

Photophysical and Photochemical Processes on Clay Surfaces

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The past two decades have witnessed an ever-increasing interest in photochemical reactions in small organized assemblies and at interfaces.²⁻⁴ In most systems studied unique chemical effects are observed that are associated with the microenvironment of the reaction zone, a small particle, or an interface. The effects are akin to the more conventional field of solid-state catalysis, and indeed some systems are used in both spheres of chemistry. The systems studied are many and span organic systems such as micelles, microemulsions, and vesicles to inorganic systems such as silica, alumina, semiconductors, and clays. The present Account outlines recent work on photochemistry in colloidal clay systems.

Clay systems either as aqueous colloids or as "dry" clays act as catalysts for photochemical reactions. The nature of the action is understood in terms of established clay chemistry in conjunction with recent photophysical studies. The latter indicates a strong sequestering of reactants on clay surfaces, which promote photochemical reactions of short-lived species. In many cases adsorption of a photoactive molecule on the clay introduces new features into the photophysics and consequently into the photochemistry also. Great attention has to be paid to the geometry of the reactive aggregate that is built on the clay surface, as reactions may be enhanced or eliminated by its exact architecture. Little photochemistry is reported with pillared clays, which are used industrially, and their importance requires future studies. This work is relevant to clay catalysis, studies of organizing assemblies, and environmental photoeffects of molecules adsorbed on clays.

Clay Reactivity and Structure

The structure of various clays has been established for some time,⁵ colloid formation in the aqueous system is understood,^{6,7} and there are many reports of the catalytic effects of clays on thermal reactions.^{7,8} The thermal reactions catalyzed vary from electron-transfer oxidation of amines such as benzidine to polymerization of monomers such as styrene and methyl methacrylate. Brønsted and Lewis sites at the clay edges and transition-metal impurities on the clay lattice are cited to account for the observed chemistry. Up until the advent of zeolites, acid clays were used quite generally as cracking catalysts in the petroleum industry. The

marked thermal reactivity and the ability to form colloids earmark clays for further study and use in photochemical studies.

Many different types of clay occur in nature. The most prominent clays in catalysis are montmorillonite, hectorite, and kaolin. The first clays are designated as 2:1 layered clays and are expandable in water, while kaolin is a 1:1 clay and nonexpandable. The expandable nature of montmorillonite and hectorite makes them particularly suitable for colloidal studies; this will emerge subsequently as the structures of the clays are outlined. Artificial clays also exist, the most prominent being laponite,⁹ which is a lithium magnesium silicate and forms excellent colloids in water. Figure 1 shows, in a diagrammatic sense, the structure of a 2:1 clay such as montmorillonite. Two clay layers are depicted in this figure. The interlayer space shown contains adsorbed cations and may also contain water. The thickness of the clay sheet is 6.6 Å from oxygen atom centers as shown, while the interlayer thickness can vary from several to tens of angstroms, depending on the water content of the clay and on the nature of the material adsorbed or placed in the layer. The clay consists of platelets with long dimensions of several microns and thickness 6.6 Å. In a colloidal solution, one platelet may exist alone or fused with others, giving particles consisting of several platelets. To a large degree, the nature of the aqueous solution controls the number of layers per particle.

Due to isomorphous substitution in the clay structure of one atom with another of lower valency, the clay possesses a net negative charge. The excess negative charge on the clay is balanced by the adsorption of cations onto the layered surfaces. The cation exchange capacity of a clay is very high and approaches 10⁻³ equiv/g of clay. Organic cations such as cetyltrimethylammonium ion may be exchanged onto the clay to produce a hydrophobically modified clay. For the most part, neutral organic molecules such as benzidine

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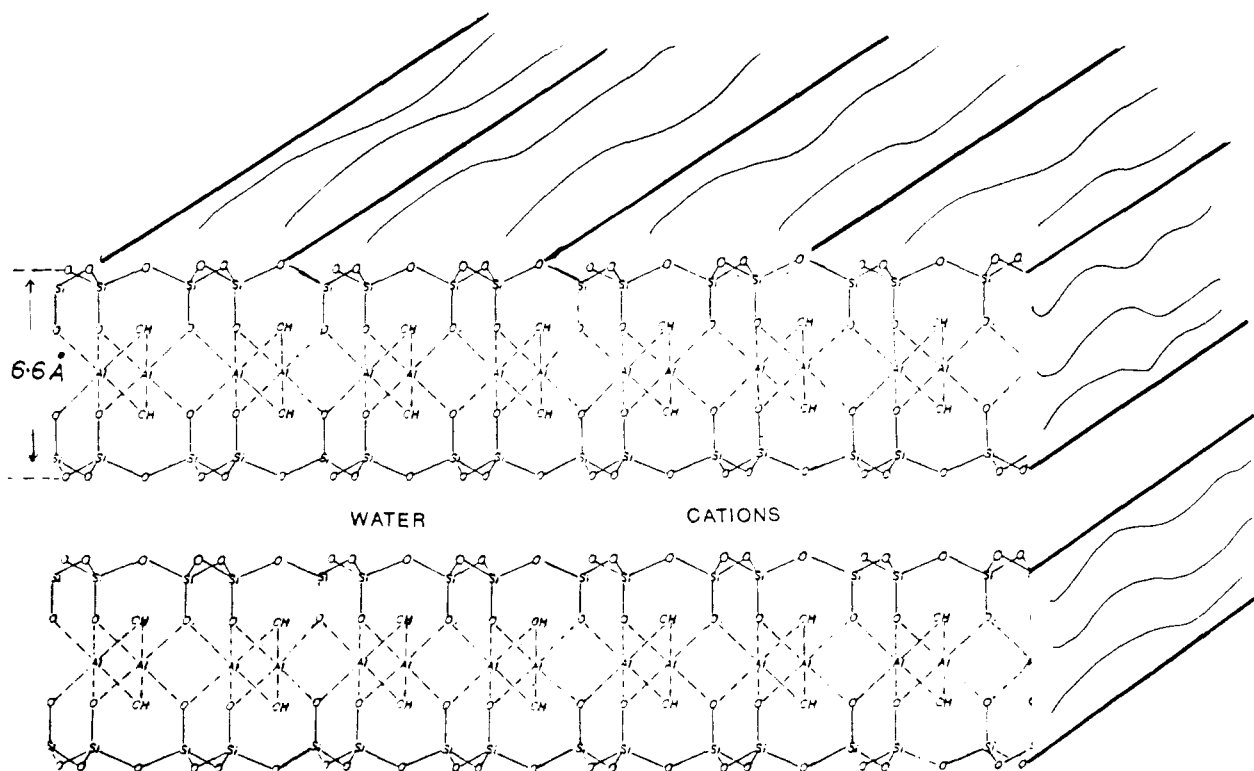


Figure 1. Diagrammatic representation of a 2:1 layer clay structure.

and pyrenes are not adsorbed on aqueous clay colloids, while hydrophobically modified colloids do act as hosts for these materials. Clay, oven dried at 104 °C, adsorbs aromatic molecules from alkane solutions to at least monolayer coverages. Studies reported here are carried out with the colloidal clay system or suspensions of clay in water.

Pillared Clays

The 2:1 layered clays, or smectites, only achieve small interlayer spacings of several angstroms. However, large molecules may be intercalated between the clay layers, and following subsequent heat treatment, large (20 Å and greater) interlayer spacings can be achieved.^{10,11} To date, no photochemistry has been reported in pillared clay systems. The need for a constant interlayer spacing will become even more important in future photochemical studies.

Basic Concepts of Photochemical Studies

The basic contention in all photochemical studies is to adsorb one or more of the reactant molecules on the clay surface. In aqueous colloids this adsorption is mainly due to electrostatic interaction of one of the reactants (a cation) with the negatively charged surface. Both reactants may be adsorbed, as with Ru^{II} and Cu²⁺, or only one may be adsorbed and the other may visit the reactive adsorbed molecule by diffusion from the aqueous phase to the clay surface. In some cases the clay itself may be reactive with the adsorbed molecule, e.g., excited adsorbed Ru^{II} with lattice-bound ferric or cupric ions. Synthetic clays may also be made that have controlled doping of the clay lattice with Cu²⁺ or Fe³⁺ ion. Laponite is a useful clay with little reactivity.

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Nonreactive molecules such as alkylammonium derivatives can be adsorbed to the clay surface, where they act as spacing or insulating units and may also control surface configuration of the adsorbed molecules.

The experimental techniques used are quite common in photochemical studies: steady-state irradiation with the monitoring of products or fluorescence, and laser flash photolysis (response $\sim 10^{-9}$ s) with the monitoring of short-lived intermediates by emission or absorption spectroscopy.³

Photochemical Studies

References 12–29 contain most of the published data on photochemistry in clay systems. Three factors play an important role in all studies: environment, e.g., polarity of clay surface and extent of clay layering, proximity of reactants due to adsorption in a limited space, and geometry of the reactants on the surface.

Aqueous Systems

The fluorescence of tris(1,2'-bipyridyl)ruthenium (Ru(bpy)₃²⁺) has been used to probe and investigate the nature of the surfaces of laponite, hectorite, and montmorillonite.^{12,13,16,17,21} Ru(bpy)₃²⁺ is strongly adsorbed onto clays, and excitation of adsorbed Ru-

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(bpy)₃²⁺ gives rise to a red luminescence with a lifetime of about 0.5 μs. Laponite exhibits fluorescence with a single-exponential decay ($X > 630 \text{ \AA}$), while natural clays tend to exhibit multiexponential decays.

By choosing clays of varying transition-metal content, e.g., iron,^{14,16} one can show that the multiexponential decay (usually double exponential) is due to quenching of excited Ru(bpy)₃²⁺ by lattice iron. Direct synthesis of clays with varying amounts of Cu²⁺ confirms this observation.²⁷ The fluorescence lifetime and quantum yield and the absorption spectrum are dependent on whether the Ru(bpy)₃²⁺ is adsorbed into the clay layers, as in the natural clays, or whether it is adsorbed on the clay surface, as with laponite. The absorption spectrum of aqueous Ru(bpy)₃²⁺ exhibits a metal-to-ligand (d-π) charge-transfer band around 460 nm and a π-π* transition of the ligands around 300 nm. Ru(bpy)₃²⁺ on clays exhibits a red shift of the charge-transfer band and a splitting of the π-π* transition into two peaks. Figure 2a shows the absorption spectrum of Ru(bpy)₃²⁺ in water and when adsorbed on a montmorillonite clay colloid. The significant alteration of the absorption spectrum by the clay is quite apparent as the Ru(bpy)₃²⁺ is adsorbed into the clay colloid layers rather than onto an external surface. Adsorption on an external clay surface is achieved with kaolin colloids, where the Ru(bpy)₃²⁺ adsorption spectrum does not exhibit π-π* splitting and where the spectrum is similar to that in water. The extent of the splitting increases with increased layer formation of the clay. At low concentrations of laponite, Ru(bpy)₃²⁺ is adsorbed on outer layers and is in contact with the aqueous phase. As the clay concentration is increased or in the presence of calcium chloride, the clay tends to form more layers. Consequently, the probe molecule is placed progressively between the layers, where its photophysics is altered. The greatest layer formation occurs with a dry film of laponite, and here the adsorbed Ru(bpy)₃²⁺ exhibits the maximum spectral change in the π-π* transition.

Emission Spectra

The phosphorescence spectra for Ru(bpy)₃²⁺ adsorbed on kaolin or montmorillonite colloids exhibit an emission maximum at 612 nm at 298 K which is identical with that observed in aqueous solution.¹⁷ The emission spectra of Ru(bpy)₃²⁺ at 77 K in 50% ethylene glycol/water glasses (v:v) are shown in Figure 2b. In the ethylene glycol/water glass there is a distinct spectral separation of two of the triplet states, yielding emission maxima at 578 and 620 nm. These results are understood in terms of a thermal redistribution of the relative populations of the triplet states and a matrix-induced distortion of the complex which shift the luminescence to lower energy.²⁸ An increase in the intensity of the emission maximum in the 630-nm region is also observed with increasing distortion of the complex. These effects are most pronounced in the ethylene

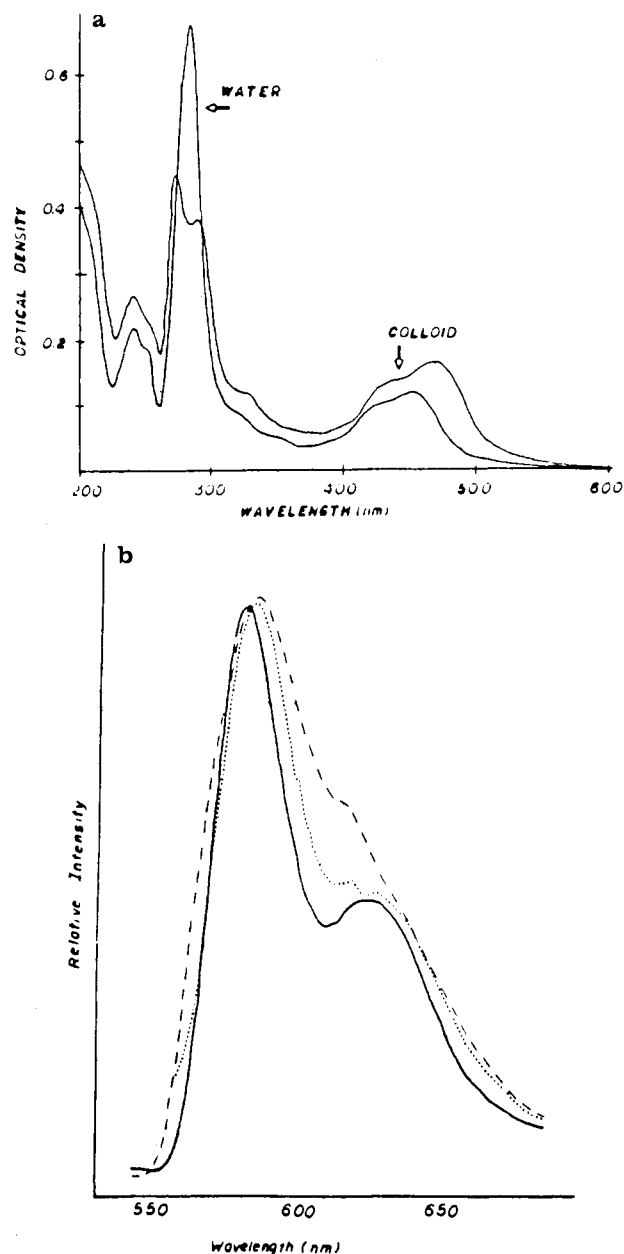


Figure 2. (a) Absorption spectrum of $8.5 \times 10^{-6} \text{ M}$ Ru(bpy)₃²⁺ in water and adsorbed on 1 g of montmorillonite/L with a montmorillonite colloid (1 g/L) in the reference cell. (b) Phosphorescence emission spectra of Ru(bpy)₃²⁺ at 77 K in an ethylene glycol/water glass (—), adsorbed on montmorillonite in an ethylene glycol/water glass (---), and adsorbed on kaolin in an ethylene glycol/water glass (···).

glycol glass. In the kaolin system Ru(bpy)₃²⁺ is adsorbed on the surface and is apparently not as immobilized and distorted by the glass matrix. This is witnessed by the appearance of only a broad shoulder in the 630-nm region. In the montmorillonite samples, intercalation in the layers of the particles separates the complex from the glass matrix to a greater extent, thereby decreasing the matrix-induced distortion such that the emission maximum is not as blue shifted, and the maximum in the 630-nm region appears as only a slight shoulder.

For ethylene glycol, kaolin, and montmorillonite the degree of polarization, p , of Ru(bpy)₃²⁺ phosphorescence at 298 and 77 K was 0, 0.20, 0.10, and 0.15, 0.11, 0.11, respectively. The larger values of p at 77 K in the ethylene glycol glass indicate greater restriction to

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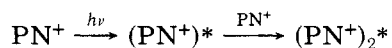
movement placed on the probe molecule. These results support the conclusions reached from the emission spectra at 77 K. For the montmorillonite samples, the lack of change in the degree of polarization upon cooling the solution to 77 K (0.11, 0.11) indicates that the local environment of the $\text{Ru}(\text{bpy})_3^{2+}$ must be such that it is still able to rotate. With kaolin, since only surface sites are available, the $\text{Ru}(\text{bpy})_3^{2+}$ is at least partially exposed to the rigid matrix that forms in the solution at 77 K, and an increase in the degree of polarization is therefore observed (0.10, 0.15). As expected, the maximum effect is observed in ethylene glycol/water mixtures, in which the $\text{Ru}(\text{bpy})_3^{2+}$ becomes trapped in the rigid matrix formed at 77 K and essentially all rotation stops. Methylviologen (MV^{2+}) shows similar effects where the yield of fluorescence is markedly increased on clays. Strong adsorption of MV^{2+} to clay keeps the molecule in a planar configuration and prevents free rotation about the center bond of MV^{2+} that reduces the fluorescence yield.

Cations such as Cu^{2+} and neutral molecules such as dimethylaniline and nitrobenzene are also adsorbed to varying extents on the clay surface. They react with excited $\text{Ru}(\text{bpy})_3^{2+}$ through electron-transfer reactions. Cu^{2+} ions are adsorbed strongly to the clay surface, and the kinetics are simplified due to the strong interaction. The reactants are considered to be concentrated in a volume within 10 Å of the clay surface, i.e., comparable to the interlayer spacing. These data show that the quenching molecules move quite freely on the clay surface in the colloid. The observed kinetics of these latter reactions are of the Poisson form, which indicates that the reactive quencher molecules are adsorbed around the $\text{Ru}(\text{bpy})_3^{2+}$ in a cluster or zone and are not adsorbed randomly throughout the system. This suggests that the adsorption sites are not uniform on the clay surface but occur in regions. This will be discussed in more detail later.

The property of the clay to concentrate reactants has also been observed in energy-transfer studies.²⁶ Energy transfer from excited rhodamine 6G to several cationic dyes is facilitated by aqueous laponite suspensions. The data indicate a variety of adsorption sites, as in the $\text{Ru}(\text{bpy})_3^{2+}$ work.

Surface Configuration

The cationic probe molecule (pyrenylbutyl)trimethylammonium bromide (PN^+) adsorbs strongly to colloidal clays^{18,21,22} and tends to cluster on the clay surface, as the predominant luminescence is that of the excited $(\text{PN}^+)_2^*$, or excimer



Addition of a cationic detergent such as cetyltrimethylammonium bromide (CTAB) decreases the excimer yield and gives a concomitant increase in the yield of monomer excited states $(\text{PN}^+)^*$. This is due to a mixing of the PN^+ and the cationic detergent on the surface, which leads to a separation of the clustered PN^+ on the surface. A cationic detergent with carbon chain >8 is needed to observe this effect. The addition of CTAB also causes a decrease in the degree of fluorescence polarization. This is due to loosening of the chromophore of PN^+ from the clay surface by the CTAB that gives it greater rotational mobility.

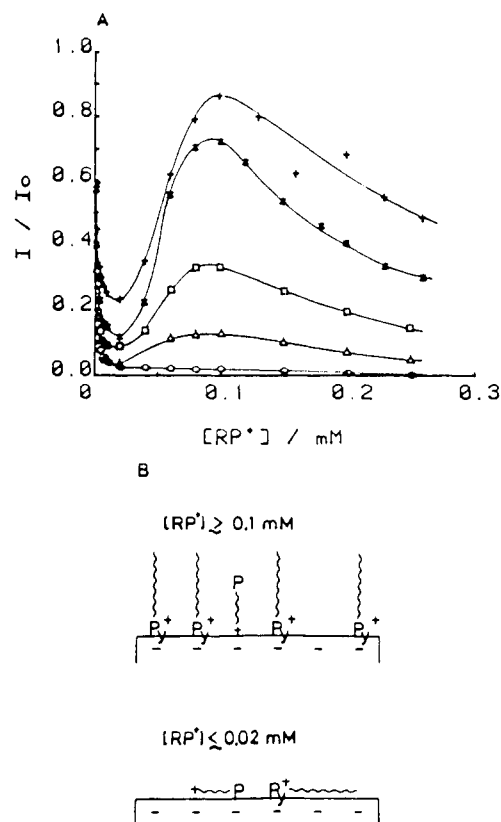


Figure 3. (A) Influence of the alkyl chain length of various alkylpyridinium ions on the PN^+ fluorescence quenching behaviors in laponite colloids (5 g/L): (○) ethyl; (Δ) pentyl; (□) octyl; (*) dodecyl; (+) hexadecyl. $[\text{PN}^+] = 5 \times 10^{-7} \text{ M}$. (B) Schematic model for PN^+ fluorescence quenching by alkylpyridinium ions: Py^+ , alkylpyridinium ions; P, PN^+ .

Recent clay^{21,22} studies have identified the nature of the configuration of adsorbed molecules on clay surfaces and indicate how the geometry of adsorbed molecules at the surface controls the photochemistry. This is borne out by steady-state and time-resolved resolved fluorescence quenching studies of excited PN^+ by cetylpyridinium chloride (CP^+), both reactants being adsorbed on colloidal laponite clay, and typical data are shown in Figure 3. Initial addition of quencher CP^+ leads to an efficient quenching of PN^+ fluorescence. Further increase of quencher gives a reverse effect, whereby the fluorescence recovers to a yield greater than that observed without quencher. The degree of recovery increases with the chain length of the alkylpyridinium ions. These results are explained in terms of a change in geometrical arrangement of PN^+ adsorbed on the clay (Figure 3). PN^+ tends to cluster on the clay surface and the molecules lie on the surfaces with the pyrene chromophore close to the surface. Co-adsorption of alkylpyridinium (AP^+) onto the clay surface places the cationic quenching pyridinium group at the clay surface in close contact with the pyrene chromophore. This leads to quenching of pyrene fluorescence. Further addition of AP^+ leads to formation of a layer of surfactant that solubilizes and locates the pyrene chromophore away from the clay surface. Fluorescence quenching decreases as the pyrene chromophore is now located in a hydrophobic organic environment, quite unlike that of the polar clay surface. The PN^+ fluorescence in hydrophobic environments is larger than that in a polar environment, which accounts

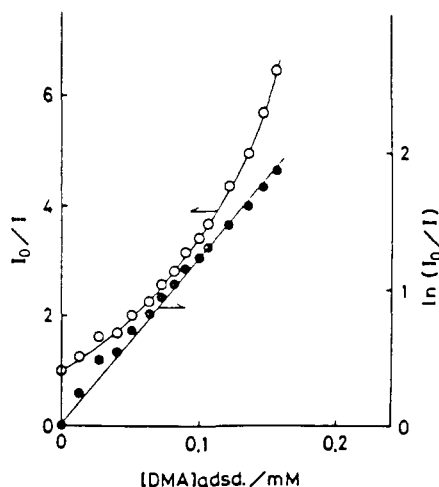


Figure 4. Stern-Volmer plot of PN^+ fluorescence quenching by DMA in the laponite-CTAB system (plot based on eq 1): $[\text{PN}^+] = 5 \times 10^{-6} \text{ M}$, $[\text{laponite}] = 5 \text{ g/L}$, $[\text{CTAB}] = 0.2 \text{ mM}$.

for the subsequent increase of PN^+ in CP^+ , which is greater than that in the absence of the quencher.

PN^+ fluorescence is quenched by dimethylaniline, nitrobenzene, and nitromethane in a CTAB-laponite system, and the kinetics are of the Poisson type. This indicates that the adsorbents exist in the form of clusters or zones on the clay surface. Figure 4 shows typical kinetics for the quenching of PN^+ fluorescence by DMA in the laponite-CTAB system. Homogeneous quenching follows Stern-Volmer kinetics.^{3,23} Here, the fluorescence intensity I in the presence of quencher at concentration $[Q]$ is related to the initial intensity I_0 ($[Q] = 0$) by

$$\frac{I_0}{I} = 1 + \frac{k_q[Q]}{k_0}$$

where k_0 refers to the rate constants for natural decay of the excited state and k_q to that with the quencher. The data in Figure 4 show the Stern-Volmer kinetics do not apply in this system. However, the data follow the Poisson form, i.e.

$$\ln(I_0/I) = [Q]/[\text{site}]$$

while $[\text{site}]$ gives the number of islands of CTAB- PN^+ in the system. With laponite the islands are finite, containing about 100 cationic exchange sites grouped together in close proximity.

Organo-Clays

Clays with a considerable organic function have been constructed by using alkyl quaternary ammonium compounds such as cetyltrimethylammonium bromide (CTAB)^{18,22,24} and dodecyl alcohol¹⁹ as adsorptive additives to the clay. These organic additives form layers of organic material on clay surfaces so that nonionic organic molecules such as pyrene are now readily adsorbed by these organo-clays.

Alkylammonium cations tend to bind tightly to the anionic sites of the clay surface. If $>50\%$ of the CEC of the clay is neutralized by an organic component, then the clay colloid tends to flocculate. Double-layered compounds can be formed with cationic surfactants. A very stable laponite (a synthetic hectorite) aqueous suspension can be prepared where the clay has a double layer of hexadecyltrimethylammonium chloride (CTAC)

adsorbed to its surface. The hydrophobic nature of the clay surface is dramatically improved in this instance; a typical CTAC/laponite system containing 2 mmol of CTAC and 1 g of laponite in 1 L of aqueous suspension dissolves 0.1 mmol of pyrene. This is to be compared to the low solubility of less than a micromole/liter for pyrene in water or clay colloids. The kinetics of pyrene fluorescence quenching of pyrene excimer formation reactions in organo-clay systems suggests that, as in other studies, the CTAC molecules form a clusterlike double layer on the clay surface. With cetyl chains a double layer of about 30-Å thickness is formed on the clay surface, and the anionic charge of the clay is reversed. Surfactant double layers in other systems such as vesicles exhibit phase transitions around ambient temperature. The double layer on a clay surface does not exhibit any phase transitions at temperatures up to 80 °C, probably due to the anchoring of one side of the bilayer to the clay surface. Pyrene excimer formation studies show that the movement of the pyrene molecules in the double layer at ambient temperatures is some 100 times slower than that observed in a long-chain hydrocarbon (with chain length comparable to that of surfactants).

Large organic cations such as rhodamine B, PN^+ , etc. are strongly adsorbed onto colloidal clay surfaces. Weak fluorescence is observed on excitation of these molecules with UV or visible light as the excited states are quenched by the clay, leading to decomposition of the dye. The probe molecule (pyrenylbutyl)trimethylammonium bromide (PN^+) fluoresces well on anionic micelles, on silica particles, and in water but is severely quenched when adsorbed on the clay particles. The yield of fluorescence increases markedly upon addition of cationic surfactants such as cetyltrimethylammonium bromide. The effect is not apparent with short-chain quaternary ammonium compounds, e.g., tetramethyl- or tetraethylammonium bromide. It is concluded that CTAB adsorbed in the vicinity of PN^+ insulates the excited (PN^+)* from the Clay, thereby preventing its photodecomposition and promoting fluorescence.^{23,27}

Formation of Semiconductors on Clays

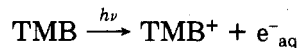
Semiconductors of small size may be synthesized on clay particles. A good example is CdS .^{23,25} The small size of the semiconductor alters its spectroscopic properties. The semiconductors are synthesized with dry clay systems with Cd^{2+} exchanged onto the clay, followed by precipitation with H_2S . With laponite, the particle size is limited by the clay interplanar spacing (11.5 Å) and the $[\text{Cd}^{2+}]$ in the clay. The spectral absorption and emission onsets of this CdS show marked blue shifts compared to those of bulk material. Increasing the local $[\text{Cd}^{2+}]$ on the clay gives rise to a red shift of both absorption and emission spectra as the CdS particle size increases in the layers. Clays provide a convenient "constrained" medium for forming semiconductors with geometries that alter their important semiconductor properties.

Photochemical Oxidation with Clays

It is well established⁷ that aromatic amines (such as benzidine (BD) and tetramethylbenzidine (TMB)) are rapidly oxidized on clays suspended in nonpolar solvents such as hexane. The oxidation takes place slowly in polar liquids with water or water/alcohol mixtures.

Efficient photochemical oxidation also occurs in these systems, yielding products that are identical with those observed in the thermal studies.

Photolysis ($\lambda < 4000 \text{ \AA}$) of BD or TMB in aqueous or alcohol/water mixtures in the presence of colloidal clay leads to a green solution.²⁰ Flash photolysis studies indicate that the initial photochemical event is photoionization in the bulk aqueous phase



as both TMB^+ and e_{aq}^- are observed spectroscopically. The hydrated electron e_{aq}^- reacts rapidly ($\tau_{1/2} < 1 \mu\text{s}$) with O_2 , giving O_2^- ; TMB^+ has a much longer lifetime ($\tau > 1 \text{ ms}$), which is shortened in the presence of clay, when the spectrum characteristic of TMB^+ ($\lambda_{\text{max}} = 4700 \text{ \AA}$) is replaced with a spectrum with λ_{max} at 3900 and 6250 \AA . The resulting species is bound tightly to the clay and is most probably cationic in nature. Unfortunately, its EPR signal is too broad for identification purposes. Addition of acid to the sample changes the color of the clay from green to orange, the color of the dication, TMB^{2+} , and the EPR signal disappears. This is typical of the behavior of TMB^+ in micellar NaLS solutions. The studies show that TMB^+ is captured by the anionic clay, and the TMB^+ -clay interaction gives rise to a dimer of TMB^+ , which is reminiscent of earlier CTAB-PN⁺ studies.

"Dry" Clays

Extremely "dry" clays, i.e., clays dried for 10 h at 105 °C, readily adsorb aromatic molecules from alkane solvents. The adsorption reaches a maximum at about a monolayer coverage, which is about 20% of the CEC

of the clay. Several arenes, e.g., dimethylaniline, tetramethylbenzidine, and aryl phosphates, are thermally decomposed rapidly on the dry clay. Other molecules, e.g., pyrene, anthracene, etc., are photochemically degraded rapidly on dry clays. In all cases colored products are produced. The exact nature of this absorption is not clearly understood.

The dry clays used in the above studies contain as much as a monolayer of adsorbed water. The further removal of this water by heating collapses the clay layers and eliminates any adsorption in the layer space. It is suggested that the monolayer of adsorbed water produces a surface with considerable OH character. By comparison of these data with adsorption studies of arenes on silica and alumina, it is suggested that the surface OH leads to adsorption of arenes and amines by the dry clay.²⁹

Energy Storage on Clays

The literature contains several reports^{12b,15a} regarding clay catalysis of reactions leading to energy storage. The old "chestnut" of photocolloid chemistry, i.e., photoinduced water splitting, has received detailed attention. The results, for the most part, are disappointing, as only small yields of H_2 are obtained. Several other photocatalytic reactions have been attempted with varying degrees of success.^{12b} The clay systems are usually doped with conventional catalysts such as RuO_2 or osmium. Again the studies are interesting but cannot compete with more conventional catalytic systems.

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