

CHARACTERIZATION OF MONTMORILLONITE SATURATED WITH SHORT-CHAIN AMINE CATIONS:

2. INTERLAYER SURFACE COVERAGE BY THE AMINE CATIONS

by

EARL B. KINTER AND SIDNEY DIAMOND

Physical Research Division, Bureau of Public Roads, Washington, D.C.

ABSTRACT

Portions of Wyoming bentonite were saturated with a series of short-chain aliphatic amine and quaternary ammonium cations, and the amine content remaining after washing was determined by combustion analysis. For those amine cations containing one or two carbon atoms, the amount of amine found was greatly in excess of the cation-exchange capacity. It is thought that this excess consists of amine cations or uncharged amine molecules which have become partly embedded in the holes associated with the oxygen rings of the silica sheet surfaces. For the larger tertiary amine cations, slightly less than the exchange capacity was found, presumably owing to blocking of some exchange sites by steric interference.

Upon treatment of the amine-saturated clays with glycerol and quantitative determination of the glycerol retained as a monolayer, it was found that these clays retain considerably less glycerol than the original bentonite. The glycerol retention values were employed to provide quantitative estimates of the interlayer clay surface left unoccupied between cation pillars. The percentage of original interlayer surface left unoccupied ranged from about 75 percent for methylamine to essentially zero for the larger tertiary amine cations.

The validity of the areas calculated from the glycerol retention results was indirectly confirmed by deriving estimates of the cross-sectional areas of the several cations from the observed reductions in amount of glycerol retained. These experimentally derived cross-sectional areas were found to be in satisfactory agreement with areas of the cations projected from atom models.

INTRODUCTION

Barrer and Reay (1957) and Barrer and MacLeod (1955) have shown that in montmorillonite saturated with certain short-chain amine and quaternary ammonium cations, the amine cations are present largely as an incomplete monolayer between the unit layers of the montmorillonite, and that the individual cations act as "pillars" in preventing collapse of the montmorillonite lattice on drying. They also demonstrated that the space between the cation pillars was available for the sorption of both polar and nonpolar gases. In attempting to measure the extent of the "interpillar" areas by applying

the Brunauer–Emmett–Teller equation to their observed data for the sorption of gases, Barrer and Reay found that calculated areas were much lower than expected from the cation exchange capacity of the clay and the size of the cations. The principal reason adduced for this discrepancy was that the B.E.T. gas sorption model apparently does not apply to the unusual sorption conditions prevailing in the sterically restricted areas between the montmorillonite unit layers.

The interlayer area in montmorillonite and related substances saturated with inorganic cations may conveniently be measured by liquid-state sorption methods employing polyhydric alcohols such as glycerol (Diamond and Kinter, 1958; Kinter and Diamond, 1958) and ethylene glycol (Dyal and Hendricks, 1950). The method involving glycerol consists of treating a sample of clay with an aqueous solution of glycerol and removing water and excess glycerol by desorption at 110°C in an atmosphere maintained at slightly less than saturation with glycerol vapor. Under these conditions, a monomolecular layer of glycerol is retained by the clay, both on the areas between the unit layers and on the exteriors of particles. Completion of the desorption of excess glycerol is signalled by the attainment of constant weight. The weight increase over the initial oven-dry weight of the clay represents the weight of the monolayer, from which, by assigning a suitable coverage area for the glycerol molecule, the surface area of the clay is estimated.

X-ray diffraction results reported by Diamond and Kinter (this Volume) indicated that glycerol molecules applied in the liquid state can also penetrate interlayer spaces when montmorillonite is saturated with any one of a number of short-chain aliphatic amine cations containing up to four carbon atoms. The entry of glycerol was revealed by an expansion of the basal spacing of the amine-cation saturated clay to provide a separation of not less than about 4 Å between the unit layers. Analogous restricted lattice expansion as a result of sorption of certain polar molecules on amine-treated montmorillonite was observed by Barrer and Reay (1957) and Greene-Kelly (1956).

In the present work, the extent of the interpillar area of a montmorillonite saturated with a series of short-chain aliphatic amine cations was estimated by means of the glycerol retention technique. The interpillar area, the total interlayer area of the original clay, and the number of amine cations present in each amine-saturated product as determined by analysis were used to estimate the area covered by the individual cations.

PREPARATION OF AMINE-SATURATED CLAY

The clay used throughout the studies was “Volclay” brand Wyoming bentonite ground to pass the no. 200 sieve and containing about 85 percent montmorillonite, the remainder being largely quartz and feldspar. This material was used as supplied, without fractionation or other purification. The group of amines used consists of a number of short-chain primary, secondary and tertiary aliphatic amine cations and two small quaternary

TABLE 1.—CHARACTERIZATION OF AMINE-SATURATED CLAY

Saturating cation	Carbon content,* based on oven-dry weight of amine-saturated clay (percent)	Amine content, based on oven-dry weight of untreated clay (meq/g)	Glycerol retention			Calculated interpillar surface area (m ² /g)
			Based on oven-dry weight of amine-saturated clay† (mg/g)	Based on oven-dry weight of untreated clay (mg/g)	Reduction from value for untreated clay (percent)	
Untreated clay	—	‡	—	192§	—	624
Methylamine	2.46	2.35	128.5	137.4	29	431
Ethylamine	3.22	1.46	101.5	109.2	44	331
Dimethylamine	2.97	1.34	106.4	126.8	34	394
Diethylamine	4.16	0.94	70.6	75.3	61	212
Di- <i>n</i> -propylamine	5.56	0.89	54.9	59.5	69	156
Trimethylamine	3.08	0.92	103.7	109.2	43	331
Triethylamine	4.16	0.93	22.5	24.6	87	33
Tri- <i>n</i> -propylamine	7.30	0.75	26.5	29.3	85	49
Tri- <i>n</i> -butylamine	8.83	0.70	13.9	15.7	92	1
Tri- <i>n</i> -amylamine	9.98	0.64	¶	¶	¶	¶
Tetramethylamine	4.26	0.95	85.8	91.7	57	270
Tetraethylamine	7.60	0.89	22.4	24.9	87	34

* Average of duplicate determinations, corrected for carbon content of untreated clay. Analysis performed by L. B. Hayes.
 † Average of duplicate determinations which agreed within 1.5 mg/g.
 ‡ The cation exchange capacity of the untreated clay is 0.91 meq/g.
 § Average of six determinations on a sample washed five times with a 9:1 acetone-water solution, the same washing procedure employed in preparation of the amine cation-saturated samples.
 || Complete interlayer surface area of untreated clay.
 ¶ Not determined; explanation given in text.

ammonium cations (Table 1). Saturation of the clay with the amine cations was accomplished using normal solutions of the amine hydrochlorides prepared by neutralizing Eastman Organic Reagent amines with hydrochloric acid to a final pH of about 7. For saturation with the quaternary ammonium cations, normal solutions of tetramethylammonium bromide and tetraethylammonium chloride, prepared from the corresponding Eastman salts, were used. For each cation saturation, 50 ml of the amine salt solution (five times the exchange capacity) was added to a 10-g portion of the clay, and the mixture was stirred until the clay was thoroughly wetted. About 100 ml distilled water was then added and the whole was vigorously stirred for 10 min with a vibration mixer. The strongly flocculated clay was sedimented by centrifugation, and the supernatant liquid decanted and discarded. The treatment was repeated four more times, and the clay was washed five times by a similar process, using 150-ml portions of a 9:1 acetone-water solution. The clay remained flocculated throughout the washing process and was easily separated from the wash liquid. The last supernatant liquid was shown to be free of chloride ion by testing with silver nitrate solution. The washed clay was dried at room temperature, lightly powdered, and stored.

CHARACTERIZATION OF AMINE-SATURATED CLAY

Determination of Amine Content

The several amine-saturated clay materials were analyzed for carbon content by the conventional dry combustion method, and the amine content in milliequivalents per gram of clay was then calculated, using the carbon content data and the theoretical carbon content of the individual amines. The values obtained are given in Table 1. For comparison with these data, the cation-exchange capacity of the raw clay (0.91 meq/g) was determined by the versenate titration method described by Jackson (1958, p. 64). The amine content varies widely among the several preparations, the values falling into three groups depending on the size of the amine (Table 1). The 1- and 2-carbon amines are found in amounts greatly in excess of the cation-exchange capacity, that of methylamine being almost three times as great; those containing from 3 to 8 carbon atoms are found in amounts approximately equal to the exchange capacity; those containing 9 or more carbon atoms are present in amounts somewhat less than the exchange capacity. The anomalously large amounts of the smaller amines are discussed later in the report. The deficiency in amine content noted for the larger amines is in agreement with findings for other relatively large amines by Hendricks (1941), Slabaugh and Kupka (1958), and others, and apparently results from a steric interference by the large cations, those involved early in the exchange process blocking the access of some of the later ones to the remaining exchange sites. Even after repeated treatments some of the original cations seemingly still remain, and the amine cations are therefore present on the clay in amounts less than the full exchange capacity.

Determination of Interpillar Area

(a) *Glycerol retention determinations.*—Duplicate glycerol retention determinations were made for the untreated clay and for each of the amine and quaternary ammonium saturated clay products, using a procedure essentially as reported earlier (Kinter and Diamond, 1958). Briefly, this involved treating a 1 g sample of clay with 10 ml of a 5 percent aqueous solution of glycerol and bringing it to constant weight (the glycerol monolayer condition) by removal of water and excess glycerol at 110°C in an atmosphere slightly less than saturated with glycerol vapor. The difference in the initial and final weight represents the glycerol retention or weight of the glycerol monolayer. The results of the glycerol retention determinations are also given in Table 1. To provide a uniform basis of comparison, the data in terms of milligrams of glycerol retained per gram of amine-saturated clay (fourth column) were converted to the basis of milligrams per gram of untreated clay, using the carbon content data from the second column and the stoichiometric compositions of the amines. The resulting values show that the amount of glycerol retained has been substantially reduced by the amine treatment. The reductions range from about 30 percent to over 90 percent of the amount retained by the untreated clay, increasing generally with increasing number of substituent alkyl groups and length of the alkyl chains.

To investigate the effect of still larger cations, an attempt was made to obtain similar glycerol retention data for the two next larger cations in the tertiary series, tri-*n*-amylamine and tri-*n*-hexylamine. This was unsuccessful, however, because after saturation and washing the samples could not be brought to constant weight upon oven drying but continued to lose weight slowly for several weeks. The weight loss was accompanied by the evolution of a characteristic amine odor, apparently as a result of the desorption of amine molecules which had been adsorbed during the saturation treatment and not removed by washing. In view of this difficulty, no further attempts were made to characterize tri-*n*-amylamine- and tri-*n*-hexylamine-treated montmorillonite by the glycerol retention technique.

(b) *External surface.*—As indicated above, it is considered that part of the retained glycerol is present in channels between the amine cations in the interlayer spaces, and the remainder as a monolayer on the external particle surfaces. Therefore, in estimating the extent of the interpillar area from these determinations, it is necessary to correct the total retention for the amount retained on external surfaces. In estimating the "external" glycerol it seems reasonable to postulate that the external surface areas of the several amine-saturated products are not significantly different from that of the untreated clay or from each other. The raw clay was treated directly with amine salt solution without prior dispersion, and flocculation was maintained throughout the saturation and washing treatments. While mechanical agitation was a necessary part of the process, it is not thought to have involved sufficient disruption of the primary particles significantly to affect the amount of external surface. The external surface area of the untreated Wyoming

bentonite material was found to be $27 \text{ m}^2/\text{g}$ by the conventional B.E.T. method using nitrogen sorption.¹ A value of $27 \text{ m}^2/\text{g}$ was also cited by Mooney, Keenan and Wood (1952) for untreated and unfractionated Wyoming bentonite of the same grade and from the same source. In subsequent calculations, therefore, the $27 \text{ m}^2/\text{g}$ value is assigned as the external surface area regardless of cation saturation.

(c) *Coverage area per glycerol molecule.*—In calculating surface area values, from glycerol retention data it is also necessary, in effect, to assign an area of surface coverage to the individual glycerol molecules. The assignment of such a coverage area for a sorbate molecule is commonly considered to be the least certain step in calculating surface area from adsorption data, whether by the B.E.T. method or by liquid state sorption as in the present study. In 1958 Diamond and Kinter had assigned a coverage area of 27 \AA^2 to the glycerol molecule, assuming liquid density for the glycerol monolayer and employing a molecular thickness of 4.5 \AA , as derived by X-ray diffraction. A basal spacing value leading to this same thickness was subsequently obtained by Brindley and Hoffman (1962) for a monolayer glycerol complex of montmorillonite. A lesser monolayer thickness of approximately 4.1 \AA has been observed by Diamond and Kinter (this Volume) for glycerol-treated specimens of montmorillonite saturated with a series of small amine cations. This value is the same as the average thickness of the glycerol molecule in a two-layer glycerol complex, and it was used by Jackson (1956, p. 336) in computing a factor for estimating surface areas from retention results for both monolayer and duolayer glycerol complexes. Jackson's computed factor leads to a slightly larger coverage area of 29 \AA^2 for the glycerol molecule.

A scale model of the glycerol molecule was assembled from a Fisher-Taylor-Hirschfelder atom model kit, and measurements of clearance thickness and coverage area were made for various conformations of the molecule, the axis of the carbon chain being maintained in an orientation approximately parallel to the assumed basal clay surface. The molecular coverage areas were measured by placing the model on a sheet of paper, drawing a smoothed outline, and estimating the area of the described figure by cutting and weighing. A number of conformations having clearance thicknesses close to the 4.1 and 4.5 \AA experimental values were examined. It was noted that more than one conformation could lead to the same value of thickness and that each conformation could have a coverage area differing somewhat from others which gave the same thickness. Coverage areas were found to be generally in the range of 27 – 31 \AA^2 , indicating the reasonableness of the 27 and 29 \AA^2 assigned values. However, inasmuch as a unique conformation could not be assigned to a given layer thickness, it was also not possible to select a unique value of coverage area corresponding to each of the two thickness values. In view of this, the 27 \AA^2 coverage area value is employed for surface area computations in the present work, irrespective of the monolayer thickness. Corresponding to this assignment, it is calculated that 1 mg of glycerol in

¹This determination was kindly performed through the courtesy of Dr. Paul Seligmann, Portland Cement Association.

the form of a monolayer occupies 1.76 m^2 of external surface, and 3.53 m^2 when interleaved between adjacent montmorillonite layers. Similarly, 1 m^2 of external surface retains 0.568 mg of glycerol, and 1 m^2 of internal surface, 0.284 mg of glycerol.

(d) *Interpretation of glycerol retention results in terms of interpillar area.*— Values of the interpillar area were derived from the glycerol retention results in the fifth column of Table 1 by subtracting the glycerol corresponding to the external surface ($27 \text{ m}^2/\text{g} \times 0.568 \text{ mg}/\text{m}^2 = 15.3 \text{ mg}/\text{g}$) and multiplying the remainder by the $3.53 \text{ mg}/\text{m}^2$ factor for glycerol on internal surfaces. The results are given in the last column of Table 1. The $624 \text{ m}^2/\text{g}$ value for the interlayer surface of the untreated clay (also given in the last column) is somewhat less than the $760\text{--}800 \text{ m}^2/\text{g}$ range commonly ascribed to pure montmorillonite but is reasonable in view of the natural impurities contained in the bentonite. The data show that in all cases the interlayer area available to glycerol after the formation of amine-cation pillars is substantially less than that of the untreated clay, being about $400 \text{ m}^2/\text{g}$ for methyl- and dimethylamine saturated clay, about $300 \text{ m}^2/\text{g}$ for ethyl-, trimethyl- and tetramethylamine, about $150\text{--}200 \text{ m}^2/\text{g}$ for diethyl- and di-*n*-propylamine, and less than $50 \text{ m}^2/\text{g}$ for the larger tertiary amines and tetraethylamine. With tri-*n*-butylamine, there appears to be no remaining interpillar surface available to glycerol, the retention found ($15.7 \text{ mg}/\text{g}$, fifth column) being essentially the same as the $15.3 \text{ mg}/\text{g}$ expected for the external surfaces of the clay. Some interlayer space apparently is still available for glycerol sorption even when the montmorillonite has been treated with such relatively large cations as triethylamine and tetraethylamine, for which a complete exchange of cations had been accomplished, and tri-*n*-propylamine, for which the exchange had been somewhat less than the full exchange capacity. On the other hand, with tri-*n*-butylamine, the even more limited amine cation population has apparently occupied the interlayer space to such an extent that glycerol molecules are unable to enter.

An explanation of these results must rest on a realistic picture of the distribution of cation sites with respect to the planar surface of the clay. In the amine-saturated clay, each cation in the monolayer is bonded to one of the two adjacent clay surfaces and occupies an area on it equal to its own cross-section. At the same time, it necessarily occupies an equal area on the other clay surface with which it is in contact. From the total surface area and the cation-exchange capacity of the original clay (Table 1), a value of 120 \AA^2 may be calculated for the average area available per exchange site; consequently, the cross-sectional area available per site is half this value or 60 \AA^2 . (On the basis of two-thirds of a charge per unit cell, the theoretical total and cross-sectional areas per unit cell of montmorillonite are 140 and 70 \AA^2 , respectively.) As a first approximation on this basis, the cation positions may be visualized as being distributed over the planar surface in the form of a rectangular net with a unit mesh area of 60 \AA^2 and the nodes representing the centers of the cation positions situated 7.7 \AA apart. Obviously, for a glycerol molecule to enter such an incompletely packed monolayer, there

must necessarily be sufficient room for it between the individual cations. Examination of an atom model has indicated that the smallest width of the glycerol molecule in an interlayer complex would be approximately 5 Å. Accordingly, if the cations were fixed in rigid positions 7.7 Å apart, such a molecule could enter between them only if the width of the cations were less than 2.7 Å. Since this critical width is much smaller than the van der Waals' diameter of even a single methyl group, saturation with any of the experimental amine cations would, on this model, virtually exclude glycerol molecules from the interlayer spaces. Inasmuch as the experimental data indicate that for saturation with most of the cations employed substantial numbers of glycerol molecules do enter and are retained in these spaces, this picture of a fixed, geometrically regular distribution of cation positions in the monolayer is clearly inadequate.

Allowing the individual cations a reasonable degree of mobility would permit the entrance of some glycerol molecules, and the generalized picture of the process would be more in accord with the experimental results. However, unless the sum of the diameters of the cation and the glycerol molecule happened to be fortuitously close to the distance between cation sites, the resulting mixed monolayer would still have a considerable extent of unoccupied space, as the lateral adjustment of a cation to widen a channel sufficiently to accommodate a glycerol molecule would correspondingly constrict the opposite channel.

Locating the interlayer cations in conjunction with the cavities of the oxygen rings of the silica sheets offers a possibly more realistic view of the cation distribution. Although the sources of charge deficiency in the octahedral or tetrahedral layers are not centered directly below these cavities, it has been demonstrated by many workers that small cations tend to enter the cavities when the clay is dried. There are two cavities for each planar face of the montmorillonite unit cell, and the total number associated with a montmorillonite of a given surface area may readily be calculated. The cation-exchange capacity of the experimental montmorillonite suggests that slightly more than one-third of these cavities may have cations associated with them. It may be assumed that although the arrangement of cavities themselves is highly regular in the silica sheets, the distribution of those that are associated with cations should be completely random. Moreover, since in a packet of unit layers the stacking with respect to the *a* and *b* axes is known to be essentially random, the upper and lower oxygen rings that face on a given interlayer space are not normally superposed. As a result of these factors, some of the cation sites must be quite closely spaced and others widely separated.

Accordingly, for saturation with an amine cation of moderate size, those cations occupying the more closely spaced sites might themselves effectively fill the space between the sites, while those on the more widely spaced sites might leave empty channels of much greater width than would be expected on the basis of a uniform spacing of the cations. A continuous distribution of channel widths thus would be expected, ranging from zero to relatively large values. If the cations were fixed in position, some channels would be

too narrow to accommodate glycerol molecules; however, if a certain degree of mobility of the cations is permitted to allow for lateral readjustment during sorption of the glycerol, the resulting mixed glycerol-amine cation monolayer might be almost completely efficient in occupying the interlayer space. On this basis, the area occupied by the pillars may be calculated as the total interlayer area ($624 \text{ m}^2/\text{g}$ in this case) minus the area found to be covered by glycerol molecules. Division of this estimate of pillar area by the numbers of pillars present would yield a value for the area occupied by an individual pillar, and half of this value would represent the cross-sectional area of the pillar. Any vacant area remaining in the mixed monolayer would, on this basis, be erroneously allocated to cation occupation, and if the amount were significant, the experimental values of cross-sectional area would be too high. Comparing such experimental values with similar values obtained from atom models should provide a test of whether the vacant channel area is in fact negligible, and thus whether the glycerol retention technique provides an accurate measurement of interpillar surface area.

In order to make this calculation for a given amine-treated clay it is necessary to estimate the number of cation pillars that are present. The total number of amine cations is readily calculated from the amine content, but it is necessary to correct for the cations that are present on external surfaces. Grim (1953, pp. 132-133), apparently citing Hendricks, Nelson and Alexander (1940), suggested that about 80 percent of the exchange capacity of montmorillonite is associated with planar surfaces, the remainder being due to "broken bond" sites on the edges of the crystallites. However, Weiss (1958) more recently obtained experimental evidence establishing that for mica, vermiculite and montmorillonite, cation exchange at near-neutral pH values is associated exclusively with planar surfaces. If this conclusion of Weiss is adopted, the "external" portion of the cation-exchange capacity may then be estimated from the values for internal and external surface area by assuming (1) that the distribution of the cation exchange sites is the same for all planar surfaces, whether internal or external, and (2) that since clay crystals are usually much larger in the *a* and *b* than in the *c* direction, almost all of their external surface is of the planar type, and the small proportion due to the edges may be ignored. As has been indicated, the external surface of the experimental clay is $27 \text{ m}^2/\text{g}$, which is about 4 percent of the total surface. According to the above assumptions, the "external" amine content would also bear this same relationship to the total amine content, and consequently the "internal" or interlayer amine content would be about 96 percent of the total amount of amine found.

The interlayer area considered to be occupied by the amine cations was calculated for each of the several amine-treated products on the basis outlined above, and the resulting values are listed in the second column of Table 2. Also listed in Table 2 are, in turn, the total number of cations per gram of clay, the estimated number of pillars (96 percent of the total), the amount of interlayer area occupied per pillar, and the cross-sectional area of the pillar. The experimental estimates of cross-sectional area range from

TABLE 2.—EXPERIMENTAL ESTIMATES OF CATION CROSS-SECTIONAL AREAS, AND COMPARISON WITH AREAS MEASURED FROM OUTLINE OF MODELS

Saturating cation	(a) Estimate of interlayer clay surface covered by cation pillars* (m ² /g)	(b) Total no. of amine cations per g of clay, × 10 ²⁰	(c) No. of cations assigned to interlayer spaces per g of clay, × 10 ²⁰ (b) × 0.96	(d) Interlayer clay surface covered per cation pillar, (a) ÷ (b) (Å ²)	Experimental estimate of cross-sectional area per cation, (d) ÷ 2 (Å ²)	Coverage area per cation from atom model outline (Å ²)
Methylamine	193	13.26	12.73	15.2	8	11
Ethylamine	293	8.78	8.43	34.8	17	17
Dimethylamine	230	8.07	7.75	29.7	15	17
Diethylamine	412	5.65	5.42	76.0	38	36
Di- <i>n</i> -propylamine	468	5.10	4.90	95.5	48	47
Trimethylamine	303	5.52	5.30	57.2	29	29
Triethylamine	601	5.57	5.35	112.3	56	48
Tri- <i>n</i> -propylamine	575	4.54	4.36	131.9	66	64
Tri- <i>n</i> -butylamine	623	4.20	4.03	154.6	77	83
Tetramethylammonium	354	5.79	5.56	63.7	32	28
Tetraethylammonium	590	5.36	5.15	114.6	57	50

 * Original interlayer surface of clay (624 m²/g) minus interpillar surface covered by glycerol molecules.

8 Å² for methylamine to 77 Å² for tri-*n*-butylamine, and as expected, increase more or less regularly with increasing chain length and number of substituent alkyl groups.

To provide for the proposed comparison of these estimates with corresponding cross-sectional areas derived from atom models of the cations, a set of the models was assembled from the Fisher-Taylor-Hirschfelder kit mentioned above. These models are designed accurately to reproduce the essential geometric features of the cations on a scale of 1 cm to 1 Å. Outline tracings of the coverage areas were made on paper, as illustrated for tri-*n*-propylamine in Fig. 1. As originally traced, the outlines contained several bulges and indentations (indicated by the dashed line), but it was thought that smoothing and relaxing the outline (indicated by the solid line) would provide a

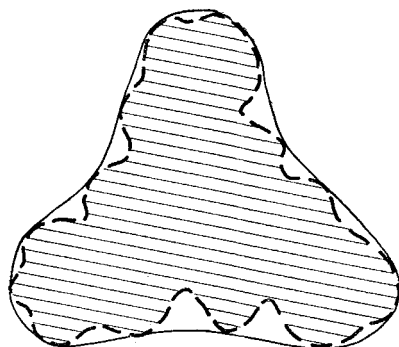


FIGURE 1.—Illustration of characteristic outline of tri-*n*-propylamine cation model (dashed line) and relaxed outline (solid line) used for measuring effective cross-sectional area.

more realistic measurement. Areas enclosed within the outlines drawn on this basis were estimated by cutting and weighing, and are listed in the last column of Table 2. Two types of orientation were used in positioning the models for outlining the coverage areas. For most of the cations, the orientation giving the minimum height, i.e. with the carbon chain parallel to the planar surface of the clay, was used. However, for the three smallest ones, which are thought to be partly embedded in the oxygen-ring cavities, the values shown in the table correspond to orientations having the long axis perpendicular to the planar surface. Outlined areas for these three cations in parallel orientations were 16 Å² for methylamine and 24 Å² for dimethylamine and ethylamine—substantially higher than those cited in the table. It seems clear that for these three amines the experimental estimates of cross-sectional area are in accord with perpendicular rather than parallel orientation. The matter of perpendicular orientation for these three cations is discussed in greater detail later in the report.

In general, there is good agreement between the experimental values of cation area and those derived from the models, the maximum deviation being

only about 15 percent, except for methylamine. There is no indication that the experimental values are systematically higher than those from the models, as would be expected if a substantial amount of vacant area were mistakenly ascribed to amine cation coverage because of incomplete penetration by glycerol. This consistently good agreement suggests that in all cases the amine cations and glycerol molecules occupy essentially all the interlayer space, and substantiates the validity of the measurement of interpillar area by glycerol retention. The virtually complete filling of the interpillar space by glycerol also supports the inference that, in general, the amine cations must have a considerable degree of mobility about the exchange sites; otherwise, they could hardly arrive at such an efficient packing with the glycerol molecules.

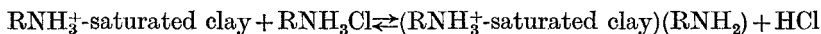
(e) *Effectiveness of triethylamine in excluding glycerol from interlayer spaces.*

In a previous study of the glycerol retention of soils and clays, Kinter and Diamond (1960) used triethylamine saturation as a pretreatment designed to prevent the entry of glycerol into the interlayer spaces. From the present work, however, although it is shown that a full exchange complement of triethylamine cations is adsorbed, it appears that a small amount of glycerol has nevertheless entered. The glycerol retained after triethylamine saturation is thus not a strict measure of the external surface of this montmorillonite. However, in a clay of higher charge density, because of the larger number of exchange sites per unit of surface area, the occurrence of widely-separated sites should be much less likely than in Wyoming bentonite. For such a clay, a cation such as triethylamine, therefore, might be large enough completely to fill the interlayer spaces. Furthermore, since in general only a small part of the internal surface of any montmorillonite is likely to be mistakenly classed as external surface by this procedure, the estimation of the amount of internal surface present in a given sample, and consequently the content of expanding minerals, should not be seriously in error.

Amine Content in Excess of the Cation-Exchange Capacity

As has been indicated, the carbon analysis data show that the smallest amines were adsorbed in amounts well above the cation-exchange capacity. This was further confirmed by ignition loss determinations interpreted by the method of McAtee (1959). Morel (1958), however, has reported the adsorption of methylamine only in amounts equal to or less than the exchange capacity, as did Cowan and White (1958) for ethylamine. Grim, Allaway and Cuthbert (1947) and Cowan and White (1958) have reported excess adsorption, but only for somewhat larger amines than the three small ones involved here. Cowan and White considered that the excess amine must be present either as molecules of the free amine or of the amine salt. Finding by analysis that their amine-treated clay did not contain adsorbed anions, they concluded that there had been no adsorption of amine salt molecules, and that the excess was therefore present as free amine. Although they did not make pH measurements, they assumed that the adsorption of free amine had caused a

lowering of the pH in their clay-amine salt solution mixture, as a consequence of the production of HCl according to the reaction:



Grim, Allaway and Cuthbert (1947) found that sorption of excess amounts of dodecylamine from a dodecylamine acetate solution was accompanied by a drop in pH from 7 to 5.6. In the present work measurements of pH were made on the mixture of dry clay and 1N methylamine hydrochloride solution, but the initial pH of 7 remained essentially unchanged.

In order to determine whether the amine content of the methylamine-treated clay, prepared and washed as previously described, was merely an intermediate stage in the process of removal of excess amine by hydrolysis, a newly prepared methylamine-treated clay was subjected to successive centrifuge washing treatments with the acetone-water wash solution, and a portion of the clay was removed at each stage and analyzed for methylamine content by ignition. The results indicated that 3.0 meq of amine per gram of clay was initially present on the treated product prior to washing; that after a single washing the amine content had dropped to 2.1 meq/g; and that as many as nine additional centrifuge washing treatments had not resulted in any significant further removal of the amine. The amine therefore apparently does not undergo significant hydrolysis on repeated washing, and thus the washed sample whose carbon analysis is reported in Table 1 must have been at equilibrium with respect to the amount of amine present. An X-ray spectrometric analysis of the same material indicated it to be essentially chloride-free. To check the possibility that chloride might have been initially adsorbed during the treatment and subsequently removed by the washing, the methylamine hydrochloride treatment and washing sequences were repeated on a fresh portion of the clay and the supernatant solutions analyzed for chloride. There was no indication of any adsorption of chloride by the clay at any stage.

In attempting to ascertain the nature of the excess adsorbed amine, it seemed reasonable to assume that a complete exchange complement of amine cations was present in the methylamine-treated clay, and that amine in excess of this could be present in one or more of three forms: additional amine cations, free amine or hydrated amine molecules, or undissociated molecules of the amine salt. For the excess to be present as amine cations would require either that an equal number of adsorbed anions (chloride or hydroxyl) also be adsorbed to preserve the electrical neutrality of the solution, or that the neutrality be preserved by a rather unlikely partial decomposition of the clay. Since the analysis showed no adsorption of chloride, the excess was definitely not in the form of amine salt. Furthermore, since there was no lowering of pH, as there would have been had hydroxyl ions been adsorbed, it does not seem likely that the excess could be in the form of cations. The remaining possibility—that the excess is free amine or hydrated amine molecules—is also not supported by the experimental data. If either of the last two species had been adsorbed in excess, the reaction suggested by

Cowan and White would have applied, and a marked lowering of pH should have been observed. The specific form of the excess amine therefore remains in doubt.

Although the adsorption of large amounts of long-chain amines and quaternary ammonium compounds on montmorillonite commonly has been attributed to van der Waals' bonding, it would not be expected that the very small amines could be held by such bonding against repeated washing of the clay or drying at 110° C. It would seem, therefore, that the retention of these must involve an additional mechanism. One possible mechanism may be found in the suggestion of Weiss (1958) that free ammonia or small amine molecules could bond to montmorillonite by replacing water molecules in octahedral coordination around aluminum atoms exposed at the edges of the clay crystallites. Weiss determined experimentally that approximately 0.2 to 0.3 meq ammonia per gram of montmorillonite can be held in this way. However, since this is much less than the approximately 1.4 meq of excess methylamine found in the present work, this mechanism can hardly account for the present effect.

An explanation more in accord with the experimental data is that the adsorbed amine material, consisting of both the complement of cations equivalent to the exchange capacity and the excess amine, may be partially embedded in the oxygen-ring cavities of the clay surface. It is thought that such embedding may account for the ability of the clay to retain the excess amine against the subsequent washing and drying treatments. The embedding would involve orientation of the amine more or less perpendicularly to the clay surface. This embedding and perpendicular orientation is in accord with the results of Rowland and Weiss (this Volume) obtained from oscillating-heating X-ray diffraction experiments, that methylamine and dimethylamine cations adsorbed by montmorillonite from solutions of moderate concentration were so located and oriented. For the methylamine, this orientation presumably would have either the amine group or the methyl group partly embedded in the cavity, with the remaining group located directly above, and the long axis of the amine thus being perpendicular to the clay surface. A similar arrangement may be visualized for ethylamine, except that since the carbon-carbon bond of the ethyl group must maintain an approximately 110° angle with the carbon-nitrogen bond, the terminal group of the ethylamine must be offset from the perpendicular axis. For dimethylamine, since the amine group is in the middle of the molecule, one of the terminal methyl groups must be embedded in the cavity, with the amine group directly above and the other methyl group offset to maintain the required bond angle.

As previously noted, the experimental cross-sectional areas given in Table 2 strongly support this perpendicular orientation for these three amines. As indicated by Diamond and Kinter (this Volume) X-ray diffraction measurements of the separation between the clay layers in montmorillonite saturated with these three amines are also consistent with perpendicular orientation and embedding. While the long dimensions of the amines as measured from models are from 1.6 to 2.3 Å greater than the observed distances between

the clay layers, the 2.4 Å depth of the cavities (Barrer and Reay, 1958) is sufficient to permit this perpendicular orientation.

The specific amount of methylamine adsorbed also suggests an association of the amine with the cavities. From the widely accepted Hofmann-Endell-Wilm structure, it may be calculated that there are approximately 1.6×10^{21} cavities per gram of pure montmorillonite. The analysis given in Table 2 for the methylamine-saturated bentonite indicates that the amine content is equivalent to approximately 1.3×10^{21} methylamine cations per gram of clay. The bentonite used was not fractionated or otherwise purified; from the observed interlayer surface of 624 m²/g as compared to the theoretical 760 m²/g for pure montmorillonite, it was estimated to contain about 82 percent of montmorillonite. Accordingly, the expected number of cavities per gram of the bentonite would be about 1.3×10^{21} , which is in agreement with the amount of amine indicated to be present by the carbon analysis. It is noted, however, that for dimethylamine and ethylamine the estimates of the total number of amine cations per gram of clay, 0.81 and 0.88×10^{21} , are considerably less than this. According to the interpretation given above, the cavities associated with exchange sites would be fully occupied by amine cations, and the excess amine would be sufficient to occupy only slightly more than half of the remaining cavities. In view of the restricted layer separations indicated by X-ray diffraction, even for wet amine-treated clay, the failure of the 2-carbon amines to occupy all the available cavities may be due to the purely physical difficulty of becoming oriented so as to be able to enter them.

SUMMARY AND CONCLUSIONS

Wyoming bentonite was treated with solutions of the hydrochlorides of several short-chain aliphatic amines and two quaternary ammonium salts, and washed with an acetone-water solution. Carbon analyses indicate that in most cases the cations were adsorbed and retained against washing in amounts consistent with the exchange capacity of the clay. However, for the 1- and 2-carbon amines, the adsorption was greatly in excess of the exchange capacity, while for the larger tertiary amines, it was less than the exchange capacity.

Glycerol retention determinations indicate that the surface available to glycerol is greatly reduced by treatment with amine cations, the reduction being most pronounced for the larger cations. After allowing for glycerol retained on external surfaces, the remaining glycerol is interpreted as having been retained between the cation "pillars" in the interlayer spaces. The glycerol retention values observed lead to estimates of "interpillar" area ranging from more than 400 m²/g for the methylamine-treated clay to essentially zero for the clay treated with tri-*n*-butylamine.

In consequence of this interpretation, the difference in glycerol-retaining capacity between untreated bentonite and the amine-treated clay is ascribed to the interlayer area physically occupied by the amine cations. From the

loss of glycerol-retaining capacity, the total area occupied by the cations and the average cross-sectional area per cation were calculated for each of the several amines. These experimental cross-sectional areas were shown to be in good agreement with coverage areas obtained from atom models of the individual amines. This agreement confirms that the interlayer space not occupied by amine cations may be virtually completely occupied by glycerol, and consequently that the glycerol retention method provides an acceptable measure of the area between the amine cation pillars. The completeness with which glycerol fills the interpillar areas suggests that at least the larger cations possess some freedom of lateral adjustment in the interlayer space.

The distribution of cations within the monolayers is considered to be somewhat irregular, with the actual distances between adjacent cation sites deviating considerably from the calculated average distance of 7.7 Å. Owing to this irregularity, saturation treatments with cations such as tri-*n*-propylamine, which are large enough to occupy all the interlayer surface of the clay on the basis of a complete exchange of cations, do not necessarily accomplish this coverage. On the one hand, the exchange of large cations is not complete because some of the sites that happen to be closely spaced may be blocked; but at the same time, in regions of widely-separated sites, some of the interlayer area may still be unoccupied. Upon glyceration a few glycerol molecules, therefore, may be adsorbed into the interlayer space, the probability of this presumably decreasing with increasing layer charge of the montmorillonite. Because of this, saturation with triethylamine cations, which has previously been suggested as a means of preventing the penetration of glycerol into the interlayer spaces, is not completely effective with Wyoming bentonite. Estimates of the external surface of some soils and clays obtained by glycerol retention after such treatment thus may be slightly high.

Methyl-, ethyl-, and dimethylamine seem to be adsorbed and retained by the clay in a manner somewhat different from the other amine cations, apparently being in perpendicular rather than parallel orientation with respect to the planar surface of the clay. The amount of methylamine adsorbed and retained corresponds to the number of oxygen-ring cavities calculated to be present on the clay surface. It is thought that a full exchange complement of methylamine cations is partly embedded in those cavities that are associated with cation sites, and that amine in excess of this is similarly embedded in the remaining ones. The adsorption of excess amine was not accompanied by either the adsorption of chloride ions or an observable drop in pH. Consequently, while it is clear that the excess amine is not adsorbed as molecules of amine salt, it is not certain whether adsorption is in the form of amine cations or as free amine molecules. The adsorption of the two-carbon amines was somewhat less than for methylamine, corresponding to occupation of all the cavities associated with cation sites, plus only about half of the remaining ones. This lesser adsorption is thought to be due to the physical difficulty of the 2-carbon amines in becoming suitably oriented for embedding in the cavities.

REFERENCES

- Barrer, R. M. and MacLeod, D. M. (1955) Activation of montmorillonite by ion-exchange and sorption complexes of tetra-alkyl ammonium montmorillonite: *Trans. Faraday Soc.*, v. 51, pp. 1290-1300.
- Barrer, R. M. and Reay, J. S. S. (1957) Sorption and intercalation by methyl ammonium montmorillonites: *Trans. Faraday Soc.*, v. 53, pp. 1253-1261.
- Barrer, R. M. and Reay, J. S. S. (1958) Sorption by NH_4^+ - Cs^+ -montmorillonites, and ion fixation: *J. Chem. Soc.*, pp. 3824-3830.
- Brindley, G. W. and Hoffman, R. W. (1962) Orientation and packing of aliphatic chain molecules on montmorillonite: in *Clays and Clay Minerals*, v. 9, Pergamon Press, New York, pp. 546-556.
- Cowan, C. T. and White, D. (1958) The mechanism of exchange reactions occurring between sodium montmorillonite and various *n*-primary aliphatic amine salts: *Trans. Faraday Soc.*, v. 54, pp. 691-697.
- Diamond, Sidney and Kinter, E. B. (1958) Surface areas of clay minerals as derived from measurements of glycerol retention: in *Clays and Clay Minerals*, Nat. Acad. Sci.-Nat. Res. Council, pub. 566, pp. 334-347.
- Diamond, Sidney and Kinter, E. B. (1962) Characterization of montmorillonite saturated with short-chain amine cations, 1. Interpretation of basal spacing measurements: This volume.
- Dyal, R. S. and Hendricks, S. B. (1950) Total surface of clays in polar liquids as characteristic index: *Soil Science*, v. 69, pp. 421-432.
- Greene-Kelly, R. (1956) The swelling of organophilic montmorillonites in liquids: *J. Colloid Science*, v. 11, pp. 77-79.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill, New York, 384 pp.
- Grim, R. E., Allaway, W. H. and Cuthbert, F. L. (1947) Reaction of different clay minerals with some organic cations: *J. Amer. Ceramic Soc.*, v. 30, pp. 137-142.
- Hendricks, S. B. (1941) Base-exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals' Forces: *J. Phys. Chem.*, v. 45, pp. 65-81.
- Hendricks, S. B., Nelson, R. A. and Alexander, L. T. (1940) Hydration mechanism of the clay mineral montmorillonite saturated with various cations: *J. Amer. Chem. Soc.*, v. 62, pp. 1457-1464.
- Jackson, M. L. (1956) *Soil Chemical Analysis—Advanced Course*: published by the author, University of Wisconsin, Madison 6, Wis.
- Jackson, M. L. (1958) *Soil Chemical Analysis*: Prentice-Hall, Inc., Englewood Cliffs, N.J.
- Kinter, E. B. and Diamond, S. (1958) Gravimetric determination of mono-layer glycerol complexes of clay minerals: in *Clays and Clay Minerals*, Nat. Acad. Sci.-Nat. Res. Council, pub. 566, pp. 318-333.
- Kinter, E. B. and Diamond, S. (1960) Pretreatment of soils and clays for measuring external surface area by glycerol retention: in *Clays and Clay Minerals*, 7th Conf., Pergamon Press, New York, pp. 125-134.
- McAtee, J. L. Jr. (1959) Inorganic-organic cation exchange on montmorillonite: *Amer. Min.*, v. 44, pp. 1230-1236.
- Mooney, R. W., Keenan, A. G. and Wood, L. A. (1952) Adsorption of water vapor by montmorillonite. I. Heat of desorption and application of B.E.T. theory: *J. Amer. Chem. Soc.*, v. 74, pp. 1367-1371.
- Morel, R. (1958) Observations sur la capacité d'échange et les phénomènes d'échange dans les argiles: *Bul. du groupe français des argiles*, v. 10, pp. 3-7.
- Rowland, R. A. and Weiss, E. J. (1962) Bentonite-methyl amine complexes: This volume.
- Slabaugh, W. H. and Kupka, F. (1958) Organic cation exchange properties of calcium montmorillonite: *J. Phys. Chem.*, v. 62, pp. 599-601.
- Weiss, A. (1958) Über des Kationenaustausch vermögen der Tonminerale—II. Der Kationenaustausch bei den Mineralen der Glimmer-, Vermikulit- und Montmorillonitgruppe: *Z. Anorg. Allg. Chemie*, v. 297, pp. 257-286.