Clays and Clay Minerals, Vol. 33, No. 6, 510–516, 1985.

SURFACE REACTIONS OF 3,3′,5,5′-TETRAMETHYL BENZIDINE ON HECTORITE

M. B. McBride

Department of Agronomy, Cornell University
Ithaca, New York 14853

Abstract—The adsorption and oxidation of 3,3′,5,5′-tetramethyl benzidine (TMB) on hectorite has been investigated using X-ray powder diffraction, ultraviolet-visible spectroscopy, electron spin resonance, and infrared spectroscopy. The molecule adsorbed by cation exchange at low adsorption levels and oxidized to the monomeric radical cation (yellow). At higher adsorption levels, intercalation of TMB occurred in amounts greater than the cation-exchange capacity of the hectorite, and the π-π charge-transfer complex (blue) became much more evident. The TMB monomers appeared to lie flat in the layer silicate interlayers, whereas the molecules in the charge-transfer complexes assumed a near-vertical orientation relative to the surface. The oxidation of adsorbed TMB was probably due to diffusion of O_2 to the surface, because the structural Fe^{3+} content of the hectorite was too low to facilitate a significant quantity of direct Fe^{3+}-TMB electron transfer.

Key Words—Benzidine, Charge-transfer complex, Color, Electron spin resonance, Hectorite, Infrared spectroscopy, Ultraviolet-visible spectroscopy.

INTRODUCTION

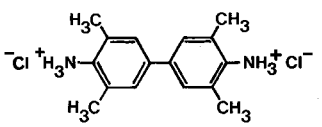
Various aromatic amines react with smectites to generate strongly colored clay-organic complexes (Hakusui *et al.*, 1970; Tennakoon *et al.*, 1974b). Studies of the interaction of benzidine with smectites to form a blue complex on the hydrated surfaces have been particularly numerous (see, for example, Lahav and Raziel, 1971). The oxidation mechanism evidently involves electron transfer from adsorbed benzidine to structural Fe^{3+} in the octahedral layer of clays (Tennakoon *et al.*, 1974a) to form the monovalent radical cation. Dehydration of the clay reversibly shifts the equilibrium in favor of the yellow quinoidal divalent cation (Hakusui *et al.*, 1970). Although oxidation of benzidine on smectites having structural Fe^{3+} is rapid, slow oxidation occurs in the presence of O_2 on smectites with no significant Fe^{3+} content (McBride, 1979). Benzidine adsorption initially occurs via ion exchange as the protonated monovalent and divalent ions (Furukawa and Brindley, 1973), but intercalation of benzidine in excess of the cation-exchange capacity can also occur on smectites (Tennakoon *et al.*, 1974a).

Certain aspects of the reactions of benzidine and related molecules with smectites remain to be clarified, most particularly the interlamellar alignment and intermolecular interactions of the amines and their oxidation products. The present study was undertaken to determine the types of clay-organic complexes formed over a range of adsorption levels on the clay. A methylated derivative of benzidine, 3,3′,5,5′-tetramethyl benzidine (TMB), was used for the study because it is much less mutagenic than benzidine, and because preliminary experiments showed it to react with smectites to form colored complexes similar to those of benzidine.

MATERIALS AND METHODS

Natural hectorite obtained from the Baroid Division of NL Industries, with a previously determined cation-exchange capacity (CEC) of 71 meq/100 g (McBride, 1979), was treated with 1 M Na-acetate (pH 4.8) to remove any free carbonates, then with citrate-bicarbonate-dithionite to dissolve Fe oxide impurities. The hectorite was then saturated with Na^+ using 3 washings containing excess NaCl and dialyzed to remove free salt.

The dihydrochloride salt of 3,3′,5,5′-tetramethyl benzidine (TMB·2HCl) with the chemical structure:



was obtained from Aldrich Chemical Company and used without further purification to prepare a 10^{-2} M TMB·2HCl aqueous solution. This solution could not be stored for long periods of time because of slow oxidation by O_2.

A range of adsorption levels of the hectorite was achieved by adding appropriate quantities of the TMB·2HCl to 100 mg of Na^+-hectorite in suspension with rapid stirring to ensure even distribution of adsorbate. The final volume was taken to 100 ml with distilled water, and the suspensions were allowed to oxidize open to air for 2 weeks. After 1 hr of equilibration, portions of the suspensions were centrifuged, and supernatants were analyzed for pH, Na^+ (by flame photometry), and TMB concentration. The latter measurement was made by adjusting all supernatants to pH 3 and measuring the ultraviolet (UV) absorbance at 320 nm. This adjustment was necessary because of

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the sensitivity of the UV spectrum of TMB to pH and the range of pH in the suspensions resulting from the differing quantities of TMB·2HCl added to the clays.

At the end of the 2-week period, the remaining suspensions were used (without washing) to prepare self-supporting films for analysis by infrared (IR), ultraviolet-visible (UV-VIS), and electron spin resonance (ESR) spectroscopy. IR spectra of films were obtained on a Perkin-Elmer Model 281 IR spectrometer, diffuse reflectance UV-VIS spectra on a Perkin-Elmer Model 200UV-VIS spectrophotometer with integrating sphere attachment, and ESR spectra of oriented films on a Varian E-104 (X-band) spectrometer. In addition, 001 spacings of the oriented hectorite films were obtained on a Philips Norelco X-ray diffractometer.

At the higher levels of TMB·2HCl addition to the hectorite (≥50 mmole/100 g), self-supporting films could not be prepared because of the highly flocculated state of the hectorite. Thus, the UV-VIS reflectance spectra and X-ray powder diffraction (XRD) traces using Ni-filtered CuKα radiation were obtained from clay dried onto ceramic plates. IR spectra were obtained on water-washed, freeze-dried clays prepared in KBr discs.

RESULTS AND DISCUSSION

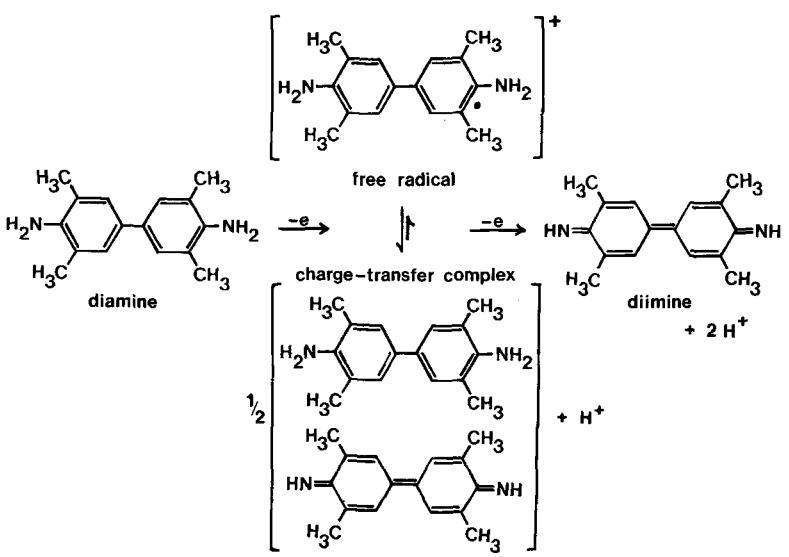
Adsorption and X-ray powder diffraction data

The immediate effect of the addition of TMB·2HCl at high loadings to Na^+-hectorite suspensions was obvious flocculation and the development of a faint green coloration. The color deepened for several hours, and clay films prepared from the suspensions after 2-weeks reaction time had the colors noted in Table 1. It was evident from the flocculation that exchange of Na^+ by either monovalent or divalent TMB occurred, depending on whether one or both amine groups remained protonated after addition of TMB·2HCl to the suspensions. A plot of Na^+ released vs. TMB adsorbed (not shown) indicated that, at the lower levels of adsorption, about 1.4 moles of TMB were adsorbed per mole of Na^+ displaced. These data suggest that both divalent and monovalent TMB was retained by the clay, a result shown for benzidine on montmorillonite (Furukawa and Brindley, 1973). In addition, some precipitation of TMB as the neutral molecule was likely at the higher pHs (low TMB-loading levels), because TMB is much less soluble in water after neutralization of the strongly acid $-NH_3^+$ groups. Whereas unsubstituted benzidine dihydrochloride has pK_a values of about 3.3 and 4.5 (Korenman and Nikolaev, 1974), the ortho substitution of $-CH_3$ groups in benzidine generates a stronger acid. Thus, the pKa of the first $-NH_3^+$ group of TMB·2HCl is about 2.8 based upon NaOH titration of TMB·2HCl.

At high levels of TMB·2HCl addition to the hectorite, the quantity of organic molecules adsorbed was greater than the CEC and the amount of Na^+ released (Figure 1), even assuming that each TMB molecule was only singly charged. Thus, with higher concentrations of TMB·2HCl in solution (which necessarily required low pH because of the very low solubility of TMB at high pH), intercalation of either neutral TMB molecules or the TMB·2HCl salt occurred. X-ray powder diffraction (Table 1) revealed a 21-Å clay-organic complex which becomes dominant relative to a 13.0–13.2-Å complex at the higher adsorption levels.

Ultraviolet-visible and electron spin resonance spectra

To understand the nature of the hectorite-TMB interaction, the solution chemistry of TMB must be more fully known. A study of the oxidation of TMB by peroxidase (Josephy *et al.*, 1982) has confirmed the following reaction sequence:



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Table 1. Properties of prepared tetramethyl benzidine-hectorite films in the air-dry and fully hydrated (excess H_2O present) states.

TMB·2HCl added (mmole/100 g)	Suspension pH	Color		d(001) (Å)	
		Wet	Dry	Wet	Dry
1	—	yellow (D)[1]	yellow	—	12.6
5	6.6	yellow (D)	yellow	12.3[2]	12.6
10	6.5	green-yellow (D)	yellow	12.3[2]	13.0
20	5.8	green (D)	yellow	13.2[3]	13.2
50	4.3	green (F)	yellow-green	13.2[3]	13.2
70	3.8	green (F)	green-yellow	13.2[3]	13.0
150	3.2	green (F)	green-yellow	21 (13.2)[4]	21 (13.2)[4]
300	2.9	green (F)	green	21 (13.2)[4]	21 (13.2)[4]

[1] D and F indicate that the suspensions were in the dispersed (D) or flocculated (F) condition.
[2] Weak, interstratified peak.
[3] Interstratified, shoulder toward higher spacings.
[4] Numbers in brackets represent less intense 001 spacings.

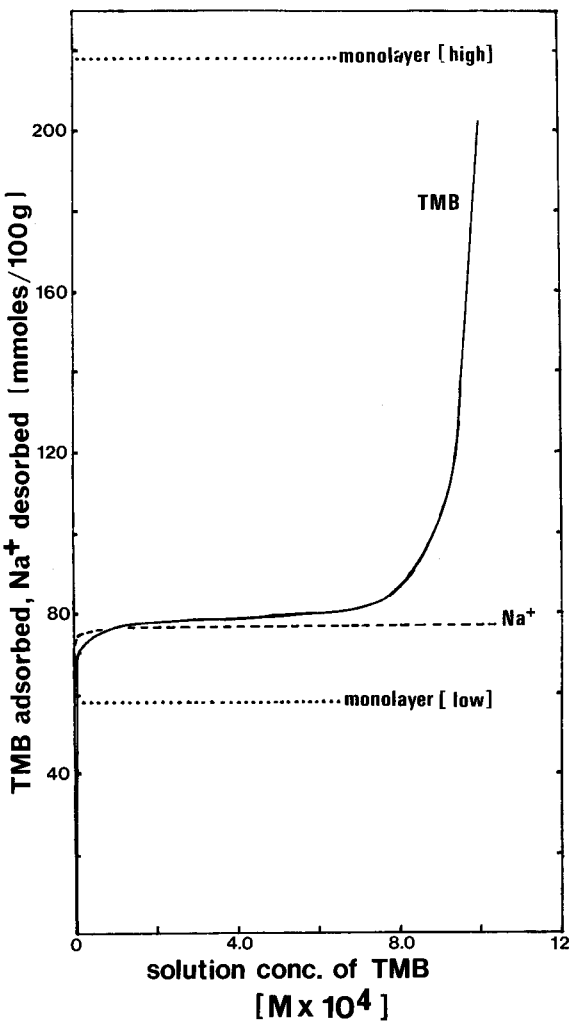


Figure 1. Adsorption of tetramethyl benzidine (TMB) and desorption of Na^+ as function of equilibrium concentration of TMB in aqueous solution. Calculated quantity of TMB required for monolayer coverage of hectorite interlayers based upon molecular dimensions of TMB are indicated for horizontal (low) and vertical (high) molecular orientations.

The absorbance maxima of these species in the UV-VIS spectrum are 285 nm (diamine), 370 and 652 nm (charge-transfer complex), and 450 nm (diimine). The UV-VIS absorbance maxima of the free radical have not been reported for TMB because of the strong tendency of the radicals to pair and form the charge-transfer complex, although the ESR spectrum of the radical has been reported (Josephy *et al.*, 1982). By analogy with benzidine, whose radical cation monomer has UV-absorption maxima at 462, 447, 428, and 413 nm (Hester and Williams, 1981), a strong, multiple absorption band near 450 nm is expected for the TMB radical.

The UV-VIS reflectance spectra of the TMB-hectorite complexes revealed the diimine (yellow) and/or free radical species over a wide range of adsorption levels, as evidenced by the strong absorption centered near 450 nm (Figure 2) and increasing concentrations of the charge-transfer (blue) complex at higher adsorption levels. As a result, the hectorite films had a yellow color at low loadings and a dark-green color at high adsorption levels. The absorbance near 640–650 nm was diminished upon drying as the color of the TMB-hectorites changed from green to yellow (Figure 2). A similar result was achieved by acidifying the TMB-hectorite with HCl. At very high TMB loadings, however, where the 21-Å complex was dominant, the green color was more stable to acidity or drying, as shown by the strong absorbance at 650 nm for the air-dry hectorite complex with 300 mmole TMB/100 g (Figure 3A).

Additional UV-VIS peaks evident in Figures 2 and 3A at 780–790 nm and near 870–900 nm are probably not due to the charge-transfer complex because they did not diminish when the wet TMB-hectorite was dried, unlike the 640-nm absorption (Figure 2). They may have been due to the free radical cation monomer, which for the unsubstituted benzidine molecule has absorption maxima at 862, 752, and 700 nm in addition to the strong multiple absorption at 454 nm (Matsunaga, 1972).

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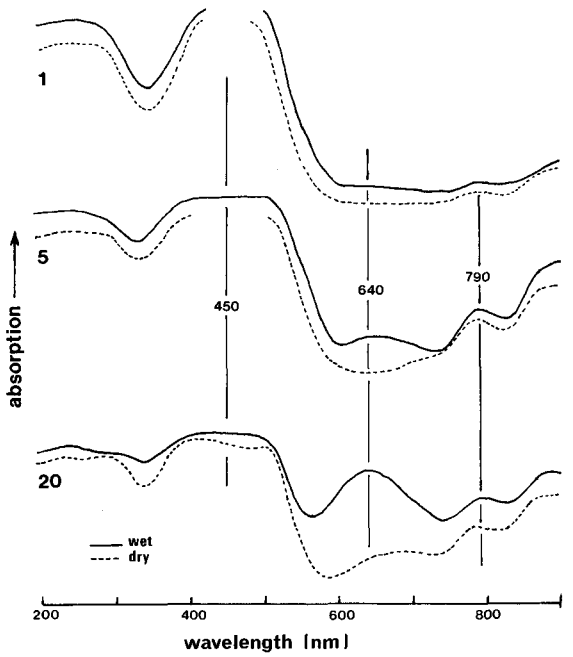


Figure 2. Ultraviolet-visible reflectance spectra of wet and dry hectorite films treated with 1, 5, and 20 mmole tetramethyl benzidine/100 g.

The oxidation of TMB·2HCl by manganese oxide in methanol generated an intense yellow-green solution, with a UV-VIS spectrum not unlike that described by Matsunaga (1972) for the benzidine radical (Figure 3B). The main features were maxima at 875, 800, and 450 nm and a shoulder near 710–720 nm. The intense 450-nm absorption had vibrational fine structure, as previously noted for benzidine (Matsunaga, 1972; Hester and Williams, 1981). The presence of the free radical in methanol was revealed by an intense ESR signal at the free electron position. In contrast, the blue charge-transfer complex of TMB in *aqueous* solution had no ESR signal, but did have UV-VIS absorption maxima at 650 nm and 370 nm. Upon acidification with HCl, it converted to a yellow solution with no ESR signal and a single absorption in the visible range at 427 nm.

The evidence, therefore, indicates that a fraction of the TMB adsorbed on hectorite underwent a single-electron oxidation to form the radical monomer and the charge-transfer complex. Evidence of radical species adsorbed on the hectorite was found at all levels of TMB adsorption, as shown by the ESR spectra in Figures 4 and 5. Whereas ESR signal intensities generally increased at higher adsorption levels, the fully wetted hectorites gave a decrease in signal intensity at the highest (≥70 mmole/100 g) adsorption levels (Figure 4). The wetted hectorite films showed two ESR signals centered near g = 2.0023, a narrow signal (2–3 gauss linewidth) which appeared to be independent of orientation, and a broader line with an orientation-dependent linewidth (see Figure 4). Drying the clays eliminated or obscured the narrow signal, and only the broad signal remained with the same orientation dependence (Figure 5). Because drying reduced the quantity of charge-transfer complex on the hectorite (from UV-VIS data), the narrow ESR resonance was probably due to rapidly exchanging unpaired electrons in the charge-transfer complex, and the broad spectrum, to the radical TMB monomer. The linewidths of the latter spectrum measured for the perpendicular (⊥) and parallel (‖) orientation of the hectorite film relative

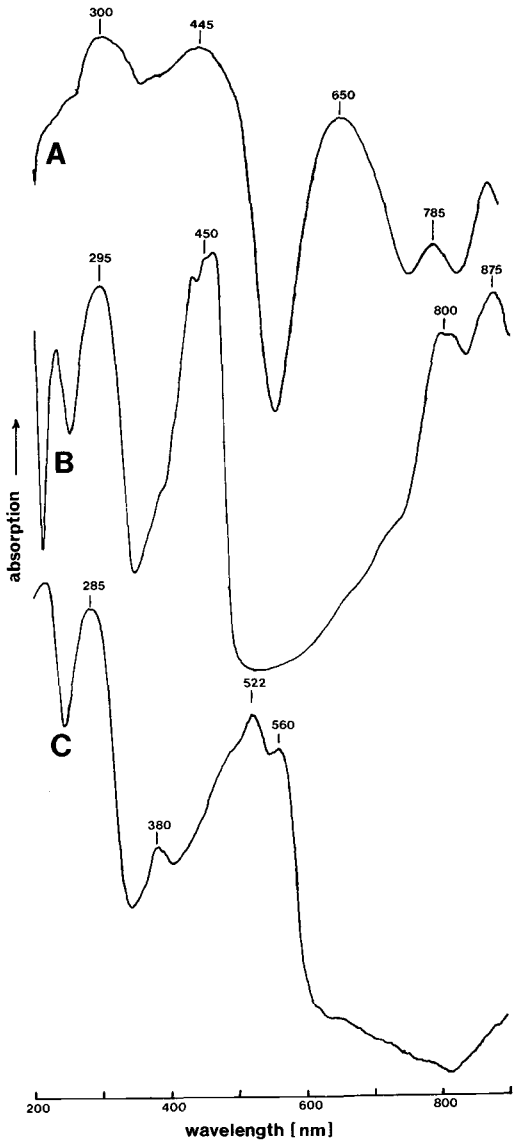


Figure 3. Ultraviolet-visible spectrum of tetramethyl benzidine: A. Adsorbed on dry hectorite film at 300 mmole/100 g level (reflectance spectrum); B. Dissolved in methanol and oxidized by manganese oxide (absorbance spectrum); C. Adsorbed on hectorite in aqueous suspension to form "red" complex (10 mmole/100 g) (absorbance spectrum).

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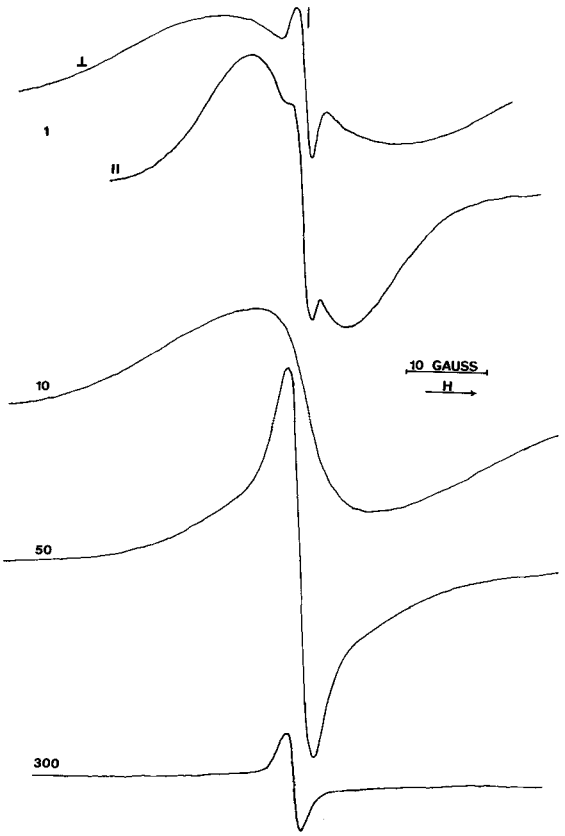


Figure 4. Electron spin resonance spectra of moist tetramethyl benzidine-treated hectorite films (1, 10, 50, and 300 mmole/100 g). Free electron (g = 2.0023) position is indicated by vertical marker.

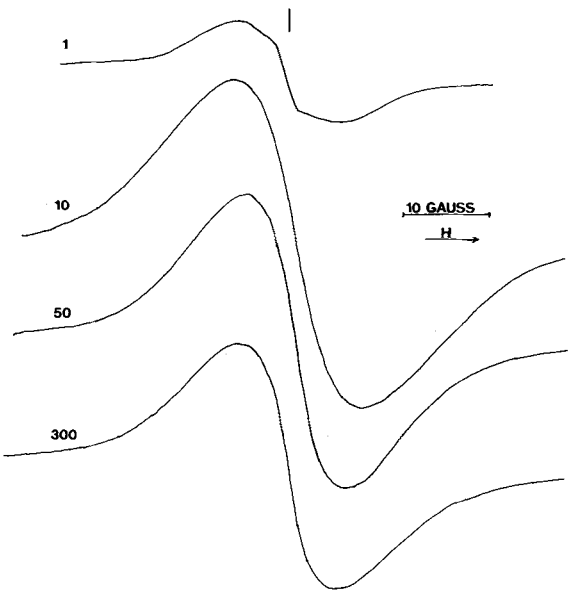


Figure 5. Electron spin resonance spectra of dry tetramethyl benzidine-treated hectorite films (1, 10, 50, and 300 mmole/100 g).

to the magnetic field (22 and 12 gauss, respectively) were similar to the linewidth of the radical generated by oxidation in methanol. The width of the resonance may have resulted from hyperfine splitting which spread the spectrum over more than 20 gauss (Josephy *et al.*, 1982), and the orientation dependence which was noted when the radical was oriented on hectorite surfaces may have arisen from anisotropy in the splitting. The inability to observe individual hyperfine lines in the spectrum may have been an effect of paramagnetics which broadened the very narrow lines.

Charge-transfer complexes have little unpaired electron density, because all but a small fraction of an electron in the donor and acceptor molecules are paired. Nevertheless, their ESR spectra can be observed, albeit at intensities much lower than expected from the degree of oxidation of the organic. Such a result has been used as evidence in support of the existence of charge-transfer complexes of oxidized benzene on smectites (Pinnavaia *et al.*, 1974).

The effect of higher temperature on the ESR signal intensity of the moist TMB-hectorite complex at the 300 mmole/100 g level (see Figure 4) was to increase the intensity of the narrow line and to generate a weak, broad signal. Possibly, higher temperatures favored molecular dissociation and the unpairing of electrons previously involved in charge-transfer. The dimerization of monomer radical cations of benzidine in ethanol is favored at low temperature (Takemoto *et al.*, 1968), a result in qualitative agreement with the present ESR results on clay. Exposure of this same TMB-hectorite complex in the air-dry state to HCl vapor changed the color from green to yellow and greatly diminished the radical ESR signal, suggesting that acidification promoted more complete oxidation to the diimine.

Infrared spectra

The IR spectra of air-dry, self-supporting clay films (prepared to loadings of 20 mmole/100 g) revealed the following features as TMB adsorption was increased: (1) a decrease in intensity of bands near 1640 cm^{-1} and 3100–3650 cm^{-1} indicating less adsorbed water as the hectorite became increasingly hydrophobic; (2) absorption bands, the most notable at 1575, 1504, 1386, 1352, 1223, and 828 cm^{-1}, which became more intense up to an adsorption level of 10–20 mmole/100 g; and (3) absorption bands, the most intense at 1480, 1270–1300, 1227, 862, and 735 cm^{-1}, appearing at very high levels of adsorbed TMB at the expense of those present at lower adsorption levels. Most of the bands listed under (2) must be assigned to oxidized species of TMB, inasmuch as TMB (unoxidized) has bands at quite different positions. Based upon the study of Hester and Williams (1981), the most intense bands at 1504 cm^{-1}

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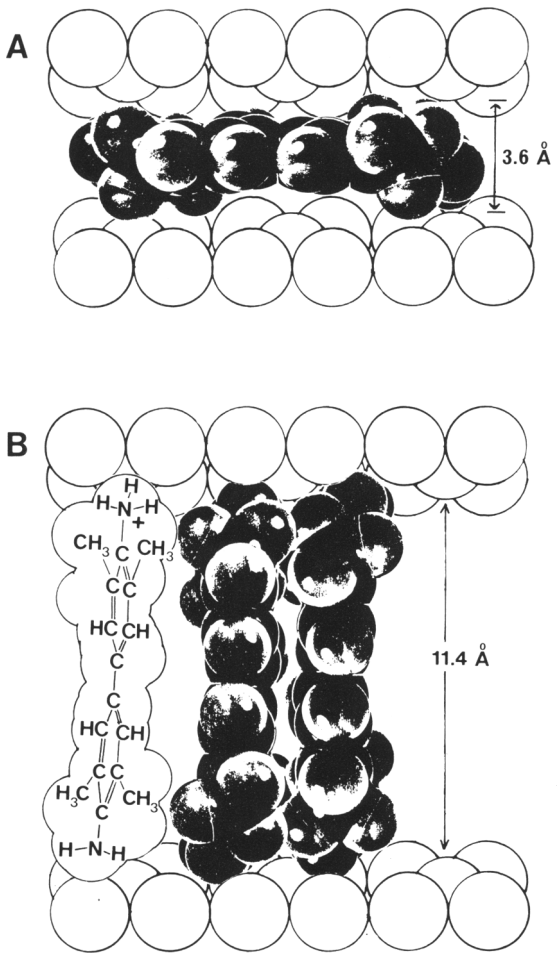


Figure 6. Proposed interlamellar alignment of tetramethyl benzidine for (A) 13.2-Å hectorite complex and (B) 21-Å hectorite complex.

and 1223 cm^{-1} are likely due to the ring C–N stretch and the ring C–H in plane bending of the radical cation; however, the IR spectrum of the diimine form of TMB has not been reported and may contribute some of the observed bands.

The change in IR spectrum with TMB adsorption level confirms the shift toward different molecular species on the hectorite with increasing additions of TMB indicated by UV-VIS spectroscopy and XRD.

Alteration of the TMB-hectorite complex

The green TMB-hectorite was altered to a different complex by adding HCl (which changed the green color to yellow) and adjusting the pH to about 12 with concentrated NaOH. The result of this procedure was a red or pink complex with a UV-VIS spectrum (Figure 3C) clearly different from any spectra reported above. The fact that acidification was necessary prior to the addition of base suggests that further oxidation of the TMB-clay complex was achieved. Matsunaga (1972) noted that acid clay complexes with benzidine produce a more oxidized state of benzidine than non-acid clays. According to the reaction sequence of oxidation described above, acidity should have favored the free radical over the charge-transfer complex. The instability of the radical exposed to O_2 may then have permitted further oxidation to the diimine despite an unfavorable pH for oxidation.

Thus, the red complex was probably the fully oxidized diimine, which at high pH may have associated on the surface to shift its main UV-VIS absorbance from near 430 nm (for the diimine monomer) to 500–560 nm (Figure 3C).

SUMMARY AND CONCLUSIONS

The protonated tetramethyl benzidine cation adsorbed instantly on hectorite by ion exchange. Partial oxidation by O_2 was then catalyzed by the surface, generating the monomeric radical cation (yellow) at low loading levels on the surface, the 13.2-Å basal spacing, and ESR spectra, all of which suggest that the radical was "flat" on the surface (Figure 6a). At higher adsorption levels, intercalation of TMB occurred beyond the CEC of the hectorite as intermolecular associations on the surface began to control adsorption behavior, and a 21-Å basal spacing was observed. The blue species observed at this high surface loading was a π-π charge-transfer complex involving 2 (or more) TMB molecules. The molecules were probably aligned nearly "vertically" on the surface, thereby permitting overlap between π-orbitals of the electron donor (diamine) and acceptor (diimine) as shown in Figure 6b. A similar complex between benzidine and vermiculite at high adsorption levels has been described (Slade and Raupach, 1982). The charge-transfer complex was oxidized to the same degree as the radical monomer, and involved an association of the 2-electron oxidation product (diimine) and the unoxidized diamine. Only a small amount of electron density was shared between these two diamagnetic molecules, so that the ESR signal for the complex was weak, as has been noted for the blue benzidine complex on hectorite (McBride, 1979). Equilibrium between the radical monomer and charge-transfer complex exists in aqueous solution (Josephy *et al.*, 1982), and the chemical equations indicate that low pH should favor the radical. Thus, the reversible shift of the equilibrium toward the yellow species from green (blue + yellow) on drying the clay can be explained, a result which may have been due to the increased acidity generated on clay surfaces by drying as well as the collapse of the 21-Å spacing to 13.2 Å (Table 1). This collapse may have been induced by the removal of interlamellar water, thereby sterically hindering intermolecular interaction. The collapse of the spacing on drying was less evident at the highest TMB adsorption levels, where the green color of the clay was not greatly diminished by drying. This

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apparently stable 21-Å intercalation complex probably retained TMB in excess of the CEC at least in part by the sharing of protons, thereby forming symmetrical hydrogen bonds as shown in Figure 6b. Similar associations between amines have been reported (Farmer and Mortland, 1965; Raman and Mortland, 1969; Mortland *et al.,* 1969) that permit the adsorption of amines in excess of the CEC because each amine molecule carries, in effect, only +½ charge.

Calculations based upon the van der Waals dimensions of the TMB molecule indicate that interlamellar packing as shown in Figure 6b could allow at most the intercalation of about 220 mmole/100 g, whereas packing as shown in Figure 6a could accommodate about 60 mmole/100 g. These two adsorption limits are indicated in Figure 1, suggesting a two-stage adsorption of TMB—ion exchange and adsorption of TMB as monomeric cations positioned horizontally on the surface, followed by intercalation of the molecules as paired molecular complexes oriented vertically on the surface.

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(Received 6 April 1985; accepted 10 June 1985; Ms. 1478)

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