

STUDIES ON THE ADSORPTION OF DYES TO KAOLINITE

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Abstract—The strong adsorption to kaolinite of four polyaromatic, cationic dyes (9-aminoacridine, 3,6-diaminoacridine, azure A and safranin O), which adsorb much less to alumina or silica, was investigated by means of acid-base titrations, measurements of adsorption at varying pH and dye concentration, and by ATR-FTIR spectroscopy. The four dyes adsorb to kaolinite to similar extents, with little change over the pH range 3–10, but at higher pH (above the pK_a s of the dyes) the adsorption of 9-aminoacridine and 3,6-diaminoacridine decreases, that of azure A increases, and that of safranin O stays approximately constant. Although the dyes adsorb to kaolinite much more strongly than metal ions do, titration and spectroscopic data show that there is only limited chemical interaction between the adsorbed dyes and the kaolinite surface. The results indicate that electrostatic interaction between the dye molecules and the kaolinite surface is necessary for adsorption, but that hydrophobic interactions also contribute. It is proposed that the relatively hydrophobic silica faces of kaolinite, which carry low-density permanent negative charge, facilitate aggregation and adsorption of the positively charged, flat, aromatic dye molecules.

Key Words—9-aminoacridine, 3,6-diaminoacridine, ATR, Azure A, Clay, Dye, Isotherm, Kaolin, pK_a , Preferential Adsorption, Safranin O.

INTRODUCTION

In an earlier paper (Harris *et al.*, 2001) we reported that a number of polyaromatic dyes adsorb selectively to kaolinite. Of 23 aromatic solutes tested, all but one adsorbed more to kaolinite than to amorphous alumina, and five of them — characterized by flat, polyaromatic, cationic dye molecules — adsorbed more than 20 times as much to kaolinite as to alumina. Further experiments with four of the dyes established that they adsorbed only slightly to silica or gibbsite, the surface structures of which are closely related to those of the basal faces of kaolinite, and that the selectivity towards kaolinite persisted over a wide pH range. The adsorption densities at the kaolinite surface exceeded monolayer coverage of the flat faces, regardless of how the dye molecules might be oriented at the kaolinite surface.

On the basis of the experimental data we suggested that the flat, rather hydrophobic, yet positively charged dye molecules adsorb in aggregates at the flat silica faces of kaolinite, which are considered to have hydrophobic character (Tunega *et al.*, 2004) but also to carry a small pH-independent negative charge due to isomorphic substitution of Al^{3+} for Si^{4+} atoms in the structure (Grim, 1962).

In previous studies of the adsorption of dyes to kaolinite (De *et al.*, 1968; Hang and Brindley, 1970; Awal, 1988; Kamel *et al.*, 1991; Yariv *et al.*, 1991; Awal and Ghimire, 1992) quantitative aspects have not been examined closely, nor have there been detailed attempts to model the adsorption behavior.

Yariv *et al.* (1991) observed metachromasy when crystal violet and ethyl violet adsorbed to kaolinite. They likened the kaolinite surface to that of a polyelectrolyte, and proposed that metachromasy was an indication of dimerization and aggregation of the adsorbed dyes at the clay surface. They proposed that the aggregation involved interaction between π -electrons of the aromatic rings of adjacent dye molecules, and concluded that the surface of kaolinite was a favorable environment for association of adsorbed organic species. Conversely, Cenens and Schoonheydt (1988) explained the metachromatic behavior of methylene blue on Laponite and hectorite purely in terms of dye aggregation (due to its high surface concentration), without reference to π -electron interaction with the surface oxygens.

A number of attempts have been made to determine the orientation of dye molecules adsorbed to clay surfaces or the extent of their aggregation (Ramachandran *et al.*, 1962; Serratos, 1966; Hang and Brindley, 1970; De *et al.*, 1974; Nikolenko *et al.*, 1997; Atun *et al.*, 1998; Sukhishvili and Granick, 1999). Models that have been proposed include adsorption with the plane of the aromatic rings parallel to the clay surface (Giles *et al.*, 1969; Rytwo *et al.*, 1995), perpendicular to the clay surface (Atun *et al.*, 1998), or at an acute angle to the clay surface (Rytwo *et al.*, 1995). There have been suggestions (Cenens and Schoonheydt, 1988; Yariv *et al.*, 1991; Breen and Rock, 1994) that dyes adsorb as monomers, dimers, trimers, micelles or a combination of these.

Fischer *et al.* (1998) concluded from NEXAFS data that crystal violet and malachite green adsorb to mica with an angle of ~ 55 – 60° between the plane of the molecule and the mica surface. Their work also suggested that only one of the amino groups of the

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adsorbate molecule was involved with adsorption, the other one or two facing away from the surface.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopic studies of the adsorption of organic compounds to minerals have been used to distinguish between inner-sphere and outer-sphere complexation. Formation of inner-sphere complexes involves breaking and forming new chemical bonds; hence vibrational states are significantly affected, causing band shifts in the order of 10–30 cm⁻¹, but shifts associated with formation of outer-sphere complexes are much smaller, generally only 3–6 cm⁻¹ (Persson *et al.*, 1998a, 1998b).

Adsorption systems that have been studied by ATR-FTIR spectroscopy include the adsorption of phthalate to alumina and goethite (Persson *et al.*, 1998b), phthalate, trimellitate and pyromellitate to goethite (Boily *et al.*, 2000), glutamic and aspartic acids to TiO₂ (Roddick-Lanzilotta and McQuillan, 2000), dicarboxylic acids to kaolinite (Specht and Frimmel, 2001) and goethite (Axe and Persson, 2005), glyphosate to goethite (Sheals *et al.*, 2002), citric acid to illite (Lackovic *et al.*, 2003b) and mellitic acid to goethite (Johnson *et al.*, 2004).

The characterization of adsorbed complexes by ATR-FTIR spectroscopy can provide a sound starting point for the development of quantitative adsorption models. For example, Persson *et al.* (1998b) found that phthalate adsorbed to boehmite via a chelating inner-sphere complex and an outer-sphere non-protonated complex. No protonated surface complex formed, irrespective of the pH of the system. These conclusions were invaluable for the formulation of a realistic surface complexation model for their system. Similarly, Lackovic *et al.* (2003b) used ATR-FTIR to determine that citrate adsorbs to goethite as an inner-sphere complex at pH 4.6 and 7, but as an outer-sphere complex at pH 8.8.

In this paper we present a more detailed study of the adsorption of four dyes that adsorb selectively to kaolinite: 9-aminoacridine (9-Aa), 3,6-diaminoacridine (3,6-Daa), azure A (Az-A) and safranin O (Saf-O). We have used a number of different techniques – acid-base titrations, quantitative adsorption measurements under varying conditions of pH and dye concentration, and ATR-FTIR spectroscopy – in order to generate a range of data that can be used to draw conclusions about the nature of the interactions between the dyes and kaolinite. These observations, together with the results of a related study (Harris *et al.*, 2006b), are used in an accompanying paper (Harris *et al.*, 2006a) as the basis for a model for dye adsorption.

MATERIALS AND METHODS

Materials

9-Aminoacridine hydrochloride hydrate (52417-22-8; 98%), 3,6-diaminoacridine hydrochloride (952-23-8; 95%), azure A (531-53-3; 98%) and safranin O (477-

73-6; 96%) were obtained from Sigma. Other reagents were of analytical reagent grade. Fresh stock solutions of the dyes (5 mM for 9-aminoacridine and 3,6-diaminoacridine; 2 mM for azure A and safranin O) were prepared weekly and stored in borosilicate glass vessels in the dark. Milli-Q[®] reagent-grade water (Millipore Corp., Bedford, USA) was used throughout.

Acid-washed kaolinite (Ajax Chemicals, Sydney, Australia), as used in several previous studies (Angove *et al.*, 1997, 1998, 1999; Harris *et al.*, 2001; Lackovic *et al.*, 2003a, 2003b) and referred to in this paper as 'Ajax kaolinite', was used without further treatment. X-ray diffraction data (Philips PW1710 X-ray diffractometer fitted with a Cu target) showed that it was highly crystalline, with a basal (*d*₀₀₁) spacing of 7.17 Å. Scanning electron micrographs (Cambridge S150 Stereoscan) showed hexagonal plate-like crystals ~1.5–2 µm across and ~0.2 µm thick. The BET surface area (measured on a Micromeritics AP2000 instrument after out-gassing at room temperature for 16 h) was 14.7±0.1 m²g⁻¹.

A second kaolinite sample, from Weipa, Queensland, Australia (kindly supplied by Comalco Research Laboratories, Melbourne, Australia), referred to here as 'Comalco kaolinite', had a BET surface area of 28.1±0.1 m²g⁻¹ and comprised thicker crystals with smaller diameter. The face:edge ratio was approximately one third that of the Ajax kaolinite. This sample was used previously by Angove *et al.* (1997).

Amorphous alumina from Queensland Alumina Limited (kindly supplied by Comalco Research Laboratories, Melbourne, Australia) was used without further treatment. X-ray diffraction data showed that it was almost entirely amorphous, with a small amount of corundum evident.

Measurement of pH

Orion Ross Sure-Flow double junction combined pH electrodes (with outer reference electrolyte 0.1 M KNO₃) and Metrohm 632 pH meters were calibrated with NBS standard buffers (pH 4.01, 6.86 and 9.18) before and after each experiment. Experimental results were accepted only if the initial and final calibrations agreed within 0.05 pH units.

Determination of dyes

Samples were centrifuged at 12,000 g for 15 min; the supernatant solutions were diluted quantitatively with buffer to give absorbances of <1, and the absorbances measured in a Varian DMS-80 UV-visible spectrophotometer (at 400 nm for 9-Aa; at 443 nm for 3,6-Daa; at 622 nm for azure A; at 518 nm for safranin O). Linear calibration curves were constructed from absorbance measurements of stock solutions diluted in the same manner. Phthalate buffer (pH 4.01) was used to dilute 3,6-Daa solutions, and borax buffer (pH 9.18) was used for the other dyes.

Adsorption experiments and titrations

Titrations and adsorption experiments were performed in borosilicate glass reaction vessels under an atmosphere of CO₂-free nitrogen. Reaction mixtures were stirred continuously and maintained at 25°C (± 0.5°C) by water circulated from a thermostated bath through the jacket of the reaction vessel. The background electrolyte was 10 mM KNO₃. Kaolinite was allowed to hydrate for at least 18 h in a stirred, CO₂-free suspension before any experiment involving suspended kaolinite.

Titration of dye solutions

To 50 mL of 1.00 mM dye in 10 mM KNO₃ small volumes (10–50 µL) of 0.0975 M KOH were added successively from a PC-controlled piston burette (Metrohm 655 Dosimat). After each addition, the pH was recorded once it was stable (drift of <0.004 min⁻¹). The process was repeated until the pH of the solution was ~11.

pH dependence of adsorption

A suspension of kaolinite (8 or 10 m²L⁻¹) in 10 mM KNO₃ was equilibrated overnight, and then the pH was decreased to ~3.5 with a measured quantity of 1 M HNO₃. Sufficient stock solution of dye was added to give a total concentration of 80 µM, and the suspension equilibrated for a further 30 min. A sample was taken and centrifuged, and the supernatant solution immediately assayed for adsorbate. Then KOH was added to the remaining suspension to raise the pH by ~0.5, the suspension re-equilibrated for 15–20 min and another sample was taken. (Preliminary experiments showed that the concentration of the adsorbate in solution became constant within 5 min.) This process was repeated until the pH of the suspension was ~12.

Adsorption isotherms

A suspension of kaolinite (8 m²L⁻¹) in 10 mM KNO₃ was equilibrated overnight. The pH was adjusted to 5.5 or 9.0 and a measured quantity of dye was added to the suspension to give a total concentration of ~5 µM. The system was allowed to equilibrate for 15 min, and then a sample was taken and centrifuged, and the supernatant solution immediately assayed for adsorbate. Further additions of dye were made, with subsequent sampling, until the total solution concentration of dye was ~150 µM. The pH of the suspension was maintained at the chosen value of 5.5 or 9.0 by addition of 0.1 M HNO₃ or KOH as required from a PC-controlled piston burette (Metrohm Dosimat 655).

Titration of kaolinite suspensions

A suspension of kaolinite (100 m²L⁻¹) in 10 mM KNO₃ was equilibrated overnight, and then titrated with standard KOH as described above for dye solutions. Approximately 70–100 additions of KOH were made

over a period of ~36 h, to raise the pH from ~4 to 10. For titrations of dye and kaolinite together, the dye was added at a total concentration of 0.6 mM after overnight pre-equilibration of the kaolinite suspension, and the system equilibrated for a further 30 min before the titration was commenced.

To obtain useful data from the titrations a surface area of 100 m²L⁻¹ was needed. Much lower concentrations of kaolinite were used for dye adsorption experiments because the dyes adsorbed strongly to kaolinite.

Infrared spectroscopy

The ATR-FTIR spectra of dyes, in solution or adsorbed to kaolinite, were collected at room temperature with a Perkin-Elmer 1720X FTIR spectrophotometer equipped with a SensIR Technologies DurasamplIR horizontal ATR attachment incorporating a diamond coated, 9-bounce ZnSe ATR crystal. The optical path was flushed with nitrogen before and during analysis to minimize interference by water vapor and CO₂. The spectra were collected and manipulated with *Spectrum for Windows v1.5* software (Perkin-Elmer).

For each sample, 200 or 500 scans, depending on the strength of signal, were taken at a resolution of 2 cm⁻¹. Aqueous dye solutions were prepared at as high a concentration as possible (near saturation): for 9-aminoacridine 10 mM; for 3,6-diaminoacridine 5 mM; for azure A 5 mM; for safranin O 2 mM. Sufficient solution was added to cover the entire surface of the crystal, and the sample covered by a concave lens pressed onto a neoprene o-ring to prevent evaporation and CO₂ contamination.

Kaolinite pastes were prepared with ~0.5 g of kaolinite. A few mL of water were added to wet the kaolinite, and then dye solution (adjusted to the desired pH) was added and the suspension agitated. It was then allowed to settle and if the supernatant suspension was clear (*i.e.* all of the dye had been adsorbed to the kaolinite) most of the supernatant solution was decanted and more dye solution was added. This was repeated until the supernatant solution remained colored, and hence the kaolinite surface saturated with dye. The pH was re-adjusted if necessary, by the addition of 1 M HNO₃ or KOH, the suspension was centrifuged, and spectra of the empty cell, the supernatant solution and the wet paste were measured. The kaolinite paste with and without adsorbed dye was placed on the ATR crystal, covered with the concave lens, and allowed to settle for a few minutes before the spectrum was recorded.

The background spectrum of the ATR crystal was subtracted from each raw spectrum, and then the appropriate supernatant solution (or water) spectrum was subtracted to yield a spectrum of the system of interest (the kaolinite surface, the dye, or the dye adsorbed to the kaolinite surface). Finally, a kaolinite spectrum was subtracted from that of the kaolinite-dye

paste to yield a spectrum of the adsorbed dye. In many cases the spectra included low-amplitude peaks arising from trace amounts of water vapor in the sample chamber: these were removed by subtracting a water-vapor spectrum.

It should be noted that much greater dye concentrations were needed for IR spectroscopy, so that, of necessity, the conditions did not match those for other experiments.

RESULTS AND DISCUSSION

Acid dissociation constants of dyes

1 mM aqueous dye solutions were titrated against standard KOH. Acid dissociation constants were estimated by fitting the titration curves by use of the curve-fitting program *GrFit* (Ludwig, 1996), and also as described by Albert and Serjeant (1971). The constants obtained from the two methods agreed within 1–2%. The uncertainties shown in Table 1 for the pK_a values represent the range of values from the two methods. The values for the aminoacridines are in good agreement with those from the literature. We were unable to find previous reports of pK_a s for the other two dyes.

The values of pK_a indicate that the molecules are positively charged over most of the pH range studied here. Were adsorption governed wholly or in part by electrostatic interactions, any noticeable change in adsorption at pH values below the dye pK_a would probably involve changes to the substrate surface, rather than the adsorbing molecule. This is discussed in more detail below.

Titration of kaolinite and dye suspensions

Potentiometric titrations of kaolinite suspensions are shown in Figure 1 (kaolinite alone) and Figure 2 (kaolinite plus dye). The symbols are for triplicate titrations; the gray line in Figure 1 represents an average, which is repeated in Figure 2 to facilitate comparison between the titrations of kaolinite suspensions with and without added dye.

The kaolinite titration curves were altered only a little by the addition of 9-Aa, 3,6-Daa or Saf-O. The protonation of the dyes in solution remains almost

constant up to \sim pH 8: in this range the greatest displacement in the titration curves represents the consumption of <1 proton for each 10 dye molecules. The presence of Az-A did affect the kaolinite titration at pHs <9 , suggesting that it may interact with the kaolinite surface more than the other three dyes.

We shall see below that the dyes adsorbed strongly to kaolinite across the pH range 3–10. The slight effect of dyes on the titration curves shows that adsorption did not involve significant uptake or release of protons, consistent with outer-sphere complexation at the permanently-charged faces.

pH dependence of adsorption

Adsorption of the four dyes onto Ajax kaolinite and amorphous alumina was measured in duplicate as a function of pH: the results are shown in Figure 3. The data for the adsorption of the dyes to alumina overlay one another: for the sake of clarity the results are shown only for one of the dyes.

None of the dyes adsorbed significantly to alumina over the pH range 4–12. All of them adsorbed much more to kaolinite, the strong preference for the kaolinite surface persisting from conditions under which the variable charge surfaces are positively charged (up to about pH 6 or 7 for the edges of the kaolinite crystals and pH 8.5 for this amorphous alumina sample – R.G. Harris, unpublished data) to conditions under which these surfaces are negatively charged. Earlier data (Harris *et al.*, 2001) showed that these dyes adsorb only slightly to gibbsite, a crystalline form of alumina

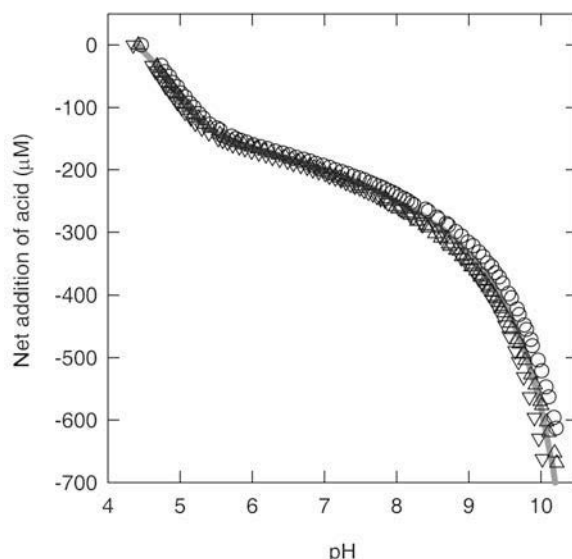


Figure 1. Potentiometric titrations of kaolinite suspensions. The symbols represent experimental data for triplicate titration experiments. The gray line is an empirical fit, which is repeated in Figure 2 to facilitate comparison with the titrations of kaolinite–dye systems presented in Figure 2. [Kaolinite] = $100 \text{ m}^2 \text{ L}^{-1}$; $[\text{KNO}_3] = 10 \text{ mM}$.

Table 1. Acid dissociation constants.

	pK_a	
	This work	Literature
Safranin-O	11.2 (± 0.1)	
Azure-A	10.6 (± 0.1)	
9-Aminoacridine	9.85 (± 0.05)	9.99 ^{a,b} , 10.0 ^c
3,6-Diaminoacridine	9.53 (± 0.05)	9.65 ^a , 9.7 ^c

^a Albert (1966)

^b Acheson (1973)

^c Albert (1968)

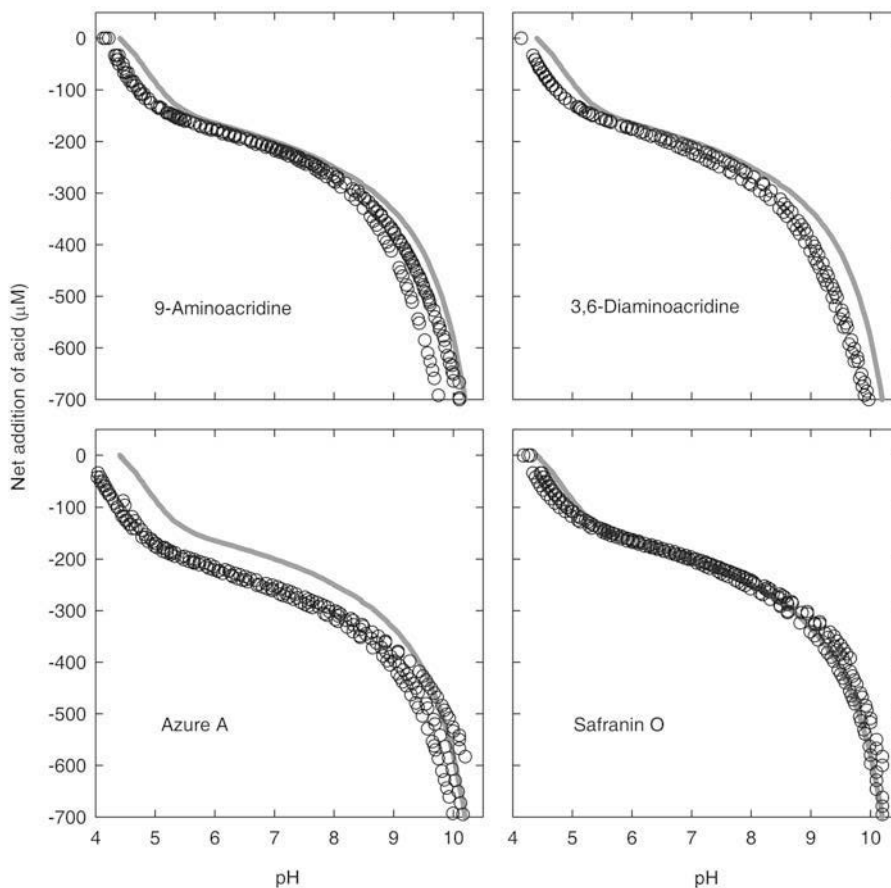


Figure 2. Potentiometric titrations of kaolinite suspensions in the presence of dyes. The symbols represent experimental data for triplicate titration experiments in the presence of dyes. The gray line is from Figure 1, to facilitate comparison with the titrations of kaolinite presented only in Figure 1. [Kaolinite] = $100 \text{ m}^2 \text{ L}^{-1}$; $[\text{KNO}_3] = 10 \text{ mM}$; [dye] = $600 \text{ } \mu\text{M}$.

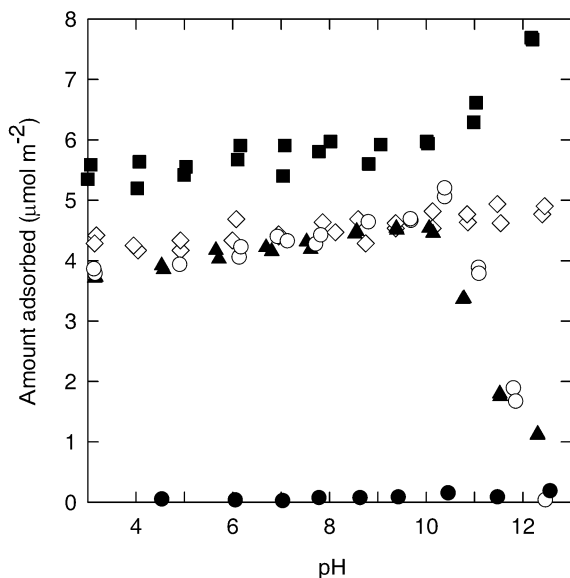


Figure 3. Adsorption of dyes to kaolinite: (○) 9-aminoacridine; (■) azure A; (▲) 3,6-diaminoacridine; (◇) safranin O; and to amorphous alumina: (●) 9-aminoacridine (representative of the four dyes studied). [Kaolinite] = $8 \text{ m}^2 \text{ L}^{-1}$; [alumina] = $80 \text{ m}^2 \text{ L}^{-1}$; [dye] = $80 \text{ } \mu\text{M}$; $[\text{KNO}_3] = 10 \text{ mM}$.

the surface structure of which is very similar to that of the alumina faces of kaolinite.

Uptake of each of the dyes by kaolinite increased gradually but steadily from pH 4 to about pH 10 or 11, at which point about half of the added dye was adsorbed. Between pH 10 and 12.5, at and above the pK_a s of the dyes, the dyes behaved differently. Adsorption of Saf-O continued to increase steadily, but that of the two aminoacridines decreased almost to zero, and that of Az-A increased more dramatically.

Dyes such as the four chosen for study are known (Bradley and Wolf, 1959; Coates, 1969; Yariv *et al.*, 1991; Breen and Rock, 1994; Wang, 2000) to form aggregates in aqueous solution, probably by π -stacking of the flat, aromatic molecules. Calculations in an earlier paper (Harris *et al.*, 2001), supported by results of the present study (see below), showed that the dyes almost certainly adsorb in layers more than one molecule thick, suggesting that adsorption is associated with aggregated clusters of molecules. The gradual increase in adsorption of the four dyes between pH 4 and 10 may result from an increase in the size of the dye aggregates as the average charge per molecule decreases.

The aminoacridines become deprotonated around their pK_{as} (9.53 for 3,6-Daa; 9.85 for 9-Aa), and hence uncharged. Thus the electrostatic attractions between the dyes and the permanent negative charges on the silica faces of kaolinite diminish, which may account for the decreased adsorption above pH 10. Az-A and Saf-O, by contrast, carry two positive charges (one due to a tertiary amine) at low pH, and remain positively charged above their pK_{as} (10.6 for Az-A; 11.2 for Saf-O), allowing continuing electrostatic attraction to the small but permanent negative charges on the silica face of the kaolinite. Although it is possible that Az-A precipitates at high pH, which would result in an apparent increase in adsorption such as that seen in Figure 3, there was no corresponding increase in the sorption of Az-A to amorphous alumina under the same conditions. This suggests that adsorption to kaolinite did indeed increase substantially at high pH.

The lack of adsorption of Az-A and Saf-O on alumina, even at high pH, indicates that while electrostatic attraction may be necessary for adsorption, it is not a sufficient condition. This is also borne out by the small pH dependence of adsorption up to pH 10, and the fact that there is no noticeable change in adsorption around pH 7 (as is often observed for metal ion adsorption) where the kaolinite edge becomes negatively charged.

It would have been advantageous to conduct some adsorption experiments at a much greater ionic strength in order to suppress electrostatic interactions, but as we noted previously (Harris *et al.*, 2001), the solubilities of the dyes are very limited at high ionic strength, so that was not possible.

Adsorption to Comalco kaolinite

The crystals of Comalco kaolinite have a smaller face:edge area ratio than those of Ajax kaolinite (Angove *et al.*, 1997). Adsorption of the dyes to Comalco kaolinite (Figure 4) follows a similar pattern to their adsorption to Ajax kaolinite, except that the amount adsorbed to Comalco kaolinite is a little less than half that for Ajax kaolinite. This corresponds closely to the ratio of the total areas of crystal faces in the experiments with the two kaolinites, giving strong support to the view that adsorption of dyes takes place only on the kaolinite faces, and not the edges.

Although the pH in this experiment was not raised as high as it was for Ajax kaolinite, desorption of 3,6-Daa at higher pH is still evident.

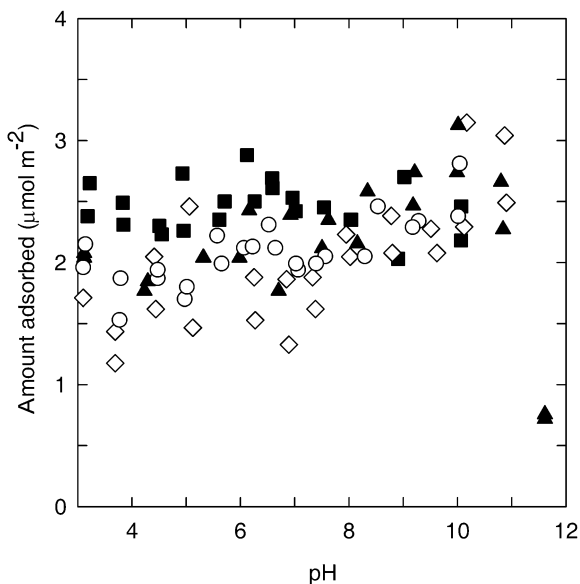


Figure 4. Adsorption of dyes to Comalco kaolinite: (○) 9-aminoacridine; (■) azure A; (▲) 3,6-diaminoacridine; (◇) safranin O. [Kaolinite] = 10 m²L⁻¹; [dye] = 100 μM; [KNO₃] = 10 mM.

Adsorption isotherms and Langmuir fitting

Adsorption of the four dyes to Ajax kaolinite was measured as a function of solution concentration at pH 5.5 and pH 9.0, with the results shown in Figure 5. All the dyes adsorbed strongly, as indicated by the initial slopes of the isotherms, and appeared to approach limiting values of adsorption at low solution concentrations. This behavior was especially apparent for Saf-O and Az-A but less so for 9-Aa.

Although a simple empirical model cannot be expected to describe the adsorption of the dyes fully, it was convenient for initial evaluation of the data to use the Langmuir isotherm:

$$N = \frac{N_m KC}{1 + KC}$$

where N is the amount adsorbed per unit area of substrate, and C is the equilibrium concentration of adsorbate in solution. Values for N_m , the maximum adsorption density, and K , the equilibrium constant for adsorption, were estimated by non-linear fitting of the data with *Sigma Plot v. 2.01* software (Jandel Scientific Software), yielding the parameters shown in Table 2.

Table 2. Langmuir parameters for adsorption of dyes onto kaolinite.

	K (m ³ mol ⁻¹)		N _m (μmol m ⁻²)	
	pH 5.5	pH 9.0	pH 5.5	pH 9.0
9-Aminoacridine	64 (±9)	70 (±6)	5.1 (±0.2)	7.2 (±0.2)
3,6-Diaminoacridine	750 (±70)	310 (±30)	3.5 (±0.2)	5.0 (±0.2)
Safranin-O	2400 (±1300)	2100 (±600)	4.3 (±0.3)	5.4 (±0.3)
Azure-A	890 (±200)	1100 (±100)	6.1 (±0.3)	6.6 (±0.3)

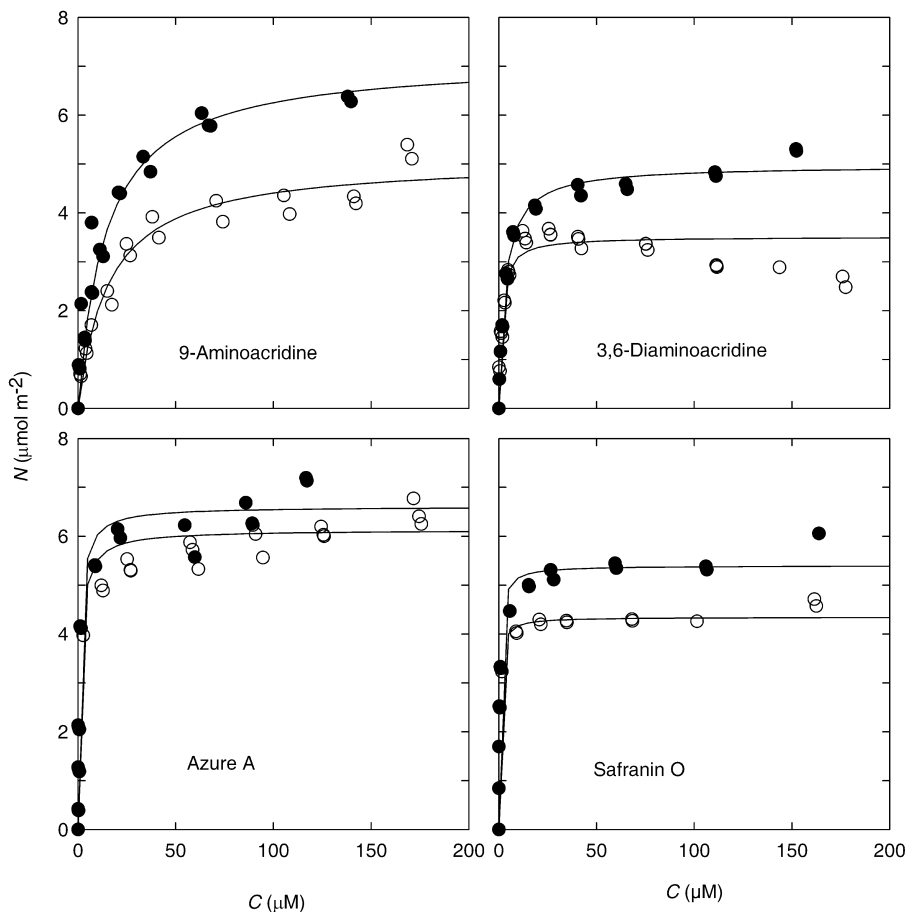


Figure 5. Adsorption of dyes to Ajax kaolinite: (○) pH 5.5; (●) pH 9.0. The fitted lines were calculated from the Langmuir equation with parameters listed in Table 2. [Kaolinite] = $8 \text{ m}^2\text{L}^{-1}$; [KNO_3] = 10 mM.

The adsorption isotherm for 3,6-Daa at pH 5.5 is anomalous. It is not clear why this dye should reach a maximum adsorption density at fairly low solution concentration and then desorb as the solution concentration is increased, especially when that behavior was not observed at pH 9, nor for any of the other three dyes. A similar isotherm has been reported (Lewis, 2000) for the adsorption of Remazol Brilliant Blue R to amorphous Fe hydroxide. Perhaps under some conditions these dyes form aggregates in solution that are more stable than the surface complexes. We do not believe our result is a kinetic artefact, as 15 min were allowed for adsorption equilibrium to be reached after each addition of solute, although initial experiments had shown that 5 min was ample. Despite these reservations, Figure 5 shows that the Langmuir isotherm fits the low-concentration data at pH 5.5 quite well, so the estimated value of K is probably realistic. However, the value of N_m must be taken with caution, and the uncertainty derived from the curve fitting is probably an underestimate.

For each of the dyes, the maximum adsorption density was greater at pH 9 than at pH 5.5, echoing the trends seen in Figure 3. The two aminoacridines

have pK_a s of ~ 9.5 , and therefore at pH 9 they would carry a significantly smaller average charge than at pH 5.5. This would favor the formation of aggregates, increasing the maximum amount it is possible to sorb to the surface. This may also be the case for Az-A and Saf-O; but because they have higher pK_a s the effect would be smaller than for the aminoacridines. The values of N_m in Table 2 support this proposition, as the increase in N_m between pH 5.5 and 9 is greater for the two aminoacridines than for Az-A and Saf-O.

By contrast, the adsorption constant, K , did not change greatly between pH 5.5 and pH 9 for any of the dyes, but its value varied markedly between them. Saf-O and Az-A ($2,400$ and $890 \text{ m}^3 \text{ mol}^{-1}$ at pH 9) adsorbed more strongly than 9-Aa and 3,6-Daa (70 and $310 \text{ m}^3 \text{ mol}^{-1}$).

It is worth noting that both the strengths of adsorption, K , and the maximum adsorption densities, N_m , are much greater than values typically found for the adsorption of heavy metal ions onto kaolinite (Ikhsan *et al.*, 1999). The adsorption of dye molecules does not seem to be limited by the charge density at the clay surface, as is the case for heavy metals.

Extent of surface coverage

The adsorption densities for monolayer coverage can be estimated from the dimensions of the dye molecules. For example, a monolayer of 3,6-Daa would represent $\sim 3\text{--}10\ \mu\text{mol m}^{-2}$, depending on whether the molecules lay flat on the surface or were stacked on their long edges or short edges (Harris *et al.*, 2001). The maximum adsorption densities in Table 2 are all higher than that estimated for a 'flat' monolayer.

However, the values of N_m in Table 2 were estimated on the basis of the total (BET) surface area of the kaolinite. If, as we propose, dye molecules adsorb only to the silica face, the area of surface to which the dyes adsorb is less than half of the total surface area: hence the adsorption density on the silica face must be more than twice the estimated N_m . For Ajax kaolinite the concentrations at the silica face would be in the range $10\text{--}20\ \mu\text{mol m}^{-2}$, corresponding to at least three or four layers of dye if adsorbed flat, and more than a monolayer even if the molecules adsorb at their short edges.

ATR-IR spectroscopy

Spectra for the dyes, in solution and adsorbed to kaolinite, are shown in Figures 6–9. In each set of spectra there were two measurements at pHs below the pK_a of the dye, and one close to the pK_a or above it. Because radiation was absorbed strongly by the ZnSe internal reflection element above $1800\ \text{cm}^{-1}$, and by kaolinite below $1200\ \text{cm}^{-1}$, analysis of the spectra is confined to the region from 1800 to $1200\ \text{cm}^{-1}$. The spectra have been scaled to similar amplitudes to facilitate comparison of the bands: before scaling, the adsorbed spectra were significantly more intense than the solution spectra, the strong adsorption to kaolinite and consequent high loading having increased the local concentration of dye adjacent to the internal reflection element.

Azure A (Figure 6). The solution spectra at pH 4.4 and 9.0, conditions under which the dye is fully protonated, were very similar, and each distinctly different from that at pH 11.5, at which the dye molecules are mostly deprotonated. On deprotonation of the dye, the band at $1338\ \text{cm}^{-1}$ resolved into two bands at 1352 and $1333\ \text{cm}^{-1}$. A new band appeared at $1520\ \text{cm}^{-1}$, the band at $1490\ \text{cm}^{-1}$ strengthened and shifted to $1480\ \text{cm}^{-1}$, while the band at $1393\ \text{cm}^{-1}$ became much weaker and shifted to $1386\ \text{cm}^{-1}$.

By contrast, the spectra of adsorbed Az-A, which were measured at pH values similar to those of the solution spectra, are almost the same, even when the pH is above the pK_a of the dye. Except for the twin bands at 1352 and $1333\ \text{cm}^{-1}$ the spectra closely match the solution spectra of protonated molecules. There is no evidence of band broadening on adsorption.

Safranin O (Figure 7). The intensities of the solution spectra were weaker than those for Az-A, as the lower

solubility of Saf-O limited the concentrations of the solutions. Furthermore, Saf-O tended to precipitate when the pH exceeded 10.6, so solution spectra could not be measured above this value. The solution spectra changed only slightly with pH, which is not surprising as the pK_a of Saf-O is 11.2, greater than the largest pH studied.

The spectra of adsorbed Saf-O are all very similar, and closely resemble those of the solution species. The bands at 1500 and $1490\ \text{cm}^{-1}$ indicate splitting of the solution band at $1497\ \text{cm}^{-1}$. If anything, band widths for adsorbed species are narrower than those in the solution spectra.

3,6-Diaminoacridine (Figure 8). At higher pH 3,6-Daa tended to precipitate from solution, with the result that the solution spectrum at pH 10.6 was weak, and probably represents a mixture of species remaining in solution together with a little precipitate. The solution spectra at pH 2.5 and pH 8.8 were similar, except for an additional band at $1468\ \text{cm}^{-1}$ at pH 8.8. That band can also be seen in the solution spectrum at pH 10.6, suggesting that it indicates deprotonated species ($pK_a = 9.5$ for 3,6-Daa).

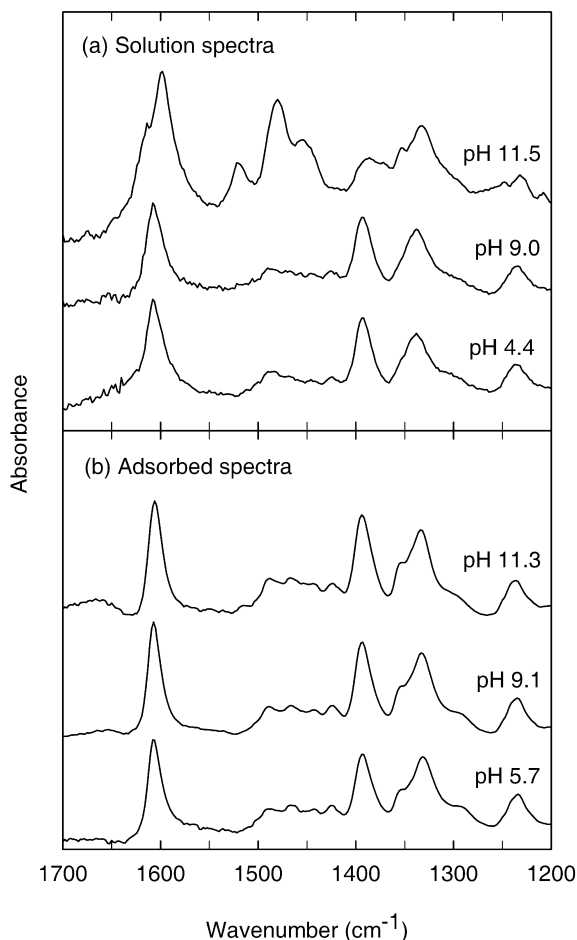


Figure 6. ATR-FTIR spectra of azure A: (a) 5 mM solution; (b) adsorbed to kaolinite.

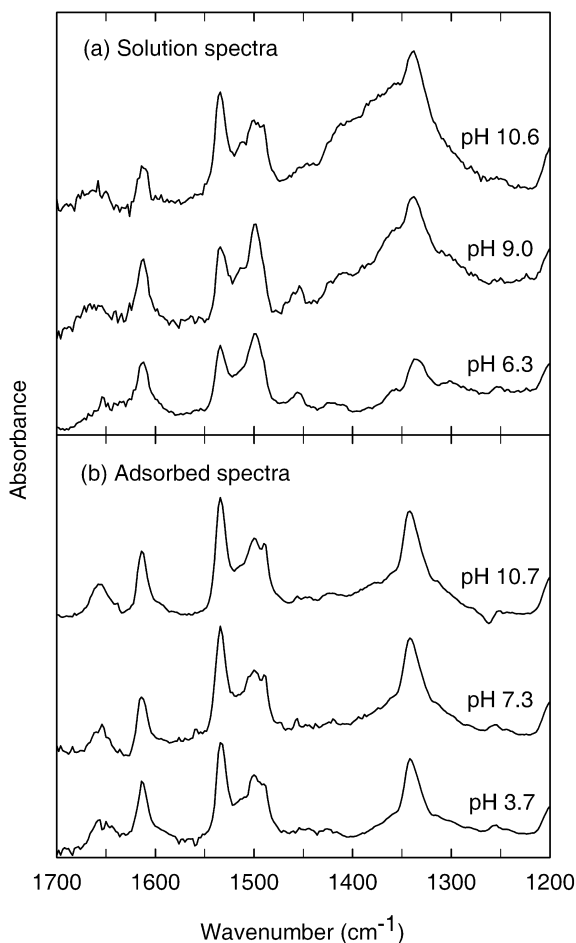


Figure 7. ATR-FTIR spectra of safranin O: (a) 2 mM solution; (b) adsorbed to kaolinite.

The spectra for 3,6-Daa adsorbed to kaolinite changed somewhat as the pH of the system was increased. At pH 9.0 there was an additional band at 1468 cm^{-1} . This band increased in intensity as the pH was increased to 11.2, and at the same time the intensity of the band at 1489 cm^{-1} decreased, an additional band appeared at 1416 cm^{-1} , and a shoulder formed on the band at 1383 cm^{-1} . Again the positions of major bands for adsorbed species are close to those found in solution, with band shifts generally $<4\text{ cm}^{-1}$.

9-Aminoacridine (Figure 9). The intensities of the solution spectra of 9-Aa were significantly lower than those for the other dyes, even though the dye concentration was twice that used for Az-A and 3,6-Daa, and five times that for Saf-O. As a consequence, the solution spectra suffer from more noise. There was also evidence of precipitation, with a further loss in spectral intensity, at the highest pH shown (10.9), which is well above the pK_a (9.9). The solution spectra of protonated species, at pH 5.0 and 8.8, are similar. The rather noisy spectrum at pH 10.9 suggests that the deprotonated dye molecules

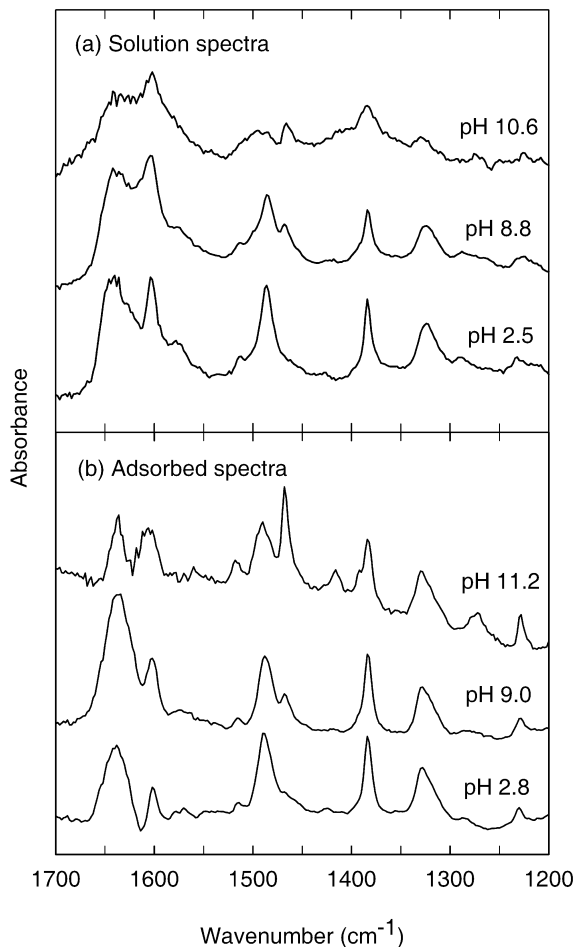


Figure 8. ATR-FTIR spectra of 3,6-diaminoacridine: (a) 5 mM solution; (b) adsorbed to kaolinite.

have a distinctly different spectrum. The nature of the bands at higher pH suggest the formation of a relatively amorphous precipitate. (Crystalline precipitates tend to result in sharp absorption bands.)

For adsorbed 9-Aa the decrease in band intensity at pH 10.7 is expected, as the quantitative adsorption data show that adsorption decreased at pH values above the pK_a of the dye. All three spectra are broadly similar, and the band positions mostly correspond to those in the solution spectra at low pH, except that at pH 8.7 and 10.7 there is evidence of an additional band at 1743 cm^{-1} in the adsorbed spectra, which is seen only in the high-pH solution sample.

Table 3 summarizes the positions of identifiable bands in the spectra of the four dyes. Because of the complexity of the dye molecules it is difficult to assign the absorption bands to particular vibrational modes. However, tentative assignments can be made for some bands that are present for all the dyes. For instance, the bands at ~ 1600 and 1490 cm^{-1} appear to be independent of pH and are probably due to ring vibrational modes. The band at $1325\text{--}1340\text{ cm}^{-1}$ is likely to be due to the

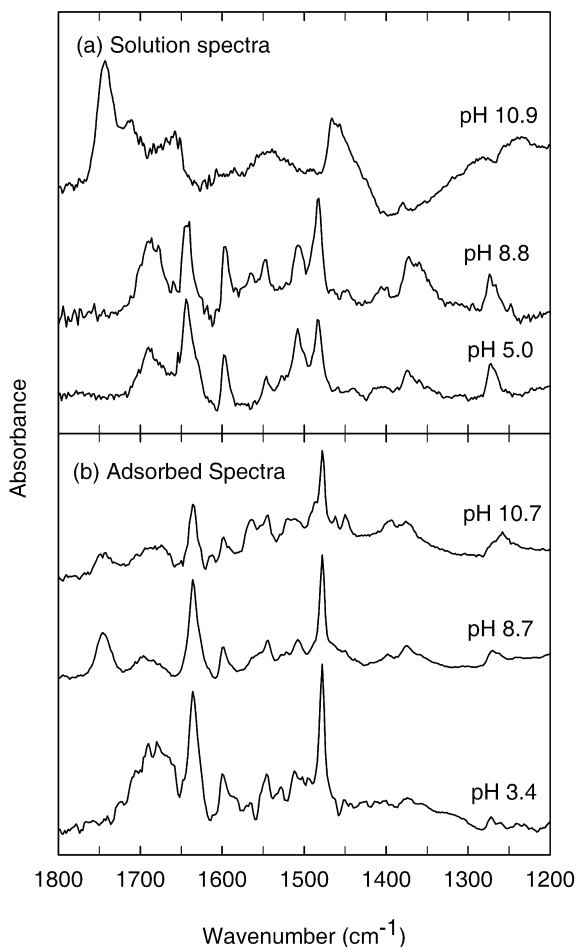


Figure 9. ATR-FTIR spectra of 9-aminoacridine: (a) 10 mM solution; (b) adsorbed to kaolinite.

C–N bond, though its absence from the spectrum for 9-Aa is surprising. It is possible that the band at 1273 cm^{-1} in 9-Aa corresponds to the C–N vibration. The band for the aminoacridines near 1640 cm^{-1} is probably a N–H bending mode of the $-\text{NH}_3^+$ group. This assignment is supported by the fact that it is weaker, or absent, in the high-pH solution spectra, where the primary amine is largely deprotonated. The band at $\sim 1465\text{ cm}^{-1}$ for the aminoacridine molecules, which occurs only at higher pH values, may be due to an –NH bending vibration.

Despite the lack of detailed assignments of the spectral bands we can draw qualitative conclusions from the spectra, and from the way that they changed with pH and on adsorption. First we note that in order to obtain solution spectra of sufficient intensity, it was necessary to use relatively high concentrations of the dyes, near their solubility limits. It is therefore likely that the solution spectra are of dye aggregates rather than dye monomers.

A surprising feature of the spectra for all of the dyes was that the bands in the adsorbed spectra were as

narrow as those in the solution spectra, and in some cases narrower. Generally, band broadening is observed when molecules adsorb as outer-sphere complexes, because the adsorbed species exist in a range of slightly different chemical environments (Persson *et al.*, 1998b; Boily *et al.*, 2000; Roddick-Lanzilotta and McQuillan, 2000). Our observation of the reverse trend suggests that the adsorbed dye molecules were in a relatively uniform environment. This is consistent with the dye molecules adsorbing as aggregates, in a rather uniform layer, such that most of the adsorbed molecules were adjacent to others of the same type. The somewhat broader bands in solution may reflect a range of aggregate sizes in the solution environment.

The spectra of adsorbed and free Az-A and Saf-O have similar characteristics, with little change over the pH range studied, even when the pH approached the pK_a of the dye. The band pattern and band positions for the adsorbed dye species were generally similar to those for the protonated dye in solution, indicating outer-sphere complexation of protonated dye aggregates.

Similarly, the band positions for the adsorbed aminoacridine species were very similar to those in solution, again showing outer-sphere complexation of aggregated dye molecules. For both aminoacridines the intensity of the spectra at the highest pH was decreased, in keeping with the observation in Figure 3 that these dyes tended to desorb above their pK_a . The spectra of the adsorbed species at low pH were similar to those for the protonated solution species, but there was evidence of progressive deprotonation of adsorbed species at higher pH values, with the intensities of bands characteristic of the deprotonated species increasing as the pH increased.

There have been few other IR spectral studies of studies of dye adsorption onto clay minerals. Rytwo *et al.* (1995) studied the adsorption of methylene blue and crystal violet onto montmorillonite, but they used DRIFT spectroscopy, and the IR samples were therefore dry rather than the wet pastes used in our study. While small shifts in some band positions and differences in band intensities between adsorbed and free dye molecules were found at low adsorbate loadings, at high loadings (similar to those used in our study) the adsorbed spectra closely resembled those for the free molecules. Results were reported at only one pH. In other studies (Axe and Persson, 2001; Specht and Frimmel, 2001) the formation of inner-sphere complexes was accompanied by significant changes in ATR spectra, such as spectral shifts ($>10\text{ cm}^{-1}$), significant changes to band shapes, the appearance of new bands or the loss of existing ones.

Orientation of adsorbed dye molecules

Our experimental data do not indicate the orientations of dye molecules in the adsorbed aggregates, except that they are likely to be stacked in an orderly array at the mineral surface. However, we can make some general observations. Alignment of the dye molecules perpendi-

Table 3. Location of bands in ATR-FTIR spectra of dyes in solution and adsorbed to kaolinite. Weaker bands are indicated by italic type.

Dye	Species	pH	Wavenumber (cm ⁻¹)		
Azure A	solution	4.4	1607	1485 1393 1338 1237	
		9.0	1608	1490 1393 1338 1233	
		11.5	1613 1599	1521 1455 1386 1352 1333 1232	
	adsorbed	5.7	1607	1489 1425 1393 1354 1332 1234	
		9.1	1607	1489 1466 1424 1394 1354 1333 1235	
		11.3	1744 1606	1489 1467 1424 1394 1354 1333 1236	
Safranin O	solution	6.3	1741	1499 1456 1336 1336	
		9.0	1615 1616	1497 1340 1338 1338	
		10.6	1740 1667	1496 1500 1489 1342 1341 1343	
	adsorbed	3.7	1613	1533 1500 1489 1341 1341	
		7.3	1653 1614	1534 1499 1489 1341 1341	
		10.7	1658 1613	1534 1499 1489 1341 1341	
3,6-Diaminoacridine	solution	2.5	1641	1487 1384 1323 1288 1232	
		8.8	1642	1485 1468 1383 1324 1288 1224	
		10.6	1602	1495 1466 1385 1329 1329 1329	
	adsorbed	2.8	1742	1489 1384 1329 1329 1230	
		9.0	1746 1634	1488 1468 1383 1329 1229 1229	
		11.2	1745 1637	1490 1468 1416 1383 1329 1229	
9-Aminoacridine	solution	5.0	1690	1508 1483 1273 1273	
		8.8	1686 1642	1509 1483 1372 1274	
		10.9	1743 1657	1540 1466 1374 1272	
	adsorbed	3.4	1746 1636	1545 1478 1374 1272	
		8.7	1746 1696	1545 1508 1478 1270	
		10.7	1743 1635	1545 1478 1450 1258	
Tentative assignment			a	b	c
		d	e		

a Ring vibrational modes

b C-N vibration

c C-N vibration?

d N-H bending (-NH₃⁺)

e N-H bending (-NH)?

cular to the surface would permit the closest approach of the maximum number of protonated amino groups to the negatively charged silica face of kaolinite, and at the same time, facilitate π -stacking interactions between adjacent dye molecules. It may be significant that 9-aminoacridine, the only one of the dyes with an amino group attached to the aromatic ring, had the weakest affinity for kaolinite, suggesting that end-on attachment may be preferred.

INTERPRETATION

The range of data from this study, together with the foregoing discussion, lead to a picture of the adsorption systems that can be summarized as follows.

Adsorption is outer sphere

Titration of kaolinite in the presence of dyes were very similar to those expected by combining the titration data for kaolinite and dye alone. Therefore, chemical bonding of titratable groups – amino groups of the dyes or surface hydroxyls of kaolinite, which are the most likely sites for inner-sphere complexation – did not occur to a significant extent.

The ATR-FTIR spectra of the adsorbed dyes were similar to those of the dyes in solution. In particular the positions of most of the absorption bands changed by $<5\text{ cm}^{-1}$ between the spectra of the free and adsorbed dye species.

These observations indicate that the dyes adsorb to kaolinite by outer-sphere complexation.

Dyes bind to the kaolinite faces only

Most of the proton-active (*i.e.* titratable) sites on kaolinite are on the crystal edges, the charge of which reverses around pH 6–7. The small change in titration behavior in the mixed (kaolinite plus dye) suspensions, and the absence of a marked change in adsorption in this pH range, suggest that the dyes do not interact significantly with the kaolinite edges. There is a good case that adsorption is at the silica face, which carries a pH-independent negative charge.

Further evidence for face-only adsorption is found in the sorption data for Comalco kaolinite, which had approximately half the face:edge ratio and approximately half the dye adsorption.

Although these lines of evidence would support adsorption to the silica face, the alumina face or both, adsorption to the alumina face is unlikely given the low adsorption to gibbsite (Harris *et al.*, 2001), which has a very similar surface structure.

Dyes bind as aggregates

The isotherms showed that the adsorption of the dyes to kaolinite is substantially stronger than that of metal ions, and also that the maximum adsorption density is too high for monolayer coverage.

The ATR-FTIR spectra suggested that dye molecules were adsorbed to the surface as relatively uniform aggregates, held to the surface by physical (outer-sphere) rather than chemical (inner-sphere) forces.

Binding is partly electrostatic

The adsorption behavior above pH 10 indicated that dye adsorption has a significant electrostatic component. As deprotonation of the dyes became significant near their pK_{as} , the two aminoacridines rapidly began to desorb, presumably because of the lack of electrostatic attraction. By contrast, Az-A and Saf-O, which remain positively charged above their pK_{as} , did not desorb.

Binding is partly hydrophobic

If dye adsorption were purely electrostatic in nature, dyes would be expected to adsorb to the kaolinite edge, with a marked change in adsorption around pH 6–7 when the surface hydroxyls are deprotonated. No such change was observed. Furthermore, the adsorption densities were greater than monolayer, and much greater than could be accounted for by electrostatic attraction to the small negative charge on the silica face. Hence, hydrophobic interactions must be significant for dye adsorption.

This conclusion is reinforced by our previous observation (Harris *et al.*, 2001) that only flat, aromatic molecules adsorb strongly to kaolinite.

CONCLUSIONS

The strong binding of the four dyes to kaolinite, which is distinctly different from their much weaker adsorption to alumina and silica (Harris *et al.*, 2001), is attributed to aggregation of dye molecules at the mineral surface, stabilized by a range of electrostatic and hydrophobic interactions.

The flat, relatively hydrophobic silica faces of kaolinite, carrying low-density permanent negative charge, facilitate aggregation and adsorption of the positively charged, flat, aromatic dye molecules. As the pH increases the average degree of protonation within the dye aggregates progressively decreases, allowing the size of the aggregates to increase, but if the cationic charge is reduced too far (above the pK_{as} of the aminoacridines) there is insufficient electrostatic attraction for the dyes to remain adsorbed.

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