

CATION EXCHANGE OF ORGANIC COMPOUNDS ON MONTMORILLONITE IN ORGANIC MEDIA

by

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ABSTRACT

Cation exchange of dimethyldioctadecylammonium (DMDO) ion for dimethylbenzyl-lauryl-ammonium (DMBL) ion previously reacted with centrifuged homoionic Na⁺ bentonite has been demonstrated. The amount of DMBL ion removed from the clay was determined by ultraviolet spectroscopy.

In order to shift the exchange equilibrium toward removal of the DMBL cation, a large excess of DMDO cation was required. At the limit of these experiments, it was found that 16 percent of the DMBL cation was exchanged.

INTRODUCTION

Many studies have been made and reported in the literature concerning the exchange of various inorganic cations on montmorillonite (Grim, 1953, pp. 126-156). Indeed, very detailed studies have been made with respect to the replaceability of one cation for another: whether it be monovalent, divalent, or trivalent; the size of the cation and the state of the ion with respect to its hydration properties. The alteration of montmorillonite from a hydrophilic to an organophilic colloid by addition of organic cations likewise has been reported in detail (Grim, 1953, p. 265; McAtee, 1959).

This paper reports observations on the cation exchange that takes place when an organophilic montmorillonite dispersed in an organic medium is brought in contact with dissolved organic cations.

Grateful acknowledgement is extended to the Baroid Division of the National Lead Company for support of part of this work and to Mr. Tyler Payton and Mr. Ernest Richter for performing many of the tedious experiments.

EXPERIMENTAL DETAILS

Centrifuged Wyoming bentonite supplied by the Baroid Division, National Lead Company was used in these experiments. This clay was taken from the Colony, Wyoming, area and was centrifuged by means of a Merco

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C-9 type centrifuge. The maximum particle size was less than 1.5μ , and less than 0.1 percent quartz was detected in the samples after centrifugation.

Homoionic Na-bentonite was prepared by passing an approximately 2 percent suspension of the clay through an ion exchange column containing Amberlite IR-120 (Rohm & Haas Co.) in the sodium form. In order to assure complete ion exchange to the Na-form, the clay slurry was passed through the column twice. Analyses by the Versenate method indicated that there remained less than 2 meq of Ca^{2+} ion per 100 g of clay solids.

The quaternary salts were commercial materials obtained from the General Mills Company. The materials are designated as Aliquat H-226 for dimethyldioctadecylammonium chloride and Aliquat H-460 for dimethylbenzylaurylammonium chloride.

To the homoionic Na-bentonite increasing amounts of the quaternary salt dimethylbenzylaurylammonium chloride (hereafter designated as DMBL) were added to separate aliquots of the clay slurry. The resulting material was filtered in a high pressure filter cell and the samples washed four to five times with distilled water. The filtrate and washings were retained and made up to a standard volume and the sodium ion was determined by flame spectrophotometry.

After the curve for the replacement of the sodium ion by DMBL cation had been established, several large samples of DMBL-bentonite were prepared in the range of 80–90 meq of organic/100 g of clay base for further study. The exact amount of quaternary cation retained by the clay was determined by standard ignition loss techniques (McAtee, 1959).

The organic cation exchange studies were conducted as follows: A weighed portion (0.100 g) of the DMBL bentonite was placed in a mortar to which was added a mixture of iso-octane (spectral grade 2,2,4-trimethyl pentane), isopropyl alcohol, and increasing amounts of the dimethyldioctadecylammonium cation (hereafter referred to as DMDO cation). The isopropyl alcohol served two functions: namely, it was necessary as the solvent for the DMDO chloride salt and secondly, as the polar dispersant for the organobentonite colloid. All samples contained 20 percent isopropyl alcohol. This amount was determined experimentally to be the optimum for dispersion of the organo-clay colloid. A total volume of 20 ml of the iso-octane mixture was prepared for each experiment.

After addition of 5 ml of the iso-octane mix to the mortar, the dispersion was produced by vigorous stirring with a pestle for 5 min. The dispersion was then transferred quantitatively to a flask with the remaining solution of isopropyl alcohol and iso-octane. This was placed on a shaking machine for a period of 1 hr. It was determined experimentally that equilibrium was established after 30–45 min, but an extra 15 min was added for assurance. The dispersion was then centrifuged and filtered using Whatman

no. 42 filter paper. The effluent was then made up to a standard volume of 20 ml with iso-octane and examined by means of a Beckman DK-1 recording ultraviolet spectrometer over the region of from 300 to 230 $m\mu$. This region includes the absorption spectra related to the benzyl group contained in the DMBL cation.

The amount of DMBL cation exchanged from the DMBL-bentonite was estimated by standard methods of comparison with calibrated samples run under the same conditions with the spectrometer.

RESULTS

Addition of the quaternary salt dimethylbenzyl-laurylammonium chloride (DMBL chloride) to centrifuged homoionic Na-Wyoming bentonite causes cation exchange replacement as shown in Fig. 1. Almost an exact 1 to 1

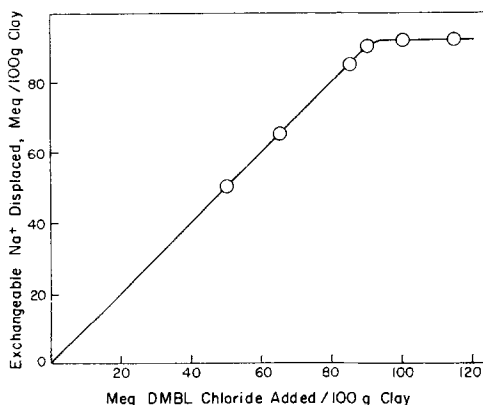


FIGURE 1.—Exchange of Na^+ from montmorillonite by dimethylbenzyl-laurylammonium cation.

replacement of sodium by the quaternary cation is obtained up to the exchange capacity of the clay (92 meq/100 g of dry clay). Since a 1 to 1 replacement was found over the region of 80–90 meq of organic cation this area was chosen for the subsequent studies concerned with organic-organic cation exchange.

When increasing amounts of dimethyldioctadecylammonium chloride (DMDO chloride) were allowed to come in contact with DMBL-bentonite dispersed in iso-octane and the effluent was examined, ultraviolet curves shown in Fig. 2 were obtained. As the amount of DMDO was increased the characteristic absorption spectra from the benzyl group contained in the exchanged DMBL cation likewise increased. The height of the first

absorption peak ($269\text{ m}\mu$) was measured for each experiment and these plotted *vs.* the amount of DMDO added (Fig.3). The experimental points shown are for two samples of DMBL-bentonite, one containing 83 meq of DMBL per 100 g dry clay and the other 88 meq DMBL.

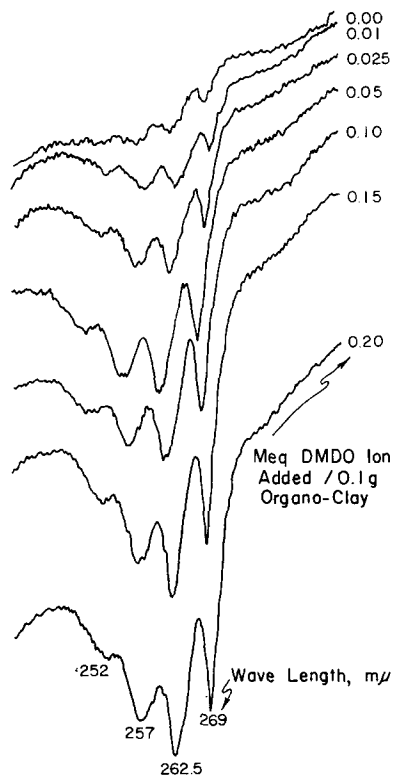


FIGURE 2.—Ultraviolet spectra of the filtrate following exchange of dimethyl-laurylammonium-montmorillonite with dimethyldioctadecylammonium cation.

DISCUSSION

It is apparent from the curve shown in Fig.3 that organic-organic cation exchange is indeed taking place. Experiments utilizing greater amounts of the DMDO cation have given all indications that increased exchange is taking place, but owing to centrifugation and filtering problems samples suitable for ultraviolet examination have not as yet been obtained. The curve shown in Fig.3 appears to be leveling off, but proof of this will have to await subsequent work.

X-ray diffraction patterns of several of the samples were obtained so as to determine the changes in basal spacings that were taking place. The ori-

ginal basal spacing for both samples of DMBL bentonite was between 18 and 19 Å. After the exchange with the maximum amount of DMDO cation used, basal spacings of from 22 to 24 Å were obtained. The approximate area of each cation was calculated to be 137 Å² for DMBL cation and 230 Å² for DMDO cation. Relating these values to the 165 Å² of average clay surface area per base exchange position (Jordan, 1949) it is apparent that as the larger DMDO cation replaces the DMBL cation on the clay expansion would take place.

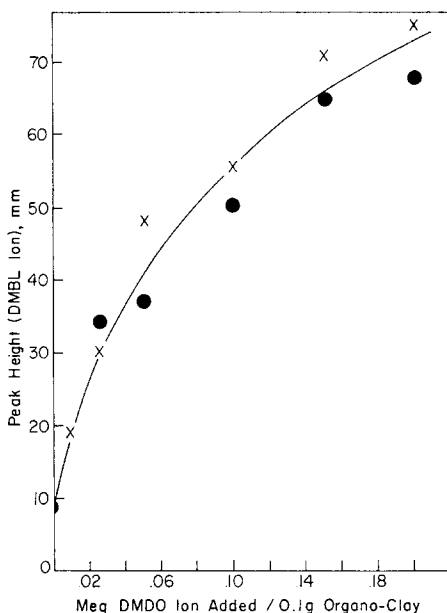


FIGURE 3.—Exchange of dimethylbenzylammonium cation from montmorillonite by dimethyldioctadecylammonium cation.

By comparing the height of the absorption peaks for the samples containing 0.2 meq DMDO/0.1 g organo-bentonite with standard absorption curves of DMBL cation, it was determined that 16 percent of the DMBL cation on the original DMBL-bentonite had been exchanged for the DMDO cation. At this exchange level, 0.2 meq DMDO/0.1 g organo-bentonite represents about 260 meq DMDO/100 g of clay base. This very large excess of DMDO cation must be related to the strong forces holding the DMBL cation to the clay anion.

Since the organic cations associated with the montmorillonite surface are held by exchange forces, it is easy to visualize that exchange of one cation for another should be fairly readily accomplished. In the case of the organo-clay complexes, however, this exchange appears to be quite

difficult for several reasons. First, after production of the hydrophobic colloid, the problem arises to set up a system in an organic medium where cations for exchange are available. It is believed that the nature of these experiments has allowed this condition to be met and cation exchange has been accomplished. Another difficulty undoubtedly is associated with the very large size of the cations involved. It generally has been concluded that as the size of an ion increases its ability to replace ions of equal valence increases. This factor results in complete exchange of sodium by the organic cation and causes the organic cation to be held quite strongly to the clay

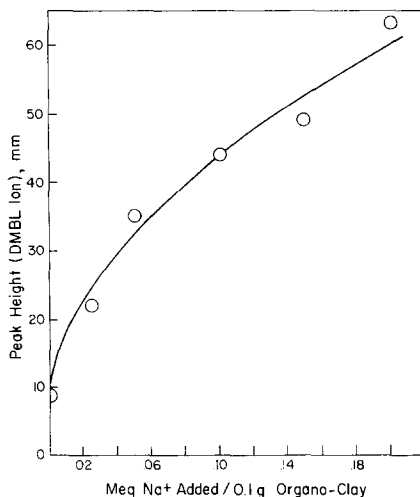


FIGURE 4.—Exchange of dimethylbenzylammonium cation from montmorillonite by sodium from sodium acetate.

surface. The same reasoning indicated the need for a still larger organic cation in order to obtain organic-organic exchange. It was partly for this reason that the particular pair of organic cations reported in these experiments were used. As the DMDO cation is somewhat larger than the DMBL cation, it was expected this exchange would be most favorable.

Somewhat as an addendum to the original objectives of these experiments, it was decided to determine if any DMBL cation on the clay could be replaced by an inorganic cation. The results of these somewhat limited experiments are shown in Fig. 4. The experimental details were the same as those previously described with the exception that sodium acetate was substituted for the DMDO chloride salt. Exchange does indeed take place over the range studied. Data with greater amounts of sodium were not obtained since the limit of solubility of the sodium acetate in isopropyl alcohol has been reached. Experiments are now being conducted, however, utilizing other sodium organic salts with greater solubility in alcohol.

The general study of organic-organic cation exchange is being extended to other clays and to other organic cations, and experiments are being conducted to extend the range of the exchange taking place.

CONCLUSIONS

The exchange of a large organic cation for another organic cation on montmorillonite clay has been accomplished. Since the organo-montmorillonite is organophilic and hydrophobic the exchange was carried out in an iso-octane-isopropyl alcohol mixture. It was found that under the conditions of the experiments up to 16 percent dimethylbenzylammonium cation can be replaced from montmorillonite with dimethyldioctadecylammonium cation. It was also shown that a large excess of sodium ion (as sodium acetate) can exchange for dimethylbenzylammonium cation on montmorillonite.

REFERENCES

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