

PROPERTIES OF REDUCED CHARGE MONTMORILLONITE: TETRA-ALKYLAMMONIUM ION EXCHANGE FORMS*

DAVID M. CLEMENTZ and M. M. MORTLAND

Departments of Crop and Soil Sciences and Geology, Michigan State University, East Lansing,
Michigan 48823, U.S.A.

(Received 13 August 1973)

Abstract—Surface properties of reduced charge montmorillonites (RCM) whose exchange capacities were saturated with tetra-alkylammonium cations, were studied with X-ray diffraction, nitrogen, and water adsorption. Methods were utilized for preparing montmorillonite of varying charge and of swelling reduced-charge clay with ethanol. As charge reduction proceeds, all layers retain some exchangeable cations until about half the original charge is reached at which point collapsed layers begin to appear and increase to about 60 per cent at maximum charge reduction. Charge reduction thus appears to proceed in a non-homogeneous fashion. When saturating exchange sites with tetra-alkylammonium ions in ethanol solvent, intercalation of salt in uncharged layers was noted if the samples were not completely washed. Nitrogen adsorption isotherms at liquid nitrogen temperatures showed considerable interlamellar penetration of tetramethylammonium (TMA^+) clays, resulting in high calculated surface areas. Much less adsorption on the tetra-*n*-propylammonium (TPA^+) clays was observed. Surface areas were increased upon reduction of charge up to the point where collapsed layers began to be appreciable, whereupon measured areas decreased. Water adsorption isotherms reflected the hydration properties of the exchangeable cation as well as the surface available for adsorption.

INTRODUCTION

Some interesting properties of reduced charge montmorillonite (RCM) have recently been revealed (Clementz *et al.*, 1973). Using the methods of Brindley and Ertem (1971) and Calvet and Prost (1971) for preparation and solvation of RCM, the authors demonstrated that charge reduction was a linear function of the fraction of Li(I) ions occupying the exchange sites prior to heat treatment. It was further demonstrated that all remaining exchange sites could be saturated with another ion [e.g. Cu(II)] via proper selection of solvent. These observations and techniques have been extended in the current study to include saturation with alkylammonium ions of all remaining exchange sites in a series of RCM's. The properties of these materials were then investigated using X-ray diffraction, and both water and nitrogen adsorption techniques.

In the previous study, RCM was shown to be heterogeneous with respect to layer charge reduction. This heterogeneity results in differential response to counter ion saturation, where layers which possess very low charge may collapse, while others with higher charge will still be expansible in water. The nature of the exchangeable cation is also a factor. The present approach was designed to eliminate collapse in those

low-charge layers by using tetra-alkylammonium ions which will resist collapse when the solvent is removed. It would seem reasonable to expect, then, that the remaining internal surface would be available for adsorption.

EXPERIMENTAL METHODS

Preparation of RCM

A series of RCM samples was prepared by the method of Brindley and Ertem (1971). Suspensions of $<2 \mu$ Li(I)-saturated and Na(I)-saturated Upton, WY, montmorillonite (A.P.I. H-25) of structural formula $\text{M}_{0.64}^+ [\text{Al}_{3.06} \text{Fe}_{0.32} \text{Mg}_{0.66}] (\text{Al}_{0.10} \text{Si}_{7.90}) \text{O}_{20} (\text{OH})_4$ were mixed in various proportions and classified with regard to the fraction of lithium ions occupying the exchange sites prior to heat treatment, *F*. The *F* values for the series were 0 (Na-montmorillonite), 0.2, 0.4, 0.6, 0.8 and 1.0 (Li(I)-montmorillonite). The aqueous suspensions (approx. 600 ml, 0.0047 g/ml) were stirred for 24 hr to allow maximum randomization of ions and then dried into large thin films (approx. 6×12 in.) on polyethylene sheets. These clay films were peeled from the polyethylene and heated for 24 hr at 220°C. It was presumed that this technique would promote homogenous distribution of ions in all layers.

After cooling, the clay films were suspended in 95 per cent ethanol and dispersed in a Waring blender. The ethanol suspensions were concentrated, and the clay was

* Michigan Agricultural Experiment Station J. Article No. 6511.

collected by vacuum filtration. One portion of each air-dried, Li(I)-Na(I) RCM sample was saved for nitrogen and water adsorption studies.

TMA⁺ and TPA⁺ exchange forms

Alkylammonium ion saturation was achieved for RCM at all *F* values by slurring the 0.5–1 g samples for 15 hr periods in 0.5 N tetramethylammonium (TMA⁺) chloride or tetra-*n*-propylammonium (TPA⁺) bromide in 95 per cent ethanol for a total of three washes. Excess salt was removed by washing with 95 per cent ethanol until a Cl⁻ or Br⁻ test with AgNO₃ was negative. The samples were allowed to air dry and then heated at 110°C for 2 hr to remove excess ethanol and then equilibrated at 20°C and 40 per cent r.h. until ready for use.

Water adsorption

The TMA⁺, TPA⁺, and the Na(I), Li(I)-RCM's were equilibrated for 3 days at 20°C under seven different partial pressures of water vapor provided by various saturated salt and sulfuric acid solutions. The resulting weight gain compared with P₂O₅-dry clay was recorded.

X-ray diffraction studies

The (001) reflections of the samples under various conditions were measured by depositing thin films of the mineral on glass slides from sonified, aqueous suspensions. A Philips X-ray diffractometer with copper radiation and a nickel filter was employed.

Nitrogen adsorption

All nitrogen adsorption data were obtained by pre-heating samples at 110°C for 2 hr under flowing helium and then obtaining isotherms on a Perkin-Elmer Model 212B Sorptometer at liquid N₂ temperatures in the manner described by Knudson and McAtee (1973).

Infra-red studies indicate this period and temperature of degassing were sufficient for complete dehydration since the tetra-alkylammonium ions have little ability to coordinate water and water is thus not tightly bound in clays saturated with these ions.

RESULTS

X-ray diffraction

Table 1 gives the (001) reflections for air-dry (40 per cent r.h.) samples of montmorillonite with varying charge and with the exchange capacity saturated with TMA⁺ or TPA⁺. The cation exchange capacity is also given. These data show that as charge is reduced in the montmorillonite, ions are present in all layers up to the *F* = 0.4 sample from which point more and more collapsed layers are formed, layers which, though easily expansible in ethanol to 17.3 Å in accord with results of Brindley and Ertem (1971), do not possess charge as indicated by the absence of TMA⁺ or TPA⁺ ions. Since the saturation of the exchange sites with TMA⁺ and TPA⁺ was carried out in ethanol soln, ample opportunity was provided for saturation of all exchange sites with the tetra-alkylammonium ions. It thus appears that charge reduction proceeds in a non-homogeneous fashion.

This confirms other work by Clementz *et al.* (1973) with Cu(II) saturated RCM systems. Some layers lose all their charge as indicated by absence of TMA⁺ or TPA⁺ ions and thus preserve some higher spacings in layers in water, while others still possess exchange capacity and maintain the appropriate *d*-spacing of the complex with TMA⁺ or TPA⁺. At first one would be tempted to explain this phenomenon by segregation of the Na(I) and Li(I) in the various layers, which, upon experiencing the 220°C heat treatment, would result in complete charge reduction in the Li(I) layers and no charge reduction in the Na(I) layers. However, if one

Table 1. The (001) reflections (Å) of alkylammonium saturated reduced charge montmorillonite

<i>F</i>	CEC* (m-equiv/100 g)	TMA ⁺	Collapsed‡ layers (%)	TPA ⁺	Collapsed‡ layers (%)
0	88	13.9	0	14.4	0
0.2	73	13.9	0	14.4	0
0.4	66	(13.9)†	N.D.	(14.4)†	N.D.
0.6	53	(13.6)	20	(14.3)	15
0.8	40	(12.5)	44	(13.4)	42
1.0	30	(11.8)	60	(12.6)	58

* Measured by saturating samples with Cu(II) and titrating conductometrically with NaOH in a 50/50 ethanol-water solvent.

† Figures in parentheses are non-rational and represent randomly interstratified systems.

‡ Calculated from Hendricks and Teller's (1942) method.

considers the $F = 1.0$ sample, this end-member had no exchangeable Na(I) at all but was completely Li(I) saturated, yet the data show the presence of some layers which were able to exchange with TMA^+ and TPA^+ ions and thus preserve some higher spacings in those systems.

Figure 1 shows the diffraction curves for the $F = 0.6, 0.8$ and 1.0 samples under air-dried conditions (40 per cent r.h.). These patterns all possess strong peaks indicating randomly interstratified layers of two kinds, those containing the TMA^+ or TPA^+ ions (13.9 or 14.4 Å respectively) and collapsed layers (9.9 Å). In addition a weak broad peak near 24 Å is apparent in some samples. An explanation for this could be the regular interstratification of collapsed (9.9 Å) and expanded (13.9 or 14.4 Å) layers. When TMA^+ -montmorillonite is completely dehydrated or devoid of solvent the d spacing is 13.6 Å; the corresponding value for TPA^+ -clay is 14.4 Å value.

Upon treatment of the RCM samples with the salts of the tetra-alkylammonium ions in ethanol, all of the samples showed complete expansion to 17.3 Å with complete rationality of higher order reflections. Thus in ethanol, all layers, whether or not they possess charge, are able to expand as shown by Brindley and Ertem (1971). If the ethanol was permitted to evaporate from the sample or if ethanol was removed by heating in an oven, rational 13.9 or 14.4 Å diffraction peaks were found regardless of the degree of charge reduction. However, if the samples were washed well with ethanol to remove excess alkylammonium salts, then

dried to remove ethanol, those layers possessing no exchangeable cations collapsed to 9.9 Å. These results prove that the tetra-alkylammonium salts can be intercalated in the layers which have lost charge, perhaps in a condition not unlike salt intercalation by kaolinite. Charge reduction in these layers has resulted in decrease in coulombic repulsion of the anion which permits intercalation of the salt.

The above results again suggest that the montmorillonite layers are to some degree non-homogeneous in regard to charge properties. The mineral does contain a small amount of tetrahedral charge which would not be eliminated by the Li(I) saturation and heating but would continue to function as cation exchange sites. It may be that the expanded layers which do remain in the $F = 1.0$ sample are indeed populated with some tetrahedral sites, while the layers which will not take on exchangeable alkylammonium ions, even though expanded to 17.3 Å in ethanol, have none at all. In the intermediate RCM samples, where mixtures of Na(I) and Li(I) were used to accomplish different levels of charge reduction, segregation of the ions may be a factor. The presence of some ordered interstratification (24 Å) in some samples could be explained by alternating layers containing Li(I) and Na(II) ions at the time of heat treatment. However, the fact is that the $F = 1.0$ sample had no Na(I) but was completely saturated with Li(I), yet an appreciable peak near 24 Å is present (Fig. 1). An explanation might be an alternation of layers with some tetrahedral sites with layers which had none.

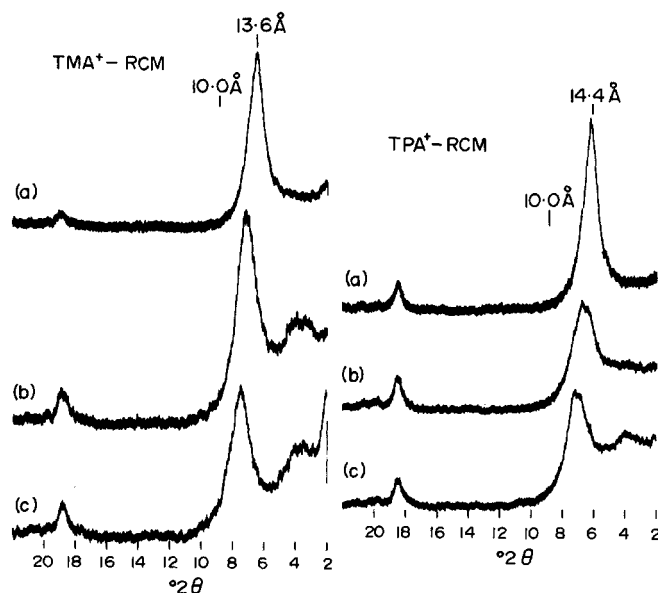


Fig. 1. X-ray diffraction curves for TMA^+ and TPA^+ saturated $F = 0.6$ (A), 0.8 (B) and 1.0 (C) samples at 40 per cent r.h.

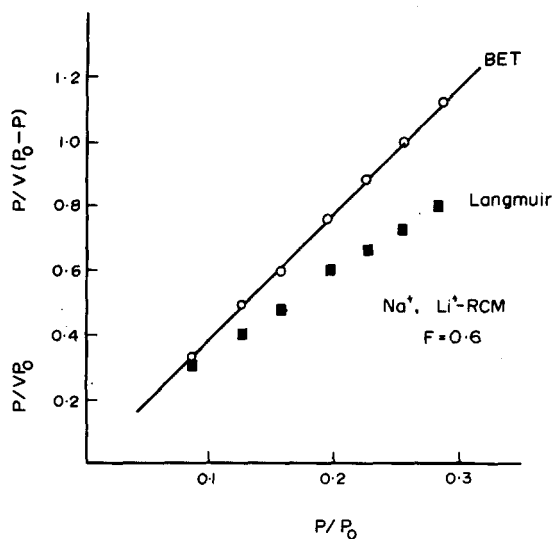


Fig. 2. Nitrogen adsorption data for sample $F = 0.6$ before saturation with TMA^+ ions. Surface area = $22 \text{ m}^2 \text{ g}^{-1}$.

Nitrogen adsorption

Representative adsorption isotherms (78°K) of nitrogen on sample $F = 0.6$ before and after saturation of the exchange sites with TMA^+ ions appear in Figs. 2 and 3 respectively. Good linearity with the Brunauer, Emmett, Teller (BET) equation appears in Fig. 2 for the Na(I) , Li(I) sample with a calculated surface area of $22 \text{ m}^2 \text{ g}^{-1}$. Barrer and MacLeod (1955) report an area of $21.5 \text{ m}^2 \text{ g}^{-1}$ for Na(I) montmorillonite by nitrogen adsorption. Less favorable obedience to the Langmuir equation will be noted. Nitrogen does not penetrate interlamellar regions in this system; thus, only external surfaces are involved. On the other hand

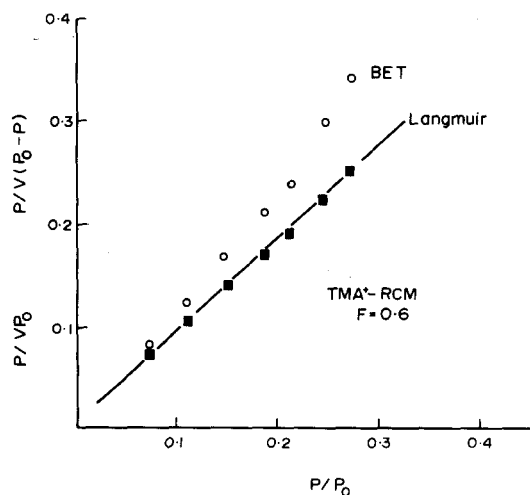


Fig. 3. Nitrogen adsorption data for sample $F = 0.6$ after saturation with TMA^+ ions. Surface area = $222 \text{ m}^2 \text{ g}^{-1}$.

the TMA^+ saturated sample (Fig. 3) better follows the Langmuir than the BET equation. The surface area calculated from the Langmuir equation was $222 \text{ m}^2 \text{ g}^{-1}$. These results are in complete agreement with those of Knudson and McAtee (1973) who found that when interlamellar penetration of montmorillonite by nitrogen took place, the Langmuir equation gave better linearity than did the BET equation. Where the build-up of multimolecular layers of nitrogen is prevented by the restrictive interlamellar space provided in these samples, it is not surprising that the Langmuir equation, which was derived on the basis of a monomolecular layer of adsorbate, is a better model for the adsorption process. This observation has been made for adsorption on other microporous solids (Gregg and Sing, 1967). The surface areas reported here were obtained utilizing whichever of the above two equations gave the best fit for the adsorption data.

Figure 4 shows the surface area of the various RCM samples as determined by nitrogen adsorption. Two factors are involved in the variation in measured surface area between the samples. On the one hand as the charge reduction increases, collapsed layers begin to occur at about $F = 0.4$ and increase to the maximum at $F = 1.0$ thus tending to reduce the measurable area. On the other hand as charge reduction proceeds, numbers of tetra-alkylammonium ions decrease, a factor which should lead to increased area. Thus in samples of lower charge reduction where the ions are present in all layers keeping all the layers apart, measured area should increase because of the reduction in

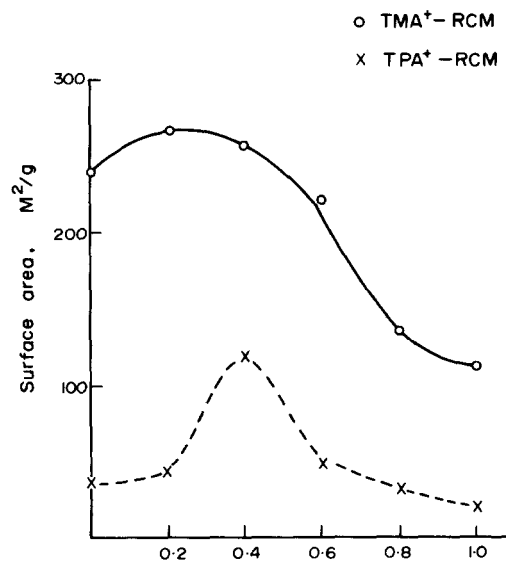


Fig. 4. Surface areas of varying charged montmorillonite (F) saturated with TMA^+ and TPA^+ ions.

numbers of interlamellar cations. However, the dominant factor which determines measured area is layer collapse. Data in Fig. 4 tend to support this reasoning.

When the total surface areas of all the samples ($F = 0-1.0$) are calculated considering the area measured by nitrogen adsorption, area occupied by exchangeable TMA^+ ions, and numbers of collapsed layers present, values ranging between 385 and 430 $\text{m}^2 \text{g}^{-1}$ were obtained. The area of the TMA^+ ion was taken as 31 \AA^2 (Theng *et al.*, 1968) and numbers of collapsed layers determined from X-ray diffraction (Table 1). The surface covered by a TMA^+ ion was assumed to be twice the 31 \AA^2 value since both opposing faces of an inter-layer would be covered and presumably unavailable for nitrogen adsorption. The relative constancy of the calculated surface areas at about 400 $\text{m}^2 \text{g}^{-1}$ suggests that at least the major factors affecting surface area were considered. One is tempted to make the assumption that a monolayer of nitrogen is formed in interlamellar layers (supported by obedience of isotherms to the Langmuir equation as well as the (001) spacing) so that when the nitrogen surface areas are doubled, (the TMA^+ areas have already been doubled, see above) a total area of 630 to 700 $\text{m}^2 \text{g}^{-1}$ results. Obviously an error in this computation is the extent of external surface area, a value which should not be doubled. However, correction for this factor would still lead to only a minor downward readjustment of the calculated values.

The data in Fig. 4 show the large differences in surface areas of the reduced charge clay depending upon whether or not the exchange sites are saturated with TMA^+ or TPA^+ ions. Obviously the large difference in size of the ions is a major factor in these results, the TMA^+ ion having a limiting area of 31 \AA^2 and TPA^+ one of 77 \AA^2 according to Theng *et al.* (1968). When the total surface area of the sample is calculated for the TPA^+ saturated samples in the same manner as was done above for the TMA^+ systems, again an average value of about 400 $\text{m}^2 \text{g}^{-1}$ is obtained.

The work of Bohor and Thomas (1968) demonstrated some interlamellar penetration of Cs(I) -montmorillonite by nitrogen and some time dependence of nitrogen penetration. With the tetra-alkylammonium ions on the exchange sites, the platelets are held much further apart (13.6 \AA for dehydrated TMA^+ and 14.4 \AA for TPA^+) so that not only is nitrogen penetration possible but also relatively rapid. Aylmore *et al.* (1970) attribute a major influence to residual water in keeping layers of metal ion saturated swelling clays apart so that nitrogen or carbon dioxide can penetrate. They state that when samples of these clays are outgassed in a standard procedure in a static system no interlamel-

lar penetration of the gases occurs. The work of Barrer and MacLeod (1951), who used a static system, and this work, which utilized a dynamic system, prove that montmorillonites saturated with tetra-alkylammonium ions and with no residual water present have internal surfaces available for nitrogen adsorption.

Barrer and MacLeod (1951) pointed out the high levels of adsorption of some organic molecules on alkylammonium montmorillonites, in some cases leading to further expansion of the clay layers beyond that defined by the exchangeable organic ions. It may be the reduced charge montmorillonite saturated with these ions could provide even greater adsorptive abilities for organic molecules because of increased area and reduced charge which might permit a greater degree of expansion.

Water adsorption

Figure 5 shows water adsorption isotherms for TMA^+ , TPA^+ , and Na(I) , Li(I) saturated $F = 0.6$ and 1.0 samples. Two observations can be made for the alkylammonium saturated systems: (1) the TMA^+ clay isotherms show more adsorption and give Type II curves in Brunauer's classification, while the TPA^+

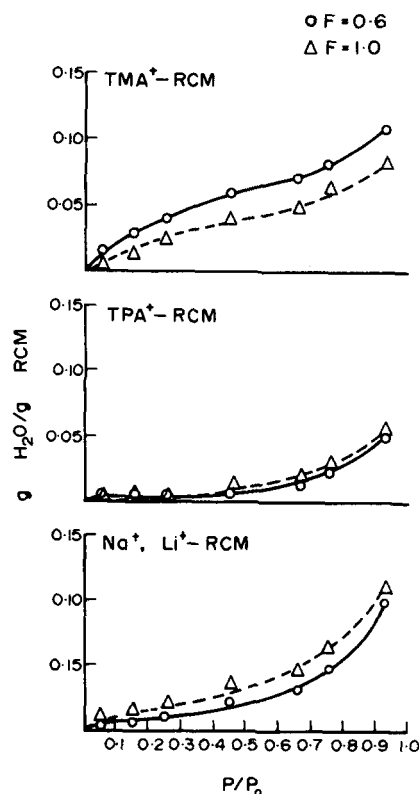


Fig. 5. Water adsorption isotherms of samples $F = 0.6$ and 1.0 before and after saturation with TMA^+ or TPA^+ ions (20°C).

samples are more like Type III; and (2) the $F = 1.0$ samples sorb less water than the $F = 0.6$, probably because they have many more collapsed layers which water cannot penetrate. The Type II curves are typical of relatively strong interaction between sorbate and the adsorbent, while Type III curves are indicative of systems where such interaction is small and less than sorbate-sorbate interaction. These curve shapes are very similar to isotherms obtained by Gast and Mortland (1971) on TMA^+ and TPA^+ saturated montmorillonite. Obviously the TMA^+ hydrates, with an energy of 32 kcal/mole. On the other hand TPA^+ would have little if any attraction for water. The other factor is the effect of ionic size on the surface available for adsorption; i.e., TPA^+ is much larger than TMA^+ . The nitrogen adsorption data clearly show the greater surface areas of the TMA^+ samples.

The isotherms obtained for the Na(I) , Li(I) -RCM show an anomaly. That is, the $F = 1.0$ sample adsorbs more water than the 0.6 sample in spite of the fact it has more collapsed layers. An important point to recognize here is that comparison is being made between samples having different ratios of exchangeable cations. For example, the $F = 0.6$ sample while having both Li(I) and Na(I) on exchange sites before heating, would have primarily Na(I) on the remaining sites with Li(I) located in the octahedral layer after heating. On the other hand the $F = 1.0$ sample was completely Li(I) saturated; thus, any exchange sites remaining after heating (those arising from tetrahedral charge, for example) would be occupied by Li(I) . The differences between these two curves, then, seem only to be accounted for by the greater hydrating ability of Li(I) . The greater adsorption by TMA^+ -RCM over the alkali metal ion clays at lower pressures may be due to the reluctance of the latter to swell.

CONCLUSIONS

The results of this work lead to the following conclusions:

1. Organic cations can be placed on the exchange sites of reduced charge montmorillonite (RCM) in ethanol solvent.
2. Organic salts may be intercalated in layers which have lost all charge yet may be expanded in ethanol.
3. The charge distribution in the reduced charge montmorillonite appears to some degree non-homogeneous, a property which could be inherent in the

mineral or the result of the method used to reduce the charge.

4. Nitrogen adsorption data indicate large amounts of internal surface for the lower levels of charge reduction of the TMA^+ saturated samples, a property that might lend itself to the use of these systems as adsorbents for various commercial purposes. TMA^+ -montmorillonite is stable up to about 260°C according to Barrer and MacLeod (1951); thus, the materials could be utilized in operations requiring relatively high temperatures.

5. Water adsorption isotherms reflected the properties of the exchangeable cations as well as the surface available for adsorption.

Acknowledgement—The support of the National Science Foundation through Grant No. GP-33878 is gratefully acknowledged.

REFERENCES

- Aylmore, L. A. G. and Quirk, J. P. (1970) Surface area of homoionic illite and montmorillonite clay minerals as measured by the sorption of nitrogen and carbon dioxide: *Clays and Clay Minerals* **18**, 91–96.
- Barrer, R. M. and MacLeod, D. M. (1951) Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkylammonium montmorillonites: *Trans. Farad. Soc.* **51**, 1290–1300.
- Brindley, G. W. and Ertem, G. (1971) Preparation and solvation properties of some variable charge montmorillonites: *Clays and Clay Minerals* **19**, 399–404.
- Calvet, R. and Prost, R. (1971) Cation migration into empty octahedral sites and surface properties of clays: *Clays and Clay Minerals* **19**, 175–186.
- Clementz, D. M., Mortland, M. M. and Pinnavaia, T. J. (1974) Properties of reduced charge montmorillonites: Hydrated Cu(II) ions as a spectroscopic probe. *Clays and Clay Minerals* **22**, 49–57.
- Gast, R. G. and Mortland, M. M. (1971) Self-diffusion of alkylammonium ions in montmorillonite: *J. Colloid Interface Sci.* **37**, 80–92.
- Gregg, S. S. and Sing, K. S. W. (1967) *Adsorption Surface Area and Porosity*. Academic Press, New York.
- Hendricks, S. B. and Teller, E. (1942) X-ray interference in partially ordered layer lattices: *J. Phys. Chem.* **10**, 147–167.
- Knudson, M. I. and McAtee, J. L. (1973) The effect of cation exchange of tris(ethylenediamine) cobalt(III) for sodium on nitrogen sorption by montmorillonite: *Clays and Clay Minerals* **21**, 19–26.
- Theng, B. K. G., Greenland, D. J. and Quirk, J. P. (1968) The effect of exchangeable alkylammonium ions in the swelling of montmorillonite in water: *Clay Minerals* **7**, 271–293.
- Thomas, J. and Bohor, B. F. (1968) Surface area of montmorillonite from the dynamic sorption of nitrogen and carbon dioxide: *Clays and Clay Minerals* **16**, 83–92.

Résumé—Les propriétés de surface de montmorillonites à charge réduite (RCM) dont la capacité d'échange est saturée par des cations tétraalkylammonium, ont été étudiées par diffraction des rayons X, adsorption d'azote et d'eau. Pour préparer la montmorillonite de charge variable et l'argile gonflante à charge réduite, on a utilisé des méthodes à l'éthanol. Lors de la réduction de la charge, tous les feuillets gardent un certain nombre de cations échangeables jusqu'à ce que la moitié de la charge initiale, environ, soit atteinte; à ce moment, des feuillets fermés commencent à apparaître et ils atteignent une proportion d'environ 60 pour cent au maximum de la réduction de charge. La réduction de charge semble donc se passer d'une manière non homogène. Lorsqu'on sature les sites d'échange avec des ions tétraalkylammonium en solution éthanolique, on note une intercalation de sel entre les feuillets non chargés si les échantillons ne sont pas complètement lavés. Les isothermes d'adsorption d'azote à la température de l'azote liquide indiquent une pénétration interlamellaire considérable des argiles tétraméthylammonium (TMA^+), ce qui entraîne l'existence de grandes surfaces spécifiques calculées. On a observé une adsorption beaucoup moindre sur les argiles tétra-*n*-propylammonium (TPA^+). Les surfaces spécifiques augmentent lors de la réduction de la charge jusqu'au moment où les feuillets fermés commencent à être en proportion appréciable; à partir de là, les surfaces spécifiques diminuent. Les isothermes d'adsorption d'eau reflètent aussi bien les propriétés d'hydratation des cations échangeables que l'existence de surfaces utiles pour l'adsorption.

Kurzreferat—Die Oberflächeneigenschaften von Montmorilloniten mit verminderter Ladung (RCM), deren Austauschkapazitäten mit Tetraalkylammoniumkationen abgesättigt waren, wurden unter Anwendung der Röntgenbeugung sowie der Stickstoff- und Wasser-adsorption untersucht. Methoden zur Herstellung von Montmorillonit mit unterschiedlicher Ladung und zur Quellung von Ton mit veränderter Ladung in Äthanol kamen zur Anwendung. Mit fortschreitender Ladungsverminderung halten alle Schichten solange einige austauschbare Kationen zurück, bis ungefähr die Hälfte der ursprünglichen Ladung erreicht ist. An diesem Punkt beginnen kontrahierte Schichten in Erscheinung zu treten, deren Anteil bei maximaler Ladungsverminderung auf 60 Prozent ansteigt. Die Ladungsverminderung scheint demnach in nicht-homogener Weise abzulaufen. Wenn die Austauschplätze mit Tetraalkylammoniumionen in Äthanol als Lösungsmittel abgesättigt wurden, wurde eine Einlagerung von Salz in die ungeladenen Zwischenschichten beobachtet, wenn die Proben nicht vollständig gewaschen waren. Die Stickstoffadsorptionsisothermen ließen im Temperaturbereich des flüssigen Stickstoffs bei Tetramethylammonium(TMA^+)-Tonen eine beträchtliche interlamellare Durchdringung erkennen, die zu hohen berechneten Oberflächen führte. Eine viel geringere Adsorption wurde in Tetra-*n*-Propylammonium(TPA^+)-Tonen beobachtet. Durch eine Verminderung der Ladung stiegen die Oberflächen bis zu dem Punkt an, bei dem kontrahierte Schichten wahrnehmbar wurden, worauf hin die gemessenen Oberflächen abnahmen. Die Wasser-adsorptionsisothermen spiegelten sowohl die Hydratationseigenschaften der austauschbaren Kationen als auch die für eine Adsorption verfügbaren Oberflächen wider.

Резюме — Дифракцией рентгеновских лучей, адсорбцией азота и адсорбцией воды исследовались поверхностные характеристики монтмориллонитов со способностями обмена насыщенными тетраалкиламмониевыми катионами. Приготовили монтмориллонит с различными зарядами и набухшую глину с уменьшенным зарядом. Во время уменьшения заряда, все слои сохраняют определенное количество обменных катионов до тех пор, пока не останется половина первоначального заряда, когда появляются разрушенные слои, увеличивающиеся до 60 процентов при максимальном понижении заряда. Таким образом, понижение заряда, очевидно, происходит неомогенным образом. При насыщении узлов обмена тетраалкиламмониевыми ионами в этиленовом растворе, в слоях без заряда замечаются тонкие включения соли, если образцы не были тщательно промыты. Изотермы адсорбции азота при температуре жидкого азота заметно проникают между слоями тетраметиламмониевых глин. Значительно меньше адсорбции видно на тетра-*n*-пропиламмониевых глинах. С понижением заряда повышаются площади поверхностей до точки, где много разрушенных слоев. Изотермы адсорбции воды отражают как характеристики гидратации обменных катионов, так и имеющуюся для адсорбции поверхность.