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# DIFFERENCES IN APPARENT INTERSTRATIFICATION OF AN ORGANO-MONTMORILLONITE DISPERSED IN VARIOUS ORGANIC SOLVENTS:

# II. ELECTRON MICROSCOPY STUDY

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## ABSTRACT

An earlier paper reported Fourier analysis of X-ray data from samples of organo-montmorillonite dispersed in various organic solvents, and classified the dispersions into four groups. Electron microscopy of the same dispersions gave the same classification, based on differences in morphology, aggregate size, particle-particle associations, and amount of curling of particles.

## INTRODUCTION

The degree and type of interstratification of dimethyldioctadecylammonium montmorillonite after dispersion in various organic solvents were studied by X-ray diffraction methods and reported in a previous paper (McAtee and Cheng, 1967). The diffraction data from oriented films of the specimens obtained at temperatures of 35°, 60° and 100° C were analyzed by Fourier analysis and Fourier transform methods. The Fourier data was then compared to the various physical properties of the organic solvents used to disperse the organo-clay and a general classification of the solvents was made as follows: Group I: methylisobutylketone and acetone; Group II: benzene and a mixture of 10 percent methanol and 90 percent toluene; Group III: butyrolactone, *n*-methyl-2-pyrrolidone, and dimethyl- formamide; and Group IV: dioxane, and cyclohexanone. It was concluded that the amount of apparent interstratification as observed by the X-ray diffraction method was related to the structure of the solvent and to the type and degree of interaction between the solvent and the organo-montmorillonite.

The present paper reports on a second phase of this study where the same group of organic solvents were used to disperse the same organo-montmorillonite, and the specimens were studied by electron microscopy. The purpose was to determine whether or not the morphology of the organo-clay particles varied in a manner which could be correlated with the results of the X-ray diffraction study. In order to reduce the possibility that the electron microscopy study would be clouded by the method used to prepare the specimen, a variety of techniques were used. Some of the sample preparation methods were found to be more enlightening than others, but in general the same conclusions could be drawn from all of the methods employed.

## MATERIAL AND EXPERIMENTAL METHODS

The clay mineral montmorillonite used in this investigation was a centrifuged Wyoming bentonite obtained from the Baroid Division of the National Lead Company, Houston Texas. X-ray diffraction of the sample indicated that it consisted principally of the clay mineral montmorillonite. The organic amine was a commercial material likewise obtained from the Baroid Division of the National Lead Company. The solvents used as dispersion media were all c.p. grade materials obtained from commercial sources. The method of preparation of the organo-montmorillonite was the same as described in the previous paper (McAtee and Cheng, 1967). The organo-montmorillonite contained 105 meq. of organic cation per 100 g of dry clay material.

Stock dispersions of the organo-clay in the various solvents were prepared by means of a Spex-mill. These stock dispersions were then used in the several methods of specimen preparation for electron microscopy evaluation.

The substrate used on the electron microscope copper grids was in all cases prepared from carbon films. The carbon films were prepared by evaporation of carbon onto clean mica in vacuum, separated from the mica by floating onto clean water and subsequently mounted on the specimen screen (Hall, 1956). The dispersed organo-clay specimens were allowed to dry on the carbon substrate film by several different methods. Without going into detail, these methods were as follows:

1. Single drop method: A drop of the organo-clay dispersion was applied to the carbon coated grid surface (supporting film side up), removal of the excess solution accomplished by blotting with a filter paper, and the remaining solution allowed to dry at room temperature.

2. Aerosol produced by supersonic dispersion: Two milliliter portions of the organo-clay dispersion were poured into a small container on a Brinkman supersonic dispersator. The apparatus was operated at a maximum frequency of 3 MHz and at 50 MA. After the aerosol was generated a special spatula containing a carbon coated grid was inserted into the aerosol for about one minute allowing some of the aerosol to settle onto the grid. This was then dried at room temperature.

3. Aerosol produced by a de Vilbiss nebulizer: In this method a portion of the sample was simply blown over the carbon coated copper grid and the aerosol allowed to settle onto the grid and dry at room temperature.

4. Freeze drying: In order to minimize the distortional effect in the drying stage, a freeze drying method as proposed by Williams, 1953, was employed. In this method a piece of metal plate was placed into a Petri dish and a portion of liquid nitrogen was slowly added to the dish until the dish and metal plate were cooled to liquid nitrogen temperature. A number of carbon coated copper grids were then placed on the surface of the chilled metal plate. As soon as the level of liquid nitrogen had receded beneath the surface of the metal plate, a portion of the clay dispersion was sprayed onto the grids by means of a de Vilbiss nebulizer. The entire assembly including the Petri dish was then placed into a vacuum chamber for quick evacuation to remove the solvent.

A slight modification of this procedure was to add to the regularly prepared dispersion, a quantity of petroleum ether and then freeze dry the resulting mixture. The presence of the petroleum ether allowed the specimen to dry more rapidly under the vacuum with apparently very little change in the morphology of the sample.

5. Replication method: In this method clean mica was chosen as a substrate material for the replication of the organo-clay particles. A metal plate holding a sheet of mica with a fresh surface was placed into a Petri dish and a portion of liquid nitrogen slowly poured into the dish as described previously. A bell jar with a small hole at the top was placed over the

metal plate supporting the clean mica sheet. A portion of the clay dispersion was then sprayed into the bell jar with a de Vilbiss nebulizer. When the aerosol had settled the mica sheet was removed and left in a desiccator until dry. A carbon film was then vaporized onto the mica sheet now supporting the organo-clay film. The carbon film was then floated off in the standard way and then shadowed using tungsten oxide.

6. Electrostatic deposition: The dispersed organo-clay particles have a negative charge, therefore when a coated copper grid was made electrically positive the clay particles were attracted toward the grid. In order to accomplish this an a-c high voltage vacuum detector was used as a holder for the coated copper grid. The high voltage detector was mounted on a ring stand and a pointed wire was placed above the tip of the detector at a distance of about 1 centimeter. A Liebig condenser wrapped with a 22 gauge resistance wire and coated with asbestos tape was attached to a second ring stand with one end of the condenser about five centimeters from the high voltage detector. By this means the nebulized specimen was flash dried in the heated condenser before being electrostatically precipitated onto the sample grid. The glass nebulizer was connected to a nitrogen tank through a pressure reduction valve so that the rate of nebulization could be varied. Since the temperature within the Liebig condenser could also be varied, the rate of drying the particles could thus be altered by changes in the drying temperature or in nebulizer pressure or both.

Before nebulizing of the clay dispersion was started the potential of the vaccum detector was increased to about 300 volts at which time an electrical discharge took place, then the clay dispersion was sprayed at various pressures through the Liebig condenser towards the electrical discharge. The specimen dried inside the condenser and then was electrostatically collected on the grid. This method was suggested by E. C. Jonas, University of Texas.

7. High vacuum drying: This method of specimen preparation was similar to the freeze drying method. The only difference was that a heating device was installed in the vacuum evaporator so that the samples could be heated to an elevated temperature while the vacuum was being maintained.

8. Spreading methods: This procedure was a modification of one suggested by Slabaugh (1964). A small piece of rubber tubing with a pinch clamp was attached to the bottom of a Buchner funnel filled with distilled water and containing a perforated metal plate in the bottom of the funnel. A desired number of uncoated copper grids were then placed on the surface of the metal plate. Several drops of clay dispersion were placed on the water surface by means of a capillary tube and the water then drained slowly from the Buchner funnel by releasing the pinch clamp, thereby lowering a thin layer of the organo-clay onto the copper grids. The entire metal plate and specimens were then removed to a desiccator for drying at room temperature.

In many cases the specimens were shadowed with heavy metals. For the most part tungsten oxide was used as the shadowing material. This was accomplished by forming a V-shaped filament of tungsten wire and heating it in air with an electric current until the filament was well coated with a layer of yellow tungsten oxide. The tungsten oxide except for that near the apex of the V was scraped away from the filament leaving a very small amount of tungsten oxide to be evaporated. The tungsten oxide was then evaporated in the usual way onto the carbon coated copper grids upon which the specimens had been previously deposited. The completion of the process was determined by the disappearance of the yellow crystals of tungsten oxide. The shadowing angles ranged from 15 to 50 degrees.

The electron microscope used in these studies was a Hitachi HU 11A. Most samples were observed with an electron potential of 75 kV but many were studied utilizing 50 or 100 kV. In all cases Kodalith LR safety film, estar base, was used to record the electron micrographs.

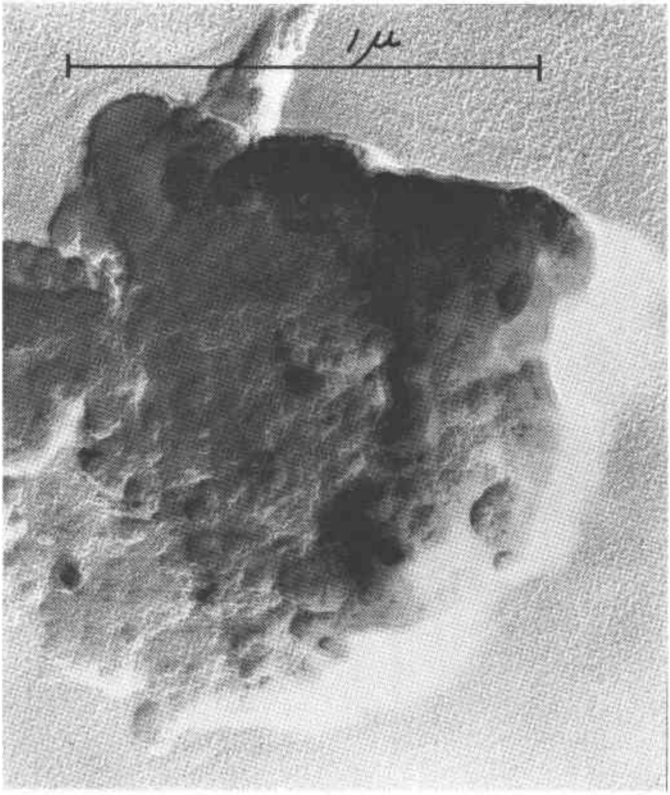

FIG. 1. Electron micrograph of organo-clay dispersed in acetone; freeze-drying method. Shadowed 39°.

## EXPERIMENTAL RESULTS AND DISCUSSION

The general trends found in the X-ray diffraction study seemed to be most closely related to the structure of the organic solvent being used. It was noted that with the exception of dimethylformamide the general changes in the complexity of the Fourier transform curves followed the dispersion media from aliphatic to aromatic compounds and from smaller to larger organic compounds. It was pointed out in the X-ray paper that these changes were most likely related to the drying mechanism. That is, the larger solvent molecules and those that interacted with organo-clay more strongly left a somewhat disordered array or stacking within the clay plates as they evaporated from the specimens which led to the changes in the Fourier transforms noted. The following general conclusions were stated.

1. Group I solvents led to transforms showing the most regular curves since the organic amine chains on the clay were apparently the least disturbed.

2. Group II solvents yielded transforms showing a greater amount of interlayering than did the Group I solvents because the quaternary ammonium molecules tended to interact with the solvent. On the other hand the solvents have low dielectric constants and probably do not in-

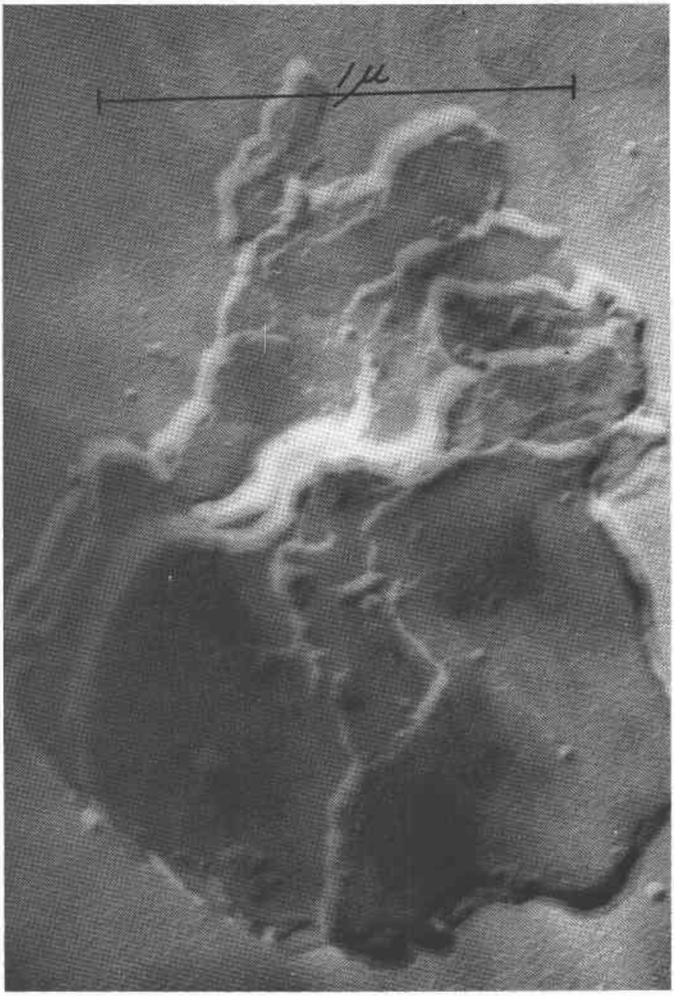

FIG. 2. Electron micrograph of organo-clay dispersed in benzene; freeze-drying method. Shadowed 39°.

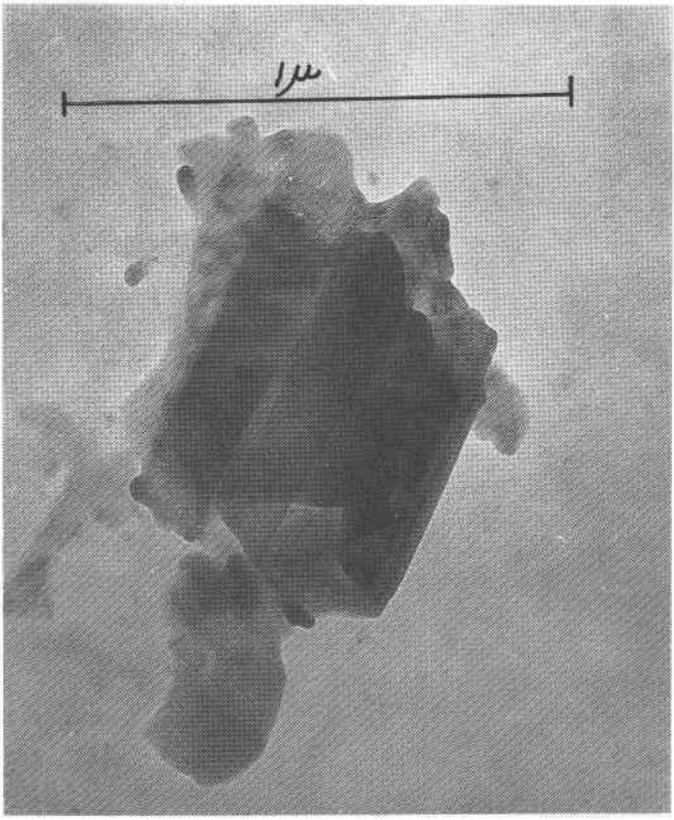

FIG. 3. Electron micrograph of organo-clay dispersed in butyrolactone; electrostatic deposition method.

teract with the clay surface to any great extent, thus not too much disruption was noted.

3. Group III solvents gave transform curves with somewhat more interstratification of high spacings than did the Group I and II solvents. It was noted that the time of penetration of the solvents through the organo-clay and the fact that the organo-clay did not swell in any of the Group III solvents was significant. It was concluded that the slow penetration of the solvent through the organo-clay was due to just the right combination of factors that allowed a large amount of interaction between the solvent and the organo-clay both with the quaternary ammonium molecules and with the clay surface itself.

4. Group IV solvents had a rather high affinity for the organo-clay and these were generally the largest solvent molecules used. Upon their

evaporation they left the most disruption of the quaternary ammonium molecules and thus the most complex Fourier transforms.

In studying the many electron micrographs taken of the specimens prepared from the various dispersions, it was concluded that the differences in the morphology of the specimens were related to similar differences observed and noted in the X-ray diffraction study. It was found in looking at the samples under the microscope that the texture of the particles, the thickness of the organo-clay particles, the apparent orientation and stacking arrangement of the organo-clay platelets and the amount of curling of the organo-clay platelets were related to the degree of interstratification observed from the X-ray diffraction data. Some of the electron micrographs taken showed rough structure or "rugged" organo-clay particles with few individual particles making up the stacked aggregate, while others showed good dispersion into small, thin particles. Furthermore it was found that the amount of solvation of the edges of the clay aggregate could be observed with the microscope and varied from one specimen to another. The meaning of solvation as used here was to imply that the resulting particles as observed under the electron microscope were somewhat diffuse and opaque which was due to irregulary

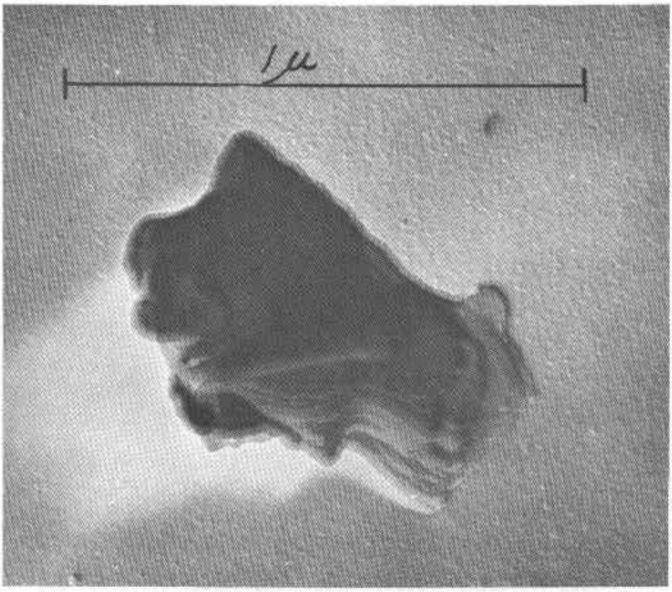

FIG. 4. Electron micrograph of organo-clay dispersed in cyclohexanone; replication method.

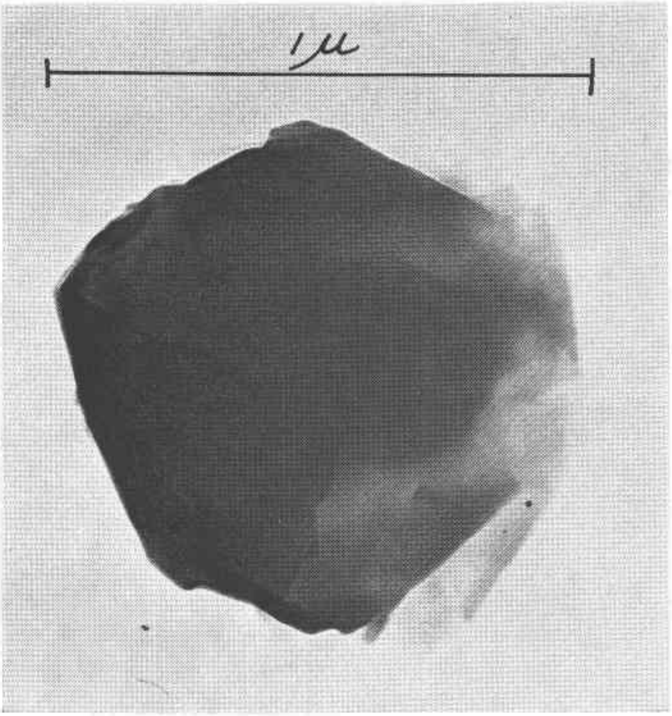

FIG. 5. Electron micrograph of organo-clay dispersed in benzene; electrostatic deposition method.

oriented organo-clay particles and apparently depended on the extent of interaction between the solvent and the organo-clay.

Electron micrographs such as shown in Figures 1, 2, 3, and 4 show the characteristic morphology for each of the clay dispersion groups. Only representative micrographs are shown from the several hundred pictures taken in this investigation.

It can be seen that the clay dispersion resulting from the acetone-dispersed sample (Group I) and freeze dried given in Figure 1 showed rough, rugged, relatively thick aggregates. The appearance was typical of both the acetone dispersed and of the methylisobutyl ketone dispersed specimens. This type of morphology was typical of the freshly prepared and dried organo-clay before being dispersed in an organic solvent. That is, if one takes the dried organo-clay and dusts it onto a microscope grid, this was the way that the specimen appeared. This is consistent with the Fourier diagrams for the Group I solvents in which they did not indicate a great deal of interaction with the organo-clay.

The benzene (Group II) dispersed and freeze dried organo-clay is shown in Figure 2. Solvents of Group II, benzene and 10 percent methanol-90 percent toluene mixture, produced specimens typified by rather smooth aggregates in which fairly thick, well defined layers were observed. Each layer probably consisted of a fairly large number of individual clay plates fairly regularly stacked. With the regular stacking, the resulting regular Fourier transforms were obtained in the X-ray study.

In Figure 3, a Group III solvent (butyrolactone) dispersed specimen, the organo-clay particles have rough appearance with some opaqueness about the edges which indicated solvation taking place. This sample was prepared by the electrostatic deposition method. Because of the irregularities in the stacking and of the disruption about the aggregate edges the Fourier transforms were consistent in that they indicated a fairly high amount of interstratification. Other solvents of Group III are dimethylformamide and n-methyl-2-pyrrolidone.

The cyclohexanone solvent of Group IV dispersed organo-clay is shown in Figure 4. This specimen was prepared by the replication method. These specimens generally had areas of fairly smooth, well stacked (but thin) particles; while within the same aggregate there would appear rough solvated appearing particles. This is in agreement with the X-ray data in that it is believed such morphology would lead to a great deal of interstratification as noted by the Fourier diagrams. Dioxane dispersed samples gave results similar to these and was also characterized as a Group IV solvent from the X-ray studies.

In order to more fully understand the relation between curling of the organo-clay particles observed in some of the micrographs and the rate of drying of the clay dispersion, other methods of specimen preparation were investigated. In one method the specimen was rapidly dried at 35°C under a vacuum of $5\times10^{-4}$mm of mercury. It was seen that curling at the edges of the clay particles was more pronounced when a faster rate of drying was employed. Another method used to study sample curling was the electrostatic deposition method of specimen preparation. Experiments were performed to determine the effect of increasing the gas spraying pressure which in effect should form smaller aerosol particles thus faster heat exchange and therefore faster drying of the clay particles. The spraying pressure was increased from 10 psig used in the previous experiments to 50 psig. It was found that as the spraying pressure increased the degree of curling at the edges of the clay particles was increased. A representative micrograph is shown in Figure 5 and can be compared to that of Figure 2. It is concluded, therefore, that the faster the rate of drying of the organo-clay particles, the more curling of the organo-clay particles takes place.

## ACKNOWLEDGMENTS

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