SELECTIVE ABSORPTION OF n-ALKYL ALCOHOL-BROMIDE MIXTURES BY MONTMORILLONITES (CLAY-ORGANIC STUDIES XIV)

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ABSTRACT

The difficulty of measuring absorption isotherms for mixed liquids on montmorillonite has been overcome by allowing equilibration to proceed via the vapor phase over periods of three to four weeks. Mixtures of $n-C_4H_9OH$ with $n-C_4H_9Br$ and $n-C_6H_{13}Br$ and $n-C_8H_{17}Br$, ranging from pure alcohol to pure bromide, have been equilibrated with Li-, Na-, Mg-, and Ca-montmorillonite. The change in composition of the liquid phase has been determined by refractive index measurements. These data, combined with the weight of material absorbed by the clay, enable the separate isotherms for alcohol and bromide absorption to be determined. Under all conditions, the alcohol is absorbed more strongly than the bromides, and when the proportion of alcohol is small, the separation factor exprssing the selectivity of the clay for alcohol may rise as high as 30. The absorption of the pure liquids is considered in terms of the number of molecules absorbed per unit cell and per exchangeable cation. The very high density of absorption of the alcohol, amounting to two molecules per unit cell in a single-layer configuration, by the Li-, Mg-, and Ca-montmorillonite is considered to arise from a predominantly hydrogen-bonded arrangement, while the considerably lower absorption density of the bromides, which decreases with increasing chain length, is regarded as being consistent with a cation-dipole attraction.

INTRODUCTION

Very few quantitative studies have been made of the absorption of binary liquid mixtures by montmorillonite when both components are strongly absorbed. While the change in composition of the liquid mixture is easily determined, there is no direct way of determining the total quantity absorbed by the clay. Barrer and Perry (1961a, p. 842) emphasised that absorption isotherms of mixtures cannot, in general, be deduced from those of the individual components and that selective absorption from mixtures can be studied only by working directly with the mixtures. Using mixtures of gases and of vapors, Barrer and his colleagues (1957, 1961a, b) found pronounced selective absorptions for certain mixtures by montmorillonites saturated with small globular organic cations, methyl- and ethylammonium ions. A special case of highly selective absorption from binary liquid mixtures occurs when a polar component is dissolved in a non-polar solvent. Greene-Kelly (1955) utilized this to study the absorption isotherm of pyridine on Na-montmorillonite from pyridine-cyclohexane solutions. More recently, Bissada, Johns and Cheng (1967) studied the absorption isotherms of ethanol and acetone on Na-, K-, Ca-, and Ba-montmorillonite from solutions in

dodecane. However, from these few examples it cannot be claimed that in all cases a non-polar solvent, which is not absorbed when alone, will not be absorbed when an absorbable component is dissolved in it.

To determine the absorption equilibria of montmorillonite with respect to binary liquid mixtures when both components are absorbed, there is no alternative to keeping the clay and the liquid mixture separated from the beginning. Consequently, equilibrium must be established through the vapor phase. If the mixed liquid is in equilibrium with the mixed vapor which in turn is in equilibrium with the clay, then the clay should also be in equilibrium with the mixed liquid. Since the present experiments were completed, the authors find that this procedure was used by Mair *et al.*, (1950, see especially p. 1285) for determining separation factors by absorption on silica gel.

The present experiments were directed towards the study of the absorption of binary organic liquid mixtures where both components are readily absorbed by the montmorillonite. The components were chosen to have similar molecular configurations with different functional groups in order to determine the role of the functional groups without complications from different configurations. It was desired also to have components which developed similar types of complexes with the montmorillonite, and which permitted a convenient method of mixture analysis. The following components were chosen: normal butanol, C_4H_9OH; and normal alkyl bromides, C_4H_9Br, $C_6H_{13}Br$ and $C_8H_{17}Br$. These compounds form single-sheet complexes with montmorillonite with basal spacings of about 14 Å. The alcohols C_2H_5OH, $C_6H_{13}OH$ and higher alcohols were excluded because C_2H_5OH readily forms double-sheet complexes and $C_6H_{13}OH$ and higher alcohols are capable of forming long spacing complexes with the molecular chains steeply inclined to (001), (Brindley and Ray, 1964). The possible influence of chain length on the absorptions was examined by using the three bromides already mentioned.

The choice of molecules with OH and Br terminations was based on the consideration that the alcohol is potentially capable of forming OH . . . O bonds to the silicate surfaces, but the bromides are likely to be absorbed principally by cation-dipole interactions with the exchangeable cations; the alcohol molecules also may be absorbed in this way. Van der Waals forces will be operative in all cases but will not be a primary cause of absorption.

The question whether alcohol molecules are absorbed by formation of hydrogen bonds or by cation-dipole forecs has been considered by Bissada *et al.* (1967) and by Dowdy and Mortland (1967) and both have favored ion-dipole forces. On the other hand, Emerson (1957) showed the possibility of a hydrogen-bonding arrangement and Brindley and Ray
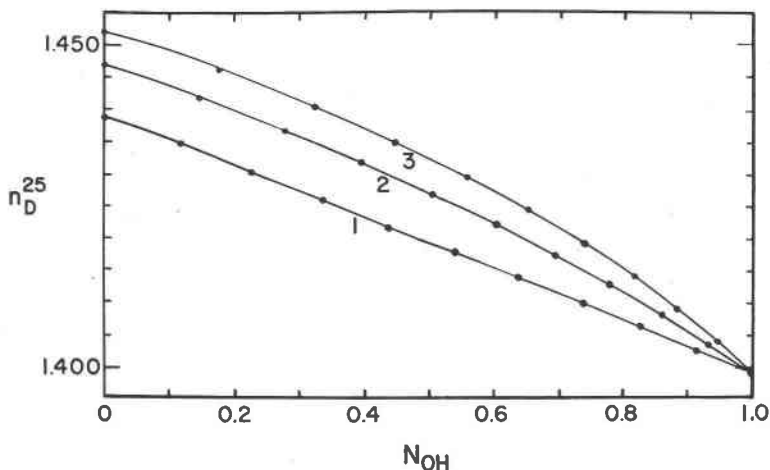
FIG. 1. Refractive index $n_D{}^{25}$ versus mole fraction of alcohol in alcohol/bromide mixed liquids.

(1) C_4H_9OH/C_4H_9Br. (2) $C_4H_9OH/C_6H_{13}Br$. (3) $C_4H_9OH/C_8H_{17}Br$.

(1964) showed that the long-spacing complexes formed by alcohols were consistent with hydrogen bonding.

Bromides were chosen in preference to alkyl chlorides so that liquid mixture compositions after absorption could be determined by careful refractive index measurements. Figure 1 gives the calibration curves of refractive index $n_D{}^{25}$ plotted against the mole fraction of alcohol, N_{OH}, obtained with a Zeiss-Abbe refractometer with temperature controlled at $25° \pm 0.2°C$ with a thermostated water circulation. The precision of the measurements was of the order of ± 0.0001, which was equivalent to about $0.002–0.003$ in the measured value of N_{OH}. Concentration changes due to evaporation during measurements were minimized by filling the liquid by small pipettes between the almost closed prisms.

A purified montmorillonite from Texas, supplied by the Georgia Kaolin Company, was used which was purified further by fractionation to give a < 1 micron fraction. The only detected impurity was a trace of kaolinite. Samples were saturated with Li, Na, Mg and Ca ions by treating with $0.5 N$ chloride solutions three times, each for two days or longer, followed by dialysis at $55°C$ until chloride ion free. The cation exchange capacity was 93 meq/100 g clay dried in vacuo at $150°C$.

A PROCEDURE FOR DETERMINING ABSORPTION ISOTHERMS FROM BINARY MIXTURES

Two series of experiments were made in parallel runs using always the same amount of montmorillonite, equilibrated with the same amount of

mixed liquid of the same initial composition, (*a*) with the montmoril-
lonite placed directly in the liquid phase, and (*b*) with the equilibrium
established through the vapor phase.

The experiments with the clay in the liquid were done as follows: 1 ml of a binary liquid mixture was pipetted into a small screwcap vial lined with aluminum foil to give a tight seal. The refractive index and the weight of the liquid phase were determined. The dried clay sample was put directly into the liquid and the vial re-weighed. Although equilibrium in these experiments was reached after 1–2 days with intermittent shaking, the vials were opened together with the parallel tests via the vapor phase. After centrifugation, the final refractive index of the liquid was measured and the change in its composition was determined.

The experiments via the vapor phase were carried out in the type of glass tube shown in Figure 2. One ml of a binary liquid of known refractive index was pipetted into the narrow lower part of the tube, and the weight of the liquid phase determined. The already weighed clay sample was transferred in its holder directly from the drying oven into the equilibration vessel. To facilitate vapor equilibrium, the glass tube was evacuated immediately after freezing the liquid phase in liquid N_2 to avoid evaporation during evacuation. Following evacuation, the equilibrium vessel was placed together with the small vial from the liquid series in a container that allowed the upper part of the glass tube with the clay sample kept
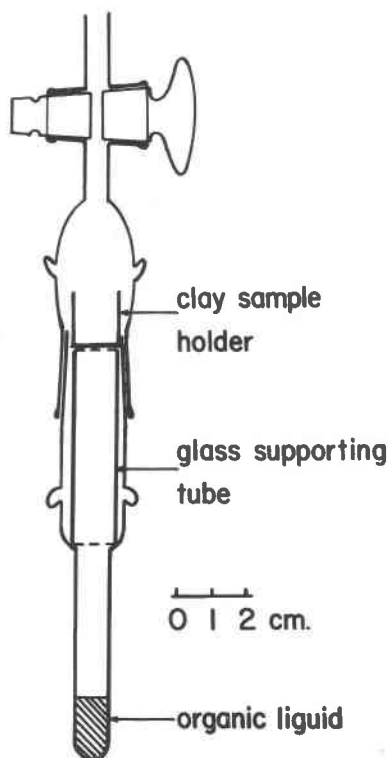

FIG. 2. Glass vessel used for equilibration between clay sample and mixed organic liquid
via the vapor phase.

at $25 \pm 1°C$ and about $3°C$ warmer than the lower part containing the liquid phase to avoid any condensation of liquid on the clay. Equilibration was allowed to proceed for three to four weeks. Preliminary experiments showed that equilibrium was attained after about three weeks under the conditions of the experiments. After this period, the glass tubes were opened, the clay sample holders removed and weighed immediately in stoppered weighing glasses. The weight of the remaining liquid and its refractive index were measured.

From the initial and final weights and compositions of the liquid phase, and the initial and final weights of the clay, the amount and composition of the absorbed material can be determined, *i.e.*, the individual absorptions of the two components can be found.

Under ideal conditions, the weight gained by the clay should equal that lost by the liquid. This was checked in all the experiments carried out and was found to be very nearly the case. Figure 3a shows data for Li-montmorillonite and mixtures of C_4H_9OH and $C_8H_{17}Br$. In fact, the weight loss of the liquid was always slightly greater than the weight gain of the clay.

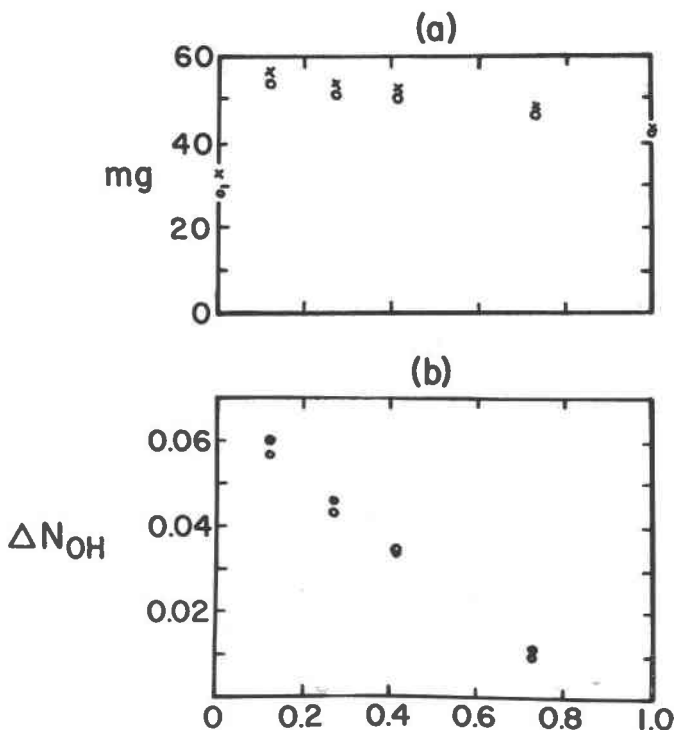Fig. 3. (a) Comparison of weight gain by 200 mg of 110°C dried Li-montmorillonite (O), and weight loss of mixed $C_4H_9OH/C_8H_{17}Br$ liquid (×), plotted against N_{OH} (equil), mole fraction of alcohol in equilibrium liquid. (b) $\triangle N_{OH} = N_{OH}$ (initial)-N_{OH} (equil) when equilibrium is reached via the vapor phase (O) and in the liquid phase (●).
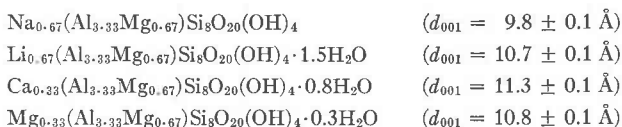
Since blank runs without clay in the tubes showed a similar loss of liquid, it seems probable that some interaction occurs between the bromides and the silicone grease.

A similar trend is exhibited in Figure 3b where $\Delta N_{OH} =$ (mole fraction of alcohol in the initial mixture)-(mole fraction in the equilibrium mixture) is plotted against the equilibrium mole fraction N_{OH} (equil.) for parallel runs in which equilibrium is established in the liquid phase and via the vapor phase. The differences in ΔN_{OH} point to the possibility of interaction between the bromides and the silicone grease in the vapor phase experiments. It should be noted that the mixtures of C_4H_9OH and $C_8H_{17}Br$, for which data are given in Figure 3, are the least favorable for vapor phase equilibration because of the low vapor pressure of the $C_8H_{17}Br$.

On the basis of these checks, which were made for all the liquid mixtures studied, it is believed that the experimental procedure determines with reasonable accuracy the absorptions of the two components on the clay.

The clays used in the experiments were dried as folows: Air-dry samples were weighed into small glass sample holders to yield about 200 mg after further drying. Na-, Li-, and Ca- montmorillonite were dried overnight at 110°C, Mg-montmorillonite was dried at 200°C, and weighed in stoppered weighing glasses to give the initial weight of clay in the absorption experiemnts. After weighing, the samples were returned to the drying oven and then were transferred directly into the equilibrium vessels.

Residual water in the clays was determined in subsidiary experiments using a vacuum thermobalance. Clay samples were weighed first after drying in air at 110°C (or 200°C), then in vacuo at 110°C (or 200°C), and then the temperature was raised slowly and weight changes followed. The weight loss on establishing the vacuum ($\sim 10^{-1}$ Torr) at 110°C (or 200°C) was attributed to release of residual interlayer water. No further weight losses occurred until a temperature of about 300°C was attained, when structural dehydroxylation may commence. On the basis of these measurements and the assumption of an ideal unit cell composition, the compositions of the 110°C (or 200°C) "dried" clays were taken as follows:

$$Na_{0.67}(Al_{3.33}Mg_{0.67})Si_8O_{20}(OH)_4 \qquad (d_{001} = 9.8 \pm 0.1 \text{ Å})$$
$$Li_{0.67}(Al_{3.33}Mg_{0.67})Si_8O_{20}(OH)_4 \cdot 1.5H_2O \qquad (d_{001} = 10.7 \pm 0.1 \text{ Å})$$
$$Ca_{0.33}(Al_{3.33}Mg_{0.67})Si_8O_{20}(OH)_4 \cdot 0.8H_2O \qquad (d_{001} = 11.3 \pm 0.1 \text{ Å})$$
$$Mg_{0.33}(Al_{3.33}Mg_{0.67})Si_8O_{20}(OH)_4 \cdot 0.3H_2O \qquad (d_{001} = 10.8 \pm 0.1 \text{ Å})$$

The spacings corresponding to the first observed X-ray reflections also are listed.

The organic liquids were dried by passing them through columns packed with molecular sieve type 4A, in 1/16 in. pellets (Fisher Scientific Co.), and subsequently were stored over this material (Hersh, 1961). The origin and quality of the liquids and their refractive indices were as follows:

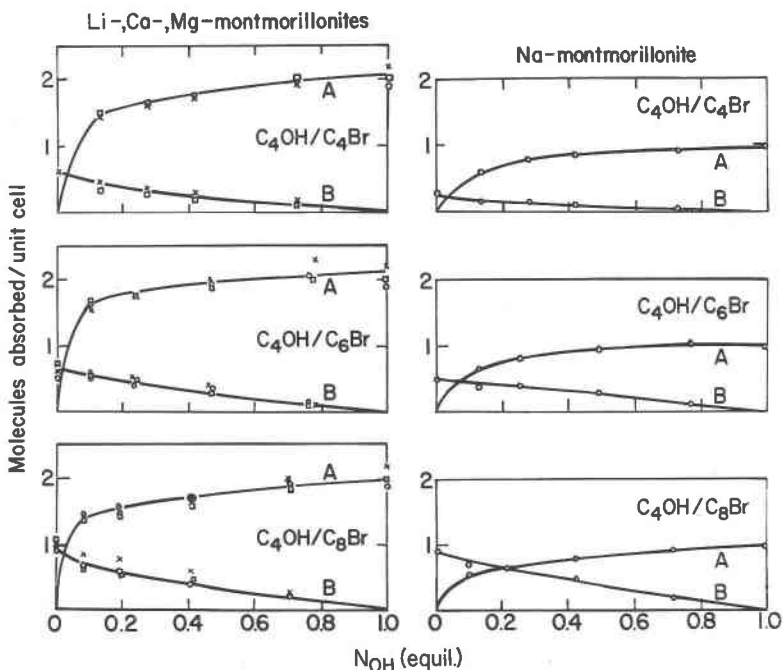|	
1-butanol, Baker analyzed reagent,	$n_D^{25} = 1.3990.$
1-bromobutane, Fisher Scientific certified reagent,	$n_D^{25} = 1.4388.$
1-bromohexane, Eastman, BP 154–155.5° C,	$n_D^{25} = 1.4469.$
1-bromooctane, Humphrey Chemical Corp.,	$n_D^{25} = 1.4519.$

FIG. 4. Molecules of organic material, A=alcohol, B=bromide, absorbed per unit cell on montmorillonite, versus N_{OH} (equil), mole fraction of alcohol in equilibrating liquid.

$$C_4OH = C_4H_9OH; \quad C_4Br = C_4H_9Br; \quad C_6Br = C_6H_{13}Br; \quad C_8Br = C_8H_{17}Br$$
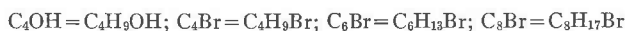
RESULTS

The experimental results, collected in Figure 4, are expressed as the number of molecules absorbed per unit cell and are plotted against the mole fraction of alcohol, N_{OH} (equil.), in the equilibrium liquid. The results for the Li-, Ca-, and Mg-montmorillonite are so closely similar that single curves have been drawn through the experimental points for the alcohol and bromide absorptions, with the individual values shown by the symbols used. The results for the Na-montmorillonite are considerably different and are shown separately. Curves marked *A* and *B* indicate respectively the alcohol and bromide absorptions.

A strong preference for alcohol absorption is exhibited in all the experiments. This preference is shown more strikingly by plotting the so-called 'separation factor' α, as defined by Mair *et al.* (1950),

$$\alpha = (N_{OH}/N_{Br})_{clay}/(N_{OH}/N_{Br})_{liquid}$$

Here N_{OH} and N_{B2} are the mole fractions of alcohol and of bromide re-

spectively on the clay and in the equilibrium liquid phase. Figure 5 shows α for the Na- and Mg-montmorillonites; the data for Li- and Ca-montmorillonites are very similar to those for Mg-montmorillonite. It is evident that with small concentrations of alcohol in the liquid phase, the preference for alcohol on the clay is very high, particularly for the Mg-, Ca- and Li- saturated clays.

DISCUSSION

The absorption data for the pure liquids are given in Table 1, (*a*) as molecules absorbed per unit cell, and (*b*) as molecules absorbed per exchangeable cation. The results will be discussed from both standpoints.

Positions of the exchangeable cations. In considering the accommodation of the organic molecules between the silicate layers, the number and positions of the exchangeable cations are important. These positions are not known with any certainty for the type of complexes under consideration but the results for hydration complexes are now reasonably well established and can be considered. Monovalent ions appear to remain closely associated with the oxygen-silicon sheets and, within limits set by the ionic radii, within the hexagonal cavities of the oxygen-silicon arrangement. This is well established for Na ions in a single water layer complex by Pezerat and Mering (1967), for Cs ions in a single layer hydrate by Mering and Brindley (1967), and for Li ions is almost certainly true because of the readiness with which they pass into octahedral positions of the structure with gentle heating (Hofmann and Klemen, 1950; Greene-Kelly, 1953; Glaeser and Mering, 1967a, b). For divalent ions, the evidence points to them taking positions between the silicate layers. This is the conclusion of Pezerat and Mering (1967) for Ca ions in a single layer hydrate and of Mering and Brindley (1967) for Ba ions in a double layer hydrate. In the ensuing discussion of the organic complexes it will be assumed that the monovalent ions lie within the hexagonal cavities, but with the Na ions less completely embedded than the Li ions, and that the divalent ions, Mg and Ca, lie between the silicate sheets.

Absorption of n-butanol. The basal spacings of the alcohol complexes with the four kinds of montmorillonite studied are about 14 Å which indicates single layer arrangements. With about two molecules absorbed per unit cell of Li-, Mg-, and Ca-montmorillonite, a highly close-packed arrangement is indicated. The close similarity in the absorptions suggests that the packing is not strongly dependent on the particular cation present of these three, but the situation is different for Na-montmorillonite. The model based on $OH \cdot \cdot O$ bonding suggested by Emerson (1957) explains
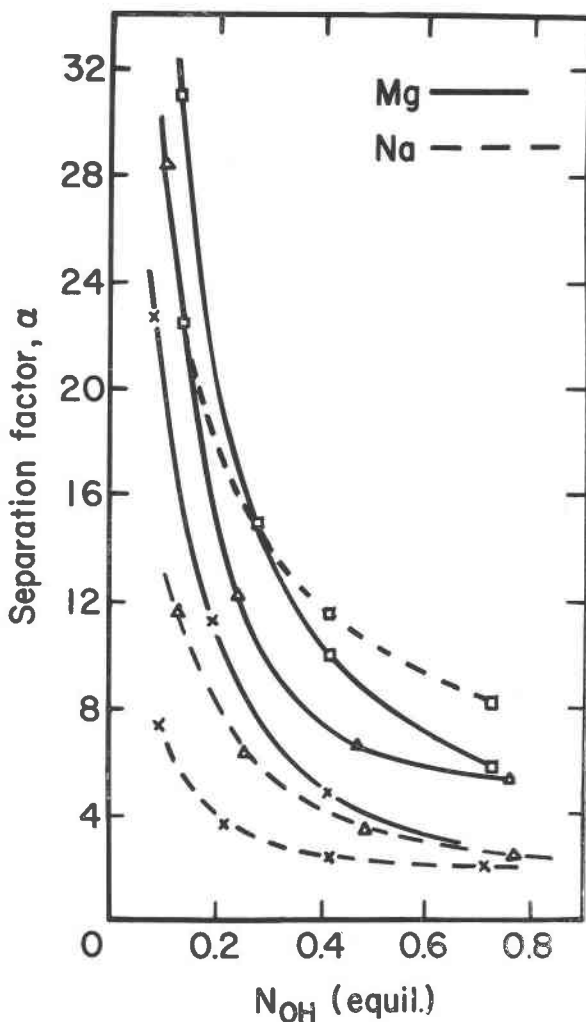
FIG. 5. Separation factor, α (see text), for C_4H_9OH/C_4H_9Br mixtures ($\times$), $C_4H_9OH/C_6H_{13}Br$ mixtures ($\triangle$), and $C_4H_9OH/C_8H_{17}Br$ mixtures ($\square$), absorbed on Na-montmorillonite (- - -) and Mg-montmorillonite (—).

very well (but not necessarily uniquely) the observed basal spacing and, by bending the molecules in the manner suggested, facilitates close-packing. The projected molecular area on (001) calculated from the Emerson arrangement is about 30 Å², which is considerably less than that of a linearly extended molecule, but packing two molecules into a 5×9 Å unit cell still requires a highly compact arrangement. The packing

TABLE 1. ABSORPTION DATA FOR THE PURE LIQUIDS, C_4H_9OH, C_4H_9Br, $C_6H_{13}Br$, AND $C_8H_{17}Br$ ON MONTMORILLONITE

(a) Molecules absorbed per unit cell

Exchange cation	C_4H_9OH	C_4H_9Br	$C_6H_{13}Br$	$C_8H_{17}Br$
Na	1.03	0.88	0.51	0.27
Li	2.16	1.04	0.61	0.55
Ca	1.94	0.90	0.49	—
Mg	1.96	1.11	0.68	0.58

Accuracy of the order ± 0.05

(b) Molecules absorbed per exchangeable cation

Na	1.5_5	1.3_0	0.7_5	0.4_0
Li	3.2	1.5	0.9_0	0.8_5
Ca	5.8	2.7	1.5	—
Mg	5.9	3.3	2.0	1.7

may be facilitated by the open hexagonal cavities of the Mg- and Ca-montmorillonite and by the unimpeded interlayer volume of the Li-montmorillonite; in fact, the Li-montmorillonite appears to absorb slightly more than the Mg- and Ca-montmorillonite. The considerably smaller absorption by Na-montmorillonite might be attributed tentatively to the partial entry of the Na ions into the hexagonal cavities, thereby impeding the interlayer volume as compared with the situation in Li-montmorillonite, and to their double number as compared with the number of Mg and Ca ions. On the other hand, the smaller absorption by Na-montmorillonite also might be attributed to the smaller field of the Na ion as compared with the much stronger fields of the Li, Mg, and Ca ions, if cation-dipole attraction is the dominant mechanism of absorption.

A cation-dipole mechanism is difficult to reconcile with the six molecules absorbed per Mg ion and per Ca ion. Bissada et al., (1967) showed that fivefold groups of the much smaller ethanol and acetone molecules could be coordinated with Ca ions and arranged in a close-packed, single-layer configuration. It does not seem possible to arrange sixfold, or even fivefold, groups of the much larger butanol molecules within the available

space. Admittedly, either six molecules per Mg or Ca ion, or two molecules per unit cell, are, in fact, accommodated within the interlayer volume, but this accommodation seems more difficult to achieve if cation-dipole coordination is the principal absorption mechanism.

Absorptions of n-C_4H_9Br, n-$C_6H_{13}Br$, and n-$C_8H_{17}Br$. Hydrogen bonding of the $OH \cdot \cdot O$ type is not involved, and bonding of the $CH \cdot \cdot O$ type is no longer considered to play any part in the absorption of such compounds, (see Greenland, 1965, p. 420; Dowdy and Mortland, 1967, p. 270). For these normal bromides, cation-dipole attraction is the most likely absorption mechanism. With approximately three molecules of n-C_4H_9Br per Mg ion and per Ca ion, there is no difficulty in visualizing single layer arrangements of cation-dipole coordinated groups. Still fewer molecules of the longer chain bromides are found in the absorption complexes.

The considerable difference between the alcohol and the bromide absorptions for molecules of the same chain length is indeed striking and is accepted by the writers as evidence for essentially different absorption mechanisms, with hydrogen bonding predominating with the alcohol molecules, and cation-dipole attractions with the bromide molecules. The marked selectivity for alcohol absorption is also seen as arising from this difference in the main bonding mechanisms.

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