

EXCHANGEABLE CATION—STRUCTURAL PARAMETER RELATIONSHIPS IN MONTMORILLONITE

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Abstract—The interaction between “unhydrated” cations (those not separated from the surface by a solvent sheath) in hole positions and the montmorillonite surface was analyzed theoretically by considering the main contributions to potential energy from the coulombic, hydration, van der Waals, induced dipole, and repulsive energies. The effects on these energy terms of the distance between the cation and the plane of basal oxygens, h , and of the angle of rotation of the silica tetrahedra, θ , were investigated. Increase of θ with h constant increases the absolute values of all but one of the energy terms. The hydration energy is an exception because it is probably independent of θ . For a small cation, the increase in attraction is greater than the increase in repulsion when the value of θ is sufficiently small. As θ increases, the repulsive energy becomes more and more dominant until a minimum potential energy is reached. For large cations, this minimum can occur only above a certain value of h . Thus, the values of the potential energy minimum and of θ at this minimum depend on the cation under study as well as on h . Since the concentration of unhydrated cations in a montmorillonite-water system increases with decreasing water content, it is concluded that θ increases during the drying of homogeneous montmorillonite–water suspensions. This provides a partial explanation for the changes in b -dimension with water content observed by other investigators.

INTRODUCTION

A PRECISE description of the state of ions and water molecules in the immediate vicinity of the solid surface of clay–water systems should include the crystallographic characteristics of the clay particles as well as the chemical and physicochemical properties of the water molecules and the ions. Montmorillonite particles are usually considered to be crystallographically stable, at neutral values of pH, except for the crystal edges. In past studies, most of the physicochemical interest in this system was focused around the ionic distribution near the clay surface and only little thought was given to the possible effect of the ions on the montmorillonite structure itself.

The ability of surface oxygen networks to change configuration with variations in the charge-balancing cations and with hydration has been demonstrated for several layer silicates (Burns and White, 1963; Leonard and Weed, 1967, 1970; Eirish and Tret'yakova, 1970). Most of these studies were limited to relatively dry clays. Low *et al.* (1970) and Ravina and Low (1972) reported

that the b -dimension of montmorillonite depends on the moisture content of the system, up to relatively high water contents. They explain this effect by the existence of epitaxy between the montmorillonite crystal and the adsorbed water and by mutual adjustment between the two with each increment of water.

In the present study we show that unhydrated charge-balancing cations can affect the b -dimension of montmorillonite and that their influence is effective up to water contents of about 3 g H₂O/g clay.

THEORETICAL CONSIDERATIONS

Consider a monionic montmorillonite suspension at equilibrium with an electrolyte solution in which the edges of the platelets have a much smaller effect than the smooth planar surfaces. When the first few ångströms of the electric double layer are studied, it is important to distinguish schematically between two types of cations (Graham, 1947; van Olphen, 1954; Bolt, 1955; Shainberg and Kemper, 1966): (a) those which are not separated from the

surface by a solvent sheath (the "unhydrated" cation, u) and (b) those which are separated by a solvent sheath one molecule thick (the "hydrated" cation, h). In calculating the relative amount of cation in each state, u and h , one can use the Boltzmann Distribution Law if the potential energy of the cation in each state can be estimated (Shainberg and Kemper, 1966). The main terms in the expression for the total potential energy, E , are (Bolt, 1955; Bolt *et al.*, 1967; Shainberg and Kemper, 1966; Lahav and Bresler, 1969) the Coulombic energy (E_{coulomb}), the hydration energy ($E_{\text{hydration}}$), and the repulsive energy ($E_{\text{repulsion}}$). Lesser terms are the induced dipole energy ($E_{i\text{-dipole}}$) and the van der Waals attraction energy ($E_{v\text{-Waals}}$) between the cation and the surface oxygens. The difference in potential energy between the states u and h can be expressed as:

$$\Delta E = E_h - E_u = \Delta E_{\text{coulomb}} + \Delta E_{\text{hydration}} + \Delta E_{i\text{-dipole}} + \Delta E_{v\text{-Waals}} + \Delta E_{\text{repulsion}} + \Delta E_x \quad (1)$$

where E_h and E_u are the total potential energy of the ions in the hydrated and unhydrated states, respectively, and ΔE_x is the difference in potential energy due to minor interactions. This latter term is assumed to be zero (Shainberg and Kemper, 1966). Equation (1) can be used to calculate the concentration of the cations in the first two layers (Shainberg and Kemper, 1966) according to:

$$C_u = C_h \exp(\Delta E/RT) \quad (2)$$

where C_h is the concentration of the cations in the first hydrated layer and C_u is the concentration of the unhydrated cations.

Let us now compare the electrostatic energy of the system under study to that of an ionic crystal (see for instance Feynman *et al.*, 1964). In calculating the electrostatic energy per ion in a crystal such as NaCl, a particular ion is considered and its potential energy with all the rest of the ions in the crystal is computed. Owing to the regularity of the crystal lattice structure, all the ions away from the edges or regions of imperfections have the same electrostatic potential energy. The calculations are similar for montmorillonite-water systems where the cation under consideration is located either at a hydrated or at an unhydrated site. As noted previously (Lahav and Bresler, 1969) the perfect ionic crystal differs from our system in two ways:

(a) The distances between the ions in the diffuse layer and the exact location of the cations near

the oxygen surface in our system are not known exactly and cannot be measured directly;

(b) The dielectric 'constant' varies throughout our system in such a way that it is difficult to estimate its values for the calculation of electrostatic interactions.

WATER CONTENT AND CATIONIC DISTRIBUTION NEAR THE CLAY SURFACE

From the foregoing discussion it is apparent that every ion in the crystal is affected by the neighboring ions in both the solid and the liquid phases. Thus, any change in the ionic distribution near the clay surface creates a change in the interaction energy between the ions and thereby affects the lattice energy of the crystal. Since the tetrahedra of montmorillonite are relatively free to rotate (Radoslovich and Norrish, 1962), it is expected that this rotation will also respond to changes in the electric double layer near the clay surface.

In a completely dry montmorillonite all the exchangeable cations are close to the surface. In an air dried clay, the cations become hydrated, and the extent of this hydration depends on the relative humidity of the air. In general, as the water content increases, the cationic concentration in the first layers near the oxygen surface decreases.

In a drying process where the distance between the clay layers is equal throughout the system and where no precipitation takes place, the concentration of the ions in the liquid phase increases. If one assumes for the moment that this increase in concentration has a small effect on the energy terms in equation (1), i.e. on ΔE , it follows from equation (2) that as the suspension dehydrates the concentration of unhydrated cations increases. At the same time, the effective charge density decreases.

The fraction of the total charge density (Γ_t) which is compensated by the unhydrated cations (Γ_u) as a function of the half distance (d) between two parallel montmorillonite platelets is given in Fig. 1a for three values of ΔE . In the calculations used to obtain Fig. 1, the structural configuration of the crystal was assumed to be constant and the values of ΔE , representing Li^+ , Na^+ and K^+ , were calculated according to Shainberg and Kemper (1966). It is evident that the value of Γ_u/Γ_t at relatively low water contents is affected and that the characteristic curves are similar for the three values of ΔE . Similarly, the magnitude of Γ_t has a small effect on the general pattern of the relation between Γ_u/Γ_t and d , although it affects the magnitude of Γ_u/Γ_t (Fig. 1b).

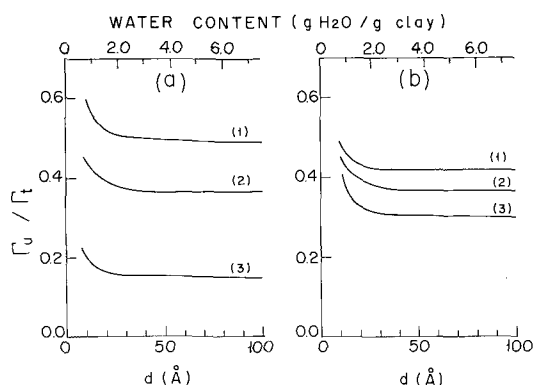


Fig. 1. Γ_v/Γ_t as a function of d , half the distance between neighboring parallel plates. (a) Three values of ΔE corresponding to K^+ , Na^+ and Li^+ (Shainberg and Kemper, 1966). (1) $\Delta E = +3.4 \times 10^{-14}$ erg/ion (K^+); (2) $\Delta E = +0.4 \times 10^{-14}$ erg/ion (Na^+); (3) $\Delta E = -5.5 \times 10^{-14}$ erg/ion (Li^+); (b) Three values of Γ_t . $\Delta E = 0.4 \times 10^{-14}$ erg/ion. (1) $\Gamma_t = 3.89 \times 10^4$ esu/cm²; (2) $\Gamma_t = 2.89 \times 10^4$ esu/cm²; (3) $\Gamma_t = 1.89 \times 10^4$ esu/cm².

The effect of the electrolyte concentration at equilibrium is relatively small and is therefore not shown here.

EFFECT OF UNHYDRATED CATIONS ON TETRAHEDRAL ROTATION

Until now we have described the distribution of the compensating cations near the montmorillonite surface without referring to the exact location of the cation near the solid phase. The exact position of the unhydrated cation in relation to the surface oxygens is of great importance and depends on all the energy terms of equation (1) (Lahav and Bresler, 1969).

Let us now examine what would be the effect of unhydrated cations at specific positions on the montmorillonite crystal lattice. For this calculation we assume that the negative charges are equally distributed throughout the lattice so that one unit cell cannot have more than one negative charge and that the compensating cations, which respond to changes in water content and become unhydrated as the clay-water system dehydrates (see Fig. 1), are located next to the ditrigonal cavity (Fig. 2); i.e. they occupy a hole position (see also van Olphen, 1954). In addition, each of the energy terms in equation (1) is assumed to depend only on the distance between the interacting ions. Furthermore, we assume that the only change in the crystal lattice which can be induced by a change of the cationic distribution near the surface oxygens is rotation of the silica tetrahedra. The angle of rota-

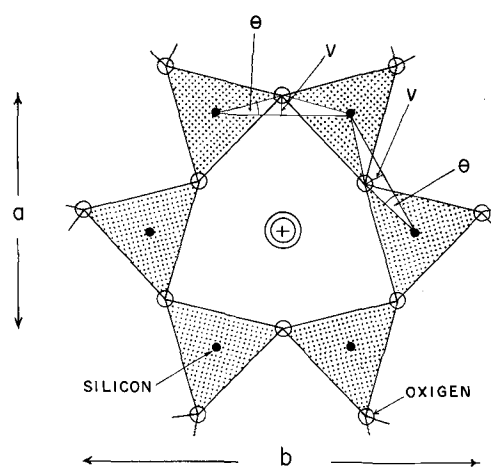


Fig. 2. Ditrigonal geometry of montmorillonite surface with the cation (+) in a central hole position.

tion, θ (see Fig. 2), can be calculated by means of the following equation (Radoslovich and Norrish, 1962):

$$\cos \theta = b_{\text{obs}}/b_{\text{tetra}} \quad (3)$$

where b_{obs} is the observed b -dimension of the unit cell of montmorillonite, and b_{tetra} is given as:

$$b_{\text{tetra}} = 6\lambda = (9.60 + 0.18p)\sin \tau. \quad (4)$$

Here τ is the $O_{\text{apex}}\text{-Si-O}_{\text{basal}}$ angle and p is the number of Al atoms at four tetrahedral sites.

As θ increases, the distance between an unhydrated cation in a hole position and each of one set of three oxygens decreases by v whereas the distance between the cation and the other three oxygens increases by v (Fig. 2). For a given distance, h , between the cation under study and the basal oxygen plane, the potential hydration energy is presumably independent of tetrahedral rotation. However, the other energy terms of equation (1) are affected by such tetrahedral rotation.

In order to calculate the relationship between θ and ΔE , the energy terms in equation (1) must be known or estimated.

The van der Waals' energy is given (Barrer, 1966) by:

$$E_{\text{v.Waals}} = \frac{k}{r^6} \alpha^2 \quad (5)$$

where α is the polarizability, r is the distance between the centers of the interacting atoms, and k is approximately 1.8×10^{-10} erg.

The repulsion energy can be written (Pauling, 1954) as:

$$E_{\text{repulsion}} = B/r^n \quad (6)$$

where B and n are constants. In order to evaluate B , the value of r should be known. Since r is not known and cannot be measured directly, a first approximation of B is made by using the calculation of hydration energy of the cation under study with the assumption that the surface oxygens are similar to the H_2O oxygens. The cation- H_2O interaction may be represented (Sposito and Babcock, 1967) as follows:

$$E_{\text{hydration}} = \frac{B}{r^{12}} - \frac{(ze)^2\alpha}{2D^2r^4} - \frac{Ze\mu}{Dr^2} \quad (7)$$

where e is the charge of an electron, μ is the dipole moment of the water molecule, and α is the polarizability of the water molecule.

The three terms in equation (7) represent repulsive, ion induced dipole and ion-dipole interactions, respectively. By applying the condition

$$\left(\frac{\partial E_{\text{hydration}}}{\partial r}\right)_{r=r_0} = 0 \quad (8)$$

B is found as

$$B = \frac{(ze)^2\alpha}{6D^2} \cdot r_0^8 + \frac{ze\mu}{6D} \cdot r_0^{10} \quad (9)$$

where r_0 is the r making $E_{\text{hydration}}$ minimum (i.e. the sum of the radii of the water molecule and cation).

The induced dipole energy between the unhydrated cation and the surface oxygens is calculated by an equation identical to the second term in equation (7) with α now the polarizability of oxygen.

We are now in a position to calculate the relationship between the energy terms of equation (1) and θ , the angle of rotation of the silica tetrahedra. It is noted that we are interested in the change δ in each of the energy terms with a change in θ . Therefore, for each value of θ the relevant δ is the difference between the potential energy at θ and that at $\theta = 0^\circ$. Each of the relevant energy terms was calculated for the interaction between the cation in a hole position at a specified value of h (the distance between the cation and the plane of the centers of the surface oxygens) and the six neighboring oxygens; three of these oxygens are close and three are far from the cation (Fig. 2). It can be shown that the effect of other ions in the lattice on the values of δ (in addition to the above

six ditrigonal oxygens) is negligible for $\delta_{v.\text{Waals}}$, $\delta_{i\text{-dipole}}$ and $\delta_{\text{repulsion}}$. As a first approximation, the same assumption can be applied also to δ_{coulomb} . Note also that the tetrahedral rotation effect on $\Delta E_{\text{hydration}}$ and ΔE_x (equation 1) is neglected.

The calculated values of δ_{coulomb} , ($\delta_{i\text{-dipole}} + \delta_{v.\text{Waals}}$), $\delta_{\text{repulsion}}$, and their sum δ_t as a function of θ are given in Fig. 3 for Na^+ and for a constant value of h . The values of $\delta_{v.\text{Waals}}$ and $\delta_{i\text{-dipole}}$ are small compared to other energy terms and therefore are not shown separately.

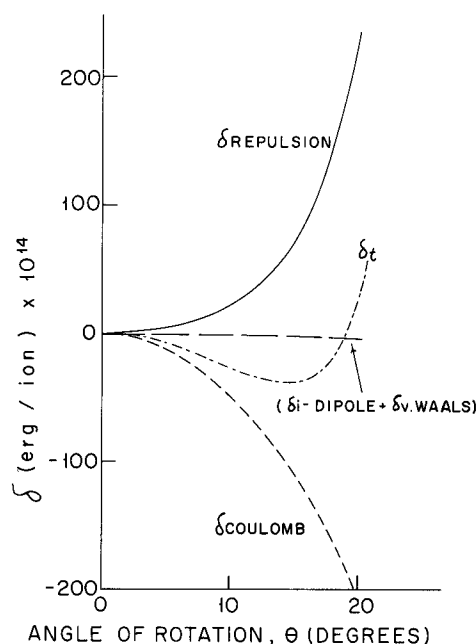


Fig. 3. δ_{coulomb} , $\delta_{\text{repulsion}}$, ($\delta_{i\text{-dipole}} + \delta_{v.\text{Waals}}$) and δ_t as a function of θ for Na^+ ($r = 0.95 \text{ \AA}$) in a central hole position, $h = 1.25 \text{ \AA}$.

It is clearly seen (Fig. 3) that an increase in θ causes an increase in the absolute value of all energy terms. At relatively low values of θ , the δ terms of the attraction energy dominate. At high values of θ where the distance between the cation and the three close oxygens becomes very small, the term $\delta_{\text{repulsion}}$ dominates. As a result, a minimum is obtained at δ_t corresponding to $\theta \approx 15^\circ$.

For a constant value of h , the angle of rotation at which δ_t becomes minimum depends on the radius of the cation (Fig. 4).

The relation between δ_t and θ for a given cation and for several values of h is given in Fig. 5.

Figures 4 and 5 show that a decrease in δ_t with θ is possible so long as the cation is not too close to the oxygens. Thus, with Li^+ and Na^+ such an

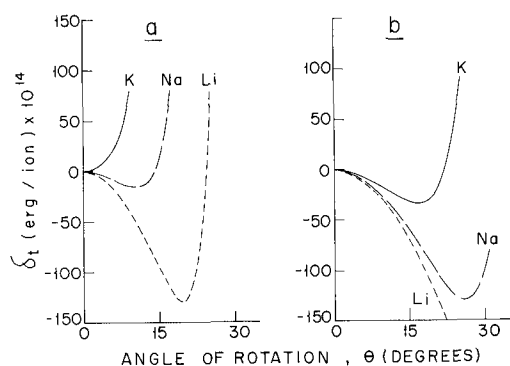


Fig. 4. δ_t of K^+ , Na^+ and Li^+ as a function of θ . (a) $h = 0$; (b) $h = 1.5 \text{ \AA}$.

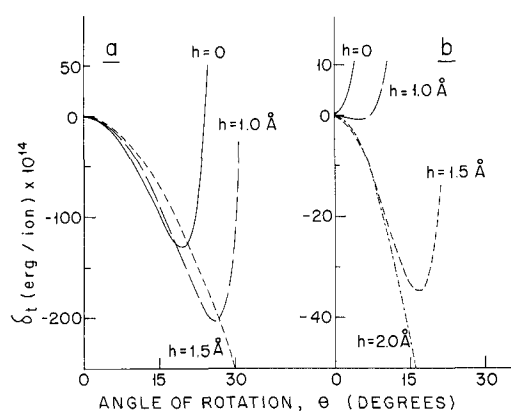


Fig. 5. δ_t at several values of h as a function of θ . (a) Li^+ ; (b) K^+ .

effect is possible even at $h = 0$. However, in the case of large cations such as K^+ , a decrease in δ_t with θ is possible only if $h \geq 0$.

EFFECT OF WATER CONTENT ON TETRAHEDRAL ROTATION

In addition to mineralogical composition (Radoslovich and Norrish, 1963), the exchangeable cations and their associated water of hydration can affect the configuration of the surface oxygens. This behavior was shown by X-ray measurements at relatively low water contents (Eirish and Tret'yakova, 1971; Leonard and Weed, 1967). The effect on tetrahedral rotation of water contents higher than the first few molecular layers can be explained by the corresponding change in the proportion of unhydrated cations (Fig. 1). An increase of the concentration of unhydrated cations increases the force exerted by these cations on the surface oxygens and thereby increases the tenden-

cy of the tetrahedra to rotate. For small cations such as Li^+ and Na^+ in a central hole position this tendency for tetrahedral rotation seems to exist even at very small values of h .

For large cations (K^+) and small values of h the cation practically touches its neighboring oxygens; therefore, the repulsive energy is very large. In the latter case one must consider the possibility that an increase in the concentration of unhydrated large cations by drying could bring about a decrease in θ .

A decrease in θ means an increase in the b -dimension of a unit cell. Low *et al.* (1970) and Ravina and Low (1972) showed that the b -dimension in six different montmorillonites increased progressively with water content from 0 to 10–15 gm H_2O/g clay. The mechanism proposed in the present study can explain changes in the b -dimension as a function of water content up to about 2–3 gm H_2O/g clay. Therefore, several mechanisms are probably responsible for the changes in b -dimension. It should be noted that in five out of the six montmorillonites used by Ravina and Low (1972) the b -dimension versus water content shows a shoulder in the range of 3–5 g H_2O/g clay. This shoulder may indicate that there are two or more mechanisms affecting the b -dimension, each of which is dominant within a different range of water content.

One must also note that Fig. 1 is a simplified description of the montmorillonite–water system because it is based on the assumption of constant structural configuration. Tetrahedral rotation increases the absolute values of all energy terms in equation (1)* for unhydrated as well as hydrated cations. However, the effect on hydrated cations in the second cationic layer can be neglected. Thus, both the b -dimension and the concentration of the unhydrated cations change with water content, and ΔE in equation (2) is not constant. However, this lack of constancy does not change the picture described above. Moreover, it seems that tetrahedral rotation tends to increase disproportionately the concentration of unhydrated cations as water content decreases.

EVALUATION

A combination of h and θ at equilibrium is obtained for each set of conditions, but the exact values of these parameters cannot be evaluated without knowing the dielectric constant. It is noted that the distance between a cation and each of the three oxygens closest to it cannot be smaller than the sum of their radii. Thus, the calculated values

*Note that hydration energy is assumed to be independent of θ .

of $E_{\text{repulsion}}$ and $\delta_{\text{repulsion}}$ must show a very steep increase as the oxygens come very close to the cation in the hole position. The procedure for the calculation of B by equations (7–9) probably underestimates this parameter. In order to compensate for this error, two values of dielectric constants were used: (a) $D = 2.0$ for the calculation of B , equation (9); and (b) $D = 5$ for the calculation of all other energy terms. A change in B does not affect the shape of the curves in Figs. 3–5 but causes a slight shift in the minimum of δ_t . Similarly, the use of different dielectric constants in the reasonable range near 5 (Shainberg and Kemper, 1966) gives curves that have similar characteristics, even though the absolute values of the energy terms and the location of the minimum value of δ_t change.

Differences between cations due to differences in their equilibrium positions near the surface oxygens cannot be calculated without taking into account the hydration energy. When all the energy terms except $E_{\text{hydration}}$ are considered, the smaller the cation, the shorter is its distance, h , from the basal oxygens plane. However, the hydration energy affects the cation in an opposite direction, i.e. the smaller the cation, the greater is its hydration energy and the lower is its tendency to penetrate into the ditrigonal hole. Measurements of dehydrated clays may give data which are easier to interpret, provided that the elevated temperature used in the dehydration process do not have an unknown effect on the clay structure. Leonard and Weed (1967) found for vermiculite that dehydration at 350° caused an increase in the b -dimension of Cs-clay and a decrease in the b -dimension of Li-clay, while the b -dimension of K-vermiculite remained unchanged. Eirish and Tert'yakova (1970) observed an increase in the b -dimension of homoionic montmorillonite samples saturated with several different cations and heated to 250°C. More experimental data are needed to have a better understanding of the role of the cation size on the b -dimension.

Our theoretical discussion leads to the following conclusions:

1. In a dehydrated clay, the penetration of cations into the ditrigonal hole is expected to be inversely related to their radii provided that the dehydration process does not bring about unknown changes in the structure of the crystal. The influence of these cations on the b -dimension should correspond to such penetration.
2. Changes in θ (or b -dimension) during the drying out of homogeneous homoionic clay suspensions (when the main mechanism of this change is the one suggested in the present paper) are expected

to start at similar values of water content and the influence of exchangeable cations and effective charge density is expected to be small. This conclusion follows from Fig. 1.

It is also interesting to note that when the distances between the unit layers are not the same throughout the system, i.e. when there is a formation of aggregates or tactoids, one expects θ to have different values at different locations. Thus, the values of θ are expected to be different in the internal and external surfaces of tactoids, provided that the silica tetrahedra do rotate and respond to the cation distribution close to the surfaces.

The above consideration suggests that the effect of compensating unhydrated cations on the configuration of the oxygen network can be explained in part by the main interactions involved. This conclusion does not exclude other mechanisms and additional effects of water molecules on the clay structure (Ravina and Low, 1972). More theoretical and experimental work is needed in order to evaluate the importance of these concepts in processes such as aggregate formation of montmorillonite and other clay minerals.

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Résumé—L'interaction entre les cations "deshydratés" situés dans les cavités (il s'agit des cations qui ne sont pas séparés de la surface par une couche de solvant) et la surface de la montmorillonite a été analysée d'une façon théorique en considérant les contributions principales à l'énergie potentielle, provenant des énergies coulombienne, d'hydratation, de Van der Waals, de dipole induit et de répulsion. On a étudié comment ces termes énergétiques étaient affectés d'une part par la distance *h* entre le cation et le plan des atomes d'oxygène de base, et d'autre part par l'angle de rotation θ des tétraèdres de silice. L'augmentation de θ à *h* constant fait augmenter les valeurs absolues de tous les termes énergétiques sauf un. L'énergie d'hydratation constitue l'exception car elle est probablement indépendante de θ . Pour un petit cation, l'augmentation de l'attraction est plus grande que l'augmentation de la répulsion quand la valeur de θ est assez petite. Lorsque θ augmente, l'énergie de répulsion devient de plus en plus importante jusqu'à ce qu'une énergie potentielle minimum soit atteinte. Pour les gros cations, ce minimum ne peut être atteint qu'au-dessus d'une certaine valeur de *h*. Ainsi, les valeurs du minimum d'énergie potentielle et de θ à ce minimum dépendent du cation étudié aussi bien que de *h*. Puisque la concentration des cations deshydratés dans un système montmorillonite-eau augmente quand la teneur en eau diminue, on conclut que θ augmente lors du séchage de suspensions aqueuses homogènes de montmorillonite. Cette variation de θ fournit une explication partielle des changements de la dimension *b* avec la teneur en eau observés par d'autres auteurs.

Kurzreferat—Die Wechselwirkung zwischen "nichthydratisierten" Kationen (solchen, die von den Oberflächen nicht durch einen Lösungsfilm getrennt sind) in Lückenpositionen und der Montmorillonit-Oberfläche werden unter Berücksichtigung der wichtigsten Bestimmungsgrößen der potentiellen Energie (Coulomb-, Hydrations-, van der Waals-, induzierte Dipol- und Abstoßungsenergie) theoretisch analysiert. Die Beeinflussung dieser Energiebeträge durch den Abstand zwischen den Kationen und der Ebene der basalen Sauerstoffionen (*h*), sowie durch den Rotationswinkel der Si-Tetraeder (θ) werden untersucht.

Durch Zunahme von θ bei konstantem *h* werden mit einer Ausnahme die Werte aller Energiegrößen erhöht. Die Hydrationsenergie stellt eine Ausnahme dar, weil sie wahrscheinlich unabhängig von θ ist. Für ein kleines Kation ist die Zunahme der Anziehung größer als die Zunahme der Abstoßung, wenn der Wert von θ hinreichend klein ist. Mit Anstieg von θ überwiegt die Abstoßungsenergie mehr und mehr, bis ein Minimum der potentiellen Energie erreicht ist. Für große Kationen kann dieses Minimum nur oberhalb bestimmter Werte von *h* auftreten. Die Größe des Minimums der potentiellen Energie und von θ bei diesem Minimum hängen folglich sowohl von dem betrachteten Kation als auch von *h* ab. Da die Konzentration des nichthydratisierten Kations in einem Montmorillonit-Wasser-System mit abnehmendem Wassergehalt zunimmt, wird die Schlußfolgerung gezogen, daß θ während des Trocknens einer homogenen Montmorillonit-Wasser-Suspension ansteigt. Diese Veränderung liefert eine teilweise Erklärung für den Wechsel der *b*-Dimension mit dem Wassergehalt, der von anderen Autoren beobachtet wurde.

Резюме — Теоретически анализировали взаимодействие негидратированных катионов (не отделенных сольватной оболочкой от поверхности) на гранях и на поверхности монтмориллонита, учитывая главные вклады в потенциальную энергию, вносимые энергиями кулоновского взаимодействия, гидратирования, Ван-дер-Ваальса, индуцированной дипольной и отталкивания. Рассматривали влияние на эти энергетические члены расстояния между катионами и плоскостью основных кислородов, *h*, и углом перемещения тетраэдра кремнезема, θ . Увеличение θ константой *h* увеличивает абсолютные значения всех членов, выражающих энергию, за исключением одного. Энергия гидратирования является исключением, так как она, очевидно, не зависит от θ . Если величина θ достаточно малая, то для небольшого катиона сила притяжения увеличивается быстрее, чем сила отталкивания. При увеличении θ преобладают силы отталкивания все время повышается до тех пор, пока не достигается минимальная потенциальная энергия. Для крупных катионов этот минимум достигается только при условии определенной величины *h*. Таким образом, величина минимума потенциальной энергии и минимума θ зависят как от исследуемого катиона, так и от *h*. В виду того, что концентрация негидратированных катионов в системе монтмориллонит-вода повышается при понижении содержания воды, заключили, что θ повышается во время высыхания гомогенных суспензий монтмориллонит-вода. Это заключение дает частичное объяснение изменениям размеров *b* в зависимости от содержания воды, замеченные другими исследователями.