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ELEMENTARY LAYERS IN THE INTERSTRATIFIED CLAY MINERALS AS REVEALED BY ELECTRON MICROSCOPY

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Abstract—Interstratified layer structures were studied by electron microscopy and electron diffraction. In order to distinguish between expansible and non-expansible layers, interstratified mica-smectite was treated with laurylamine hydrochloride solution. Electron micrographs of the layers at the curled edges of the crystals show expanded basal spacings of 24 Å and unexpanded spacings of 10 Å. It was observed that adjacent pairs of expanded and unexpanded layers in the micrographs form non-expansible units. Arrangement of the expanded and unexpanded layers shows that the layers expanded by sorption of laurylammonium ions have expansible and non-expansible surface characteristics on opposite sides of the layer. The relationships between the ratio of component layers and basal spacings in two component systems are discussed.

INTRODUCTION

LAYER expansion of clay minerals, caused by interlayer sorption of molecules or ions, is greatly affected by the nature of the interlayer cations which balance the charge resulting from lattice substitution. If the substitution is in the octahedral sheet, these interlayer cations are exchangeable for other cations by treatment with an aqueous solution of the replacing cation. Since octahedral replacements usually occur less frequently than one per average unit cell, these clays can be expanded by chemical treatment. However, if the substitution is in the tetrahedral sheet, the charge-balancing cations may or may not be easily exchangeable for other cations, dependent on the magnitude of the surface charge density resulting from the substitution. The expansibility is similarly dependent on charge density. A typical example of the expansible clays is montmorillonite with a 2/3 replacement of Al^{3+} by Mg^{2+} per average unit cell; a non-expansible example is mica with 2 replacements of Si^{4+} by Al^{3+} per average unit cell. The basal spacing of mica remains at 10 Å independent of chemical treatment.

In interstratified minerals, such as mica–smectite, it is obvious that expansible pairs will expand by chemical treatment and non-expansible pairs will not. However, the behavior of a pair consisting of an expansible and a non-expansible layer is questionable. The structural model very often used to analyze X-ray diffraction by interstratified structures is a mixture of a unit which remains at 10 Å independent of treatment, and another unit of variable spacing which varies according to the treatment (Brown, 1961; Sato, 1969). In general, however, clay crystals are colloidal in dimension. For such materials, a combination of transmission electron microscopy and electron diffraction is very useful for studying the structure. These methods have been applied to the study of organo-montmorillonites (Suito, Arakawa and Yoshida, 1969). Electron micrographs of the layers of some organo–montmorillonites showed regular and irregular layer expansion caused by the interlayer sorption of the organic compounds. Some micrographs exhibited local variations of layer expansion even within one particular layer. Layer expansion was interpreted on the basis of arrangement of sorbed interlayer molecules and ions. Local variation of the layer expansion caused by ion exchange sorption of *n*-alkyl–ammonium ions was interpreted as due to local differences in the charge density between the layers (Yoshida and Suito, 1972).

In this paper, the expansibility of layers and the nature of the surfaces of pairs of adjacent layers in a crystal, composed of both expansible and non-expansible layers, will be discussed on the basis of the layer arrangement as observed by the transmission electron microscope. To distinguish between expansible and non-expansible layers, the sample was treated with a *n*-alkylamine hydrochloride solution. Since the interlayer arrangements of the alkyl chains mainly depends on the layer charge, and since the interlayer distances are related to definite configurations of the interlayer molecules or ions (Lagaly and Weiss, 1969), it should be possible to examine the characteristics of the surfaces of layers from analysis of the expansion caused by interlayer sorption of alkyl–ammonium ions.

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EXPERIMENTAL

The organo–clay complex was prepared as follows. The clay powder (No. 1 interstratified mica–smectite, supplied by the editorial subcommittee for *The Clays of Japan*, 1969) was suspended in 0·1 N laurylamine hydrochloride solution and allowed to stand, with frequent stirring, for 24 hr at about 65°C. Then the suspension was cooled to room temperature and allowed to stand for 1 month with occasional stirring. The precipitate was filtered and washed with a solution of alcohol and water. The precipitate was again suspended in 0·1N laurylamine hydrochloride and allowed to stand for 1 week with occasional stirring. The precipitate was filtered and placed into a solution of alcohol and water. After 1 day, the alcohol–water solution was replaced with a fresh one by decantation. This procedure was repeated until no sedimentation took place. The precipitate then was dried at 65°C (Lagaly and Weiss, 1969).

The specimens for electron microscopy were prepared as follows: the organo–clay powder was dispersed in water by 5 min of exposure to ultrasonic vibration, and a small drop of this suspension was dried on a specimen grid covered with an evaporated carbon film. A specimen of raw sample was prepared similarly for examination.

Electron micrographs and diffraction patterns were obtained at 100 kV with a JEM 7A instrument.

RESULTS

An electron micrograph (a) and selected area diffraction pattern of the organo–clay crystal (b) are shown in Fig. 1. Hexagonal symmetry of the sports in the diffraction pattern shows oriented stacking of several layers in the crystal, and the weak rings joining the spots show that some of the stacking layers are disoriented with respect to one another by rotation around an axis perpendicular to (001). On the innermost ring, the index of the main spot being parallel to the edge of crystal is (02) or (11). Electron micrographs of the layers observed at the curled edge marked A and B in Fig. 1a are shown in Fig. 2. The distances between adjacent lines in the images were measured as 10 and 24 Å. In Fig. 2b, dislocations are visible in the region marked by the arrows. Since the layers are parallel to the edge of crystal, and since the diffraction pattern given in Fig. 1 shows that the edge is parallel to b^* or [11], the direction of curling of the crystal is perpendicular to the b^* or [11]. Such curling of a crystal has been observed in an organo-montmorillonite (Suito and Yoshida, 1971). The electron micrograph shown in Fig. 3 is taken from the region marked *C* in Fig. 1.

Figure 4 is an electron micrograph in which unexpanded layers are the main component.

The electron micrograph shown in Fig. 5 was taken from the raw sample. Distance between lines was measured as 10 Å, a result which indicates either that the interlayer water was desorbed because of the high vacuum in the electron microscope, or that the observed region was originally composed of non-expansible layers.

DISCUSSION

Layer expansion caused by interlayer sorption of lauryl–ammonium ions

Since the *c*-spacing of both micas and untreated smectites under high vacuum in an electron micro-

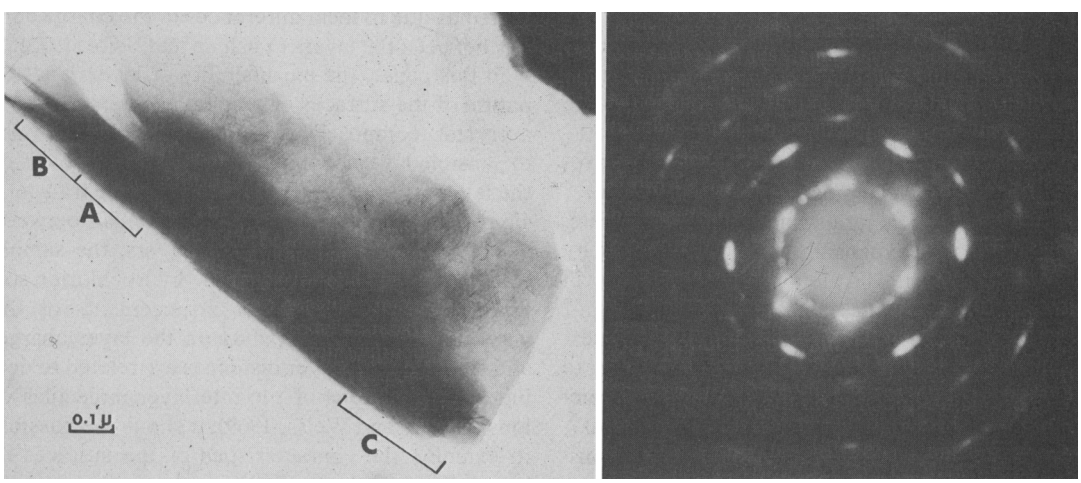


Fig. 1. Electron migrograph of an interstratified organo–clay crystal and its selected area electron diffraction pattern.

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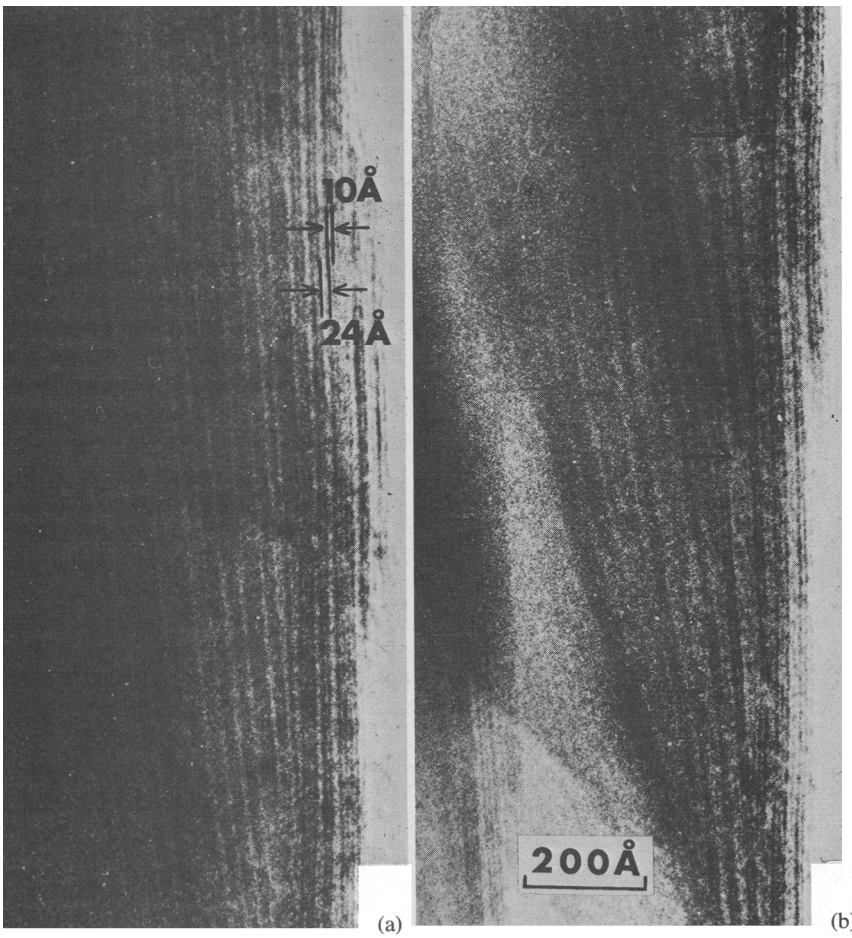


Fig. 2. Electron micrographs of the layers observed at the curled edge of the crystal shown in Fig. 1. a and b were taken from the region marked *A* and *B* respectively. Line distances in the images were measured as 24 and 10 Å. Dislocations are visible in the region marked by arrows in b.

scope is about 10 Å, an interlamellar spacing of 10 Å in the micrograph implies that no sorption of organic material took place between these layers. The expanded layers at 24 Å, a distance which represent an increase of about 14 Å over this 10 Å value, result from interlamellar sorption of alkylammonium ions.

As to the structure of the expanded interlayer space, the following may be deduced. The unit cell surface area is $5{\cdot}21 \times 9{\cdot}12 = 47{\cdot}8$ Å^2 on each side. Since the layer charge of normal montmorillonite is 0·33 per half-unit cell, the area available to each univalent cation in a monolayer between the two silicate layers is $47{\cdot}8/0{\cdot}33 \times 2 \fallingdotseq 70$ Å^2. For normal vermiculite with a layer charge of 0·67 per half-unit cell, this equivalent area is 37 Å^2. Biotite has the highest layer charge, 1 per half-unit cell, which corresponds to an equivalent area of 24 Å^2. If the laurylammonium ions are arranged in double layers parallel to the silicate sheets, the area occupied by each laurylammonium ion is just 70 Å^2 (Lagaly and Weiss, 1969). In this configuration, the basal spacing must be about 18 Å.

However, if the alkyl chains are in a paraffin-type arrangement perpendicular to the silicate layer, the area occupied by a laurylammonium ion is 20 Å^2 (cross-section of the alkyl chain) on each side. Since the length of the alkyl chain is 17 Å in this configuration (Lagaly and Weiss, 1969), the basal spacing must be about 27 Å. Therefore, a layer dimension of 24 Å suggests that the layer charge balanced by the organic ions is close to that of vermiculite, and that the sorbed alkylammonium ions are arranged in paraffin-type arrays, making some angle between the chain axis and the silicate layers.

If the ion exchange has occurred at one side only

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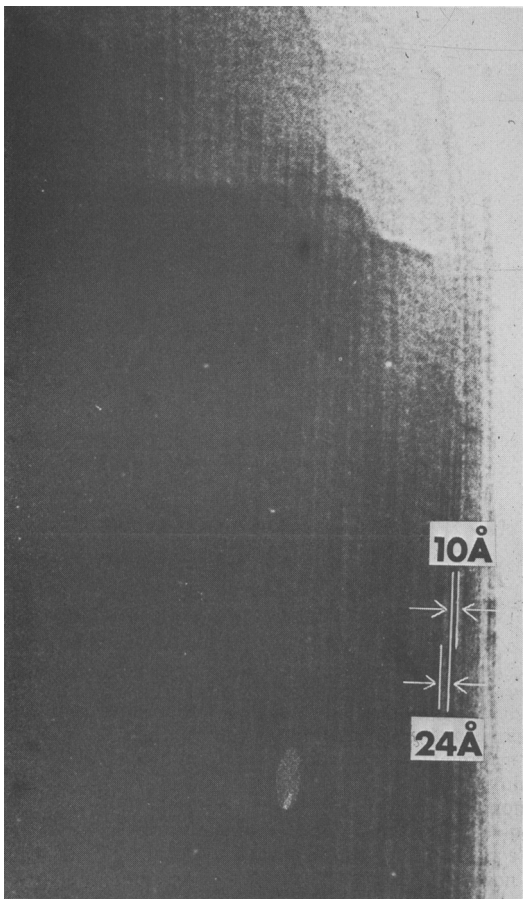


Fig. 3. Electron micrograph of the layers observed at the region marked *C* in Fig. 1.

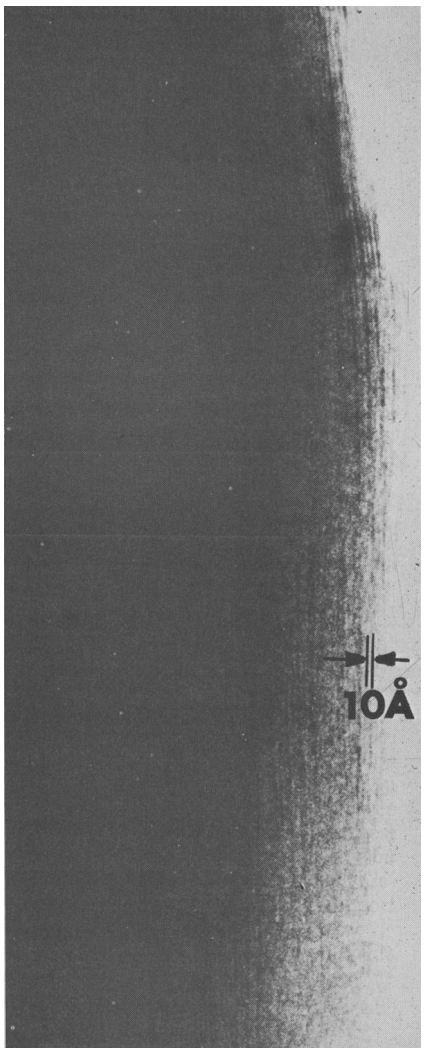


Fig. 4. An example of electron micrograph of layers showing the layer structure in which unexpanded layers are a major component.

of the internal surface of adjacent layers, the layer charge of expanded layers with a 24 Å dimension is close to 1·34 (0·67×2) per half-unit cell. This value is too high. Therefore it is reasonable to consider that the ion exchange of organic ions occurred equally on each internal surface of adjacent layers.

Layer structure and surface characteristics of the component layers

It is clear that pairs of expansible layers will be expanded by water and organic ions, and that pairs of non-expansible layers will not. However, the behavior of the mixed pairs of expansible and non-expansible layers is questionable. If such pairs are expanded by water, they should also be expanded by organic ions, since the sample is treated with a water solution. Interlayer configurations of the sorbed organic ions depend on the surface characteristics of the layers; the layers expand according to the types of configurations (Weiss, 1963).

First, let us discuss the interstratified layer structure of an organo–montmorillonite. Figure 6 shows an electron micrograph of the expanded layers of mixed trimethyloctadecylammonium-stearamide–montmorillonite. Distances between lines on the image are measured as 19, 26 and 40 Å (Yoshida and Suito, 1972). The lines are regularly arranged, but the 26 Å line is bent at the point marked by an arrow. The micrograph is represented schematically in Fig. 7. It is clear that the characteristics of both surfaces of this particular layer labeled *X* were changed at the region of the bend point. The layers designated *C* formed 40 Å spacings at both

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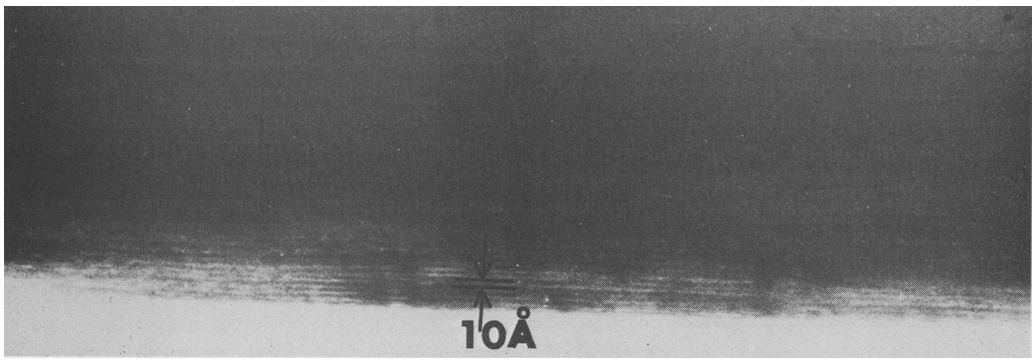


Fig. 5. Electron micrograph taken from the raw sample showing unexpanded layer structure ($d = 10$ Å).

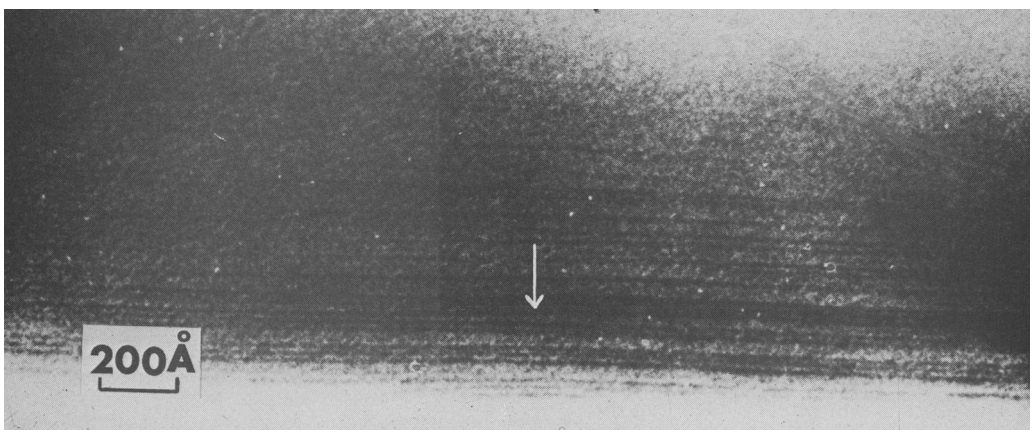


Fig. 6. Electron micrograph showing interstratified structure with the 19, 26 and 40 Å spacings observed at the curled edge of mixed trimethyloctadecylammonium/stearamide–montmorillonite (Yoshida and Suito, 1972). The line forming a 26 Å spacing is deflected at the point shown by an arrow.

sides of the *A* layer, and these spacings had the same characteristics on each surface. Similarly, the layers labeled *B* which formed 19 Å spacings on both sides of the *A* layer have the same characteristics on each surface, but the characteristics of the *B* layers differ from those of the *C* layers. The spacings of 40 and 19 Å on opposite sides of the *A* layers (i.e. *C*–*A* and *B*–*A*) show that the characteristics of each surface differ. One of the characteristics is probably identical with that of the *C* layer, the other one probably identical with that of the *B* layers.

Tuning to the interstratified layer structure, the most important problem is the behavior of pairs of adjacent expanded and unexpanded layers, Figure 2 clearly shows unexpanded pairs of expanded and unexpanded layers. Figure 8 is a schematic representation of part of the layer arrangement observed in the micrograph shown in Fig. 3. In arrangement (1), there are two kinds of the layers. One of the layers labeled *A*, is drawn with thin and thick lines, and another layer designated *B*, is drawn with two thin lines. Thick lines represent internal surface covered by organic ions, and thin lines show the internal surface of the unexpanded uncoated layers. Since one side of the expanded layers is in contact with an organic layer and another side of the layer is in contact with a plain silicate layer, it is clear that both internal surfaces of all of the expanded layers differ in characteristics on each side of the layer. If the expansible layers have the same surface characteristics on each side of the layer, as shown by thick lines in arrangement (11), the expansibility of adjacent expansible and non-expansible layers becomes very important (Hower, 1967). Since the pairs *CB* and

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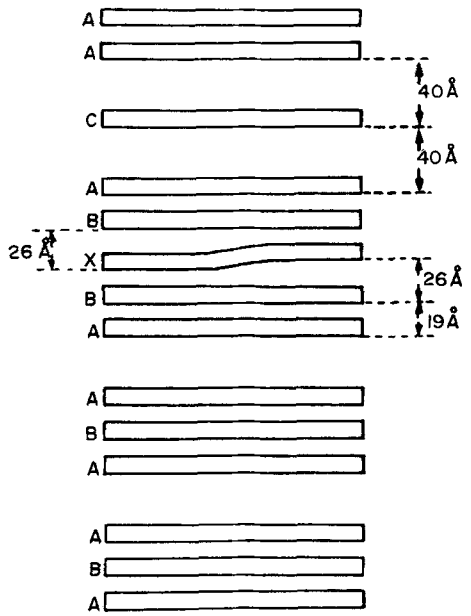


Fig. 7. Schematic representation of the electron micrograph shown in Fig. 6.

BC are in the same situation, the expansion of the *C* layers must show the same interlayer distances on each side of the layers. If the pairs *CB* and *BC* are non-expansible, then the expanded pairs are the *CC* pairs, and it is impossible to arrange the layers in the form shown in Fig. 8 without any discrepancy. Therefore, it can be concluded that the layer structure is composed of unexpanded *B* layers and expanded *A* layers. It is interesting that there are no layers the surface of which carries the expansible characteristic and faces a surface carrying the non-expansible characteristic (i.e. contiguous dissimilar surface). If there are such layers in the layer structure, the structure must be composed of three different spacings, and this situation is not observed.

Next, let us discuss the relationship between the ratio of the component layers and the basal spacings in the two component system. Although the characteristics of the surfaces of many real layers may be more complicated, it can be assumed that the layers are similar to those labeled *A*, *B* and *C*. Namely, *A* layers have expansible and non-expansible surface characteristics on opposite sides of the layer. *B* layers have non-expansible surface characteristics on both sides of the layer. *C* layers have expansible surface characteristics on both sides of the layer. Discussion will be limited to a system composed of only two basal spacings.

1. The system composed of the layers *A* and *B* is a mixture of the units AB^iA, where i shows the number of *B* layers sandwiched between *A* layers. Let d_1 be the unexpanded layer distance, and d_2 the expanded layer distance.

nd_1 = number of occurrences of d_1 in the crystallites
= $NA/2+NB$, where NA and NB are the number of layers of types *A* and *B* respectively.
nd_2 = number of occurrences of d_2 in the crystallites
= $NA/2$
$nd_1/nd_2 = 1+2\,(NB)/NA$.

In the case of the crystal shown in Fig. 1, for a portion of the crystal the micrograph shown in Fig.

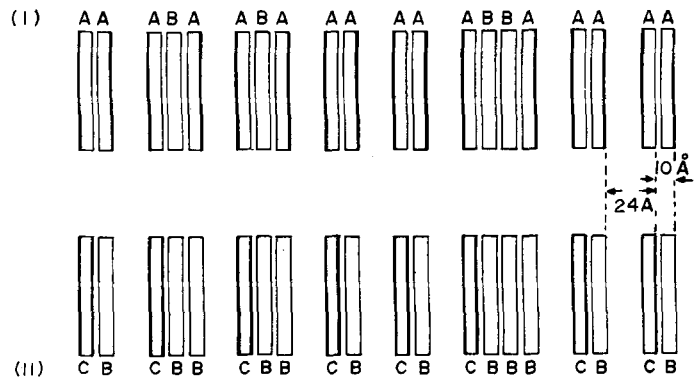


Fig. 8. Schematic representation of the layer structure shown in Fig. 3. In the layer arrangement (I), the internal surfaces on which the organic ions are sorbed are shown by thick lines. The layers labeled A have different surface characteristics on each side of the layer. If the expanded layers have same surface characteristics on each side of the layer, as shown by *C* in layer arrangement (II), the pairs *CB* must be expanded, since the pairs *CB* and *BC* are in the same situation.

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3 gives $nd_1/nd_2 = 34/24$ and $NB/NA = 10/48$.

If the system exists under the conditions $NB > NA$, and PAA = probability of an AA pair = 0, the system is a mixture of the units BAB, and a different relationship is obtained:

$$nd_1/nd_2 = NB/NA.$$

This relationship implies that nd_1 and nd_2 are equal to NB and NA respectively.

2. The system composed of the layers A and C is a mixture of the units AAC^iAA, where i shows the number of C layers sandwiched between AA pairs. Let L be a AA pair, then the expansible pairs are LL, LC and CL.

Since $NL = NA/2$,

$$nd_1/nd_2 = NA/2(NC) + NA.$$

Therefore, $nd_1/nd_2 < 1$.

3. For the system composed of the layers B and C, there are two relationships corresponding to expansion or non-expansion of BC pairs, since the system is assumed to be composed of two different basal spacings.

For the system having expanded $BC(CB)$ pairs, under the following condition:

$$Pcc = \text{probability of a } CC \text{ pair} = 0,$$

let NBB, NBC, NCB and NCC be the number of BB, BC, CB and CC pairs respectively. Then

$$\begin{aligned} nd_1 &= NBB \\ nd_2 &= NBC + NCB \\ N^* &= \text{total number of layers} \\ &= \text{NBB} + \text{NBC} + \text{NCB} \\ nd_1/nd_2 &= NBB/N^* - NBB. \end{aligned}$$

The relationship depends on the probability of a BB pair.

For the system having unexpanded $BC(CB)$ pairs and expanded CC pairs

$$\begin{aligned} nd_1 &= NBB + NBC \\ nd_2 &= NCC \end{aligned}$$

$$nd_1/nd_2 = N^* - NCC/NCC.$$

This relationship depends on the probability of CC pairs.

The layer structure of the organo-montmorillonite given in Fig. 6 is an example of a system composed of the three species of layers differing in expansibility, with the exception of the layer pair forming 26 Å spacing. Perhaps many crystals are not necessarily a simple mixture of the units as discussed above. For example, Fig. 4 shows more complicated layer structure. However, the layer unit having expansible and non-expansible surface characteristics on opposite sides of the layer may be an important elementary layer.

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Résumé—Des structures feuilletées interstratifiées ont été étudiées par microscopie et diffraction électroniques. Afin de faire la distinction entre les feuillets expansibles et non expansibles, un interstratifié micasmectite a été traité par une solution de chlorhydrate de laurylamine. Les micrographies électroniques des feuillets sur les bords enroulés des cristaux montrent des espacements basals ouverts à 24 Å et des espacements fermés à 10 Å. Il a été observé que les paires adjacentes de feuillets gonflés et nonet formés forment des unités non gonflantes. L'arrangement des feuillets gonflés et non gonflés montre que les feuillets gonflés par sorption d'ions laurylammonium ont des caractéristiques superficielles gonflables et non gonflables sur les faces opposées du feuillet. On discute des relations existant entre le rapport des feuillets composants et les espaces basals dans les systèmes à deux composants.

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Kurzreferat – Schichtstrukturen mit Wechsellagerung wurden mit Hilfe des Elektronenmikroskopes und der Elektronenbeugung untersucht. Um zwischen aufgeweiteten und nichtaufgeweiteten Schichten zu unterscheiden, wurden wechselgelagerte Glimmer-Smectite mit Laurylaminhydrochloridlösung behandelt. Elektronenmikroskopische Aufnahmen der Schichten an den gekräuselten Kanten der Kristalle zeigen aufgeweitete Basisebenenabstände von 24 Å und nichtaufgeweitete Abstände von 10 Å. Es wurde beobachtet, daß benachbarte Paare von aufgeweiteten und nichtaufgeweiteten Schichten in den Aufnahmen nichtaufweitbare Einheiten bilden. Die Anordnung der aufgeweiteten und nichtaufgeweiteten Schichten zeigt, daß die durch Sorption von Laurylammonium-Ionen aufgeweiteten Schichten auf den gegenüberliegenden Seiten der Schicht aufweitbare und nichtaufweitbare Oberflächeneigenschaften aufweisen. Die Beziehungen zwischen dem Mengenverhältnis der Schichtkomponenten und den Basisebenenabständen in aus zwei Komponenten bestehenden Systemen werden diskutiert.

Резюме — Электронной микроскопией и дифракцией электронов изучалось впластованное строение слоев. Чтобы отличить вспучившийся слой от невспучившегося переслаивающийся слюдяной смектит обрабатывали раствором хлористоводородного лауриламина. Электронномикроскопические снимки слоев показывают на крючковатых гранях кристаллов разбухшие базальные параметры порядка 24 Å, а неразбухшие — порядка 10 Å. Заметили, что пара смежных разбухших и неразбухших слоев на микроснимках образуют невспучивающиеся агрегаты. Характер укладки вспученного и невспученного слоев показывают, что слои разбухшие вследствие сорбции ионов аммиачного лаурила имеют вспученные и невспученные характеристики поверхностей на противоположных сторонах слоя. Рассматривали соотношение между коэффициентами составных частей слоев и базальными параметрами двух систем.

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