

INFRARED ABSORPTION AND X-RAY DIFFRACTION STUDY OF BUTYLAMMONIUM COMPLEXES OF PHYLLOSILICATES

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Abstract—I.R. absorption and X-ray diffraction data on butylammonium complexes of vermiculites show, when compared with the Wyoming montmorillonite complex, that the tetrahedral location of charge determines the keying of the $-\text{NH}_3^+$ groups into the ditrigonal cavities and that these groups have their C_3 axes perpendicular to the layers. The aliphatic chains adopt different conformations depending on the area available per exchange position; they will either: (a) adopt an 'all-trans' conformation with their axes inclined 55° to the silicate planes, when the area available is small; (b) rotate 120° around the C_1-C_2 bond to adopt a flat disposition relative to the layers, when the area available is larger than the area covered by the organic ion.

INTRODUCTION

Since the early work of Jordan (1949), considerable attention has been given to the study of *n*-alkylammonium complexes of montmorillonite and vermiculite (Weiss *et al.*, 1956, 1957; Walker, 1960; Garrett and Walker, 1962). The existing work was summarized by Weiss (1963), and one finds inconsistencies in experimental data concerning the (001) periodicities of the complexes obtained by the different authors.

More recently Johns and Sen Gupta (1967) and Serratosa *et al.* (1970) have added evidence, by X-ray diffraction and by i.r. absorption techniques, concerning the disposition of the organic cations in the interlayer space of the silicate structure. Since then it has been generally accepted that in complexes with vermiculite, where the surface charge density is high and tetrahedrally located, the organic cations are adsorbed in such a way that the terminal $-\text{NH}_3^+$ groups are deeply keyed into the cavities formed by the oxygen atoms of the tetrahedral sheets, and that the aliphatic chains are inclined to the silicate layer at angles of around 55° .

Complexes with long alkylammonium ions frequently give (001) periodicities which are shorter by $\approx 2\text{Å}$ than expected. Conformational changes in the alkyl chains, departing from the 'all-trans' conformation, could explain the observed data (Walker, 1967; MacEwan, 1967; Weiss, 1969).

Based on calculations by Hagele and Pechhold (1970), Lagaly and Weiss (1973) proposed that rotations of alkylammonium chains around $C-C$ bonds are possible, as relatively low energy barriers have to be overcome and that formation of 'kinks'

may be the cause of the apparent shortening of the length of the adsorbed molecules. The 'kink' concept appears to be particularly relevant for bilayer complexes of long alkylammonium ions with vermiculite.

In support of their argument, evidence is presented in this paper confirming the existence of such conformational changes via rotation around $C-C$ bonds, even in monolayer complexes of short alkylammonium chains.

EXPERIMENTAL

Butylammonium complexes were prepared with Wyoming montmorillonite (unit cell charge 0.66), vermiculite from Beni-Buxera (unit cell charge 1.44) and Llano vermiculite (unit cell charge 1.90) by treating Na-saturated samples with 1 N butylammonium chloride at 60°C , followed by repeated washing with alcohol-water mixtures to eliminate butylammonium chloride in excess over the exchange capacity.

Single crystals of the vermiculite complexes were used for X-ray diffraction examination. Self supporting oriented films were prepared to obtain the X-ray diffraction data on the montmorillonite complex, and for recording the i.r. spectra of the three complexes.

RESULTS AND DISCUSSION

Figure 1 gives the i.r. spectra of the three complexes in the region of $-\text{OH}$ stretching and $-\text{NH}_3^+$ deformation vibrations. The spectra show differences in the position and dichroic properties of corresponding bands.

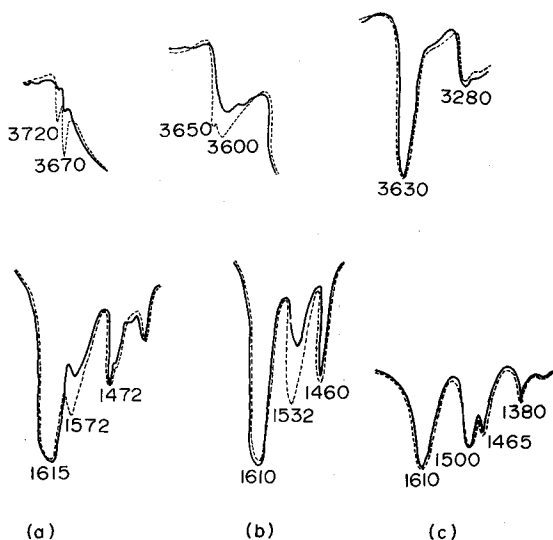


Fig. 1. IR spectra in the regions of OH stretching and NH_3 deformation vibrations of butylammonium complexes with: (a) Llano vermiculite; (b) vermiculite from Beni-Buxera; and (c) Wyoming montmorillonite. — 0° Incidence, ---- 40° incidence.

In the complex with montmorillonite, where the charge density is low and predominantly octahedral, the symmetric deformation vibration of the $-\text{NH}_3^+$ groups appears at 1500 cm^{-1} and is not dichroic, indicating weak *H*-bonding and a direction of the C_3 axis of the $-\text{NH}_3^+$ that is essentially parallel to the layers. The X-ray basal spacing is 13.5 \AA . Both results are consistent with a structure in which butylammonium chains with an 'all-trans' conformation lie parallel to the layers of montmorillonite.

In the complex with Llano vermiculite, the band is dichroic and has shifted to 1572 cm^{-1} , indicating that the C_3 axis is normal to the layers and that there is *H*-bonding of the $-\text{NH}_3^+$ to the surface oxygens. At the same time, two dichroic bands appear in the $-\text{OH}$ stretching region, one at 3670 cm^{-1} corresponding to unperturbed structural $-\text{OH}$ with a 3 Mg^{2+} environment and another at 3720 cm^{-1} corresponding to structural $-\text{OH}$ strongly perturbed by the presence of $-\text{NH}_3^+$ groups sitting closely above them. The basal spacing is 14.7 \AA and the i.r. and X-ray data agree with the structure found by Johns and Sen Gupta (1967) in which the organic molecules are in 'all-trans' conformation, with the aliphatic chains standing at an angle of 55° to the *a*-*b* plane and with the $-\text{NH}_3^+$ groups keyed into the ditrigonal cavities of the silicate (nitrogen atom at 4.65 \AA from the octahedral Mg plane). The high surface charge density and the tetrahedral location of the charge in Llano vermiculite both determine the structure of the complex.

A different situation occurs in the case of the complex with vermiculite from Beni-Buxera. There, the X-ray basal spacing is 13.2 \AA , which must be interpreted as indicative of a disposition of the organic molecules parallel to the silicate layers. In that vermiculite an area of 35 \AA^2 is available per exchange position, which is higher than the 28 \AA^2 available in the Llano vermiculite, and allows a flat disposition of the molecules as in the montmorillonite complex. However, Fig. 1 shows that the symmetric deformation band of the $-\text{NH}_3^+$ groups is dichroic and its location is at 1532 cm^{-1} . As in the Llano vermiculite complex, the axis of the $-\text{NH}_3^+$ group must be perpendicular to the layers, with the group associated to the surface oxygens by *H*-bonding. Similarly, two bands appear in the $-\text{OH}$ stretching region at 3600 and 3650 cm^{-1} indicating the presence of perturbed $-\text{OH}$ groups.

The above results may be explained if it is assumed that, on account of the tetrahedral location of charge in the vermiculite, the terminal $-\text{NH}_3^+$ groups are keyed into the ditrigonal cavities, so that the direction of the *N*-*C* bond in the butylammonium molecules is perpendicular to the layers, but that the rest of the molecule has rotated 120° around the C_1 - C_2 bond to adopt a flat disposition. With such conformation the

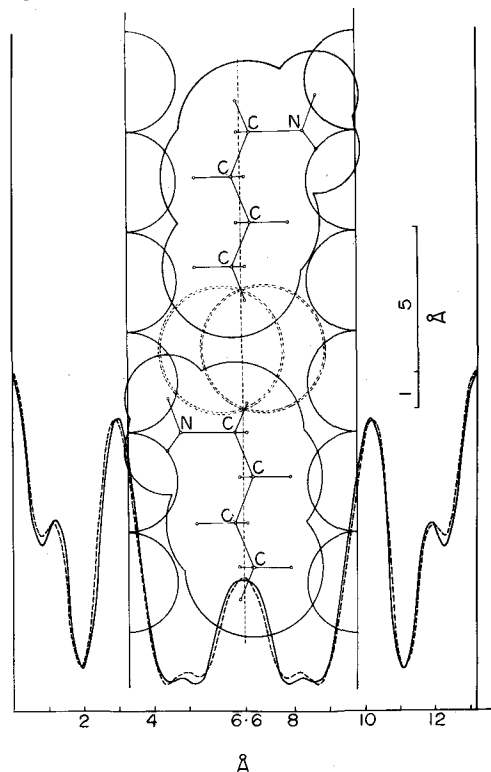


Fig. 2. Monodimensional electron density profiles for butylammonium complex with vermiculite from Beni-Buxera. — From F_{obs} , ---- from F_{cal} .

Table 1. Observed and calculated structure factors for the butylammonium complex with vermiculite from Beni-Buxera*
 $(\text{Si}_{2.75}\text{Al}_{1.23}\text{Fe}_{0.02})(\text{Fe}_{0.46}\text{Ti}_{0.06}\text{Mg}_{2.48})\text{O}_{10}(\text{OH})_2 \times 0.72$
 $\text{CH}_3-(\text{CH}_2)_3-\text{NH}_3^+ \times 1\text{H}_2\text{O}$

001	F_{obs}	F_{cal}	F_{cal} (silicate)
1	118.41	121.89	193.90
2	0.00	3.34	-47.89
3	19.65	-16.33	14.89
4	143.12	150.03	131.17
5	41.51	47.92	61.63
6	37.25	-33.07	-44.92
7	41.34	-44.47	-34.96
8	27.82	27.23	21.57
9	52.16	58.76	40.66
10	30.59	31.01	31.80
11	25.24	23.75	21.92

F_{obs} corrected for absorption. F_{cal} with $B = 6.22\text{\AA}^2$, $R = 0.085$.

F_{cal} (silicate) with coordinates of atoms of silicate alone, $R_s = 0.347$.

* Mineral formula from Luzon Cuesta (1968).

molecule will occupy an area of 30\AA^2 , just smaller than the area available.

Figure 2 and Table 1 show the result of the one dimensional Fourier analysis of the complex. The nitrogen atom has been located at 4.85\AA from the octahedral Mg plane. The carbon atoms are in two planes, at 6.34\AA and at 6.86\AA , with the plane of the zig-zag chain making an angle of 60° to the layers. Hydrogen atoms are located at 5.27 and 6.50\AA . Based on the area under $\rho(z)$, one water molecule per half unit cell at $z = 6.00\text{\AA}$ has been included in the structure. Electron density profiles obtained with F_{obs} (11 rational orders observed) and with values of F_{calc} based on the above model are almost identical.

An isotropic temperature coefficient, B , of 6.22\AA^2 was obtained by the method of Wilson (1942). This value seems rather high for a layer silicate. Corresponding values for Mg-vermiculite and for the complexes of Llano vermiculite are 1.2\AA^2 (Mathieson and Walker, 1954) and 3.75\AA^2 (Johns and Sen Gupta, 1967). Calculation of the root mean square vibrational amplitude gives 0.12\AA for Mg-vermiculite, 0.22\AA for the Llano complex, and 0.28\AA for the Beni-Buxera complex. If real, these amplitudes would indicate considerably more vibration, which could suggest poorer bonding between layers. Because the Beni-Buxera complex can have no interlocking of the organic chains (as with Llano), then perhaps the complex is more poorly held together. If so, such a high value for B might be expected.

The position of the N atom found by Johns and Sen Gupta (1967) for the Llano complex is at 4.65\AA . In the present complex, steric hindrance due to the disposition of the aliphatic chains prevents the $-\text{NH}_3^+$ from keying deeper into the cavities. This fact agrees well

with the smaller shift observed for the $-\text{NH}_3^+$ symmetric deformation band (located at 1532cm^{-1} in the Beni-Buxera complex and at 1570cm^{-1} in the Llano complex).

The interlayer water contained in air-dried samples is just sufficient to complete surface coverage. Most of it is probably lost under the heat from the i.r. beam (see Fig. 1).

In summary, while the tetrahedral location of the charge determines the keying of the $-\text{NH}_3^+$ groups into the ditrigonal cavities and the disposition of their C_3 axis normal to the layers, the aliphatic chains will either:

(a) Remain in an 'all-trans' conformation with their axes inclined 55° to the silicate planes, when the area available is small; or else

(b) Rotate around the C_1-C_2 bond to adopt a disposition parallel to the surfaces, when the area available is larger than the area covered by the organic ion.

With the second conformation the $d_{(001)}$ spacing of the complex is smaller. It may be reasonably assumed that the variation of van der Waals attractive potential is sufficient to overcome the energy required for the change of conformation of the molecules.

REFERENCES

- Garrett, W. G. and Walker, G. F. (1962) Swelling of some vermiculite complexes in water: *Clays and Clay Minerals* **9**, 557-567.
- Hagele, P. C. and Pechhold, W. (1970) Struktur- und Konformationsberechnungen in Polymeren: *Kolloid Z.Z. Polymere* **241**, 977-984.
- Johns, W. D. and Sen Gupta, P. K. (1967) Vermiculite alkylammonium complexes: *Amer. Mineral.* **52**, 1706-1724.
- Jordan, J. W. (1949) Organophilic bentonites—I. Swelling in organic liquids: *J. Phys. Coll. Chem.* **53**, 294-306.

- Lagaly, G. and Weiss, A. (1973) Conformational changes of long chain molecules in the interlayer space of swelling mica-type layer silicates: *Proc. Int. Clay Conference, Madrid*, 637–649.
- Luzon Cuesta, R. (1968) Estudio del procesode activacion acide de la vermiculita: Doctoral Thesis. *Publ. Facultad de Ciencias de Granada*.
- MacEwan, D. M. C. (1967) Complejos interlaminares de sorcion: *An. Edaf. Agrobiol.* **26**, 1115–1127.
- Mathieson, A. McL. and Walker, G. F. (1954) Crystal structure of Mg-vermiculite: *Amer. Mineral* **39**, 231.
- Serratosa, J. M., Johns, W. D. and Shimoyama, A. (1970) I.R. study of alkylammonium vermiculite complexes: *Clays and Clay Minerals* **18**, 107–113.
- Sutherland, H. H. and MacEwan, D. M. C. (1961) Organic complexes of vermiculite: *Clay Minerals Bull.* **4**, 229–233.
- Walker, G. F. (1960) Macroscopic swelling of vermiculite crystals in water: *Nature* **187**, 312.
- Walker, G. F. (1967) Interactions of *n*-alkylammonium ions with mica-type layer lattices: *Clay Minerals* **7**, 129–143.
- Weiss, A. (1963) Mica-type layer silicates with alkylammonium ions: *Clays and Clay Minerals* **10**, 191–224.
- Weiss, A. (1969) Organic derivatives of clay minerals, zeolites and related minerals. In *Organic Geochemistry*, (Edited by Eglinton and Murphy), pp. 736–781. Springer, Berlin.
- Weiss, A., Mehler, A. and Hoffmann, U. (1956) Zu Kenntniss von Organophilenn Vermikulit: *Z. Naturforschung* **11b**, 431–434.
- Weiss, A., Michel, E. and Weiss, A. (1957) Über den Einfluss von Wasserstoffbruecken-bindungen auf ein—und zwei-dimensionale Innerkristalline Quellungs Vorgaerge: In *Hydrogen Bonding*, pp. 495–508. Pergamon Press, Oxford.
- Wilson, A. J. C. (1942) Determination of absolute from relative X-ray intensity data: *Nature* **150**, 152.

Résumé—Les résultats de la spectrométrie infrarouge et de la diffraction X montrent dans le cas des complexes butylammonium-vermiculite comparé au cas du complexe avec la montmorillonite du Wyoming, que la localisation tétraédrique de la charge détermine la fixation des groupes NH_3^+ dans les cavités ditrigonales et que ces groupes ont leur axe C_3 perpendiculaire au feuillet. Les chaînes aliphatiques adoptent différentes conformations qui dépendent de la surface disponible par position d'échange; elles pourront soit (a) adopter une conformation 'entièrement *trans*' avec leurs axes inclinés à 55° par rapport au feuillet lorsque la surface disponible est petite, soit (b) tourner de 120° autour de la liaison $\text{C}_1\text{—C}_2$ pour se mettre à plat par rapport au feuillet, lorsque la surface disponible est plus grande que la surface occupée par l'ion organique.

Kurzreferat—Die Ergebnisse von Infrarotabsorptions- und Röntgenbeugungsuntersuchungen an Butylammoniumkomplexen von Vermiculiten zeigen bei einem Vergleich mit Wyoming Montmorillonitkomplexen, daß die Anordnung der Ladungen in den Tetraedern das Einpassen der —NH_3^+ -Gruppen in die ditrigonalen Hohlräume bestimmt, und daß diese Gruppen ihre C_3 -Achsen senkrecht zu den Silicatschichten stellen. Die aliphatischen Ketten nehmen in Abhängigkeit von der für eine Austauschposition verfügbaren Oberfläche unterschiedliche Zuordnungen an. Sie bilden entweder (a) eine 'all-*trans*'-Zuordnung mit um 55° zu den Silicatoberflächen geneigten Achsen bei geringer verfügbarer Oberfläche oder (b) rotieren um 120° um die $\text{C}_1\text{—C}_2$ -Bindung, um eine flache Anordnung zu den Schichten einzunehmen, wenn die verfügbare Fläche größer als die durch das organische Ion eingenommene Fläche ist.

Резюме — Данные инфракрасных спектров поглощения и рентгенографических исследований бутиламмониевых комплексов вермикулита показывают, при сравнении с комплексом монтмориллонита Вйоминг, что тетраэдральное местнахождение заряда определяет манипулирование групп —NH_3^+ в дитригональные трещины, и что оси C_3 этих групп лежат перпендикулярно к слоям. Алифатические цепи принимают различные конформации в зависимости от имеющейся при обмене площади: они либо а) если имеющаяся площадь небольшая примут конформацию «all-*trans*» с осями наклоненными на 55° по направлению к плоскостям силикатов, либо б) повернутся 120° вокруг связи $\text{C}_1\text{—C}_2$, чтобы принять плоское положение по отношению к слоям, если имеющаяся площадь больше, чем площадь занимаемая органическим ионом.