

ORIENTATION OF TRIMETHYLPHENYLAMMONIUM (TMPA) ON WYOMING MONTMORILLONITE: IMPLICATIONS FOR SORPTION OF AROMATIC COMPOUNDS

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Abstract—The orientation of TMPA cations on montmorillonite affects the adsorbate-accessible siloxane surface area and determines whether the TMPA phenyl ring can interact with other aromatic adsorbates by π - π interactions. The purpose of this study was to determine the orientation of TMPA ions in the interlayer of normal-charge and reduced-charge Wyoming montmorillonite. The orientation of TMPA's phenyl group was investigated using infrared dichroism of selected aromatic ring vibrations. X-ray diffraction (XRD) and MacEwan Fourier transforms were used to determine interlayer spacings and to ascertain whether reduced-charge Wyoming montmorillonite is a randomly interstratified mixture of layers with two different d-spacings. For normal-charge montmorillonite, the infrared results showed that the C-N bond axis is neither perpendicular nor parallel to the surface, yet X-ray data suggested that the TMPA phenyl ring is perpendicular or nearly perpendicular to the siloxane surface. In this orientation, the average adsorbate-accessible space between adjacent TMPA ions is 24 Å², or about 1/3 of the total surface. When the phenyl ring of TMPA is perpendicular to the clay surface, aromatic compounds should be able to interact with TMPA's aromatic ring by π - π interactions, while polar compounds such as water can interact with positively charged nitrogen atom. The reduced-charge montmorillonite used in this study is a randomly interstratified mixture of about 25% collapsed layers with no adsorbed cations and 75% expanded layers that are propped open by TMPA's methyl groups, not by the aromatic ring. The adsorbate-accessible surface area on expanded layers of reduced-charge montmorillonite is 1.5 to 2 times that on normal-charge TMPA-clay, depending on the orientation of TMPA's aromatic ring.

Key Words—Adsorbate, Infrared dichroism, Montmorillonite, Trimethylphenylammonium (TMPA).

INTRODUCTION

Smectite and other expanding 2:1 clay minerals sorb aromatic hydrocarbons from water when small quaternary alkylammonium cations such as trimethylphenylammonium (TMPA) occupy the clay's cation exchange sites (Boyd et al. 1991). Information about the orientation and distribution of organocations within clay interlayers will aid in developing suitable organoclay sorbents for a particular waste stream because these properties affect sorption capacity and sorption mechanisms. For example, the surface-charge density of a clay may affect the orientation of an adsorbed organic cation's aromatic ring (Serratosa 1966), which in turn may affect the interlayer surface area accessible to uncharged organic sorbates such as aromatic pollutants. The orientation of TMPA phenyl rings may also determine whether TMPA's π -electrons can interact with other aromatic sorbates by π - π interactions.

Infrared dichroism experiments can be used to determine the orientation of adsorbed aromatic compounds such as TMPA. When an infrared beam is parallel to an axis of molecular vibration (for example, x-, y-, and z-axes in Figure 1), the absorption intensity of that vibration will be minimized. If the sample is rotated so that the infrared beam is no longer parallel to the infrared vibration, the absorption intensity will increase. Thus, if the C-N bond of TMPA is either par-

allel or perpendicular to the siloxane surface, or if the phenyl ring is parallel to the surface, the intensity of the appropriate vibrational band will change when an oriented clay film is rotated in an infrared beam. Infrared dichroism experiments have shown that uncharged polar aromatic molecules like pyridine (Farmer and Mortland 1966; Serratosa 1966) and benzonitrile (Serratosa 1968) lie perpendicular to the siloxane surface of montmorillonite, with the polar functional group midway between opposing clay surfaces. This orientation allows the polar group to either solvate adsorbed inorganic cations directly or to interact with water molecules in the hydration shell of the inorganic cation. In contrast, when pyridinium ions satisfy a clay's negative charge, infrared dichroism experiments have shown that the pyridinium ring lies parallel to montmorillonite but perpendicular to vermiculite surfaces (Serratosa 1966). The difference in orientation between these two clays was attributed to the higher charge density of vermiculite. The surface area per negative charge on Wyoming montmorillonite can accommodate pyridinium ions lying flat on the clay surface, whereas pyridinium can only satisfy the structural charge of vermiculite when in an upright position (Serratosa 1966). On both montmorillonite and vermiculite, the pyridinium ring is oriented in a manner that minimizes charge separation between the NH⁺

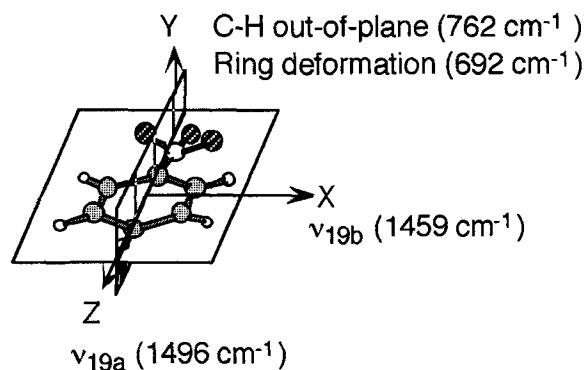


Figure 1. Symmetry axes of TMPA and infrared band assignments for TMPA- d_6 vibrations along these axes.

group of pyridinium and the clay's structural charge sites. As with pyridinium, adsorbed TMPA cations should also adopt an orientation that minimizes charge separation within steric constraints imposed by the size of the TMPA ion and the clay's layer charge.

The objective of this research was to determine the orientation of TMPA cations on normal-charge and reduced-charge Wyoming montmorillonite. Specifically, infrared dichroism experiments were used to test the hypothesis that TMPA phenyl groups are perpendicular to the surface of normal-charge montmorillonite and parallel to the surface of reduced-charge montmorillonite. Infrared dichroism will not be observed if the principal vibration axes of TMPA are randomly oriented or if the preferred orientation is such that none of the principal vibration axes is perpendicular to the surface. Additionally, little or no dichroism will be observed if a clay comprises interstratified layers with different TMPA orientations. XRD d-spacings were used to further constrain the orientation of adsorbed TMPA, and MacEwan transforms of the XRD data were calculated to test the hypothesis that reduced-charge montmorillonite comprises a randomly interstratified mixture either of layers with different TMPA orientations and hence with different d-spacings, or of collapsed and expanded layers.

MATERIALS AND METHODS

Preparation of Reduced- and Normal-Charge TMPA Montmorillonite

Wyoming montmorillonite (SWy-1) was obtained from the Clay Minerals Society Source Clays Repository at the University of Missouri-Columbia. The $<2\text{-}\mu\text{m}$ fraction was separated from the coarser material by sedimentation. Half of the $<2\text{-}\mu\text{m}$ clay was saturated with Na^+ and the other half with Li^+ by shaking 4 g of clay with 200 ml of the appropriate 0.1 M chloride solution, centrifuging the suspensions, and decanting the supernatant solutions. This shaking-centrifugation-decantation process was repeated three times. Excess salts were removed from the homoionic clays by dialysis until an AgNO_3 test for chloride was negative. Part of the dialyzed Na^+ -saturated clay suspension ("normal-charge" clay) was freeze-dried and set aside.

The layer charge of the remaining clay was reduced by a method similar to that described by Brindley and Ertem (1971). Briefly, a suspension composed of 50% Li^+ -saturated montmorillonite and 50% Na^+ -saturated montmorillonite by mass was freeze-dried, then heated 18 h in quartz crucibles at 250°C to dehydrate adsorbed Li and promote Li migration into vacant octahedral sites. The collapsed, reduced-charge clay was re-expanded by sonicating 2-g subsamples of clay in 200 ml of a 70% methanol-water mixture for 20 min in an ice-water bath (Greene-Kelly 1953; Brindley and Ertem 1971; Jaynes and Bigham 1987). A Heat Systems, Ultrasonic Inc. model W-385 sonicator with a 7-mm diameter probe tip on a setting of 7 (out of 10) was used.

To prepare TMPA-saturated montmorillonites for the XRD studies described below, TMPA-Br was added to both normal- and reduced-charge montmorillonites in 70% methanol-water suspensions (10 g clay l^{-1}) and stirred for 72 h. The amount of TMPA added was ten times the CEC. After the suspensions were stirred, clays were dialyzed until bromide-free and then were freeze-dried. Selected properties of normal- and reduced-charge TMPA-clays are reported in Table 1.

Table 1. Selected physical and chemical properties of normal- and reduced-charge TMPA-montmorillonite.

Treatment	d(001) Å	N_2 surface area ¹ $\text{m}^2\text{ g}^{-1}$	Total C ² g kg^{-1}	Adsorbed TMPA ³ mmol kg^{-1}	CEC ⁴ mmol kg^{-1}
Reduced	13.57	318 ± 14	48.6 ± 0.9	449 ± 8	390 ± 30
Normal	14.84	252 ± 28	88.1 ± 1.0	814 ± 11	870 ± 80

¹ Avg \pm SD (N = 2 or 3) from three-point BET N_2 adsorption isotherms using a Quantachrome Quantasorb Jr. surface area analyzer.

² Avg \pm SD (N = 2) of total C determined by combustion at 900°C using a Dohrmann DC-190 high-temperature carbon analyzer.

³ Avg \pm SD (N = 2) calculated with the equation: Adsorbed TMPA = g C/kg clay \times mmol TMPA/g C.

⁴ Avg \pm SD (N = 3) Determined by Na^+ saturation and ammonium displacement of the parent normal-charge and reduced-charge clays. Statistically identical values were obtained with Mg^{2+} saturation and Ba^{2+} extraction.

Infrared Dichroism

PREPARATION OF METHYL-DEUTERATED TMPA. As will be discussed later, accurate assignment and identification of the ν_{19a} and ν_{19b} infrared bands of TMPA (Figure 1) is essential for using infrared dichroism to determine the orientation of adsorbed TMPA. Methyl C-H deformation vibrations of TMPA overlap at least partially with the ν_{19a} and ν_{19b} ring stretching vibrations, but the ring vibrations are distinct in methyl-deuterated TMPA. Montmorillonites saturated with TMPA- d_9 were used in the infrared dichroism experiments described below.

Methyl-deuterated TMPA (TMPA- d_9) was synthesized using a procedure modified from that of Cope et al. (1960). Aniline, NaHCO_3 , and CD_3I in a mole ratio of 1:3:3 were refluxed in methanol [10:1 methanol:aniline (v:v)] with constant stirring for 75 h. Deuterated methyl iodide was added after 24 and 48 h to give a final CD_3I :aniline mole ratio of 4.5:1. After the mixture was refluxed, it was evaporated to dryness in the reflux flask. The residual solid was extracted three times with boiling chloroform. The volume of chloroform for each extraction was equal to the volume of methanol used during reflux. The hot chloroform extracts, which contained the deuterated TMPA-iodide, were decanted from the solid material remaining in the flask and were filtered. Much of the deuterated TMPA-iodide crystallized on the filter because the boiling chloroform cooled rapidly at room temperature. Deuteration of the TMPA methyl groups was verified by obtaining the FTIR spectrum of the white crystalline product in a pressed KBr pellet.

CLAY FILM PREPARATION. Oriented, self-supporting TMPA- d_9 -saturated clay films were prepared by sedimenting Na^+ -saturated normal-charge and reduced-charge montmorillonite suspensions onto glass slides. The Na-montmorillonite films were air-dried at room temperature and then were reacted overnight at 60°C with 20 ml of TMPA- d_9 in ethanol (5 mmol TMPA- d_9 kg^{-1} solution) in covered Petri dishes. During this reaction, the clay films partially separated from the glass slides. Next, the ethanol was allowed to evaporate, and the dry films were removed from the slides and washed gently with 20 ml of ethanol to remove excess salts. The ethanol wash solutions were removed with a Pasteur pipette, and the clay was allowed to dry. The normal-charge film contained 2.8 mg clay cm^{-2} , and the reduced-charge film contained 2.2 mg clay cm^{-2} .

SPECTRAL COLLECTION. Self-supporting TMPA- d_9 montmorillonite films were placed in the sample holder of a Perkin-Elmer 1710 FTIR that was purged with high-purity N_2 . Single-beam background (empty, purged sample compartment) and clay spectra were collected with a DTGS detector using 2 cm^{-1} resolution, no apodisation and 100 scans. After spectra were collect-

ed with the montmorillonite films normal to the beam, a second spectrum of each film was collected with the film tilted approximately 45°. Spectra were stored on diskette and converted from single-beam spectra to absorbance using the MS-DOS program SpectraCalc (Galactic Software, Inc.). Baselines were leveled in spectral regions of interest and zeroed. To correct for small differences (<10%) in absorbance that might be caused by differences in the amount of clay probed by the infrared beam with the clay films 90° and 45° to the infrared beam, the spectra were normalized to make the absorbance of the clay lattice O-H stretching band (3628 cm^{-1}) equal at the two angles of incidence. To determine whether the TMPA phenyl group adopts a preferred orientation with respect to the siloxane surface in either the normal-charge or reduced-charge montmorillonite, the normalized 90° absorbance of each TMPA ring vibration was compared with the normalized absorbance at 45°.

X-Ray Diffraction and Fourier Transform

X-ray diffraction (XRD) patterns were obtained for normal-charge and reduced-charge TMPA montmorillonites to determine the interlayer spacings and to determine whether reduced-charge TMPA-montmorillonite is a randomly interstratified mixture, as was indicated by previous research (Clementz and Mortland 1974; Clementz et al. 1974). Although TMPA-montmorillonites are the focus of this study, glycerol-solvated Na-montmorillonites also were X-rayed to give unambiguous information about the clays themselves, because the d-spacings of glycerated Na-montmorillonites are well known.

To prepare slides for XRD, replicate aqueous suspensions of normal- and reduced-charge Na-montmorillonites were sedimented onto X-ray slides to give clay film densities near 4 g cm^{-2} . The slides were allowed to dry overnight. To prepare TMPA-saturated montmorillonite, one set of Na-montmorillonite slides was reacted overnight at 60°C with 40 mL of 5 mM TMPA bromide in ethanol. Excess solution was then removed, and the slides were rinsed gently with ethanol to remove excess salts. The TMPA-saturated montmorillonites were allowed to dry overnight prior to XRD. To prepare glycerol-solvated Na-montmorillonite slides, the other set of slides was sprayed with an aqueous solution of 10% glycerol, then placed in a desiccator over CaCl_2 to dry overnight. All slides were X-rayed from 3 to 90° 2 θ , typically in 50-s, 0.05° steps at 10 mA and 25 kV, using a Phillips APD 3270 diffractometer with Ni-filtered $\text{Cu-K}\alpha$ radiation, a theta-compensating slit and a graphite monochromator between the sample and the detector.

To determine whether the d(001) spacing of each sample was a true interlayer spacing or if it resulted from a randomly interstratified mixture of expanded and collapsed layers, electron probabilities [$W(R)$] for

layer spacings (R values) from 0 to 45 Å were calculated at 0.05 Å intervals with the equation (MacEwan 1956):

$$W(R) = \sum_{n=1}^x \frac{I_o}{\sqrt{L_p F^2}} \cos(360R/d) \quad [1]$$

In this equation, I_o is the corrected integrated peak area of the n^{th} XRD peak, L_p is the Lorentz polarization factor, F^2 is the form factor (structure factor) and d is the d-spacing the n^{th} XRD peak.

Values of I_o used in equation [1] were calculated from measured peak intensities (areas) by correcting for the angular dependence of the volume of sample irradiated (Moore and Reynolds 1989):

$$I_o = \frac{I_{meas}}{\frac{\sin \theta}{2\mu^* g} \left[1 - \exp\left(\frac{-2\mu^* g}{\sin \theta}\right) \right]} \quad [2]$$

where I_{meas} is the measured peak area (after subtracting any overlapping quartz peaks); μ^* is the mass absorption coefficient and is equal to 35 for montmorillonite (Moore and Reynolds 1989, p. 280); g is the density of the clay film (4 g cm⁻² in this study). Because our diffractometer's theta-compensating slit irradiates a constant sample area, the correction for the angular dependence of the volume irradiated is the same for depth of irradiation.

Form factors (F^2) in Equation [1] were estimated from Figure 8-2 of MacEwan (1956). Some form factors approached zero, which caused amplitude factors to approach infinity. As recommended by Reynolds (1980), X-ray peaks that caused the amplitude factor to approach infinity were not used to calculate the Fourier transform.

The Lorentz polarization factor for random powders [i.e., $(1 + \cos^2 2\theta)/(\sin \theta \sin 2\theta)$] was used in Equation [1] even though it is only an approximation for oriented clay films. We did not attempt to derive the exact Lorentz polarization factor for our diffractometer geometry and slit/monochromator arrangement because a sensitivity analysis showed that the peak positions in the electron probability plots were insensitive to the equation used to describe the angular dependence of the Lorentz polarization factor.

RESULTS

Infrared Dichroism

To determine whether the TMPA phenyl ring is perpendicular or parallel to the siloxane surface, the normalized absorbances of the ν_{19a} , ν_{19b} , C-H out-of-plane and ring deformation bands of TMPA-d₉ (Figure 1) with a clay film perpendicular to the infrared beam can be compared to the normalized absorbances for the clay film tilted 45° with respect to the infrared beam. If the x-axis of the phenyl ring (ν_{19b} vibration) is perpendicular to the siloxane surface, the absor-

bance of the ν_{19b} vibration should increase by as much as a factor of two (Serratosa 1966) when a TMPA-d₉-montmorillonite film perpendicular to the infrared beam is rotated 45°. The ν_{19a} absorbance should exhibit dichroism if the phenyl ring and z-axis (C-N bond axis) are perpendicular to the infrared beam, whereas the C-H out-of-plane and ring deformation vibrations should be dichroic if the phenyl ring is parallel to the siloxane surface.

For TMPA-d₉ adsorbed on normal-charge montmorillonite, the normalized absorbance of all of the TMPA ring vibrations increased slightly when the clay film was rotated in the infrared beam, but none of the vibrations exhibited significant dichroism (Figure 2a). The phenyl ring itself may be perpendicular to the siloxane surface even though neither the x-axis nor z-axis is perpendicular, but infrared dichroism alone cannot show the orientation of the phenyl ring when neither the x-, y-, nor z-axis is perpendicular.

For reduced-charge montmorillonite, none of the TMPA ring vibrations showed significant dichroism (Figure 2b). Thus, none of the axes is perpendicular to the clay surface and the phenyl ring is not parallel to the siloxane surface. The original hypothesis that the phenyl ring of TMPA is parallel to the surface of reduced-charge Wyoming montmorillonite is therefore false.

X-Ray Diffraction Analysis

The X-ray diffraction pattern for normal-charge TMPA-montmorillonite gives $d(001)$ of 14.9 Å (Figure 3a). Higher order peaks are rational and suggest that the actual d-spacing is 15.0 Å, a result that is supported by the 15-Å maximum in the MacEwan electron probability plot (Figure 4a). The small discrepancy between the $d(001)$ spacing and the electron probability maximum (14.9 vs 15.0 Å) can be accounted for by a 0.04 °2θ error in the $d(001)$ position and thus is negligible, given the breadth and asymmetry of this peak. There also is good agreement between the raw XRD pattern and the MacEwan transform for normal-charge, glycerol-solvated Na-montmorillonite (Figures 5a and 6a).

For reduced-charge TMPA-montmorillonite, XRD peaks (Figure 3b) are much broader and more poorly defined peaks than for normal-charge TMPA-montmorillonite. The $d(001)$ spacing is at 13.6 Å, and the higher order peaks are irrational. The breadth and irrationality of the XRD peaks suggest that reduced-charge TMPA-montmorillonite is an interstratified mixture of layers with two different d-spacings. This result is consistent with previous studies in which reduced-charge montmorillonites with greater than 50% charge-reduction gave irrational XRD peaks and were thus presumed to be interstratified mixtures of layers with two different d-spacings (Clementz and Mortland 1974; Clementz et al. 1974). Clementz and Mortland

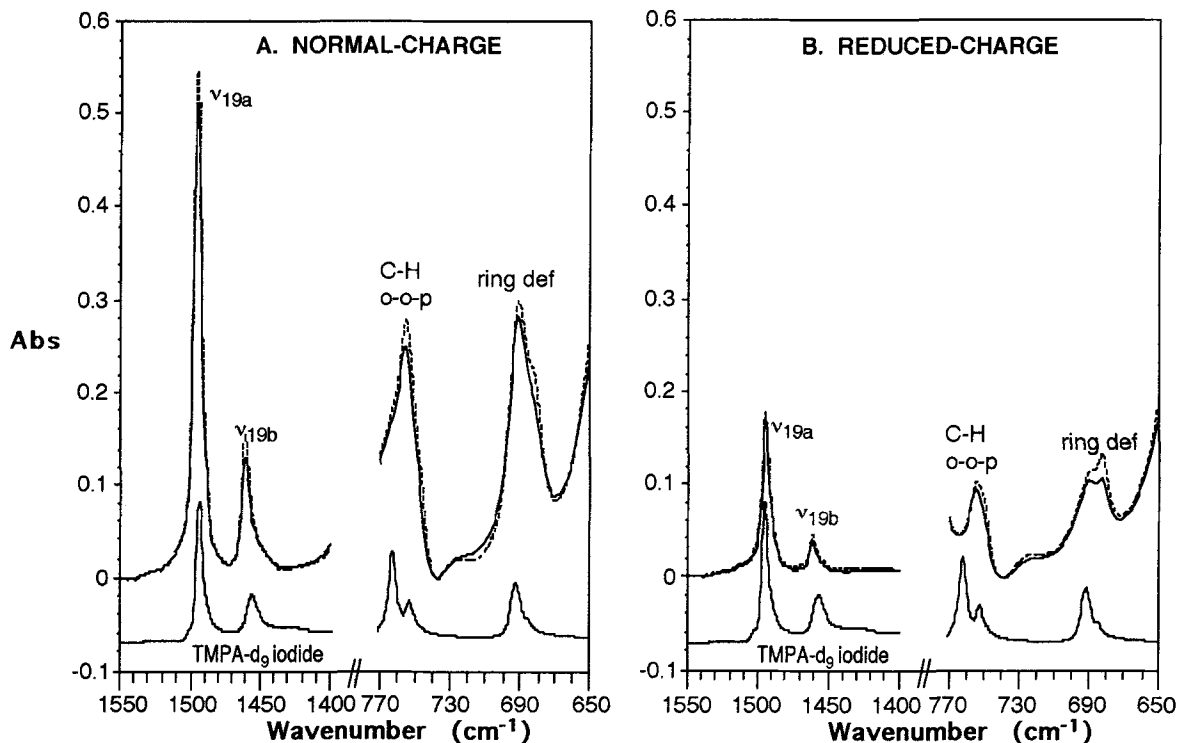


Figure 2. Selected infrared vibrations of TMPA adsorbed on normal-charge and reduced-charge Wyoming montmorillonite for 90° (—) and 45° (---) angles of incidence and for TMPA- d_9 iodide pressed in a KBr pellet (bottom spectrum). Molecular axes associated with each vibration are shown in Figure 1.

(1974) proposed that some layers cannot be re-expanded after charge reduction because their structural charge is completely neutralized by Li atoms and no exchangeable cations can be adsorbed in the interlayer.

The MacEwan electron probability plot for reduced-charge TMPA-montmorillonite (Figure 3b) has strong maxima at 13.52 Å and at integral multiples of 13.5 Å. In addition, there are smaller maxima at 9.55 Å and at linear combinations of 13.5 and 9.5 Å. The peak at 13.5 Å represents layers with TMPA adsorbed in the interlayer, whereas the peak at about 9.5 Å represents collapsed layers with no TMPA. Thus, reduced-charge TMPA-montmorillonite comprises a randomly interstratified mixture of collapsed layers and layers with 13.5 Å d-spacings. The 13.5 Å d-spacing for TMPA-containing layers of reduced-charge montmorillonite is about 1.5 Å smaller than for normal-charge TMPA-montmorillonite and is evidence that the orientation of TMPA is different on reduced-charge montmorillonite than on normal-charge montmorillonite. There is some uncertainty (up to 0.2 Å, based on the 9.55 spacing for the collapsed layers in Figure 4b) in the MacEwan transform because it is difficult to accurately determine peak areas and peak positions when XRD peaks are broad and overlapping as they are for reduced-charge TMPA-montmorillonite. The XRD pattern for reduced-charge, glycerol-solvated Na-montmorillonite

(Figure 5b) contains much sharper peaks and should provide clearer evidence for or against interstratification. In the X-ray diffractogram (Figure 5b), the irrationality of the d-spacings, the high intensity of the even-ordered peaks (compared with normal-charge montmorillonite) and the breadth of the odd-ordered peaks strongly indicate random interstratification. The MacEwan electron probability plot (Figure 6b) has prominent maxima at 18 and 36 Å from expanded layers, with smaller peaks at 9.35 and 27.35 Å (18 + 9.35) from collapsed layers and from expanded + collapsed layers. The proportion of 18-Å expanded and 9.35-Å collapsed layers cannot be estimated accurately from the MacEwan electron probability plots because of uncertainties about the location of the baseline. However, the proportions of each layer type can be calculated from the positions of the XRD peaks using Mering's methods (Reynolds 1980). Diffraction peaks at 9.06, 4.54 and 3.03 Å require that reduced-charge montmorillonite comprises 65–75% expanded layers and 25–35% collapsed layers. Values of Q (Moore and Reynolds 1989), calculated based on 17.95 Å and 9.35 Å spacings of expanded and collapsed layers, exhibited a linear dependence on (peak width * $\cos 2\theta$) (Figure 5b inset). This linear relationship is further evidence for random interstratification of collapsed and expanded layers.

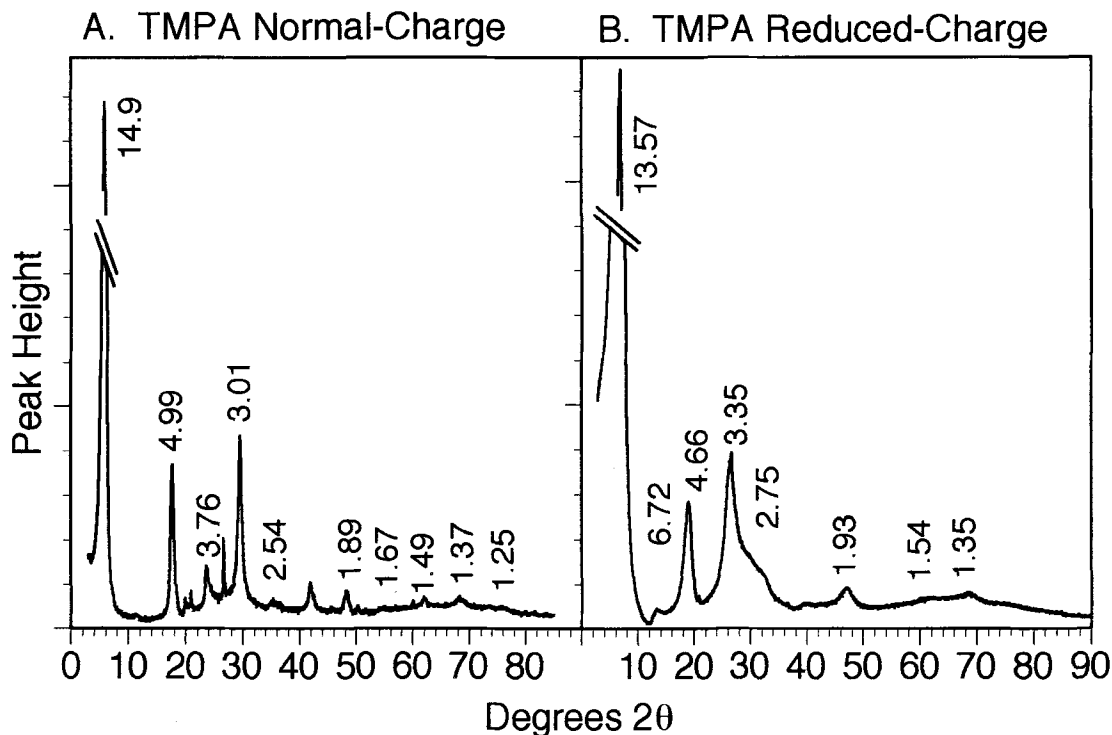


Figure 3. X-ray diffractogram for normal-charge and reduced-charge TMPA-montmorillonites. Only the peaks used to calculate the MacEwan Fourier transform are labeled.

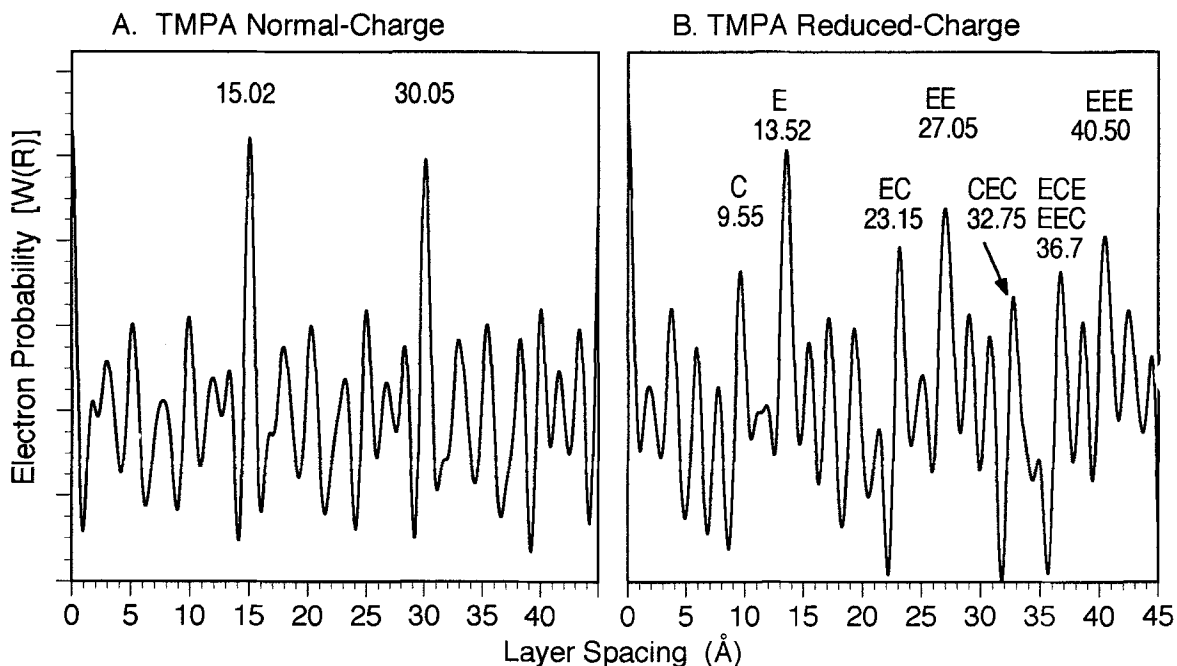


Figure 4. MacEwan Fourier transforms for normal-charge and reduced-charge TMPA-montmorillonites. Peaks due to expanded (E) and collapsed (C) layers and combinations are labeled for reduced-charge montmorillonite.

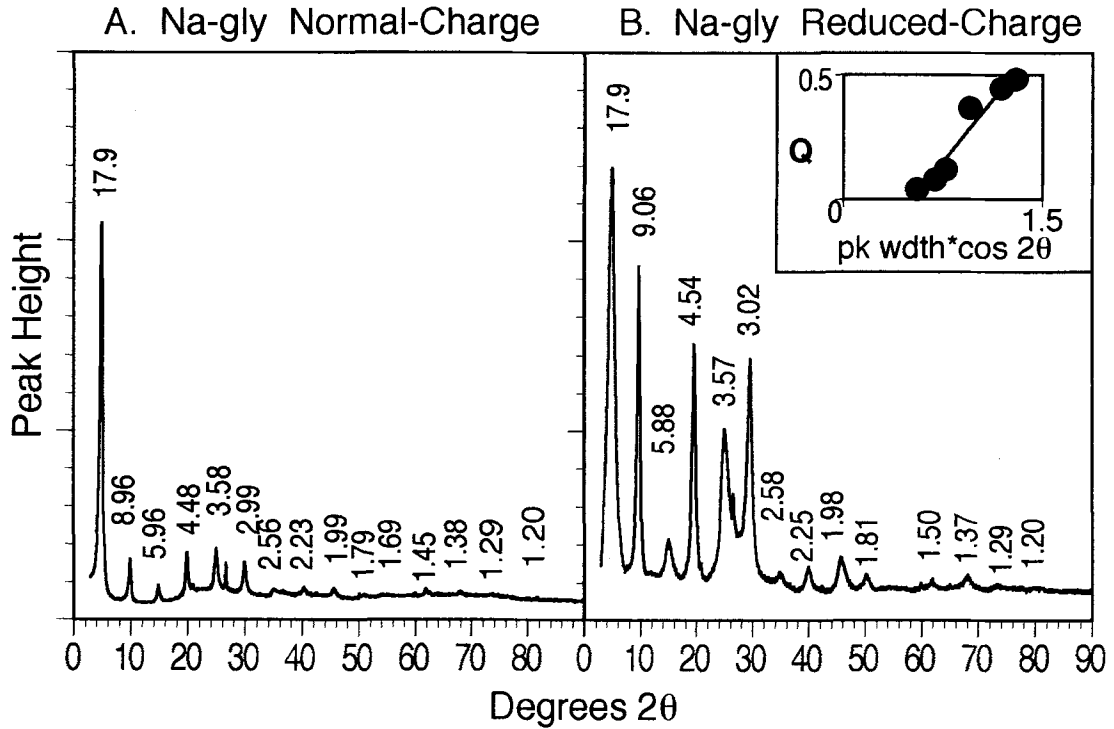


Figure 5. X-ray diffractogram for normal-charge and reduced-charge glycerol-solvated Na-montmorillonites. Only the peaks used to calculate the MacEwan Fourier transform are labeled.

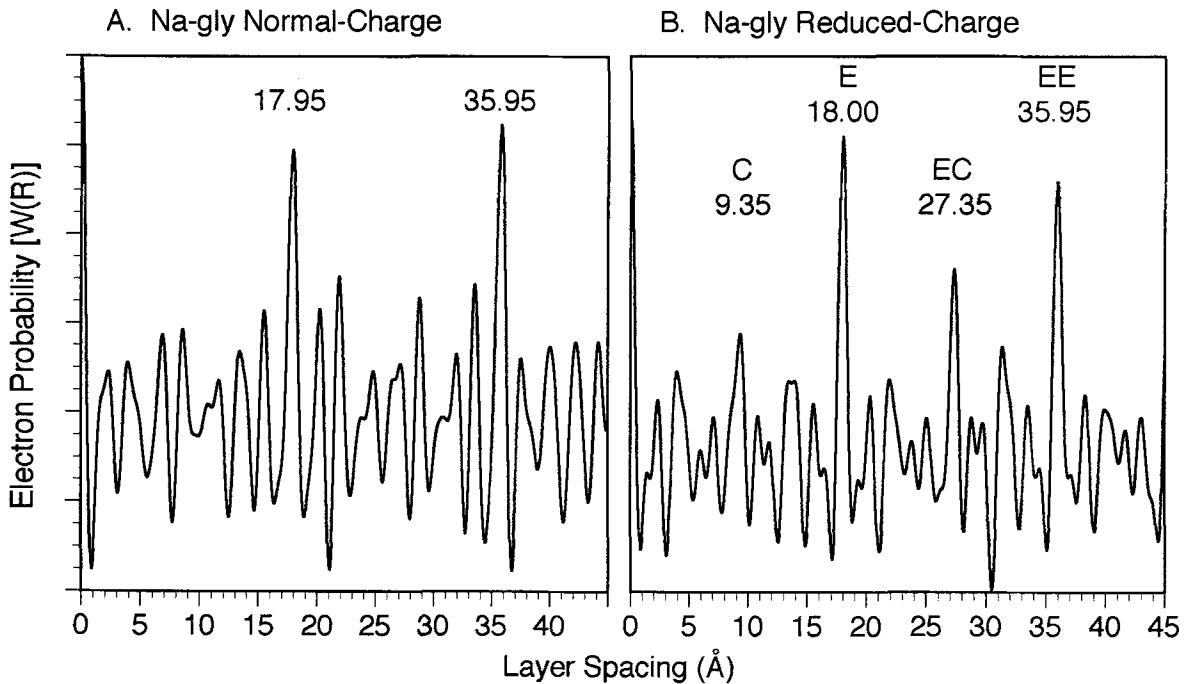


Figure 6. MacEwan Fourier transforms for glycerol-solvated Na-montmorillonites. Peaks due to expanded (E) and collapsed (C) layers and combinations are labeled for reduced-charge montmorillonite.

DISCUSSION AND CONCLUSIONS

For normal-charge TMPA-montmorillonite, the 15-Å d-spacing measured by XRD indicates that TMPA's aromatic ring may be perpendicular or nearly perpendicular to the siloxane surface, based on previous XRD and infrared dichroism studies that reported d-spacings near 15 Å when polar aromatic compounds were adsorbed with their aromatic ring and x-axis perpendicular to the siloxane surface of montmorillonite (Greene-Kelly 1955; Serratos 1966). Our infrared dichroism experiments (Figure 2a) revealed that the x-axis of TMPA is not perpendicular to the siloxane surface of normal-charge montmorillonite, but the aromatic ring could be perpendicular or nearly perpendicular to the clay surface even though none of the molecular vibrations is perpendicular to the surface. The x- and y-axes might be tilted with respect to the surface in order to minimize the distance between the positively charged N atom of TMPA and the clay's structural charge.

If TMPA's phenyl ring is perpendicular to the siloxane surface of normal-charge montmorillonite, the average accessible space between adjacent TMPA cations is 25 Å², which is approximately 1/3 the total siloxane surface area per cation (see Appendix for calculation details). This molecular-level picture is supported by the fact that the measured N₂-accessible surface area [252 m² g⁻¹ (Table 1)] is approximately 1/3 of the theoretical surface area [770 m² g⁻¹ (Gast 1977)]. Jaynes and Boyd previously suggested that adsorbed TMPA acts as pillars to hold open layers; the surface area between adjacent TMPA ions is accessible to N₂ and other sorbates.

The perpendicular orientation of TMPA on normal-charge montmorillonite would allow other aromatic compounds such as benzene to sorb in the clay interlayer with their aromatic ring perpendicular to the surface. A perpendicular orientation would allow aromatic sorbates to interact with TMPA or with one another by π - π interactions. A benzene ring oriented perpendicular to the siloxane surface requires 25 Å² of space between adjacent TMPA ions, which is exactly the average accessible space per TMPA ion on dry normal-charge TMPA-montmorillonite. Thus, if TMPA ions were uniformly distributed on the surface, no aromatic molecule larger than benzene could adsorb on normal-charge TMPA-montmorillonite, particularly in the presence of water, where the accessible surface area would be even smaller. The fact that small amounts of alkylbenzenes and naphthalene are sorbed from aqueous solution by high-charge TMPA-montmorillonites (Jaynes and Boyd 1991) is evidence that TMPA ions are not uniformly distributed on the surface and that some of the interlayer pore spaces between adjacent TMPA ions are sufficiently large to accommodate large arenes. The structural charge of

montmorillonite may be distributed non-uniformly such that TMPA ions are densely packed and have their aromatic rings perpendicular to the surface in high-charge regions, with little or no surface accessible to other sorbates. In low-charge regions, more siloxane surface area would be accessible to other adsorbates, and there would be sufficient space between TMPA ions such that TMPA's aromatic ring need not be perpendicular to the siloxane surface. Thus a non-uniform distribution of structural charge and TMPA ions is consistent with both the absence of infrared dichroism and with the 15-Å d-spacing of normal-charge TMPA-montmorillonite. Jaynes and Boyd (1991) previously proposed that adsorbed TMPA ions are clustered in some interlayer regions but assumed that structural-charge sites were uniformly distributed and that the clustering of TMPA ions was caused by "staggering" of alternating clay layers.

The reduced-charge TMPA-montmorillonite used in these experiments is a randomly interstratified mixture composed of about 25% collapsed layers with no interlayer cations and about 75% expanded layers with a 13.6-Å d-spacing. The 13.6-Å d-spacing is the same as that reported for tetramethylammonium (TMA)-montmorillonite (Barrer and Reay 1957; Barrer and Perry 1961) and may suggest that TMPA's methyl groups prop open adjacent clay layers. Apparently, the structural charge of expanded layers of reduced-charge montmorillonite is sufficiently low that the aromatic ring need not be perpendicular to the surface, as was also shown by infrared dichroism. The phenyl ring of TMPA may be free to rotate within the interlayer at angles intermediate between parallel and perpendicular. Previous research has shown that benzene sorption causes TMA-montmorillonite to expand from 13.6 to 15.0 Å so that the benzene ring can adsorb perpendicular to the siloxane surface (Barrer and Reay 1957; Barrer and Perry 1961) and preliminary experiments in our laboratory confirm that reduced charge TMPA montmorillonite also expands to about 15 Å when benzene is sorbed. This would allow π - π interactions between adjacent aromatic sorbates.

On 13.6 Å layers of reduced-charge TMPA-montmorillonite, the average accessible space between adjacent TMPA ions is between 38 and 52 Å², depending on the exact orientation of TMPA's phenyl ring (see Appendix). Thus, the accessible area per cation is 1.5 to 2.1 times that on normal-charge TMPA montmorillonite. For comparison, the N₂ BET surface area of expanded layers of reduced-charge TMPA-montmorillonite is 1.7 times the N₂-accessible area on normal-charge montmorillonite (424 m² g⁻¹ = 318 m² g⁻¹ ÷ 0.75 g expanded clay/g total clay). The larger accessible surface area of reduced-charge TMPA-montmorillonite should allow more sorption, particularly of larger aromatic compounds (Jaynes and Boyd

1991), and should permit faster diffusion into the interlayer.

Rotation of TMPA's phenyl ring into a perpendicular orientation during arene sorption on reduced-charge TMPA-montmorillonite would increase both the arene-accessible surface area per cation and the interlayer pore dimensions to more than twice those in the normal-charge montmorillonite. Thus, macroscopic surface area measurements, in which the N₂-accessible surface area of reduced-charge montmorillonite is only 1.25 times that of normal-charge montmorillonite, give an incomplete picture of interlayer accessibility to aromatic sorbates. Measured surface areas do not reflect the fact that essentially all of the accessible surface area on reduced-charge montmorillonite resides on 75% of the layers that are expanded, and that the phenyl ring of TMPA likely rotates in the presence of aromatic sorbates (but not N₂) to create additional adsorbate-accessible surface area on reduced-charge montmorillonite.

APPENDIX

Calculation of Accessible Surface Area

The area per negative charge on normal-charge Wyoming montmorillonite can be calculated from the siloxane surface area per unit cell ($5.2 \text{ \AA} \times 9.0 \text{ \AA} \times 2$ siloxane surfaces = 93.6 \AA^2 per unit cell) and the structural formula (0.62 negative charges per unit cell) to give 151 \AA^2 per negative charge. The lateral space per charge would be half that, or 75.5 \AA^2 . When the aromatic ring of TMPA is perpendicular to the siloxane surface, each TMPA ion occupies 50 \AA^2 of lateral space [(25 \AA^2 for the edge area of the aromatic ring + 25 \AA^2 for the methyl groups (Pauling 1960)]. Thus 25.5 \AA^2 per TMPA ion is accessible to other sorbates, which is $\frac{1}{3}$ of the total lateral space.

On reduced-charge montmorillonite, the existence of collapsed and expanded layers makes the calculations somewhat more complex because TMPA ions are sorbed only on expanded layers. Based on Mering's method, about 75% of the layers are expanded and thus accessible to TMPA and other sorbates. Assuming that all of the CEC resides in the expanded layers, the CEC of the expanded layers is $600 \text{ mmol}_c \text{ kg}^{-1}$ ($449 \text{ mmol}_c \text{ kg}^{-1} \div 0.75$). The area per charge on expanded layers of reduced charge montmorillonite (ExRCM) is about 102.5 \AA^2 , calculated from the ratio of $\text{CEC}_{\text{NCM}} : \text{CEC}_{\text{ExRCM}}$ ($1.356 = 814 \text{ mmol}_c \text{ kg NCM}^{-1} \div 600 \text{ mmol}_c \text{ kg ExRCM}^{-1}$) $\times 75.5 \text{ \AA}^2$ per charge on normal-charge montmorillonite (NCM).

On reduced-charge TMPA-montmorillonite, TMPA's phenyl ring likely is oriented intermediate between parallel and perpendicular. If the phenyl ring were parallel to the siloxane surface, each TMPA would occupy 65 \AA^2 [40 \AA^2 for the aromatic ring +

25 \AA^2 for the methyl groups (Pauling 1960)]. Thus, each TMPA requires a lateral space of 50 to 65 \AA^2 , which leaves 37.5 to 52.5 \AA^2 accessible to other sorbates.

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