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KINK BLOCK STRUCTURES IN CLAY ORGANIC COMPLEXES

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Abstract—Complexes of *n*–tetradecylammonium–beidellite with *n*–alkanols

$$(n\text{-}C_{14}H_{29}NH_3^+)_{0,44}(n\text{-}C_xH_{2x+1}OH)_{1,56}\{Mg_{0,28}Al_{1,81}(OH)_2Si_{3,56}Al_{0,44}O_{10}\}^{0,44-}$$

($x = 8$ –22) have been prepared and characterized by their basal spacings and by measurements of the specific heat c_p.

The compounds undergo a series of reversible phase transitions

$$\beta_1 \rightleftharpoons \ldots \rightleftharpoons \beta_i \rightleftharpoons \ldots \rightleftharpoons \beta_\omega \rightleftharpoons \alpha_1 \rightleftharpoons \ldots \rightleftharpoons \alpha_j$$

with rising temperature. The maximum number ω of β-phases depends upon the chain lengths and increases from 1 with decanol to 6 with docosanol. Due to the evaporation of alkanol the number of α-phases is not yet established in all details.

The β-transitions correspond to conformational changes of the alkyl chains via rotational isomerisation, especially kink formation. The β-phases become unstable if the kink concentration exceeds 0,14 kinks/-CH_2-. The β/α-transition is probably caused by a rearrangement into special gauche-block structures.

INTRODUCTION

Complexes of montmorillonite with alkanols were reported for the first time by Bradley (1945). Later on, several papers dealt with these compounds: orientation of alkanol molecules (MacEwan, 1948), influence of inorganic (Dowdy and Mortland, 1967; Bissada *et al.*, 1967) and organic (Weiss, 1963) interlayer cations and of charge density (Lagaly and Weiss, 1967) onto the alkanol orientation, selectivities for distinct alkanols from mixtures (Heydemann and Brindley, 1968; Slabaugh and Hanson, 1969; Aragon de la Cruz, 1969) and temperature dependent phase transitions with inorganic interlayer cations (Brindley and Ray, 1964; Pfirrmann *et al.*, 1973).

In this paper temperature dependent phase transitions in alkanol complexes of alkylammonium–montmorillonite will be discussed, using the *n*–alkanol complexes of *n*–tetradecylammonium–beidellite as examples.

MATERIAL AND METHODS

Beidellite

The beidellite $Ca_{0.22}(H_2O)_x\{Mg_{0.28}Al_{1.81}(OH)_2Si_{3.56}Al_{0.44}O_{10}\}$ was a pure white sample collected at Unterrupsroth/Rhön in Germany. It has only a slightly inhomogeneous charge distribution with a mean layer charge of 0·44 eq./$(Si,Al)_4O_{10}$ and a lower and upper limit of interlayer cation density of 0·36 and 0·48 resp. (Lagaly and Weiss, 1970 a and b). The CEC is about 120 m-equiv./100 g.

n–tetradecylammonium–beidellite

n–tetradecylammonium–beidellite was prepared by cation exchange with *n*–tetradecylammonium chloride (Grade: puriss., Fluka, CH-Buchs) in 0·1 N aqueous solutions (pH = 6–7) from the purified Na^+/Ca^{2+}-beidellite at 65°C as described in other papers (Lagaly and Weiss, 1969, 1970 a and b). The removal of excess alkylammonium salt and free alkylamine had to be controlled carefully.

n–tetradecylammonium–n–alkanol–beidellite

In order to prepare the complexes of *n*–tetradecylammonium–beidellite with *n*–alkanols (*n*–octanol ..... *n*–docosanol), *n*–tetradecylammonium–beidellite was dried in high vacuum ($P < 0{\cdot}01$ Torr) at 65°C and then carefully mixed with 4 moles alkanol per mole beidellite. The mixture was stored at 65–80°C for 24 hr, ground and again stored at 65°C for another 24 hr. Then, the sample was slowly cooled down to room temperature and kept there for at least 24 hr before the measurements of the basal spacings were started.

Measurements of basal spacings

The basal spacings at room temperature were measured in Debye–Scherrer powder cameras and with a Philips Norelco diffractometer. For measurements above room temperature, a special sample holder for the diffractometer was constructed (Fig. 1), which could be heated electrically up to 140°C. Using a precision NTC resistance thermometer, the temperature could be maintained constant within ±0·1°C. The

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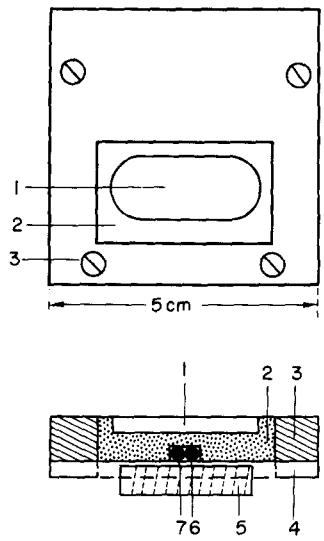


Fig. 1. Sample holder for the Norelco Diffractometer (Philips, Eindhoven) allowing temperature dependent basal spacing measurements up to 140°C.
1: Sample; 2: Cu-Block; 3: Teflon; 4: Al-Support; 5: Heater; 6: Thermocouple; 7: NTC-Resistance.

temperature was measured with an Ni–NiCr thermocouple. The adjustment of the sample was controlled by dodecylammonium–dodecanol–beidellite as reference sample.

The complex was transferred into the sample holder at room temperature with a preferential orientation of the layers. The first 6 or 7 (001)-reflections were measured. Thereafter, the temperature was raised by about 3°C. After 15–20 minutes the (001)-reflections were recorded again. In this way the temperature dependency of the basal spacings was followed with increasing temperature up to a maximum temperature, and with decreasing temperature from the maximum temperature to room temperature. Since the alkanol was in large excess, errors due to evaporation of the alkanol could not be observed up to 80°C for decanol and up to 120–140°C for the longer chain alkanols. Therefore a maximum temperature of 80°C for decanol and 120–140°C for dodecanol, tetradecanol etc. had not been exceeded during the runs.

One series of measurements from room temperature up to the maximum temperature took about 6–8 hr. During the measurements the samples were carefully controlled in order to avoid errors by deformation of the sample surface. The measurements from room temperature to maximum temperature and vice versa were repeated 4–6 times, using new sample preparations as well as previously used ones.

Specific heat

The specific heat of the tetradecylammonium–tetradecanol–beidellite was measured with an adiabatic calorimeter. The sample—a mixture of 0·9265 g (=2 mmole) *n*–tetradecylammonium–beidellite and 1·9325 g (=9 mmole) *n*–tetradecanol—was introduced into a small glass vessel which was immersed in liquid paraffin. The specific heats were calculated from the temperature change of the paraffin by electrical heating. The temperatures were measured with a precision NTC resistance (sensitivity: 2×10^{-4}°C). The sensitivity of the calorimeter was better than 60 mJ/hour.

RESULTS AND DISCUSSION

Complexes of tetradecylammonium–beidellite with tetradecanol

Figure 2 gives the temperature dependency of basal spacings for the tetradecanol complex of tetradecylammonium–beidellite. In general, the first 6–8 orders of (001)-reflections could easily be analysed, still higher orders (10–15) also were accessible. Deviation of the values of the individual (001)-reflections from the mean value is generally less than 0·1 Å, indicating integral (001)-series.

With rising temperature, the basal spacing decreases in distinct steps at 49°C, 60°C and 72°C, the step height being constant at 1·2 ± 0·1 Å. At 94°C the basal spacing decreases more drastically by about 6 Å from 46 Å to 40 Å. At still higher temperatures the decreases are again in small steps.

This temperature dependency of the basal spacings is exactly reproducible during the heating runs. On cooling hysteresis effects may occur; with fast cooling rates the transformation temperatures may be shifted to lower values.

The sharp decrease in the basal spacing at 90° indicates a drastic rearrangement of the interlayer structure. Low temperature forms (β) and high temperature

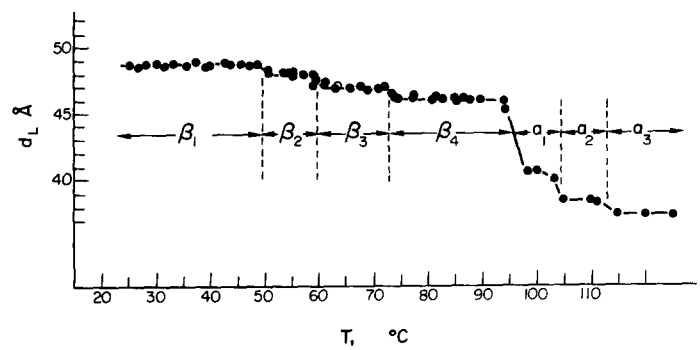


Fig. 2. Temperature dependency of the basal spacings d_L of *n*–tetradecylammonium–tetradecanol–beidellite showing the stability ranges of the low temperature phases β_1, β_2, β_3, β_4 and of the high temperature phases α_1, α_2, α_3.

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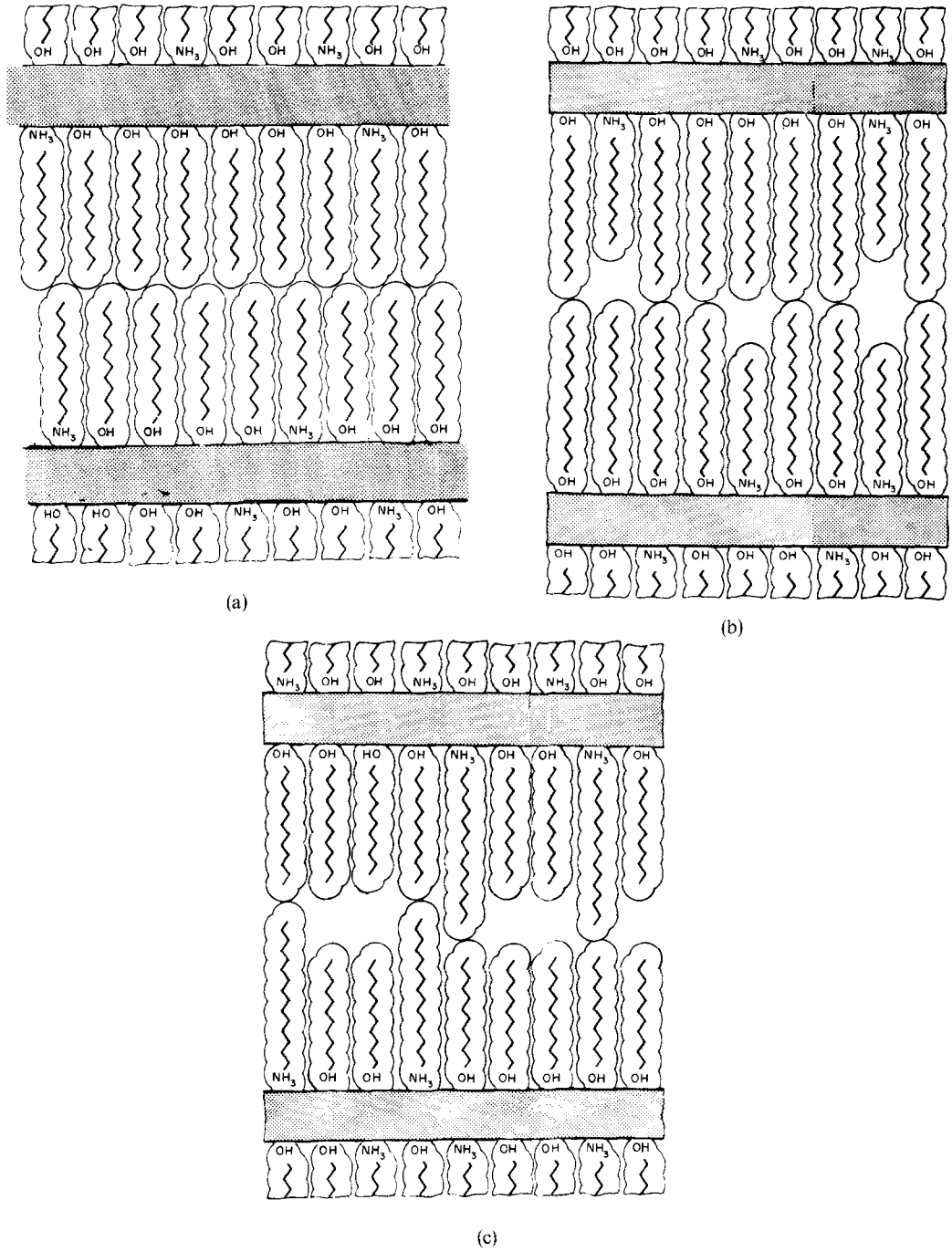


Fig. 3. Structure of the bimolecular film of alkyl compounds between the silicate layers: (a) $n_A = n_C$ spacing determining pairings: $\{n_A + n_A\} = \{n_A + n_C\} = \{n_C + n_C\}$; (b) $n_A > n_C$ spacing determining pairings: $\{n_A + n_A\}$; (c) $n_A < n_C$ spacing determing pairings: $\{n_A + n_C\}$.

forms (α) may be distinguished and the whole range may be described by

$$\beta_1 \overset{49^\circ C}{\rightleftharpoons} \beta_2 \overset{60^\circ C}{\rightleftharpoons} \beta_3 \overset{72^\circ C}{\rightleftharpoons} \beta_4 \overset{94^\circ C}{\rightleftharpoons} \alpha_1 \overset{100^\circ C}{\rightleftharpoons} \alpha_2 \overset{110^\circ C}{\rightleftharpoons} \alpha_3 \rightleftharpoons \ldots$$

Interlayer structure in the low temperature forms (β-phases)

A simple model for the interlayer structure has been established from the basal spacings and the analytical composition (Lagaly and Weiss, 1971 a).

There are about two chains per $(Si, Al)_4O_{10}$ unit, 0·44 belonging to the cations and 1·56 to the alkanol molecules. The average composition is therefore $(R\text{-}NH_3^+)_{0.44}$ $(R\text{-}OH)_{1.56}$ $\{Mg_{0.28}Al_{1.81}(OH)_2$ $Si_{3.56}Al_{0.44}O_{10}\}^{0.44+}$. The chains of both the alkylammonium ions and alkanol molecules have all-trans conformation; they are arranged in bilayers and stand upright perpendicular to the silicate layers (Fig. 3a).

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In order to explain the steps in the spacing versus temperature plots, one might assume that the chains stand perpendicular to the silicate layer at room temperature and become tilted to distinct angles with rising temperature. Such distinct angles could be caused by special reorientations of the terminal $-NH_3^+$ and –OH groups to the silicate layers (Tettenhorst and McGuire, 1970). However, since the step height does not increase with the chain length (Lagaly and Weiss, 1971b) one must assume distinct, but different orientations for each small step, e.g. angles of 79°, 74° and 67° for the steps of tetradecylammonium–tetradecanol–beidellite and angles of 81°, 75°, 70° and 66° for the steps of octadecylammonium–octadecanol–beidellite. In general, in the system alkylammonium–alkanol–beidellite with 10–18 C-atoms in the alkyl chains of the alkylammonium ions and alkanol molecules, at least 20 different angles would be necessary for explanation of the steps! There is no rational reason for reorientation leading to such numerous distinct tilting angles.

It is more probable that the steps are produced by some kind of conformational changes in the alkyl chains. From the great number of possible conformation isomers, only a relatively small number are of importance in more or less regular structures. These are discussed in the papers of Pechhold about phase transitions in paraffins and relaxation properties of polymers (Pechhold, 1968; Blasenbrey and Pechhold, 1967).

Conformational changes in the alkyl chains

The energetically most favored conformation changes of alkyl chains are rearrangements of trans-bonds t into gauche bonds $g.\bar{g}$. The activation energy

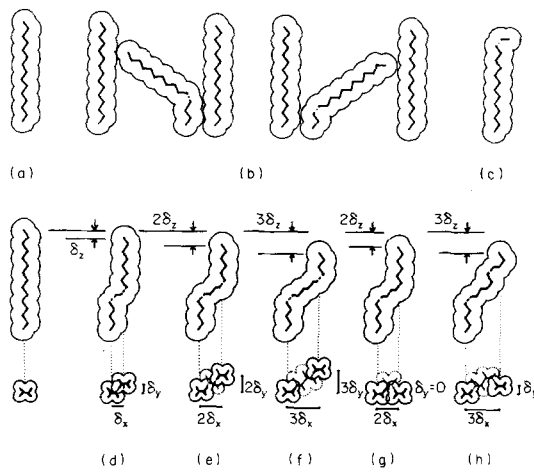


Fig. 4. Rotation isomers of alkyl chains: (a) all-trans chain; (b) alkyl chains with isolated +gauche g and −gauche $\bar{g}$ bond resp. in an assembly of trans alkyl chains; (c) isolated gauche bond at chain end (position 2 or (ω–1)); (d) alkyl chain with 2g1-kink (conformation ....*tttgtḡttt*...); (e) alkyl chain with 2g2-kink (conformation ...*ttgtttḡtt*...); (f) alkyl chain with 2g3-kink (conformation ...*tgttttḡt*...); (g) alkyl chain with 3g2-kink (conformation ...*ttgtḡtgtt*...); (h) alkyl chain with 3g3-kink (conformation ...*tgtttḡtgt*...).
– – – gauche bonds.
δ_x = 1,78 Å, δ_y = 1,27 Å, δ_z = 1,27 Å.

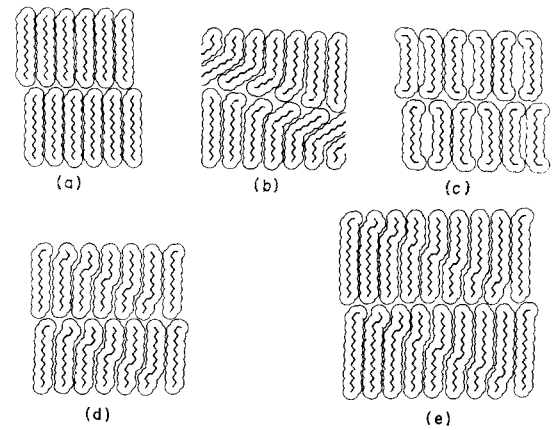


Fig. 5. Assemblies of alkyl chains: (a) block of all-trans chains; (b) gauche block; (c) block of alkyl chains with gauche bonds in 2- and (ω-1) positions; (d) kink block with shorter alkyl chains; (e) kink block with longer alkyl chains.

is only 3·6 kcal/mole (= 15·1 kJ/mole), the increase in internal energy 0·6 kcal/mole (= 2·5 kJ/mole). (Hägele and Pechhold, 1970; Wobser and Blasenbrey, 1970; Hoyland, 1968; Sovers, 1968; Volkenstein, 1963). Thus, such transitions can easily occur even at room temperature.

By transition of one trans-bond within an all-trans chain into a gauche bond, the two chain parts before and after the gauche bond form an angle of 125° with each other (Fig. 4b). Therefore, the formation of such an isolated gauche bond within a regular assembly of parallel all-trans chains would require a large activation volume and is unlikely to occur. Long range ordering into 'gauche blocks' (Fig. 5b) should be favored. The transition of a block of all-trans chains into gauche blocks is connected with a large decrease of the spacings in directions normal to the layers and seems to be unlikely in structures with low chain mobilities. It has been postulated for melts of polymers by Pechhold (Pechhold and Blasenbrey, 1970; Pechhold, *et al.*, 1972). In our system the decrease of the basal spacing by transition into gauche blocks would exceed the observed step heights of 1·1–1·3 Å very much and should increase with the chain length from about 5 Å for decylammonium–decanol–beidellite to about 12 Å for octadecylammonium–octadecanol–beidellite.

The activation volume for isolated gauche bonds should become less, the closer the gauche bonds lie to the chain ends. Therefore they might occur also in ordered structures close to the chain ends (Fig. 4c). In 2- and (ω-1)-positions the decrease in the basal spacing would be exactly 1·27 Å. Since there are 4 terminal groups in the bilayer, up to 4 isolated gauche bonds could be formed (Fig. 4c, 5c) producing up to 4 steps of 1·27 Å in the d_L versus temperature plots. Gauche bonds in 2- and (ω-1)-position, however, have to enlarge the lateral distances between the chains. Therefore space filling would be poor and the stabilizing van der Waals energy of the bilayer structure would be drastically reduced.

High activation volumes and large decreases in the packing density as a consequence of isolated gauche

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Table 1. Different Types of Kinks (Pechhold 1968)

Term	Conformation	δ_x	δ_y (cp. Fig. 4)	δ_z
all-trans	*ttttttttt*	0	0	0
$2g1$-kink	*ttttgtḡttt*	1·78	1·27	−1·27
$2g2$-kink	*tttgtttḡttt*	2 × 1·78	2 × 1·27	−2 × 1·27
$3g2$-kink	*tttgtḡtgttt*	2 × 1·78	0	−2 × 1·27
$2g3$-kink	*ttgttttḡtt*	3 × 1·78	3 × 1·27	−3 × 1·27
$3g3$-kink	*ttgtttḡtgtt*	3 × 1·78	1·27	−3 × 1·27
$4g3$-kink	*ttgtḡtgtḡtt*	3 × 1·78	1·27	−3 × 1·27

bonds are drastically reduced if combinations of +gauche g and −gauche $\bar{g}$ bonds are formed, e.g. conformations such as ...*tttḡtgttt*... or ...*ttgtttḡtt*... and ...*ttgtḡtgtt*... In these cases the $\bar{g}$-bond brings the two chain parts back again to a parallel orientation (Figs. 4d–h). Rotational isomerization into such conformations are thermodynamically probable. The activation energy of formation of pairs g and $\bar{g}$ with one chain does not exceed 7·2 kcal (=30·1 kJ) and the internal energy does not differ by more than 1·2 kcal/mole (=5·0 kJ/mole) (Hägele and Pechhold, 1970; Wobser and Blasenbrey, 1970).

A special term 'kink' has been proposed for conformations ...$gt\bar{g}$... (Fig. 4d). Kinks of higher order ('jogs' Figs. 4e and f) are formed with $(2n-1)$ trans bonds between g and $\bar{g}$ ($n = 2,3\ldots$). The most characteristic features of the kinks are the shortening of the overall length of the chains by multiples of 1·27 Å (Fig. 4d–h) and displacements of the parallel parts of the chains by multiples of δ_x and δ_y in x and y directions. Some types of kinks are tabulated in Table 1 together with their displacements.

The conformity of the step heights observed in our experiments makes it highly probable that the steps are produced by formation of kinks in the alkyl chains. Thus, from the decrease of the basal spacing by 1·2 Å at 49°C (transition β_1/β_2) (Fig. 2) one kink per pair of chains has to be postulated. Two further steps of 1·2 Å in the basal spacings at 60°C and 72°C (transition β_2/β_3 and β_3/β_4) may be explained in different ways:

1. Formation of a kink in the all-trans chain of the pair at 60° and insertion of a further kink in one of the kinked chains at 72°C.
2. Insertion of a second kink in the kinked chain of a pair at 60°C and then formation of a kink in the all-trans chain of the pair at 72°C.
3. Formation of a second kink at 60°C and a third kink at 72°C in the kinked chain of the pair, the other chain remaining in all-trans conformation over the whole temperature range.
4. Transition of the $2g1$-kink in one chain of a pair in a $2g2$- or $3g2$ kink at 60°C and into kinks of still higher order ($2g3$ etc.) at 72°C.

No distinction can be made between these possibilities from basal spacing measurements only. Possibilities 1 and 2 seem to be more probable than the others, since higher order kinks require more drastic structural rearrangements than insertion of additional first order kinks. This assumption is supported by the experimentally determined transformation enthalpies and entropies (Lagaly *et al.*, 1973).

Kink block structures

Formation of isolated 'kinked' chains in random distribution should not show up in sharp steps. Stepwise decrease is possible only in case of equal numbers or equivalent orders of kinks in each pair of alkyl chains. Kink formation is connected with an increase of the lateral space requirement. Since the number of chains per formula unit does not change beyond experimental error in the β-phases, the space requirement must be minimized. This is possible by formation of 'kink blocks' in which the kinks of neighboring pairs of chains are well ordered. Then the formation of kinks in these ordered structures should occur in a highly cooperative reaction, the formation of kinks being highly favored by neighboring kinks.

The dimensions of the 'kink-blocks' should depend upon the chain lengths. An optimal packing is reached if kinks in neighbor chains are displaced by 2·5 Å (= 2 *C*–*C*-bonds) in the direction of the chain axes. Therefore, the position of the kinks within a kink block should move from the polar end to the hydrophobic end of the chains or vice versa. The borders are represented by chains with kinks near the polar or the hydrophobic end. Unfortunately, experimental data on the dimensions of the kink blocks are not yet available, but investigations have been started.

Nature of phase transitions

Interpretations of the nature of phase transitions are often based on experimental results of measurements

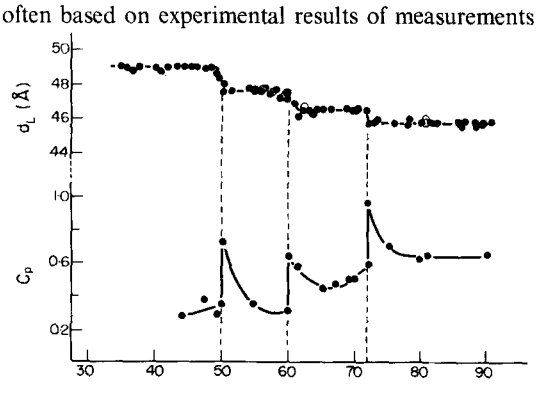


Fig. 6. Specific heats c_p (kcal/deg mol) and basal spacings d_L for the β-phases of tetradecylammonium–tetradecanol–beidellite.

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Table 2. Transition Enthalpies and Entropies for Tetradecylammonium–Tetradecanol–Beidellite

Transition Temperature °C	ΔH kcal/mole Beid.	(kJ/mole)	ΔS cal/deg. mole Beid.	(deg. mole)
50	0·73	(3·06)	2·3	(9·6)
60	0·72	(3·01)	2·3	(9·6)
72	0·68	(2·84)	2·3	(9·6)

of the specific heat c_p. The results of our investigations are shown on Fig. 6. The specific heat does not change continuously throughout the investigated temperature range (30–90°C). There are three marked discontinuities in the c_p versus temperature plot at exactly the same temperatures as the steps in the basal spacings. Integration of the experimental c_p and c_p/T-curves leads to the phase transition enthalpies and entropies. The data in Table 2 refer to one mole (Si, Al)$_4$O$_{10}$. Since there are 2 alkyl chains (= one pair) per (Si, Al)$_4$O$_{10}$ and since an additional kink is formed at each transition point, the data represent the enthalpy and entropy of the formation of one kink, ordered in a block structure. From the constancy of the entropy at the three transition temperatures, it may be assumed that the 2nd and 3rd transitions are probably due to formation of additional $2g1$-kinks and not to rearrangements of $2g1$-kinks into kinks of higher order.

The transition enthalpy approximates the enthalpy values given by Pechhold for formation of a kink in an isolated chain (1·2 Kcal/mole, 5·0 kJ/mole) and in a chain bundle (0·95 kcal/mole, 4·0 kJ/mole). The still lower value in the investigated system may be a consequence of the lower packing density of the alkyl chains.

The shapes of the c_p-discontinuities resemble Λ-transitions and from this one should assume second order transitions. In contrast to well known second order transitions, however, there are distinct deviations, which need additional investigation. They may be due to cooperativity and block ordering.

COMPLEXES OF TETRADECYLAMMONIUM–BEIDELLITE WITH DECANOL, DODECANOL, HEXADECANOL, OCTADECANOL, EICOSANOL AND DOCOSANOL

Experimental results

The temperature dependency of the basal spacings for tetradecyl–ammonium–beidellite with decanol, dodecanol, hexadecanol, octadecanol, eicosanol and docosanol is shown on Fig. 7. As in the tetradecanol complex the basal spacings decrease stepwise. Again only two types of steps are observed: small steps with 1·0–1·3 Å height (transitions $\beta_i \rightleftharpoons \beta_{i+1}$ and $\alpha_i \rightleftharpoons \alpha_{i+1}$) and large steps—one in each curve—with heights increasing with chain length of the alkanol (transitions $\beta_\omega \rightleftharpoons \alpha_1$).

The (001)-reflections are in general as intensive as in the case of the *n*-tetradecanol complexes. This is especially true for higher temperatures.

Interlayer structure in the β-phases

The analytical composition in systems with differing numbers of *C*-atoms in the alkylammonium ion ($= n_C$) and the alkanol molecule ($= n_A$) is the same as in the system $n_A = n_C$, i.e. $(\text{R-NH}_3)^+_{0.44}$ $(\text{R-OH})_{1.56}$ $\{Mg_{0.28}Al_{1.81}(OH)_2\ Si_{3.56}Al_{0.44}O_{10}\}$. A reliable model for the interlayer structure can be deduced from Fig. 3a by substituting the alkanol molecules having the same chain length as the alkylammonium ions by longer or shorter chain alkanols (Figs. 3b or 3c).

With $n_A = n_C$ (Fig. 3a) each alkyl chain in one of the two layers is adjoining an alkyl chain with the same length in the other layer (in simplified model, neglecting ordering of the terminal groups). For $n_A \neq n_C$ (Fig. 3b and 3c), instead of pairs of chains with equal length, there occur three types of pairs:

longer chains + longer chains,
longer chains + shorter chains, and
shorter chains + shorter chains.

The probability of finding an alkylammonium ion in the monolayer is 0·44/(0·44 + 1·56) = 0·22 and to find an alkanol molecule 1·56/(0·44 + 1·56) = 0·78. Therefore, the probability for pairs alkylammonium ion + alkylammonium ion (symbol = $\{n_C + n_C\}$) is 0·22 × 0·22 = 0·048, for pairs alkanol molecule + alkanol molecule (symbol = $\{n_A + n_A\}$) 0·78 × 0·78 = 0·608 and for pairs alkylammonium ion + alkanol molecule (symbol = $\{n_C + n_A\}$) 2 × 0·22 × 0·78 = 0·344.

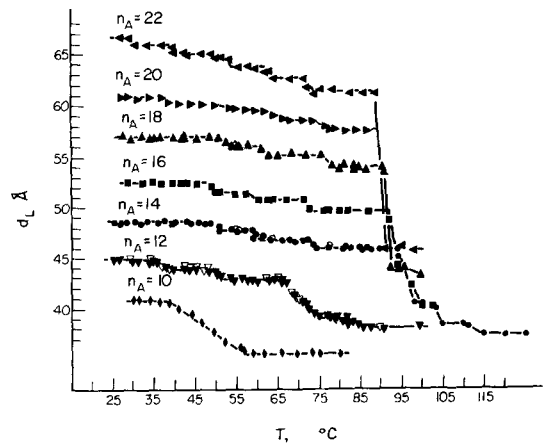


Fig. 7. Temperature dependency of basal spacings d_L of *n*-tetradecylammonium–alkanol complexes.
Alkanol = Decanol (◆), Dodecanol (▼), Tetradecanol (●), Hexadecanol (■), Octadecanol (▲), Eicosanol (▶), Docosanol (◀).

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Table 3. Experimental and Theoretical Basal Spacings d_L (in Å) calculated for the Models $\{n_A + n_A\}$, $\{n_A + n_C\}$ and $\{n_C + n_C\}$

			$d_{L(calc)}$ (Å), calculated* for spacing-determining pairings					
		$d_{L(obs.)}$	$\{n_A + n_A\}$		$\{n_A + n_C\}$		$\{n_C + n_C\}$	
n_C	n_A	(Å)	$d_{L(calc)}$	Δd_L†	$d_{L(calc)}$	Δd_L†	$d_{L(calc)}$	Δd_L†
14	22	65·8	69·1‡	−2·3	59·0	+7·8	48·8	+18·0
	20	61·7	67·0‡	−2·3	56·4	+5·3		+12·9
	19	59·2	61·5‡	−2·3	55·1	+4·1		+10·4
	18	56·8	59·0‡	−2·2	53·9	+2·9		+8·0
	17	54·8	56·4‡	−1·6	52·6	+2·2		+6·0
	16	52·6	53·9‡	−1·3	51·3	+1·3		+3·8
	15	50·3	51·4‡	−1·1	50·1	+0·2		+1·5
	14	48·8	48·8‡	0	48·8‡	0		0
	13	47·2	46·3	+0·9	47·5‡	−0·3		−1·6
	12	45·0	43·7	+1·3	46·3‡	−1·3		−3·8
	11	42·7	41·2	+1·5	45·0‡	−2·3		−6·1
	10	40·6	38·6	+2·0	43·7‡	−3·1		−8·2
	9	35·6	35·3	+0·3	42·1	−7·1		−13·2
	8	32·8	32·8	0	40·4	−7·6		−16·0

* Parameters adjusted to give $d_L = 48{\cdot}8$ for $n_A = n_C = 14$.
† $\Delta d_L = d_{L(obs)} - d_{L(calc)}$.
‡ Most probable structure.

If $n_A > n_C$, the most numerous pairs alkanol + alkanol produce a larger interlayer spacing (Fig. 3b) than all other pairs would do. Therefore, it seems likely that the basal spacing is mainly determined by the pairs alkanol + alkanol. Between the hydrophobic chain ends of the pairs cation + alkanol and between those of the pairs cation + cation holes are generated. For $n_A < n_C$ the most numerous pairs $\{n_A + n_A\}$ give a smaller basal spacing than the pairs $\{n_A + n_C\}$. It is thus likely that the interlayer distance is now determined by the pairs $\{n_A + n_C\}$ and holes are formed within the pairs $\{n_A + n_A\}$. The pairs $\{n_C + n_C\}$ would lead to still higher spacings, their probability, however, is so small (4·8 per cent) in comparison to the other pairs (60·8 per cent resp. 34·4 per cent), that their influence on the structure will be negligible.

In Table 3, the observed basal spacings (at room temperature) are compared with theoretical basal spacings. They were calculated in case that the interlayer distance is determined by pairs $\{n_A + n_A\}$, $\{n_C + n_A\}$ or $\{n_C + n_C\}$. As expected, the differences $\Delta d_L = d_{L(obs)} - d_{L(calc)}$ become < 0 with the spacing determining pairings $\{n_A + n_A\}$ for $n_A > n_C$ and $\{n_A + n_C\}$ for $n_A < n_C$. They are multiples of $1{\cdot}15 \pm 0{\cdot}19$ Å. This leads to the assumption that the volume of the holes in the interlayer structure is reduced by formation of kinks in the longer alkyl chain pairs even at room temperature. With rising temperature the stepwise decrease of the basal spacing indicates that, similar to the system $n_A = n_C$, the number of kinks per chain increases still further, probably under formation of distinct kink block structures. The steps in the basal spacings indicate that the number of these additional kinks per chain pair increases: 0 for $n_A = 10$, 1 for $n_A = 11$, 2 for $n_A = 12$, 3 for $n_A = 13$–19, and 5 for $n_A = 22$.

TRANSITIONS INTO THE α-PHASES (HIGH TEMPERATURE FORM)

Brindley and Ray (1964) first observed the transition of a low temperature form with high basal spacing into a high temperature form with low spacing in alkanol

Table 4. Transition Temperatures T_u for the β/α-transition of tetradecylammonium–alkanol–beidellite

Number of C-Atoms in Alkanol n_A	Melting Point of pure Alkanol °C	Transition Temperature °C	ω
10	7	39	1
11	16	52	2
12	24	66	3
13		79	4
14	38	94	4
15	44	94	4
16	49	92	4
17	54	93	4
18	59	91	4
19	62	91	4
20	66	91	4
22	74	89	5

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Table 5. Kink Concentrations in the Kink Block Structures of Tetradecylammonium–Beidellite at 25°C

n_A	Structure Determining Pairs	Number n_K of Kinks in the pairs* $\{n_A + n_A\}$	$\{n_A + n_C\}$	$\{n_C + n_C\}$	Mean Kink Concentration c_K (Kinks/-CH_2-)
22	$\{n_A + n_A\}$	2	0	0	0·030
20		2	0	0	0·033
19		2	0	0	0·034
18		2	0	0	0·036
17		1	0	0	0·019
16		1	0	0	0·020
15		1	0	0	0·021
14		0	0	0	0
13	$\{n_A + n_C\}$	0	0	2	0·004
12		0	1	3	0·020
11		0	2	5	0·040
10		0	3	6	0·060

* Taken from $n_K \approx \Delta d_L/1{\cdot}27$ with Δd_L referred to the model $\{n_A + n_A\}$, $\{n_A + n_C\}$ and $\{n_C + n_C\}$, resp. (cp. Table 3).

complexes of calcium montmorillonite. They related the transition temperatures to the melting points of the pure alkanols and distinguished 'below and above melting point' series.

The similar transition β_ω/α_1 in alkylammonium–alkanol–beidellite may be of the same nature. The transition temperatures, however, are generally higher than the melting points of the pure alkanols (Table 4). The constancy of the basal spacings at high temperatures and the further decrease in distinct steps ($\alpha_1 \rightleftharpoons \alpha_2 \rightleftharpoons \ldots$) contradict the assumption, that the β_ω/α_1-transition is merely a 'melting' of the chains in the interlayer space with transition in highly disordered structures. Since the basal spacings in the α-forms are larger than expected for a monolayer structure, a bimolecular structure has to be postulated also in these structures. The decrease in the basal spacings is probably due to a drastic rearrangement into well ordered gauche block structures.

Kink and gauche block arrangements have been proposed for the structure in melts of polyethylene and long chain paraffins (Pechhold and Blasenbrey, 1967; Blasenbrey and Pechhold, 1970). Using statistical thermodynamics and experimental data about melting enthalpies, specific volume changes, pressure dependency of the melting points, expansion coefficients and compressibilities, Pechhold assumed melting of these long chain alkyl compounds to be connected with a sudden increase in kink concentration from a lower limit of about 0·02 kinks/-CH_2- to a value of about 0·25 kinks/-CH_2-.

By analogy one might speculate that in the tetradecylammonium–alkanol–beidellite systems the concentration of kinks in the β-forms will increase up to a critical value only, beyond that the β-form will rearrange into the α-form. This view is supported by a calculation of the kink concentrations in the different phases. With $n_A = n_C = 14$ four β-phases or up to three kinks are found in each pair of chains with $2 \times 14 = 28$ C-atoms. The kink concentration then amounts to $3/28 = 0{\cdot}107$ kinks/-CH_2-.

With $n_A \neq n_C$ kinks already exist at room temperature in the β_1-phase in the longest pairs only. For $n_A > n_C$ kinks are in the pairs $\{n_A + n_A\}$ which are

Table 6. Kink concentrations c_K in the β_ω-Phases of Tetradecylammonium–Alkanol–Beidellite

n_A	Spacing Determining Pairings	Number of Kinks in these Pairs for β_1	β_ω	Mean Kink Conc. $\bar{c}_K$* (Kinks/-CH_2-) for β_ω	Kink Conc. c_K† (Kinks/-CH_2-) for β_ω
22	$\{n_A + n_A\}$	2	7	0·144	0·159
20		2	6	0·103	0·150
19		2	5	0·118	0·132
18		2	5	0·124	0·139
17		1	4	0·102	0·118
16		1	4	0·116	0·125
15		1	4	0·122	0·133
14		0	3	0·107	0·107
13	$\{n_A + n_C\}$	0	3	0·113	0·111
12		1	3	0·100	0·115
11		2	3	0·083	0·120
10		3	3	0·060	0·125

* Assuming that the additional kinks (3 for $n_A = 18$–13, 2 for $n_A = 12$) occur in all the pairs.
† Related only to spacing determining pairs.

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longer than the pairs $\{n_A + n_C\}$ and $\{n_C + n_C\}$. When $n_A < n_C$ they are in the pairs $\{n_A + n_C\}$ and $\{n_C + n_C\}$. The calculated kink concentrations at room temperature are given in Table 5.

As an example the calculation is shown in detail for the system $n_A = 12$, $n_C = 14$. From Table 3 the pairs $\{n_A + n_C\}$ and $\{n_C + n_C\}$ are 1·3 Å and 3·8 Å (= 3 × 1·27 Å) longer than the observed basal spacings. This may be explained with the assumption of 1 kink in each of the 0·344 pairs $\{n_A + n_C\}$, 3 kinks in each of the 0·048 pairs $\{n_C + n_C\}$ and no kink in the 0·608 shorter pairs $\{n_A + n_A\}$. Hence, the total number of kinks is $1 \times 0{\cdot}344 + 3 \times 0{\cdot}048 + 0 \times 0{\cdot}608 = 0{\cdot}488$. Since the total number of C-atoms per $(Si, Al)_4O_{10}$ unit amounts to $0{\cdot}344 \times (14 + 12) + 0{\cdot}048 \times (14 + 14) + 0{\cdot}608 \times (12 + 12) = 24{\cdot}88$, the mean kink concentration $\bar{c}_K$ at room temperature is 0·488/24·88 = 0·020 kinks/-CH_2-.

With rising temperature, it may be assumed that additional kinks are formed in all pairs, their number per pair being equal to the number of steps in the β-range of the d_L versus T-plot. For $n_A = 12$, $n_C = 14$ with two steps ($\beta_1 \rightleftharpoons \beta_2 \rightleftharpoons \beta_3$) the kink concentration increases by 2/24·88 = 0·080.

Table 6 gives the mean kink concentrations of the β_ω-phases. The values are not constant, but increase with the chain length strongly from $n_A = 10$ to $n_A = 12$ and slightly for longer chain alkanols.

If there is a relation between kink concentration and transformation temperature, not the mean concentration, but the concentration in the spacing determining pairs should be crucial. This value c_K is calculated from the number of kinks in these pairs divided by the number of C-atoms in the same pairs; e.g. with $n_A = 12$, $n_C = 14$: 3/12 + 14 = 0·115 kinks/-CH_2-. The data for the other alkanols are given on Table 6. They are plotted on Fig. 8 against the number of C-atoms in the spacing determining pairs (= $n_A + n_A$ and $n_A + n_C$, resp.). In addition c_K-values for $(n + 1)$ and $(n - 1)$ kinks are inserted. It is evident that the maximum kink concentration cannot exceed a line which slightly increases from 1·2 kinks/-CH_2- for pairs with 20 C-atoms to 1·6 kinks/-CH_2- for pairs with 44 C-atoms. This limiting value determines the maximum number of kinks in the β-form and thereby ω, the number of β-phases. For $n_A = 16$, e.g., with 3 or 4 kinks in the pairs $\{16 + 16\}$ the kink concentration (0·094 and 0·125) is smaller than 0·14 and the corresponding kink block structures are stable. With 5 kinks per pair, however, the concentration (0·156) would exceed the limit for β-phases; the structure has to rearrange into the α_1-form.

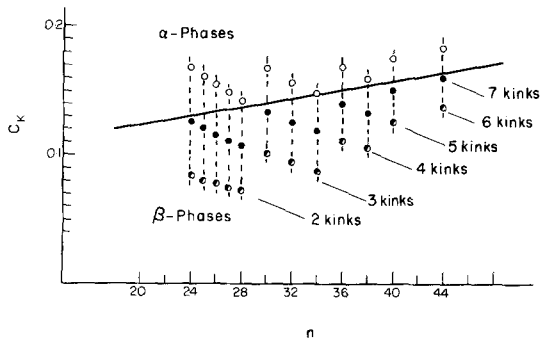


Fig. 8. Dependency of kink concentration c_K (kinks/-CH_2-) in the spacing determining pairs on the number n of C-atoms in these pairs ($n = n_A + n_A$ for $n_A > n_C$; $n = n_A + n_C$ for $n_A < n_C$).
○ for not observed hypothetical phases $\beta_{\omega+1}$
● in the observed phases β_ω
◐ in the observed phases $\beta_{\omega-1}$

The behaviour of the $n_A = 10$, $n_C = 14$-system may be explained in the same way. In this system only a β/α-transition and no β_i/β_{i+1}-transitions have been found. At room temperature there are already three kinks in the spacing determining pairs $\{14 + 10\}$, which correspond to $c_K = 3/24 = 0{\cdot}125$. Formation of an additional kink would increase c_K to 0·167. This value is considerably higher than the limiting value for β-phases and rearrangement to the α_1-form has to take place.

Our model also explains the behaviour of systems with $n_c = 14$ and $n_A < 10$. In these the observed basal spacings at room temperature are much shorter than those calculated for $\{n_A + n_C\}$ as spacing determining pairings and even no β/α-transformation is found with rising temperature. Comparison of observed and calculated basal spacings shows that at least 4 kinks per pair $\{n_A + n_C\}$ are built in at room temperature, probably due to space filling requirements. With $n_A + n_C = 24$ the kink concentration ($c_K = 4/24 = 0{\cdot}166$) becomes higher than the critical value for β-phases. Thus only α-phases are observed at room temperature.

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