

A STUDY OF THE MORPHOLOGY AND PROPERTIES OF ARYL AND ALKYL AMMONIUM MONTMORILLONITES: AN ELECTRON MICROSCOPE INVESTIGATION

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Abstract—The effect of exchanging selected aryl and alkyl ammonium cations for sodium ions on the morphology and the hydrophobicity of a sodium montmorillonite was studied. It was found that the morphology of the organo-clays as observed by transmission electron microscopy depended on the type of and the amount of exchanged organic cation. An attempt was made to correlate the observed morphology of organo-clays with their hydrophobicity.

INTRODUCTION

The purpose of this report is to study the effects of the type and the amount of exchanged organic cations on the morphology and hydrophobicity of montmorillonite. The properties and structure of alkyl and aryl ammonium complexes of montmorillonite have been extensively studied, although apparently more attention has been given to the alkyl ammonium complexes. The early studies of Jordan (1949) were extensive both with regard to the structure of *n*-alkylammonium complexes and the organophilicity of such complexes. The arylammonium complexes have been primarily studied with an emphasis on structural properties by McAtee and Concilio (1959), Hoffmann and Brindley (1960), Bradley (1945), and McAtee and Hawthorne (1964).

Besides Jordan's (1949) work, others have studied the organophilic properties of *n*-alkylammonium montmorillonites. Slabaugh (1964) found that certain such complexes of montmorillonite would spread to form a film on water, and that hydrophobicity increased with increasing length of the alkyl chain. In an electron microscope investigation, McAtee and Cheng (1967) showed the effect of dispersion in various organic solvents on the interstratification of dimethyldioctadecylammonium montmorillonite.

EXPERIMENTAL

The organo-montmorillonites were prepared by exchanging the desired arylammonium cation for sodium ion on an ion exchanged, freeze dried sodium-montmorillonite obtained from Baroid Division, NL Industries. This clay according to its X-ray diffraction pattern is 99.8 per cent montmorillonite of the typical Wyoming type. It has an ammonium acetate C.E.C. value of 96 m-equiv./100 g dry clay.

Since the clay was commercially prepared, it is probably a composite of the several mines in operation by Baroid at the time of its production. Two of the organo-montmorillonites studied were obtained already exchanged (100 per cent) from the Baroid Division. These two were the dimethyldioctadecylammonium montmorillonite (Bentone-34) and the dimethylbenzyl-octadecylammonium montmorillonite (Baragel-24). The starting clay for both of these commercial products is probably similar to the sodium-montmorillonite described above.

In preparing the other samples, the desired number of m-equiv. of the organic salt in solution was added, with stirring, to a 1 per cent dispersion of the sodium montmorillonite. Stirring was continued for 15 min and the dispersion then allowed to stand for 24 hr to complete the exchange. The exchanged clay was then removed by centrifuging and washed repeatedly to remove excess electrolyte. Completeness of washing was determined by analyzing the wash water for chloride ion. The samples were then dried at 80°C and pulverized.

Samples for electron microscope investigation were prepared in a manner previously described (Jernigan and McAtee, 1975). In the majority of cases, the dried clay was dispersed in amyl acetate and then critical point dried. All of the samples were carefully prepared under identical conditions using 400 mesh copper grids with a carbon film. In one particular series, the undried centrifuged clay was dispersed directly in amyl acetate and then critical point dried. The clays were all dispersed (0.1 per cent suspension) ultrasonically and critical point dried using liquid CO₂ in the DCP-1 Critical Point Drying Apparatus (Denton Vacuum, Inc., Cherry Hill, New Jersey). The prepared samples were examined in a Hitachi HU-11A electron microscope.

Gel volume data for the organo-montmorillonites in several solvents was determined by a procedure similar to the one used by Jordan (1949). A 25.0 ml

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graduated cylinder containing exactly 25.0 ml of the desired solvent was used to determine the gel volume of a 0.50 g sample of the clay. The dry clay was added slowly and carefully to the graduate cylinder in such a way that there was no clumping of the sample or sticking to the sides of the graduated cylinder. The clay in the graduate cylinder was then allowed to sit for a minimum of 24 hr before the apparent volume of the gel was then read in units of ml/g.

RESULTS AND DISCUSSION

The organo-montmorillonites examined in this study were as follows: dimethyldioctadecylammonium montmorillonite; *n*-dodecylammonium montmorillonite; dimethylbenzyl-octadecylammonium montmorillonite; dibenzylammonium montmorillonite; benzylammonium montmorillonite; β -phenylethylammonium montmorillonite; and diisopropylchloroethylammonium montmorillonite.

Two parts of the electron microscope investigation are reported here. In one study, the above organo-montmorillonites were studied as a series to determine what effect the different types of exchange cations had on particle morphology. In this series, all of the montmorillonites were 100 per cent exchanged, i.e. 100 m-equiv. alkylammonium salt was added to 100 g clay in the preparation. In the second study, the effect of extent of exchange was investigated for the diisopropylchloroethylammonium complex. A series of exchanged clays were prepared by adding 20, 40, 60, 80 and 100 m-equiv. salt to 100 g original sodium montmorillonite in 1 per cent dispersion. Hereafter, these samples will be referred to as 20, 40, 60, 80 and 100 per cent exchanged. An electron microscope investigation was made of each of these samples.

Figures 1-5 are electron micrographs representative of the type of morphology observed for the various 100 per cent exchanged organo-montmorillonites. The micrographs reveal a striking difference in observed morphology between the strictly arylammonium substituted clays and those exchanged with alkylammonium ions. For example, Fig. 1 showing dimethyldioctadecylammonium montmorillonite shows very extensive particle to particle interactions with unusual orientations and curling of the sample. Similar micrographs were obtained for *n*-dodecylammonium and dimethylbenzyl-octadecylammonium montmorillonites. Among these three, the extent of curling is greatest for the dimethyldioctadecylammonium complex with the *n*-dodecylammonium and dimethylbenzyl-octadecylammonium clays showing a lesser amount of curling and being roughly comparable to each other in the extent of curling.

Figure 2 is typical of the diisopropylchloroethylammonium montmorillonite. This clay shows the smallest degree of curling in the sense that the system appears to be somewhat more heterogeneous than the other alkylammonium montmorillonites. In some areas there is very pronounced interaction and curl-

ing, but in other areas the clay particles are platelike and flattened. In this respect, the particles resemble the precursor sodium montmorillonite.

Figure 3 shows an electron micrograph for the dibenzylammonium montmorillonite studied. Electron micrographs for benzylammonium and β -phenylethylammonium montmorillonites gave similar results. It should be pointed out, however, that the strict classification of these clays into aryl and alkylammonium types can be only approximate in the case of the dimethylbenzyl-octadecyl and β -phenylethylammonium montmorillonites. On the basis of the results, however, the classification does seem to be justified. The clays (illustrated by Fig. 3) show little particle-particle interaction and a lack of curling in comparison to the alkylammonium montmorillonites. The smaller particles and aggregates with the flattened plates are, in this respect, much more similar in morphology to sodium montmorillonite.

Figure 4 shows a typical area photographed from the 20 per cent exchanged sample of diisopropylchloroethylammonium montmorillonite. Figure 5 is an electron micrograph of two aggregates of a 100 per cent exchanged diisopropylchloroethylammonium montmorillonite which shows considerable greater amount of curling than shown in Fig. 4. For the sake of brevity, electron micrographs were not included for the entire exchange series from 20-100 per cent. Only the extremes of the series are shown here. However, the study clearly revealed, as is shown in Figs. 4 and 5, that the extent of interaction and curling of particles increased as the amount of organic cation was increased. The observed unique morphology involving curling was directly the result of the interaction of the diisopropylchloroethylammonium ion on the clay surface. The entire series revealed in addition that there was a rather uniform change in particle morphology from a morphology near to that of sodium montmorillonite (the starting material) to the morphology of the 100 per cent exchanged clay shown in Fig. 5.

The electron micrographs presented demonstrate that the morphology of the organo-montmorillonites is a function both of the type of organic cation present and the extent of exchange of the organic cation for the sodium ion in a sodium montmorillonite. The curling and particle-particle interaction of the alkylammonium montmorillonites is particularly striking. In an attempt to understand the origin of this phenomenon, other observations made in the course of this study are of importance.

As Jordan (1949) originally demonstrated, the organophilicity (and hydrophobicity) of an alkylammonium montmorillonite increases both with extent of exchange (for a particular cation), and with increasing length of carbon chain for a fixed amount of exchange. We observed, in addition, that for the 100 per cent exchanged clays there was a marked difference in hydrophobicity between the various clays. Dimethyldioctadecylammonium, dimethylbenzyl-octadecylammonium, and *n*-dodecylammonium mont-

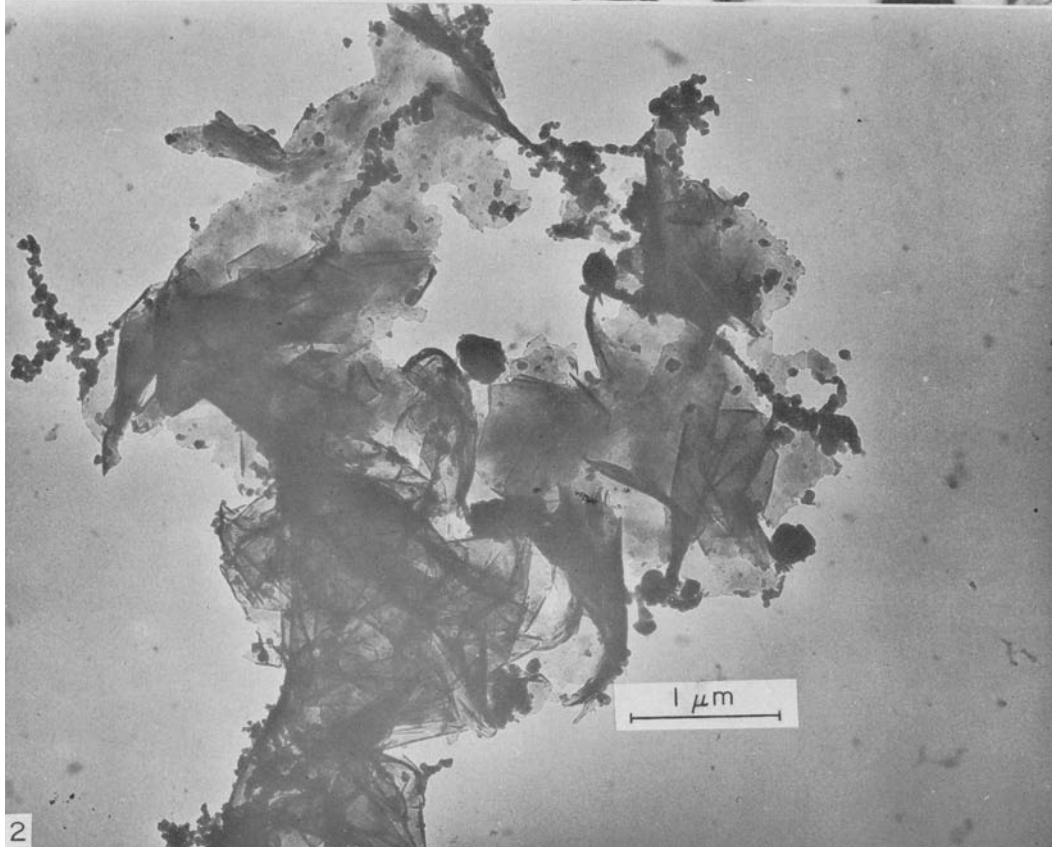


Fig. 1. Electron photomicrograph of dimethyldioctadecyl-ammonium montmorillonite (100 per cent exchanged).

Fig. 2. Electron photomicrograph of diisopropylchloroethylammonium montmorillonite (100 per cent exchanged).



Fig. 3. Electron photomicrograph of dibenzylammonium montmorillonite (100 per cent exchanged). Magnification 24,000 \times .

Fig. 4. Electron photomicrograph of diisopropylchloroethylammonium montmorillonite (20 per cent exchanged). Magnification 41,000 \times .

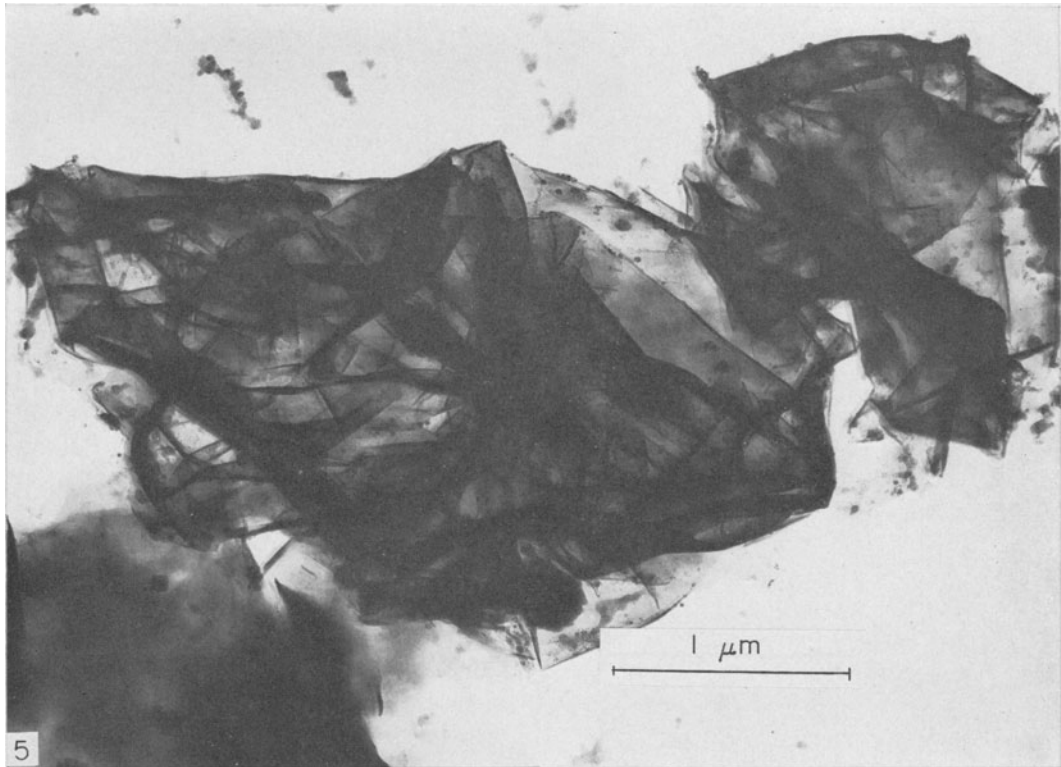


Fig. 5. Electron photomicrograph of diisopropylchloroethylammonium montmorillonite (100 per cent exchanged). Magnification 52,000 \times .

Table 1. Gel volumes of organo-montmorillonites

Exchange Cation	Gel volume (ml/g)	Solvent
benzylammonium	2.0	n-octanol
dibenzylammonium	2.0	n-octanol
β -phenylethylammonium	4.2	n-octanol
n-dodecylammonium	5.8	n-octanol
diisopropylchloroethylammonium	2.0	n-octanol
dimethyldioctadecylammonium	6.0	n-octanol
dimethylbenzyloctadecylammonium	2.0	n-octanol
dibenzylammonium	3.0	\pm toluene-methanol
β -phenylethylammonium	3.3	\pm toluene-methanol
n-dodecylammonium	4.0	\pm toluene-methanol
dimethyldioctadecylammonium	28.0	\pm toluene-methanol
dimethyldioctadecylammonium	12.4	amyl acetate
dimethylbenzyloctadecylammonium	5.0	amyl acetate
benzylammonium	2.5	amyl acetate

\pm 80 per cent toluene and 20 per cent methanol (by volume)

morillonite all showed strong hydrophobicity. For example, all three of these dried clays formed surface films on water when an attempt was made to disperse them. These three clays would disperse to only a very small extent in water even with strenuous ultrasonic methods. It must be remembered that these three clays were the ones which showed the largest amount of curling and association according to the electron micrographs. In contrast to these, the three arylammonium montmorillonites (benzyl, dibenzyl, and β -phenylethylammonium) went into the water system and dispersed much more readily. The diisopropylchloroethylammonium montmorillonite, which was intermediate in morphology, was also intermediate between the two general groups of clays mentioned above.

In an attempt to gain more quantitative information about the organophilic character of the clays, gel volumes were determined in several solvents by a method similar to the one used by Jordan (1949). Table 1 contains the gel volume data. It has been pointed out (Jordan, 1949), that it is difficult to make general conclusions about organophilicity from such data, because an organo-clay has both polar and non-polar characteristics even after extensive exchange. We find this to be true in the data reported in Table 1. For example, the largest gel volume reported is for perhaps the most organophilic of all the samples (dimethyldioctadecylammonium montmorillonite) in a non-polar solvent (toluene) containing a small amount of a polar component (methanol). However, the general trend of the data is such that the overall differences in organophilicity are apparent even though some individual exceptions are noted. These exceptions point to the fact that it is difficult to make generalizations about a series of clays which may have very unique individual characteristics.

In considering the origin of the curling and association seen in Figs. 1–3, two possibilities seem to exist. The curling and association may occur in the aqueous dispersion at the time when exchange of the organic

cation for sodium ion is occurring. As the exchange process proceeds, the clay is being transformed from a hydrophilic to a hydrophobic material in an aqueous phase. It is very possible that the particles may aggregate with overlapping of sheets in order to reduce the surface area exposed to the polar solvent and, at the same time, to increase the interaction between adjacent particles. Another possibility is that the curling and interaction occurs at the point when the dried clays are dispersed in amyl acetate for sample preparation. Several observations point to the first possibility.

When the series of diisopropylchloroethylammonium montmorillonites were prepared, the nature of the resulting aqueous dispersions of organo-clay after standing for 24 hr, showed an interesting trend. At the time of adding the organic cation, all the samples showed flocculation and the flocculation increased from the 20 per cent to the 100 per cent exchanged samples. Also, after 24 hr, the 80 and 100 per cent samples had gelled with only a 1 per cent montmorillonite dispersion. The 60 per cent exchanged sample showed some evidence of gellation but the 20 and 40 per cent samples showed none. It seems possible that the unusual phenomenon of gelling in a 1 per cent dispersion shows that an extensive particle-particle association and perhaps curling have taken place.

In studying the exchange series for diisopropylchloroethylammonium montmorillonite, samples were prepared in two different ways. In one study, the clay samples were dispersed in amyl acetate directly after washing and centrifuging but before drying. At a later time, the series was repeated with samples prepared from the dried and pulverized clay. The particle morphology observed was the same regardless of whether the clay was dispersed before or after drying. In fact, Fig. 2 shows a sample dispersed before drying and Fig. 5 a sample dispersed after drying. This observation suggests the possibility that the observed association and interaction was already present in the water dispersed clay.

Lastly, in examining the gel volume data in Table 1 in amyl acetate, the large difference in gel volume between the dimethyldioctadecylammonium and dimethylbenzyloctadecylammonium montmorillonites appears to be consistent with the similarity in morphology of the samples as seen by electron microscopy. In other words, if the amyl acetate produces the curling and association, then the observed similarities in morphology would not lead one to expect as large a difference in gel volume as observed. The degree of curling as seen in the electron micrographs does reveal a difference between these two samples, but does not suggest a difference of such magnitude as that in the gel volume data.

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REFERENCES

- Bradley, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Am. Chem. Soc.* **67**, 975–981.
- Hoffmann, R. W. and Brindley, G. W. (1960) Adsorption of non-aliphatic molecules from aqueous solutions on montmorillonite: *Geochim. Cosmochim. Acta* **20**, 15–29.
- Jernigan, D. L. and McAtee, J. L., Jr. (1975) Critical point drying of electron microscope samples of clay minerals: *Clays and Clay Minerals* **23**, 161–162.
- Jordan, J. W. (1949) Organophilic bentonites—I. Swelling in organic liquids: *J. Phys. Coll. Chem.* **53**, 294–306.
- McAtee, J. L., Jr. and Concilio, C. B. (1959) Effect of heat on an organo–montmorillonite complex: *Am. Miner.* **44**, 1219–1229.
- McAtee, J. L., Jr. and Hawthorne, J. M. (1964) Heating–oscillating X-ray diffraction studies of some organo–montmorillonites: *Am. Miner.* **49**, 247–257.
- McAtee, J. L., Jr. and Cheng, F. S. (1967) Differences in apparent interstratification of an organo–montmorillonite dispersed in various organic solvents—II. Electron microscopy study: *Am. Miner.* **52**, 1725–1734.
- Slabaugh, W. H. (1964) The spreading of organo–bentonites on water: *J. Coll. Sci.* **19**, 165–172.