

INORGANIC-ORGANIC CATION EXCHANGE ON MONTMORILLONITE

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ABSTRACT

Replacement of the inorganic cations on montmorillonite by base exchange with organic compounds has been followed by step-wise additions of the organic compound to the clay. It has been shown that a primary amine has enough basic character to react with montmorillonite by the base exchange mechanism. Data are also given showing the replacement of sodium, calcium and magnesium for montmorillonite and hectorite treated with a large quaternary ammonium salt. The sodium on montmorillonite is replaced stoichiometrically while calcium and magnesium require greater than the stoichiometric amount of organic for replacement.

INTRODUCTION

The alteration of montmorillonite from a hydrophilic to an organophilic material by the addition of organic compounds has led to many interesting uses of montmorillonite. The study of montmorillonite-organic reactions has also led to important analytical procedures whereby montmorillonite can be differentiated from other clay minerals, base exchange values determined, surface areas calculated, etc. To understand more fully the reaction between montmorillonite and organic amines and amine salts, a study was initiated to follow the displacement of montmorillonite exchangeable cations by these organic substances.

EXPERIMENTAL DETAILS

Centrifuged Wyoming bentonite and centrifuged hectorite were used as the clay minerals in these experiments. The Wyoming bentonite was from the Colony, Wyoming area. Centrifugation was accomplished by means of a commercial Merco C-9 type centrifuge. The maximum particle size in both samples was less than 1.5 microns.

Homoionic Na-bentonite was prepared by passing a 1-2% suspension of the clay through an ion exchange column containing Amberlite IR-120 (Rohm and Haas Company) in the sodium form. The clay slurry and the column were preheated to about 65° C. so as to get complete ion exchange of the clay with a single pass.

The amine, amine salt and quaternary salts were commercial materials produced by Armour Chemical Division and by Onyx Oil & Chemical Company.

Increasing amounts of the amine, amine salt and quaternary salts were added to separate aliquots of the clay slurry. The resulting material was filtered in a high pressure filter cell and the sample washed four to

five times with distilled water. The filtrate and washings were retained and made up to a standard volume and the various cations determined by routine analytical methods.

Blanks were run on the bentonite and hectorite samples as follows: Portions of each clay slurry were filtered in the high pressure filter cell. The filtrate and washings were made up to a standard volume and the total cations determined. These values were considered as excess soluble cations and were subtracted from the values obtained with the organic treated clays.

In order to determine the amount of amine or quaternary salt being retained by the clay after washing, a portion of the filtered and washed residue was dried at 105° C. The dried residue along with a sample of the dried clay base were ignited at 1000° C. in a muffle furnace. From the differences in the loss on ignition of the sample and blank and the molecular weight of the organic compound, the milliequivalents (*me*) of the organic substance retained by the clay were calculated as follows:

$$me \text{ organic}/100 \text{ g. clay} = \frac{(I - C) \times 100,000}{(100 - I)W}$$

where

I = Ignition loss of clay-organic complex in per cent.

C = Ignition loss of the clay in per cent.

W = Molecular weight of the amine or quaternary ammonium cation.

RESULTS

Cation replacement curves resulting from the addition of octadecylamine and octadecylamine hydrochloride to centrifuged Wyoming bentonite are shown in Fig. 1. The curves demonstrate the ability of

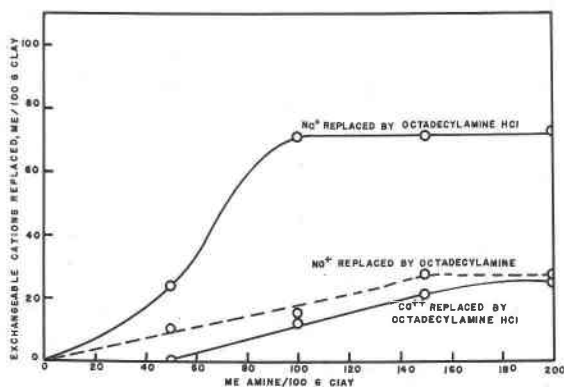


FIG. 1

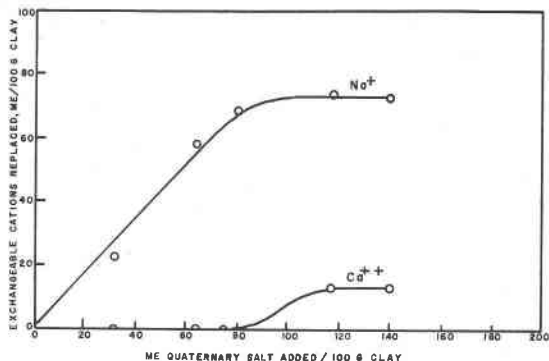


FIG. 2

octadecylamine hydrochloride to replace sodium and calcium exchangeable ions. It will be noted that half or more of the sodium is replaced before any of the calcium ions are removed from the clay.

The third curve shown in Fig. 1 is the replacement of sodium ions by the octadecylamine. This curve shows that octadecylamine has some basic character, indeed enough to replace 27 *me* of the sodium ions upon the addition of 150 *me* of the amine. The addition of 50 *me* amine replaces about 10 *me* of sodium. No calcium was replaced by the amine.

Figure 2 shows curves for the exchangeable sodium and calcium replaced upon the addition of the quaternary salt, dimethyldioctadecylammonium chloride. The replacement of the sodium ion by the quaternary is practically a 1:1 relationship, with all of the sodium being replaced before any calcium is removed.

The addition of the quaternary salt, dimethylbenzylaurylammonium chloride, to centrifuged Wyoming bentonite causes cation exchange replacement as shown in Fig. 3. Again as with the dimethyldioctadecyl-

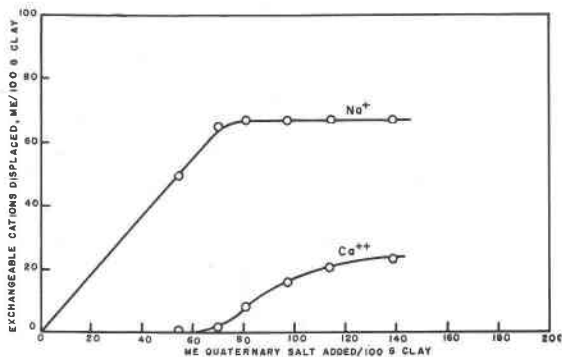


FIG. 3

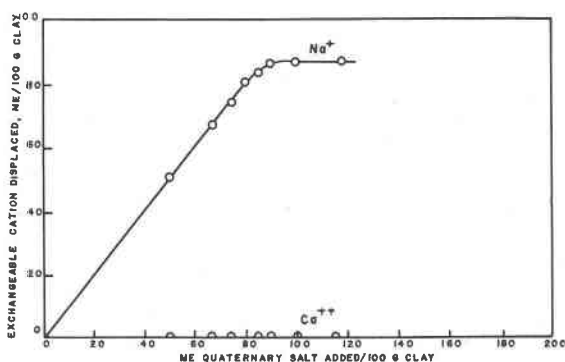


FIG. 4

ammonium quaternary, sodium is replaced stoichiometrically. At the start of calcium replacement there is required about one and a half *me* of quaternary to remove one *me* of the calcium ion. As more and more calcium is removed, it takes greater amounts of the quaternary cation to remove a single *me* of the calcium ion. Between the addition of 97 and 111 *me* of the quaternary cation, only 4 *me* of calcium are removed, indicating, therefore, that it is becoming increasingly more difficult to remove the remaining exchangeable cations.

Homoionic Na-bentonite was reacted with varying amounts of dimethylbenzylammonium chloride. The resulting cation exchange curves are shown in Fig. 4. It will be noted that almost an exact 1:1 replacement of sodium by the quaternary cation is obtained up to the exchange capacity of the clay (the B.E.C. value was found to be 92 *me*/100 g. dry clay).

The curves shown in Fig. 5 are for the replacement of divalent cations, Ca⁺⁺ and Mg⁺⁺, from a centrifuged Wyoming clay passed through a

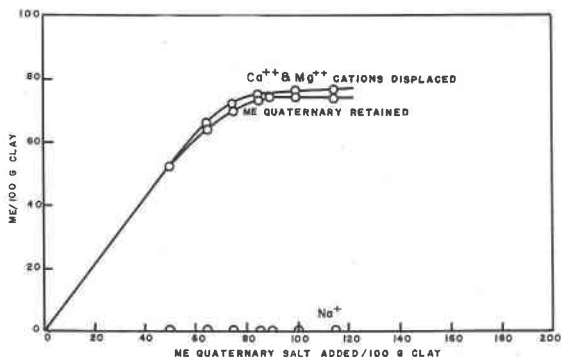


FIG. 5

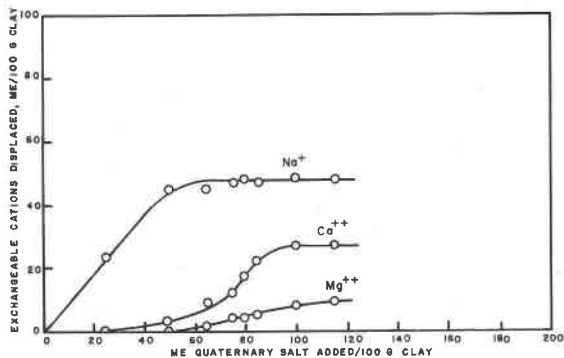


FIG. 6

calcium ion exchange column. The clay blank contained 62 *me* Ca⁺⁺, 13 *me* Mg⁺⁺ and 1 *me* Na⁺/100 g. dry sample. Also shown in Fig. 5 is a curve for the *me* of quaternary salt actually retained by the clay after washing and drying compared with the amount added. It is interesting to note that the two curves coincide up to an addition of 115 *me* of quaternary salt.

Hectorite, the trioctahedral magnesium montmorillonite, was reacted with dimethylbenzylaurylammonium chloride. The resulting cation exchange curves are shown in Fig. 6. It will be observed that most of the sodium is replaced by the quaternary ion, then the calcium and finally the magnesium.

Curves showing the retention of dimethylbenzylaurylammonium chloride by various samples after washing with distilled water and drying are shown in Fig. 7. It will be noted that the homoionic sodium bentonite and the hectorite retain practically all of the quaternary ion

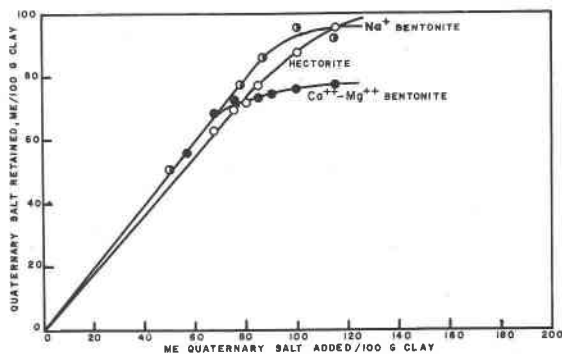
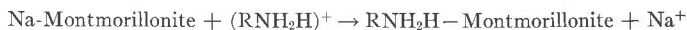
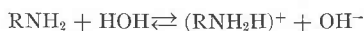


FIG. 7

that was added. The Ca^{++} - Mg^{++} clay, on the other hand, retains only approximately 70 *me*.

DISCUSSION

A comparison of the curves shown in Figs. 1, 2, 3 and 6 show that the sodium exchangeable cation is the first to be replaced by the amine salt or quaternary salts. It is of interest to note that the large quaternary compounds replace sodium much easier than does the octadecylamine hydrochloride. Furthermore, from the rates of calcium removal shown in the various curves, the larger organic cations also remove calcium ions at a greater rate than does the simple primary amine ion. As already shown, the primary amine, octadecylamine has enough basic character (probably due to hydrolysis with water) so that it will replace some of the sodium ion from exchange positions of centrifuged Wyoming bentonite. This is demonstrated by the following equations:



This replacement is not as rapid, nor as complete as with the corresponding amine hydrochloride, but certainly takes place to an extent corresponding to its relative basic character.

A comparison of the replacement of sodium from the homoionic Na-bentonite with the replacement of divalent Ca^{++} and Mg^{++} from the Ca-Mg bentonite is of interest. These curves again show the relative ease with which sodium is replaced by the large organic cation compared to the divalent ions. It is of particular interest to note the much greater retention of the organic cation by the Na-bentonite compared to the Ca-Mg bentonite (Fig. 7). Due to the large groups of flocculated clay in the Ca-Mg system, the quaternary cation probably cannot effectively exchange onto the clay nor even have room to become adsorbed after approximately 75 *me* has been added. On the other hand, the sodium bentonite and hectorite both retain all of the organic cation added up to at least 100 *me*/100 g. clay.

The centrifuged Wyoming bentonite used in these experiments had an ammonium acetate base exchange capacity of 92 *me*/100 g. dry clay. The total exchangeable cations and soluble cations were 113 *me* Na^+ , 30 *me* Ca^{++} , and 13 *me* Mg^{++} . After subtracting the values found for the soluble cations, the exchangeable cations were found to be 67 *me* Na^+ , 30 *me* Ca^{++} and 13 *me* Mg^{++} . Comparing the B.E.C. values of bentonite with the various curves, it can be seen that upon the addition of 92 *me* of amine or quaternary salt, only the homoionic sodium clay has an almost exact stoichiometric replacement of cations. The difference be-

tween the amount of organic added and cations removed at 92 *me* organic for the octadecylamine salt is 13 *me*, 17 *me* for the dimethyldioctadecyl quaternary and 12 *me* for the dimethylbenzylauryl quaternary on centrifuged bentonite. The difference for the dimethylbenzylauryl quaternary on the Na and Ca-Mg bentonites is 5 *me* and 18 *me*, respectively.

The centrifuged hectorite used had a B.E.C. of 93 *me*/100 g. dry clay and 47, 37 and 24 *me* Na⁺, Ca⁺⁺ and Mg⁺⁺ exchangeable cations, respectively. A total of 90 *me* of cations are replaced upon the addition of 93 *me* of dimethylbenzylauryl quaternary. This indicates that the cations on hectorite are somewhat easier to replace than those on Wyoming bentonite.

Further examination of Fig. 6 shows that for hectorite the calcium ion starts being removed slightly before all of the sodium ion is replaced. Between the addition of 65 and 90 *me* of the dimethylbenzylaurylammonium chloride, a total of 25 *me* of Ca⁺⁺ and Mg⁺⁺ are removed. This is a 1:1 replacement of divalent ions, which is totally unlike that found with centrifuged Wyoming bentonite.

The differences shown in Figs. 3 and 6 for the replacement of the cations of hectorite and Wyoming bentonite are probably due to the differences in the origin of the cation exchange. The Wyoming bentonite used has roughly 50% of its cation exchange capacity originating in the tetrahedral layer and 50% originating in the octahedral layer (1). On the other hand hectorite has almost all of its cation exchange originating in the octahedral layer resulting from substitution of the magnesium by lithium (2). Grim (3) states: "Since the charges resulting from substitutions in the octahedral sheet would act through a greater distance than the charges resulting from substitutions in the tetrahedral sheet, it would be expected that cations held because of the latter substitutions would be bonded by a stronger force than those held by forces resulting from substitutions in the octahedral sheet." It would be expected, therefore, that the exchangeable hectorite cations would be easier to replace than the exchangeable cations on Wyoming bentonite which is indeed shown by the results of these studies.

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