

## Adsorption and spectral studies of 3,6-diaminoacridine adsorbed on montmorillonite clay and cellulose

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**Abstract.** Montmorillonite- and cellulose-adsorbed 3,6-diaminoacridine are prepared. The adsorption isotherm studies show that while 3,6-diaminoacridine molecules are adsorbed in the interlayer spaces of the montmorillonite clay, the dye molecules are adsorbed on the surface of cellulose. Quenching studies reveal that the  $Al^{3+}$  ions of the aluminosilicate layers of the clay also quench the excited state emission of the adsorbed 3,6-diaminoacridine.

**Keywords.** Montmorillonite clay; 3,6-diaminoacridine; intercalation.

### 1. Introduction

Clay systems either as aqueous colloids or as dry clays act as catalysts for photochemical reactions. In many cases, adsorption of photoactive molecules like  $Ru(bpy)_3^{2+}$ , pyrene, etc. on the clay introduces new features into the photophysics and consequently into the photochemistry (Thomas 1988). Clay minerals are interesting supports for organic photochemical reactions because of their ion exchange, swelling and adsorptive properties (Theng 1978). In addition, they offer the possibility of organizing the adsorbed molecules in monolayers. The heterogenization of homogeneous catalysts and their reduced mobilities in the adsorbed state with respect to their mobility in solution and the increase of the selectivity of photochemical reactions are some of the benefits expected from surface photochemistry.

3,6-Diaminoacridine is known to reduce water to hydrogen photochemically (Kirch *et al* 1979; Krasna 1979; Kalyanasundaram and Graetzel 1980) in aqueous and micellar solution. Recently, clay minerals have been utilized as supports for photosensitizers (Thomas 1988). We have reported our preliminary results on the adsorption characteristics and spectroscopic studies of 3,6-diaminoacridine on bentonite and kaolin clays and on silica gel (Ramaraj *et al* 1991). The use of solid supports (clay related adsorbants) in the study of photoinduced electron transfer reaction in the heterogeneous state is becoming an alternative assembly for micelle, monolayer, vesicle and polymer systems since the clay support induces a different environment on the adsorbed molecule and new geometries of the reactants in between layers of the clay (Kalyanasundaram 1987; Ramamoorthy 1991) and leads to a wealth of new

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information. Therefore, we studied the adsorption of 3,6-diaminoacridine (PFH<sup>+</sup>) on montmorillonite clay, [(OH)<sub>4</sub>Si<sub>8</sub>(Al<sub>3.34</sub>Mg<sub>0.66</sub>)O<sub>20</sub>], and cellulose and the spectral characteristics of the dye on these supports.

## 2. Experimental

The dye 3,6-diaminoacridine (PFH<sup>+</sup>) (Aldrich) was used after purification (Millich and Oster 1959). Montmorillonite clay (Aldrich) and cellulose powder (SD fine chemical) were used as received. Na<sup>+</sup>-treated montmorillonite was prepared according to the reported procedure (Castro-Acuna *et al* 1987; Kotkar and Ghosh 1987). All other chemicals used in these investigations are of AnalaR grade. Water used was obtained by double-distillation in all-glass apparatus.

For adsorption studies, a mixture of 25 ml of a known concentration of 3,6-diaminoacridine and 0.5 g of montmorillonite clay or cellulose was taken in a beaker and stirred uniformly for 8 hours and the suspension obtained was centrifuged at 5000 rpm for 30 minutes. The sediments were separated, washed and dried. The amount of dye adsorbed on clay or cellulose was determined by spectrophotometrically measuring the absorbance of the dye in the filtrate. Absorption and emission spectral measurements were made for the irreversibly adsorbed dye molecule on clay or cellulose by suspending the solid samples in water.

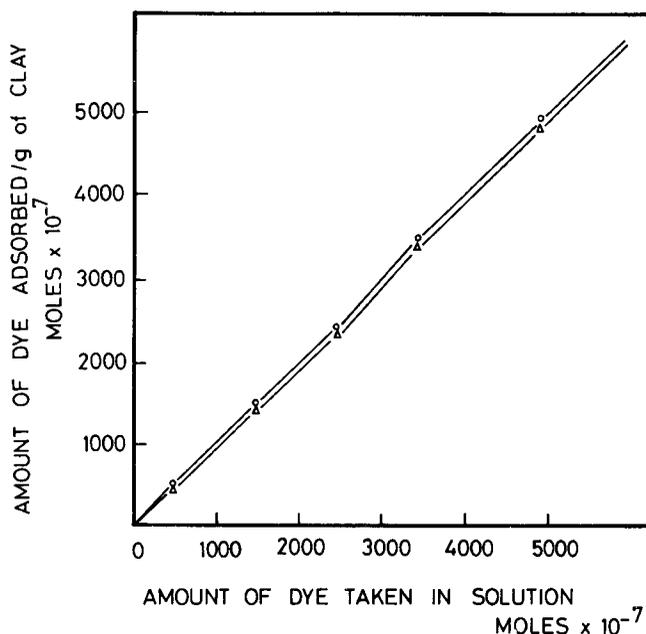
Absorption spectra were recorded with a Perkin 402 spectrophotometer and emission spectral measurements and quenching studies were carried out on a Jasco FP 770 spectrofluorometer. The bimolecular quenching rate constants were calculated using the Stern–Volmer equation.

## 3. Results and discussion

The photochemistry of 3,6-diaminoacridine has been studied in solution and in micellar systems (Kirch *et al* 1979; Krasna 1979; Kalyanasundaram and Graetzel 1980). The absorption spectrum of 3,6-diaminoacridine in water and at pH = 1 shows an intense band around 444 nm ( $\epsilon_{444} = 40,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) (Schoonheyelt *et al* 1986). The emission spectrum of the dye in aqueous solution at pH = 1 shows an intense band around 514 nm. At higher concentrations of 3,6-diaminoacridine, the emission intensity decreases due to self-quenching of the dye and also due to the formation of photochemically inert dimers and aggregates (Haugen and Melhuish 1964).

### 3.1 Adsorption characteristics of 3,6-diaminoacridine adsorbed on montmorillonite and cellulose

Giles *et al* (1960) classified the adsorption behaviour of the solutes on solid particles into four main classes according to the initial slope as *S*, *L* (Langmuir type), *H* (high affinity) and *C* (constant partition). *C* curves are linear and exhibited by solutes which penetrate into solid more readily than the solvent. On the other hand, *L* curves indicate that molecules are adsorbed on the surface.



**Figure 1.** The adsorption of 3,6-diaminoacridine on montmorillonite clay. 3,6-diaminoacridine adsorbed onto Na<sup>+</sup>-montmorillonite clay in water, -Δ-, and onto untreated montmorillonite clay, -○-.

The adsorption isotherms of 3,6-diaminoacridine adsorbed on untreated montmorillonite and Na<sup>+</sup>-montmorillonite in water belong to the C-type as shown in figure 1. Montmorillonite is a 2:1 layered clay which expands in water and the interlayer spaces contain exchangeable cations and water molecules (Grim 1968). The dye 3,6-diaminoacridine is adsorbed into the interlayer spaces of the clay and the process takes place largely by exchange of cations. Exchangeable metallic cations from the interlayer spaces are released into the solution when cationic molecules are equilibrated with clay (Thomas 1988). Hence the adsorbed dye is intercalated into the interlayer spaces of montmorillonite clay and the amount of adsorbed dye increases with the concentration of the added dye. The interlayer spaces of montmorillonite expand (Grim 1968; Thomas 1988) in water to several ångströms (> 6.6 Å). Therefore, more dye molecules can be adsorbed in the interlayer spaces. At very low amounts of 3,6-diaminoacridine (< 10<sup>-5</sup> mol) there is complete adsorption of the dye molecules on 1 g of montmorillonite clay.

The adsorption of 3,6-diaminoacridine on cellulose in water follows the L-type adsorption isotherm (figure 2) (Giles *et al* 1960). The initial slope of the curve shows that as more sites on the surface of cellulose particles are filled it becomes increasingly difficult for the dye molecule to find a vacant site on cellulose. As the concentration of the dye is increased, the adsorption of the dye on cellulose reaches a saturation level (figure 2). It is therefore inferred that all the sites are occupied by the molecules, which leads to the formation of a monolayer on the surface of cellulose. This behaviour is analogous to the adsorption of Rhodamine B on silica gel (Mirza *et al* 1988).

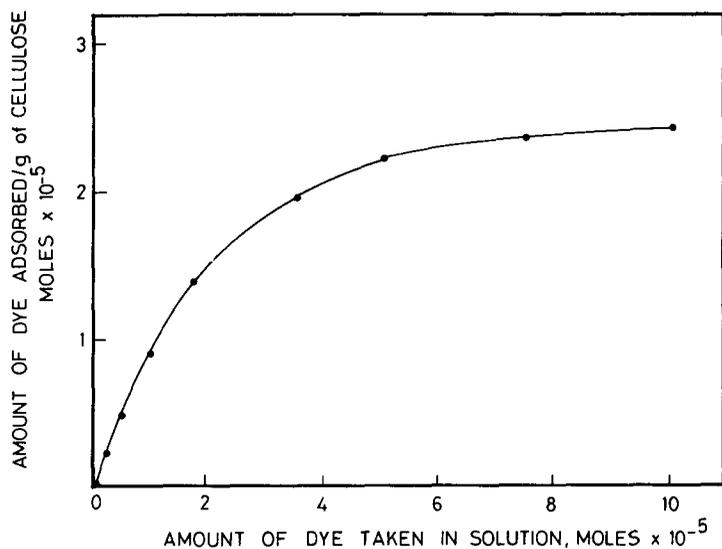
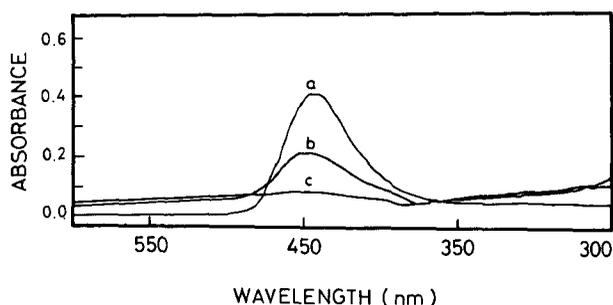


Figure 2. The adsorption of 3,6-diaminoacridine on cellulose in water.

### 3.2 Absorption spectra of the dye adsorbed on clay

A large decrease in absorbance at 444 nm for  $\text{Na}^+$ -montmorillonite clay adsorbed 3,6-diaminoacridine has been observed as shown in figure 3 and this may be attributed to the ready formation of dimers  $(\text{PFH}^+)_2$  and diprotonated species  $(\text{PFH}_2^{2+})$  ( $\epsilon_{\text{max}} = 20,000$  and  $30,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for the diprotonated and dimer species respectively) of the dye when it is adsorbed into the highly acidic clay. While the pH of the free dye solution in the concentration range employed is  $\sim 6.7$ , a perceptible decrease occurs in the pH of the supernatant solution after adsorption (table 1). This not only shows that hydrogen ions are replaced by dye in the case of untreated montmorillonite clay, but also that they are available for protonation. Such a protonation has also been observed for the adsorption of acridine orange and methylene blue on montmorillonite in water (Bergmann and O'Konski 1963; Cohen and Yariv 1984). In the case of  $\text{Na}^+$ -montmorillonite clay, when higher amounts of dye are adsorbed, protons are released and this shows that actually not all protons are replaced by  $\text{Na}^+$  ions during the  $\text{Na}^+$ -montmorillonite clay preparation. However, when low amounts of dye were adsorbed by  $\text{Na}^+$ -montmorillonite clay, the pH of the supernatant liquid is  $\sim 6$  showing that protons are not released. Even though we followed the reported procedure (Castro-Acuna *et al* 1987; Kotkar and Ghosh 1987) to prepare  $\text{Na}^+$ -montmorillonite, this observation clearly shows that not all protons are removed by  $\text{Na}^+$  ions in the montmorillonite clay. This may be due to the ionization of water molecules in the interlayer spaces of the clay.

The absorption spectra of cellulose-adsorbed 3,6-diaminoacridine could not be studied because of the large particle size of cellulose which leads to light scattering.



**Figure 3.** Absorption spectra of 3,6-diaminoacridine adsorbed onto  $\text{Na}^+$ -montmorillonite clay (per gram): (a) free dye ( $10^{-5}$ ); (b)  $1.2 \times 10^{-6}$ ; (c)  $2 \times 10^{-7}$  mol.

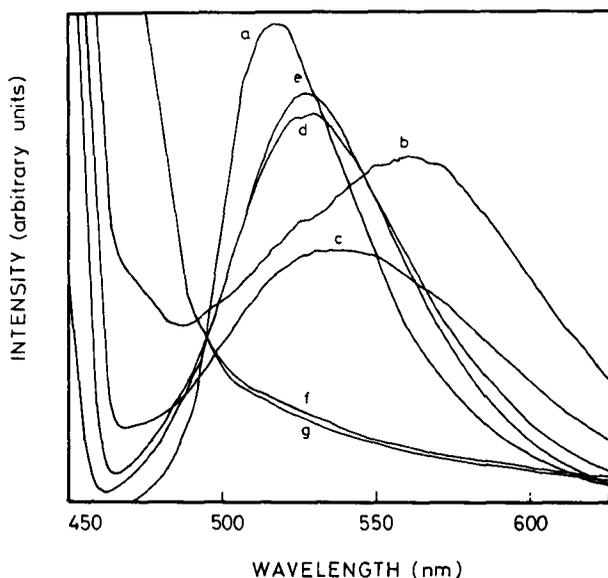
**Table 1.** Effect of the acidic nature of montmorillonite clay on the adsorption of 3,6-diaminoacridine.

Amount of $\text{PFH}^+$ (mol/g clay)	pH of the solution after adsorption (montmorillonite)	pH of the solution after adsorption ( $\text{Na}^+$ -montmorillonite)
$5.0 \times 10^{-4}$	2.9	3.4
$3.5 \times 10^{-4}$	3.0	4.4
$2.5 \times 10^{-4}$	3.1	5.2
$1.5 \times 10^{-4}$	3.3	5.5
$5.0 \times 10^{-5}$	3.5	5.7
$5.0 \times 10^{-6}$	4.1	6.0

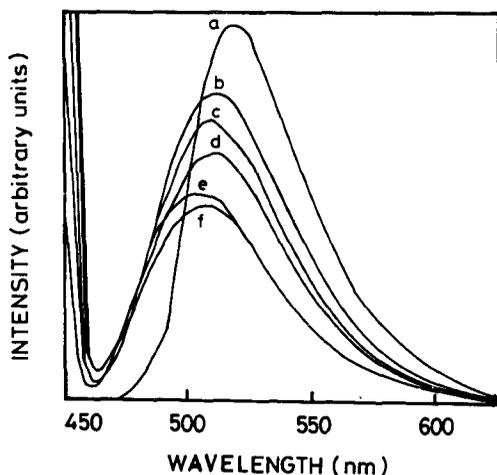
pH of free 3,6-diaminoacridine solution is 6.7

### 3.3 Emission spectral studies

The emission spectra of irreversibly adsorbed 3,6-diaminoacridine on montmorillonite in water show an intense band at 582 nm at the highest loading ( $4.98 \times 10^{-4}$  mol per gram clay) of the dye whereas the free dye in water shows an emission maximum at 514 nm (figure 4). As the loading of the dye decreases, a blue shift is observed and the intensity of the band becomes very weak. When the amount of dye adsorbed onto montmorillonite clay is lower than  $4.99 \times 10^{-5}$  mol per gram clay, the emission of the adsorbed dye is completely quenched. At higher loadings of 3,6-diaminoacridine, dimers and higher aggregates may form easily since montmorillonite clay expands. Schoonheyelt *et al* (1986) believe that the emission around 550 nm is due to the formation of  $\text{PFH}_2^+$  species in the interlayer spaces of clay. Therefore, the formation of dimers or higher aggregates of the dye cations in the interlayer spaces of the clay or  $\text{PFH}_2^+$  may result in metachromasy at higher concentration. At lower loadings of the dye, the dye cation is oriented parallel to the aluminosilicate layers of the clay and the metachromasy is due to the  $\pi$ -interactions between the aromatic ring of the dye and the oxygen plane of the aluminosilicate layer of the clay. At lower loadings of the dye (amount of dye  $< 4.99 \times 10^{-5}$  mol per gram of clay), the emission is completely quenched which may be due to the presence of iron impurities in the clay (Grauer *et al* 1984; Schoonheyelt *et al* 1986; Thomas 1988).



**Figure 4.** Emission spectra of 3,6-diaminoacridine adsorbed on montmorillonite clay (per gram): (a) free dye ( $10^{-5}$ ); (b)  $4.98 \times 10^{-4}$ ; (c)  $3.49 \times 10^{-4}$ ; (d)  $2.49 \times 10^{-4}$ ; (e)  $1.49 \times 10^{-4}$ ; (f)  $4.99 \times 10^{-5}$  and (g)  $4.98 \times 10^{-6}$  mol.



**Figure 5.** Emission spectra of 3,6-diaminoacridine adsorbed on cellulose (per gram): (a) free dye ( $10^{-5}$ ); (b)  $2.4 \times 10^{-5}$ ; (c)  $2.25 \times 10^{-5}$ ; (d)  $1.41 \times 10^{-5}$ ; (e)  $4.83 \times 10^{-6}$  and (f)  $2.36 \times 10^{-6}$  mol.

While the emission spectrum of the free dye shows a maximum at 514 nm, the emission spectrum of 3,6-diaminoacridine adsorbed on cellulose exhibits a band around 510 nm ( $2.25 \times 10^{-5}$  mol  $g^{-1}$  cellulose) (figure 5). When the loading of the dye decreases, the emission intensity also gradually decreases with concomitant shifting of the band to the high energy side of the spectrum. As discussed earlier, the dye molecules are adsorbed on the surface of cellulose particles and  $\pi$ -interaction may occur leading to decrease in emission intensity. Unlike in montmorillonite clay-

adsorbed 3,6-diaminoacridine where the emission is quenched, emission is observed at all loadings of the dye on cellulose.

### 3.4 Quenching of 3,6-diaminoacridine in water by metal ions

When the amount of dye adsorbed on montmorillonite is lower, we observe that the emission of 3,6-diaminoacridine is completely absent. Concentration quenching is ruled out as, at this concentration, the dye cannot exist as a dimer. It has been suggested that  $\text{Fe}^{3+}$  ions present in the clay may quench the emission of the adsorbed dye (Grauer *et al* 1984; Schoonheyelt *et al* 1986; Thomas 1988). We thought that the study of quenching of 3,6-diaminoacridine in water by various metal ions may provide valuable information. Therefore, quenching studies were carried out using 3,6-diaminoacridine as sensitizer and  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  as quenchers at  $\text{pH} = 1$ . From the emission spectral intensities linear Stern–Volmer plots were obtained for the quenching of emission of 3,6-diaminoacridine in solution (figure 6). The bimolecular quenching rate constants are given in table 2. The results clearly show that in addition to  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions also quench the emission of 3,6-diaminoacridine in solution.

In the ground state, there is no interaction between the quencher and the sensitizer,

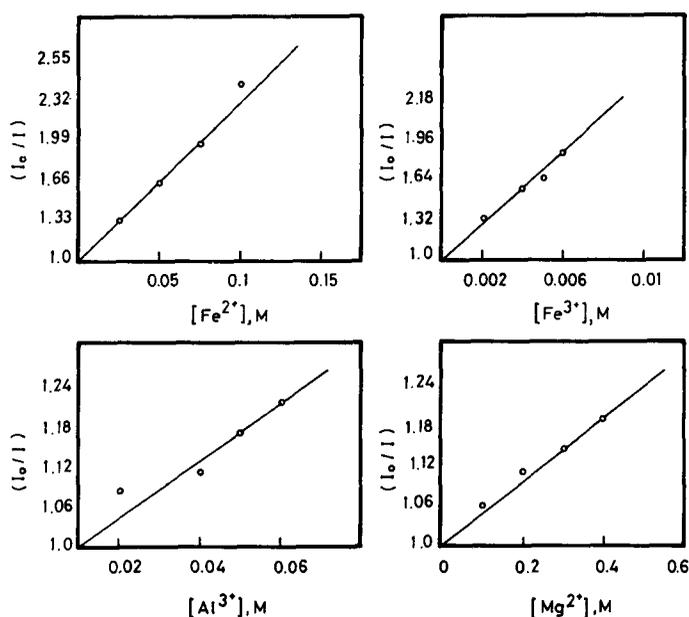


Figure 6. Stern-Volmer plots for the quenching of 3,6-diaminoacridine by  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions.

Table 2. The quenching rate constants for 3,6-diaminoacridine by metal ions in aqueous solution.

Quencher	$\text{Al}^{3+}$	$\text{Mg}^{2+}$	$\text{Fe}^{3+}$	$\text{Fe}^{2+}$
$k_q \times 10^9 (\text{M}^{-1} \text{s}^{-1})$	1.6	0.2	78.3	11.7

as evidenced from the absorption spectrum recorded for a mixture of quencher and sensitizer in solution. Though the emission quenching by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is 10–80 times higher than the quenching by  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions, the latter is also significant. We believe that in addition to quenching by the iron impurities, quenching of 3,6-diaminoacridine in clay may also be caused by ions like  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ . It is not unreasonable to conclude that the  $\text{Al}^{3+}$  of the aluminosilicate layers of the clay may also be responsible for the quenching of the emission of adsorbed 3,6-diaminoacridine in addition to that by iron impurities at low loading. The thickness of the aluminosilicate layer is around 10 Å (Grim 1968). The  $\text{Al}^{3+}$  is located at the centre of the aluminosilicate layer (Grim 1968) and the quenching process can easily take place when the dye is adsorbed between the aluminosilicate layers of the clay.

The weak charge transfer interaction between the excited state dye molecules and the metal centre does not obviously change the absorption characteristics whereas it can lead to quenching of the dye molecules. It appears that (i) the immobilization of the adsorbed dye molecules between the aluminosilicate layers of the clay, and (ii) the parallel configuration of the planar 3,6-diaminoacridine molecule and the aluminosilicate layer favour the efficient quenching of 3,6-diaminoacridine by the  $\text{Al}^{3+}$  of the aluminosilicate layer of the clay.

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