

ADSORPTION OF SAFRANINE BY Na⁺, Ni²⁺ AND Fe³⁺ MONTMORILLONITES

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Abstract—The adsorption of the cationic oxidized safranine S⁺ by a Na⁺, Ni²⁺ and Fe³⁺ montmorillonite has been studied with X-ray powder diffraction, u.v., visible and i.r. spectroscopy. In solution S⁺ may be protonated: S⁺, SH²⁺ and SH₃⁺ have characteristic spectra in the 500–600 nm region where the clay structure does not absorb. In the Na⁺ as well as in the Ni²⁺ and Fe³⁺ clays, the adsorption of S⁺ is a cation exchange process accompanied by the protonation of the adsorbed dye such as variable concentrations of M⁺ (Na⁺, Ni²⁺ or Fe³⁺), S⁺ and SH²⁺ are simultaneously present. Protonation activity decreases from Fe³⁺ to Ni²⁺ and Na⁺, being the protonation site the amine group as shown by i.r. In the interlamellar space it seems that a SH²⁺..S⁺ association exists that could be described as a sandwich structure 6.5 Å thick.

INTRODUCTION

Smectites such as montmorillonite have been used widely as adsorbents for various kinds of dyes (Grim, 1968). Safranine Y has been shown to stain acid treated clays in relation to their mineralogical origin. Methylene blue has been studied by Pham Thi Hang and Brindley (1970) who have shown that both surface area and cation exchange capacity of clay minerals can be measured by adsorption from aqueous solutions.

Safranine T, whose oxidized and reduced structure are shown in Figure 1, is a molecule of particular interest because its standard oxidation potential should allow redox reactions within the interlamellar space. The E_m-pH relationship is given by:

$$E_m = E_0 + \frac{RT}{2F} \ln \frac{[S^+]}{[SH]} + \frac{RT}{2F} \times \ln \left[[H^+]^3 + K_{r1}[H^+]^2 + K_{r1}K_{r2}[H^+] \right] \quad (1)$$

(Stiehler *et al.*, 1933), where E₀ = 0.235, K_{r1} = 2.10⁻⁵ and K_{r2} = 2.10⁻⁸. S⁺ and SH represent the oxidized and reduced forms respectively (Fig. 1). The oxidized form of Safranine T also exists in two protonated forms: SH²⁺ and SH₃⁺. This explains why E_m is pH dependent. In addition, as shown by Jacobi and Kuhn (1961), each form may be characterized by a defined

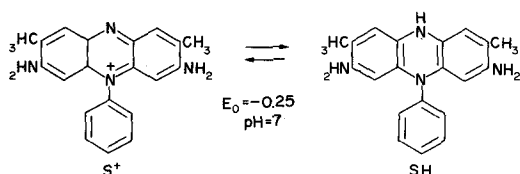


Fig. 1. Structures of the oxidized and reduced forms of safranine, S⁺ and SH respectively.

absorption spectrum between 200 and 700 nm. Table 1 shows the main absorption bands and their extinction coefficients.

Because the phenyl group is not coplanar with the heterocyclic ring, the introduction of safranine within the interlamellar space should expand the d₀₀₁ spacing by more than 5 Å. The surface area covered by the molecule is of the order of 320 Å² whereas the thickness is of the order of 5 Å when the phenyl group is rotated around the C₂ axis at the maximum of repulsion between its CH bonds and those of the heterocyclic ring.

On the other hand it is known that many dyes aggregate in aqueous solution (Duff and Giles 1975). There is only limited evidence of this phenomenon in organic solvents. Aggregation induces spectral changes. In the case of cationic dyes such as safranine, an increase in concentration produces a decrease in intensity of the long wavelength band in the visible spectrum (M band) assigned to the monomeric ion and a new band appears at shorter wavelength (D band) attributed to the dimeric species. Therefore, from various points of view, safranine seems to be an interesting probe to study the surface properties of Montmorillonite.

Table 1. Spectral characteristics of the oxidized and protonated forms of safranine T

	ε (M ⁻¹ cm ⁻¹)	λ (nm)
S ⁺	44,000	278
	41,000	528
SH ²⁺	31,500	265
	35,000	290
	5800	394
	28,000	579
SH ₃ ⁺	54,000	304
	13,800	425
	8500	630

EXPERIMENTAL

The clay mineral from a Wyoming bentonite was dispersed in deionized water and purified by centrifugation in order to remove the quartz and other impurities. The purification process was followed by X-ray powder diffraction. The fine quartz free fraction was redispersed in a 1 N NaCl solution and centrifuged. The treatment was repeated five times with fresh solutions. Aliquots from the sodium clay were saturated in the same manner with other cations, namely Ni^{2+} and Fe^{3+} . In the case of Fe^{3+} , alcohol solutions of the salt were used in order to minimize hydrolysis.

About 5 g of cation exchanged montmorillonite were shaken with a concentrated aqueous solution of safranin (13.5×10^{-3} mole $\text{S}^+\text{Cl}^-/\text{l}$ for several hr. The suspension was centrifuged and washed about fifteen times with distilled water until the supernatant was chlorine free. Self-supported films for X-ray powder diffraction, i.r., visible and u.v. spectroscopy were prepared readily by slowly evaporating to dryness on thin polyethylene sheets. If needed the samples were heated at 160°C during 24 hr into a vacuum i.r. cell to remove the interlayer water. For X-ray powder diffraction the films were transferred inside a dry box from the i.r. cell to a vacuum camera. The patterns were recorded by a CGR diffractometer using Ni filtered Cu K_α radiation. Infrared spectra were recorded from 4000 to 200 cm^{-1} with a 180 Perkin-Elmer spectrophotometer. Infrared spectra of a reference safranin were obtained from KBr disks. Visible and u.v. spectra were recorded under various conditions. Pure safranin at different concentrations and its protonated homologues were examined in aqueous solutions. Clay samples were run either as 1% suspensions or as clay films deposited on a quartz window. The spectra were recorded with a Beckman u.v.-visible spectrophotometer model 25. Chemical analysis were performed in order to determine the nitrogen and cation contents. Ni, Na and Fe were analyzed by atomic absorption.

RESULTS

Chemical analysis

Data about the total safranin content and exchangeable cations are shown in Table 2. They suggest that in the case of the Na Montmorillonite about

Table 2. Surface species concentrations (meq/100 g clay, except for the safranin contents expressed in mM/100 g clay)

	Total safranin content	S^+	SH^{2+}	Metal cation	Total charge
Na-safranin montmorillonite	43.5	24.4	19.1	33	95.6
Ni-safranin montmorillonite	19.3	9.6	9.6	60	88.8
Fe-safranin montmorillonite	25	5	20	72.5	117.5

2/3 of the exchangeable cations have been replaced by S^+ while the replacement was only 1/3 in the case of the Ni clay. The amount of substitution seems to be lower in the Ni^{2+} than in the Na^+ montmorillonite.

The total cation exchange capacity obtained by adding the total safranin content and the Na^+ or Ni^{2+} content in 10^{-3} equivalent/100 g of air dried clay is 76.5 meq/100 g for the Na^+ montmorillonite and 79.3 meq/100 g for the Ni^{2+} montmorillonite. This is appreciably lower than the expected value (between 90 and 100 meq/100 g of air dried clay).

U.v. and visible spectra

Figure 2 shows the visible spectra of aqueous solutions of safranin at different concentrations, from 10^{-4} to 5.10^{-3} M. As expected, an increase in concentration produces a shift towards lower wavelengths. The blue acid treated form was run at a concentration of 5.10^{-4} M. In this region protonation results in a shift towards longer wavelengths and a marked asymmetry of the band. In the u.v. region the band at 275 nm splits into two components at 265 and 280–289 nm respectively.

Visible spectra of suspensions of safranin treated clays saturated with different cations are shown in Figure 3a. In the adsorbed state the splitting of the 275 nm band is not observed. At longer wavelengths a complex band, containing two and, in most cases, three components, replaces the single band at 518 nm observed in solution. In the case of the Fe-safranin heated sample the longer wavelength band is particularly well developed. The observation of a band at

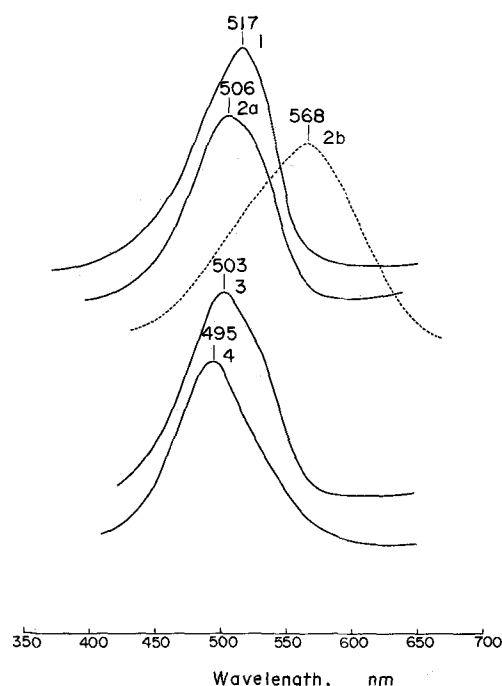


Fig. 2. Visible spectra of safranin (1) 10^{-4} M, in water; (2a) 5.10^{-4} M, in water; (2b) 5.10^{-4} M, in HCl; (3) 10^{-3} M, in water; (4) 5.10^{-3} M, in water.

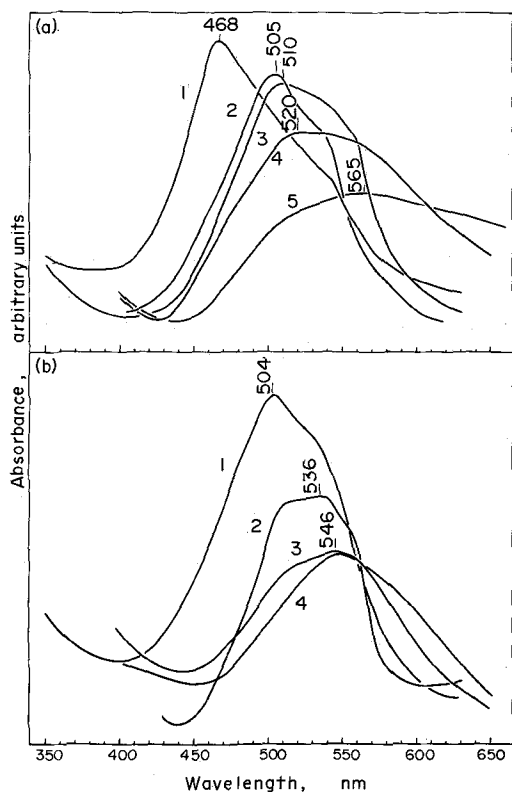


Fig. 3. (a) visible spectra of safranine treated montmorillonite suspensions (1) Na clay; (2) "Well dispersed" Ni clay; (3) Ni clay; (4) Fe clay; (5) Fe clay resuspended after drying and heating at 160°C. (b) visible spectra of safranine treated montmorillonite films (1) Na clay; (2) Ni clay; (3) Fe clay; (4) Fe clay heated at 160°C.

468 nm for the suspension of a safranine treated Na montmorillonite seems to be most curious.

It must be reminded that the particles dispersion of a given clay depends partially upon the nature of the charge balancing cation. Whereas for a Na montmorillonite suspension the single clay platelets are separated from one another, the divalent Ca suspension forms stable tactoids of about 5–15 parallel plates (Banin and Lahav 1968). Air-drying the clays results in larger tactoids.

The shift of bands towards shorter wavelength seems to be related to the degree of dispersion of the clay. Two samples of Ni montmorillonite differing in the degree of dispersion were studied. The better dispersed obtained by a special preparation (Banin 1973) gave the band at lower frequency.

In the safranine treated air-dry films, some differences can be pointed out. The Na sample 468 nm band shifts to 504 nm. For the heated Fe montmorillonite film, the band at 550 nm is practically the only one apparent. Taking into consideration the intensities of the band in this wavelength range, it must be concluded that safranine has undergone a protonation reaction which may be more pronounced for the Ni than for the Na sample but which does not produce the same spectrum as that observed for the violet protonated form in solution.

Because the extinction coefficients are known it is possible to evaluate the concentration of SH^{2+} and S^+ from the optical density at 510 and 555 nm. By reference to Table 1, it is assumed that the 524 nm and the 579 nm bands observed in the dissolved state correspond to those observed at 510 and 555 nm in the adsorbed state, the respective extinction coefficients being the same in both states.

The total content in safranine from the chemical analysis and the concentration of the three species are shown in Table 2. Indeed the $\text{SH}^{2+}/\text{S}^+$ ratio is smaller in the Na (0.79) than in the Ni (1.0) montmorillonite but the amount of divalent cations removed from the clay by treatment with the saturated solution of safranine is smaller than the amount of monovalent extracted. In the case of the iron clay, it follows from an approximate deconvolution of the bands that the ratio $\text{SH}^{2+}/\text{S}^+$ is about 4.

Clay films were prepared with very small known quantities of safranine such as 0.1 g/100 g clay and 0.5 g/100 g clay. In the first case the film was green (as SH_3^{3+} in solution), in the second the sample was reddish-blue (SH^{2+} in solution). The reflection spectra for the low safranine concentration sample showed one absorption band at 592 nm. A sharper band at about 400 nm could not be entirely recorded because of instrumental limitations. A much broader band centered at 570 nm was observed for the more concentrated sample. The colour together with the band positions indicate that safranine is readily protonated when small quantities are adsorbed. The change from green to reddish-blue would suggest that the first molecules can be biprotonated (SH_3^{3+}) when many protons are available. By increasing the surface concentration in safranine, the monoprotonated form SH^{2+} is obtained and upon further increase, S^+ becomes dominant.

The higher degree of protonation observed in going from Na^+ to Ni^{2+} , and finally Fe^{3+} , is in line with the relative polarizing effect of the cations on the hydration water. A trivalent metal cation is more selectively adsorbed than a di- or monovalent cation.

An interesting illustration of the acid buffer properties of a clay mineral surface was obtained by wetting a film of safranine-Na montmorillonite with a concentrated H_2SO_4 solution and recording its reflection spectrum as a function of time. The band at 495 nm was progressively substituted by another band at 460 nm as the green color vanished at the expense of the blue color. Table 3 accounts for the positions of some of the bands referred above.

X-ray powder diffraction

The adsorption of safranine within the interlamellar space is expected to provoke a considerable swelling along the C^* axis. Figure 4 contains some X-ray powder diffraction spectra. The Na-safranine montmorillonite complex outgassed at 160°C for 24 hr has a d_{001} spacing of 15.8 Å with a third and a fifth order at 5.2 and 3.2 Å, respectively. With these reflections

Table 3. Characteristic features of the u.v.-visible spectra of safranine and safranine-treated montmorillonite (wavelength in nm)

	Protonated oxidized safranine	Na montmorillonite (suspended)	Na montmorillonite (film)	Ni montmorillonite (well dispersed)	Ni montmorillonite (suspended)	Ni montmorillonite (film)	Fe montmorillonite (suspended)	Fe montmorillonite heated (suspended)	Fe montmorillonite (film)	Fe montmorillonite heated (film)
207 m										
239 w		249 st	*		247 m	*	*	*	*	*
246 m		265 m			275 m					
275 st		275 w								
	289 st									
	390 m									
		468 st								
518 st			504 st	505 st	510 m	510 m	520 m	520 m		510 sh
			528 m		530 m					
			550 sh	535 m	553 m	535 m				
						555 m				
	568 st						560 w	565 m	546 m	546 m
									very broad	very broad

st = strong; m = medium; w = weak; sh = shoulder.

* optical density too high.

are weaker reflections at 9.9 and 4.85 Å. The Na montmorillonite outgassed under the same conditions has reflections at 9.9, 4.85 and 3.21 Å. It may be concluded that the Na-safranine complex is actually a mixture of a large amount of clay expanded to 15.8 Å and a smaller amount of collapsed Na montmorillonite.

On the basis of the results shown in Table 2 this result could have been anticipated. Indeed if all the 43.5×10^{-3} moles of safranine that have been adsorbed by 100 g of Na clay are assumed to be within the interlamellar space, they should cover about $830 \text{ m}^2/\text{g}$. Because the total internal and external surface of montmorillonite is about $800 \text{ m}^2/\text{g}$, two layers of safranine should be superimposed between the layers in such a way that the phenyl rings, belonging to two superimposed heterocyclic rings, would be on both sides of the sandwich. In addition, some molecular aggregation between the individual tactoids should be present.

Between the layers the separation is about $15.8 - 9.3 = 6.5 \text{ Å}$. Assuming as usual that keying the organic molecules between the clay structure surface atoms occurs to some extent, 6.5 Å should accommodate the suggested association.

For the Ni sample the situation is different since, according to Table 2, the safranine content would not allow more than 40% of the layers to be expanded. This is in agreement with the X-ray diffractogram shown in Figure 4. After outgassing the Ni-safranine complex at 160°C , the diffraction pattern strongly suggests that interstratification is obtained. The first peak occurs at 13.7 Å . For a 1/1 arrangement of layers

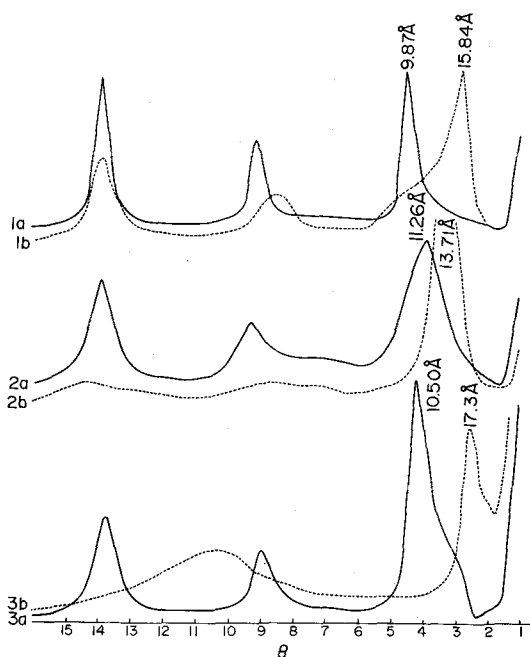


Fig. 4. X-ray powder diffraction patterns (degree θ) of (1a) Na mont; (1b) Na-saf mont; (2a) Ni mont; (2b) Ni-saf mont; (3a) Fe mont; (3b) Fe-saf mont. Pretreatment: 24 hr outgassing at 160°C .

with d_{001} spacings at 10 and 15.4 Å , the graphs calculated by Mac Ewan (Brown 1961) indicate that the first reflection should occur at 13.9 Å . The system can be even more complicated since a Ni montmorillonite sample treated in the same manner exhibits a typical pattern of interstratification with the first reflection at 11.26 Å . The Ni^{2+} being able to fix water very tenaciously it follows that expanded and unexpanded layers are present in the same microcrystal of clay. For the Fe-safranine montmorillonite sample dried at 100°C a simple set of reflections is obtained, d_{001} being at 17.3 Å . The identically treated Fe montmorillonite sample gives a broad peak at 10.5 Å with a shoulder at 14.5 Å . Fe^{3+} retains water strongly but the adsorption of safranine between the layers seems to have provoked a complete swelling with an interlamellar spacing of 8 Å .

Infra-red spectroscopy

As shown in Figures 5 and 6, the air-dried Na, Ni and Fe montmorillonite-safranine complexes and safranine chloride have quite comparable i.r. spectra in the $1800-1200 \text{ cm}^{-1}$ spectral domain but they differ appreciably in the $3500-3100 \text{ cm}^{-1}$ region. Three distinct bands at 3470 , 3390 and 3240 cm^{-1} in the adsorbed state replace two less defined bands at 3180 and 3330 cm^{-1} . For the Na complex, a very broad band, which could be attributed to residual safranine chlorhydrate, appears at 2450 cm^{-1} (The Aldrich library of Infrared Spectra, 1975).

The structural OH stretching of montmorillonite is at 3620 cm^{-1} and the $\text{C}=\text{C}$ stretching of the benzenic rings could be responsible for bands in the $1400-1600 \text{ cm}^{-1}$ region. The NH_3^+ asymmetric deformation could contribute to the absorption at 1610 cm^{-1} . Water can also interfere in this region. The $\text{C}=\text{N}$ stretching could appear also as the 1635 cm^{-1} band and it is probably responsible for the band at 1320 cm^{-1} which is observed in the free state as well as in the adsorbed state.

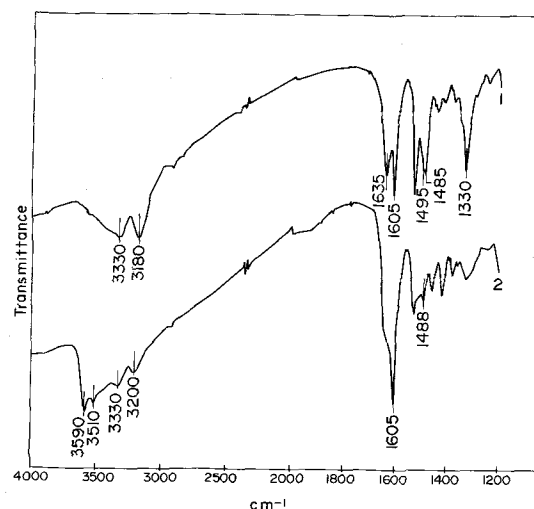


Fig. 5. I.r. spectra of safranine (1), and protonated safranine (2) in KBr pellets.

Primary amines exhibit two N-H stretching modes near 3500 and 3400 cm^{-1} respectively. The frequency is generally lowered in the solid state. The bands at 3470 and 3380 cm^{-1} in the adsorbed state could be due to NH_2 groups involved in weak hydrogen bonds.

The protonated blue form of safranin in KBr pellets has bands at 3180 and 3330 cm^{-1} as in the crystalline state of the red form, but in addition, two well defined bands are observed at 3510 and 3590 cm^{-1} .

A comparison between the i.r. spectra of the adsorbed and protonated form suggests that if protonation occurs in the adsorbed state, as suggested by the visible spectra, it does not occur to the same extent as in the material obtained from crystallization in acid solution and incorporated in KBr pellets. This conclusion is reinforced by the inspection of the low frequency region, where the adsorbed state for the Na as well as for the Ni clay is characterized by a strong band at 1485 cm^{-1} whereas a much weaker doublet at 1485 and 1495 cm^{-1} is characteristic of both the safranin chloride and the protonated form.

In methyl and ethylammonium cations adsorbed by montmorillonite, the NH_3^+ symmetric deformation has been observed at about 1490 cm^{-1} and the NH_3^+ stretching at 3105 and 3247 cm^{-1} respectively. There-

fore the 1485 and 3240 cm^{-1} bands could be due to the protonated $-\text{NH}_2$ groups in the adsorbed safranin.

Protonation of safranin appears clearly in the Fe-safranin montmorillonite heated for 24 hr at 160°C . A very strong asymmetric band at 1615 cm^{-1} very similar to that at 1605 cm^{-1} in the protonated blue crystal, substitutes for a couple of bands at 1635 and 1605 cm^{-1} in the pure safranin.

Reduction of adsorbed safranin

Assuming that the local pH on the clay surface is of the order of $\text{pH} = 2$ (Fripiat *et al.* 1965), it follows from equation (1) that the standard oxidation potential is about $+0.065\text{ V}$. Safranin should thus be able to oxidize Na thiosulfite into sulfite ($E_0 = -0.83\text{ V}$ at $\text{pH} = 2$). The action of thiosulfite is spectacular since it leads to a drastic color change of the clay safranin complex. The characteristic red-orange color turns to yellow-brown. After two hours at room temperature the decoloration is complete but traces of oxygen suffice to restore the original color. It is not certain that this redox reaction occurs exclusively between the layers of the clay since some safranin may be attached to the external surface. On the other hand the possibility of exchanging S^+ by Na^+ from the thiosulfite solution can not be neglected. In this case the reduction will take place outside the layers.

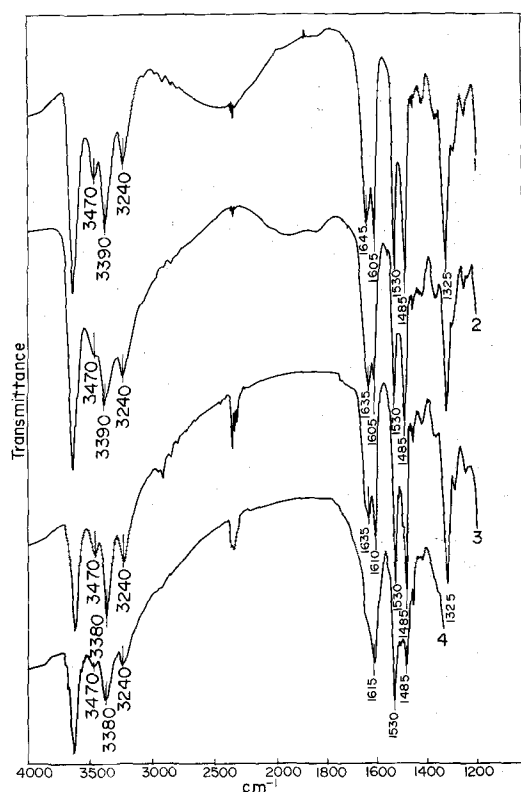


Fig. 6. I.r. spectra of the safranin-montmorillonite films: (1) Na clay; (2) Ni clay; (3) Fe clay and (4) Fe clay heated at 160°C .

DISCUSSION

The adsorption of safranin by Montmorillonite is essentially a cation exchange process. In addition, when adsorbed, safranin undergoes a partial protonation due to the high acidity of the surface water. Therefore the balance of the structure charge results from the simultaneous presence on the surface of a fraction of the original metal cations and of S^+ and SH^{2+} . In the case of the Fe-safranin montmorillonite some SH_2^{3+} also was present with small safranin coverage. In this complex surface association the proportions of the different species are not the same for all cations. The ratio $\text{SH}^{2+}/\text{S}^+$ is 4.0, 1.0 and 0.80 for Fe^{3+} , Ni^{2+} and Na^+ respectively. The introduction of the safranin molecules removes the hydration water.

In their study of the adsorption of methylene blue by montmorillonite Hang and Brindley (1970) have shown that after removing the excess water, a d_{001} spacing of 15.6 \AA was observed. This was interpreted as the formation of a bimolecular layer within the interlamellar space. The safranin heterocycle has about the same thickness. However because of the presence of the additional phenyl ring the overall thickness of the molecule is not greatly different from that of the association of two molecules (about 7 \AA). Therefore the observation of a $d_{001} = 15.8\text{ \AA}$ spacing in the Na-safranin montmorillonite complex and a

possible 15.8–10 Å interstratification in the Ni-safranine montmorillonite complex seems to result from the association of two molecules "face to face". In the case of the Fe-safranine montmorillonite complex, the 17.3 Å spacing could indicate that the dimer is slightly tilted with respect to the C* axis perhaps to reduce the surface packing in view of the larger adsorption.

Perhaps the cohesion between the superposed safranine heterocyclic rings finds its origin in hydrogen bonding between the protonated NH₂ group of SH²⁺ and a nitrogen atom of the adjacent molecule. Such an association is not unexpected since many dyes aggregate in aqueous solution.

At increasing concentration, the main long wavelength band in the visible spectrum (the M band) loses its intensity, whereas a new band (D band) appears on the short-wavelength side of the monomeric band (Duff and Giles 1975). This shift towards a smaller wavelength due to the association process is thus in the opposite direction to that observed upon protonation of S⁺ into SH²⁺. That protonation occurs is clearly shown by the shift towards a longer wavelength observed in clay films as compared to S⁺ in solution (Figures 2 and 3b). Nevertheless, the wavelengths of the S⁺ and SH²⁺ main bands are lower in the films than in solution (Figure 3b and Table 1), which is in favor of a higher degree of association.

That association also occurs and that it is influenced by the dispersion of the clay is illustrated clearly by comparison of the visible spectra of well dispersed Na and Ni safranine montmorillonites with those of the corresponding films. A noticeable shift towards shorter wavelength is observed in the dispersed state (Figure 3), which may be attributed essentially to the disappearance of the protonation effects. A high degree of protonation is not compatible with a high dilution of the clay. For instance, the green iron-safranine montmorillonite film where SH₂³⁺ is abundant turns pink (SH²⁺ and S⁺) upon dispersion in water.

By comparison with S⁺ in highly diluted solutions, the shift for the Na-safranine montmorillonite is drastic; 49 nm (compare to the 22 nm obtained in Figure 2). It could be that the presence of completely separated clay sheets, as for Na montmorillonite, favors the adsorption of associated safranine molecules in a special type of arrangement. Suppose for instance that a dimer (S⁺)₂ is adsorbed by individual separated sheets. As water is removed from the suspension to

form a clay film, protonation of (S⁺)₂ occurs forming SH²⁺ . . . S⁺. Maybe a small quantity of SH₂³⁺ is present in all cases which cannot be observed because of an excess of the other species. As already outlined these sandwiches will expand the 001 spacing by about 7 Å in agreement with the X-ray powder diffraction data. This association could result from or provoke the interaction of the protonated -NH₃⁺ groups with one among the nitrogen atoms in the unprotonated S⁺.

In summary the safranine clay interaction is ruled by three effects: the cation exchange process, the protonation and the association of molecules, when in dry or wetted state. It is only by pondering these factors that the assemblage of experimental observations can be explained.

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REFERENCES

- Banin, A. (1973) Quantitative ion exchange process for clay. U.S. Patent 3,725,528. 3 April, 1973.
- Banin, A. and Lahav (1968) Particle size and optical properties of Montmorillonite in suspension: *Israel J. Chem.* **6**, 235–250.
- Duff, D. G. and Giles, C. H. (1975) *Water—A comprehensive treatise, Volume 4* (Edited by Felix Franks) pp. 169–208. Plenum Press, New York.
- Fripiat, J. J., Jelli, A., Poncelet, G. and André, J. (1965) Thermodynamic properties of adsorbed water molecules and electrical conduction in montmorillonites and silicas: *J. Phys. Chem.* **69**, 2185–2197.
- Grim, R. E. (1968) *Clay Mineralogy*. McGraw-Hill, New York.
- Hang, P. T. and Brindley, G. W. (1970) Methylene blue adsorption by clay minerals: Determination of surface areas and cation exchange capacities (Clay organic studies XVIII): *Clays & Clay Minerals* **18**, 203–212.
- Jacobi, H. and Kuhn, W. (1972) Richtungen der übergangsmomente des absorptionsbanden von Acridin-, Phenazin-, und Xanthenfarbstoffen aus dichroismus und fluoreszenz-polarisation. *Ber. Bunsenges. Phys. Chem.* **66**, 46–53.
- Mac Ewan, D. M. C., Ruiz, Amil A. and Brown, G. (1961) *The X-ray Identification and Crystal Structures of Clay Minerals* (Edited by Brown) p. 393. Mineralogical Society of London.
- Stiehler, R. D., Chem, T. T. and Clark, W. M. (1933) Studies on oxidation-reduction XVII: Simple Safranine: *J. Am. Chem. Soc.* **55**, 891–907.
- The Aldrich Library of Infrared Spectra (1975).