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# CATION MIGRATION INTO EMPTY OCTAHEDRAL SITES AND SURFACE PROPERTIES OF CLAYS

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**Abstract**—The migration of small cations into the empty octahedral sites of dioctahedral clays allows one to study the local effects in the trioctahedral structure and the consequences of the exchange capacity decrease on the solvation properties. The results concern essentially the montmorillonite saturated by lithium. Computations based on a point charge model shows the necessity for the OH groups to undergo a reorientation when the lithium ions are within the octahedral sites. This change of orientation was studied by i.r. spectroscopy which permits one to estimate the amounts of lithium present in the structure. By analogy with i.r. results obtained for the Li, Mg, Ca and K montmorillonites, one can say that the non-exchangeable lithium which is not within the octahedral sites must be in the bottom of the hexagonal cavities. Moreover, it is shown that the solvation properties of the clay depend on the number of exchangeable cations and on the nature of the solvent. The clay does not swell with water when the amount of exchangeable cation is lower than 50 per cent of the exchange capacity. This limit is 30 per cent with glycerol, and 20 per cent with ethylene glycol.

## INTRODUCTION

THE THERMAL treatment of a montmorillonite saturated by cations of small radius (less than 0·7 Å) results in marked decrease of its exchange capacity. This was first shown for lithium (Hoffman and Klemen, 1950) and then for $Mg^{2+}$ and $Al^{3+}$ (Greene-Kelly, 1955; Glaeser and Mering, 1967).

Hoffman and Klemen have suggested that lithium ions migrate from the interlayer positions to the vacant octahedral sites. While Greene-Kelly and Glaeser and Mering agree with this hypothesis, Tettenhorst does not (Tettenhorst, 1962).

If lithium ions are really in vacant octahedral sites two consequences can be predicted:

(1) The existence of local trioctahedral configurations which would result in some special spectroscopic properties.

(2) A decrease of exchangeability of interlamellar cations which would certainly lead to changes in the solvation properties.

## THE I.R. SPECTRA OF HEATED MONTMORILLONITE AND THE PROPERTIES OF LATTICE HYDROXYL

### *I.R. spectra*

The clay used in this study is the montmorillonite of Camp Berteaux. The formula is:

$$(Si_4)[(Al^{3+}_{1\cdot46}\,Fe^{3+}_{0\cdot16})Mg_{0\cdot38}]O_{10}(OH)_2M^{+}_{0\cdot38}$$

The theoretical exchange capacity is 103 meq./100 g. The experimental exchange capacity is: 107 meq./100 g of clay dried at 250°C.

Infrared spectra were recorded with a Beckman i.r. 12 spectrophotometer. All the samples are oriented clay films heated to a given temperature. When the clay is treated by $D_2O$ at spectrophotometer temperature, the lattice OH groups are not affected, while the water OH are deuterated. Accordingly, all the samples are deuterated before recording, in order to shift the $H_2O$ spectrum and observe the structure OH vibrations alone. The dichroïc properties are observed by tilting the film in the incident beam from 0 to 45°C.

OH *stretching*. 3300–3800 $cm^{-1}$ region (Fig. 1). Before heating, the spectrum shows a single band with a regular profile at 3630 $cm^{-1}$. After heating, one can observe:

a dichroïc narrow band at 3670 $cm^{-1}$

a well-defined shoulder at 3700 $cm^{-1}$

a shift of the apparent maximum of the main band from 3630 $cm^{-1}$ to 3640 $cm^{-1}$. This shift is stressed (3643 $cm^{-1}$) when the film is tilted in the incident beam, which indicates some dichroïc properties.

The dichroïc band at 3670 $cm^{-1}$ has been observed in a previous work (Prost and Calvet, 1969). It was attributed to hydroxyl groups perpendicular to the (*a*, *b*) plane. This change in the orientation of some OH groups was related to the cation migration into octahedral sites in the structure. Such hydroxyl groups do not contribute to



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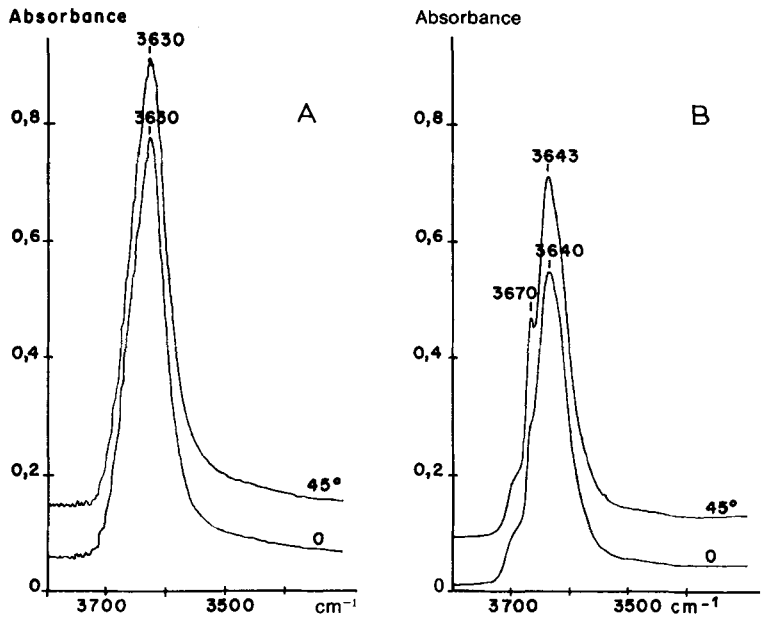



Fig. 1. Stretching vibrations of structural OH groups of Li-montmorillonite; A: unheated; B: heated at 220°C during 24 hr.

the absorption under normal incidence, and consequently the integrated intensity of unperturbed OH is decreased. The structure of montmorillonite shows that the migration of one cation into a vacant octahedral site must be accompanied by the change of orientation of two OH groups. Thus, comparison of the integrated intensity of the OH band, before and after heating, allows us to estimate the proportion of lithium ions present in the structure.

If we take into account the relative proportion of $Al^{3+}$ and $Mg^{2+}$ and if we suppose that the lithium migrates into the vacant sites near the isomorphic substitutions, we shall observe in the octahedral layer the configurations shown in Fig. 2.

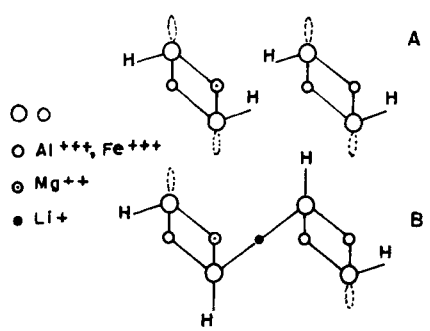



Fig. 2. Relative positions of octahedral cations and structural OH. A: before heating; B: after heating.

According to Vedder (1964), one can say that the dichroïc 3670 $cm^{-1}$ band is due to a Al, Mg, Li configuration, and the Al, Al, Li configuration must give a dichroïc band at lower frequencies. The shift of the main band maximum from 3640 to 3643 $cm^{-1}$ is probably due to this band, the shoulder at 3700 $cm^{-1}$ being related to a configuration Mg, Mg, Li. The appearance of several bands in the spectrum of heated Li-montmorillonite shows that the hydroxyl band of unheated montmorillonite is not a single band but is formed by several unresolved bands.

OH *bending*. 650–1000 $cm^{-1}$ region (Fig. 3). Before heating, the spectra of the montmorillonite saturated by different cations are similar. The assignments are the following (Farmer, 1967):

920 $cm^{-1}$: OH associated with Al–Al pair
890 $cm^{-1}$: OH associated with $Fe^{3+}$–$Fe^{3+}$ pair
845 $cm^{-1}$: OH associated with Al–Mg pair.

The fourth band at 800 $cm^{-1}$ can be eventually attributed to OH associated with Mg–Mg pair.

Marked changes are observed on the spectra after heating and the absorption pattern depends on the nature of the exchangeable cations. The intensity of the 920 $cm^{-1}$ band decreases chiefly for lithium-montmorillonite. This was also observed on muscovite treated by fused lithium-nitrate (White; 1961). No shift of the frequencies is observed for K- and Ca-montmorillonite. On

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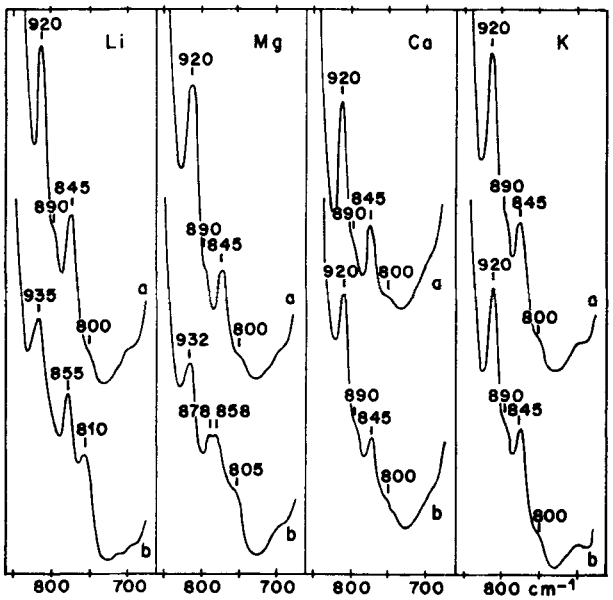



Fig. 3. Bending vibrations of structural OH groups of Li, Mg, Ca and K–montmorillonite obtained from oriented film. a: unheated; b: heated at 220°C during 24 hr for Li-montmorillonite and at 400°C during 6 hr for Mg, Ca and K-montmorillonite.

the contrary, for Li- and Mg-montmorillonite there are shifts towards high frequencies. The new values are:

Li-montmorillonite: 935 $cm^{-1}$, 855 $cm^{-1}$, 810 $cm^{-1}$

Mg-montmorillonite: 932 $cm^{-1}$, 858–878 $cm^{-1}$, 805 $cm^{-1}$.

The migration of lithium ions into the vacant octahedral sites, as shown by the OH stretching vibrations, is accompanied by a shift of the OH bending frequencies. For the K-montmorillonite, when no migration occurs, one does not observe any change in the absorption spectra either in the OH-stretching or bending regions. Consequently, the examination of the OH bending bands shows that the Mg ions migrate into the octahedral site, whereas the calcium ions do not. Moreover we have observed similar shifts for heated Ni and Be-montmorillonite. Thus, it appears that the migration of little cations into the structure is a general phenomenon, as was claimed by Glaeser and Mering (1967).

*One interaction model between* OH *groups and lithium ions*

A decrease in the exchangeability of lithium ions can be observed simultaneously with the change in the orientation of OH groups. An important question is thus raised: can lithium ions lie in octahedral sites without change in the orientation of OH groups? In order to answer this, a rough description of electrostatic interactions between the structural OH groups and the lithium ions is given. Such an evaluation encounters two difficulties:

(1) The first one is related to the position of the negative charge due to isomorphic substitutions. We have assumed that this charge is distributed over the six oxygen atoms of the substituted octahedron. This octahedron would include:

6 oxygen charges $q_o$

2 hydrogen charges $q_H$

1 cation (Mg) charge $q_c$

The hydrogen charge was evaluated according to its value in the water molecule (0·343 $e$). The charges $q_o$ and $q_c$ are calculated in order to have a minimum of electrostatic energy of the octahedron. Taking into account the relation:

$$q_c + q_o + 2q_H = -e$$

we can find:

$$q_o = -0{\cdot}454\, e$$
$$q_c = +1{\cdot}036\, e$$

$e$: electronic charge.

We have made the same calculation with a hydrogen charge of 0·25 $e$. This value has been

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proposed by Vedder (Vedder and McDonald, 1963) from the results of i.r. spectroscopy relative to the structure OH of the muscovite. In this case the charges are slightly different:

$$q_o = -0{\cdot}447\,e, \quad q_c = 1{\cdot}18\,e.$$

(2) The second difficulty deals with the screening effects. They are different for each charge, and can be expressed by the dielectric constant $\epsilon$. In order to simplify the calculation, we chose a constant value for $\epsilon$ ($\epsilon = 1$). Consequently, the interaction energy between cation and charges $q_o$ are over-estimated when the cation is within a hexagonal cavity. This approximation is less important when the cation–OH distance is short, i.e. when the lithium is within an octahedral site.

Figure 4 shows a possible path followed by the lithium ion when migrating from the interlayer positions to the vacant octahedral sites. The potential at a point $P$ is:

$$\phi = \sum_i \frac{e_i}{s_i}$$

$e_i$: charge of the $i^{th}$ atom (oxygen or hydrogen)
$s_i$: distance between the atom $i$ and the point $P$.

The potential energy of the lithium ion (which is treated as a point charge) is: $W = e \,.\, \phi$. Figure 5 represents a plot of $W$ along the trajectory in three cases:

(1) with the structural OH tilted over the $(a, b)$ plane by $+16°$ (curve $OH_2$) and $-16°$ (curve $OH_1$).

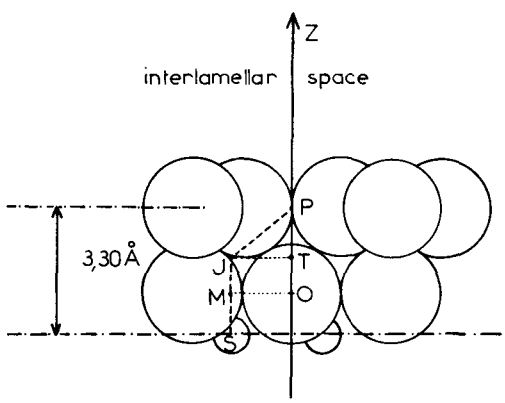



Fig. 4. Model used for the calculation of the potential energy of lithium ion moving along the trajectory ZPJMS.
OM = 1·54 Å SM = 1·09 Å
SJ = 2·0 Å PT = 1·3 Å
JM = 0·91 Å PJ = 2·015 Å
The plane PJMS in the symmetry plane of the unit cell. S is the vacant octahedral site.

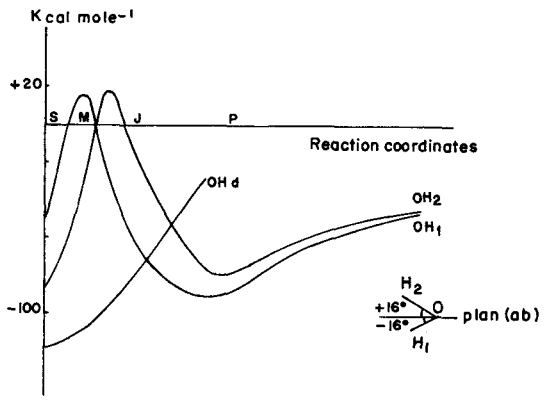



Fig. 5. Potential energy of the lithium in the electric field of the structure. Reaction coordinates: position of $Li^+$ on the structure. $OH_1$, $OH_2$ and $OH_d$ correspond to a particular orientation of OH with respect to the $(a, b)$ plane (see the text). Hydrogen-charge: 0·343 $e$.

(2) with the structural OH perpendicular to the $(a, b)$ plane (curve $OH_d$). We have taken the values of $\pm 16°$ as in muscovite, because we do not have any knowledge relative to this structural property for montmorillonite.

With the hydrogen charge of $+0{\cdot}25\,e$, the variation of $W$ presents the same general features. However, the height of the potential barrier is lowered by an amount of 35 kcal mole$^{-1}$. Whatever the hydrogen charge used in the calculation, the potential barrier remains too great. In fact it is certainly over-estimated for several reasons:

The two values used for the hydrogen charge constitute only a rough estimate of the true value. One can think that it is certainly smaller than $+0{\cdot}25\,e$, because some detailed calculations on the ($OH^-$) ion have shown a marked electron delocalization on the proton (Grahn, 1964).

The value of the dielectric constant is certainly greater than unity.

A rigorous calculation should be performed on mobile charges.

On the other hand, it is possible that the cation movement is not a simple phenomenon which can be described by electrostatic interactions only. The intervention of processes such as proton delocalization (Fripiat *et al.*, 1965) can certainly play a part.

The most important result of this calculation is that filling of the third octahedral site results in stability only if the neighbouring structural OH groups are perpendicular to the $(a, b)$ plane. Hence, the lithium migration in the structure can be visualized and studied by i.r. spectroscopy which enables us to distinguish between differently oriented structural OH groups.

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The octahedral site is not always the more stable. As a matter of fact, the migration can take place from the octahedral site to the interlamellar position when a Li–montmorillonite is heated at 250°C in a N/10 NaCl solution (Greene-Kelly, 1955). This can explain the results obtained with samples which have been completely re-expanded with $NH_3$ vapour, where nearly half of the original lithium content is exchangeable (Farmer and Russell, 1967).

## STUDY OF LITHIUM TRANSITION TO NON-EXCHANGEABLE STATES

The thermal treatment of Li–montmorillonite gives rise to a decrease of lithium exchangeability. This decrease can be measured either through direct determination of the exchangeable lithium or, through estimate of the lithium amount present in the structure by i.r. spectroscopy.

### *Experimental results*

*Data from the chemical analysis.* After the clay has been heated to the desired temperature for a fixed time, the exchangeable lithium is determined by exchange against $NH_4^+$ ions in a $CH_3COONH_4$ solution. This exchange is accomplished after treatment by ethylene glycol to facilitate the opening of the layers. Table 1 gives the amount of non-exchangeable lithium after heating for 24 hr at different temperatures.

Table 2 gives the amount of non-exchangeable lithium after heating at 120°C and 180°C for variable periods of time.

*Data from the i.r. analysis.* The intensities of the OH band are determined when the beam is normal to the clay film. Under these conditions the i.r. radiation exhibits perpendicular incidence to the totality of the layers which constitute the clay particles of the film.

If $A_o$ is the integrated intensity of the OH band before heating for normal incidence, and if $A_T$ is the integrated intensity of the OH band after heating, always for normal incidence, the ratio $A_T/A_o \times 100$ represents the percentage of unperturbed OH. The ratio $(1-A_T/A_o)\,100$ represents the percentage of OH perpendicular to the layer.

Seeing that each cation penetration gives rise to two OH groups perpendicular to the layer, there will be per unit cell, a maximum number of $(0{\cdot}76 \times 2)$ OH groups which are likely to become perpendicular to the layer (the clay charge is 0·76 per unit cell). This number represents $[(0{\cdot}76 \times 2)/4 \times 100]$ per cent of the total number of OH, therefore the amount $(1-A_T/A_o) \times 4/(0{\cdot}76 \times 2) \times 100$ represents the percentage of OH groups perpendicular to the layer, as compared with the number of OH groups which are likely to become perpendicular to the layer. This percentage is also equivalent to the number of lithium ions present in the lattice. Table 3 gives this percentage for different heating temperatures during 24 hr obtained under the same experimental conditions as for Table 1.

Similar determinations are also made on a single film heated during 24 hr at 110°C, then 24 hr at 120°C, etc... up to 220°C. Table 4 gives the corresponding values of the lithium percentage which has penetrated into the structure.

The results of the chemical and spectroscopic analysis show clearly that the lithium transition to a non-exchangeable state is related to the temperature and to the duration of heating. Moreover, the results of Table 2 show that the reaction rate increases with increasing temperature and is very high at the beginning.

Table 1

| Temp. (°C) | 108 | 120 | 135 | 150 | 180 | 220 |
|---|---|---|---|---|---|---|
| % of non exchangeable $Li^+$ as compared with the total quantity of $Li^+$. (107 meq./100 g) | 31 | 36 | 53 | 67 | 84 | 92 |

Table 2

| Duration of heating | | 1 hr | 2 hr | 8 hr | 16 hr | 24 hr |
|---|---|---|---|---|---|---|
| % of non-exchangeable lithium as compared with the total quantity of lithium (107 meq./100 g) | at 120°C | 20 | 25 | 34 | 35 | 36 |
| | at 180°C | 68 | 71 | 79 | 81 | 84 |

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Table 3

| Temp. (°C) | 90 | 120 | 135 | 150 | 180 | 220 |
|---|---|---|---|---|---|---|
| % of lithium in the lattice as compared with the total quantity of lithium | 9 | 22 | 26 | 32 | 55 | 68 |

Table 4

| Temp. (°C) | 90 | 110 | 120 | 150 | 180 | 220 |
|---|---|---|---|---|---|---|
| Duration of heating (see the text) | 24 | 48 | 72 | 96 | 120 | 144 |
| % of lithium in the lattice as compared with the total quantity of lithium | 0 | 20 | 26 | 73 | 84 | 93 |

*Discussion: the states of non-exchangeable* Li

As was observed by Glaeser and Mering (1967) and Greene-Kelly (1955), a prolonged thermal treatment does not lead to a total disappearance of the exchangeable lithium. Even though all the crystallites are collapsed, after a heating of 24 hr at 220°C exchangeable lithium is about 8 meq./100 g. Greene-Kelly considers that these ions are fixed outside of the crystallites. Since the ions which are on the basal surface corresponding to the external surface should become non-exchangeable, it follows that the 8 meq. probably represent the cations fixed on the sites due to the broken bonds located on the edges of the layers. Therefore, these ions are not concerned in the migration process. The percentages given in the Tables 1, 2 and 4 should be modified in order to be expressed in terms of the quantity of ions amounting to 107–8 = 99 meq. (Tables 1a and 2a).

As we have already noticed, there is no equality between the amounts of non-exchangeable lithium (Table 1a) and the amounts of lithium fixed in the octahedral sites, as determined by i.r study (Table 3) and is illustrated in Fig. 6.

The chemical and spectroscopic determinations of lithium quantities allow us to follow the reactions kinetics. Tables 1a and 3 represent the yield after 24 hr. If we assume that the reaction takes place in a homogeneous medium the reaction rate is

Table 1a

| Heating temp. | 108 | 120 | 135 | 150 | 180 | 220 |
|---|---|---|---|---|---|---|
| % of non-exchangeable $Li^+$ with regard to 99 meq. of lithium after 24 hr heating | 34 | 39 | 58 | 72 | 91 | 100 |

Table 2a

| Duration of heating | | 1 hr | 2 hr | 8 hr | 16 hr | 24 hr |
|---|---|---|---|---|---|---|
| % of non-exchangeable $Li^+$ with regard to | at 180°C | 22 | 27 | 37 | 38 | 39 |
| 99 meq. of lithium after 24 hr heating | at 180°C | 73 | 77 | 85 | 88 | 91 |

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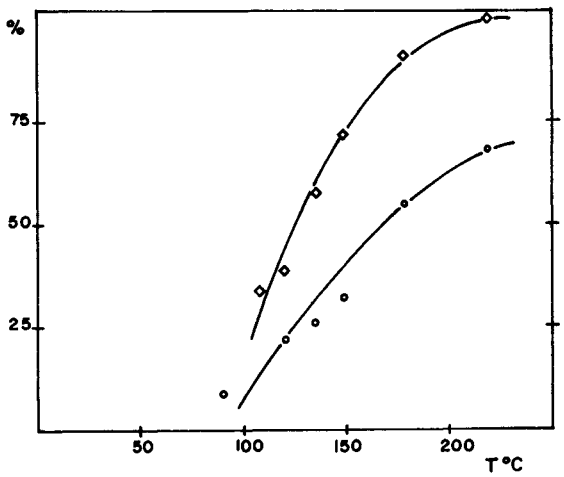



Fig. 6. The influence of temperature on the percentage of non-exchangeable $Li^+$ and the percentage of $Li^+$ in the structure. ◇—non-exchangeable $Li^+$; ○—$Li^+$ in the structure.

given by:

$$V = a^n K(1-p)^n \qquad (1)$$

where $a$ = initial concentration
$p$ = yield
$n$ = reaction order
$K$ = specific reaction rate.

The theory of rate processes allows us to write:

$$K = e\frac{kT}{h}\exp\left(\frac{-E}{RT}\right)\exp\left(\frac{\Delta S\ddagger}{R}\right) = K_o \exp\left(\frac{-E}{RT}\right) \qquad (2)$$

where $\Delta S\ddagger$ = entropy change accompanying the activation process
$e$ = base of logarithms
$k$ = Boltzman constant
$h$ = Planck constant
$R$ = Gas constant
$E$ = Activation energy
$T$ = Absolute temperature.

Taking the logarithm of (1) and with (2) we have:

$$\log(1-p) = \frac{1}{n}\log V - n\log a - n\log K_o + \frac{E}{2{\cdot}3\,RT}$$

Figure 7 represents $\log(1-p) = f(1/T)$. If the reaction formalism in homogeneous phase were applicable, the variation of $\log(1-p)$ as a function of $1/T$ should be linear.

In point of fact, it would seem that this occurs in a high temperature range (> 135°C), suggesting

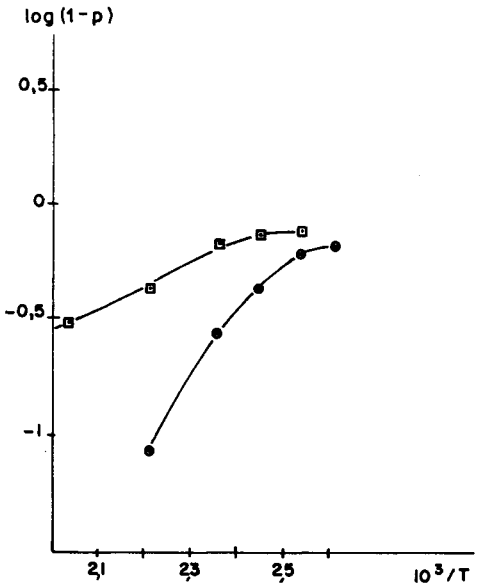



Fig. 7. Log $(1-p)$ vs. $10^3/T$. ⊙—non-exchangeable $Li^+$; ⊡—$Li^+$ in the structure.

that for this range, the transformations take place in homogeneous phase. Moreover, it becomes evident that the two types of determination do not concern the same reaction.

The existence of non-exchangeable lithium which is not in the structure can be explained in two ways:

(1) Ions are not exchangeable as a consequence of the inaccessibility of the interlayer spaces.

(2) After heating, ions are blocked in the hexagonal cavities and are not exchangeable even if the interlayer space is accessible.

In the first hypothesis some layers are collapsed and some ions, which ordinarily would be exchangeable, are non-exchangeable. This can account for the observed discrepancies between the amounts of non-exchangeable lithium and the amounts of lithium in the structure. We are then led to assume that the decimal fractions of collapsed layers are the following, provided that the percentage of non-exchangeable lithium is approximately that of the collapsed layers:

120°C: 0·4
150°C: 0·7
180°C: 0·9

X-ray diffraction studies performed on clays after heating at 120°C and 150°C indicate a complete swelling in each case. The beginning of interstratification (observed for the clay heated at 180°C) indicates that the clay is not totally expanded.



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These results are in contradiction with the proposed proportion of collapsed crystallites. It follows that the non-exchangeable lithium cations situated on accessible surfaces are probably trapped in the hexagonal cavities.

The i.r. spectrum of heated Ca–montmorillonite shows, in the stretching region, the development of a weak sharp band at 3533 $cm^{-1}$ which persists until dehydroxylation. This band is due to structural OH vibrations perturbed by $Ca^{2+}$ localized in the bottom of the hexagonal cavity (Russell and Farmer, 1964). In the case of Mg–montmorillonite, a similar weak sharp band which has the same origin appears at 3496 $cm^{-1}$ when the sample is heated at 300°C for 5 mn only (Fig. 8). It disappears if the heating is longer.

These observations are consistent with the results obtained from the preceding study of the OH bending vibrations in Mg- and Ca–montmorillonite. We have concluded that Mg ions could migrate in the structure and Ca ions could not. This implies that the migration of magnesium from the interlayer space to the vacant octahedral site takes place through a transition state which is the bottom of the hexagonal cavity. Consequently the OH stretching vibration should be dichroïc, but this is difficult to observe because of the small number of perturbed OH.

For the lithium clay it could be assumed that the same situation may occur. Accordingly, lithium ion could lie in the bottom of the hexagonal cavity. However, the electric field of lithium is not so high as that of calcium or magnesium; the resulting shift of OH frequency is then probably too small and therefore cannot be observed even after a short heating. The determination of exchangeable lithium would allow the study of the trapping of lithium in hexagonal cavities and the migration in the structure. This last reaction can only be observed by i.r. spectroscopy.

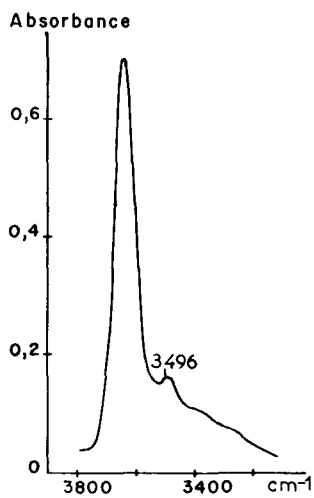



Fig. 8. Stretching vibrations of Mg–montmorillonite heated at 220°C during 5 mn.

## THE NUMBER OF EXCHANGEABLE CATIONS AND THE SORPTION OF POLAR SOLVENTS

A heated lithium montmorillonite shows two important features:

(1) The number of exchangeable cations is smaller than the number of exchangeable cations of an unheated montmorillonite.

(2) The structure possesses some local sites which belong to the trioctahedral type.

Since a montmorillonite (dioctahedral mineral) and hectorite (trioctahedral mineral) have similar solvation properties, the difference in crystallographic structure may be not as important as the existence of interlamellar cations. The important role of the cations was stressed in several works (Dyal and Hendricks, 1950; Bissada *et al.*, 1967). Hence, the heated Li–montmorillonite provides a quite useful material to study the relations between the number of exchangeable cations and the solvation properties of the clay-surface.

### *Sorption of polar solvents on biionic montmorillonite*

Biionic sodium–lithium clays are obtained by mixing two suspensions of monoionic sodium and lithium clay in a given ratio. The mixtures were shaken during 3 days before use.

As we have seen, a lithium montmorillonite, heated at 220°C during 24 hr, has a very small number of exchangeable cations. A biionic clay saturated by sodium and lithium, heated in the same conditions has only one exchangeable cation: the sodium.

The amounts of exchangeable sodium for different biionic clays are listed in Table 5.

One can see that nearly all the sodium is exchangeable. This was not observed by Greene-Kelly, but we think that this author, because of his use of glycerol instead of glycol to treat the clay before exchange, was not able to recover all of the sodium.

In order to study the sorption on biionic clay, we measured the $d_{001}$ spacing on oriented films exposed to water, ethylene glycol and glycerol vapor. The obtained values are recorded in Table 6.

The sorption in the interlamellar space is different for the three solvents. When the amount of exchangeable cations ($Na^+$) is less than 50 per cent, the clay cannot swell with water. This means that the water molecules cannot reach the internal surface when the number of interlamellar cations

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Table 5

| Initial amount of sodium meq./100 g of dried clay (250°C) | Amount of exchangeable sodium after heating meq./100 g of dried clay (250°C) |
|---|---|
| 86·5 | 83 |
| 75 | 72 |
| 65·5 | 63 |
| 44 | 40 |
| 22 | 17 |

Table 6

| % $Na^+$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| $H_2O$ 100% HR | O | O | O | O | N | N | N | N | N |
| Glycerol | OR | OR | OR | OR | OR | O | N | N | N |
| Glycol | OR | OR | OR | OR | OR | OR | O | O | |

2 Water layers $H_2O$: $d_{001} = 15{\cdot}5$ Å; 2 Glycerol layers: $d_{001} = 17{\cdot}9$ Å; 2 Glycol layers: $d_{001} = 16{\cdot}9$ Å.

OR – Expanded clay with a rational series; O – interstratified expanded clay; N – collapsed clay.

is less than 50 per cent. The limit value is 30 per cent for glycerol and 20 per cent for ethylene glycol. When the content in exchangeable cations is greater than 40 per cent, the glycol gives X-ray spectra with rational series; it is also the case for glycerol when the content exceeds 50 per cent. Hence all the interlamellar spaces are accessible and have certainly the same ionic population. It suggests to us that sodium and lithium cations are evenly distributed on the clay surface.

*Water sorption on homoionic clay: the lithium–montmorillonite*

We have studied the water absorption on powdered clay heated at different temperatures for 24 hr. The samples are kept in dessicators immersed in a constant temperature bath. The partial pressure of water vapour is fixed by a solution of sulfuric acid and water contents are determined by weighing. Adsorption isotherms are shown in Fig. 9. One can see that the amount of adsorbed water decreases as the quantity of exchangeable cations decreases.

There is no satisfying theory to describe the water adsorption on clay. However, we think that a theory which takes into account the variation of the adsorption energy in relation to the surface coverage can be useful. This is the case for Halsey's theory (Halsey, 1948) in which the adsorption energy is given by the formula:

$$E = a\theta^{-r} \quad \text{with } \theta = \frac{V}{Ve}$$

where $\theta$ = surface coverage
$V$ = volume of adsorbed water under the partial pressure $p$
$Ve$ = volume of adsorbed water under the partial pressure $p = 1/e$
$a, r$ = constant
$e$ = base of natural logarithm.

The constant value of $r$ during the adsorption process means that a single mechanism takes place. When the adsorbed volume is greater than $Ve$, a cooperative adsorption begins. A cooperative adsorption is characterized by the existence of lateral interactions between adsorbed solvent molecules.

If $p_o$ is the saturated pressure, $\theta$ and $p$ are related by the following formula:

$$\frac{p}{p_o} = \exp(-\theta^{-r})$$

A plot of $\log(\log p_o/p)$ vs. $\log\theta$ gives $r$. Fig. 10 shows such a plot.

Table 7 gives the values of $Ve$ and $V_T$. $V_T$ is called the transition volume: it is the volume of adsorbed water which corresponds to a change of the value of $r$. This representation reveals the existence of two domains of hydration.

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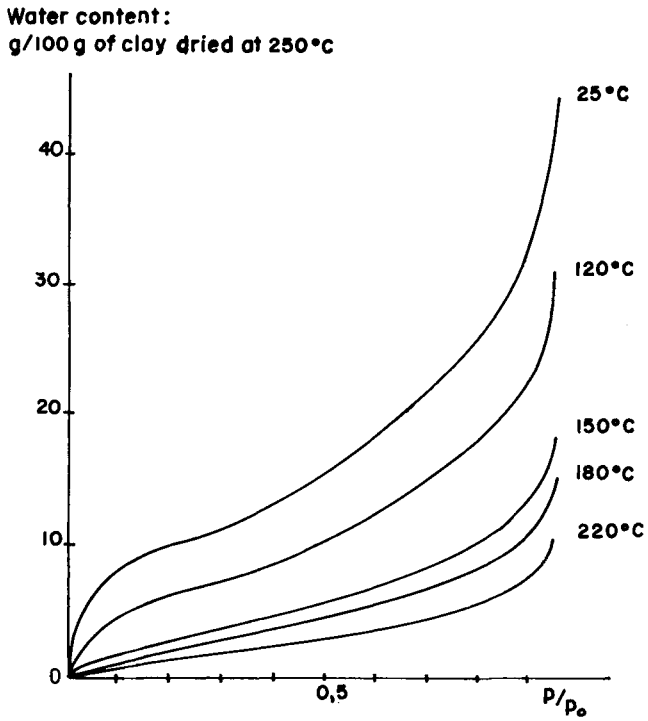



Fig. 9. Adsorption isotherms of water at 20°C on heated Li-montmorillonite.

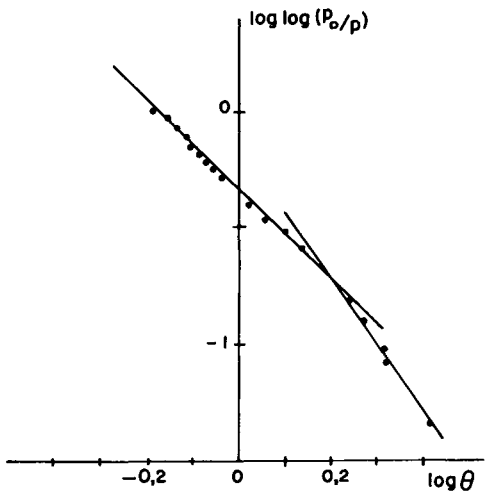



Fig. 10. log log/($P_0/P$) vs. log $\theta$ for clay dried at 25°C.

Table 7

| | Ve | Vt | Quantity of exchangeable lithium |
|---|---|---|---|
| Unheated clay | 12·7 | 20·1 | 107 |
| Clay heated at 120°C | 8·1 | 15·6 | 68 |
| Clay heated at 150°C | 4·4 | 8·1 | 35 |
| Clay heated at 180°C | 3·2 | 4·4 | 17 |

Quantity of exchangeable lithium: meq./100 g of dried clay (250°C) Ve and Vt: g of water/100 g of dried clay (250°C).

Table 8

| V in mole/cation | Ve | Vt |
|---|---|---|
| Unheated clay | 6·6 | 10·4 |
| Clay heated at 120°C | 6·6 | 12·7 |

We have seen that an amount of exchangeable cations less than 50 per cent prevents the swelling of the clay. Since the clays heated at 150, 180 and 220°C have an amount of exchangeable cations less than this limit, the adsorbed water on such clays must be distributed over the external surface.

The comparison between *Ve* and *Vt* is easy only for the clay heated at 120°C and the non-heated clay (the two swelling clays).

For these clays, the processes of hydration can be described in the following way:

(1) The first adsorbed molecules are localized in a little space near the cations. The number of these molecules is constant.

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(2) Then the cooperative adsorption begins in spaces distant from the cations and concerns a great number of molecules.

The importance of interlamellar cations in the first stage of water adsorption was suggested by Low (Low, 1961). Application of the Halsey's theory supports this view.

## CONCLUSION

The study of the properties of heated lithium montmorillonite shows some important features of the (structure + cations) system dynamics.

I.R. spectroscopy indicates that the lithium ions move within the structure towards the octahedral sites which lie near the isomorphic substitutions. The analysis of the electrostatic interactions allows us to establish the stable character of this position that leads to a better neutralization of the lattice negative charges. As a consequence, these negative charges are probably localized in a small volume around the isomorphic substitution in the octahedral layer. However only a fraction of the non-exchangeable lithium lies in the lattice, the remainder being in the hexagonal cavities. Structural modifications take place with the cation migration and create local trioctahedral configurations.

The absorption of polar solvents reveals the role of the two following factors:

The nature of the polar solvent
The number of exchangeable cations.

The importance of these two factors is obvious, but it is interesting to emphasize their interdependence which can be a useful source of information concerning the mechanisms of swelling.

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**Résumé** – La migration des petits cations vers les sites octaédriques libres des argiles dioctaédriques permet d'étudier l'apparition locale dans le réseau d'une structure trioctaédrique et les conséquences de la diminution de la capacité d'échange sur les propriétés de solvatation. Les résultats concernent essentiellement la montmorillonite saturée par le lithium. Des calculs basés sur un modèle de charges ponctuelles montrent la nécessité pour les groupes OH de se réorienter quand les ions lithium sont à l'intérieur des cavités octaédriques. Ce changement d'orientation a été étudié par spectroscopie i.r. Cette technique permet une évaluation de la quantité de lithium présente dans le réseau. Par analogie avec les résultats i.r. obtenus pour des montmorillonites saturées par Li, Mg, Ca et K on peut dire que le lithium non échangeable qui n'est pas à l'intérieur d'une cavité octaédrique doit se trouver dans le fond des cavités hexagonales. En outre, on montre que les propriétés de solvatation de l'argile dépendent du nombre des cations échangeables et de la nature du solvant. L'argile ne gonfle pas avec l'eau quand la quantité de cation échangeable est inférieure à 50 pour cent de la capacité d'échange. Cette limite est de 30 pour cent avec le glycérol et de 20 pour cent avec l'éthylène glycol.

**Kurzreferat** – Die Wanderung kleiner Kationen in die leeren oktaedrischen Gitterstellen gestattet die Untersuchung der örtlichen Effekte im trioktaedrischen Gefüge und die Auswirkungen der Abnahme in Austauschkapazität auf die Solvatationseigenschaften. Die Ergebnisse beziehen sich insbesonders auf den mit Lithium gesättigten Montmorillonit. Berechnungen auf Grund eines Spitzeladungmodells erwiesen die Notwendigkeit einer Reorientierung der OH-Gruppen wenn die Lithiumionen in den oktaedrischen Gitterstellen sind. Diese Änderung der Orientierung wurde durch Ultrarotspecktroskopie untersucht, die es erlaubt die in dem Gefüge gegenwärtigen Lithiummengen abzuschätzen. In


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Analogie mit Ultrarotergebnissen, die für die Li, Mg, Ca und K Montmorillonite erhalten wurden, kann gesagt werden, dass das nichtaustauschbare Lithium, das nicht innerhalb der oktaedrischen Gitterstellen ist am Boden der hexagonalen Hohlräume sein muss. Ferner wird gezeigt, dass die Solvatationseigenschaften des Tons von der Zahl der austauschbaren Kationen und vom Wesen des Lösungsmittels abhängen. Der Ton quellt nicht mit Wasser auf wenn die Menge von austauschbarem Kation geringer ist als 50% der Austauschkapazität. Diese Grenze ist 30% mit Glyzerin, und 20% mit Äthylenglykol.

**Резюме** — Вхождение малых катионов в пустые октаэдрические положения диоктаэдрических глин дает возможность изучить локальные особенности структур триоктаэдрических слюд и следствия влияния уменьшения обменной емкости на сольватационные свойства. Основные результаты получены, главным образом, на примере монтмориллонита, насыщенного литием. Вычисления, основанные на определении точечного заряда, показали необходимость реориентировки групп OH при вхождении ионов лития в октаэдрические положения. Это изменение ориентировки было изучено методом инфракрасной спектроскопии, который позволил оценить количество лития, находящегося в структуре. При сопоставлении данных ИКС для Li-, Mg-, Ca- и K-монтмориллонитов можно сделать вывод о том, что необменные ионы лития, которые не входят в октаэдрические положения, должны находиться в основании гексагональных полостей. Кроме того, показано, что особенности сольватационных свойств глин зависят от количества обменных катионов и от природы растворителя. При насыщении водой разбухание глин не наблюдается в тех случаях, когда количество обменных катионов ниже 50% обменной емкости. Этот предел составляет 30% для глицерина и 20% для этиленгликоля.

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