

PHASE TRANSITIONS IN COMPLEXES OF NONTRONITE WITH *n*-ALKANOLS

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Abstract—The basal spacings of long chain *n*-alkanol complexes of nontronite saturated with Li⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ were measured for temperatures increasing from –70°C up to 130°C. With rising temperatures the complexes rearrange from a low temperature form into a high temperature form.

In the low temperature form the alkyl chains of the alkanol molecules form bilayers with their chain axes perpendicular to the silicate layers. The chains may not be in all cases in the planar all trans conformation but in special 'kink'-conformations.

The transition into the high temperature form is explained by cooperative transition from a form with a low number of 'jogs' to one with a high number of 'jogs' and 'kinks'.

INTRODUCTION

IN SWELLING mica-type layer silicates with long chain compounds in the interlayer space a characteristic phase transition was observed with increasing temperature. The transition was characterized by a major decrease in the basal spacing (Brindley and Ray, 1964; Weiss and Roloff, 1966). In a recent paper (Lagaly and Weiss, 1971 a,b) on the *n*-alkylammonium silicate–*n*-alkanol complexes it has been shown that besides the high–low temperature phase transition, additional characteristic transitions can occur within the regions of both the low and high temperature form. The transitions are connected with changes in basal spacings of only 1.1–1.3 Å and are probably due to the formation of kinks and jogs within the alkyl chains. In the present paper the measurements of Brindley and Ray were extended to the alkanol complexes of nontronite with different inorganic interlayer cations.

EXPERIMENTAL

Materials

A nontronite from Kropfmuehl (Grube Ficht Bavaria, Germany) was used. It consists of lath-like crystals of about 3–10 μm length and 300–500 Å breadth. The layer charge (0.4 eq./[(Si, Al)₄O₁₀]) and the CEC (110 mval/100 g) are similar in the

highly charged montmorillonite from Cyprus and are higher than those of the Dakota montmorillonite used by Brindley. The Li⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺-saturated samples were prepared by treating the natural clay several times with 1 N solutions of the appropriate chlorides for several days. After the cation exchange reaction the samples were washed free of chloride and dried at 110°C in vacuum over P₄O₁₀.

Methods

The alkanol complexes were obtained by the 'propping open' procedure of Brindley and Ray (1964), starting from the ethanol complex. From this the butanol complex was obtained by the following method: the slurry of nontronite and ethanol was transferred to a Buchner funnel and a large amount of butanol was slowly sucked through. Attention was paid to keeping the nontronite always under alcohol and to careful exclusion of water. The completeness of this displacement reaction was monitored by X-ray diffraction, following the criteria of Brindley and Ray (1964) and checking the integrality of the (00*l*)-reflections. The hexanol complex was prepared in the same way from the butanol complex and then the octanol complex from the hexanol complex, etc. In this procedure the long chain alkanols (*n_A* > 12)† had to be dissolved in a mixture of hydrocarbons (b.p. 40–60°C). Prior to X-ray examination, adhering solvent was removed by passing a dry air stream over the sample. In order to prove the

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†*n_A* = number of carbon atoms in the alkyl chain of the alkanol molecules.

absence of hydrocarbon from the interlayer region, some samples were prepared without any solvent by using molten long chain alkanol, others by use of hexanol as a solvent. The three different methods yielded samples of identical basal spacings with rational (00 l)-sequences.

The basal spacings were measured with the Siemens diffractometer (Type Kristalloflex III). In order to get exact 2θ -values, a standard kaolinite was used for calibration. The sample holder was connected with a cryostat and thermostat, resp., so that temperatures between -70 and $+140^\circ\text{C}$ could be applied. The temperature of the sample was constant within $\pm 2^\circ\text{C}$.

In measurements below room temperature water vapor from the air is condensed onto the sample. The water molecules would replace intercalated alkanol molecules, thus leading to erroneous data. Therefore, the entire apparatus was protected by polyethylene film. In addition, at temperatures below 0°C dry nitrogen was blown through the apparatus.

Attempts at determining the exact amount of intercalated alkanol failed, since it was impossible to remove all the adhering alkanol without extracting some alkanol from the interlayer region. Extrapolation from thermogravimetric analysis tended to about 2 moles alkanol per mole $(\text{Si}, \text{Al})_4\text{O}_{10}$ for the low temperature form and to about 1.3 moles alkanol per mole $(\text{Si}, \text{Al})_4\text{O}_{10}$ in the high temperature form.

RESULTS

Influence of the chain length on the basal spacings

In Fig. 1a the basal spacings d_l of the Mg-nontronite- n -alkanol complexes are plotted versus the temperature. Within the experimental limits of error the basal spacing of the hexanol complex is independent of temperature. All the longer chain complexes exhibit a marked dependency of basal spacings on temperature, with a large decrease at a transition temperature and small or negligible changes below and above this temperature. The decrease occurs over a more or less broad temperature range. With increasing chain length this range narrows and shifts to higher temperatures and the difference in the basal spacings of the complexes below and above the transition temperature increases. Obviously, for the shorter chain alkanols the transition temperature range includes the melting points of the pure alkanols (arrows in Fig. 1a), thus justifying the nomenclature "above and below melting point series" of Brindley and Ray (1964). With increas-

ing chain lengths, however, the transition shifts to appreciably higher temperatures.

Influence of the interlayer cations on the basal spacings

The basal spacings of the various complexes

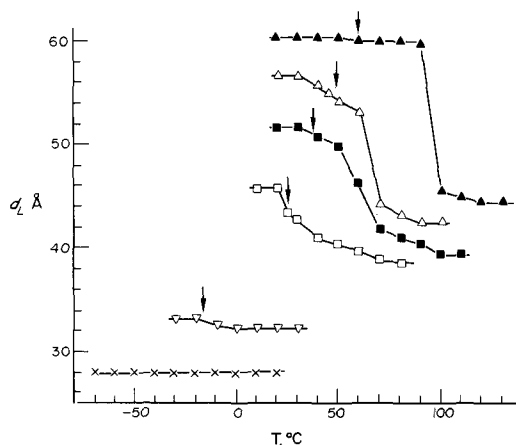


Fig. 1a

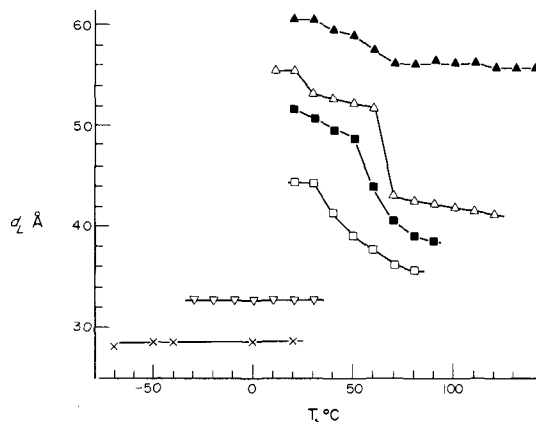


Fig. 1b

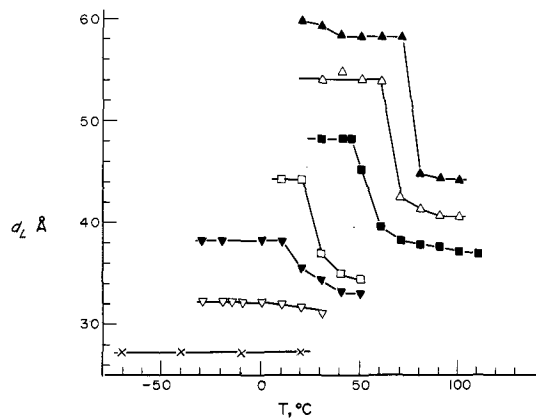


Fig. 1c

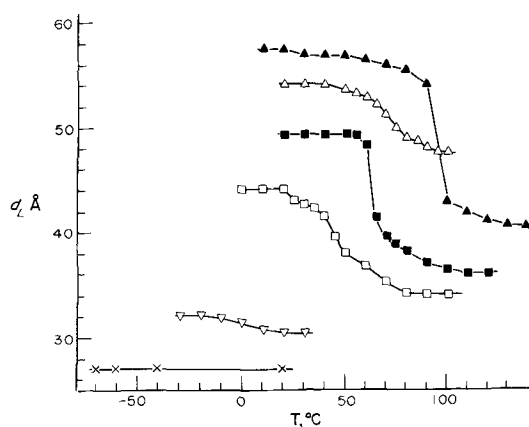


Fig. 1d

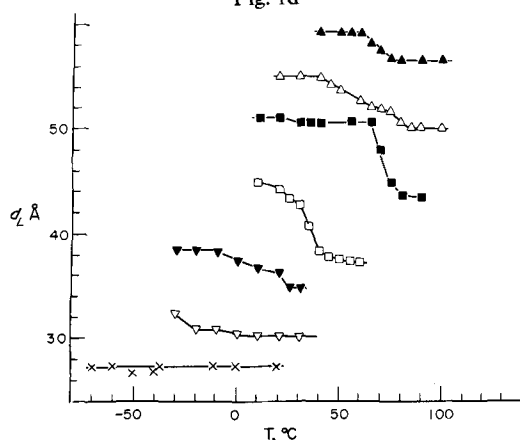


Fig. 1e

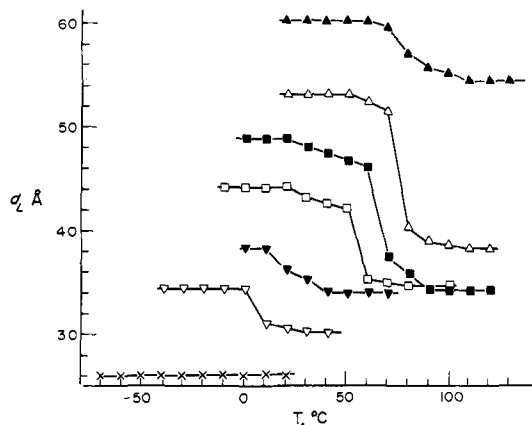


Fig. 1f

Fig. 1. Variation of the basal spacings of nontronite-*n*-alcohol complexes with temperature. —X—X— Hexanol —∇—∇— Dodecanol —▼—▼— Octadecanol —□—□— Octanol —■—■— Tetradecanol —△—△— Decanol —▲—▲— Hexadecanol (a) Mg-nontronite (b) Ca-nontronite (c) Sr-nontronite (d) Ba-nontronite (e) Li-nontronite (f) K-nontronite (the arrows in Fig. 1a indicate the m.p. of the pure *n*-alkanols)

with other mono- or divalent interlayer cations (Figs. 1b–f) change in a similar way with rising temperature. However, distinct differences up to 3 Å are introduced by the different interlayer cations. The temperature intervals for the low/high-transition are listed in Table 1. The transition temperatures increase with rising chain length. The influence of the interlayer cations is small; no simple relation to cation size and valency can be seen.

Table 1. Temperature range for the transition of the low temperature form into the high temperature form: (= temperatures for $\Delta d_L/\Delta T = \text{maximum}$)

Cation	Temperature range (°C) for				
	$n_A = 10$	12	14	16	18
Mg ²⁺		20–30	50–70	60–70	90–100
Ca ²⁺		30–40	50–60	60–70	
Sr ²⁺	10–20	20–30	45–60	60–70	70–80
Ba ²⁺		40–50	60–65		90–100
Li ⁺	20–25	30–40	65–80		
K ⁺	10–20	50–60	60–70	70–80	

With Li⁺, K⁺, Ca²⁺ complexes of octadecanol and Li⁺ and Ba²⁺ complexes of hexadecanol the transition low/high seems to be impeded. The decrease of the basal spacing is very small and the sequence exhibits some randomness.

The experimental data suggest that the structure in the interlayer space may be similar for the different interlayer cations but not exactly the same. A model should make allowance for such differences without drastic rearrangement of the interlayer structure. For Li-complexes, in addition, a shift of the Li⁺ cations from exchange positions into octahedral holes may be considered. However, this change is unlikely, since the charge distribution is highly beidellitic and the measured spacings are reversible.

INTERPRETATION AND DISCUSSION

Models for the interlayer structure in the low temperature form

The arrangement of long chain molecules in the interlayer space of swelling layer silicates can often be deduced from basal spacings measured for different chain lengths. If the basal spacings increase with increasing chain lengths in a regular manner, it can be assumed that the long chain molecules are stretched and tilted at distinct angles α to the silicate layers. The tilting angle can be calculated from the average increase of the basal spacing with chain length (= $\Delta d_L/\Delta n_A$). If $\Delta d_L/\Delta n_A$

is $1.27 \text{ \AA}/\text{C-atom}$, the chains are perpendicular to the silicate layers. (The projection of the C-C bond of an alkyl chain to their chain axis is 1.27 \AA). A value less than 1.27 \AA indicates tilting angles smaller than 90° , which can be calculated from the formula $1.27 \sin \alpha = \Delta d_L/\Delta n_A$. If $\Delta d_L/\Delta n_A$ becomes larger than 1.27 \AA , the chains are either arranged in bilayers between the silicate sheets or the tilting angle increases with increasing chain length. If the chains in both layers are perpendicular to the silicate sheets, the maximum increase per carbon atom is $\Delta d_L/\Delta n_A = 2 \cdot 1.27 \text{ \AA} = 2.54 \text{ \AA}$.

The described procedure was used by Brindley and Ray (1964) in order to learn about the arrangement of long chain alkanol molecules in the interlayer space of Ca-montmorillonite-alkanol complexes. In these, the alkanol molecules are reported to be arranged in bimolecular layers with their chain axes tilted at angles of 77° with respect to the silicate layers. This value is close to the 70° angle required for a distinct type of hydrogen bonding to the silicate layers (Tettenhorst and McGuire, 1970). The basal spacings of the nontronite complexes, however, cannot be interpreted easily in this way. Since the decrease in basal spacing with rising temperature is non-linear, calculation of the tilting angle from an average seems to be meaningless.

Instead of using $\Delta d_L/\Delta n_A$, the tilting angle α can also be estimated from the absolute value of the basal spacing d_L . This procedure requires exact values for the distance between the OH-groups and the silicate layers and between the CH_3 terminations within the bilayers. Since these values are known only within certain limits, the calculation of tilting angle is somewhat arbitrary. In addition it must be taken into consideration that the orientations of the end groups can change with the chain length, the interlayer cation and the temperature.

For these reasons we propose another model. We assume that the chains are nearly perpendicular to the silicate layers but undergo conformational changes with increasing temperature, especially a transformation of trans C-C bonds into their gauche forms.

If the chain axes are perpendicular to the silicate layers (Fig. 2), the basal spacings for the all-trans conformation can be calculated by the equation:

$$d_L = 6.6 + 2\{x_1 + 1.20 + (n_A - 1)1.27\} + x_2 [\text{\AA}] \\ = 12.7 + 2.54n_A [\text{\AA}].$$

The terms in this equation have the following

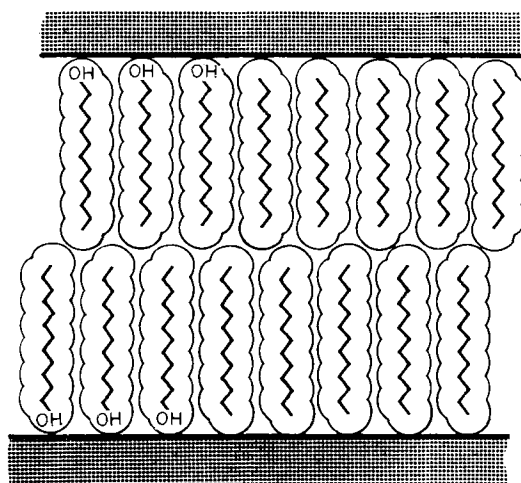


Fig. 2. Idealized arrangement of the alkanol molecules in the interlayer space of the nontronite-*n*-alkanol complexes in the low temperature form (without regard to interlayer cations).

meanings: 6.6 is the separation between the centers of the oxygen atoms on opposite sites of a silicate layer; x_1 gives the distance of the OH-groups from the surface oxygen atoms of the silicate sheet (normal to the silicate layer); x_2 denotes the distance between the CH_3 -endgroups in the medial plane of the interlayer space; the term $1.20 + (n_A - 1)1.27$ is the length of the alkyl chain between the O-atom and the terminal C-atom for the all-trans conformation. The most favorable positions of the OH-groups of the alkanol molecules are positions above the pseudo-hexagonal array of surface oxygens. In this case x_1 is $1.6 \pm 0.3 \text{ \AA}$ (Lagaly and Weiss, 1971). If the CH_3 -terminations of the alkyl chains make van der Waals contacts within the bilayer, x_2 is $3.0 \pm 0.3 \text{ \AA}$.

In these models the influence of the interlayer cations has not been considered. The cations cause defects in the regular arrangement of the alkyl chains. The distortion should depend upon the size of these ions and their coordination to the surface oxygens. Large cations, such as K^+ , Sr^{2+} and Ba^{2+} , probably will occupy positions above the oxygen hexagons, which will permit coordination numbers higher than 6, whereas small cations like Li^+ , Mg^{2+} and probably Ca^{2+} may be arranged above the centers of the SiO_4 -tetrahedra with a tendency to coordination number 6. In both cases the coordination of the cations can be completed by the alkanol oxygens, which requires a shift of these alkanol molecules out of the oxygen hexagons.

The displacement of the alkanol molecules from

the energetically stable positions above the hexagon centers is favored by the ion-dipole interaction (cation-OH group of alkanol) and probably by an increase of the van der Waals energy between the chains. In the idealized structure with interlayer cations and alkanol molecules occupying only the hexagon centers, $2-\zeta$ alkanol molecules can be bound (per formula unit, i.e. $(\text{Si}, \text{Al})_4\text{O}_{10}$ -unit, there are 2 hexagons and ζ cations). Here the packing of the chains is not as close as in the crystalline alkanols (Lagaly and Weiss, 1971a). If, however, the influence of the cations forces the adjacent chains out of their positions in the oxygen hexagons, the alkanol content in the interlayer space is no longer determined by the number of hexagon positions and becomes somewhat higher than $2-\zeta$ molecules per unit, thus producing a closer packing of the chains. The less favorable arrangement of the OH groups to the surface oxygen atoms of the silicate layers is then compensated by the enhanced van der Waals energy between the chains as a consequence of the closer packing. In this view, the cations can be regarded as point defects which produce dislocations of the alkanol molecules in the sense of positive or negative clustering of these molecules around the cation. If most of the chains still remain in the all-trans conformation, the OH distance from the silicate layers is enhanced and the basal spacing can be up to 2.5 \AA higher than the calculated values.

In another model it can be assumed that the

*The first number in the kink notation denotes the number of gauche bonds, the second the shortening of the overall length in multiples of 1.27 \AA . Kinks which produce a shortening $> 1.27 \text{ \AA}$ are called jogs.

cation point defects in the interlayer structure give rise to structural deviations from the all-trans conformation. The most probable conformational isomers are the kink and jog isomers. These isomers are formed if trans-bonds in the chain turn into gauche-bonds. In the case that three adjacent trans-bonds ($\dots ttt \dots$) change into a $\dots gt\bar{g} \dots$ conformation, the new conformation is called a $2g1$ kink (Fig. 3). The two parts of such alkyl chains are parallel to each other, but the overall length is 1.27 \AA shorter than in the all-trans chain. Other types of kinks have conformations such as $\dots gtt\bar{g} \dots$ ($= 2g2$ kink*), $\dots gt\bar{g}tg \dots$ ($= 3g2$ kink) or $\dots gtttt\bar{g} \dots$ ($= 2g3$ kink). Recently, kink isomers are supposed to cause the rotational phase transition in paraffin crystals (Blasenbrey and Pechhold, 1967) and to contribute to the relaxation properties of polymers (Pechhold, 1968; Pechhold and Blasenbrey, 1970). The model in Fig. 4 shows how the formation of kinks near the interlayer cations produce kink block structures. Their dimensions depend upon the chain length and the special type of kinks (Table 2). It seems evident that those types of kink block structures should be preferred whose areas are comparable with the area available for each cation on the silicate surface (twice the equivalent area for monovalent cations and four times the equivalent area for divalent cations). It can be seen from Table 2 that, according to cationic radius and chain length, different kink block structures ($2g1/2g1/\dots ttt \dots$, $2g2/2g1/\dots ttt \dots$, $2g1/2g1$ etc.) may be formed. The formation of such structures should reduce the basal spacing by 1.3 ($2g1$ -kink block) or $2 \times 1.27 \text{ \AA}$ ($2g2$ or $3g2$ kink block), but this decrease can be more or less com-

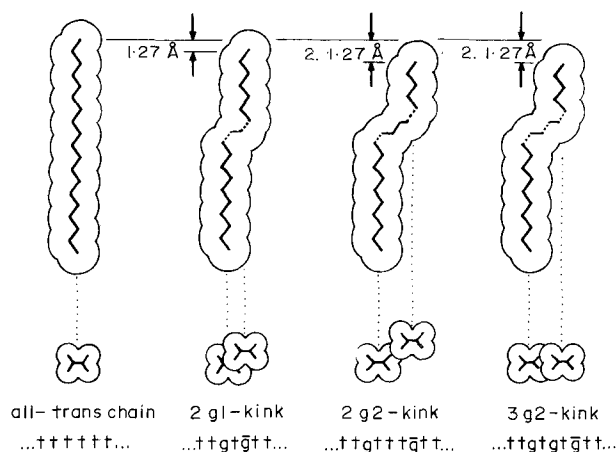


Fig. 3. Rotational isomers of alkyl chains: (— trans bonds, gauche bonds).

Table 2. Dimensions of kink block structures in nontronite-*n*-alkanol complexes

Interlayer cation	Ionic radius (Å)	Combination of kinks to accommodate the cation	Model	Area for each cation on the silicate sheet* (Å) ²	Area of the kink block for	
					$n_A = 12$ (Å) ²	$n_A = 18$ (Å) ²
Li ⁺	0.60	2g1/... ttt...	Fig. 4a	120	110	170
K ⁺	1.33	2g1/2g1	Fig. 4b	120	220	340
		or			100	160
Mg ²⁺	0.65	2g2/... ttt...	Fig. 4a	240	110	170
Ca ²⁺	0.99	2g1/2g1	Fig. 4b	240	220	340
Sr ²⁺	1.13	or				
Ba ²⁺	1.35	2g2/... ttt...			100	160

* = 2 × equivalent area for monovalent cations;

= 4 × equivalent area for monovalent cations.

† = the areas were calculated for a linear arrangement of the chains like Fig. 4, the mean distance between the chains in one row being 4.8 Å, between the rows 4.2 Å.

compensated by changes in the distance of the OH groups from the silicate layers and the distance between the CH₃ terminations.

The experimental results are given in Table 3. It may be seen that for the small interlayer cations the basal spacing lies at the upper limit of the calculated data or exceeds these values. In these cases the first model seems to be more probable. The formation of kink block structures may be realized only for the large interlayer cations and long alkyl chains.

Phase transitions in the low temperature form

Within the temperature range of the low temperature form, in most samples the basal spacing decreases with rising temperature in a quite irregular manner. The decrease in the basal spacing can be interpreted as the formation of kinks. In well ordered systems with cooperative kink formation

the basal spacing should decrease in steps of 1.3 Å as observed in the *n*-alkylammonium-*n*-alkanol complexes (Lagaly and Weiss, 1970 a,b). In the system under investigation, however, the regular stepwise decrease in the basal spacing by kink formation seems to be more or less outweighed by changes in the arrangement of the end groups or by the fact that rotational isomers with the same conformation are arranged in clusters in the interlayer spaces which change their conformation at different temperatures. Due to such clusters the spacings of succeeding interlayer spaces would differ by about 1.3 Å and the measured basal spacing would be only an average. The very regular decrease in the basal spacing of the *n*-alkylammonium silicate-*n*-alkanol complexes comes from the fact that here the cations do not represent point defects in the interlayer structure since their long chains are incorporated in the bimolecular film of

Table 3. Basal spacings of the low temperature form of nontronite-*n*-alkanol complexes (ca 20°C below melting point of pure *n*-alkanol)

Number of C-atoms in the chain	Calculated for bimol. arrangements equation (1)	Basal spacings (Å)					
		Experimental interlayer cations =					
$n_A =$		Li ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	K ⁺	Ba ²⁺
6	27.9 (30.4)*	27.3	28.0	28.6	27.2	26.0	27.0
8	33.0 (35.5)	32.3	33.0	32.7	32.1	34.3	32.0
10	38.1 (40.6)	38.4			38.0	38.2	
12	43.2 (45.7)	45.0	45.8	44.2	44.2	44.1	44.0
14	48.3 (50.8)	51.2	51.4	51.5	48.2	48.4	49.4
16	53.3 (55.8)	55.2	56.4	55.3	54.0	53.1	54.3
18	58.4 (60.9)	59.6	60.4	60.4	59.7	60.0	57.6

*Maximal values.

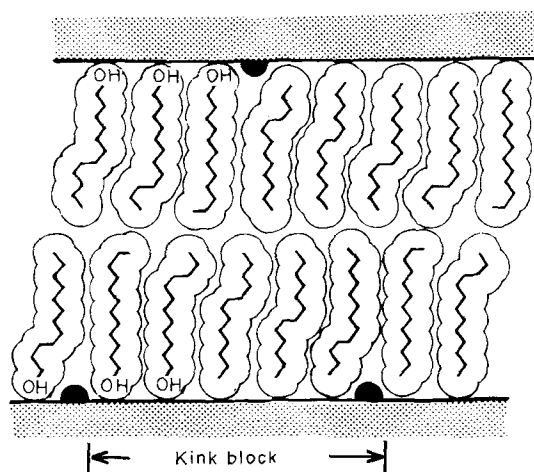


Fig. 4a

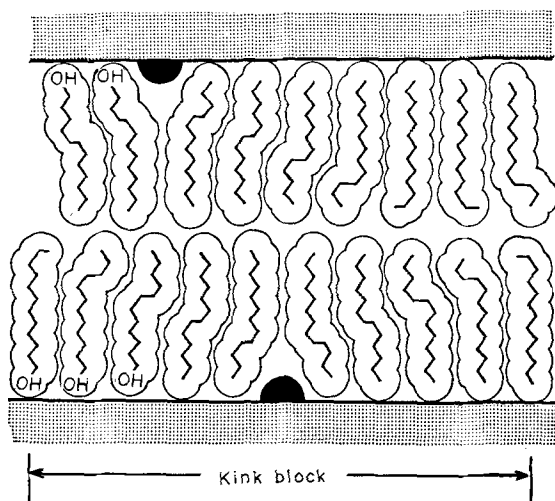


Fig. 4b

Fig. 4. Formation of kink block structures as a consequence of point defects caused by the interlayer cations: (a) small interlayer cations and combinations $2g1/\dots tt\dots$ at the kink block boundaries. (b) large interlayer cations and combinations $2g1/2g1$ at the kink block centers.

the alkanol molecules in the interlayer space and cooperate in the conformational changes of the alkanol molecules.

For alkanol complexes with less than 8 C-atoms in the chain the basal spacing is constant in the investigated temperature range (Figs. 1a-f). This constancy indicates the formation of kinks and jogs to be less probable in short chains ($n_A < 8$).

Transition to the high temperature form

As shown in Table 1 the transition into the high temperature form starts at temperatures which in general are not markedly influenced by the cations

but increase with increasing chain length. This situation suggests that the transition is primarily caused by alkyl chain conformation changes.

There seems to exist a certain relation between the basal spacings in the low temperature form and the high temperature form. Since no phase transitions are observed for the hexanol complexes it is possible to compare the differences in the basal spacings $d_{n_A > 6} - d_{n_A = 6}$ for the low temperature form (l.t.f.) and the high temperature form (h.t.f.). The ratio:

$$\frac{(d_{n_A > 6} - d_{n_A = 6}) \text{ l.t.f.}}{(d_{n_A > 6} - d_{n_A = 6}) \text{ h.t.f.}}$$

was found to be about 2.0, thus suggesting a mechanism for the phase transition which is independent of the chain length ($n_A \geq 8$) and the interlayer cation.

Models for the high temperature form

In order to interpret the low-high temperature phase transition, one might assume at first glance that the bimolecular layer of the low temperature form rearranges to a monolayer structure at higher temperatures. This assumption seems to be supported by the measured loss of alkanol from the interlayer space. However, the observed basal spacings are remarkably higher than the values which are calculated for the monolayer structure (Table 4). Thus, a bimolecular arrangement in the interlayer space must be discussed. The simplest model which corresponds to the observed data is pictured schematically in Fig. 5a and is similar to the model of Brindley and Ray (1964). In other models the rearrangement in the interlayer space may be caused by a cooperative transition of structures with low kink concentrations into structures with high kink concentrations or in structures with predominant jogs (Fig. 5b). Since chains with jogs require two neighboring positions in the interlayer space, the formation of jogs must lead to a drastic rearrangement of the interlayer structure, connected with a release of alkanol out of the interlayer space. Probably both layers of alkanol molecules are interlocked with each other, but total interlocking is prevented by the jogs.

In some cases the basal spacings in the high temperature form are unexpectedly high, particularly with Li^+ cations. The low temperature form appears to be stabilized up to high temperatures. Perhaps the release of the alkanol from the interlayer space is hindered so that special types of rotational isomers (e.g. $\dots tgtg\dots$ helix) may be formed. A different view would be that the alkanol

Table 4. Basal spacings of the high temperature form of nontronite-*n*-alkanol complexes (*ca* 40°C above melting point of the pure alkanol)

Number of C-atoms in the chain	Calculated for monolayer arrangement	Basal spacings (Å)					
		Experimental interlayer cations =					
		Li ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	K ⁺	Ba ²⁺
8	21.1	30.1	32.1			30.0	30.3
10	23.6	34.8			33.0	34.0	
12	26.2	37.4	38.4	35.6	34.4	34.6	34.2
14	28.7	43.6	39.2	38.4	37.0	34.2	36.2
16	31.3	50.4	42.3	41.2	40.5	38.2	40.7
18	33.8	56.9	44.1	55.6	44.2	54.3	47.8

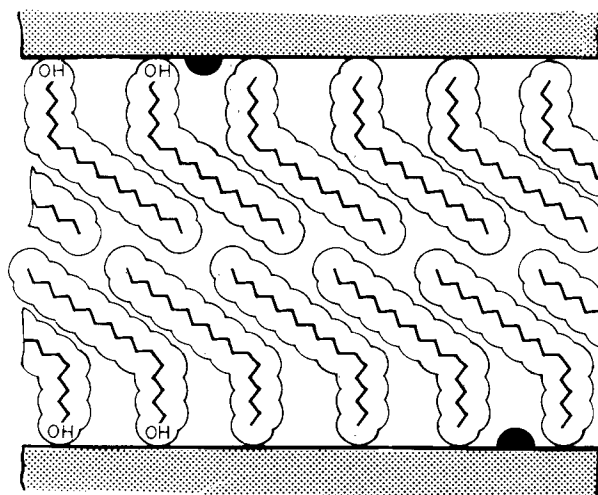


Fig. 5a

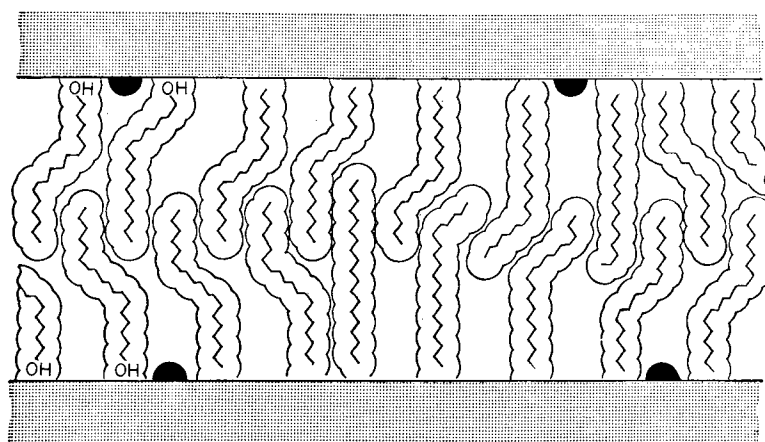


Fig. 5a,b. Models for the interlayer structure in the high temperature form. (There is some experimental evidence for an increased porous volume in the high temperature form. Some of the holes may be occupied by alkanol molecules flatly lying on the silicate surface.)

molecules may not interlock to the same extent as in the other complexes. The differences between the proposed or other possible models lie mainly in the type of the conformational changes of the alkyl

chains. A detailed discussion, however, does not seem to be meaningful, since from the basal spacings alone no distinction can be made between the different models.

The crucial point of the above interpretation is the absence of randomness within low and high temperature range. Only within the transition interval some randomness has been observed. Calculation of the basal spacings d_l from the individual orders l of the (00 l)-reflexions give identical values within $\pm 0.1 \text{ \AA}$ at spacings up to about 40 \AA and within $\pm 0.3 \text{ \AA}$ at spacings above 50 \AA .

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Résumé—Les espacements basaux des complexes formés entre des *n*-alcanols et la nontronite saturée par Li^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} et Ba^+ ont été mesurés aux températures allant de -70°C à 130°C . Lorsque la température s'élève, les complexes subissent un réarrangement d'une forme basse température à une forme haute température.

Dans la forme basse température les chaînes alkyle des molécules d'alcanol forment des couches doubles dans lesquelles les axes des chaînes sont perpendiculaires aux feuillets du silicate. Il peut arriver que les chaînes n'adoptent pas dans tous les cas la conformation plane "all trans", mais qu'elles aient des conformations spéciales ("kinks").

Le passage de la forme basse température à la forme haute température est expliqué par une transition coopérative d'une forme à nombre réduit de "jogs" vers une forme à nombre élevé de "jogs" und "kinks".

Kurzreferat—Die Basisebenenabstände von langkettigen *n*-Alkanolkomplexen mit Li^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} und Ba^+ -gesättigtem Nontronit wurden im Temperaturbereich von -70°C bis 130°C gemessen. Mit ansteigender Temperatur ordnen sich die Komplexe von einer Tieftemperaturform in eine Hochtemperaturform um.

In der Tieftemperaturform bilden die Alkylketten der Alkanolmoleküle bimolekulare Schichten mit senkrecht zu den Silikatschichten angeordneten Kettenachsen. Die Ketten brauchen nicht in allen Fällen in der ebenen all-trans Konformation vorzuliegen, sie können auch in speziellen Kinkkonformationen auftreten.

Der Übergang in die Hochtemperaturform wird als eine kooperative Umwandlung von einem Zustand mit einer geringen Zahl von "Jogs" in einen solchen mit einer großen Zahl von "Jogs" und "Kinken" gedeutet.

Резюме—Наблюдали изменения базисных параметров длинной цепи комплексов *n*-алканолом нонтронита, насыщенного Li^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} и Ba^{2+} , при повышении температуры от -70°C до 130°C . С повышением температуры комплексы перегруппировываются из низкотемпературной формы в высокотемпературную.

При низкотемпературной форме алкиловые цепи молекул алканолом формируют бинарные слои при чем оси их цепей находятся перпендикулярно к слоям силиката. Не во всех случаях цепи ориентированы в планарной цельной трансформации, иногда они ориентированы в особых «петлевых» конформациях.

Переход в высокотемпературную форму объясняется объединенным переходом из формы с малым числом «ступенек» в форму с большим числом «ступенек» и «петель».