ORGANIC CATION EXCHANGE ON MONTMORILLONITE AS OBSERVED BY ULTRAVIOLET ANALYSIS

by

JAMES L. McATEE, JR.

Department of Chemistry, Baylor University, Waco, Texas

ABSTRACT

An analytical method is described whereby the exchange of various organic cations for other organic cations on montmorillonite is determined. The exchange is followed by means of a Beckman DK-1 ultraviolet spectrometer.

It has been observed that organic cations from compounds such as primary, secondary, and tertiary amine salts and quaternary ammonium salts can be exchanged for one another on the natural cation exchange substance, montmorillonite. The exchange is carried out in isooctane to which a small amount of isopropyl alcohol has been added to aid in dispersion of the organic–clay complex. By choosing pairs of organic substances, of which one has strong absorbance in the ultraviolet and the other does not, the exchange can be followed quantitatively with the u.v. spectrometer.

INTRODUCTION

It has been observed that under some conditions of use, some types of organo–clay complexes appear to undergo decomposition. One mechanism that has been proposed is that the organic cations that are originally exchanged on to the clay become exchanged for some other cation present in the dispersion system. If an exchange does take place the nature of the clay–organic may be altered sufficiently to cause a change in its rheological properties.

The investigation described herein shows that organic–organic cation exchange on bentonite and hectorite does take place. By utilizing an ultraviolet spectrometer, the amount of exchange was determined for a number of primary, secondary, and tertiary amine salts, and quaternary ammonium salts.

EXPERIMENTAL DETAILS

Centrifuged Wyoming bentonite and centrifuged hectorite supplied by the Baroid Division, National Lead Company, were used in these experiments. The Wyoming bentonite after centrifugation had a maximum particle size of 1.5 μ and less than 0.1 percent quartz. The hectorite contained less than

153

0.5 percent calcite and less than 0.1 percent quartz after centrifugation and its particle size did not exceed 1.5 μ.

Monoionic sodium clays were prepared by passing approximately 2 percent dispersions through ion exchange columns containing Amberlite IR-120 (Rohm and Haas Company) in the sodium form. Analysis by the Versenate (Cheng and Bray, 1951) method indicated that there remained less than 2 meq of calcium and magnesium ion per 100 g of clay solids.

The quaternary salts were commercial materials obtained from the General Mills Company. The amines were commercial materials obtained from Armour, General Mills, Onyx Oil and Chemical, Archer-Daniels Midland, and Eastman Chemicals Companies.

To hot dispersions of the homoionic sodium bentonite or hectorite, approximately 85 meq/100 g of dry clay of dimethylbenzyllauryl ammonium chloride (hereafter designated as DMBL) were added. The resulting organic–clay complex was filtered, washed four or five times with distilled water and then allowed to air dry. This material was then ground in a mortar for use in the exchange experiments. The exact amount of the DMBL cation on the clay was determined by standard ignition loss techniques (McAtee, 1959).

A weighed portion (0.100 g) of the DMBL-clay complex was placed in a mortar to which was added a mixture of isooctane (spectral grade 2,2,4-trimethyl pentane), isopropyl alcohol and increasing amounts of the amine salt or quaternary salts being tested. The isopropyl alcohol served two functions. Namely, it was necessary as the solvent for the amine and quaternary salts and, secondly, as the polar dispersant for the organo–bentonite colloid. All samples contained a final concentration of 20 percent alcohol. This amount was determined experimentally to be the optimum for dispersion of the organo–clay complex. A total volume of 20 ml of the isooctane, alcohol–amine salt was prepared for each experiment.

After addition of 15 ml of the isooctane mix to the mortar, a 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 isooctane mix. This was then placed on a shaking machine for 1 hr. The dispersion was then filtered in a high pressure filter cell and the filtrate made up to a standard volume. The filtrate was examined by means of a Beckman DK-1 recording spectrometer over the region of 300 to 230 mμ. This region includes the absorption spectra related to the benzyl group contained in the DMBL cation. The amount of DMBL cation exchanged from the clay was determined by comparison of the experimental curves to curves prepared from standard solutions of DMBL in isooctane–20 percent isopropyl alcohol mixture.

RESULTS

When bentonite containing the inorganic cation sodium is reacted with a quaternary ammonium cation an almost exact 1:1 replacement of sodium by the quaternary cation is obtained up to the exchange capacity of the clay

(92 meq/100 g dry clay) (McAtee, 1959). Since a 1:1 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.

One of the major requirements that had to be met in this study was the finding of an organic system in which the organophilic clay colloid could be dispersed and which at the same time acted as a solvent for the various organic amine and quaternary salts that were to be studied. Furthermore, it was also necessary that the system lend itself to a quantitative method for the determination of the amount of exchange, if any, taking place. These problems were solved by using combinations of organic cations such that one had some characteristic absorption spectrum in the ultraviolet while the other did not, but both were soluble in isooctane isopropyl alcohol mixtures. Since the benzyl group has a very characteristic absorption spectrum in the ultraviolet region and straight chain hydrocarbons do not, various combinations of these contained in amines and quaternaries were selected for study. Spectral grade isooctane was used as the dispersant and isopropyl alcohol was used as the dispersion aid and as a carrier for the organic exchange cation.

By starting with clays that consisted of approximately 85 meq of an organic cation containing at least one benzyl group and allowing other organic cations to come into contact with it, organic–organic exchange was studied. As any exchange took place, the filtrate from the dispersion system contained the organic cation with the benzyl group. The amount of exchange was then determined by comparing the intensity of the ultraviolet absorption bands with absorption bands obtained from standards (McAtee, 1962).

Starting with either bentonite–dimethylbenzyllaurylammonium (DMBL) complex or hectorite–dimethylbenzyllaurylammonium (DMBL) complex various exchange studies were made. Primary, secondary and tertiary amine salts and quaternary salts were all allowed to exchange with the DMBL cation of the clay. The amounts of exchanges that take place under the conditions of these experiments are illustrated in Figs. 1 to 9.

DISCUSSION

Figure 1 illustrates the type of exchange that takes place between the clay–DMBL complex and a relatively large organic quaternary salt dimethyldioctadecylammonium (DMDO) chloride. It will be noted that at an addition of 266 meq of the DMDO cation approximately 35 meq of the DMBL is replaced on both the bentonite and hectorite complexes. A comparison of the two curves indicates that the DMBL cation is slightly more easily replaced by the DMDO cation on hectorite than it is on bentonite. This probably results from the fact that the exchange forces on hectorite are weaker than those on bentonite (McAtee, 1959, pp. 1230–1231). Wyoming bentonite has almost 50 percent of its cation exchange originating in the octahedral layer and 50 percent in the tetrahedral layer while hectorite has
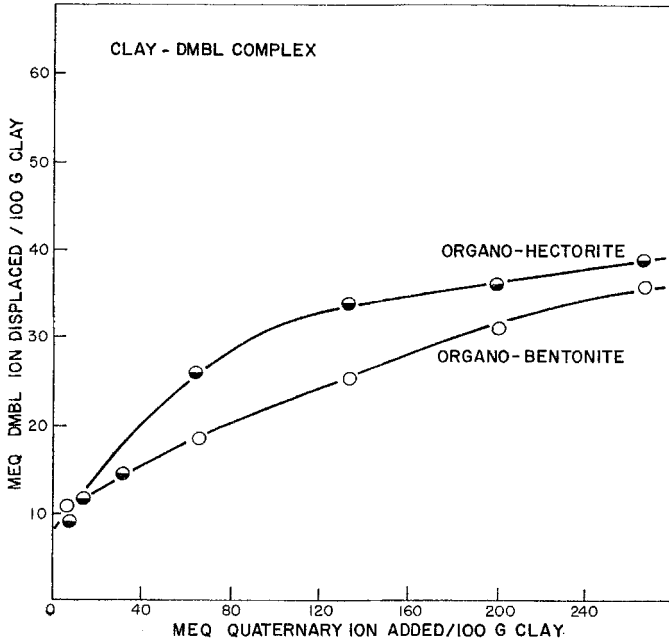
FIGURE 1.—Displacement of DMBL cations from hectorite and bentonite by DMDO cation.
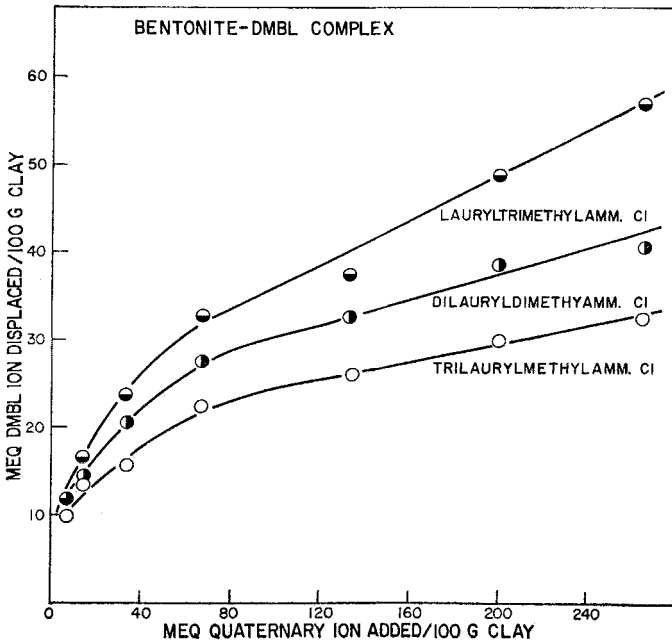

FIGURE 2.—Displacement of DMBL cations from bentonite by lauryl–methyl quarternary cations.

all its cation exchange originating in the octahedral layer (Grim, 1953, p. 133). These differences cause the average exchange forces of bentonite to be somewhat stronger than those of hectorite.

A series of quaternary ammonium salts consisting of lauryl and methyl groups were exchanged for the DMBL cation on bentonite and hectorite. Curves illustrating these results are shown in Figs. 2 and 3. The amount of exchange increases as one goes from the trilaurylmethyl- to the dilauryl-dimethyl- to the lauryltrimethylammonium cation. It will also be noticed in
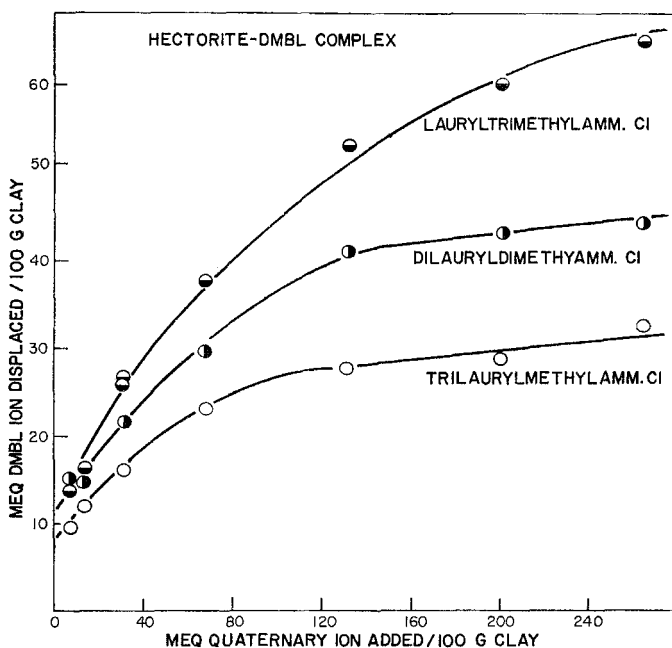

FIGURE 3.—Displacement of DMBL cations from hectorite by lauryl–methyl quarternary cations.

these curves that the amount of exchange experienced with hectorite–DMBL complex is greater than with bentonite–DMBL complex.

When relatively short chained primary amines are exchanged for the DMBL cation on bentonite, results afford the curves shown in Fig. 4. The curve for methyl amine HCl lies between the curves produced by ethylamine and butylamine HCl salts. The ionization constants for the free amines are as follows: 5.6×10^{-4} for ethylamine, 4.4×10^{-4} for methylamine and 4.1×10^{-4} for butylamine. It is thus indicated that as the ionization constant increases the amount of exchange experienced increases.

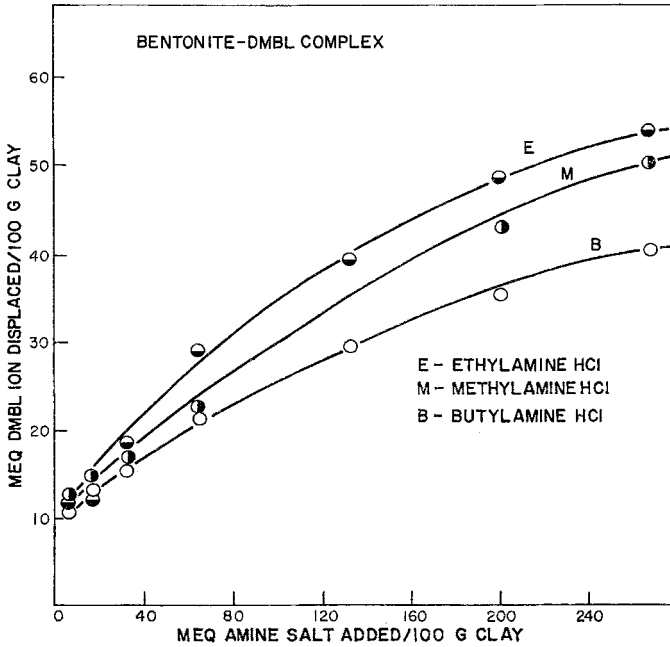In order to test further the effect of basicity, the curves shown in Fig. 5

Figure 4.—Displacement of DMBL cations from bentonite by primary amines.
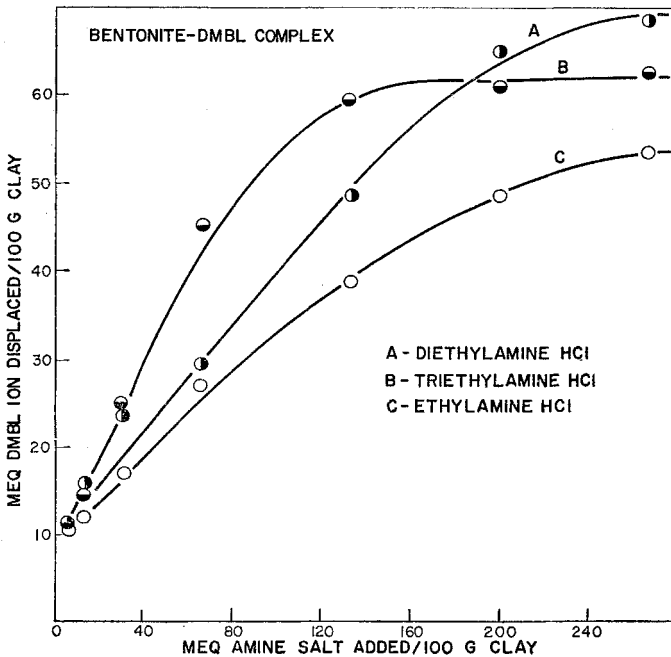

Figure 5.—Displacement of DMBL cations from bentonite by a series of ethylamines.

were obtained. These curves depict the exchange of ethyl-, diethyl-, and triethylamine HCl with bentonite–DMBL complex. The K_i values for these free amines are 5.6×10^{-4}, 1.3×10^{-3} and 5.7×10^{-4} respectively. Of all the amine ionization constants found in the literature diethylamine has the largest value and is therefore the strongest base. It will be noted that of all the amines tested, diethylamine gives the greatest amount of exchange. Why the curve for the triethylamine results shows the very rapid initial increase is not known, but it does level off at a value that would be predicted from its K_i value.
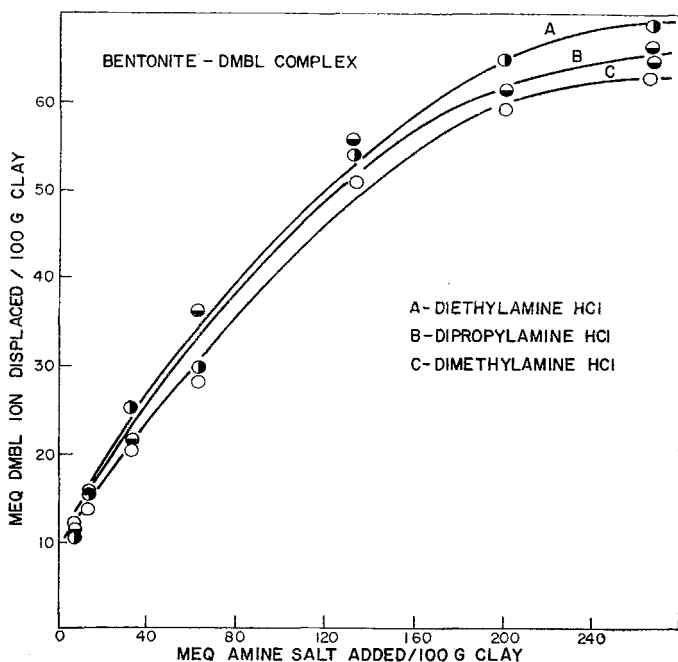

FIGURE 6.—Displacement of DMBL cations from bentonite by secondary amines.

Results for the exchange by short chained secondary amines are shown in Fig. 6 and for exchange by several tertiary amines are shown in Fig. 7. The ionization constants for the secondary amines are 1.3×10^{-3} for diethylamine, 8.2×10^{-4} for dipropylamine and 5.1×10^{-4} for dimethylamine. These curves again show the influence of the basicity of the free amine. The exchange curves shown in Fig. 7 illustrate another important factor which influences the amount of exchange. It is seen that the amount of dimethyloctadecyl-ammonium HCl exchanged compared to the short chained amines and even to the N,N-diethylcyclohexylamine HCl is relatively small. It will be recalled that the amount of dimethyldioctadecylammonium salt exchanged on
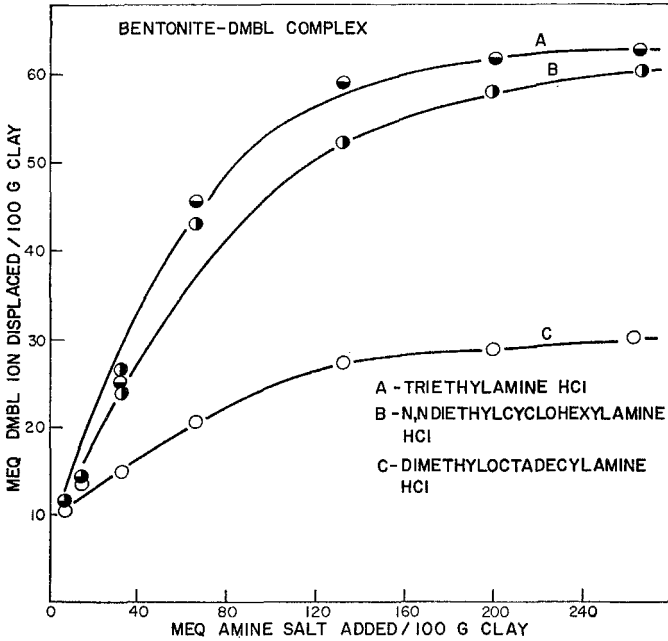
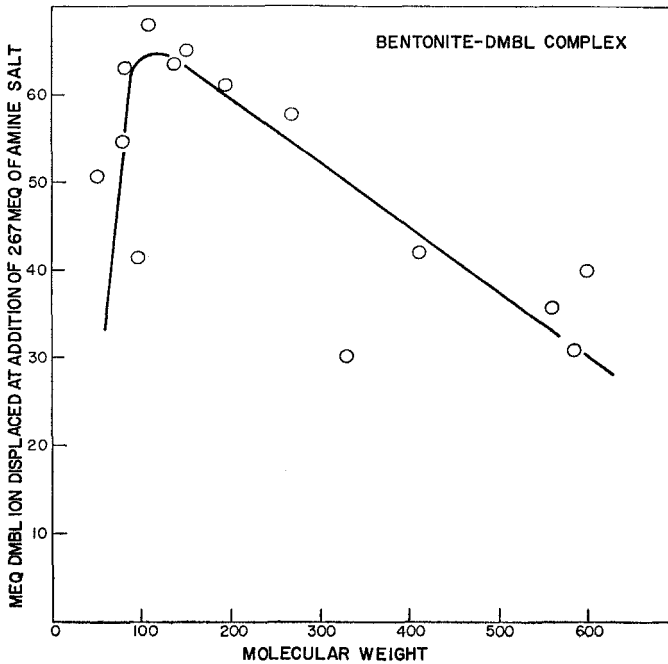FIGURE 7.—Displacement of DMBL cations from bentonite by tertiary amines.

FIGURE 8.—DMBL cations displaced from bentonite by amine and quaternary cations as related to the molecular weight of the displacing cation.

bentonite and hectorite as shown in Fig. 1 is also relatively small. Figures 2 and 3 also show that as the number of lauryl groups increase the methyl–lauryl quaternaries also exchange less and less. It is apparent, therefore, that the size of the organic cation can greatly affect the exchange. Seemingly if the exchanging cation is compact or relatively small, or both, it can exchange for the DMBL cation with ease, while if it has long chains these chains interfere with the exchange.
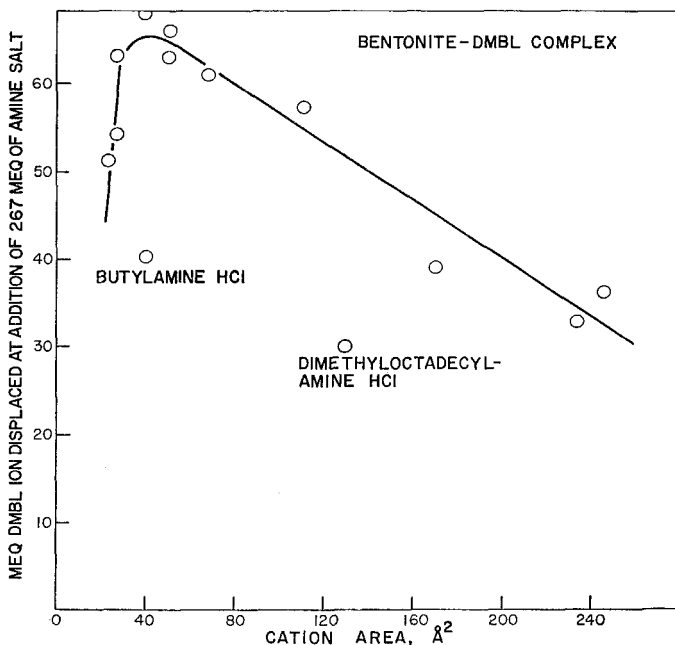

FIGURE 9.—DMBL cations displaced from bentonite by amine and quaternary cations as related to the molecular weight of the cation area of the displacing cation.

Figures 8 and 9 give curves which illustrate the effect of molecular weight and cation area with respect to the exchange for DMBL cation on bentonite where 266 meq of the exchanging cation has been added. As already discussed, the relative basicity of the amine greatly influences the exchange, so it was not expected that all the points should fall on the curves. It is believed, however, that the trends shown in Figs. 8 and 9 are significant. Both curves show a maximum for cations in the C_2–C_4 range and then the amount of exchange drops off fairly rapidly as the molecular weight or cation size increases. This decrease is probably due to a decrease in the mobility of the large cation or to steric hindrance, or both.

11

CONCLUSIONS

From the data presented it appears that the exchange of organic cations for DMBL cation on bentonite and hectorite is a function of the relative basicity and of the size of the cation. As the basicity of the amine increases so does the amount of exchange increase. As the size of cation increases the amount of exchange decreases. Thus the amount of organic–organic exchange is a direct function with respect to the basicity of the exchanging compound and an inverse function with respect to the size.

REFERENCES

Cheng, J. L. and Bray, R. N. (1951) Determination of calcium and magnesium in soil and plant materials: *Soil Sci.*, v. 72, pp. 449–459.

Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill, New York, 384 pp.

McAtee, J. L., Jr. (1959) Inorganic–organic cation exchange on montmorillonite: *Amer. Min.*, v. 44, pp. 1230–1236.

McAtee, J. L., Jr. (1962) Cation exchange of organic compounds on montmorillonite: *Clays and Clay Minerals*, v. 9, Pergamon Press, New York, pp. 440–450.