

ADSORPTION OF 1-*n*-ALKYL PYRIDINIUM BROMIDES BY MONTMORILLONITE

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ABSTRACT

Adsorption isotherms of 1-*n*-alkyl pyridinium bromides on Na-montmorillonite, and in addition of cetyl pyridinium bromide on Ca-montmorillonite, have been determined. For up to eight carbon atoms in the alkyl chain adsorption has a limit close to the exchange capacity of the clay. With larger ions adsorption occurs beyond this and is accompanied by adsorption of the bromide ion. Adsorption of the cetyl pyridinium ion beyond the exchange capacity is greater on Na- than on Ca-montmorillonite. Replacement of the cation initially present is incomplete. X-ray diffraction analysis shows that the adsorbed ions normally lie flat on the clay surface, but cetyl pyridinium ions may stand up in a plane at right angles to the surface. Interlamellar separations somewhat less than the minimum molecular thicknesses, found for the methyl and ethyl pyridinium ions, are attributed to a combination of (1) "keying" of the alkyl groups into the clay surface, and (2) the effect of the attractive forces between the clay and the pyridinium ring. It is concluded that adsorption is due to ionic and dispersion forces between the pyridinium ions and the clay. For the cetyl compound the dispersion forces are larger than ionic forces. The exchangeable cation initially present influences the adsorption by its effect on the exchange reaction and probably also by its influence on the domain structure of the clay and hence the accessibility of external surfaces of the crystallites.

INTRODUCTION

The present paper is a preliminary report of an investigation of certain features of the adsorption of 1-*n*-alkyl pyridinium compounds by montmorillonite. It is well known that the physical properties of clays can be modified considerably by combination with quaternary ammonium salts and related compounds (Clare, 1947; Grossey and Woolsey, 1955; Chakravarti, 1956). To understand how these changes in physical properties can best be controlled it is important to understand the adsorption mechanisms which operate. In addition to older investigations of the adsorption of amino-compounds by clays, summarized by Grim (1953), a number of recent reports have appeared (Chakravarti, 1957; Sieskind and Wey, 1958; Cowan

and White, 1958; Weiss, 1958a and 1958b; Kurilenko and Mikhalyuk, 1959). These are in general agreement in showing that the smaller cationic organic compounds are readily adsorbed in amounts approximately equal to the cation exchange capacity of the clay. Where the aliphatic part of the organic cation contains more than 10 or 12 carbon atoms much larger amounts may be adsorbed (Grim, Allaway and Cuthbert, 1947; Jordan, 1949b; Mukherjee, 1954; Franzen, 1955; Cowan and White, 1958; Kurilenko and Mikhalyuk, 1959; Williams, 1959). It was considered that the *n*-alkyl pyridinium compounds provided a convenient series in which the effect of molecular size and other factors on this adsorption could be studied, and which could be directly related to the adsorption of the important surface-active reagent, cetyl-pyridinium bromide. Greene-Kelly (1955a, 1955b) investigated the adsorption of a number of simple pyridinium compounds on montmorillonite, but did not examine the 1-*n*-alkyl derivatives.

MATERIALS

The montmorillonite used was a sample of Wyoming bentonite from the John C. Lane Tract, Upton, Wyoming (A.P.I. reference no. 25). The clay as obtained contained less than 2 percent of material greater than 2μ e.s.d and was not further fractionated. The cation exchange capacity determined by the standard ammonium acetate leaching technique was 90 meq per 100 g of air-dry material (water content as determined by drying at 100°C for 24 hr over phosphorus pentoxide *in vacuo*, 12 percent). The clay was converted to the pure sodium or calcium form by shaking a 2 percent suspension with the acid form of Amberlite IR 120 or Dowex 50 for 20 min, to give the hydrogen saturated clay. This was separated from the exchange resin by filtering through nylon gauze. Dilute NaOH or $\text{Ca}(\text{OH})_2$ was added immediately to the suspension to bring the pH to 7. The pH was redetermined and adjusted if necessary after 24 hr.

The 1-*n*-alkyl pyridinium bromides other than cetyl were prepared by refluxing the appropriate alkyl bromide and pyridine in benzene solution (Knight and Shaw, 1937). The reaction was followed by bromide determinations. At completion of the reaction the alkyl pyridinium compounds were washed with benzene and taken into aqueous solution where further washing with benzene was carried out. These aqueous solutions were the stock solutions from which aliquots were taken and diluted as required for the adsorption experiments. They were shown to be initially free from pyridine by determination of the bromide ion concentrations and the molecular extinction coefficients at 259μ .

The cetyl pyridinium bromide was obtained from Fluka AG Chemische Fabrik, and was used without further purification.

METHODS

Adsorption isotherms were obtained by shaking suspensions of the clay in the appropriate solution for 16 hr at 23 °C, centrifuging and determining the change in the concentration of the supernatant solution. It was shown that shaking times longer than 16 hr did not lead to higher adsorptions. The concentration of montmorillonite was generally close to 0.6 percent, but varied slightly in different preparations. This may have produced some of the minor irregularities observed in the adsorption isotherms. All operations were carried out in a constant-temperature room.

The concentrations of the alkyl pyridinium solutions were determined by the intensity of adsorption of ultraviolet light at 259 m μ , using a Hilger spectrophotometer. It was possible to determine the concentrations to within 0.1 percent by this method. Thus, provided the concentration change on adsorption was at least 10 percent, the accuracy in the determination of the amount of adsorption was better than 1 percent.

Bromide determinations were made by conductometric titrations with silver nitrate solutions. The accuracy of this determination at the concentrations employed was ± 1 percent, but the actual error in the amount of bromide adsorbed depended on the bromide ion concentration in the supernatant solution. Since the supernatant concentrations varied over a considerable range, estimated errors have been included with the corresponding results. Sodium was determined with the flame photometer and pH with a Cambridge pH-meter and standard calomel and glass electrodes.

The samples obtained after centrifuging and decanting the supernatants were dried and examined by standard X-ray diffraction techniques, using a Philips PW1010 X-ray generating set and PW1050 (17 cm radius) diffractometer, with CoK α radiation. Flat powder specimens were employed and no attempt was made to produce preferential orientation.

RESULTS

The adsorption isotherms for ethyl, butyl, octyl, dodecyl and cetyl pyridinium bromides on montmorillonite are shown in Fig.1. The extent to which the pyridinium compound was adsorbed by mechanisms other than cation exchange was assessed by measuring the change in the bromide concentration of the supernatant solution. The extent to which sodium was replaced from the clay was also determined. These results are collected in Table 1.

The basal spacings of the montmorillonite-pyridinium complexes determined by X-ray diffraction are given in Tables 2, 3 and 4, and in Fig.2 the relative intensities of the reflections obtained from some of the cetyl pyridinium complexes are shown.

TABLE I.—ADSORPTION OF 1-*n*-ALKYL PYRIDINIUM BROMIDES BY NA-MONTMORILLONITE

Pyridinium Compound	Equilibrium Concentration (g/100 ml) (m-moles/l.)		Pyridinium Adsorbed (meq/100 g of Air-dry Clay ¹)	Bromide Adsorbed (meq/100 g of Air-dry Clay)	Na ⁺ Replaced from Clay (meq/100 g of Air-dry Clay)	Final pH of Suspension
Ethyl	0.004	0.213	26.3	—	—	—
	0.112	5.90	47.8	3.3 ± 1.5	55.0	7.0
	0.165	8.76	75.3	4.9 ± 2.5	59.0	7.0
	0.248	13.1	75.7	11.5 ± 3.0	59.0	6.9
Butyl	0.028	1.25	65.5	2.0 ± 1.0	55.0	6.7
	0.158	7.30	94.9	—	59.0	5.2
	0.320	14.8	102.0	9.1 ± 4.0	61.0	4.8
	0.400	18.5	83.8	8.3 ± 4.5	61.0	4.65
Octyl	0.050	1.84	78.0	—	—	—
	0.290	10.3	74.4	5.8 ± 3.0	57.0	6.9
	0.345	12.7	76.9	9.4 ± 4.0	58.0	7.0
	0.415	15.2	65.8	8.1 ± 4.5	58.0	7.0
Dodecyl	0.510	18.7	59.9	8.1 ± 5.0	60.0	6.75
	0.006	0.183	82.6	1.0 ± 1.0	89.0	5.7
	0.055	1.68	106.0	12.5 ± 1.5	87.0	4.3
	0.124	3.78	121.0	25.5 ± 2.0	87.0	3.9
	0.190	5.79	140.0	42.0 ± 2.5	87.0	3.9
	0.220	6.80	151.0	58.0 ± 2.5	91.0	3.7
Cetyl	0.330	10.1	171.0	75.0 ± 3.0	92.0	3.65
	0.400	12.2	163.0	89.0 ± 3.5	—	3.6
	0.005	0.12	70.0	0.0 ± 0.0	49.0	6.45
	0.006	0.14	107.0	22.0 ± 1.0	61.0	6.25
	0.009	0.22	125.0	37.0 ± 1.5	49.0	6.05
	0.016	0.385	210.0	120.0 ± 2.0	67.0	5.30
	0.145	3.50	264.0	—	65.0	—

¹ Water content of the oven-dry clay determined by drying over P₂O₅ *in vacuo* at 100 °C was 12 percent.

DISCUSSION

The Adsorption Isotherms

The adsorption isotherms for the ethyl, butyl and octyl compounds show an increasingly rapid approach to a maximum adsorption at or close to the exchange capacity of the clay. The increase in the readiness with which the organic cation is adsorbed as its size increases may be explained by the increase in magnitude of the van der Waals forces between clay and organic cation with increasing size of the cation. The dipole and induced dipole effects will not vary greatly as they will be primarily associated with the pyridine nucleus which is common to all three. The dispersion forces,

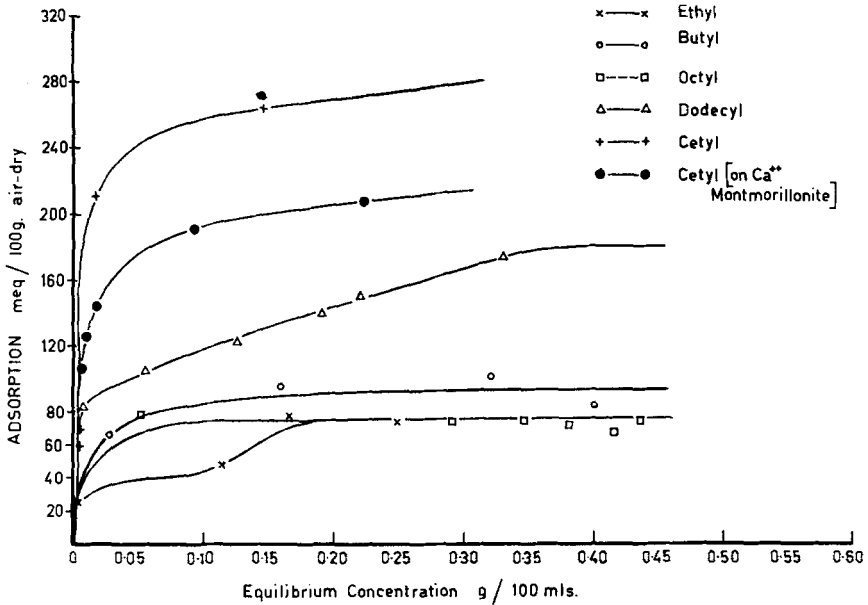


FIGURE 1.—Adsorption isotherms of 1-*n*-alkyl pyridinium bromides on Na-montmorillonite.

TABLE 2.—BASAL SPACINGS OF 1-*n*-ALKYL PYRIDINIUM MONTMORILLONITES

Pyridinium Compound	Meq Pyridinium Compound per 100 g Clay	Condition of Sample	<i>d</i> (001) (Å)	Interlamellar Separation (Å)
Methyl	80.0	O-d ¹	12.6	3.1
		Moist	12.6	3.1
Ethyl	63.6	O-d	12.8	3.3
		Moist	12.8	3.3
Butyl	93.7	O-d	14.0	4.5
		Moist	14.0	4.5
Octyl	77.0	O-d	14.2	4.7
		Moist	14.0	4.5
Dodecyl	76.3	O-d	14.3	4.8
		Moist	15.9	6.4
Cetyl	33.5	O-d	14.4	4.9
		Moist	17.0	7.5

¹ Oven-dry: dried 16 hr at 105 °C in air.

TABLE 3.—BASAL SPACINGS OF MONTMORILLONITE COMPLEXES WITH DODECYL PYRIDINIUM BROMIDE IN EXCESS OF THE EXCHANGE CAPACITY

Meq per 100 g	Exchange Cation Initially Present	Basal Spacing (Å)
140	Na	22.0 (A-d) ¹ 17.1 (O-d) ²
160	Na	20.5 (A-d) 16.3 (O-d)
140	Ca	20.0 (A-d) 18.0 (O-d)

¹ Air-dry.

² Oven-dry.

TABLE 4.—BASAL SPACINGS OF MONTMORILLONITE COMPLEXES WITH VARYING AMOUNTS OF CETYL PYRIDINIUM BROMIDE (ALL DATA REFER TO SAMPLES DRIED 16 hr AT 105 °C IN AIR)

Meq CPB per 100 g	Exchange Cation Initially Present	<i>d</i> (001) (Å)	No. of Higher Orders
60	Na	42 and 21	8 and 3
70	Na	18.0	Nil
98	Na	(42) and 21	(1) and 1
107	Na	21	1
114	Na	17.0	Nil
116	Na	42 and 21	3 and 1
125	Na	(42) and 21	3 and 1
136	Na	(42) and 21	3 and 1
148	Na	21	1
210	Na	42 and 21	9 and 4
264	Na	42 and 21	11 and 4
299	Na	42 and 21	8 and 4
305	Na	42 (and 21)	13 (and 6)
70	Ca	17.8	Nil
154	Ca	42 and 21	4 and 2
191	Ca	42 and 21	7 and 3
206	Ca	42 (and 21)	9 (and 3)

Very weak reflections are indicated by parentheses.

however, are additive for each atom in the ion. Barrer and Ibbitson (1944) have in fact shown that for the adsorption of straight chain aliphatic hydrocarbons by chabazite, a cubic lattice zeolite type silicate, the heat of adsorption increases linearly with the size of the molecule and for molecules containing more than eight carbon atoms can attain a magnitude similar

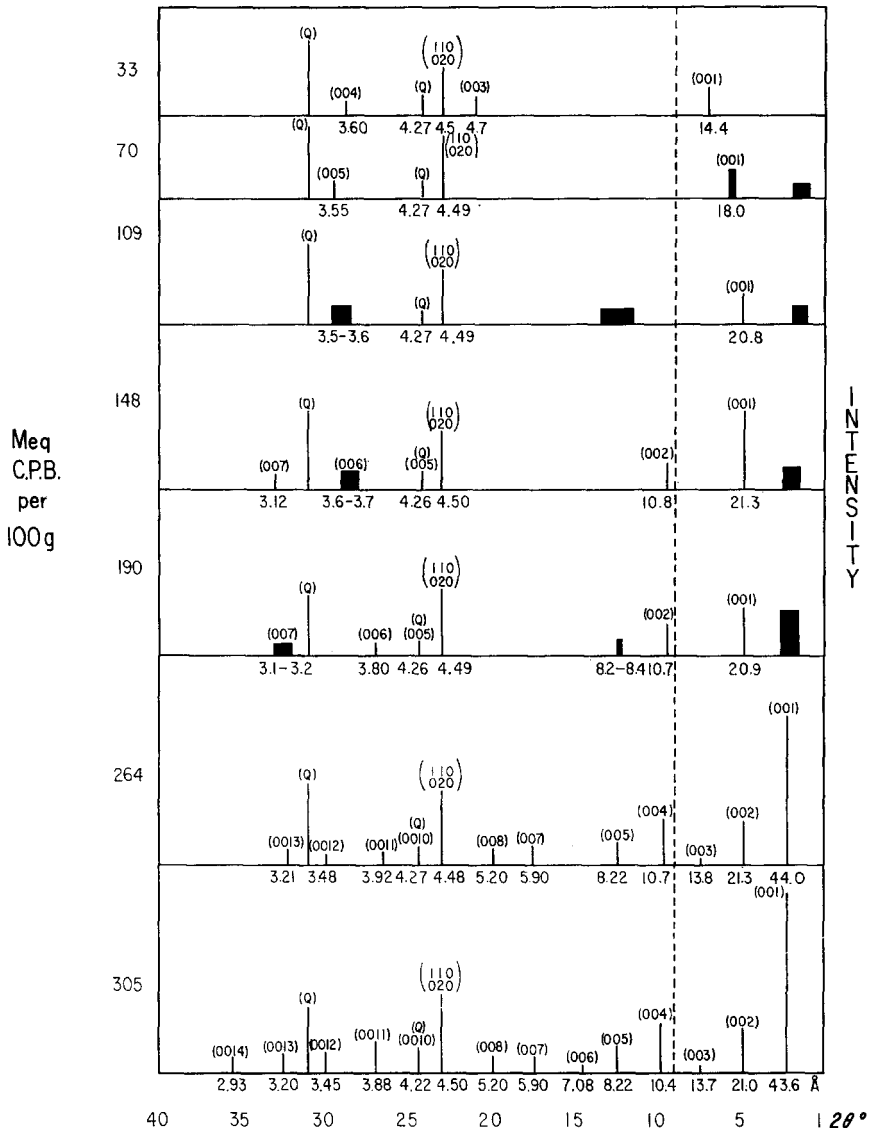
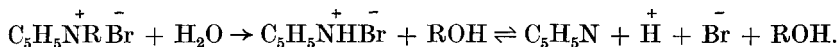


FIGURE 2.—Relative intensities and positions of peaks in X-ray diffractometer traces of cetyl pyridinium bromide-montmorillonite complexes. The intensities of peaks to the left of the broken line are increased relative to those to the right, owing to a change in slit size.

to that for a covalent bond. The adsorption of the hydrocarbon must be due predominantly to dispersion forces similar to those operating in the present instance between the aliphatic chain and the alumino-silicate surface. In addition to the obviously important effect of the increasing contribution from the dispersion forces, the solubility of the organic cation decreases as the size increases, and there is therefore less tendency for the larger ions, once adsorbed, to escape back into solution.

While it is possible to explain why the isotherms of the octyl and butyl compounds should rise more steeply than that of the ethyl, it is not possible to see why the maximum level attained by the butyl compound should be rather higher than that of the other two. In spite of all efforts to maintain perfectly uniform conditions, exact reproducibility of the isotherms was not attained. The differences were larger than could be explained by experimental error, being often 5 to 10 meq per 100 g whereas the experimental error associated with the analytical techniques was never greater than 2 meq per 100 g.

In the present instance the pH of the suspensions after adsorption was found to vary quite widely (Table 1). The variations are associated in part with varying degrees of hydrolysis of the pyridinium compounds:



It is therefore not possible to be certain that the observed increased adsorption of the butyl compound is significant. The results shown in Fig. 1 and Table 1 all refer to a single set of adsorption determinations made consecutively and under similar conditions.

In accordance with the greater size and reduced solubility of the dodecyl and cetyl compounds these are adsorbed more strongly than the others. The adsorption isotherm for the dodecyl compound shows a pronounced change of slope at an adsorption about equal to the exchange capacity of the clay. This is to be expected when the adsorption beyond the exchange capacity takes place by somewhat weaker forces. Up to the exchange capacity, adsorption is due to ionic forces plus van der Waals; beyond this, only van der Waals. The absence of such discontinuity in the slope of the cetyl isotherm indicates that the non-ionic adsorption forces must be larger than those producing ionic adsorption. It is difficult to be certain without more detailed investigation whether this can be attributed to the length of the carbon chain alone. The possibility exists that adsorption of the complete micelle takes place, and that this acts as a single very large unit in the adsorption.

One further point of particular interest arises from the adsorption isotherms for the cetyl compound. This is the difference between the isotherms obtained with Na- and Ca-montmorillonite. It is to be expected that the increased difficulty of replacing the calcium ion from the clay might

lead to a less steeply sloping isotherm, for adsorption up to the exchange capacity, but it is not to be expected that the adsorption beyond the exchange capacity would be affected. In fact the maximum adsorption observed was 205 meq per 100 g, compared with 305 meq per 100 g adsorbed by the sodium clay. Williams (1959) has reported a similar effect with cetyl pyridinium bromide and other clays, and Kurilenko and Mikhalyuk (1959) with various aliphatic amines and montmorillonite.

It may be that the inorganic cations influence the later stages of the adsorption because they determine the arrangement taken up by those organic molecules adsorbed while some of the cations are still present and the arrangement of these molecules determines that of those subsequently adsorbed. The X-ray results, to be discussed below, give no support to such an hypothesis.

The nature of the adsorbate micelles may be important. When the final stage of adsorption is approached the supernatant solution has a concentration of 0.03 N in sodium or calcium bromide, and micelle size may be differentially affected by this concentration.

Even for the same amount of cetyl compound adsorbed the Na-clay is more voluminous than the Ca-clay and it appears therefore that the structural features of the clay mass influence the final adsorption. Aylmore and Quirk (1959) have suggested that the differences in swelling behavior of Na- and Ca-montmorillonite are most satisfactorily interpreted as arising from the greater stability of the domains of the Ca-clay, and hence the observed difference in adsorption and physical properties of the cetyl pyridinium complexes could be due to differences in the extent and accessibility of the external surfaces of the two materials. If crystals are held within a domain structure adsorption on the external surfaces of crystals will be limited, whereas if these crystals are separated as a result of domain breakdown then enhanced adsorption is possible.

If a difference in external surface area and accessibility of this surface accounts for the observed adsorption difference it is necessary for the domain structure to persist after exchange of the ions initially present for pyridinium ions. Determinations of the quantities of sodium ions displaced showed that in fact up to 30 meq of sodium ions per 100 g remained with the clay even when the quantity of pyridinium adsorbed was equal to or greater than the exchange capacity (Table 1).

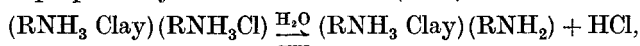
Bromide Adsorption and Displacement of Inorganic Cations from the Clay

It is probably correct to assume that bromide ion adsorption by montmorillonite in the presence of only inorganic cations is very small. The observed adsorptions in the present study therefore may be considered to arise from the adsorption of pyridinium cations in excess of those ad-

sorbed by exchange. The results in Table 1 show that even for the ethyl, butyl and octyl compounds adsorptions of up to 10 meq per 100 g occur. The sodium displaced from the clay was 55–61 meq per 100 g, whereas the total exchangeable sodium was 90 meq per 100 g. This further establishes that not all the adsorption is due to ion exchange, even when the maximum attained lies close to the exchange capacity of the clay. The bromide and sodium displacement results for the butyl compound are similar to those for the ethyl and octyl compounds, but the adsorption of the butyl compound is associated with a significantly lower pH.

With the dodecyl and cetyl compounds, where adsorption much beyond the exchange capacity occurs, the expected higher adsorptions of bromide are observed. The amount of sodium displaced is rather larger for the dodecyl compound, around 90 meq per 100 g, and rather less, 50–70 meq per 100 g, for the cetyl. A fall in pH with adsorption beyond the exchange capacity was again observed.

The agreement between the quantities of pyridinium ions adsorbed and sodium ions displaced is not good, even allowing for the rather high experimental errors involved. These discrepancies can be explained by hydrolysis of the pyridinium solution, so that some hydrogen ions are present which may displace sodium, and by the further possibility that adsorption of the pyridinium ion may be accompanied by displacement of aluminum or hydrogen ions rather than sodium. The simple hydrolysis mechanism proposed by Cowan and White (1958),



to account for the nonadsorption of chloride ions and the fall in pH when primary amines are adsorbed in amounts greater than the exchange capacity of the clay, cannot apply to a quaternary compound. It is therefore not surprising that in contrast to their findings and those of Grim, Allaway and Cuthbert (1947) adsorption of the bromide ions was found to occur. As mentioned earlier, the low pH levels found in the supernatants in the present instance must be attributed to hydrolysis of the pyridinium ions to release free pyridine and the alcohol of the *n*-alkyl group. It is known that this hydrolysis can occur slowly in solution, and it is possible that the breakdown is to some extent catalyzed by the clay. Mukherjee (1954) reported that the adsorption of cetyl trimethyl ammonium bromide on an electro-dialyzed montmorillonite took place in amounts much in excess of the exchange capacity, but that considerable residual exchange acidity remained with the clay.

The Basal Spacings of the Montmorillonite–Pyridinium Complexes

The data in Table 2 show that the complexes containing 60 to 100 meq per 100 g of the butyl, octyl and dodecyl compounds have interlamellar

separations slightly larger than the minimum thickness of an aliphatic carbon chain (4.0 Å) but corresponding very well with the thickness of the chain in the plane of the carbon atoms (4.5 Å). It is to be expected that this spacing will be attained if the molecule retains some degree of free rotation about the C–N bond. The spacings observed for the methyl and ethyl compounds are much less and the corresponding interlamellar separations not only less than the minimum thickness of the aliphatic chain but also less than that of the pyridinium ring (3.7 Å). Greene-Kelly (1955a) has made similar observations for complexes of montmorillonite with pyridine and various C-substituted aliphatic derivatives of pyridine. The shortening of the van der Waals contact distance has also been observed with a large number of other small organic molecules (Bradley, 1945; MacEwan, 1948; Glaeser, 1951) but many large organic molecules such as proteins (Hendricks, 1941), long-chain amines (Jordan, 1949a) and sugars (Greenland, 1956) apparently make normal van der Waals contact with the clay surface. The reasons that have been suggested for the shortening include C–H...O hydrogen bond formation (Bradley, 1945; MacEwan, 1948), keying of the organic molecule into the open-packed oxygen sheet at the clay surface (Glaeser, 1951), and the general attractive forces between the silicate sheets and between the silicate sheets and the adsorbed molecules (Greene-Kelly, 1953). None of these appears to be entirely satisfactory. Hydrogen bonds between carbon and oxygen atoms could only be extremely weak and therefore unlikely to produce the observed shortenings of contact distance, and furthermore with the aromatic compounds angles of approach are unsuited to the formation of such bonds. Keying of aromatic molecules into the surface is also not possible. If the attractive forces themselves were sufficient to produce the shortening, the shortening would be expected to be at least as great with the larger and more strongly adsorbed molecules, but in fact just the reverse is found.

It may well be that the attractive forces are sufficient to produce a shortening where the molecule consists predominantly of an aromatic nucleus, as in most of the compounds examined by Greene-Kelly. In small aliphatic compounds such as methyl alcohol and acetone, keying of the molecule to the clay surface may be important. A combination of these two theories could well explain the present results, since keying of the methyl and, to a lesser extent, the ethyl groups attached to the pyridine nucleus is possible, whereas for larger aliphatic groups, it is not possible and therefore they take up their full van der Waals distance.

For the complexes formed from pyridinium compounds with up to eight carbon atoms in the aliphatic chain there is no difference in the basal spacings of the moist and oven-dried samples. The dodecyl compound gives a complex which in the moist state shows a basal spacing of 15.9 Å contracting to 14.3 Å on air-drying and showing no further change when

dried at higher temperatures. The moist samples, which were taken directly from the pastes thrown down in centrifuging the montmorillonite in the pyridinium solutions, gave only weak reflections so that only very strong peaks could be observed. Hence higher orders were not obtained in the diffraction patterns and it was not possible to tell whether the observed 15.9 Å spacing corresponded to a rational reflection or to an interstratified complex. Most probably it was obtained from an interstratified complex, possibly of a two-layer type such as that depicted for the cetyl pyridinium complex in Fig. 3 (a), and the single layer complex, with some water present in the interlamellar spaces so that there is insufficient room for all the dodecyl compound to be contained in a single layer. The 15.9 Å spacing does not agree with any obvious orientation of the molecule in a single layer and is too small to accommodate a double layer.

When larger quantities of the dodecyl compound are adsorbed (Table 3) the moist or air-dry samples give diffuse basal spacings of 20–22 Å, contracting to 16–18 Å on oven-drying. It is difficult to interpret these spacings in terms of the orientation of the molecule at the surface, as the spacings greater than 20 Å yield only one or two irrational orders, and the smaller spacings no higher orders, but it seems probable that they are due to interstratified systems containing varying proportions of the one-layer ($d(001) = 14 \text{ \AA}$), two-layer ($d(001) = 18 \text{ \AA}$) and three-layer ($d(001) = 22 \text{ \AA}$) complexes.

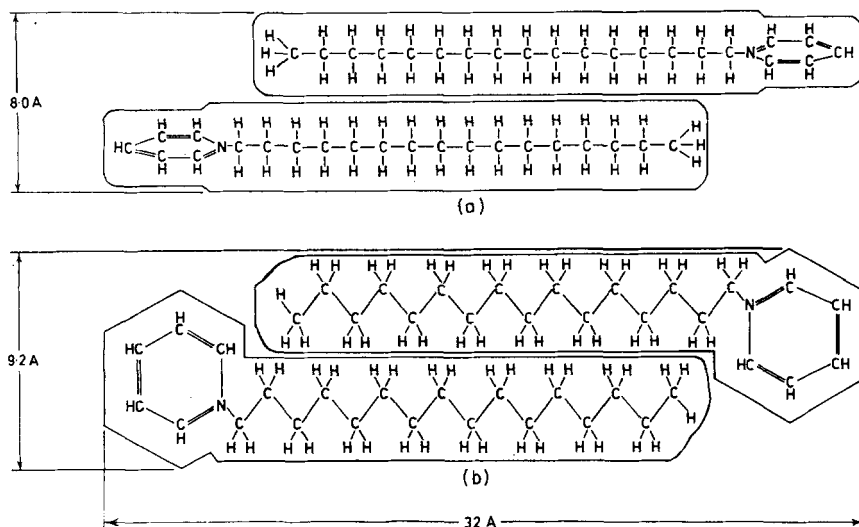


FIGURE 3.—Possible orientations of the cetyl pyridinium ion on the surface of montmorillonite: (a) in a two-layer complex; (b) in the 42 Å complex, and in an orientation which may be interstratified with the two-layer (17 Å) and three-layer (21 Å) complexes.

The X-ray diffraction patterns obtained from the cetyl complexes also indicate that interstratified systems of one-, two- and three-layer complexes probably are formed. With 33 meq of the cetyl pyridinium compound present, a rational series of reflections is obtained corresponding to a basal spacing of 14.3 Å. With from 50 to 150 meq present, the first-order reflection is either close to 17 Å or 21 Å. Higher orders of the 21 Å reflection are obtained but not of the 17 Å reflection. The situation is further complicated by the fact that some of the systems giving a 21 Å reflection also give a weak diffuse reflection at about 42 Å.

The 42 Å reflection is obtained regularly from the complexes containing more than 150 meq of the cetyl compound but only when 250 meq is adsorbed does the intensity of the reflection at 42 Å much exceed that at 21 Å (Fig. 2).

Williams (1959) obtained complexes containing 80 meq of cetyl pyridinium bromide which gave reflections corresponding to basal spacings of 56 Å. In the course of the present investigations such a reflection has been obtained only once, from a moist complex containing 199 meq per 100 g.

The interlamellar volume corresponding to a basal spacing of 42 Å is $(42 - 9.5) \times 0.5 \times 700 \times 10^{22}$ Å³ per 100 g or approximately 11×10^{25} Å³ per 100 g, taking the total interlamellar surface area as 700 m² per g. The volume of one cetyl pyridinium ion is 470 Å³, so that 300 meq occupies 8.5×10^{25} Å³. If allowance is made for the fact that some of the inorganic cations initially present remain in the interlamellar region and that 250 meq of bromide ion must also be accommodated, it is evident that there is a reasonable correlation between the observed maximum in the adsorption isotherm at approximately 300 meq of cetyl pyridinium bromide per 100 g and a densely packed interlamellar volume corresponding to the 42 Å basal spacing.

The basal spacing of 21 Å corresponds to an interlamellar separation of 11.5 Å and an interlamellar volume of approximately 4×10^{25} Å³ per 100 g, which can accommodate approximately 100 meq of cetyl pyridinium ions. It is to be expected, therefore, that complexes containing more than this quantity of the cetyl pyridinium compound will show both the 21 Å and 42 Å spacings. Only a small proportion of the 42 Å complex is necessary to accommodate a considerable amount of the cetyl pyridinium ion, and it is not surprising, therefore, that the reflections obtained from the 42 Å spacing are weak until about 250 meq of the cetyl compound is adsorbed. The basal spacings of 21 Å and less probably arise from 1-, 2- and 3-layer complexes. McAtee (1958) has obtained evidence from Fourier transforms that 2- to 6-layer complexes of montmorillonite with dimethyldioctadecyl ammonium chloride may be formed. However, in the present instance no evidence for any spacing between 21 and 42 Å was obtained. The 42 Å spacing could correspond to an eight-layer complex, but it is more probable

that it arises from the adsorption of the pyridinium compound perpendicularly to the clay surface in the arrangement indicated in Fig. 3 (b). In this complex the pyridine ring is oriented at right angles to the plane of the montmorillonite sheet, so that the maximum contribution to the adsorption energy from the polarization of the pyridinium part of the molecule may be obtained. Only the pyridinium part of the ion is in contact with the surface, but there is the maximum possible contact between adjacent aliphatic chains. Similar complexes in which an aliphatic chain extends in a vertical plane from the clay surface have been described by Franzen (1955), Weiss (1958a) and others. The tendency for the aliphatic parts of such molecules to be in contact with each other, and for the charged part of the molecule to form the outer surface, is also seen in the ready formation of micelles. These are formed by cetyl pyridinium bromide solutions as dilute as 0.02 per cent (Addison and Furnidge, 1956).

However, the possibility arises that the 42 Å reflection is due to some impurity precipitated on the clay-organic complex. Sodium palmitate, for instance, which could be formed by hydrolysis and oxidation of the cetyl pyridinium ions, gives rise to a strong reflection at 42 Å. The reflection cannot be due to cetyl pyridinium bromide itself since this gives no low-angle reflection beyond 28.6 Å. If the reflection is due to an impurity, it would be expected to be soluble in either water or benzene. In fact extensive washing of the complex with these two reagents did not alter the intensity or the position of the 42 Å peak. The impurity, if it exists, either must then be peculiarly insoluble or the reflection must be due to the complex containing the very strongly bound cetyl pyridinium bromide. The close coincidence of the calculated value of the cetyl pyridinium bromide adsorbed at the plateau of the isotherm (300 meq per 100 g) and the interlamellar volume corresponding to a basal spacing of 42 Å is further strong evidence that the 42 Å reflection is due to the complex.

With both the dodecyl and cetyl compounds, similar basal spacings are observed whether adsorption takes place initially onto a Ca- or Na-montmorillonite. This suggests that the inorganic cation itself does not affect the orientation of the adsorbed molecules. The maximum amount of the cetyl compound adsorbed on a Ca-clay is very much less than that adsorbed on a Na-clay. If the interlamellar volume remains the same this must be due to the Ca-clay retaining more water in the interlamellar regions. The much stronger tendency for calcium to retain a hydration shell is well known, so that this is quite possible. However, if the explanation of the difference in adsorption in terms of domain structure is correct, then the greater adsorption on the Na-clay is associated with the greater external surface. The magnitude of the difference, 100 meq per 100 g, is probably larger than the difference to be expected from either of the causes above, and it therefore seems probable that they both contribute.

CONCLUSIONS

Adsorption of 1-*n*-alkyl pyridinium bromides is associated with ionic and dispersion forces, the magnitude of the latter increasing with the size of the adsorbed molecule or ion. However, even when a large ion such as cetyl pyridinium is adsorbed replacement of the cation initially present is incomplete. When the pyridinium ions are adsorbed in excess of the exchange reaction with the initial cation, bromide ions are also adsorbed. The adsorption is then associated with a low pH in the external solution, probably due to hydrolysis of the pyridinium compound.

Since the initial exchangeable cation appears to affect not only the exchange reaction but adsorption beyond this, it is concluded that those ions not replaced have an important influence. This most probably is due to their influence on the domain structure of the clay, and hence the availability of external surfaces for adsorption, although other explanations are possible.

The results of the X-ray diffraction analyses show that the adsorbed ions normally lie along the clay surface, adsorption of larger amounts of the bigger ions giving rise to two- and three-layer complexes. This is in conformity with the idea that the adsorption is due primarily to dispersion forces. When cetyl pyridinium bromide is adsorbed an alternative position with the molecules standing up on the clay sheets may occur. This phenomenon appears to be the analogue in the adsorbed phase of micelle formation in solution. Further work is required to establish to what extent solution micelles act as single units in adsorption. The relative importance of external surfaces of crystals and interlamellar surfaces also requires further investigation, particularly in relation to the possible importance of domain structure.

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