

SEGREGATION AND EXCHANGE PROPERTIES OF ALKYLAMMONIUM IONS IN A SMECTITE AND VERMICULITE*

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Abstract—X-ray diffraction analysis of mixed alkylammonium-exchanged smectite revealed segregation of different ion species into randomly ordered layers. Vermiculite, however, showed segregation into crystallites, a behavior attributed to clay inhomogeneity. Ion segregation is explained by the hydration properties of cations as well as the energy requirements of layer expansion. Quaternary ammonium ions of different size were used to exchange ethylammonium-clays, and the effectiveness, as well as steric hindrance, of cation size in ion exchange was demonstrated. Layer charge density was related to the degree of ease of large cation adsorption. Basal spacing in suspension was found to be important in determining the preference of vermiculite for certain cations, while more freely-expanding, lower layer charge smectite did not demonstrate this phenomenon.

INTRODUCTION

CATION segregation in clay interlayer regions has been studied by various workers. Glaeser and Merling (1954, 1958) first hypothesized demixing of Ca^{2+} and Na^+ ions in smectite on the basis of hydration properties, and noted a critical Ca^{2+} -ion fraction (f -value) at which segregation became evident. Below this fraction, the clays had X-ray spacings and hydration properties of the pure Na^+ -clay. Glaeser (1958) described the broadened nature of X-ray peaks of interstratified clays and the 001 peak position between the diffraction peaks of the pure Na^+ - and Ca^{2+} -clays. Demixing of Na^+ and Ca^{2+} ions in free-swelling bentonites was detected by Fink *et al.* (1971) using X-ray diffraction methods. Random interstratification of inorganic and organic cations in clays has been reported as well. Mortland and Barake (1964) found ethylammonium- Ca^{2+} (Li^+) ion segregation in montmorillonite, using X-ray data to distinguish the interstratified systems from clays having a homogeneous mixture of interlayer cations. Barrer and Brummer (1963) studied Na^+ -methylammonium and Na^+ -tetramethylammonium cation mixtures on montmorillonite, and also observed segregation. The investigation of alkylammonium ion adsorption by clays was carried

out by Theng *et al.* (1967, 1968) and some exchange properties of these ions were described.

In this study, the objective was to determine if different organic cations segregated in partially exchanged clays. In addition, the characteristics of alkylammonium ion adsorption by clays were studied and compared with the Na^+ and Ca^{2+} exchange properties of those clays.

METHODS

The clays utilized in this work were smectite from Upton, Wyoming bentonite and a Libby, Montana vermiculite. The clay fractions were obtained from these minerals by conventional methods and saturated with ethylammonium (EA^+) ion by addition of large excesses of the chloride salt to the clay suspension. The clay was centrifuged, the supernatant solution discarded, and more ethylammonium chloride added. The above procedure was repeated four times after which the suspensions were dialyzed in distilled water until no chloride appeared in the dialysate. The smectite was found to have 93 m-equiv. of EA^+ /100 g after saturation and the vermiculite 115 m-equiv./100 g. Since the value found for the vermiculite is considerably lower than the CEC of homogenous vermiculites, it was obvious that the material still contained unexpanded layers, a conclusion which was confirmed by X-ray diffraction. To obtain mixed ionic systems, various amounts of alkylammonium chlorides were equilibrated for 24 hr with 0.2 g of the EA^+ saturated clays in 50 ml volumetric flasks.

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Experiments at several days equilibration produced the same results indicating 24 hr were sufficient for equilibrium. The suspensions were centrifuged, and the clear supernatant solution analyzed for ethylammonium ion by making the solution alkaline with NaOH, distilling the ethylamine into boric acid and titrating with standard HCl. Under such conditions the quaternary ammonium ions are not distilled so that an analysis is obtained which reflects the concentration of EA⁺ in a mixture with quaternary ammonium ions. The Na⁺ and Ca²⁺ analyses were made with an atomic absorption spectrophotometer. X-ray diffraction patterns of air-dried clay films deposited on glass slides were obtained utilizing a Philips diffractometer with filtered Cu K α radiation.

DISCUSSION OF RESULTS

The X-ray diffraction data for pure ethylammonium and tetra-*n*-propylammonium (TPA⁺) smectites, and for systems which contained various proportions these two species, are reported in Fig. 1. The basal spacings of the pure EA⁺ and TPA⁺ smectites are 12.9 and 14.5 Å, respectively. These samples possess rational higher orders of the (001) sequence which suggests homogeneous systems. In the systems where ethylammonium was partially exchanged by tetrapropyl ammonium at various levels up to about 55 per cent, only the basal reflection was usually observed at values intermediate between the two homogeneous systems. These results point to random interstratification of 12.9 and 14.5 layers in the 0–55 per cent exchanged EA–smectite and lead to the con-

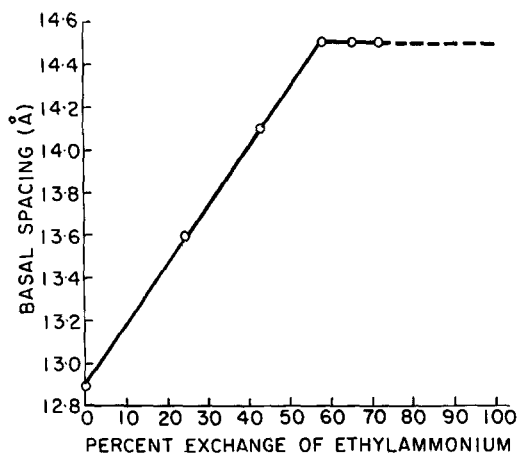


Fig. 1. The 001 spacing of smectite at 40 per cent relative humidity as a function of the proportion of EA⁺ exchanged by TPA⁺.

clusion that segregation of the two species of organic cations occurred in the partially exchanged systems. If the ions were uniformly distributed in all layers in these partially exchanged samples, the basal spacing would be defined by the larger TPA⁺ ion and would occur at 14.5 Å, probably with rational higher order reflections. This situation is observed with the 55–100 per cent exchanged smectites, and is evidence for homogeneity. These results are similar to those found with mixed metal ion systems (Na–Ca smectite, Glaeser and Mering 1954, 1958 and Fink *et al.*, 1971) and mixed metal and organic cation smectites (Barrer and Brummer, 1963, and Mortland and Barake, 1964). These results do not prove that segregated systems contain no layers with mixed cationic species, but do establish the preference of ion species for definite inter-layer regions. The basal spacings of EA⁺–smectite and EA⁺–vermiculite in suspension were 12.9 and 12.7 Å, respectively.

The exchange isotherms of TPA⁺, tetraethylammonium (TEA⁺), tetramethylammonium (TMA⁺) and hexadecyltrimethylammonium ions on EA⁺–smectite are given in Fig. 2. At low exchange levels, the effectiveness of replacement of EA⁺ is directly related to the molecular weight of the replacing ions. At higher replacement of EA⁺, the low molecular weight quaternary ammonium ions (TMA⁺ and TEA⁺) are the most effective, the TEA⁺ being better than TMA⁺ due to its size. TEA has a molecular weight high enough to make it very effective in exchange, yet not large enough to encounter

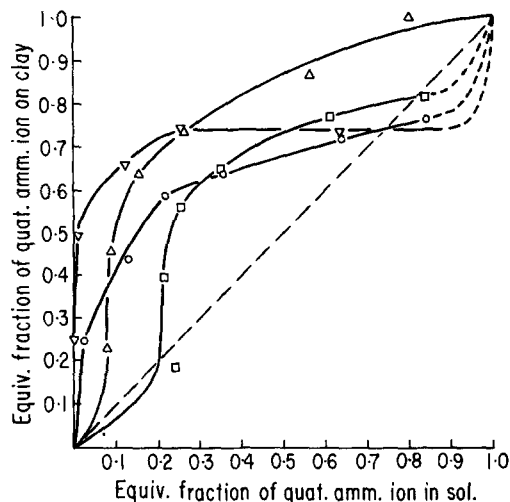


Fig. 2. Exchange isotherms of quaternary ammonium ions on EA⁺–smectite. Rectangles □ TMA⁺, circles ○ TPA⁺, triangles △ TEA⁺, inverted triangles ▽ hexadecyltrimethylammonium.

steric hindrance. A similar result, which might also be explained in this way, was obtained by Greenland and Quirk (1962), who observed that *n*-butyl pyridinium was more effective than either *n*-ethyl pyridinium or *n*-octyl pyridinium in exchanging Na-smectite. The intermediate size cation may be large enough to exchange other cations easily, yet small enough not to have to contend with repulsive forces associated with close-packing in the interlamellar space. Close-packing is necessary for the symmetrical quaternary ammonium ions (TMA⁺, TEA⁺, TPA⁺) because of their apparent inability to form more than a single interlamellar molecular layer. Hexadecyltrimethyl ammonium exchanged only about 74 per cent of the EA⁺, probably because of this steric effect. High concentrations of quaternary ammonium ion in equilibrium with the clay may overcome the repulsive forces; in fact, total EA⁺ exchange can be achieved with very high TPA⁺ concentrations. TPA⁺ covers a surface area on smectite so as to barely permit total monolayer adsorption (Theng *et al.*, 1967). The isotherms of Fig. 2 differ considerably from those of Theng *et al.* (1967) mainly because EA⁺, rather than Na⁺-smectite, was used in the present study. The greater mass of EA⁺, as well as its effect in contracting the clay in suspension, results in isotherms with the quaternary ammonium ions less preferred than Theng *et al.* (1967) observed for Na⁺ clay.

Studies on the exchange of EA⁺-vermiculite with quaternary ammonium ions contrasted sharply with the smectite system. For partial exchange by quaternary ammonium ions, random interstratification was not observed. Sharp peaks characteristic

of the EA⁺-vermiculite or of the quaternary ammonium ion forms were observed. This result suggests that entire vermiculite crystallites (domains) were exchanged while others remained saturated with EA⁺. Inhomogeneity of the vermiculite is the most likely explanation for this behavior. That is, the vermiculite contained a spectrum of charge densities rather than all particles possessing a similar charge density. In support of this explanation, Na⁺-vermiculite, when air dried, gave two discrete basal reflections at 12.4 and 14.7 Å although Ca²⁺-vermiculite gave but one at 14.8 Å.

Exchange isotherms of TMA⁺, TEA⁺, and TPA⁺ on EA⁺-vermiculite are reported in Fig. 3. These are in sharp contrast to the smectite isotherms in Fig. 2. The exchange of EA⁺ by quaternary ammonium ion was much more difficult for vermiculite than for smectite, and the effectiveness of exchange was inversely related to ionic size. Thus, TPA⁺ ions are too large for entry into the higher charged vermiculite, although exchange of EA⁺ from smectite of lower charge density occurred with little difficulty. The coulombic forces in the vermiculite are too strong for layer expansion from the 12.7 Å of EA⁺-vermiculite in suspension to the 14.5 Å required by the TPA⁺. The highest observed exchange of about 7 per cent was mostly from external surface sites. At this highest level of TPA⁺ exchange, however, a small peak at 14.5 Å was found, indicating some of the lower charged portion of the inhomogeneous vermiculite was exchanged. TEA⁺ and TMA⁺ were successively better exchangers because their decreasing size required less interlayer expansion for adsorption. The basal spac-

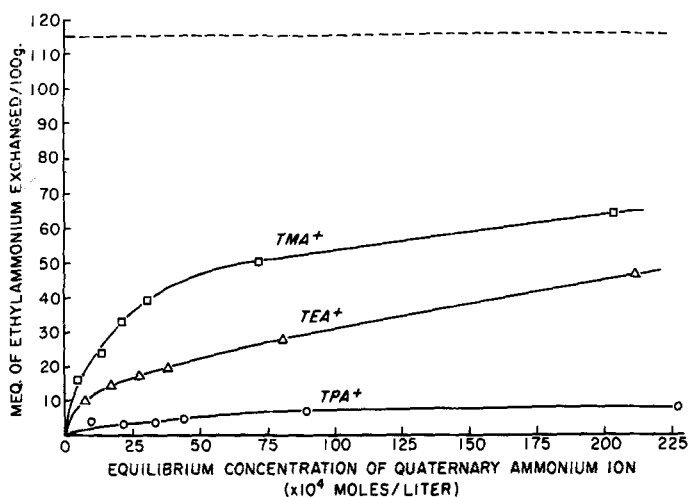


Fig. 3. Exchange isotherms of quaternary ammonium ions on EA⁺-vermiculite. Dashed line represents total exchangeable EA⁺ on saturated vermiculite.

ings of TEA⁺ and TMA⁺-vermiculite in suspension are 14.2 and 13.6 Å respectively. In accordance with their greater ease of exchange, the peak intensities at 14.2 and 13.6 increased as amount of exchange with EA⁺ increased. In comparing quaternary ammonium ion concentrations required for appreciable exchange, it is apparent that none of these ions were very effective with EA⁺-vermiculite. High concentrations were required to cause exchange, and even TMA⁺ showed somewhat less ability to replace EA⁺ than Na⁺ (Fig. 6) despite its greater molecular weight (compare the TMA⁺ isotherm in Fig. 3 with the Na⁺-vermiculite isotherm in Fig. 6). In contrast, EA⁺-smectite exchange by TMA⁺ (Fig. 2) was much more effective than exchange by Na⁺ (Fig. 6). Thus, significant ion exclusion effects are observed for TMA⁺, TEA⁺, and TPA⁺, increasing in the order: TMA < TEA < TPA. This sequence is related to ion size, although hydration energies of the quaternary ammonium ions may also be important.

Experiments on exchange of Na⁺ and Ca²⁺ from vermiculite by TPA⁺ were carried out for comparison with the EA⁺-vermiculite system. The exchange isotherms for TPA⁺ on Na⁺ and Ca²⁺-vermiculite are reported in Fig. 4 and for Ca²⁺ and EA⁺ smectite in Fig. 5. For the vermiculite systems (Fig. 4) very little Na⁺ or Ca²⁺ was exchanged by TPA⁺, similar to the results with EA⁺-vermiculite in Fig. 3, while in the smectite system (Fig. 5) much greater amounts were exchanged. For the vermiculite most of the metal ion exchange must have been from external surfaces, although Na⁺-vermiculite showed significantly higher exchange than did the Ca²⁺ form. Since the vermicu-

lite was non-homogeneous, a fraction of the sample of sufficiently low charge could, when Na⁺ saturated, swell beyond the 14.7 Å spacing and thus permit some interlamellar exchange by TPA⁺. In the smectite system shown in Fig. 5, the metal ions are obviously more accessible as evidenced by the relatively easy exchange of Ca²⁺ with TPA⁺. In water suspension the basal spacings would be about 19 Å for the Ca²⁺ and much more for the Na⁺ smectite. Ca²⁺ and Na⁺ with hydration energies of 377 and 95 kcal/mole respectively (Kittrick, 1969) result in vermiculite expansion to 14.7 Å, while EA⁺ with a hydration energy lower than K⁺ results in a 12.7 Å spacing in suspension. TPA⁺ has a lower hydration energy than EA⁺ as evidenced by its lack of association with water in smectites (Gast and Mortland, 1971), which is expected for a quaternary ammonium ion. TMA⁺ has a hydration energy of only 32 kcal/mole (Halliwell and Nyburg, 1963); TPA⁺ and TEA⁺ should have lower values. In order to replace highly hydrated Na⁺ or Ca²⁺ ions on vermiculite, TPA⁺ would have to penetrate an interlayer no wider than its own diameter, since the energy requirement for further expansion would be too large to overcome. Further hydration of the already hydrated Ca²⁺ and Na⁺ ions will not furnish sufficient energy for further expansion. Van der Waals forces are negligible for TPA⁺ (Theng *et al.*, 1967), unlike aliphatic single chain molecules, so the tendency for TPA⁺ penetration is small beyond the mass effect.

TPA⁺, due to its molecular weight and the greater distance between sheets, can replace highly hydrated cations from smectite surfaces exposed by swelling beyond 14.7 Å. However, in comparing

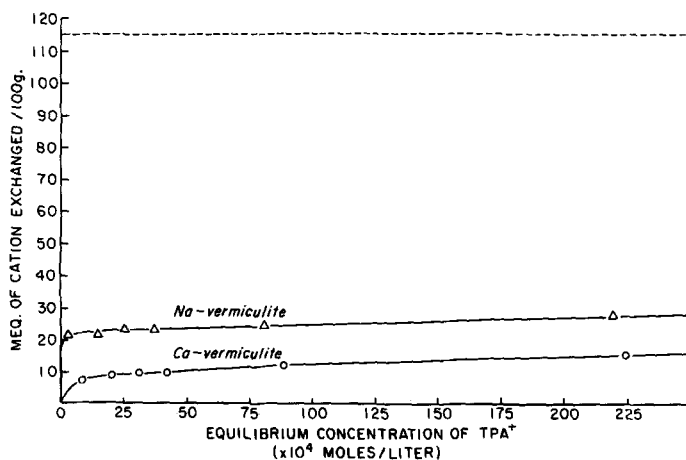


Fig. 4. Exchange isotherms of TPA⁺ on Na⁺ and Ca²⁺-vermiculite. Dashed line represents total exchangeable Na⁺ or Ca²⁺ on the saturated vermiculite.

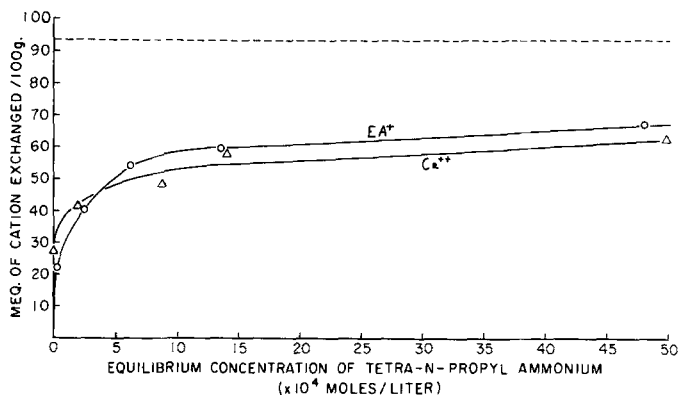


Fig. 5. Exchange isotherms of TPA^+ on Ca^{2+} and EA^+ -smectite. Dashed line represents total exchangeable cations on smectite.

Figs. 3 and 4, note that TPA^+ exchanges Na^+ from vermiculite more readily than it does EA^+ . This difference can be related to the 12.7 \AA spacing of the EA^+ -vermiculite, and the energy required for expansion of the layers to permit TPA^+ entry. For the most part, TPA^+ appears to replace EA^+ from external surfaces and is unable to expand effectively even the lower charged portion of the vermiculite. As shown by the data, Na^+ -vermiculite readily allows exchange by TPA^+ in this lower charged fraction.

The above explanation would predict no difficulty in the exchange of EA^+ from vermiculite by small hydrated ions, and this is in fact demonstrated in Fig. 6 where EA^+ is exchanged from vermiculite by Na^+ and Ca^{2+} .

SUMMARY AND CONCLUSIONS

Organic ions of different size and chemical properties tend to segregate in smectite interlayers. However, in the non-homogeneous vermiculite used, segregation appears to be on the less microscopic scale of domains or crystallites. The TPA^+ cation, due to its size, probably hinders its own complete interlayer replacement of smaller cations in smectite; thus, segregation may not be perfect. Segregation appears to be favored because of an enthalpy factor larger than the opposing entropy of mixing which would favor ion homogeneity. After a large ion expands an interlayer, complete exchange of that interlayer would be preferred to expanding other layers. This enthalpy factor may best explain EA^+ - TPA^+ segregation in smectite. However, this

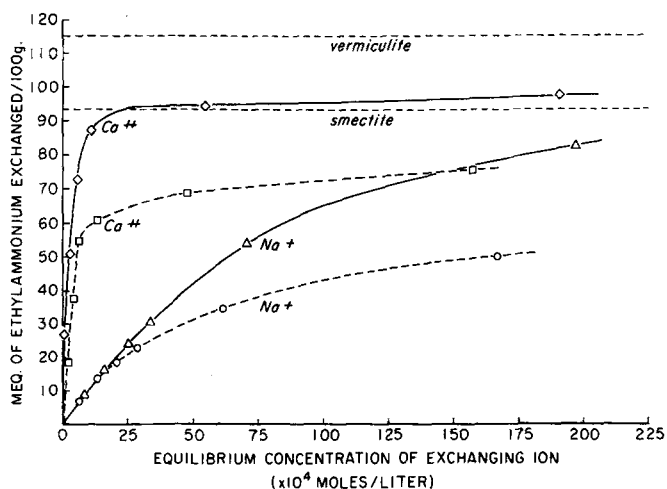


Fig. 6. Exchange isotherms of Ca^{2+} and Na^+ on EA^+ -vermiculite and smectite. Dashed level lines represent total exchangeable EA^+ on vermiculite and smectite. Solid curves are isotherms on vermiculite, dashed curves on smectite.

argument is not in agreement with Vansant and Uytterhoeven (1971), who used thermodynamic data to support a model of a homogeneous Na^+ -alkylammonium mixture on montmorillonite in suspension. Their explanation of possible segregation upon drying contrasts with the observations of Fink *et al.* (1971), who observed cation segregation in certain proportions of mixed Na^+ - Ca^{2+} bentonite suspensions. Segregation appears to be a direct result of differences in cationic properties, the most important being ion size and hydration energy. It should be observed in both wet and air-dry clays, unless the wet clays are more fully expanded in suspension, in which case the size of cations in relation to the interlayer spacing has less importance. Homogeneity in such a system would be expected until drying restricted the distribution of the ions. The EA^+ - TPA^+ -smectite is very likely segregated in suspension because it does not swell freely.

Cation size is an important factor in exchange reactions of smectites, larger ions generally being preferred. Cation size may also have a limiting effect as is observed in exchange of EA^+ -smectite with TPA^+ and hexadecyltrimethylammonium. However, when the silicate layer charge is high (as in vermiculite), large cations of low hydration energy (TPA^+) are not able to expand the clay layers to replace smaller organic ions (EA^+). Clays partially expanded with smaller hydrated cations such as Na^+ and Ca^{2+} show only limited exchange with TPA^+ if the layer charge is fairly high. However, low layer charge Ca^{2+} -smectite exchanges with TPA^+ because interlayer expansion in suspension allows less hindered entry of TPA^+ between the clay layers. EA^+ is easily replaced from vermiculite and smectite by small, hydrated cations (Ca^{2+} and Na^+). This observation supports the argument that the interlayer spacing of the clay in suspension is of crucial importance in explaining ca-

tion preference in exchange. This is especially true of contracted, higher layer charge clays, where energy must be provided for interlayer expansion so that exchange by large cations can occur.

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Résumé—L'analyse par diffraction X d'une smectite partiellement échangée par des ions alkylammonium révèle une ségrégation des différentes espèces ioniques dans des feuilletés ordonnés au hasard. La vermiculite, au contraire, montre une ségrégation dans des cristallites; ce comportement est attribué à l'hétérogénéité de l'argile. La ségrégation ionique est expliquée par les propriétés d'hydratation des cations et par l'énergie requise pour l'ouverture des feuilletés. Des ions ammonium quaternaire de différentes tailles ont été utilisés pour échanger des argiles etylammonium et on a pu démontrer l'efficacité et le rôle dans l'empêchement stérique de la taille du cation lors de l'échange d'ion. La densité de charge du feuillet a été reliée à la facilité avec laquelle le gros cation est adsorbé. Il a été montré que l'espacement basal en suspension joue un rôle important pour déterminer la préférence de la vermiculite pour certains cations alors que la smectite à plus basse charge et à caractère de gonflement non limité plus marqué, ne met pas ce phénomène en évidence.

Kurzreferat—Die Röntgenbeugungsanalyse von Smectiten, die mit gemischten Alkylammoniumionen ausgetauscht wurden, ließ eine Auftrennung der verschiedenen Ionenarten in zufällig geordnete Schichten erkennen. Vermiculit zeigte dagegen Auftrennung in Kristallite. Dieses Verhalten wurde

auf Inhomogenität des Tons zurückgeführt. Die Auftrennung der Ionen wird sowohl mit den Hydratationseigenschaften der Kationen als auch mit dem Energiebedarf für eine Schichtaufweitung erklärt. Quarternäre Ammoniumionen verschiedener Größe wurden mit Äthylammonium-Ton zum Austausch gebracht und der Wirkungsgrad sowie die durch die Kationengröße bedingte sterische Hemmung des Ionenaustausches dargestellt. Zwischen der Ladungsdichte der Silicatschichten und dem Ausmaß des Eintausches großer Kationen bestand eine Beziehung. Der Basisebenenabstand in Suspension stellte sich als wichtige Bestimmungsgröße der Selektivität von Vermiculit für bestimmte Kationen heraus. Smectit mit niedrigerer Schichtladung zeigte diese Erscheinung nicht.

Резюме — При рентгеновском исследовании смешанного смектита с обменным алкиламонием обнаружили сегрегацию различного рода ионов в произвольно регулярные слои. Вермикулит, однако, выявил сегрегацию в мелкие кристаллы; это поведение приписывается неоднородности глины. Сегрегация ионов объясняется как свойствами гидратации катионов, так и энергией разложения на слои. Для обмена этиламмониевых глин использовались четвертичные аммониевые ионы различных размеров, что продемонстрировало как эффективность, так и стерическое препятствие размера катионов в ионообмене. Плотность заряда слоя соответствовала легкости адсорбции крупных катионов. Нашли, что базальный параметр в суспензии является важным фактором причины предпочтения вермикулитом некоторых катионов, в то время как смектит, разлагающийся более свободно, этой особенности не проявляет.