

## PREPARATION AND SOLVATION PROPERTIES OF SOME VARIABLE CHARGE MONTMORILLONITES

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**Abstract**—Li-, Na-, K- and Ca-saturated Wyoming montmorillonites have been prepared and used to obtain Li,Na-, Li,K-, and Li,Ca-montmorillonites with a range of Li contents. These were heated at 220°C for 24 hr, causing the Li<sup>+</sup> ions to migrate mainly into the layer structure and leaving varying amounts of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> ions in the interlayer positions as determined by exchange with NH<sub>4</sub><sup>+</sup> ions. The results are only partially consistent with a migration of the Li<sup>+</sup> ions into vacant octahedral sites up to the limit of the octahedral layer charge. Solvation of the resulting clays with water and various organic liquids showed the following results: With water, acetone and 3-pentanone, expansion of the montmorillonites increased in a step-wise manner with increasing numbers of interlayer cations qualitatively in accord with the field strength of the cations and the dipole moments of the molecules. With ethanol, ethylene glycol and morpholine, swelling with each liquid was practically independent of the number of interlayer cations, within the limits of the prepared materials. It is suggested that for the second group of liquids some mechanism additional to cation-dipole interactions, such as hydrogen bonding to silicate oxygen surfaces, may play an important part.

### INTRODUCTION

EXPERIMENTS have been carried out on the production and swelling properties of some charge-modified montmorillonites. By starting with clays containing variable proportions of Li<sup>+</sup> ions in the exchangeable positions and subjecting them to a heat-treatment at 220°C for 24 hr in air, the Li<sup>+</sup> ions move into the layer structure and thereby reduce the layer charge and the number of interlayer cations.

Various opinions are held regarding the migration of Li<sup>+</sup> ions in montmorillonites. It is widely considered that Li<sup>+</sup> ions (and other small cations) migrate into vacant octahedral cation sites until the octahedral charge imbalance is neutralized (Hofmann and Klemen, 1950; Green-Kelly, 1953, 1955; Quirk and Theng, 1960; Glaeser and Mering, 1967; Mering and Glaeser, 1967; Schultz, 1969; Prost and Calvet, 1969). A lower limit to the layer charge and to the number of interlayer cations will be set by the amount of Al replacing Si in tetrahedral positions. A second point of view, based largely on infrared observations, is that Li<sup>+</sup> ions move partly, or even wholly, into the quasi-hexagonal holes of the Si-O networks (Tettenhorst, 1962; Russell and Farmer, 1964, see especially pp. 458-9; Farmer and Russell, 1967, see especially pp. 128-9; Calvet and Prost, 1971). On this basis it is conceivable that Li<sup>+</sup> ions which have migrated into the tetrahedral sheets will be less firmly fixed with respect to subsequent cation

exchange reactions than Li<sup>+</sup> ions which have moved into the octahedral sheets and some evidence for differential fixation has been obtained in the course of the present work.

The present experiments are oriented principally towards the solvation behavior of partially Li-saturated and 220°C/24 hr treated montmorillonites. The results obtained fall into a largely consistent pattern with respect to the nature of the solvating liquid and probably reflect the character of the solvation processes involved.

### EXPERIMENTAL

#### *Material preparation and chemical analysis*

A Wyoming montmorillonite, supplied by the American Colloid Company under the name "Volclay", has been used for the experiments reported. After the Na-saturation with 1 N sodium chloride solution and removal of excess electrolyte by centrifugation and washing and subsequently by dialysis at around 60°C, the < 1 μ fraction was removed. This fraction appeared to be without crystalline impurities as shown by X-ray diffraction analysis. A chemical analysis of the < 1 μ material gave the results shown in Table 1, where the structural formula calculated on the basis of O<sub>10</sub>(OH)<sub>2</sub>, i.e. cation valence = +22, also is given. Li-, K-, and Ca-saturated montmorillonites were prepared from the Na-saturated material by treatment with the respective 1 N chloride solutions and with subsequent removal of excess chlorides as des-

cribed above. Stock suspensions of the Li-, Na-, K-, and Ca-saturated clays containing about 20 g clay/l. were stored in polyethylene bottles.

#### Cation exchange capacity

The exchange capacity was determined by displacing the Na<sup>+</sup>, or Li<sup>+</sup>, ions by treatment with 1 N ammonium chloride solution and measuring the displaced cations by atomic absorption spectrometry. The results gave 88 meq Na/100 g clay and 82 meq Li/100 g clay, which are close to the value calculated from the chemical formula, 89 meq/100 g clay.

#### Preparation of Li, Na- and Li, K-montmorillonites

The Li-, Na-, and K-montmorillonites were fully dispersed in water when freed from excess electrolyte. Absence of basal 00l reflections from the moist clays was confirmed. Mixed Li,Na- and Li,K- clays were prepared by mechanically mixing appropriate volumes of the stock solutions with intermittent agitation over a period of several hours. Clay-coated slides were prepared by pipetting about 2 mg clay/cm<sup>2</sup> on to glass slides which were left to dry slowly in air to form oriented aggregates. Thin bands of aluminum foil were wrapped tightly around the clay-coated slides without touching the areas to be subsequently X-rayed. The slides were heated at 220°C for 24 hr and then cooled in a desiccator. The aluminum foil prevented curling of the clay films during heating.

For cation exchange determinations of the 220°C-heated clays, air-dried films of clay were heated at 220°C for 24 hr and then suspended in

ethanol. The amounts of Li<sup>+</sup> and Na<sup>+</sup> ions displaced by ammonium chloride were measured by atomic absorption spectrometry. The use of ethanol to assist the dispersion of the heated clays is important in this procedure.

#### Preparation of Li,Ca-montmorillonites

Because Ca-montmorillonite does not expand in water beyond a basal spacing of about 19 Å, it was considered that mixed Li,Ca-clays would not form readily nor homogeneously by mechanically mixing the separate clays. Therefore Ca-clay suspensions were treated with appropriate concentrations of lithium chloride solutions for periods of 2 hr and analyses were made of the Ca<sup>2+</sup> ions removed. Clay-coated slides were prepared in air-dry condition and then given the 220°C/24 hr treatment.

The exchangeable cations on the air-dried Li,Ca-clays were obtained by replacing the Ca<sup>2+</sup> ions by Li<sup>+</sup> ions and measuring the Ca<sup>2+</sup> ions displaced. The exchangeable cations on the 220°C/24 hr treated clays were determined by dispersing the clays in ethanol-water mixtures and measuring the Li<sup>+</sup> and Ca<sup>2+</sup> ions displaced by 1 N ammonium chloride solution.

Experiments were made to convert the 220°C/24 hr treated Li,Ca-clays wholly to the Ca-form by treatment with calcium chloride solutions. The resulting clays appeared to have considerably more exchangeable calcium than corresponded to their exchangeable (Li<sup>+</sup> + Ca<sup>2+</sup>) content. The results suggested that some of the Li<sup>+</sup> ions, not exchangeable with NH<sub>4</sub><sup>+</sup> ions, became exchangeable with Ca<sup>2+</sup> ions. The diversity of results obtained in these experiments, which were performed rather late in the program of work, indicated that further study will be required of these phenomena. Therefore in the present report, the solvation data will be restricted to the mixed Li,Ca-clays after 220°C/24 hr treatment.

#### Solvation experiments

These were carried out by taking the clay-coated slides cooled in a desiccator after 220°C/24 hr treatment, and adding drops of the solvating liquid to the edges of the clay film until the diffusing liquid made the entire clay film visibly moist. A stock of solvated clay slides was then stored over the corresponding liquid in a desiccator for a period of 24 hr. Diffractometer recordings with filtered CuK<sub>α</sub> radiation were made, usually at 1°(2θ)/min, with the clay-coated slide in a sealed enclosure on the diffractometer with excess liquid present to prevent any drying out of the clay films.

Table 1. Composition and structural formula of the Na-montmorillonite employed

	Weight Per cent	Cations normalized to valence 22	
SiO <sub>2</sub>	61.3	Si	3.89
Al <sub>2</sub> O <sub>3</sub>	22.4	Al	0.11
Fe <sub>2</sub> O <sub>3</sub>	3.55	Al	1.57
FeO	0.39	Fe <sup>3+</sup>	0.17
TiO <sub>2</sub>	0.11	Fe <sup>2+</sup>	0.02
CaO	n.d.	Mg	0.27
MgO	2.81	Na	0.33
Na <sub>2</sub> O	2.71	K	0.00
K <sub>2</sub> O	0.044	O <sub>10</sub> (OH) <sub>2</sub>	
Ignition loss 110°-550°C	1.27	H <sub>2</sub> O	0.23
Ignition loss 550-1050°C	4.55		
Total	99.13		

RESULTS AND DISCUSSION

*Exchangeable ions on the prepared clays*

Figure 1 shows on the horizontal axes the proportions of Na and Ca equivalents in the prepared clays prior to heat-treatment measured after exchange by  $\text{NH}_4^+$  ions from ammonium chloride solution. The milliequivalents of exchangeable cations, Li and Na, and Li and Ca, per 100 g dry clay after 220°C/24 hr treatment are shown vertically and by the full curves. The cations non-exchangeable by  $\text{NH}_4^+$  ions are shown by dashed lines.

As would be expected, the  $\text{Ca}^{2+}$  ions remain fully exchangeable after the heat-treatment, but surprisingly not all the  $\text{Na}^+$  ions remain exchangeable by  $\text{NH}_4^+$  ions. Greene-Kelly (1955) also found that "the amount of sodium recovered [after glycerol treatment of heated Li,Na-clay] was still somewhat less than that introduced" and when his results are plotted in the manner of Fig. 1a, the amount of non-exchangeable sodium is found to vary in a very similar manner to that found in the present experiments.

The behavior of the  $\text{Li}^+$  ions also is not wholly in accordance with what would be expected from the simple Hofmann-Klemen principle. Some  $\text{Li}^+$  ions remain exchangeable even when the amount of Li in the system is small, i.e. when the conditions are most favorable for their migration into octahedral positions. Possibly some of these exchangeable  $\text{Li}^+$  ions come from sites on the external surfaces of the mineral. Perhaps some  $\text{Li}^+$  ions entered the tetrahedral sheets where they were less firmly "fixed" and subsequently were exchangeable by  $\text{NH}_4^+$  ions. In both series of experiments, the amount of  $\text{Li}^+$  which becomes non-exchangeable to  $\text{NH}_4^+$ , as shown by the dashed lines in Fig. 1, increases almost linearly with the amount of Li in the initial clay. This result is broadly consistent with the Hofmann-Klemen

principle, but it has to be remarked that there is no obvious saturation of the layer structure by  $\text{Li}^+$  ions corresponding to the octahedral layer charge. In neither of the systems studied is there a "levelling-off" of the total exchange capacity after 220°C/24 hr treatment at a value corresponding to the tetrahedral layer charge, about 30 meq/100 g, as indicated by the chemical analysis and structural formula of the mineral given in Table 1. The question arises whether, under conditions where the exchangeable cations are mainly  $\text{Li}^+$  ions, some of these enter the tetrahedral sheets and become non-exchangeable to  $\text{NH}_4^+$ .

Evidently further study is required to elucidate the detailed thermal behavior of montmorillonite saturated partly with  $\text{Li}^+$  and partly with other cations. So far it appears that the view that  $\text{Li}^+$  ions enter octahedral positions up to the limit of the octahedral layer charge and that the remaining layer charge comes from the tetrahedral sheets is probably an over-simplification.

*Solvation data for 220°C/24 hr heat-treated Na,Li-, K,Li-, and Ca,Li-montmorillonite\**

Table 2 summarizes the basal spacings of the prepared clays after solvation by immersion for 24 hr in the liquids indicated. The proportions of  $\text{Li}^+$  ions occupying exchange positions prior to heat-treatment are indicated from left to right across the table. The basal X-ray reflections from the heat-treated and solvated clays in most cases were sufficiently sharp, symmetrical and regular that a spacing accurate to about 0.05 Å could be

\*From here on, the order of the cations is reversed, e.g. Na,Li rather than Li,Na, because after heat-treatment the  $\text{Li}^+$  ions are mainly non-exchangeable and the solvation behavior will depend mainly on the cation other than  $\text{Li}^+$ .

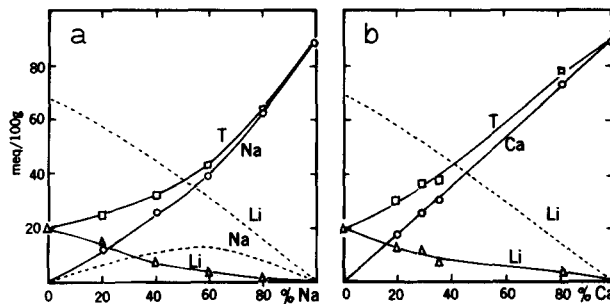


Fig. 1. Milliequivalents/100 g clay of exchangeable and non-exchangeable cations on Li,Na- and Li,Ca-montmorillonites after 220°C heat-treatment for 24 hr in air. The horizontal axis shows the proportion of equivalents of Na and Ca in the initial, pre-heated clays. Full lines show exchangeable cations, dashed lines non-exchangeable cations after heat-treatment. T signifies total exchange capacity after heat-treatment.

Table 2. Basal spacings of heat-treated clays after solvation with the liquids indicated. Exchangeable cations in the heat-treated clays are obtained from Fig. 1, by using the fraction of exchangeable Na, or Ca in the pre-heated clays. Data for K ions are taken to be similar to the data for Na ions. Stippled areas indicate changes in state of solvation

Solvating liquid	Cation other than Li	Basal spacings, in Å, of 220°C/24 hr treated clays						
		Fraction of exchangeable Li ions in pre-heated clays						
		0	0.2	0.4	0.6	0.8	1.0	
Water	Na	∞	∞	∞	9.8 <sub>s</sub> vb	9.6 vb	9.5 <sub>s</sub> sh	9.5
	K	∞	10.5 vb	9.9 <sub>o</sub> b	9.8 <sub>s</sub>	9.8 <sub>s</sub> sh		9.6 <sub>o</sub>
	Ca	19.1 <sub>o</sub> sh	19.1 <sub>o</sub>		19.2 <sub>o</sub>	9.5 <sub>s</sub>		9.6 <sub>o</sub>
Acetone	Na		18.5 <sub>o</sub>	18.5 <sub>o</sub>	13.0 <sub>o</sub> sh	13. m-l	9.3 <sub>s</sub> m-l	
	K	13.1 sh	13.0 sh	13.0	12.9 <sub>s</sub>			9.4 <sub>s</sub> *
	Ca	17.4 <sub>s</sub> sh	17.4 <sub>s</sub> sh		17.5 <sub>o</sub> sh	13.1 <sub>s</sub> irreg		13.1 irreg
3-Pentanone	Na	13.2 <sub>o</sub> v sh	13.1 <sub>s</sub> v sh	13.2 <sub>s</sub> v sh	13.1 <sub>o</sub> sh	13.2 <sub>o</sub> sh	9.4 <sub>s</sub> (12.8)**	9.6(13.2)
	K	13.4	13.2 <sub>s</sub>		13.2 <sub>s</sub> sh			
Ethanol	Na	16.8 <sub>o</sub>	17.0 <sub>s</sub>	17.1 <sub>o</sub>	17.1 <sub>o</sub>	17.0	17(18.5) m-l	
Ethylene glycol	Na	17.0 <sub>o</sub> v sh	17.2 <sub>o</sub> v sh	17.0 <sub>s</sub> v sh	17.1 <sub>o</sub> v sh	17.1 <sub>s</sub> sh	17.1 <sub>s</sub> sh	17.1 irreg
	Ca		16.8 <sub>s</sub> v sh	16.9 <sub>s</sub> v sh	17.0 <sub>s</sub> sh	17.0 <sub>s</sub> v sh	17.0 <sub>s</sub> v sh	
Morpholine	Na	14.8 <sub>o</sub> (9.6)	14.8 <sub>o</sub> (9.6)			14.8 (9.6)		15.1 <sub>s</sub> (9.5)
	K	9.9						

v sh—very sharp; sh—sharp; b—broad; vb—very broad; irreg—irregular; m-l—mixed layered; ( )—also present; ∞—no basal spacing observed; \*\*—trace of 22 Å spacing  $9.45 + 128 = 22.25$  Å; \*—trace of long spacing.

determined. Reflections up to 005 normally were recorded, but in some cases they could be followed to 008 and occasionally to 00·10. The regularity of the diffraction data indicated that the prepared clays were predominantly homogeneous; in very few cases was evidence obtained for any formation of long spacings such as might have arisen from a demixing of cations in the mixed cation clays.

In this exploratory survey, interest attaches mainly to the broad features of the solvation results. It will be seen that the liquids studied appear to fall into two groups, which will be considered separately.

#### Solvation by water, acetone and 3-pentanone

Solvation by water and by acetone is generally considered to arise from a grouping of the polar molecules around the interlayer cations due to cation-dipole interaction. The tendency to solvation will increase as the electric fields of the cations increase, in the order  $K^+ < Na^+ < Ca^{2+}$ , and as the dipole moments of the molecules increase (water,  $1.84 \times 10^{-18}$  e.s.u.; acetone and pentanone, both close to  $2.71 \times 10^{-18}$  e.s.u.). In the case of water, however, hydrogen bonding of

the molecules to each other and to the silicate oxygen surfaces also may play some part.

The results in Table 2 combined with those in Fig. 1 show that the solvation data for water, acetone and 3-pentanone are broadly what would be expected from the cations and molecules involved. For Na,Li- and Ca,Li-clays, the cations available for solvation can be read from the curves of Fig. 1; for K,Li-clays, similar analyses were not made but are likely to be similar to those for Na,Li-clays, because K-clay like Na- and Li-clay shows large expansions in water. With water as the solvating liquid, full expansion of the heated Na,Li-clays ceases when the exchangeable cations, mainly  $Na^+$ , fall below about 60 meq/100 g. For K,Li-clays, the corresponding value is about 75 meq/100 g and for Ca,Li-clays it is about 60 meq/100 g. Evidently, the greater the energy of solvation, the smaller the number of interlayer cations required to expand the clay. It is seen that the clays are either fully expanded, 19.1 Å with  $Ca^{2+}$  ions and large distances, given as ∞, with  $Na^+$  and  $K^+$  ions, or non-expanded with a basal spacing of 9.6–9.8 Å; intermediate spacings are not obtained.

With acetone,  $(\text{CH}_3)_2\text{CO}$ , the overall picture is very similar, but intermediate spacings around 13.0 Å are obtained. With Na,Li-clays, expansion to 18.5 Å ceases at exchange capacities below about 50 meq and expansion to 13.0 Å ceases around 27 meq. With K,Li-clays, the lower solvation energy of the  $\text{K}^+$  ion does not give rise to the 18.5 Å spacing, and expansion to 13.0 Å ceases when the exchange capacity falls to about 30–35 meq. With Ca,Li-clays, full expansion to 17.4 Å occurs until the exchange capacity is reduced to about 60 meq/100 g; below this value, the expansion is somewhat irregular with an average spacing around 13.1 Å.

With 3-pentanone,  $(\text{C}_2\text{H}_5)_2\text{CO}$ , the expansion is approximately the same as with acetone, but expansion to 18.5 Å was not obtained; possibly the larger size of the molecule as compared with that of acetone is a hindrance to the greater expansion.

*Solvation by ethanol, ethylene glycol, and morpholine*

The solvation of montmorillonite by ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , has been attributed to dipole attractions to the interlayer cations (Bissada, Johns and Cheng, 1967; Dowdy and Mortland, 1967) and also to hydrogen bonding to oxygen surfaces (Emerson, 1957; Brindley and Ray, 1964). Both mechanisms may play a part and this holds also for ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , doubly terminated by  $-\text{OH}$  groups, and for morpholine,  $\text{NHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ , with an  $\text{NH}$  group.

The outstanding characteristics of the results for these three liquids are that full expansion occurs at all compositions examined in Table 2. There is even a small tendency for the heat-treated clays to show slightly greater spacings when the exchange capacity after heat-treatment is diminished towards the right-hand side of Table 2. Figure 1 shows that the exchange capacity diminishes from 88 meq/100 g when no Li is present to 20 meq/100 g when the clay is saturated with Li, yet the expansion of the clay with ethanol, ethylene glycol and morpholine takes place to the same extent irrespective of the change in exchange capacity. This behavior contrasts strongly with that of the liquids in the first group and suggests that a different mechanism or an additional mechanism, such as hydrogen bonding of these molecules to the silicate surfaces, may be involved. Evidently the residual interlayer cations must play some role, for if there were *no* interlayer cations, as in pyrophyllite, then penetration of solvating liquids would be impossible or extremely difficult.

#### CONCLUSIONS

The preparation of montmorillonites with

variable numbers of exchangeable interlayer cations is made possible by forming mixed-cation clays with  $\text{Li}^+$  ions as one of the cations. Heat-treatment at 220°C for 24 hr renders most of the  $\text{Li}^+$  ions non-exchangeable by  $\text{NH}_4^+$  ions. When considered in detail, the results obtained for the numbers of exchangeable cations after heat-treatment are not entirely in accordance with migration of  $\text{Li}^+$  ions into vacant octahedral sites up to the limit of the octahedral charge deficiency and further study is required of the phenomena involved.

Swelling of the heat-treated clays in liquids is shown to fall into two categories. With water, acetone and 3-pentanone, the swelling proceeds broadly in accordance with the number and field strength of the exchangeable cations and the dipole moments of the molecules. The results are qualitatively consistent with cation-dipole interactions. With ethanol, ethylene glycol and morpholine, swelling appears to be largely independent of the number of exchangeable cations within the range of exchange capacities studied, 88–20 meq/100 g, and may even be slightly greater when the number of exchangeable cations is small. The results suggest that for the second group of liquids some mechanism additional to cation-dipole interactions, possibly hydrogen-bonding to the silicate oxygen surfaces, becomes important.

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**Résumé** – Des échantillons de montmorillonite du Wyoming saturés par Li, Na, K et Ca ont été préparés et utilisés pour obtenir des montmorillonites Li–Na, Li–K, Li–Ca, à différentes teneurs en Li. Ces argiles ont été chauffées à 220°C pendant 24 heures, ce qui entraîne une migration des ions Li<sup>+</sup> principalement à l'intérieur du réseau et ce qui laisse en position interfeuillet des quantités variables d'ions Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> et Ca<sup>2+</sup> qui sont dosés par échange avec l'ion NH<sub>4</sub><sup>+</sup>. Les résultats ne sont seulement que partiellement compatibles avec une migration des ions Li<sup>+</sup> dans les sites octaédriques vacants, dans la limite de la charge de la couche octaédrique. La solvation des argiles résultantes, avec l'eau et divers liquides organiques, donne les résultats suivants: avec l'eau, l'acétone et la 3-pentanone, l'ouverture des montmorillonites progresse par paliers quand le nombre de cations interlamellaires augmente, en accord qualitatif avec l'intensité du champ des cations et les moments dipolaires des molécules. Avec l'éthanol, l'éthylène glycol et la morpholine, le gonflement est pratiquement indépendant du nombre de cations interlamellaires, à l'intérieur des limites correspondant aux matériaux préparés. Il est suggéré que pour le second groupe de liquides, un mécanisme qui s'ajoute aux interactions cation-dipole, comme une liaison hydrogène avec les atomes d'oxygène de la surface du silicate, puisse jouer un rôle important.

**Kurzreferat** – Li-, Na-, K- und Ca-gesättigte Wyoming Montmorillonite wurden bereitet und dazu verwendet Li, Na-, Li, K-, und Li,Ca-Montmorillonite mit einem Bereich von Li-Gehalten zu erhalten. Diese wurden für 24 Stunden auf 220°C erhitzt wobei die Li<sup>+</sup> Ionen hauptsächlich in das Schichtgefüge wanderten und verschiedene Mengen an Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, und Ca<sup>2+</sup> in den Zwischenschichtpositionen zurückblieben, was durch Austausch mit NH<sub>4</sub><sup>+</sup> Ionen nachgewiesen wurde. Die Ergebnisse sind nur teilweise mit einer Wanderung der Li<sup>+</sup> Ionen in die oktaedrischen Leerstellen bis zur Grenze der oktaedrischen Schichtladung vereinbar. Solvation der sich ergebenden Tone mit Wasser und verschiedenen organischen Flüssigkeiten führte zu folgenden Resultaten: Mit Wasser, Aceton und 3-Pentanon nahm die Expansion der Montmorillonite mit wachsender Zahl der Zwischenschichtkationen qualitative im Einklang mit der Feldstärke der Kationen und den Dipolmomenten der Moleküle zu. Bei Äthanol, Äthylenglykol und Morphin war die Quellung mit der jeweiligen Flüssigkeit praktisch unabhängig von der Zahl der Zwischenschichtkationen, innerhalb der Grenzen der hergestellten Stoffe. Es wird die Vermutung ausgesprochen, dass bei der zweiten Gruppe von Flüssigkeiten ein Mechanismus zusätzlich zu den Kation-Dipolwechselwirkungen, wie etwa Wasserstoffbindung an Silikatsauerstoffoberflächen, eine wichtige Rolle spielen könnte.

**Резюме** — Специально приготовленные насыщенные Li-, Na-, K-, и Ca-монтмориллониты Вайоминга использовались для получения Li, Na-, Li, K-и Li, Ca-монтмориллонитов с различным содержанием Li. Эти монтмориллониты нагревались при температуре 220°C в течение 24 часов, в результате чего ионы Li<sup>+</sup> мигрировали, главным образом, вглубь слоистой структуры; некоторые количества ионов Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> и Ca<sup>2+</sup> оставались в межслоевых положениях, что определялось по обмену с ионами NH<sub>4</sub><sup>+</sup>. Полученные результаты лишь частично согласуются с представлением о миграции ионов Li<sup>+</sup> в вакантные октаэдрические положения до достижения предельного заряда октаэдрической сетки. Обработка полученных глин водой и различными органическими жидкостями привела к следующим результатам: при обработке водой, ацетоном и 3-пентанолом разбухание монтмориллонита возрастало ступенчато, что сопровождалось возрастанием числа межслоевых катионов, в приближенном соответствии с силовым полем катионов и дипольным моментом молекул. При обработке этанолом, этиленгликолем и морфолином разбухание в каждой жидкости практически не зависело от числа межслоевых катионов в препаратах. Предполагается, что для второй группы жидкостей важную роль может играть какой-либо дополнительный механизм к катион-дипольному взаимодействию, например, водородные связи с кислородными поверхностями силикатных слоев.