

BENTONITE-METHYLAMINE COMPLEXES¹

by

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ABSTRACT

Suspensions containing 3 percent sodium bentonite (Wyoming) and each of the four methylamine hydrochlorides were prepared so that the latter were present in amounts equal to 25, 50, 75, 100, 125, 200, 400, 600, 800, and 1000 percent of the exchange capacity of the clay. The flocculated clay was removed by decantation, and an oscillating-heating X-ray diffraction (Cu $K\alpha$) pattern was made of the first-order diffraction maximum. With these patterns, the thermal stability, mixed layering, and multilayering of the amine-bentonite complex were followed. For methylamine, the data suggest that the first cations to enter lie in the holes with their C-N axes as close to the oxygen surface as possible. As additional methylamine hydrochloride enters, the C-N axis stands perpendicular in the holes to accommodate the chloride, and after all the holes are filled a second layer forms. Although the geometry of the dimethylamine cation permits it to occupy only two out of three holes, it also forms a second layer. The trimethylamine and tetramethyl ammonium cations are so large that they can occupy only one hole in three; this distribution satisfies the cation-exchange capacity, but a second layer does not form.

INTRODUCTION

The four methylamines are uniquely suited for the study of montmorillonite-organic complexes because the structure of the small molecules is known (Structure Reports, 1945-46) and the water-soluble hydrochloride readily exchanges for the inorganic cation held between the layers of the montmorillonite.

Of these, only the tetramethyl ammonium salt supplies a cation. The methyl-, dimethyl-, and trimethylamine hydrochlorides react with the clay by substituting hydrogen for the exchange cation and are bonded to the clay through this hydrogen. Dimethylamine is slightly more basic than methylamine, and both are an order of magnitude more basic than trimethylamine. For convenience, the form attached to the clay can be called a cation.

Cowan and White (1958) investigated the retention by montmorillonite of

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primary aliphatic amines of increasing chain length. For chain lengths of eight carbons or less, they found that the amount of amine retained by the clay does not increase even when ten times the cation exchange capacity is added and that this amount is retained even with water washing.

Barrer and MacLeod (1955) and Barrer and Reay (1957) reported on the surface activation of montmorillonite which had adsorbed tetramethyl and tetraethyl ammonium cations. Their work includes basal spacings for these complexes. Jordan (1949) presented data on the adsorption of longer carbon chain amine complexes. Very little information is available, however, on the arrangement of the methylamines on the oxygen surface of the clay.

EXPERIMENTAL

Suspensions containing 3 percent sodium Wyoming bentonite and each of the four methylamine hydrochlorides were prepared so that the latter

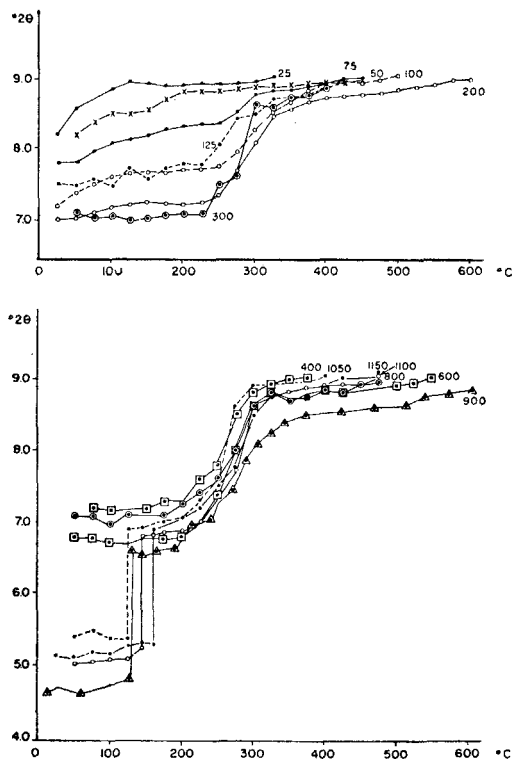


FIGURE 1.—Change in $d_{(001)}$ (degrees 2θ) of methylamine hydrochloride bentonite with increasing temperature ($5^\circ\text{C}/\text{min}$). Each curve presents data from an oscillating-heating pattern. The number on each curve is the total amount of amine expressed as percentage of the base-exchange capacity.

were present in amounts equal to 25, 50, 75, 100, 125, 200, 400, 600, 800, and 1000 percent of the exchange capacity of the clay. The bentonite, which has a cation-exchange capacity (C.E.C.) of 90 meq/100 g, was a -1μ fraction converted to the sodium form on a sodium Dowex 50 resin column. These mixtures were allowed to react for several days, during which they were frequently agitated. The clay complex was then removed by decantation and

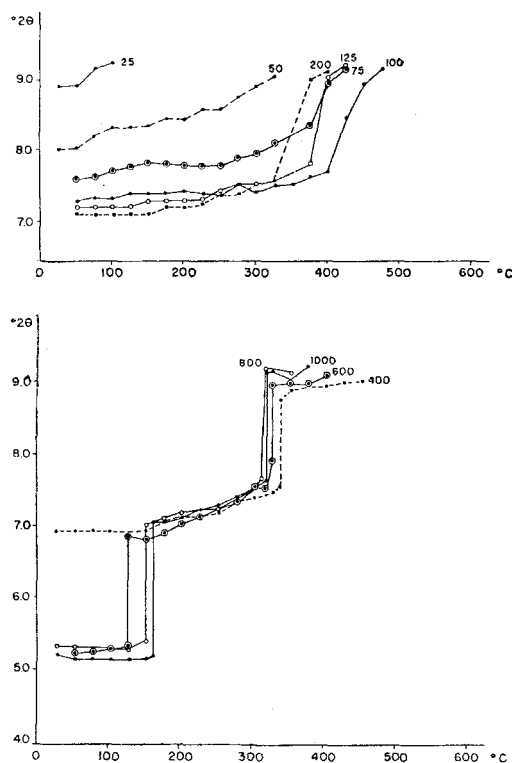


FIGURE 2.—Changes in $d_{(001)}$ of dimethylamine hydrochloride bentonite.

was mounted on the specimen holder of the oscillating-heating X-ray powder diffraction apparatus (Weiss and Rowland, 1956). With Cu $K\alpha$ radiation, the first-order diffraction maximum was recorded while the sample temperature was raised at the rate of $5^{\circ}\text{C}/\text{min}$ until the 001 spacing had collapsed to $9.2^{\circ}2\theta$ (9.6 \AA). The resulting basal spacing in degrees 2θ is plotted against temperature in Figs. 1, 2, 3, and 4.

At atmospheric temperature and humidity, sodium bentonite usually contains one layer of water, and the first-order basal spacing is 12.6 \AA ($7.0^{\circ}2\theta$). This water is lost between 50° and 60°C , and the basal spacing collapses to 9.6 \AA ($9.2^{\circ}2\theta$).

Methylamine hydrochloride forms a series of complexes at concentrations below 300 percent of the C.E.C. Below 100 percent of the C.E.C. these complexes contain some water, some methylamine, and some collapsed layers. The 125 percent and 200 percent curves are close together at a spacing of about 11.7 Å. Infrared patterns show that the mixtures below 300 percent contain more water than those above 300 percent. Between 300 and 600 percent the

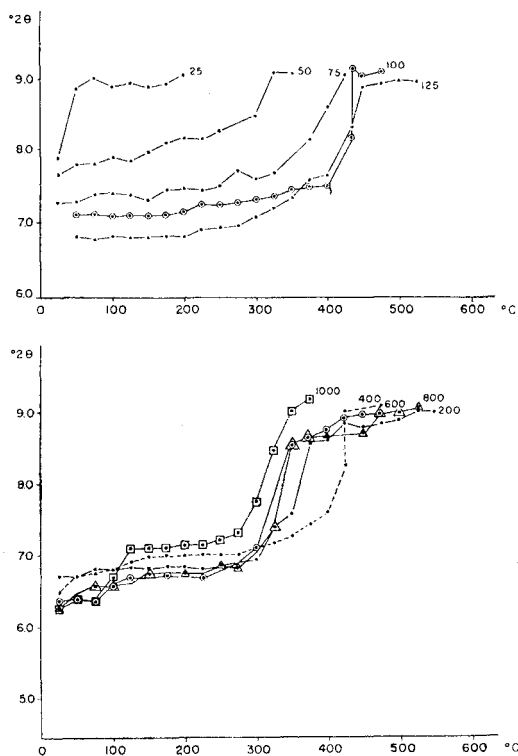


FIGURE 3.—Changes in $d_{(001)}$ of trimethylamine hydrochloride bentonite.

spacing varies from 12.4 Å to 12.9 Å as the combination passes through a one-layer configuration of the $\text{CH}_3\text{NH}_2 \cdot \text{H}^+$ cation. At concentrations above 600 percent of the C.E.C. a second layer, with an average spacing of about 17.4 Å, begins to form. This second layer desorbs at temperatures between 130° and 160° C, leaving one layer at about 12.9 Å. When samples above 300 percent of the C.E.C. are washed with water, the spacing returns to 11.7 Å. For all concentrations the complex is destroyed at temperatures near 300° C, and the clay is essentially collapsed.

Dimethylamine hydrochloride expands the clay to approximately a one-layer spacing at 100 per cent of the C.E.C. At concentrations between 100 and

400 percent of the C.E.C. the spacing expands from 12.5 Å to 12.7 Å. Above 600 percent a second layer forms at 17.0 Å. This layer is desorbed between 130° and 160° C. All the amine is desorbed at about 320° C, except the 100 percent and 125 percent samples, in which the amine persists to almost 400° C.

The trimethylamine hydrochloride props open most of the interlayer space at a concentration equal to 75 percent of the C.E.C. As the concentration of

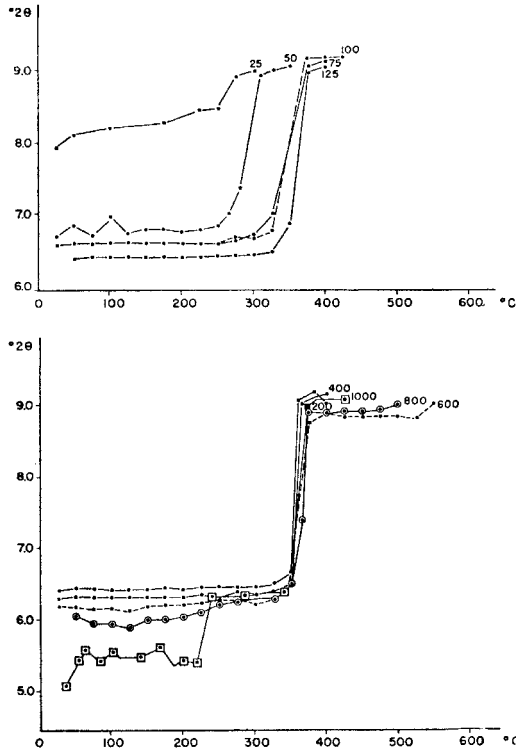


FIGURE 4.—Changes in $d_{(001)}$ of tetramethyl ammonium chloride bentonite.

the amine is increased, the spacing increases from about 12.3 Å to 13.6 Å at 1000 percent of the exchange capacity, but no second layer develops. After the excess water is driven off around 100° C, the most preferred spacing is around 13.5 Å.

Tetramethyl ammonium chloride props open many of the layers at a concentration equal to 50 percent of the C.E.C. The spacing of 13.4 Å increases steadily to 14.5 Å at 800 percent of the exchange capacity. The 100 percent sample loses excess water below 100° C and collapses to the general level of 14.5 Å at 200° C. All the samples desorb the organic at 350° C.

DISCUSSION

Hendricks (1941) has pointed out that organic cations are held to the surface not only by the coulombic forces due to the ionic nature of the compound but also by van der Waals' forces between the molecule and the neighboring oxygen surface of the clay. The interlayer space is equal to a distance characteristic of these forces plus the orientation of the molecule. In general, the orientation of the molecule would tend to maximize these forces.

The X-ray diffraction patterns from the methylamine-bentonite complexes are not suitable for a one-dimensional Fourier analysis to determine the orientation of the interlayered organic molecule because they consist of an intense first order of (00 ℓ) and low-intensity, diffuse higher orders up to the fifth. However, some information about the orientation of these molecules can be inferred from the first-order spacing by observing its changes with increasing concentration of the organic molecule and desorption on heating. Although the dimensions of the organic molecule are not known under exactly these conditions, dimensions free of the influence of the oxygen surfaces are available (Structure Reports, 1945-46).

Because it becomes increasingly difficult, with these small molecules, to decide whether the nitrogen determined by analysis comes from an amine ion attached to the clay, an amine salt lying between the clay layers, or an amine salt simply included with the clay, solution isotherms were not attempted.

In the following discussion it is assumed that the charge on the oxygen surface of the clay is statistically distributed with one charge in every three holes, although there is no evidence for such an even pattern. Similarly, the bond angle difference between the amines is assumed to remain at 109°, because a few degrees variation makes little difference in these results.

The positively charged methylamine $\text{CH}_3\text{NH}_2 \cdot \text{H}^+$ cation consists of a carbon atom bonded to a nitrogen atom, with three hydrogens arranged at the remaining vertices of a tetrahedron about each carbon and nitrogen atom. Since the diameter of the carbon atom is about the same as that of the nitrogen atom ($\text{C-N} = 1.56 \text{ \AA}$), either would fit into the hexagonal ring of the oxygen surface of the clay if the hydrogen atoms were not present. If the height of the methylamine ion is 4.28 \AA (4.30 \AA with Fisher-Taylor-Hirschfelder models), then the complex will have a repeat distance (001) of 13.9 \AA when the organic is positioned directly over an oxygen. Positioned over a hole, as in Plate 1*b*, or sitting on the three oxygens of the base of a silica tetrahedron, the ion can penetrate the oxygen surface as much as 0.4 \AA at either end, and the 001 spacing will be about 13.1 \AA . If the hydrogens of the ion slide down into the hole between two oxygens (Plate 1*a*), then the amine end can penetrate 0.7 \AA and the methyl end can penetrate about 0.6 \AA , which reduces the 001 spacing to 12.65 \AA . When the axis of the amine tilts in the hole (Plate 2), the distance from oxygen surface to oxygen surface is 2 \AA , and the 001 spacing becomes 11.6 \AA . For this minimum to obtain, however, each molecule must be oriented in the same direction.

Since there is no spacing greater than 13.3 \AA (Fig. 1) in the one-layer range, the condition which requires the methylamine to sit on top of an oxygen (13.9 \AA) is not realized. However, one end, but not the other, may penetrate a hole, giving a spacing of 13.3 \AA . This is suggested by the triangles for the 900 percent curve of Fig. 1. Most of the curves lie within a range in which fitting into both holes would likely apply. However, the 125 percent and 200 percent curves may be either the result of tilting of the methylamine molecule or a combination of some of the molecules standing in the holes of some layers, whereas other layers have not been penetrated and are still collapsed.

The oxygen surface area covered by the methylamine molecule is 14 \AA^2 when the long axis of the amine is perpendicular to the oxygen surface, or 17 \AA^2 when the long axis is parallel to the oxygen surface. Since each unit cell contains two-thirds of an exchange charge, or one charge per 72 \AA^2 , the exchange capacity is satisfied when 19 percent of the oxygen surface is covered by methylamine molecules standing perpendicular or when 23.5 percent of the oxygen surface is covered by methylamine molecules that are tilted.

Each unit cell has two oxygen rings, and there is room for two methylamine molecules. When these two molecules are tilted, the area is 70 percent covered, and there is no room for the chloride ion associated with the amine in excess of the exchange capacity. When the molecules are perpendicular, 58 percent of the area is covered, and there is room for the extra chloride ions.

As the methylamine ions penetrate between the layers, those entering first probably lie in the holes with their long axes as close as possible to the oxygen surface (Plate 2). This may continue until the exchange capacity is satisfied, or when one-third of the holes are occupied. The entrance of an additional methylamine cation is accompanied by an associated chloride ion which is retained between the clay layers. With one hole already occupied, there is room for one additional methylamine hydrochloride in the two remaining holes. In order for room to be provided for the chloride ion of the third methylamine hydrochloride, the molecule must rotate until its axis is perpendicular to the oxygen surface (Plate 1). In this position, there is adequate room for one methylamine ion and two methylamine hydrochloride molecules. The entrance of additional methylamine hydrochloride then begins to form a second layer.

The dimethylamine ($\text{CH}_3)_2\text{NH} \cdot \text{H}^+$ cation differs geometrically from the methylamine cation in that a methyl group has replaced one of the hydrogens on the nitrogen. It resembles the beginning of a zigzag carbon chain, except that the nitrogen in the middle is the site of the charge. There are three positions which this cation may assume on the oxygen surface. In one position the plane of the zigzag chain may be parallel to the oxygen surfaces (Plate 3a). The area of the molecule is 32 \AA^2 , and it covers 67 percent of the unit cell, or 44.5 percent of the unit charge area. In this position the calculated repeat distance is 12.6 \AA . In another position (Plate 3b), the plane of the zigzag chain is perpendicular to the oxygen surface. In this position, it covers 28 \AA^2 , which

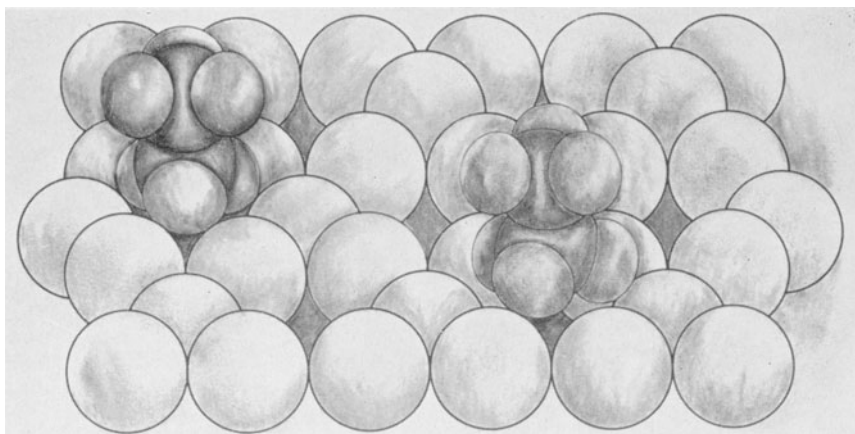


PLATE 1.—(a) Methylamine ion located over hole in oxygen surface with each hydrogen of the amine touching two oxygens and penetrating into the surface 0.7 \AA ($d_{(001)} = 12.65 \text{ \AA}$). (b) Each hydrogen of the amine touches one oxygen and penetrates into the surface 0.4 \AA ($d_{(001)} = 13.1 \text{ \AA}$). After the exchange capacity has been satisfied (one amine in every third hole), methylamine hydrochloride can fill the remaining holes with room for the chloride between the amine molecules.

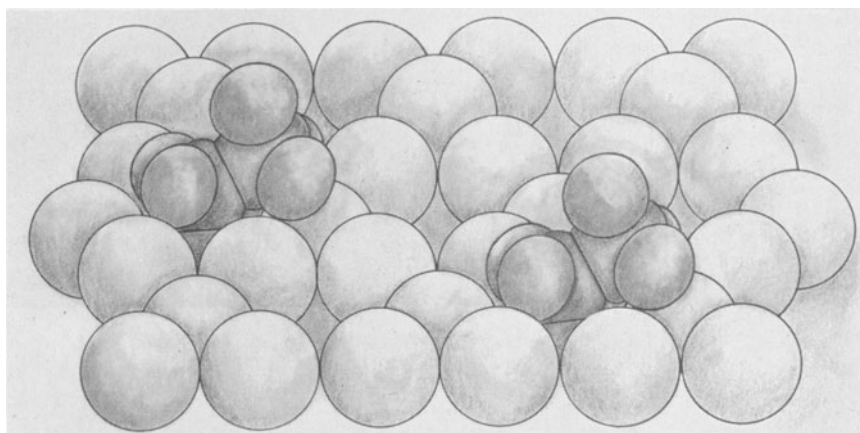


PLATE 2.—Methylamine ion with one hydrogen penetrating into the hole. All molecules must have the same orientation in order to fit the overlying oxygen surface and to account for the observed spacing $d_{(001)} = 11.6 \text{ \AA}$. Only one of the other two holes may be occupied by a molecule of the amine hydrochloride.

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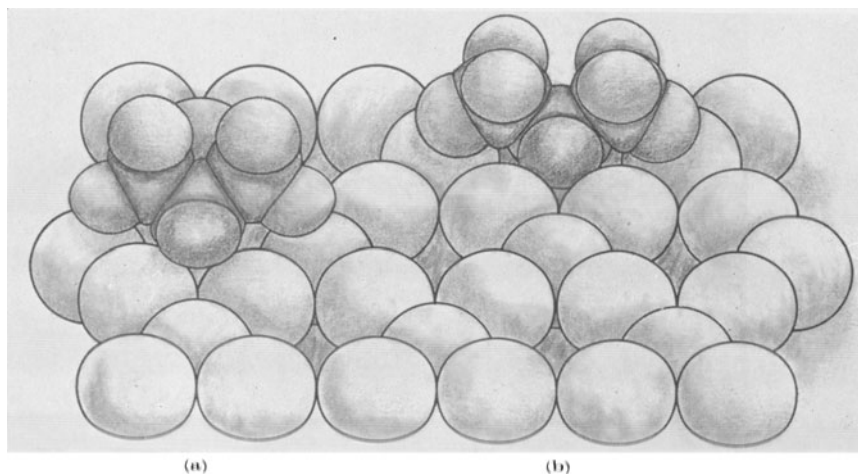


PLATE 3.—(a) Dimethylamine ion with the plane of the zigzag chain parallel to the oxygen surface; one hydrogen penetrates the hole; $d_{(001)} = 12.6 \text{ \AA}$. (b) Plane of dimethylamine zigzag chain perpendicular to the oxygen surface; $d_{(001)} = 12.8 \text{ \AA}$. After the charge is satisfied, an additional dimethylamine hydrochloride molecule may occupy one of the two remaining holes.

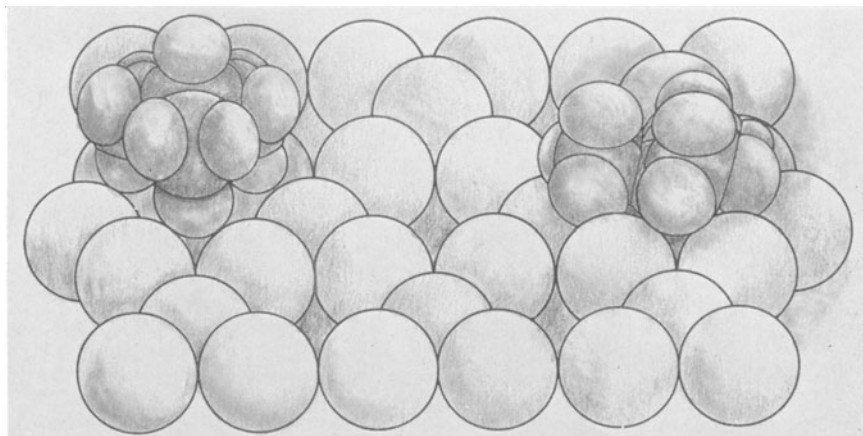


PLATE 4.—Trimethylamine ions lying flat over holes in the oxygen surface, one with the single hydrogen uppermost, and the other with this hydrogen in the hole; $d_{(001)} = 12.6 \text{ \AA}$. The size of the molecule precludes the occupancy of surrounding holes, and only one hole out of every three can be occupied by the trimethylamine ion.

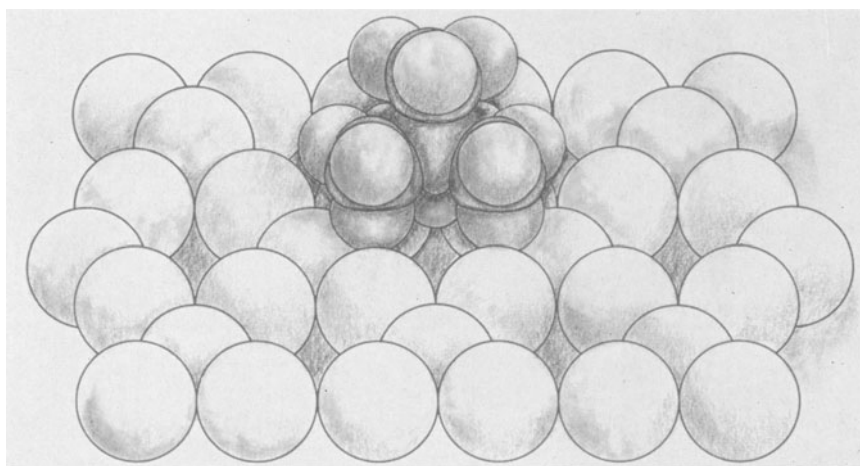


PLATE 5.—Tetramethyl ammonium ion located with one hydrogen of each of three methyl groups contacting two adjacent oxygens. The nitrogen is centered over a hole in the oxygen surface; $d_{(001)} = 14.6 \text{ \AA}$. Only one hole in three can be occupied, and therefore no additional salt can be sorbed.

is 59 percent of the unit cell area, or 40 percent of the unit charge area, and has a calculated repeat distance of 12.8 Å. These calculated repeat distances compare well with the observed distances of 12.5 Å to 12.7 Å. The maximum coverage for either of these positions is one molecule in every other hole, and there is space for diamethylamine hydrochloride after the charge is satisfied and before the second layer begins.

A third position, with the axis of the carbon and the nitrogen almost perpendicular, covers an area of 20 Å², which is 41 percent of the unit cell area or 26 percent of the unit charge area. In this position there would be room for an amine in every hole, but the calculated repeat distance was not observed.

The trimethylamine (CH₃)₃N·H⁺ cation is almost disc-shaped, since the three methyl groups form the base of an obtuse pyramid with nitrogen almost in the plane of the carbon. Because of its size and shape, it must lie flat over the hole, with the cation as close to the negative charge on the oxygen surface as possible (Plate 4). In this position only one of each three holes can be occupied. Additional trimethylamine hydrochloride cannot lie flat on the surface, even with crowding. The area of a trimethylamine cation lying flat is 28 Å², which covers 59 percent of the unit cell area and 39 percent of the area per unit charge. The calculated spacing of one layer in which every third hole is occupied is 12.6 Å, which agrees with the range of data obtained. Perhaps the lack of additional space on the oxygen surface accounts for the lack of a second layer.

The tetramethyl ammonium cation (CH₃)₄N⁺ is symmetrical, with four methyl groups arranged tetrahedrally around the nitrogen. If one of these methyl groups is allowed to point upward, then the cation will fit over the hole in the same position as the trimethylamine and be subject to the same coverage; one hole in three (Plate 5). However, the methyl group on top of the tetramethyl ammonium ion cannot penetrate the upper layer of the trimethylamine, as did the hydrogen, and this makes a greater separation of the oxygen surfaces. Such an arrangement would result in a calculated spacing of about 14.6 Å, which is in good agreement with the upper limit observed (14.7 Å).

The exact attitude of the symmetrical cation has a negligible effect on the spacing and coverage. Because the 001 spacing for other quaternary ammonium salts is essentially the same as that for tetramethyl, a position with the planes of the two "zigzag" chains perpendicular to the oxygen surface (as in Plate 3) may be more logical. In this position additional carbons can be added to the chain without affecting the spacing.

The temperature of the flexures in each family of curves does not correspond to melting, sublimation, or boiling temperatures for the amine hydrochloride. The sharp break at 135°C in the methylamine hydrochloride curves and around 150°C in the dimethylamine hydrochloride curves probably indicates the departure of water and the amine hydrochloride.

The collapse of the clay above 220°C on the methylamine curves and above 300°C for the other amines is associated with the dissociation of the

organic compound. Some of the high-temperature products remain between the layers even at the highest temperatures shown.

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