

THE ORDERING OF CETYLPYRIDINIUM BROMIDE ON VERMICULITE

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Abstract—X-ray superlattice reflections, infrared spectroscopy, and chemical analyses have established that cetylpyridinium bromide (CPB) is highly ordered when adsorbed on vermiculite. The molecules, which stand at about 57° to the silicate surface, form close-packed arrays. Full surface coverage is achieved only for the most highly charged vermiculites. The packing within the arrays accounted for the superlattice observed and each adsorbed molecule had an area of 18.4 \AA^2 at the surface. The implications of these findings for the CPB method used in soil surface area studies are discussed.

Key Words—Adsorption, Cetylpyridinium, Exchange, Interlayer, Superlattice, Vermiculite.

INTRODUCTION

The organization of cetylpyridinium bromide (CPB, 1-hexadecyl-pyridinium bromide) on clay surfaces is of interest from several points of view. CPB is a powerful cationic detergent. Various pyridinium salts, including dodecylpyridinium, have been used as coenzyme models (Slifkin, 1971). In particular, because CPB has been used to determine surface areas of clays, the packing of aliphatic and aromatic groups at the surface needs to be known. This paper combines single crystal diffraction techniques with polarized attenuated total reflectance, i.r. spectroscopy, and chemical analyses to determine the packing and orientation of CPB at the surfaces of three differently charged vermiculites. The application of the results to surface area determinations of soil clays is discussed.

To determine the surface area of clays, Greenland and Quirk (1960, 1962, 1964) suggested using CPB as an alternative to water or ethylene glycol which had been used previously. These two materials had presented difficulties because monomolecular coverage at a standardized vapor pressure was required. Because of their polar nature, water and ethylene glycol molecules cluster about exchangeable cation sites thus invalidating the assumption of monomolecular coverage (Quirk, 1955).

Earlier Greenland and Quirk (1960) found CPB to be adsorbed strongly by montmorillonite and concluded that the adsorption initially took place by a degree of replacement of exchangeable inorganic cations followed by van der Waals attraction between the alkyl chains. They made two assumptions viz. that there was complete surface coverage and that the alkyl chains extended perpendicular to the clay surface. To obtain the area occupied by a single CPB molecule Greenland and Quirk (1962) measured the amount adsorbed on a sodium montmorillonite, whose internal surface area was calculated by using a correction for the area of the external surfaces based upon nitrogen sorption. With this calibration Greenland and Quirk (1962) determined the surface areas of several clay minerals from their adsorption isotherms with CPB. They compared their

results with those based upon water and nitrogen sorption and concluded that CPB adsorption was a valuable method to determine the surface areas of soil clays. At the same time they realized that surface areas of materials having a low density of charge could be underestimated with the CPB technique. The CPB method subsequently has been used to deduce the surface area of soils (Burford et al., 1964, Aringhieri and Sequi, 1978).

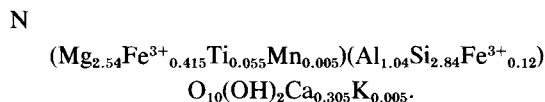
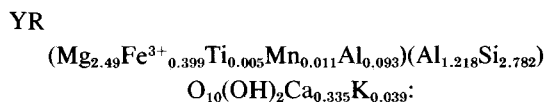
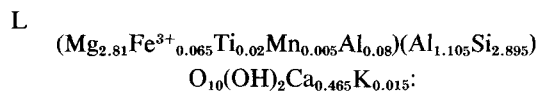
In earlier work Greene-Kelly (1955a,b) had used a combination of X-ray powder diffraction spacing measurements and one-dimensional Fourier syntheses to examine some simple pyridinium complexes formed by montmorillonite. The work was not extended to the 1-alkyl derivatives. Raupach et al., (1975) reported on a lysine-vermiculite complex and advanced the argument that arrays of superlattice reflections, observed in the X-ray powder diffraction patterns, were evidence for a high degree of ordering of the organic molecules in the vermiculite interlayers. X-ray and i.r. studies of other organic complexes with vermiculite (Slade et al., 1976; Raupach and Janik, 1976) have examined the arrangement of organic molecules in the interlamellar spaces of vermiculites. These studies demonstrated the advantages of using vermiculite flakes to elucidate clay-organic interactions.

CPB is here shown to form close-packed, highly orientated arrays at vermiculite surfaces. Further, the packing of the molecules which form these arrays exactly accounts for the excellent superlattice reflections observed.

EXPERIMENTAL

Materials used

Three vermiculites, each with different charge, were studied. They were from the following localities: Llano, Texas; Young River, Western Australia, and Nyasaland, now Malawi. Norrish (1973) reported the analyses of calcium saturated samples of the Llano (L) and Nyasaland (N) vermiculites after igniting at 960°C ; the Young River sample (YR) was similarly calcium saturated and analyzed for this work. The structural formulae are given below:



Natural flakes 1–2 mm across were refluxed with 2 M LiCl or NaCl at 80°C for 1 week; the solution was renewed daily to achieve complete saturation. Residual salt was removed by water-washing and finally the flakes were air-dried. The loss in weight of each vermiculite was determined both after oven drying at 105°C and after heating to 960°C.

Cetylpyridinium bromide (B.D.H.). The proportions of carbon, hydrogen, nitrogen, and bromine present agreed within 0.1% with the theoretical composition based upon $\text{C}_{21}\text{H}_{38}\text{NBr}$. Standard 0.01 M solutions were prepared from CPB dried over P_2O_5 . The percentage absorption of a 0.01 M solution at 259 $\text{m}\mu$ in a 1-cm cell was 45.5.

Preliminary study

After flakes of sodium saturated YR had been immersed in 0.01 M CPB at 40°C for 1 week, an X-ray powder diffractogram showed a set of 12 rational orders based upon a d_{001} of 30.15 Å. After 3 weeks reaction, diffractograms of selected flakes showed a rational set of 30 orders based upon a d_{001} of 40 Å. Weissenberg photographs taken of portions of these flakes revealed an additional 14 orders in the 00l spectra. Measurements of flake thickness showed the swelling of this vermiculite in CPB solution to be almost complete after 5 days, and quite complete at 12 days. Air-dry flakes increased in thickness by 250% in the solutions. Twelve days was therefore taken as the reaction time in the absorption experiments.

Methods

Absorption experiments were carried out in triplicate by shaking 2–3-mg samples of air-dry vermiculite, in tared 4-ml sealed tubes, with 2–3 ml of CPB solution. After the tubes had been shaken at 29°C for 12 days, the supernatant solutions were poured off and the concentrations of CPB, and sodium or lithium in these were determined. The experiments were continued after fresh CPB solutions had been added to the tubes; any residual solution carried forward was determined by weight difference.

To monitor the progress of reactions and to record the 00l X-ray spectra, single flakes were pressed gently onto glass slides for examination with filtered cobalt

radiation in a Norelco diffractometer fitted with the following slits: divergence 0.25°, receiving 0.146 mm before a 1° slit. The scan speed was 1°/minute. For Fourier analyses, integrated counts associated with reflections were recorded while scanning the X-ray diffraction peaks at 0.5°/minute. Background counts, measured in a fixed time mode on either side of the peak, were used to correct the integrated intensities before applying the angle factors necessary to compute structure factors. To obtain the intensities of the (generally weak) reflections between 0030 and 0044 visual estimations were made from a zero level ‘a’ or ‘b’ axis Weissenberg film. These measurements were tied to those from the diffractometer by comparison with suitable reflections between 001 and 0030. A Unicam rotation camera with iron-filtered cobalt radiation was used to record oscillation photographs about either ‘a’ or ‘b’ axes of those crystals displaying rational sets of orders based on fundamental spacings of either 30 or 40 Å. The crystals were set with their basal planes initially perpendicular to the X-ray beam.

The i.r. measurements were made using a Perkin-Elmer 521 double beam grating spectrophotometer, equipped with a wire grid polarizer, RIIC TR-5 ATR assemblies in both beams and with dry air purging to compensate for atmospheric bands. Measurements were made on single flakes and on orientated films using both germanium and KRS-5 hemicylinders. The flakes were pressed onto the reflecting surface of the sample hemicylinder with a teflon backing piece until adequate adhesion occurred. The backing piece was then removed. Deuteration was achieved by direct exchange with D_2O vapor and drying under vacuum. Perpendicular and parallel polarized spectra were recorded at a series of known angles of incidence well above the critical angle for the hemicylinder used. Transmission and ATR spectra on pure cetylpyridinium halides and on related pyridinium and cetyl compounds assisted the band assignments.

Calculations of transmission moment directions were made with the assumption of isotropic refractive indices in the interlamellar region as previously described (Raupach et al., 1975; Raupach and Janik, 1976). The individual band intensities were obtained by splitting the polarized i.r. spectra into their component bands using a least squares program on a 9830B Hewlett Packard programmable calculator. From these, the calculated angle (ψ) representing the direction of the transition moment of the assigned band with respect to the silicate surface was obtained by applying the optical equations of Flournoy and Schaffers (1966).

RESULTS

The chemical analyses

The amounts of CPB and cetylpyridinium (CP) ions sorbed and cation released into solution are shown in

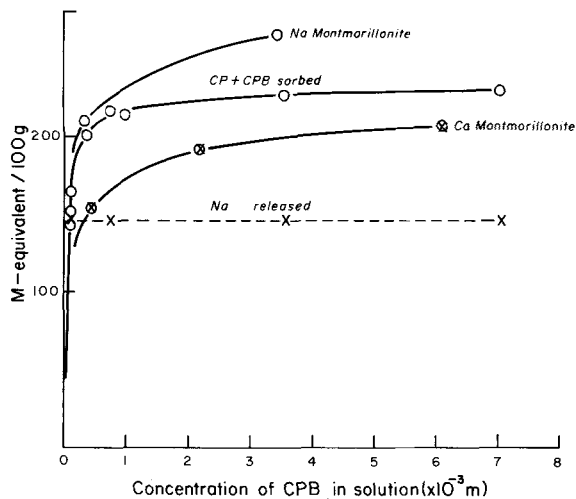


Fig. 1. The sorption of CPB and the corresponding release of Na from Na-YR vermiculite (O D. basis). Together with data for montmorillonite (air-dry basis) from Greenland and Quirk (1960).

Table 1 and Figure 1. One CP ion was assumed to displace one sodium or lithium ion, the total number released being equal to the effective charge. On this basis the CP sorbed (Table 1) was calculated and the ratio of CPB/CP in the vermiculites was established. For the 40 Å complexes these ratios varied with charge; however, they were similar for the 40 Å complexes formed from lithium and sodium saturated YR. The number of CP ions in the 30 Å complex of YR approximately satisfied the charge but the low CPB/CP ratio showed the number of adsorbed CPB molecules to be considerably less than for the 40 Å complexes. The ratio for the 30 Å material was confirmed by microanalysis for carbon, nitrogen, and bromine.

X-ray diffraction

Oscillation photographs of crystals of both 30 and 40 Å complexes formed by CPB and each of the vermiculites

showed not only the usual reflections for vermiculite, but also superlattice reflections near the direct beam as shown in Figures 2a and 2b.

These arrays of superlattice reflections form an interesting comparison with those found in lysine-vermiculite complexes by Raupach et al. (1975) and provide evidence for a high degree of ordering of the organic molecules in the interlayer region of the vermiculite. Inspection of the superlattice reflections for the 30 Å complex reveals them to be a subset of the array characteristic of the 40 Å complex.

The superlattice patterns are direct projections of the reciprocal lattice planes nearest the Ewald sphere and because the reciprocal lattice section is planar and the photographic film curved, the image of the diffraction pattern is geometrically distorted. To interpret the distorted pattern, an unweighted transcription of it was made onto a scale drawing of an a*b* net for vermiculite; see Figure 2c.

The interpretation of this pattern was based upon the realization that it could be built up from a simpler array rotated successively through 120°. This simpler array (Figure 3b) is the diffraction pattern formed by the mask (shown in Figure 3a) when placed into the tube of a light microscope which had been converted into an optical diffractometer by the method of Gall (1967). The mask illustrated in Figure 3a is essentially a hexagonal set of scattering points with one row in six missing. Such rows would be perpendicular to the direction defined crystallographically as "a" on a silicate surface if a one to one correspondence is allowed between the scattering centers of the mask and say the centers of the rings of oxygen atoms forming the surface of a silicate sheet. Inspection of the diffraction pattern (Figure 3b) confirms that there are five true-cell (superlattice) reflections between each pair of primitive-cell reflections in the a* direction. The true cell for CPB-vermiculite has its "a" cell dimension equal to only three times the "a" dimension for a standard vermiculite cell because

Table 1. Characteristics of the vermiculites after reaction with cetylpyridinium bromide.

Vermiculite Used	Spacing (Å)	CP + CPB sorbed (m-equiv./100g O.D. vermiculite)	Li or Na released	CPB/CP calc.	Charge	No of Li or Na ions released (effective charge) (.....per unit cell.....)	No of CP + CPB molecules sorbed
Li-Nyasaland	40.0	185	132	0.40	1.22	1.10	1.55
Li-Young River	40.0	247	151	0.64	1.43	1.25	2.06
Li-Llano	40.0	335	207	0.62	1.90	1.72	2.74
Na-Young River	30.15	167	147	0.14	1.43	1.25	1.28
"	40.0	230	146	0.58	1.43	1.25	1.76

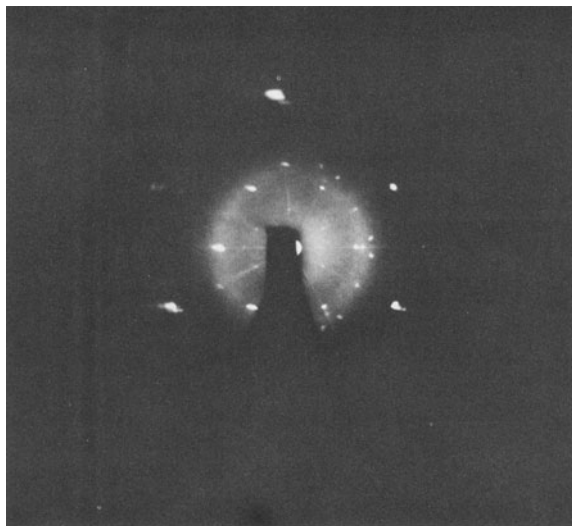


FIGURE 2a.

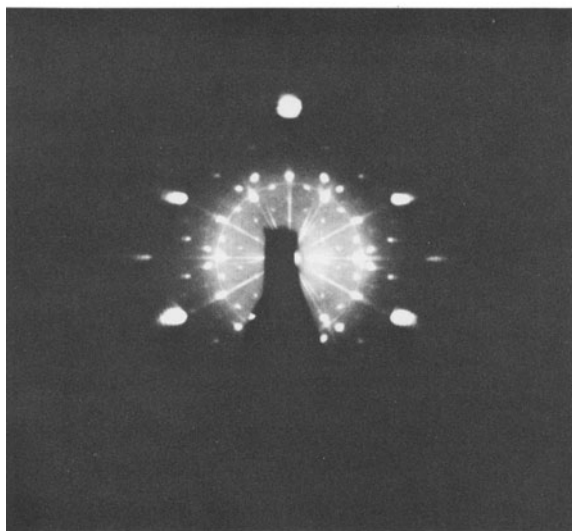


FIGURE 2b.

Fig. 2. a) Oscillation photograph of Young River vermiculite after reaction for 1 week with CPB (0.01 M), 30 Å phase. Oscillation axis = "a"; exposure time 4 hr; CoK α radiation. b) Oscillation photograph of Young River vermiculite after reaction with CPB (0.01 M) for 3 weeks, 40 Å phase. Oscillation axis = "a"; exposure time 4 hr; CoK α radiation.

such cells are c-face centered and as such will only give rise to reflections with $(h + k) = 2n$. The threefold symmetry of the X-ray diffraction patterns shown in Figures 2a and 2b seems likely to arise from a pattern within single sheets on which the organic molecules are grouped in parallel arrangements within domains, each domain being rotated 60° (or 120°) to a neighboring do-

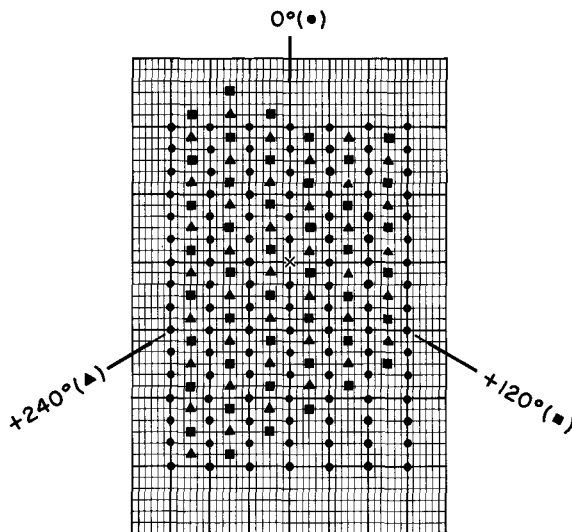


FIGURE 2c.

Fig. 2. c) Transcription of the a^*b^* reciprocal plane of the superlattice for CPB-vermiculite complex.

main. Or the pattern may be the statistical result from stacking a number of sheets, on each of which there is a parallel arrangement of linear members. Between sheets the lineation is randomly rotated through 60° in the basal plane. The evidence from the single crystal diffraction work showed that after reaction with CPB the true repeat distance along "a" for the complex was increased by three times the original "a" cell edge for vermiculite. Although it displays only the strongest reflections of the 40 Å complex, the diffraction pattern for the 30 Å complex is founded upon the same geometrical parameters as those for the 40 Å phase; hence the ordering of the organic molecules on the surfaces of the vermiculite sheets seems to be substantially achieved in the 30 Å phase.

Figure 4 shows the electron density distribution projected onto the c-axes of the unit cells. From these Fourier images a positive identification of the strong peaks expected for the halogen ions proved difficult, but this was overcome by determining the corresponding c-axis projection for the complex formed between cetylpyridinium iodide (CPI) and the L vermiculite. Figure 4 includes this projection for comparison. A considerable enhancement of the peak at a distance of 9 Å from the center of the octahedral layer is seen for the CPI complex. This enhancement, ascribed to the greater scattering power of iodine, allowed the coordinate for the bromine ions to be established.

Each of the one-dimensional projections shows a broad high region adjacent to the silicate section of the projection. The peak at 6 Å is part of this region and might suggest that the pyridinium ions lie flat on the

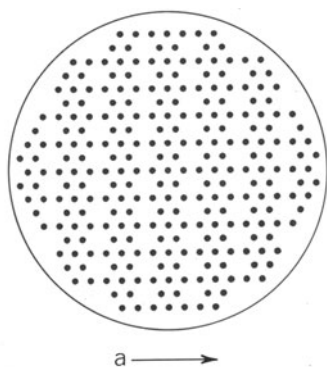


FIGURE 3a.

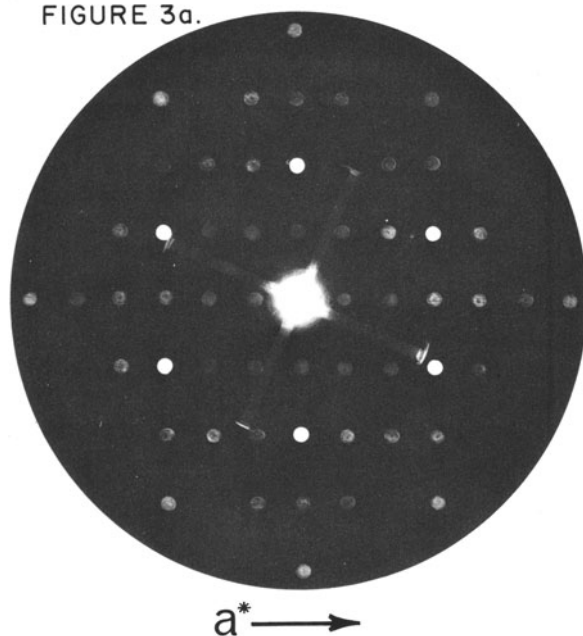


FIGURE 3b.

Fig. 3. a) Portion of mask formed from a hexagonal set of scattering points; one row in six missing in a direction perpendicular to "a." b) Optical diffraction pattern formed by the mask shown in Figure 3a.

surface. However the general height of the region from 6 Å through to 10 Å, considered in conjunction with the unexpectedly close proximity between the 6 Å peak and that at 7.3 Å, seems incompatible with a system of flat rings. A more complete understanding of the one-dimensional projections followed from the interpretation of the i.r. spectra.

I.R. spectroscopy

The spectra of the CPB complexes formed by the various vermiculites may be represented by the result given in Figure 5 for the 40 Å complex produced by the L vermiculite. No significant differences were found for the cetylpyridinium chloride, bromide or iodide complexes of the L, N, and YR vermiculites. Nor were the

spectra for the 30 Å complexes very different, except that a slightly smaller angle ($\psi = 51^\circ$) between the alkyl chains and the silicate surfaces was indicated.

The frequencies noted as the important features of the spectra (Table 2) are the means of peak maxima from splitting a number of reflectivity spectra. The assignment of the peaks was made by comparison with pure pyridinium salts and with results previously recorded in the literature for 1-methylpyridinium iodide (Spinner, 1967; Foglizzo and Novak, 1970) and for pyridinium chloride (Foglizzo and Novak, 1969).

The three high frequency peaks at 3682, 3545 and 3380 cm^{-1} are due to OH vibrations in L vermiculite. The bands between 3100 and 3000 cm^{-1} did not shift on deuteration and are from CH stretching and associated deformation vibrations of the pyridine ring; in the complex these have been displaced towards shorter wavelengths by about 50 cm^{-1} in comparison with pure pyridinium salts, reflecting a modification of the environment for the ring and indicating a different degree of charge transfer. The two main bands below 3000 cm^{-1} are due to the asymmetric (2923 cm^{-1}) and symmetric (2855 cm^{-1}) methylene stretching vibrations, with shoulders contributed by the methyl group. The transition moments of these two methylene vibrations are at right angles to one another and are in a plane normal to the long axis of the alkyl chain, with the symmetric mode lying in the plane of the carbon atoms forming the chain.

The most useful bands below 1700 cm^{-1} for determining the orientation of the pyridine ring are at 1635 and 1175 cm^{-1} , each of which are A_1 vibrations (see Theng, 1974; Foglizzo and Novak, 1969, 1970, but the latter assignment is Spinner's, 1967), and at 1489 and 1585 cm^{-1} , each of which are B_1 vibrations. A_1 and B_1 are both in-plane vibrations, A_1 being directed through N(1) and C(4), Figure 6, and B_1 bisecting the ring at right angles to A_1 . Although the 1491 cm^{-1} band for the pyridinium ion has been assigned to the symmetry class A_1 by Serratosa (1966), the 19b mode (see Spinner, 1967; Foglizzo and Novak, 1970) of 1-methylpyridinium which is necessarily B_1 , is given at 1486 and 1485 cm^{-1} by these authors. Therefore B_1 is the correct assignment for our 1489 cm^{-1} band. The band at 1670 cm^{-1} which is shifted completely on deuteration, is due to the HOH bending of hydrogen bonded water because it is at a higher frequency than for normal water. Bands at 1502 and 1216 cm^{-1} were not suitable for orientation work as the first appeared to be strongly coupled with extraneous influences giving deviations from its usual assignment (19a, A_1) and the second was too weak. The scissoring and wagging vibrations of the alkyl chain were not as useful as the stretching vibrations for the determination of the orientation of the chain. Mean transition moment orientation angles are given in Table 2, together with the standard deviations for the mean results of the different vermiculites studied.

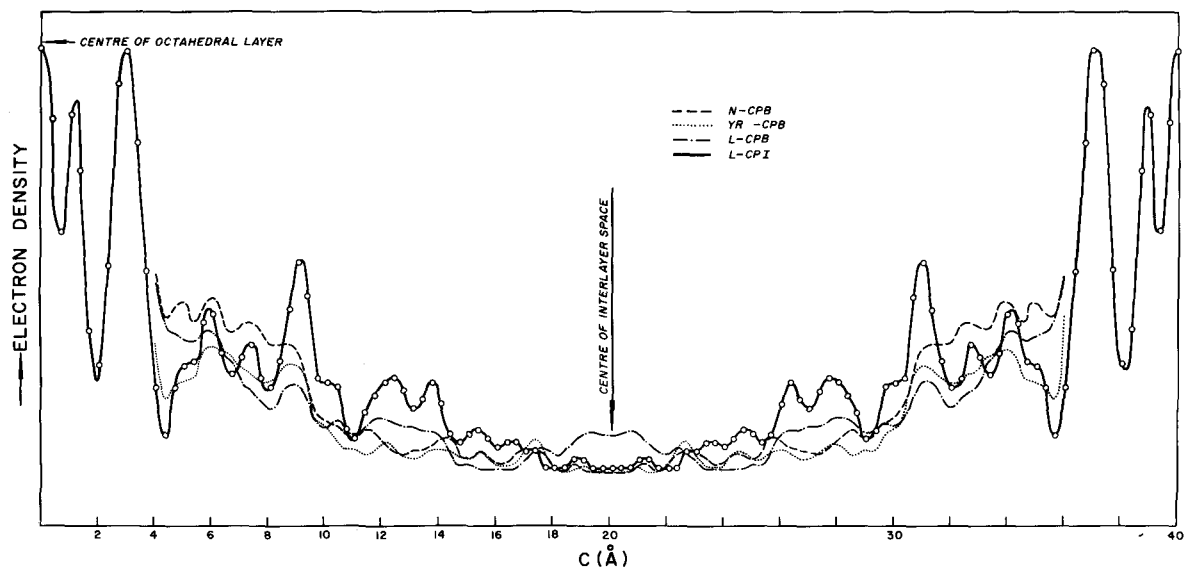


Fig. 4. One dimensional electron density functions for the CPB-vermiculite complexes studied. The corresponding curve for the L vermiculite complex with cetylpyridinium iodide is shown for comparison.

From Table 2 it is concluded that, on average, the alkyl chains make an angle of 57° with the surface. This angle determines the rise of the chain, although projections along the unit cell "a" and "b" axes would be at higher angles. The proposed orientation of the molecules in the interlayer region is illustrated in Figure 6. This representation has been constructed from the data given in Table 2, in conjunction with the distances for

van der Waals contacts between the molecules and the oxygens of the silicate surface. As argued below, the plane containing the carbons of the alkyl chain is along "b."

DISCUSSION

As previously mentioned, oscillation photographs of the 30 Å phase of the vermiculite-CPB complex showed

Table 2. Mean i.r. frequencies and transition moment directions with respect to the silicate surface for the CPB-vermiculite complexes as determined from polarized ATR. The approximate orientations of the moments with respect to the CPB molecule are indicated. The standard deviations of the mean angular directions had 27 degrees of freedom for the 2923 and 2855 cm^{-1} vibrations and the others listed had 5 degrees of freedom.

Frequency (cm^{-1})	Assignment and moment	Transition moment direction (ψ°)	Standard deviation
3096	pyridinium	48	3
2923	CH_2 antisymmetric stretching	\perp chain axis [†]	1
2855	CH_2 symmetric stretching	\perp chain axis [†]	1
1670	H_2O bending?	49	
1635	pyridinium 8a	A_1	5
1585	pyridinium 8b	B_1	6
1502	pyridinium	50	
1489	pyridinium 19b	B_1	1
1467	(CH_2 and CH_3 scissoring deformation) largely \perp chain axis [†]	27	3
1445		32	1
1365	CH_2 wagging deformation	//chain axis [†]	3
1216	pyridinium	34	
1175	pyridinium 18a	A_1	2

[†] Mutually perpendicular

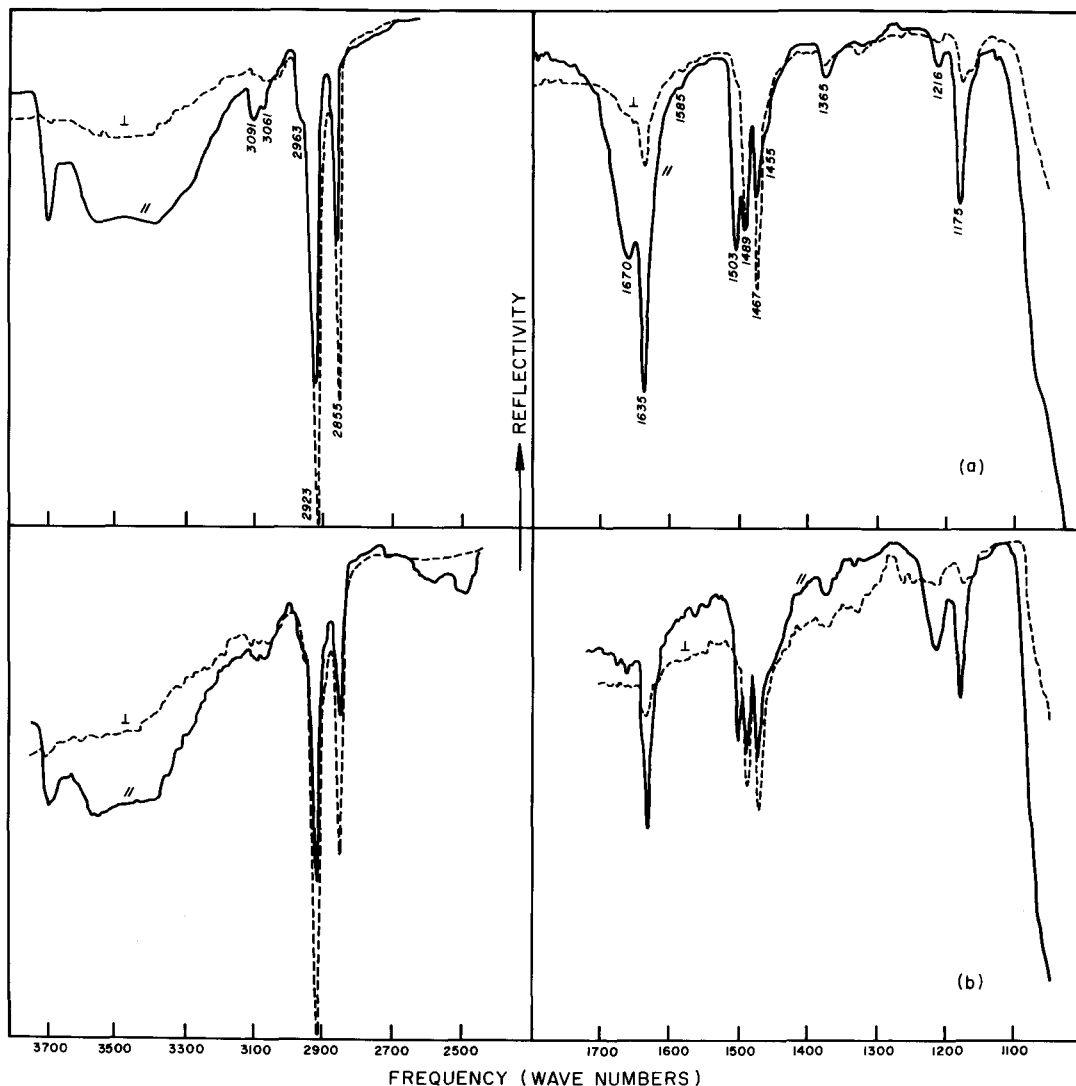


Fig. 5. Polarized ATR spectra of the cetylpyridinium vermiculite complex with a KRS-5 hemicylinder and at polarizations of $0^\circ(\perp)$ and $90^\circ(\parallel)$: (a) undecuterated and (b) deuterated at angles of incidence of 50° and 55° respectively.

a subset of reflections when compared with similar photographs of the 40 \AA complex. However for both materials the unweighted a^*b^* reciprocal nets are the same. This suggests a similar packing arrangement of the organic molecules in the two complexes. The configuration proposed in Figure 6 not only provides for contact between the pyridinium sections of the molecules and the silicate surfaces but also allows a maximum possible contact between adjacent aliphatic chains. That such an arrangement leads naturally to an explanation for the superlattice reflections observed in the diffraction patterns for the complexes is seen from the following.

The area occupied by an aliphatic chain, when viewed along its own axis and inclined steeply as in Figure 6, can be inscribed within a rectangle 4.0×4.6

\AA . Figure 7 shows an extended array of such rectangles superimposed upon a similarly scaled drawing of vermiculite unit cells. This figure shows that one cell edge, as measured along the b -axis, is equal to the total van der Waals thickness of two aliphatic chains measured in the plane of their zigzags (9.18 \AA). However along the a -axis, three unit cells are exactly matched by four molecules measured with their van der Waals thicknesses perpendicular to the zigzag plane ($3 \times 5.33 \approx 4 \times 4.0 = 16.0$). These coincidences, which involve eight neighboring aliphatic chains, provide the explanation for why the true crystallographic cell (as deduced from the superlattice phenomena) is actually 3 times " a " in the a -direction and only 1 times " b " in the b -direction.

The chemical data showed the 30 \AA complex to have

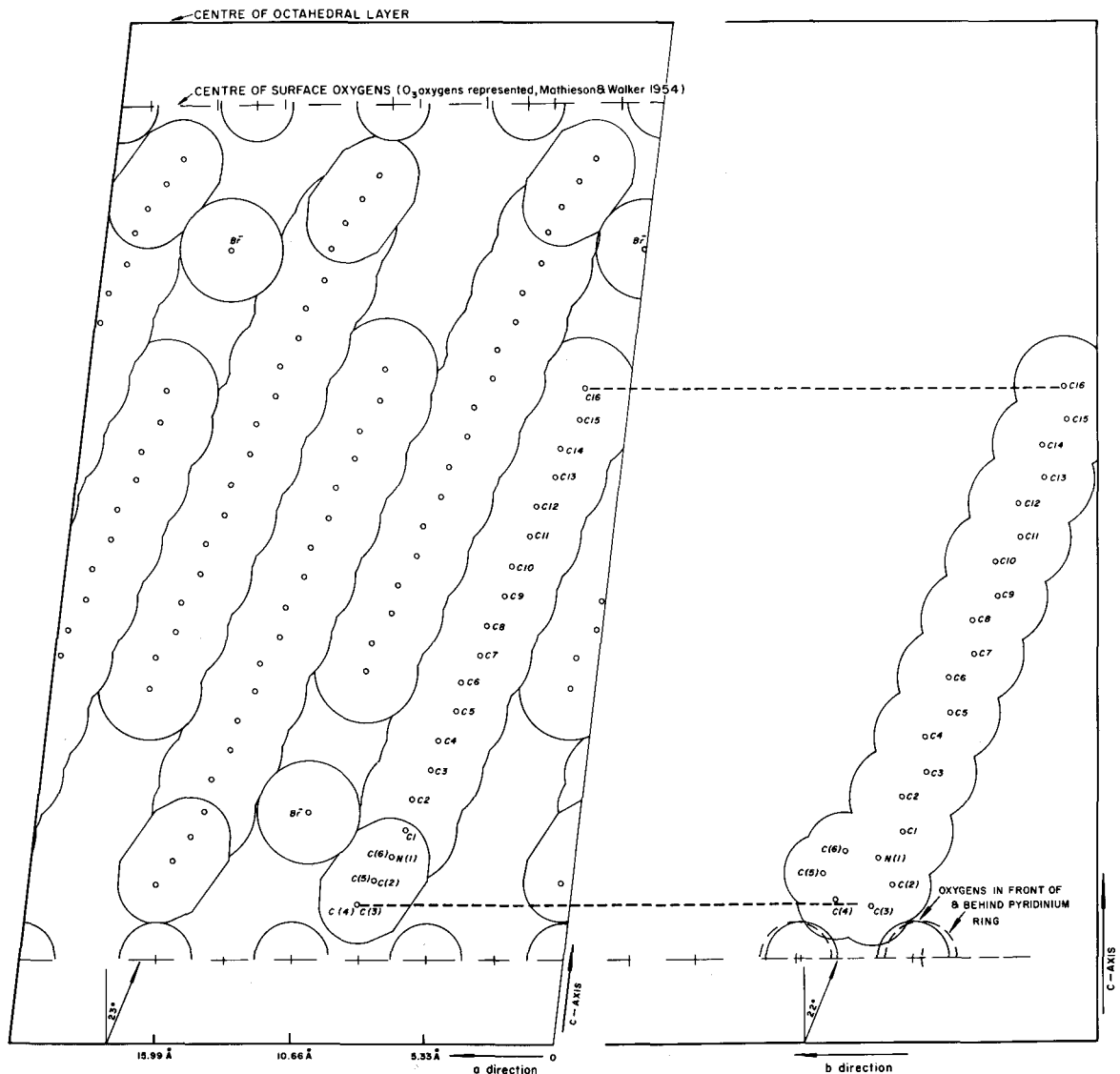


Fig. 6. Projections of the orientation of the cetylpyridinium molecules at the vermiculite surface and in the interlayer region—from i.r. spectroscopy. A cross section perpendicular to the b-direction shows the contents of a unit cell. The orientation of a single molecule perpendicular to the a-direction is also shown.

a lower ratio of bromine to carbon than the 40 Å material. Using our model, this fact explains the observed enhancement in the intensity and clarity of the diffraction patterns as the 40 Å phase is approached. In the final stages of reaction the basic packing arrangement of the organic molecules is decorated by the incorporation of additional ions (bromine) into specific sites. It is these heavy ions which reinforce the scattering from the existing arrays of organic molecules as reactions go to completion. Concurrently, water molecules are probably lost from the interlayer region.

From Figure 7 the maximum number of organic molecules which can be incorporated into a unit cell is $16/6 = 2\frac{2}{3}$. The chemical data in Table 1 shows that this

number is only achieved for the CPB complex of the highly charged Llano vermiculite. Although the degree of surface cover is less than complete for lower charged vermiculites the ideal packing must also occur over considerable areas of their surfaces in order to produce the observed superlattice reflections.

The charge probably influences the extent of the cover in the following way. Initially the charges upon the silicate surfaces are satisfied by organic cations entering the interlayer spaces to prop the structure open. Each charged molecule then endeavors to surround itself with eight organic moieties held by van der Waals forces (Figure 7). Greenland and Quirk's (1962) observation that CPB absorption experiments returned low

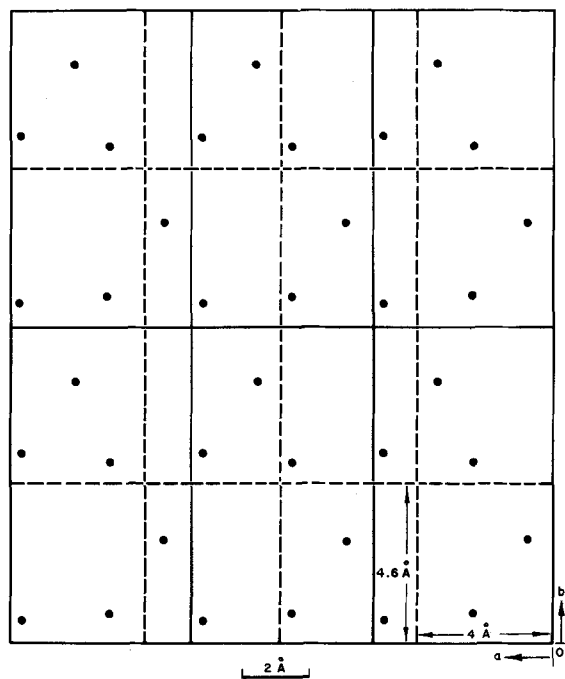


Fig. 7. The network of rectangles (dashed lines) representing the limits to the projections of the van der Waals radii for the aliphatic chains, at the deduced orientation, shown superimposed upon outlines of vermiculite unit cells (solid lines).

surface areas for low charged materials could therefore be expected.

Figure 1 shows that montmorillonite and moderately charged vermiculite have similar adsorption curves. The sorption behavior of the two materials differs because of variations in relative coverage and extent of external surfaces and the degree to which inorganic cations are replaced by CP-ions. The external surfaces of montmorillonite possibly absorb CPB as micelles which would inflate the adsorption values in concentrated CPB solutions (Malik et al. 1972). Our model does not invalidate the CP-CPB adsorption technique for the determination of the internal surface areas of soil clays but as a result of this model and of previous studies, the following cautionary remarks are made.

(1) The CPB method should, if suitably calibrated, hold for materials whose surface density of charge does not deviate markedly from that of the calibrating material. The surface density of charge of most common clay minerals of soil origin does not vary greatly from an average value of between 0.23 and 0.28 m-equiv. per 100 m² (Fripiat, 1964; Farrar and Coleman, 1967) and therefore further work should be based on a standard or range of standards having charge densities close to these values.

(2) The d-spacing of the sorption complex formed by the unknown should be equal to that of the calibrating material.

(3) In order to favor complete exchange, unknowns should be saturated with a cation such as lithium, as should be the standard.

After all this, the effective internal surface area occupied per adsorbed organic moiety may be larger than the minimum possible value of 18.4 Å² reported here.

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Резюме- Рентгеновские сверхрешетчатые отражения, инфракрасная спектроскопия и химические анализы показали, что цетилпиридиновый бромид /ЦПБ/ в высшей степени упорядочен, когда адсорбирован вермикулитом. Молекулы, которые расположены под углом около 57° к поверхности силиката, образуют тесно упакованные системы. Покрытие всей поверхности достигается только для вермикулитов с наиболее высокими зарядами. Наблюдалась упаковка в пределах систем, обусловленная свехрешеткой, и было установлено, что каждая адсорбированная молекула имеет на поверхности площадь $18,4 \text{ \AA}^2$. Обсуждаются возможности использования этих выводов для изучения поверхности почвы методом ЦПБ.

Kurzreferat- Röntgenüberstrukturreflectionen, Infrarotspektroskopie und chemische Analyse haben bewiesen, daß Cetylpyridiniumbromid (CPB) in hohem Grade geordnet ist, wenn es an Kieselgur adsorbiert ist. Die Moleküle, welche sich in einem etwa 57° Winkel zu der Silikatoberfläche befinden, formen kompakte Anordnungen. Nur die am höchst geladenen Kieselgure bedecken die ganze Oberfläche des Silikates. Das Aufsichten innerhalb der Anordnungen erklärt die Überstruktur, welche gesehen wurde. Jedes Molekül maß $18,4 \text{ \AA}^2$ an der Oberfläche. Die Bedeutung dieser Befunde für die CPB-Methode, welche in Untersuchungen von Erdoberflächen benutzt wird, ist diskutiert.