

## ADSORPTION OF ETHYLENE GLYCOL ON AMINE-SUBSTITUTED MONTMORILLONITES

JOHN L. BURBA, 3RD<sup>1</sup> AND JAMES L. MCATEE, JR.

Chemistry Department, Baylor University, Waco, Texas 76703

**Abstract**—To determine the reason why the adsorption of ethylene glycol on organo-smectites does not result in an expansion along the *c*-axis of the clays, smectites containing relatively small organo-ammonium ions (lauryl-, benzyl-, dibenzyl-, and dicyclohexylammonium), larger organic cations (dimethylbenzylotadecyl- and methylbenzylododecylammonium), and the heterocyclic organo-ammonium ion 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethylammonium and the corresponding ethoxylated compound were exposed to ethylene glycol vapor for up to several months and examined by X-ray powder diffraction (XRD), surface area, and thermogravimetric methods. Weight loss data showed that all samples adsorbed ethylene glycol. XRD data for oriented samples indicated that lauryl-, benzyl-, dicyclohexyl-, and ethoxylated heterocyclic ammonium clays expanded by one layer of ethylene glycol and that methylbenzylododecylammonium smectite expanded by two layers. Dibenzyl-, dimethylbenzylotadecyl-, and heterocyclic smectites did not expand because the clay oriented in such a manner as to leave free clay surface between the organo-ammonium cations.

**Key Words**—Adsorption, Amine, Ethylene glycol, Expansion, Montmorillonite.

### INTRODUCTION

Complexes of ethylene glycol and glycerol with montmorillonite have been studied more than any other organo-clay complex (Brindley, 1966). Ethylene glycol and glycerol are also commonly used in surface area determinations of clays. Kinter and Diamond (1963) and Diamond and Kinter (1958) determined the area covered by an amine ion associated with the clay surface by dispersing an amine-substituted montmorillonite in an aqueous glycerol solution and drying the clay to constant weight at about 100°C to remove the water and excess glycerol. They showed that as the size of the exchange amine ion increased (from methylamine to tri-*n*-amylamine), the amount of glycerol taken up by the clay decreased until the surface was completely covered by amine ions. A clay whose surface was completely covered by amine ions would not be expected to take up glycerol, and consequently, it should not expand along its *c*-axis.

Surface areas of organo-smectites have been measured for several years in this laboratory by the Kinter and Diamond method, but when organo-smectites were studied by this method, it was found that although all samples adsorbed ethylene glycol, not all samples expanded along the *c*-axis, as shown by X-ray powder diffraction analysis. The present study was made to determine why some organo-clays expanded under these conditions and others did not.

### EXPERIMENTAL

The amine-substituted montmorillonite samples were prepared by the Baroid Division of NL Industries

or at Baylor University by reacting amine salts with centrifuged, spray-dried, sodium-substituted Wyoming montmorillonite in aqueous dispersion and drying the products at about 100°C. Each amine-substituted montmorillonite was ground in a ball mill and passed through a 250 mesh sieve. The samples were then dispersed ultrasonically in enough methylethylketone to yield a 1% clay dispersion by weight. Oriented samples were prepared by sedimenting the clay dispersions on petrographic microscope slides and drying them at 80°C for 24 hr. Drying at elevated temperature was necessary to remove the strongly adsorbed methylethylketone. After drying, the samples were examined by X-ray powder diffraction (XRD) using a Picker X-ray diffractometer and Ni-filtered CuK $\alpha$  radiation. Following the recording of the initial XRD patterns, the samples were placed in an atmosphere of saturated ethylene glycol vapor. After 24 hr, the samples were re-examined by XRD and replaced in the ethylene glycol vapor. This process was repeated periodically over the next 4 to 6 months.

External surface areas were determined by N<sub>2</sub> adsorption at -196°C at varying N<sub>2</sub> partial pressures so that isotherms were obtained for each sample. The data were then fitted to the BET isotherm, and the surface areas were determined. Adsorption measurements were made with a Perkin Elmer Model 212C Sorptometer. The organic compounds exchanged onto the clay were lauryl-, benzyl-, dibenzyl-, dicyclohexyl-, dimethylbenzylododecyl-, methylbenzylododecyl-, 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethyl-(heterocyclic-), and ethoxylated heterocyclic-ammonium cations. The amount of amine present in the amine-substituted montmorillonite samples and the amount of adsorbed ethylene glycol were

<sup>1</sup> Present address: Dow Chemical Company, Freeport, Texas 77541.

Table 1. X-ray powder diffraction data for amine-substituted montmorillonites.

Substituted ammonium cation	Before exposure to ethylene glycol (Å)		After exposure to ethylene glycol <sup>1</sup> (Å)		Expansion of the clay lattice (Å)	Theoretical amine area, (Å <sup>2</sup> )
	001	Δ <sup>2</sup>	001	Δ <sup>2</sup>		
Lauryl	13.6 ± 0.2	4.0	17.0 ± 0.1	7.4	3.4	60
Benzyl	12.7 ± 0.5	3.1	16.7 ± 0.0	7.1	4.0	45
Dibenzyl	15.2 ± 0.0	5.6	15.2 ± 0.0	5.6	0.0	90
Dicyclohexyl	14.2 ± 0.0	4.6	15.5 ± 0.3	8.4	1.3	—
			16.5 ± 0.1	6.9 <sup>3</sup>		
Dimethylbenzyl octadecyl	17.7 ± 0.2	8.1	18.0 ± 0.0	8.4	0.3	150
Methylbenzyl dioctadecyl	29.0 ± 0.1	19.4	36.8 ± 0.0	11.4	7.8	240
Heterocyclic <sup>4</sup>	21.0 ± 0.0	11.4	21.0 ± 0.0	11.4	0.0	100
Ethylated heterocyclic	26.8 ± 0.8	17.2	30.4 ± 0.0	20.8	3.6	160

<sup>1</sup> Exposure for 24 to 48 hr.<sup>2</sup> Δ = 001 spacing - 9.6 Å.<sup>3</sup> Exposure for 7 days.<sup>4</sup> 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethyl.

determined by thermal gravimetric analysis (TGA) with a Perkin Elmer TSG-1 thermal balance which was calibrated with NBS class M weights for the range 0°–1000°C.

#### DATA AND DISCUSSION

Kinter and Diamond (1963) found that the amount of glycerol adsorbed from an aqueous phase by relatively small primary, secondary, and tertiary amine-montmorillonite complexes decreased with the area of the clay covered by a particular amine ion. Their results indicated that if the surface of a montmorillonite was completely covered by a large amine ion, no glycerol would be intercalated. In contrast, the c-axis of the clays in the present study that contained large ions expanded upon exposure to ethylene glycol vapor. Table 1 lists the 001 spacing and interplanar spacing, Δ (Δ = 001 spacing - 9.6 Å), obtained before and after exposure of the samples to ethylene glycol; the expansions of the montmorillonite lattice; and the theoretical areas

of the substituted amines (Fischer-Hirshfelder-Topfel models were used to determine theoretical areas of the various amines).

Table 2 lists the exchanged amine ions, the milliequivalents of amine per gram of clay, the experimentally determined external surface area, the weight of adsorbed ethylene glycol, the number of molecules of ethylene glycol per exchange site, and the available area per ion. The amount of ethylene glycol that was adsorbed to the basal surfaces of the montmorillonites is arbitrarily expressed in molecules of ethylene glycol per cation-exchange site. Variation in the available area per exchange ion from sample to sample is due to the fact that while the surface area of the basal planes and the average charge density of montmorillonite are constant, the amount of the substituted amine ions changes from one montmorillonite sample to another.

After a 24-hr period, the only samples that did not expand were dibenzylammonium, dimethylbenzyl octadecylammonium, and 1,4a-dimethyl-7-isopropyl-

Table 2. Thermal gravimetric analysis data for amine-substituted montmorillonite.

Substituted ammonium cation	Meq ammonium cation/100 g clay	External surface area (m <sup>2</sup> /g)	Molecules of ethylene glycol/exchange site	Available area/ion (Å <sup>2</sup> )	Weight of ethylene glycol + amine/gram of clay (g)	Weight of amine/gram of clay (g)	Weight of ethylene glycol/gram of clay (g)
Lauryl	1.16	10	0.7	115	0.277	0.215	0.062
Benzyl	0.94	15	2.0	142	0.117	0.102	0.015
Dibenzyl	0.97	53	0.8	138	0.281	0.193	0.088
Dicyclohexyl	N.M. <sup>1</sup>	negligible	N.M.	N.M.	N.M.	N.M.	N.M.
Dimethyl benzyl octadecyl	0.95	negligible	0.8	140	0.427	0.370	0.057
Methylbenzyl dioctadecyl	1.09	negligible	4.0	122	0.792	0.507	0.285
Heterocyclic <sup>2</sup>	0.99	negligible	1.6	135	0.473	0.357	0.116
Ethylated heterocyclic	0.81	negligible	0.4	164	0.635	0.622	0.013

<sup>1</sup> N.M.—not measured.<sup>2</sup> See Table 1.

1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethylammonium (hereafter referred to as heterocyclic ammonium) montmorillonite. The expansion of amine-substituted montmorillonites may be controlled by: (1) the orientation of the amine cation with respect to the montmorillonite surface, and (2) the amount of the montmorillonite surface that the amine molecule is capable of covering. Such a model requires the following assumptions:

1. Due to hydrogen bonding, ethylene glycol has a greater affinity for clay surfaces than do hydrocarbon chains and rings.
2. Ethylene glycol will adsorb to uncovered clay surfaces before competing for clay surface with other adsorbed or exchanged material.
3. If a clay surface is completely covered by a large amine cation, where the organic chains are in contact with the clay surface, it will be difficult for ethylene glycol to migrate under these molecules to adsorb on the clay surface.
4. If a long alkyl chain is buckled due to crowding from other chains, ethylene glycol can adsorb under the chain, lifting it off of the clay surface and allowing other ethylene glycol molecules to adsorb more readily.

To prove or disprove this model, the data for some of the organo-clays studied will be examined in light of the assumptions.

#### Laurylammonium montmorillonite

The XRD pattern of laurylammonium montmorillonite yielded four integral orders of the 001 reflection. The 001 spacing of 13.6 Å represents an interplanar distance of 4.0 Å which corresponds closely to the average thickness of a straight hydrocarbon chain. The area covered by each laurylammonium ion is about 60 Å<sup>2</sup> and comprises only 50–60% of the area of an exchange site (about 130 Å<sup>2</sup>). To account for the observed 001 spacing obtained before the sample was exposed to ethylene glycol, the chains associated with adjacent faces must have been staggered in such a way that all of the chains were virtually coplanar; otherwise the 001 spacing would have been greater than 13.6 Å.

When the sample was exposed to ethylene glycol vapor for 24 hr the clay expanded along the c-axis to a final 001 spacing of 17.0 Å, a value that is 0.6 Å less than the predicted value of 17.6 Å. Before exposure to ethylene glycol, each laurylammonium ion was apparently in contact with two montmorillonite particles. Because the projected area attributed to the laurylammonium cation is ~50% of the area of an exchange site, the entire internal surface of the clay is presumed to have been covered by organic material. As the particles were forced apart by adsorption of ethylene glycol, the amine cations remained with their respective clay par-

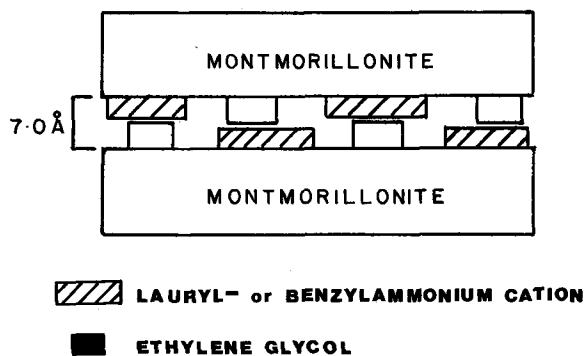


Figure 1. Schematic illustration of the proposed complexes of laurylammonium and benzylammonium montmorillonite and ethylene glycol.

ticles to which they were exchanged, thus creating “uncovered” surface on the clay on which further ethylene glycol molecules could have been adsorbed. A schematic representation of these resulting complexes is shown in Figure 1. Figure 1 represents a model where ethylene glycol molecules adsorbed to one clay particle are oriented above laurylammonium ions of the adjacent clay particles yielding an 001 spacing of 4 Å (ethylene glycol) + 4 Å (laurylammonium) + 9.6 Å (clay) = 17.6 Å, which compares well with the observed 001 spacing.

#### Benzylammonium montmorillonite

XRD spacings of benzylammonium montmorillonite samples expanded from 12.7 Å to 16.7 Å with the adsorption of ethylene glycol. The theoretical area covered by a benzylammonium ion is 45 Å<sup>2</sup>. The maximum thickness of this ion is about 4 Å; whereas a benzene ring has a thickness of 3 Å. The interlayer space of 3.1 Å (12.7 Å – 9.6 Å) can be accounted for by a keying of the nitrogen into hexagonal holes in the silicate surface. Since the benzylammonium ion covered less than half of the available exchange site area (Table 2), only one layer of organic material could have resulted between adjacent plates.

As with laurylammonium montmorillonite, each benzylammonium ion is expected to contact two clay surfaces. The 001 spacing of the ethylene glycol-adsorbed benzylammonium montmorillonite complex was 16.7 Å, indicating that ethylene glycol adsorbed in a manner similar to that shown in Figure 1.

#### Dibenzylammonium montmorillonite

The dibenzylammonium montmorillonite samples exhibited the most uniform XRD patterns of all of the organo-clays investigated. Deviations between the 001 spacings of the samples before and after exposure to ethylene glycol were observed in the third, fifth, and sixth orders, but the differences were too small to be significant.

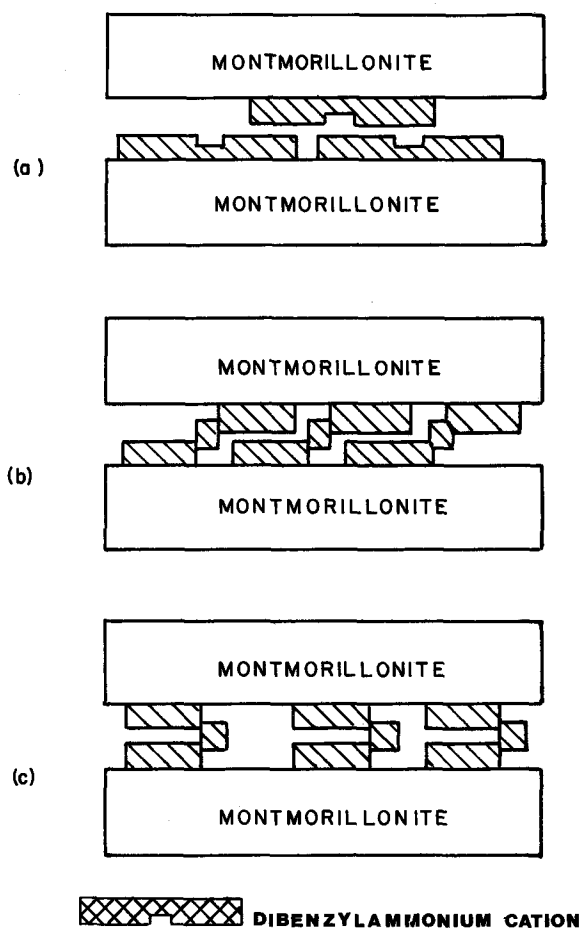


Figure 2. Schematic illustrations of three possible orientations of dibenzylammonium ion adsorbed on montmorillonite surfaces.

Dibenzylammonium montmorillonite samples were so resistant to expansion by ethylene glycol adsorption that no change in the 001 values was noted even after several months of exposure to the reagent. However, TGA data indicated that 0.8 molecule of ethylene glycol adsorbed per exchange site. Furthermore, dibenzylammonium ion covered only about 60% of the surface, leaving 40% of uncovered surface available for ethylene glycol adsorption.

Dibenzylammonium ions may take on a number of configurations on a clay surface when unhindered, but tilt when crowded (Theng, 1974). Since the amount of amine ion exchanged was less than the exchange capacity of the clay, the packing should not have been dense enough to cause tilting of the rings. The 001 spacing of 15.2 Å allows 5.6 Å between the clay particles, which corresponds roughly to the thickness of two aromatic rings, each 2.8 Å thick. Conformations a, b, and c in Figure 2 are consistent with the observed 001 spacing. Since benzyl groups lie flat on the clay surface,

ethylene glycol apparently cannot adsorb under them; thus ethylene glycol can adsorb only to areas that are not covered by the amine. However, unlike the benzylammonium ion discussed above which covers only about 45 Å<sup>2</sup>, there is a substantial amount of overlapping of the aromatic rings in this case.

Expansion of the c-axis would be expected if dibenzylammonium ions assume either configuration a or b in Figure 2 because ethylene glycol would be expected to adsorb in the same way as it adsorbs on benzylammonium montmorillonite. The resulting 001 spacing of such a complex would be 16.6 Å or greater. Configuration c in Figure 2 is consistent with the observed data because the ions are about 5.6 Å thick as calculated from Fischer-Hirschfelder-Topfel models. Ethylene glycol could have adsorbed on the "free" clay surface and not cause expansion because these molecules are only about 4 Å thick.

#### *Dicyclohexylammonium montmorillonite*

Dicyclohexylammonium samples had c-axis spacings of 14.2 Å. After exposure to ethylene glycol for 24 hr, the samples expanded to 15.5 Å and to 16.5 Å after 7 days of exposure. The long period of time involved in the adsorption indicates that adsorption of glycol was sterically hindered. The final 001 spacing of 16.5 Å suggests a glycolated structure similar to that of laurylammonium montmorillonite.

#### *Dimethylbenzyl-octadecylammonium montmorillonite*

XRD patterns obtained from the dimethylbenzyl-octadecylammonium complex exhibited a high degree of uniformity. After exposure to ethylene glycol for 24 to 48 hr, the diffraction patterns of the three samples were identical, and expansion was 0.4 Å. The 001 spacing for the sample before exposure to ethylene glycol was 17.7 Å, allowing 8.1 Å for interlayer material. This distance corresponds to two layers of organic material between the clay platelets. The slight increase in the 001 spacing after exposure to ethylene glycol might have been due to a configuration change of the amine chains on the clay surfaces. This change could have been caused by ethylene glycol molecules adsorbing on the clay surfaces in such a way as to cause the hydrocarbon chains to lift up slightly.

As shown in Figure 3, after the samples had been exposed to ethylene glycol for six months, anomalous peaks appeared at about 36 Å. These peaks disappeared when the samples were heated at 80°C for 30 min. The only significant change occurred in the 36-Å peak. Furthermore, from Figure 4, it can be seen that the ethylene glycol adsorption was very slow, with the 36-Å peak appearing after one week, but not becoming very significant until after two weeks. It took about six months for the peak to reach its maximum observed intensity.

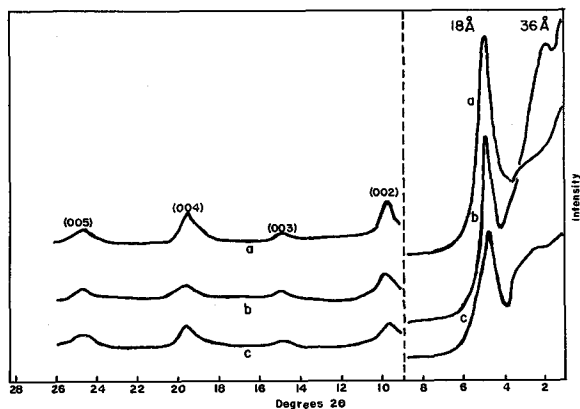


Figure 3. X-ray powder diffraction patterns of dimethylbenzyl-octadecylammonium montmorillonite (a) before exposure to ethylene glycol, (b) after exposure to ethylene glycol for 6 months, and (c) after exposure to ethylene glycol for 6 months and heating at 80°C for 30 min.

It might seem that a substantial expansion took place in this sample and that the new 001 spacing was 36 Å. However, if the surfaces of two associated clay particles had been completely covered with ethylene glycol so that the octadecyl chains were lifted off of the basal surface, the resulting expected 001 spacing would have been  $2 \times (4 \text{ Å}) + 8.1 \text{ Å} + 9.6 \text{ Å} = 25.7 \text{ Å}$ , which is 10 Å less than the observed 001 value. This discrepancy can be accounted for if the octadecyl chains were oriented perpendicular to the clay surfaces. However, such an effect should have been observed only if the clay surface was packed with long chain amines in amounts exceeding its cation-exchange capacity, or with long chain alcohols (Kinter and Diamond, 1963). Ethylene glycol is not large enough to have caused the chains to orient in such a manner.

An alternative explanation of the above observations is that the ethylene glycol molecules that adsorbed on uncovered clay surfaces caused the octadecyl chains to assume different configurations. Eventually, the packing of organic material on the clay surface became uniform, causing opposing clay particles to face one another in such a manner as to yield constant interparticle distances over the entire interparticle region, giving rise to two-unit-cell diffraction. The result of a diffraction by two "unit cells" is that the observed spacing is twice the value of the 001. If the 36 Å peak is assigned Miller indices of  $00\frac{1}{2}$  and the 18.0 Å peak is assigned Miller indices of 001, the remaining reflections would be assigned Miller indices of 003 and 004. These reflections are the same as those that were observed after only 24 hr of exposure to ethylene glycol.

#### *Methylbenzyl-dioctadecylammonium montmorillonite*

Only the 001 reflection of methylbenzyl-dioctadecylammonium montmorillonite, 29.0 Å, was observed

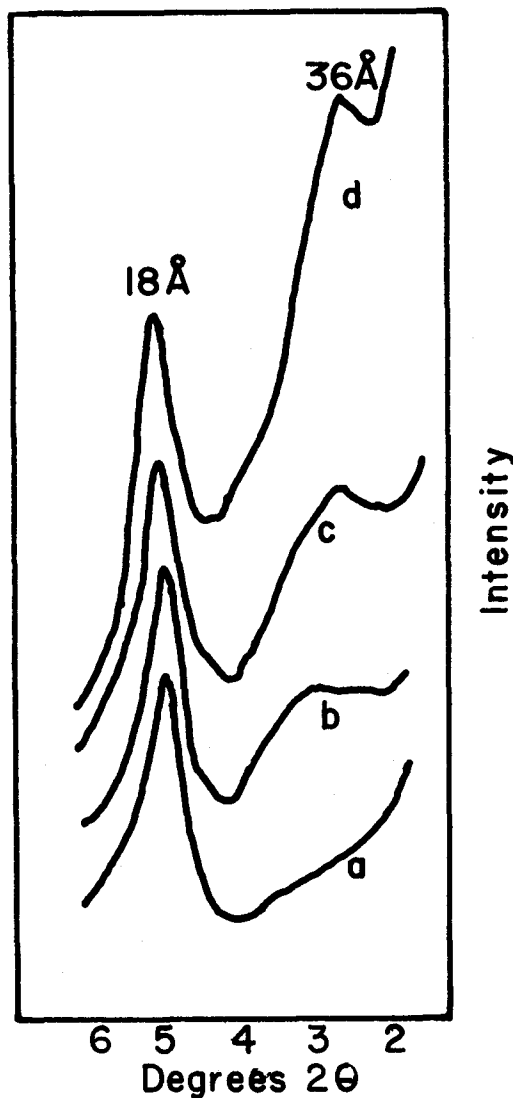


Figure 4. X-ray powder diffraction patterns of dimethylbenzyl-octadecylammonium montmorillonite (a) before exposure to ethylene glycol, (b) after exposure for one week, (c) after exposure for 2 weeks, and (d) after exposure for 6 months.

before the samples were exposed to ethylene glycol. After exposure; the 001 spacing increased to 36.8 Å, and higher order reflections at 18.7 Å and 9.4 Å were observed. The appearance of these peaks suggests that adsorption of ethylene glycol caused increased uniformity of particle stacking.

A methylbenzyl-dioctadecylammonium cation is capable of covering 250 Å<sup>2</sup> of clay surface. However, since there was 1.09 meq of amine per gram of clay, the average area available for an ion was 122 Å<sup>2</sup>. Thus, the octadecyl chains must have been situated on top of one another, yielding four layers of organic material with an 001 spacing of  $4 \times (4 \text{ Å}) + 9.6 \text{ Å} = 25.6 \text{ Å}$ . The observed 001 spacing was 29.0 Å. A concentration of 1.09



meq of amine per gram of clay caused the separation of the clay particles to be greater than the expected 16 Å for four layers of aliphatic chain.

Methylbenzylidioctadecylammonium montmorillonite took up about four ethylene glycol molecules per exchange site, which is a large amount of ethylene glycol compared with the amounts adsorbed by the other samples in this study. The amount of expansion of the c-axis was 7.8 Å, which corresponds to two layers of ethylene glycol. The most significant property of this sample is that its c-axis expanded even though the surface of the clay was completely covered by the exchange ion. Ethylene glycol apparently adsorbed because the octadecyl chains were lifted up off of the surface due to the buckling.

*1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethylammonium montmorillonite*

In addition to the main 001 reflection at 21 Å, a pronounced shoulder was present at 26 Å in each pattern before and after exposure to ethylene glycol, as well as an integral multiple of this shoulder at 13 Å. This shoulder may have been due to heterogeneity in the packing of the heterocyclic ion on the clay. If some of the ions were not parallel to the clay surface, a larger 001 spacing would have resulted.

The amount of organic ion was 0.99 meq of amine per gram of clay, providing 135 Å<sup>2</sup> of surface area covered per ion. The ions apparently stacked in a manner similar to that shown in Figure 5. The resulting thickness of two ions was approximately 11.7 Å producing a 001 spacing of about 21 Å. Such a stacking arrangement would have left a substantial amount of the internal surface that was uncovered and available for adsorption of ethylene glycol. Experimentally, the samples adsorbed about one ethylene glycol molecule per exchange site; however, no c-axis expansion occurred because the ion is so thick that even a double layer of ethylene glycol was not enough to cause expansion. Also, the ion was too rigid for ethylene glycol to displace it from the clay surface.

*Ethoxylated 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethylammonium montmorillonite*

This heterocyclic ammonium ion is similar to the heterocyclic ion described above except that the nitrogen has additional hydrocarbon chains added, thereby increasing its size. After exposure to ethylene glycol, the sample expanded to an 001 spacing of 30.4 Å, which corresponds to five layers of hydrocarbon material. Before adsorption of ethylene glycol, four layers of amine ions were between clay plates.

A comparison of the results obtained on this sample

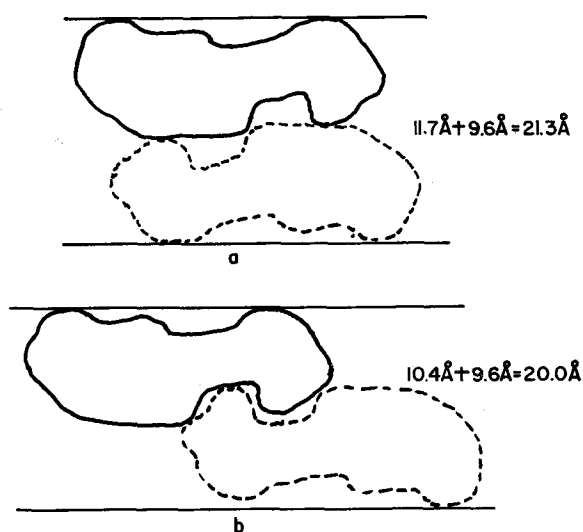


Figure 5. Schematic illustration of the packing of two 1,4-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenemethylammonium ions between montmorillonite plates yielding a 20.0-Å 001 spacing (the organic part of the schematic illustration was obtained from a projection of a Fischer-Hirschfelder-Topfel model).

with the previously discussed heterocyclic clay indicates that the addition of the ethoxy groups resulted in the clay surface being covered with organic molecules, and that the adsorption of ethylene glycol on the clay surface caused an expansion along the c-axis. The ethylated nitrogen group is a fairly flexible part of the molecule, compared to the rigid heterocyclic groups.

## CONCLUSIONS

XRD and TGA analysis of amine-substituted montmorillonites indicate that although the samples adsorbed ethylene glycol from the vapor phase, their c-axes did not necessarily expand. Expansion depended on the orientation and thickness of the substituted amine as well as on the amount of clay surface that was available for adsorption. During adsorption, ethylene glycol was capable of displacing hydrocarbon chains only if they had already raised from the clay surface. Ethylene glycol did not displace large, rigid organic cations.

## ACKNOWLEDGMENT

The authors thank the Robert A. Welch Foundation for support of this research.

## REFERENCES

- Brindley, G. W. (1966) Ethylene glycol and glycol complexes of smectites and vermiculites: *Clays & Clay Minerals* **6**, 237-259.
- Diamond, S. and Kinter, E. B. (1958) Surface areas of clay minerals as derived from measurements of glycerol reten-

tion: in *Clays and Clay Minerals*, Proc. 5th Natl. Conf. Clays and Clay Minerals, Urbana, Illinois, 1956, Ada Swinford, ed., *Natl. Acad. Sci. Natl. Res. Council. Publ.* 566, Washington, D.C., 334-347.

Kinter, E. B. and Diamond, S. (1963) Characterization of montmorillonite saturated with short-chain amine cations: 2. Interlayer surface coverage by amine cations: in *Clays*

and *Clay Minerals*, Proc. 10th Natl. Conf. Clays and Clay Minerals, Austin, Texas, 1961, Ada Swinford and P. C. Franks, eds., Pergamon Press, New York, 174-190.

Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions*: Halsted Press, London, 48-62, 64-67.

(Received 13 August 1979; accepted 11 May 1980)

**Резюме**—Для того, чтобы найти причину почему адсорбция этиленгликоля органо-сметтитами не вызывает расширения вдоль оси с глин, сметтиты, содержащие сравнительно небольшие органо-аммониевые ионы (лорил-, бензил-, лобезил-, и дициклогексиламмоний), большие органические катионы (диметилбензилоктадил- и метилбензилдиокт адециламмоний), и гетероциклический органо-аммониевый ион 1,4а-диметил-7-изопропил-1,2,3,4,4а,9,10,10а-октагидро-1-фенатренеметиламмоний и соответствующее этоксилазированное соединение были подвергнуты обработке паром этилена гликоля на протяжении нескольких месяцев и исследованы порошковым методом рентгено-структурного анализа (РСА), методом поверхностной площади, и термогравиметрическим методом. Данные потери веса указывают на то, что все образцы адсорбировали этилен гликоль. Данные РСА ориентированных образцов показали, что лорил-, бензил-, дициклогексил-, и этоксилазированные гетероциклические аммониевые глины расширились на один слой этилена гликоля и что метилбензилдиоктадециламмониевый сметтит расширился на два слоя. Дибензил-, диметилбензил-, октадецил-, и гетероциклические сметтиты не расширились потому что глина ориентирована так, что оставляет свободную глинистую поверхность между органо-аммониевыми катионами. [N.R.]

**Resümee**—Um zu untersuchen, warum die Adsorption von Ethylenglycol an Organo-Smektiten kein Quellen der Tone in Richtung der c-Achse verursacht, wurden Smektitte, die die folgenden Ionen enthielten, für einige Monate Ethylenglycoldampf ausgesetzt und anschließend mittels Röntgendiffraktometrie, Oberflächen- und thermogravimetrischen Methoden untersucht: relativ kleine Organo-Ammoniumionen (Lauryl-, Benzyl-, Dibenzyl-, und Dicyclohexylammonium), größere organische Kationen (Dimethylbenzyl-octadecyl- und Methylbenzyl-dioctadecylammonium), und das heterocyclische Organo-Ammoniumion 1,4a-Dimethyl-7-Isopropyl-1,2,3,4,4a,9,10,10a-Octahydro-1-Phenanthrenemethylammonium und die entsprechende ethoxylierte Verbindung. Ergebnisse über den Gewichtsverlust zeigen, daß alle Proben Ethylenglycol adsorbieren. Röntgendiffraktometerdaten von orientierten Proben deuten darauf hin, daß Lauryl-, Benzyl-, Dicyclohexyl-, und ethoxylierte heterocyclische Ammonium-Tone um eine Schicht Ethylenglycol quellen und Methylbenzyl-dioctadecylammonium-Smektit um zwei Schichten. Dibenzyl-, Dimethylbenzyl-octadecyl-, und heterocyclische Smektitte quellen nicht, da diese Tone in einer Weise orientiert sind, die freie Tonoberflächen zwischen den Organo-Ammoniumkationen übrig läßt. [U.W.]

**Résumé**—Pour déterminer la raison pour laquelle l'adsorption de glycol éthylène sur des organo-smectites ne résulte pas en une expansion le long de l'axe-c des argiles, des smectites contenant des ions organo-ammonium relativement petits (ammonium-lauryl-, -benzyl-, -dobenzyl, et -dicyclohexyl), des cations organiques plus grands (ammonium-diméthylbenzyl-octadyl et -méthylbenzyl-dioctadecyl), et l'ion organo-ammonium hétérocyclique ammonium 1,4a-diméthyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-1-phénanthreneméthyl et le composé éthoxylaté correspondant ont été exposés à la vapeur de glycol éthylène pendant plusieurs mois et examinés par des méthodes de diffraction poudrée aux rayons-X (XRD), d'aire de surface, et thermogravimétriques. Des données de perte de poids ont montré que tous les échantillons avaient adsorbé le glycol éthylène. Des données XRD pour des échantillons orientés ont indiqué que les argiles ammonium-lauryl-, -benzyl-, -dicyclohexyl, et hétérocycliques éthoxylatés se sont dilatés par une couche de glycol éthylène et que la smectite méthylbenzyl-dioctadecylammonium s'est dilatée par deux couches. Les smectites-dibenzyl-, -diméthylbenzyl-octadecyl et hétérocycliques ne se sont pas dilatées parce que l'argile s'était orientée de telle manière qu'une surface libre d'argile était laissée entre les cations organo-ammonium. [D.J.]