsorbed molecule as the coverage increases, with the maximum deviation occurring for a surface containing equal numbers of the two constituents. For dissociative adsorption, the deviation of the adsorption isotherm from the Langmuir equation is due to the limitations imposed by the surface constituent present in smaller concentration, these becoming more important as the concentrations of the two surface constituents become more unequal. The deviations from Langmuirian behavior for both associative and dissociative adsorption on pair sites may be observed experimentally when surface coverages are measured with an uncertainty less than about 5–10% of the saturation coverage.

Introduction

In modeling adsorption on uniform surfaces it is generally assumed that the number of surface sites blocked by each adsorbed molecule is a constant, independent of surface coverage. For example, associative adsorption is assumed to involve one surface site per adsorbed molecule and dissociative adsorption is described in terms of two or more identical surface sites per molecule. The corresponding adsorption behavior is represented by well-known Langmuir isotherms. In the present paper, adsorption of