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Adsorption of Cationic Monomeric and Gemini Surfactants on Montmorillonite and Adsolubilization of Vitamin E

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(iii) However, phonon-scattering processes must tend to zero with T , whereas both delayed fluorescence in this paper and transfer to supertraps in a previous paper⁷ tend toward concentration-dependent finite limits at the very lowest temperatures reached, $T \sim 1.6$ K. This leads us to reexamine whether emissions at very low temperatures may be explained by microscopic quantum delocalized states. At any event, whether the low-tem-

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Photoprocesses on Colloidal Clay Systems. 3. Interaction of Dodecanol and Its Micelles with Colloidal Montmorillonite

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The fluorescent probe pyrene and 1-dodecanol have been incorporated in the interlamellar spaces of the clay mineral montmorillonite. This powder has been suspended in aqueous solution to form colloidal clay particles containing these molecules. Upon suspension, a fraction of the pyrene and dodecanol molecules form micelles that incorporate pyrene. The critical micelle concentration (cmc) of these micelles is approximately 3×10^{-4} M. They render a nonpolar environment, and fluorescence quenching studies with hydrophobic and hydrophilic molecules show the expected trends of enhanced quenching rates in the former case and reduced rates in the latter. Quenching studies with the suspension containing pyrene in the interlamellar spaces of the clay and in the dodecanol micelles indicate that the pyrene excimer exists only in the micelles but not in the clay particles. The results show that the diffusion of molecules within the domain of the montmorillonite particles is significantly reduced compared to that of homogeneous aqueous solution. The system models natural conditions when clay colloids coexist with organic micelles. Fluorescence techniques enable kinetics in both particles to be observed independently in addition to ions interacting between the two colloids.

Introduction

There is currently a large interest among photochemists in interfacial photochemistry. Colloidal systems, i.e., micelles, microemulsions, vesicles, and semiconductors, are of interest because of their ability to promote specific photochemical reactions and inhibit others.¹⁻⁶ Recently, work has appeared that involves the photochemistry that occurs on the surface of colloidal clay minerals.^{7,8} As a continuation of this work, results are presented for colloids of montmorillonite particles that have pyrene and 1-dodecanol incorporated in their interlamellar spaces. The luminescence quenching techniques employed in this work have been especially useful in characterizing the nature of these systems and explaining their catalytic effects.

The clay mineral used in this work was montmorillonite. It is an aluminosilicate containing aluminum in an octahedral configuration sharing oxygen atoms with silicon, which is in a 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. There then occurs an expandable layer into which water, organic molecules, or cations may be intercalated. The mineral possesses a periodic negative charge along its structure due to the isomorphous replacement of aluminum for ferrous or magnesium ions. The small size of these atoms permits them to take the place of the Si and Al atoms. 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 mineral's surface. In the presence of water, these charge-balancing cations may be exchanged with other cations available in solution.

Several studies have investigated the adsorption and nature of primary alcohols in montmorillonite powders.⁹⁻¹⁶ The alcohols can be adsorbed from the vapor phase, pure liquid, aqueous solution, or in the presence of another solvent.⁹ The results obtained from these clays depend on several factors, especially on the counterion that is adsorbed on the clay's surface and the method of preparation. All of these previous investigations involved powders, and no studies have been undertaken on the colloidal nature of these "organoclays". It was found in this work that a fraction of the dodecanol is released into the aqueous phase upon suspension of these particles and that the dodecanol molecules subsequently form micelles. The fluorescent probe pyrene was also incorporated into the interlamellar spaces with the dodecanol. It is also released from the clay and solubilized in the dodecanol micelles. The resulting suspension contains pyrene solubilized in two distinct environments: cosolubilized with dodecanol in the interlamellar spaces of the montmorillonite particles and in the hydrophobic core of the dodecanol micelles in the aqueous phase. The colloidal properties of this system are unique in that selected photochemical reactions can be carried out either on the surface of the clay particles or in the dodecanol micelles or simultaneously in both systems. This work represents, to our knowledge, the first

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presentation of the suspension of a montmorillonite powder containing a hydrophobic molecule and a fluorescent probe in its interlamellar spaces as well as the first demonstration of the formation of dodecanol micelles in aqueous solution.

Experimental Section

A. Chemicals. Nitrobenzene (Eastman), nitromethane (J. T. Baker), cobaltic chloride (Mallinckrodt), cupric sulfate (J. T. Baker), silver nitrate (Alpha), sodium iodide (Fisher), and 100% ethanol (Aaper) were used as received. The cetylpyridinium chloride (Sigma) was recrystallized three times from ethanol. The cetyltrimethylammonium bromide (Sigma) was recrystallized twice from a 50/50 ethanol/water mixture. The cetyltrimethylammonium chloride was recrystallized three times from 50/50 ethanol/ethyl acetate. *N,N*-Dimethylaniline (Matheson Coleman and Bell) and 1-dodecanol (Aldrich) were vacuum distilled prior to use. Since 1-dodecanol is not readily soluble in water, a standard solution was sonicated for approximately 30 min prior to dilution. Pyrene was recrystallized three times from ethanol.

B. 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 Tetrionix 546 B storage oscilloscope. All data were analyzed by using a Tetrionix 4051 computer, which was interfaced to the digitizer for rapid data reduction. The absorption spectra were obtained with a Perkin-Elmer 552 spectrophotometer. Fluorescence spectra 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. The X-ray powder diffraction measurements were made on a Philips-Norelco instrument using filtered Cu K α radiation.¹⁷

C. 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 a 0.1 M AgNO₃ solution.

It is difficult to obtain interlamellar penetration of *n*-alcohols with more than seven carbons, especially when the montmorillonite is in the sodium form.⁹ However, it has been observed that certain nonvolatile materials may readily be adsorbed by equilibrating them with the mineral in combination with a volatile solvent such as ethanol and allowing the solvent to evaporate.¹⁸ Complexes are formed on drying because the solvent evaporates, leaving the clay and nonvolatile material behind. Since ethanol is easily intercalated in montmorillonite, it evidently aids the intercalation of dodecanol and pyrene and can subsequently be evaporated.

To prepare the montmorillonite powders with pyrene and dodecanol intercalated in the internal layers, 5 g of the air-dried clay was first dispersed in 100 mL of ethanol with a Waring blender. The suspension was transferred to a beaker, made 0.5 M in dodecanol and 5×10^{-4} M in pyrene, and allowed to mix for 1 day. The clay was then allowed to settle out of solution for several days and the supernatant poured off. The remainder of the solution was then allowed to evaporate for approximately 2 weeks. The clay had hardened to a dried cake after this period and was reground with a mortar and pestle. It was then placed in a Buchner funnel and, with use of high suction, quickly washed several times with ethanol. This was done to remove any excess pyrene or dodecanol that may have been weakly adsorbed on the outside surface of the particles. The sample was then placed in a vacuum oven at 50 °C for 24 h to remove excess ethanol.¹⁹ The

powder diffraction measurements of these samples yielded basal (*d*(001)) spacing measurements of 15 and 23 Å. No interpretation is given to these measurements with regard to the orientation of pyrene and dodecanol in the interlamellar space. It is known that straight-chain alcohols take up a variety of orientations depending on numerous factors.^{9,12} However, the long spacing of 23 Å can only be attributed to the intercalation of dodecanol. Since the spacing of the silicate sheet is approximately 10 Å, the interlamellar space is swollen to 13 Å. The shorter *d*(001) spacing of 15 Å is attributed to either residual water or a partially expanded layer containing ethanol in contrast to a fully expanded ethanol layer of 17 Å.

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 the quencher molecules is much greater than the bulk solution concentration. Use of the bulk concentration of quencher for the calculation of quenching rate constants results in inaccurate values for these systems where the quencher is adsorbed (i.e. cationic quenchers). 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 9.2 Å between each negative charge. Based on the cation-exchange capacity (cec) and surface area of this mineral, this value is in reasonable agreement with other estimates of the surface area per charge for montmorillonite.^{20,21} 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 that contain layered particles of similar size and structure.²²

Results and Discussion

Centrifugation of the clay colloid and subsequent spectroscopic examination of the supernatant revealed that a fraction of the pyrene was not intercalated into the layers of the clay but resided in the aqueous bulk of the mixture. Upon suspension of the montmorillonite particles, the high shear produced by the blender severs the particles along their layers and releases both pyrene and dodecanol into the solution. It was found that micelles of dodecanol are formed in the aqueous phase and solubilize the pyrene released from the clay. Therefore, suspension of the montmorillonite particles containing both dodecanol and pyrene resulted in a solution with pyrene solubilized in two distinct environments: in the layers of the montmorillonite particles and in the dodecanol micelles. In order to understand the fluorescence quenching of pyrene observed in this compound system, experiments were first performed in aqueous solutions of pyrene and dodecanol.

Evidence for the Formation of Dodecanol Micelles. One of the most convincing measurements that demonstrates the formation of micelles in aqueous solutions is that of the measurement of the change in surface tension with concentration of surface-active agent. The surface activity of the agent (as reflected by the surface tension) increases with concentration below the cmc and thereafter changes only slightly. Accordingly, the cmc can be determined from the inflection point of the surface tension vs. log concentration curve.²³⁻²⁶ This method is fairly successful when

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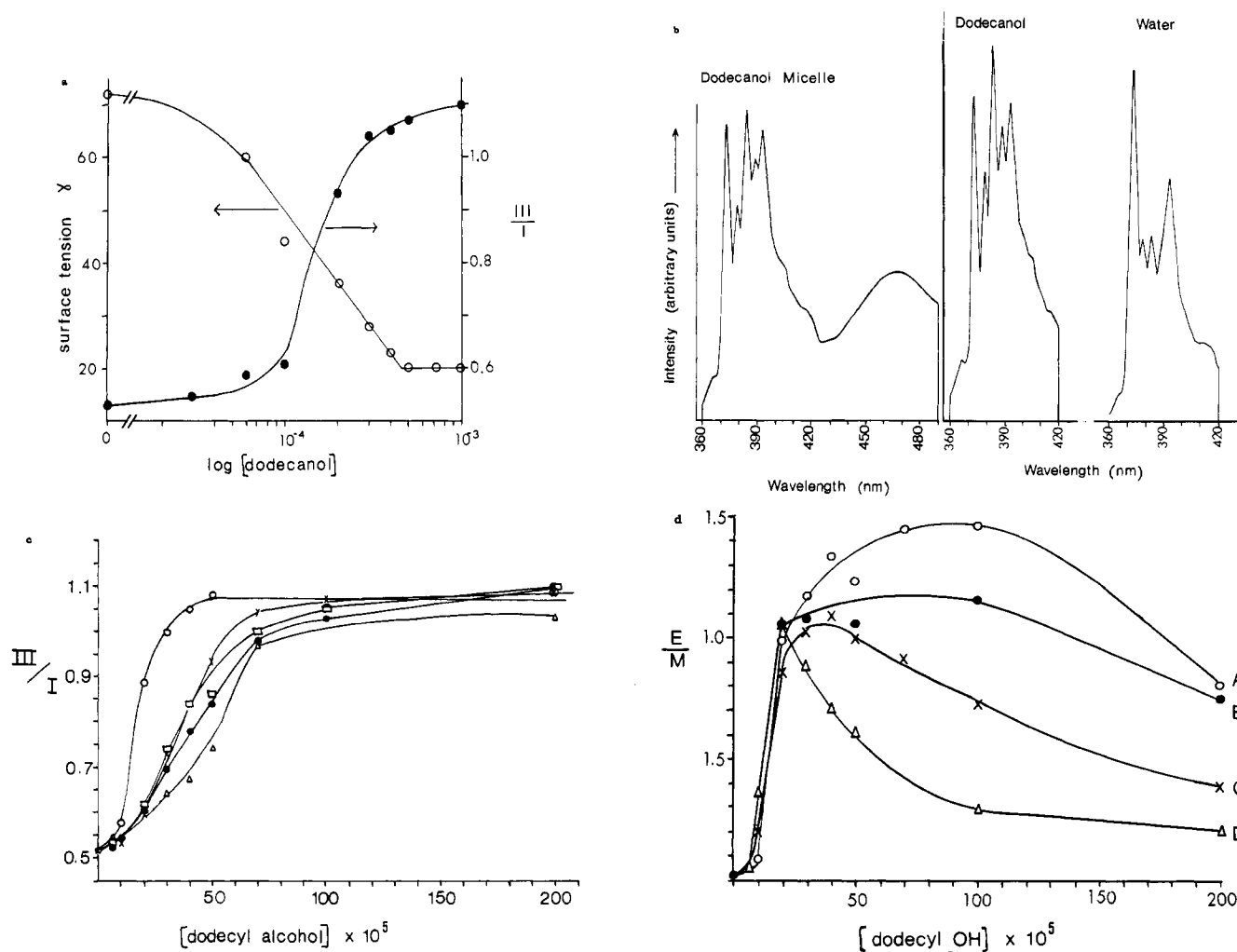


Figure 1. (a) Plots of surface tension and III/I ratio vs. dodecanol concentration. The cmc's determined by these methods were 4×10^{-4} and 3×10^{-4} M, respectively. (b) The steady-state emission spectra of pyrene in pure dodecanol, water, and an aqueous solution of 7×10^{-4} M dodecanol. (c) The change in the III/I ratio for pyrene concentrations with increasing dodecanol concentration: (O) 1×10^{-6} , (X) 2×10^{-6} , (\square) 3×10^{-6} , (\bullet) 4×10^{-6} , (Δ) 5×10^{-6} M pyrene. (d) The excimer to monomer ratio for various concentrations of pyrene dissolved in increasing concentrations of dodecanol: (A) 4×10^{-6} , (B) 3×10^{-6} , (C) 2×10^{-6} , (D) 1×10^{-6} M pyrene.

applied to nonionic surface-active agents,^{27,28} and the results obtained from the addition of increasing concentrations of dodecanol to water containing 1×10^{-7} M pyrene are shown in Figure 1a. The critical micelle concentration obtained by this method was 3.5×10^{-4} M.

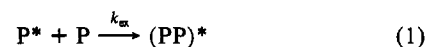
Figure 1b shows the emission spectrum of pyrene in three different solvents: water, pure dodecanol, and a solution of 7×10^{-4} M dodecanol in water. The III/I ratio obtained from pyrene's emission spectrum has been shown to be very sensitive to the polarity of its environment.^{29,30} It is determined by dividing the relative emission intensity of the third vibronic band by the emission intensity of the first. The emission spectra in Figure 1b suggest that pyrene dissolved in 7×10^{-4} M dodecanol is in an environment similar to that in pure dodecanol.

This ratio has also been used to determine the onset of micellization of various surfactants in aqueous solution.³¹ As shown

in Figure 1a, micellization of dodecanol in aqueous solution occurs at about 3×10^{-4} M as determined by this method. As the pyrene is incorporated into the hydrocarbon-like environment, the III/I ratio changes from approximately 0.5 to 1.1. This ratio remains constant as the dodecanol concentration is increased beyond 3×10^{-4} M because this concentration is sufficient to completely solubilize 1×10^{-7} M pyrene.

Figure 1c shows that larger concentrations of dodecyl alcohol are needed to solubilize larger concentrations of pyrene. All of the pyrene is assumed to be solubilized when the III/I ratio remains constant upon further addition of dodecanol. In the cases depicted, a dodecanol concentration of 1×10^{-3} M was sufficient to solubilize all of the pyrene into a moderately nonpolar environment (III/I = 1).

Further experimental evidence of the formation of dodecanol micelles is the appearance of the pyrene excimer as very low pyrene concentrations. Excimer formation is due to the dimerization of an excited and unexcited pyrene molecule, i.e.



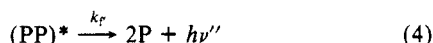
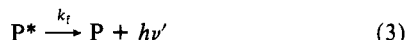
This dimerization only occurs at very high pyrene concentrations in homogeneous solution ($\sim 10^{-3}$ M in hexane) but can be induced at much lower concentrations in micellar solutions due to the solubilization of more than one pyrene molecule by the micelle. The onset of excimer formation is rapid and again is an indication of a micellization or premicellization process. At all concentrations of pyrene studied, there is a sudden appearance of excimer between

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1×10^{-4} and 3×10^{-4} M dodecanol.

Figure 1d shows the results obtained in pyrene solutions containing increasing amounts of dodecanol. At 1×10^{-6} M pyrene and 2×10^{-4} M dodecanol, a significant fraction of the excited pyrene molecules form excimers due to their confinement within a limited number of dodecanol micelles. However, as the number of these micelles is increased (increasing dodecanol concentration), a redistribution occurs that favors fewer pyrene molecules per micelle and the amount of pyrene excimer decreases. As the pyrene concentration is increased, more excimer is formed and more dodecanol is therefore required to reduce excimer concentration. Identical behavior has been observed to occur in anionic and cationic micellar solutions.³

Excimer formation can also be detected by an increase in the rate of decay of the transient fluorescence signal of the pyrene monomer since the reaction quenches the monomer emission:



With a dodecanol concentration of 7×10^{-4} M, which completely solubilizes pyrene in the concentration range $(1-5) \times 10^{-6}$ M (Figure 1d), an apparent self-quenching rate constant for pyrene was obtained by use of the equation

$$k = k_0 + k_q[Q] \quad (I)$$

where k and k_0 are the observed decay constants in the presence and absence of quencher, Q , k_q is the quenching rate constant, and $[Q]$ is the bulk concentration of pyrene. This method yields a rate constant of approximately $3 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$, well beyond that obtainable for a diffusion-controlled quenching reaction, and is a result of the confinement of the pyrene molecules within the dodecanol micelles thereby dramatically increasing its effective concentration.

Various physical methods were used to determine the formation and properties of these dodecanol micelles. Turbidity and dynamic light-scattering measurements all indicated that a micellization process occurred between 2×10^{-4} and 4×10^{-4} M dodecanol. The light-scattering measurements yielded a radius for this structure of approximately 1400 Å. These preliminary measurements would indicate the existence of a large, rodlike or prolate micelle structure. Further light-scattering studies are necessary for more quantitative details of the shape and aggregation number of these structures.

Fluorescence Quenching of Pyrene in Dodecanol Micelles. Steady-state and transient decay methods were used simultaneously to measure the fluorescence quenching of pyrene and to obtain quenching rate constants. Steady-state methods made use of the well-known Stern-Volmer equation

$$I_0/I = 1 + \tau k_q[Q] \quad (II)$$

where I_0 and I are the measured emission intensity in the absence and presence of quencher, Q , k_q is the quenching rate constant, and τ is the natural lifetime of the pyrene in the system under study.

Transient decay measurements of 1×10^{-6} M pyrene solubilized in dodecanol micelles yielded a lifetime in the range of 120 ns for the pyrene monomer. This decay of the monomer was found to be first order and is shown in Figure 2a. This value is somewhat less than that of pyrene in pure dodecanol, ~350 ns, and is due to excimer formation. Measurement of the monomer lifetime below the cmc coincided with that of pyrene in water, i.e., ~200 ns. However, as the cmc was approached and the excimer became apparent in the emission spectrum, the transient decay of the monomer was observed to exhibit the same characteristics as those observed in other micellar systems.³ Figure 2b shows the steady-state emission spectrum of pyrene monomer and excimer

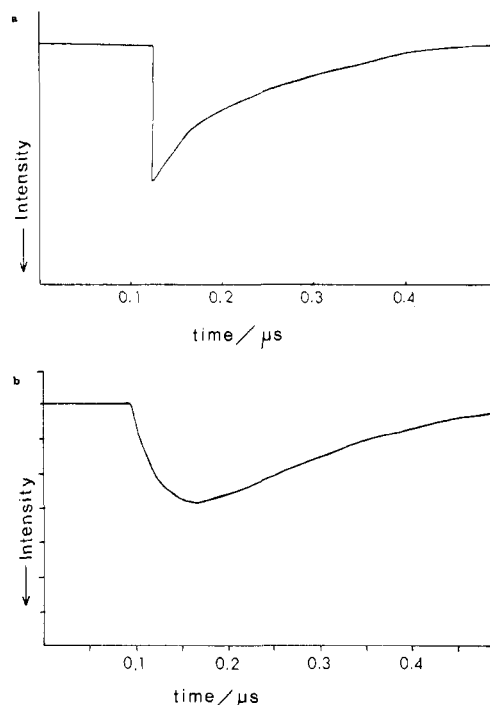


Figure 2. (a) The transient decay of the pyrene monomer ($\lambda = 400$ nm) for a solution of 1×10^{-6} M pyrene dissolved in an aqueous solution of 7×10^{-4} M dodecanol. (b) The transient decay of the pyrene excimer ($\lambda = 475$ nm) in the same solution. The excimer formation time is estimated to be approximately 80 ns in this system.

TABLE I: Quenching Rate Constants ($\times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$) of Pyrene

quencher	0.017 M ethanol monomer	1-dodecanol micelle		1-dodecanol micelle and dodecanol clay	
		monomer	excimer	monomer	excimer
oxygen	200	200	200		
nitromethane	81	4.3	2.7	0.83	1.2
dimethylaniline	40	1230	750	1150	790
iodide ion	30	8	6	0.1	0.9
nitrobenzene	126	1220	980	870	840
cetylpyridinium	100	2000		220	0 ^a
cupric ion	55	33	23	340	0 ^b
silver ion	51	6.4	2.6	94	0 ^c
cobaltic ion	7	10	11	138	0 ^c

^a Up to cetylpyridinium concentration of 1×10^{-4} M. ^b Up to a Cu^{2+} concentration of 4×10^{-4} M. ^c Up to a concentration equal to ccc of clay colloid.

in these systems. Figure 2c shows the slow formation of excimer in these systems, which indicates that the pyrene molecules must diffuse together to form the excimer.³ In all of the quenching experiments except those involving cetylpyridinium, the transient decay was found to be first order and the quenching rate constants were obtained by use of eq I.

Fluorescence quenching of pyrene in dodecanol micelles was studied and compared to homogeneous solutions containing pyrene. The results are given in Table I. The rates for monomer and excimer quenching are similar but not identical. The quenching behavior in these systems exhibits the general trends expected for the solubilization of a probe molecule in a hydrophobic micelle; i.e., ionic or hydrophilic quencher molecules demonstrate reduced quenching rates compared to those for homogeneous solution in contrast to hydrophobic quenchers with rates increased by at least 1 order of magnitude. Figure 3a shows the results obtained for the quenching of the pyrene excimer with Cu^{2+} , I^- , and Co^{2+} ions. The pyrene excimer quenching is depicted to demonstrate the relative impenetrability of these micelles by ionic species. Although the pyrene monomer may be in dynamic equilibrium with the aqueous solution,³² the excimer can only be formed and exist within

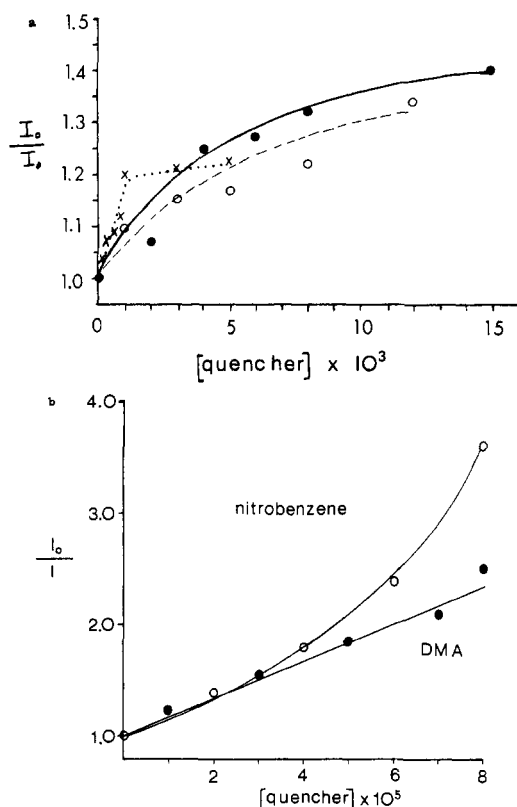


Figure 3. (a) Steady-state pyrene excimer quenching by Co^{2+} (●), Cu^{2+} (○), and I^- (×) ions in solutions of 1×10^{-6} M pyrene and 7×10^{-4} M dodecanol. (b) Steady-state pyrene excimer quenching by nitrobenzene and dimethylaniline in solutions of 1×10^{-6} M pyrene and 7×10^{-4} M dodecanol.

the micelle at a pyrene concentration of 1×10^{-6} M. The quenching rates and the fraction of the fluorescence quenched for the monomer were higher than those for the excimer, but the Stern–Volmer plots for monomer quenching also showed a reduced rate (leveling off) of quenching at higher quencher concentrations.

In contrast to these results, Figure 3b shows typical Stern–Volmer plots for nitrobenzene and dimethylaniline quenching of the pyrene excimer. For nitrobenzene, the fluorescence quenching starts to exhibit static behavior at higher concentrations due to its preferential incorporation within the micelle. Table I shows that the monomer quenching rate constants are increased by a factor of 30 and 10 for dimethylaniline and nitrobenzene, respectively.

Complex results were obtained with cetylpyridinium that appear to be due, in part, to interaction of its long hydrocarbon tail with the dodecanol structure. Figure 4a shows the steady-state results obtained from quenching experiments in these systems. The monomer quenching rises to a plateau at about 3×10^{-5} M cetylpyridinium and then decreases while the excimer quenching shows significant upward curvature. The transient fluorescence results, however, yielded similar monomer and excimer quenching rates. These quenching rate constants were obtained by the use of eq 1 and as such are a measure of dynamic quenching that takes place.

Physical changes occur in these systems upon the addition of cetylpyridinium. Figure 4b shows the changes that occur in the III/I and E/M ratios. As previously discussed, these are good indicators of the environment of pyrene. The changes in the III/I ratio from 1.15 to 0.65 suggest that the pyridinium head group becomes incorporated in the dodecanol micelle and not only quenches the pyrene but also leads to a structure with an increased polarity for the probe environment. The III/I ratio of pyrene in a cetyltrimethylammonium micelle is 0.74.³¹

In order to confirm that the C_{16} hydrocarbon tail of cetylpyridinium becomes incorporated in the dodecanol micelle, the cationic surfactant cetyltrimethylammonium bromide (ctab) was added to an identical system containing only pyrene and dodecanol. Parts c and d of Figure 4 show that for systems containing the same concentration of pyrene as in the cetylpyridinium quenching experiments, identical changes in the III/I and E/M ratios occurred upon the addition of ctab. When ctab was added to these solutions over the same concentration range, the excimer emission was observed to slowly disappear in the steady-state emission spectrum while the monomer emission intensity increased. Measurements of the transient decay rates of the monomer and excimer showed that the excimer formation time decreased from 80 to 15 ns as ctab was added up to a concentration of 2×10^{-4} M. This data indicates that the surfactant chain becomes incorporated in the dodecanol micelle. The presence of the charged head group initiates a curvature in the surface of the prolate micelles, causing rearrangement to smaller micelles. The pyrene molecules are then distributed among more, and a smaller size, of dodecanol micelles. Excimer formation is then less likely, and the excimer formation that does occur requires less time.

Fluorescence Quenching in Clay/Micelle Systems. The data in Table I summarize the results obtained from quenching experiments with a colloidal solution containing pyrene in dodecanol micelles as well as in the internal layers of montmorillonite particles. As discussed previously and shown from X-ray powder diffraction measurements, the dodecanol and pyrene are intercalated in the internal layers of the montmorillonite powder. However, the clay is suspended in water with a blender, which produces very high-shear forces. These forces sever the montmorillonite particles along the interstitial layers, which release a fraction of the pyrene and dodecanol into the aqueous phase. The dodecanol molecules subsequently form micelles that incorporate pyrene. There is probably a small percentage of pyrene in the aqueous phase, but due to its very low solubility in water ($\leq 1 \mu\text{mol}$)³³ and its preference for the nonpolar environment in a micelle's core,³² this fraction is assumed to be insignificant with regard to the overall results obtained in the quenching experiments.

There is extensive information on the binding of inorganic cations by colloidal montmorillonite.³⁴ The influence of cation hydration, ionic size, charge, and polarizability has been studied in regard to the strength of the binding forces with clays.^{35–39} Swartzen-Allen and Matijevic have made three generalizations concerning the tendency of a cation to exchange onto a negative surface.⁴⁰ The exchangeability of the bound cation increases (a) with decreasing hydrated radius and increasing polarizability, (b) with decreasing counterion charge, and (c) as the negative free energy of hydration decreases for monocations and increases for dications.

The order of increasing preference of alkali ions for a montmorillonite colloid is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, and for divalent transition-metal cations it is $Mn^{2+} \approx Ni^{2+} \approx Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$.⁴⁰

It has been suggested that, in general, among mono-, di-, and trivalent cations, the greatest affinity is for cations of the highest charge.^{34,40} (Although, there may be reversals when comparing a low-affinity dication with a high-affinity monocation.) Therefore, the binding strengths of the ions present in the quenching studies performed using a Na^+ -exchanged montmorillonite would be $Na^+ < Ag^+ < Co^{2+} < Cu^{2+}$.

Quenching experiments were performed with Ag^+ , Co^{2+} , and Cu^{2+} cations, and results very different from those in homogeneous or micellar solutions were obtained. The most striking and im-

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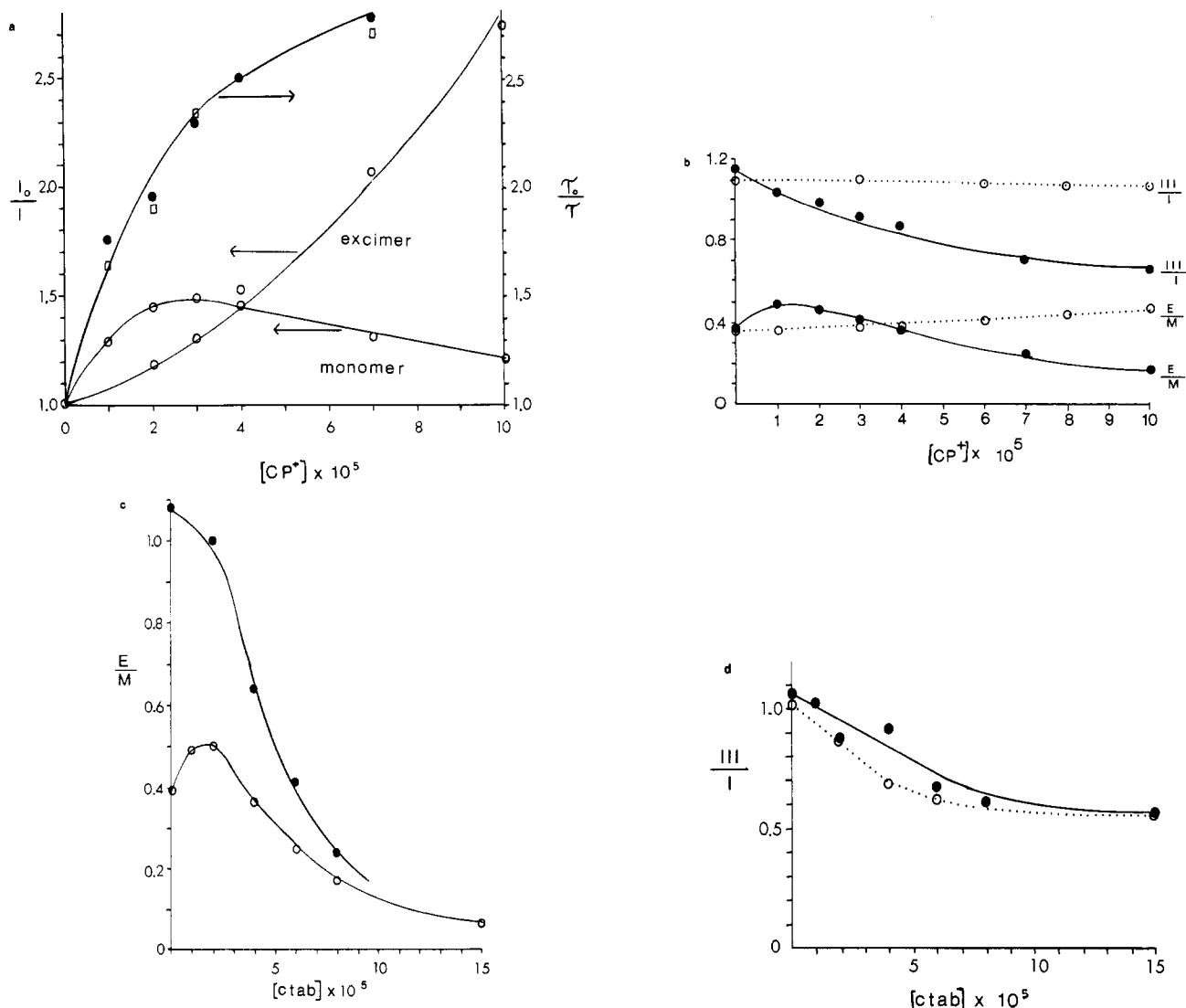


Figure 4. (a) Cetylpyridinium quenching of the pyrene monomer and excimer in dodecanol micellar solutions. For the transient measurements, ○ is for the monomer and ● is for the excimer. Solution contained 1×10^{-6} M pyrene and 7×10^{-4} M dodecanol. (b) Change in the excimer to monomer and III/I ratios of pyrene upon addition of cetylpyridinium to a dodecanol micelle solution or dodecanol micelle + dodecanol clay colloid mixture. Note that both ratios remain constant in the presence of the clay colloid. (c) Effect of ctab on the excimer to monomer ratio of pyrene: (●) 1×10^{-6} M, (○) 4×10^{-6} M pyrene; dodecanol concentration = 7×10^{-4} M. (d) Effect of ctab on the III/I ratio of (●) 1×10^{-6} and (○) 4×10^{-6} M pyrene in 7×10^{-4} M dodecanol.

portant feature is that for cation concentrations below the cation-exchange capacity (cec) of the clay colloid, where the cation is exclusively bound to the clay particles, there is a complete absence of pyrene excimer quenching. The monomer quenching in this cation concentration range proceeds at apparent rates many times those observed in homogeneous solutions or in dodecanol micelles (Table I). However, beyond the cation-exchange capacity of the colloid, the cations are no longer bound to the clay and excimer quenching was observed. These results suggest that the pyrene excimer is only located in the micelles and not in the layers of the clay particles.

Previous work with clay colloids containing a cationic luminescent probe showed that the apparent quenching rate constants for cationic and many nonionic quenchers were increased compared to those for homogeneous solution.^{7,8} This was due to a large increase in the local concentration of quencher as a result of its confinement within the domain of the colloidal clay particles. As described in the Experimental Section, the local or effective concentration of bound cations can be calculated. This treatment yields quenching rate constants of 2×10^7 , 8×10^6 , and 5×10^6 $M^{-1} s^{-1}$ for Cu^{2+} , Co^{2+} , and Ag^+ ions, respectively. These dramatic reductions in the effective rate constants are in agreement with previous work which demonstrated that quenching reactions on the clay particles in the absence of adsorbed surfactants proceeded

at rates close to those for homogeneous solution while rates were reduced by at least 1 order of magnitude in the presence of adsorbed surfactants.⁸ It was shown that diffusion of the quencher and probe on the clay surface is reduced by the adsorbed surfactant. During the preparation of these clay powders, the dodecanol and pyrene become completely intercalated in the layers of the montmorillonite. After suspension in water, the diffusion of the clay counterions (Na^+ or Co^{2+} , Cu^{2+} , and Ag^+ in the quenching experiments) as well as of pyrene and dodecanol in the layers of the particle is evidently reduced significantly compared to the case for aqueous solutions. This may account for the lack of formation of pyrene excimer in these colloidal clay particles. When large concentrations of montmorillonite are suspended in methanol or ethanol, significant reductions in the conductance of the clay counterions are observed compared to those of suspension in aqueous solution.³⁶ This effect has been attributed to an increase in the association of these cations with the clay surface, which decreases their diffusion along its surface. When the ratio of the effective rate constant (given above) to that obtained for homogeneous solution (column 1, Table I) is multiplied by 100, the relative percent of the rate of quenching in aqueous solution is obtained. These were 1, 0.4, and 0.1% for Co^{2+} , Cu^{2+} , and Ag^+ , respectively. Although dodecanol greatly reduces the diffusion of these ions along the clay surface by increasing their interaction

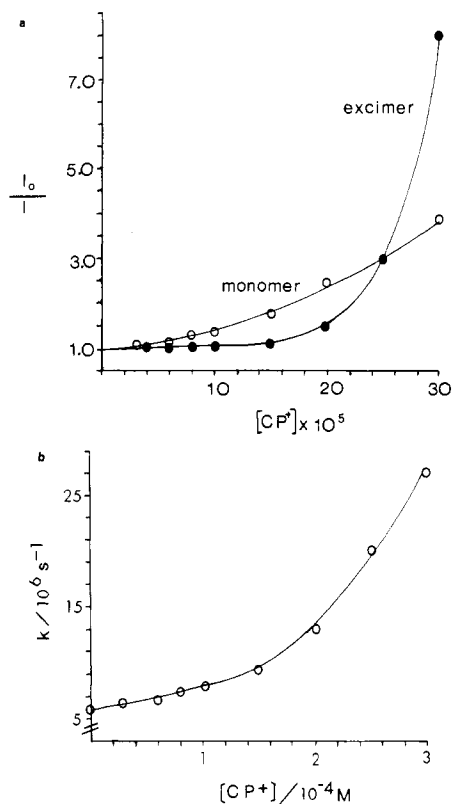


Figure 5. (a) Steady-state quenching of the pyrene monomer (O) and excimer (●) by cetylpyridinium in a dodecanol micelle + dodecanol clay solution. Clay concentration = 1 g/L. (b) The measured transient decay constant of the pyrene monomer vs. the concentration of cetylpyridinium added to a dodecanol micelle + dodecanol clay solution. Note that the inflection point occurs at approximately the same concentration as in Figure 5a, indicating cetylpyridinium quenching on the clay at low concentrations and in the micelle at higher concentrations.

with it, the data suggest that the extent of interaction is slightly different for these cations and increases as $Co^{2+} < Cu^{2+} < Ag^+$.

Figure 5a shows the steady-state monomer and excimer quenching by cetylpyridinium. In the concentration range from 0 to 1×10^{-4} M, a significant difference is evident in this system when compared to a solution containing only dodecanol micelles (Figure 4a). There is a slower rate of monomer quenching while the excimer quenching is nonexistent. In dodecanol micellar solutions, the monomer quenching increased and then decreased while the apparent excimer quenching increased rapidly. The quenching behavior observed in the presence of clay is consistent with that obtained for the inorganic cations. That is, cetylpyridinium is bound to the clay particles and only quenches the monomer that exists in these particles.

As previously discussed, at very low concentrations of cetylpyridinium, incorporation into dodecanol micelles occurs. Evidence for this phenomenon is obtained from the change in the III/I and E/M ratios. Figure 4b demonstrates that for cetylpyridinium concentrations below 1×10^{-4} M in dodecanol micelle/clay colloid systems, the III/I ratio remains constant while the E/M ratio increases slightly due to quenching of the monomer. Adsorption isotherms for this system indicate that up to 1×10^{-4} M, all the cetylpyridinium is bound to the clay particles. Beyond 1.5×10^{-4} M, the cetylpyridinium is distributed between the aqueous phase (containing dodecanol micelles) and the clay particles. There is an extremely rapid increase in the apparent excimer quenching beyond 2×10^{-4} M cetylpyridinium due to its increased concentration in the aqueous phase and subsequent alteration of the micellar structure. These results are similar to those observed at high concentrations in the micellar solutions.

Figure 5b shows the observed decay constant of the pyrene monomer plotted against the cetylpyridinium concentration with an inflection point occurring at approximately 1.7×10^{-4} M. The

initial rate observed when the cetylpyridinium is localized on the clay particles is $2.2 \times 10^{10} M^{-1} s^{-1}$. The faster rate occurs at concentrations in which it exists in the aqueous phase and is $1.4 \times 10^{11} M^{-1} s^{-1}$. This data is in agreement with the adsorption isotherm for cetylpyridinium in these colloids and with the steady-state quenching data which demonstrate that initially it is bound to the clay particles where only monomer quenching occurs. However, at higher concentrations it exists in the aqueous phase where it is incorporated into the dodecanol micelles and quenches both the pyrene monomer and excimer.

Other significant differences noted in the quenching experiments occurred with the iodide ion and nitromethane. As shown in previous work with clay colloids, neither of these molecules has an affinity for the clay surface.^{7,8} In fact, I^- is repelled from the negatively charged particles, which is reflected by a 300-fold reduction in the monomer quenching rate compared to that for homogeneous solution. Since the excimer exists in the dodecanol micelles, it is quenched dynamically at a rate only slightly reduced from that in pure dodecanol micellar solution. A reduction in the monomer quenching was also observed with nitromethane.

Conclusions

(1) The formation of dodecanol micelles in aqueous solution has been demonstrated by surface tension and fluorescence measurements. They have a cmc of approximately 3×10^{-4} M and a measured radius of 1400 Å.

(2) The micelles render a nonpolar environment as evidenced by the III/I ratio of solubilized pyrene. Complete solubilization occurs with excimer formation evident at concentrations of 1×10^{-6} M. Quenching studies with hydrophobic and hydrophilic molecules show the expected trends of enhanced quenching rates in the former case and reduced rates in the latter.

(3) A combination of dodecanol and pyrene have been intercalated into the layers of the montmorillonite as demonstrated from powder diffraction measurements, yielding an interlayer spacing of 13 Å, and quenching studies that indicated two distinct locations for the pyrene.

(4) When these dodecanol/pyrene/montmorillonite powders are suspended in water, a fraction of the dodecanol and pyrene is released into the aqueous phase, forming dodecanol micelles into which the released pyrene is solubilized. The resulting suspension then contains a mixture of colloidal clay particles containing both pyrene and dodecanol in addition to dodecanol micelles containing pyrene.

(5) Due to the large cation-exchange capacity of the clay, the quenching cations are completely bound below the cmc of the colloid. This allowed an interpretation of the quenching reactions occurring solely on the clay particles. No excimer quenching was observed even when large concentrations of quenching cations were adsorbed on the colloid. Beyond the cec when the cations are also in solution, excimer quenching occurs. These results indicate that the pyrene excimer is formed only in the dodecanol micelles and not in the clay particles. It may also suggest that movement of pyrene molecules in the domain of these particles is significantly reduced. Further work is in progress on the diffusion of pyrene within the particles.

(6) The apparent quenching rate constants for the cations Co^{2+} , Cu^{2+} , Ag^+ , and cetylpyridinium are increased compared to those for homogeneous solution. This is due to their increased effective concentration on the clay particles. Reevaluation of these rate constants based on the calculated volume rendered by the clay colloid demonstrates that the actual rates are 1% of those in homogeneous aqueous solution. These results also demonstrated that the adsorbed dodecanol inhibited diffusion of molecules along the clay's surface.

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Registry No. Cu, 7440-50-8; Ag, 7440-22-4; Co, 7440-48-4; I^- , 20461-54-5; ctab, 57-09-0; 1-dodecanol, 112-53-8; pyrene, 129-00-0; cetylpyridinium chloride, 123-03-5; nitromethane, 75-52-5; *N,N*-dimethylaniline, 121-69-7; nitrobenzene, 98-95-3; montmorillonite, 1318-93-0.