

Leading Contribution

Intercalation and exchange reactions of clay minerals and non-clay layer compounds

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Abstract: Presently, a large variety of layered materials are synthesized that are able to intercalate neutral guest molecules or to exchange inorganic and organic ions for interlayer ions. Several of these materials are also found as minerals.

The intracrystalline reactivity of a few selected compounds will be described and compared to clay minerals:

- intercalation into crystalline silicic acids;
- reactions of phosphates, arsenates, and sulfates;
- reactions of titanates, niobates, and molybdates with long chain alkylammonium ions, and
- anion exchange properties of double hydroxides.

A general conclusion is that the non-clay minerals in many ways behave like clay minerals, but there is no doubt that the reactivity of clay minerals and the variety of their reactions cannot be exceeded by any other material.

Key words: Alkylammonium ions; cation exchange; clay minerals; intercalation; layered materials; silicic acids; surfactants

Introduction

An increasing number of colloid scientists are interested in studying layered materials, the interlayer space of which is accessible to certain reactions. The best known group of these compounds is the clay minerals. However, many scientists (including the majority of colloid scientists) refuse to study these materials because clay minerals are the constituents of clays, and clays are “dirty” materials, a mixture of minerals, generally deteriorated by large proportions of impurities, of variable analytical composition, with particles of irregular shape and with high degrees of disorder. In general, with their unpredictable behavior and properties, they are even a horror to inorganic chemists.

Nevertheless, the smectites (the largest group of clay minerals; for instance see [1]) are enticing for colloid scientists. When dispersed in water the crystals with lithium or sodium as gegen ions dis-

articulate (delaminate) into the individual silicate layers or thin packets of them. An interesting fact is that delamination is also observed for vermiculites (a group of clay minerals more highly charged than smectites) when short chain alkylammonium ions (methylammonium . . . butylammonium ions) or certain α , ω -amino acids are adsorbed between the layers [2]. Preparation and properties of colloiddally disarticulated clay minerals have been recently reviewed [3].

The process of reversible disaggregation/reaggregation of the elementary layers of layered compounds is very exceptional in that only a few oxidic compounds disarticulate in water: zirconium phosphate (and related compounds) after interlamellar adsorption of propylamine [4, 5] and crystalline silicic acids under the influence of surface active agents [6]. $V_2O_5 \cdot xH_2O$ xerogels exhibit a series of (001)-reflections when deposited onto a flat substrate. The V_2O_5 ribbons aggregate to layers which behave as a host structure for intercalation. When

water is added, the basal spacing increases in 0.28 nm steps. Beyond $x = 5$ (three water layers) a continuous swelling process finally leads to colloidal dispersions of the V_2O_5 -ribbons [7].

Intracrystalline reactivity of layered compounds is the ability to bind guest molecules between the layers or to exchange interlayer ions (Fig. 1). For a long time, graphite, three-layer clay minerals, and kaolinite were the only intracrystalline-reactive materials. The number of intracrystalline-reactive materials increased rapidly in the last 15 years; and it seems that this trend continues.

Two classes of intracrystalline-reactive compounds are usually distinguished: materials with neutral layers and materials composed of charged layers and gegen ions between them (Table 1). This classification is only schematic. A noticeable number of compounds contain OH groups (Si-OH, P-OH, As-OH) pointing into the interlayer space. When the interlayer space is filled with water molecules, a part of the OH groups dissociate, the layers obtain a certain charge density, and hydronium ions are the gegen ions in the interlayer space. These compounds could be listed in both groups. Intercalation (= adsorption of *neutral* guest compounds between uncharged layers) also can be accompanied by electron [8, 9] or proton transfer (see below), so that the reaction product is composed of charged layers and ionic guest compounds. The layer charge of several host materials

(in particular, sulfides, which are not discussed here; e.g., see [8, 10]) results from electrochemical redox processes in the presence of the guest compounds.

Crystalline silicic acids

Many chemistry textbooks refer to the ortho silicic acid H_4SiO_4 as the only oxo acid of silicon, disregarding the fact that crystalline silicic acids have been known for more than 65 years! Presently, about 20 different forms are known; they are obtained by proton exchange of layered alkali silicates and several other silicates [11–13] (Fig. 2).

Several hydrated alkali silicates are found as minerals (kenyaite: $Na_2Si_{20}O_{41} \cdot xH_2O$, $x \approx 10$; magadiite: $Na_2Si_{14}O_{29} \cdot xH_2O$, $x \approx 9$; makatite: $Na_2Si_4O_9 \cdot xH_2O$, $x \approx 3$; kanemite: $NaHSi_2O_5 \cdot xH_2O$, $x \approx 3$; revdite: $Na_2Si_2O_5 \cdot 5H_2O$, [14]; and grumantite: $\approx NaHSi_2O_5 \cdot xH_2O$, $x \approx 0.9$ [15]). As the conditions of their formation are very particular [16–18], the minerals are only found in a few regions. Possible practical uses refer to synthetic materials [19, 20]. The hydrated alkali silicates can easily be prepared from dispersions of silica in aqueous solutions of sodium or potassium hydroxide, or from water glass solutions at 70–150 °C [11, 19–24].

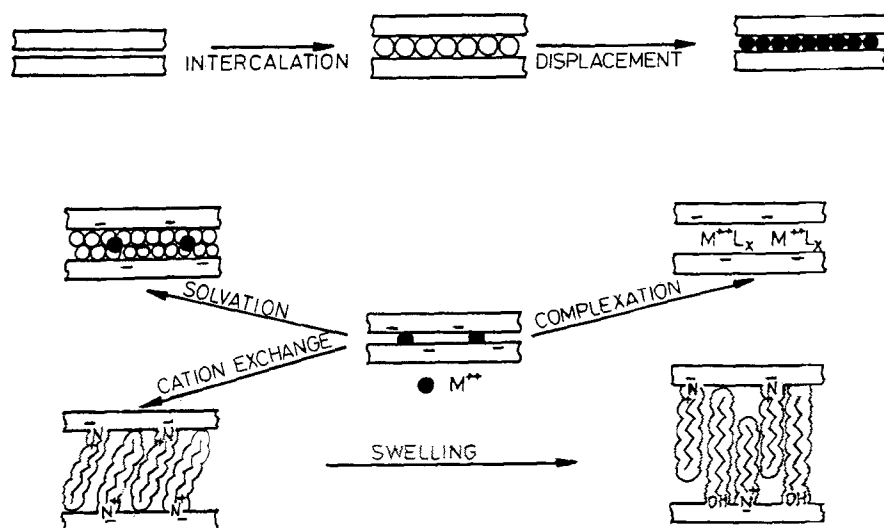


Fig. 1. Intracrystalline reactions of layered host compounds

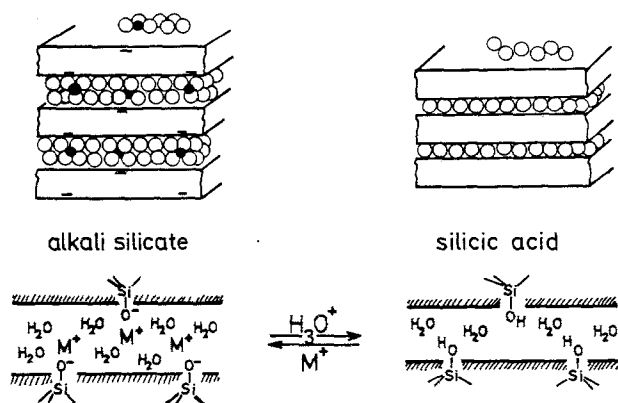


Fig. 2. Preparation of crystalline silicic acids from hydrated alkali silicates

The crystals of $\text{H}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ and $\text{H}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ *) are intergrown to dense or loose spherical aggregates. A particular property of $\text{H}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ is a large gas adsorption hysteresis open to very low pressures of nitrogen [25]. The nitrogen molecules penetrate more deeply between the layers with increasing relative pressure and remain wedged between the layers at decreasing pressure. The gas adsorption measurements also reveal that the entry to the interlayer space is reversibly widened with increasing p/p_0 .

Various types of guest molecules are intercalated. The reactivity increases from $\text{H}_2\text{Si}_2\text{O}_5$ to the highly condensed acids $\text{H}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ and $\text{H}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ [12]. Typical classes of guest molecules (listed in order of decreasing reactivity) are alkyl- and arylamines, N-, S-, and P-oxides (e.g., trimethyl amine-N-oxide, dimethyl sulfoxide, trimethyl phosphine oxide), fatty acid amides (formamide, acetamide, and derivatives) and urea and derivatives. Intercalation proceeds quickly, and complete conversion is generally achieved. A very reactive acid from the parent silicate $\text{K}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ has been recently described [23]. It intercalates several compounds (alcohols, nitriles, ketones and certain amino acids) that are usually not intercalated.

The reaction between guest molecules and most of the crystalline silicic acids does not proceed as

intercalation in a strength sense, but as displacement of interlamellar water by the guest molecules.

The acidity of the silanol groups depends on the type of acid. The highly condensed acids are strongly acidic (Hammett values: amorphous SiO_2 , $H_0 \approx 6-7$; $\text{H}_2\text{Si}_2\text{O}_5$, $H_0 = 2.3-3.3$; $\text{H}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$, $-5 - (-3)$). The Hammett values of the acids extend into the range of acidities which are required for Brønsted acid-catalyzed reactions. In fact, the crystalline acids may be considered, not only as possible catalyst supports, but also as direct catalysts [26].

The exact crystal structure is only known for several modifications of $\text{H}_2\text{Si}_2\text{O}_5$ and the parent materials $\text{Na}_2\text{Si}_2\text{O}_5$, KHSi_2O_5 , and makatite. Structural models were proposed for $\text{H}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ and $\text{H}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ on the basis of MAS-NMR measurements [27, 28]. Results of NMR measurements [27–31] are indicative of broad structural variations (see also [32]). The x-ray patterns are less sensitive to such variations, but particularities of intracrystalline reactions point in the same direction. An important result from ^1H and ^2H -NMR relaxation measurements is that even isolated water molecules in the structure remain highly mobile down to 200 K.

Crystalline silicic acids dehydrate at higher temperatures. The dehydrated forms of several acids remain crystalline up to 1000–1200 °C before they transform into cristobalite. The presence of intercalated organic material can strongly influence type and morphology of the products. For instance, $\text{H}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ reacted with N,N'-diethyl urea and heated to 800 °C transforms into a fine-meshed network of cristobalite rods [33]. The x-ray powder patterns of heated organic derivatives are often remarkably better developed (increased sharpness and number of reflections) than in the absence of organic material. During decomposition, the interlamellar organic material acts as a "lubricant" and facilitates gliding of the layers. The number of unfavorable contacts between neighboring layers (for instance, by siloxane bridges) is reduced and the structure becomes less disordered. A silica with high surface area (BET surface area about $900 \text{ m}^2\text{g}^{-1}$) can be obtained from alkyl trimethylammonium kanemite after heating at 700 °C [34].

*) The formulae are written as often found in literature. They report the number of acidic protons which are neutralized by bases; the total amount of silanol groups is higher and corresponds approximately to $\text{H}_4\text{Si}_{14}\text{O}_{30} \cdot x'\text{H}_2\text{O}$ and $\text{H}_4\text{Si}_{20}\text{O}_{42} \cdot x'\text{H}_2\text{O}$

Intercalation compounds may also be used for Si_3N_4 production; for instance, Si_3N_4 is formed at about 1400°C from magadiite with poly acrylonitrile intercalated [35].

Phosphates, arsenates, and sulfates

The best known members of this group are zirconium phosphate, $\text{H}_2\{\text{Zr}(\text{PO}_4)_2\} \cdot \text{H}_2\text{O}$, and other M^{IV} phosphates and arsenates ($M^{\text{IV}} = \text{Zr}, \text{Ti}, \text{Ge}, \text{Sn}, \text{Pb}$) (Fig. 3). They intercalate a variety of neutral compounds (for review see [36, 37]). Possible guest molecules are those listed for the silicic acids. Again, the alkyl- and arylamines are highly effective. The reaction proceeds by displacement of water molecules. The rate of reaction decreases with increasing particle size and crystallinity. It also depends on the absence or presence of salts. This influence is very complex. The salts act as structure-promoting or structure-breaking agents towards the liquid guest compounds. They can also induce structural changes around the

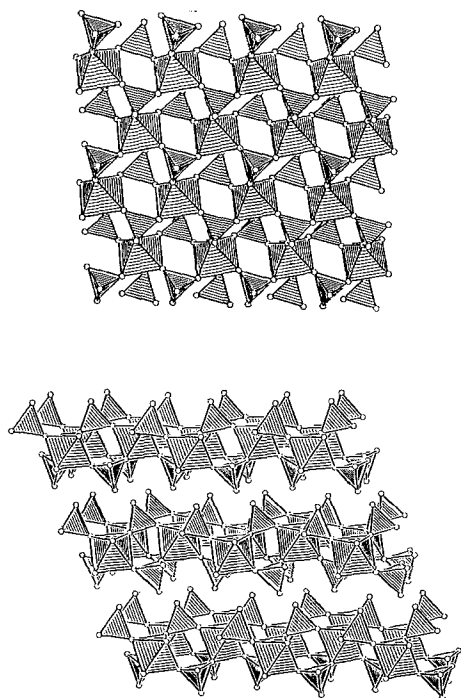


Fig. 3. The continuous sheets of $[\text{PO}_4]$ tetrahedra and $[\text{ZrO}_6]$ octahedra in zirconium phosphate

opening of the interlayer spaces which impede or accelerate intercalation [38].

Current activities result from a possible use of the M^{IV} phosphates as catalysts [39–42] or supports for dispersed metals [43]. In this connection an effort was made to prepare derivatives with zeolitic properties. Derivatives are prepared with “pendant” organic groups which are covalently attached to the phosphate sheets (Fig. 4). One way to prepare these derivatives is the reaction of M^{IV} -salts with arylphosphonic esters [44]. Because of the high density of P–OH groups on the surface, the interlayer is almost completely filled with the pendant groups. Therefore, a series of zirconium phosphates was prepared with two different pendant groups or with a partial substitution of the phosphate groups by phosphite groups [39, 45]. A fascinating attempt to impart microporosity is the intercalation of aminated cyclodextrins (Fig. 5) [46, 47].

Another group of zirconium phosphate derivatives is prepared from agents with two functional groups such as sulfopropyl phosphonic acid. The pendant groups are then accessible to further reactions. If the free end group of the pendant entity contains acidic protons ($-\text{COOH}$, $-\text{SO}_3\text{H}$, >POH) (Fig. 4), a new class of inorganic-organic ion exchangers is formed [36, 45, 48, 49].

Disarticulation of zirconium phosphate crystals was described by Alberti et al. [4]. In the presence of distinct amounts of short chain alkylamines

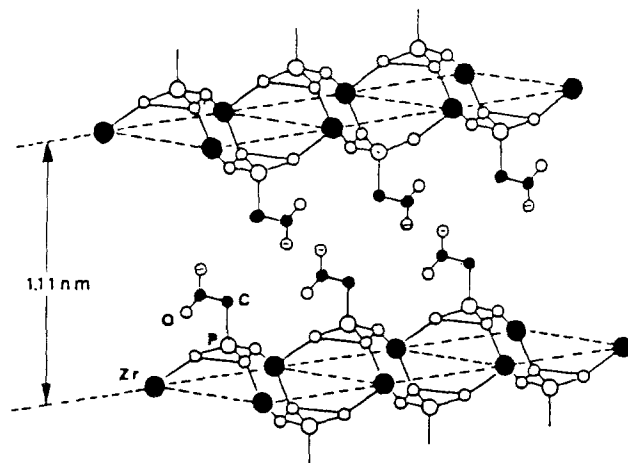


Fig. 4. Zirconium phosphate with pendant groups (carboxymethanephosphonate) (from [36])

(e.g., propylamine) zirconium phosphate is delaminated like sodium smectites in water (Fig. 6). Thin films showing high degrees of texture can be obtained from these colloidal solutions ("pelicular" zirconium phosphate). Some practical applications come to mind, in particular on the basis of the increased ionic conductivity [50–52].

A further group of phosphates and arsenates which recently generated some interest are vanadium and niobium phosphates [53–56]. Niobyl phosphate $\text{NbOPO}_4 \cdot 3\text{H}_2\text{O}$ intercalates a large variety of organic amines. Long-chain alkylamines are arranged in bilayers between the $\{\text{NbO}(\text{H}_2\text{O})\text{PO}_4\}$ -layers with the chain axes tilted at angles of about 60° to the layers (Fig. 7).

Vanadyl phosphate $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is a very reactive host material which even intercalates alcohols which are not intercalated by most host

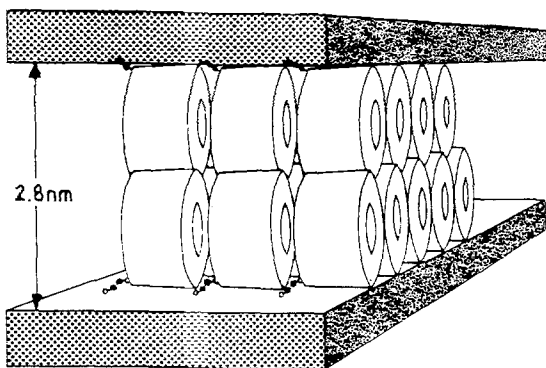


Fig. 5. Aminated cyclodextrine molecules intercalated into zirconium phosphate (from [46])

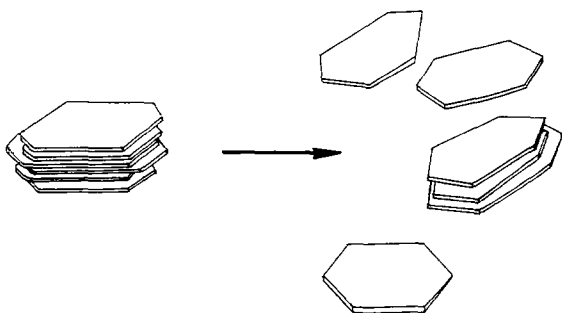


Fig. 6. Disarticulation of zirconium phosphate crystals in water after adsorption of propylamine (the propylamine molecules attached to the layers are not shown)

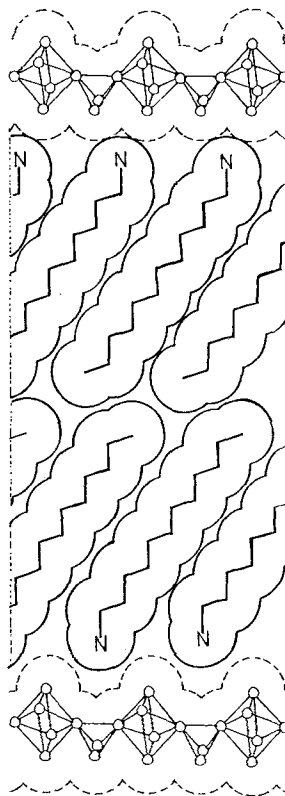


Fig. 7. Alkylamine bilayers between the $\{\text{NbO}(\text{H}_2\text{O})\text{PO}_4\}$ layers of niobyl phosphate

compounds. In the presence of reducing agents (for instance iodide ions) $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ readily undergoes redox reactions which lead to interlamellar insertion of alkali, alkaline-earth, transition metal cations, and alkylammonium ions (see below) [57, 58]. Organic derivatives with longer alkyl chains pendant into the interlayer space show pronounced selectivity against isomeric alcohols [59]. These derivatives are prepared from V_2O_5 and alkylphosphonic acids. The main interest on vanadyl phosphates arises from possible uses as catalysts [60].

VOSO_4 , isostructural to $\alpha_1\text{-VOPO}_4$, and its hydrates are also reactive host compounds and intercalate alcohols in bilayers. The reaction of VOSO_4 with mixtures of aliphatic alcohols proceeds in a typical way. At low molar fractions of the longer alcohol, x_j , the basal spacing remains virtually constant, and longer alcohols are incorporated as defects. With increasing x_j , the spacing reaches a plateau (around $x_j \approx 0.5$) which corresponds to an

interlayer expansion by pairs consisting of a short- and a long-chain alcohol. At $x_j \rightarrow 1$, the large spacings are maintained by pairs of two long-chain alcohols (Fig. 8) [61, 62]. The intercalation of pairs of different long alcohol molecules may be compared to the interlamellar sorption of long-chain alcohols by the long-chain alkylammonium derivatives of various layer compounds where the basal spacing is also determined by pairs of alkylammonium ions and alcohol molecules (for instance [63], see also [64]).

Comparison with kaolinite

The most striking difference between kaolinite and other oxidic host compounds is its reaction to DMSO and alkyl- and arylamines. Kaolinite easily intercalates DMSO, but does not react directly with amines. The other oxidic compounds intercalate amines, but many of them do not react with DMSO. Preparation of alkylamine kaolinite by displacement reactions indicates the direct reaction to be kinetically hindered.

A decisive step is nucleation of the intercalation reaction (Fig. 9). The interlayer adsorption of amines is probably initiated by proton transfer from the layer to the nitrogen atom. Thus, alkyl-

ammonium ions are bound in the edge regions, pry open the interlayer space, and the multitude of alkylamine molecules penetrate between the layers. A strong surface acidity is not imperative as only a few alkylamine molecules must be protonated to initiate intercalation. In the case of FeOCl , the reaction may be initiated by protons which are bound in the structure as a consequence of defects $\text{Fe}_{\text{Fe}^{3+}}^{2+}$. Complex formation between the host compound and the alkylamine may also initiate intercalation, for instance, between silver ions of the silver molybdate $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ and alkylamine molecules [65].

Protonation does not play a major role for DMSO intercalation. Too high surface acidity (for instance, uranium mica) even impedes this reaction. A possible mechanism of initiation has been proposed by Weiss (cf. [66]). Highly polar molecules such as DMSO adsorbed on the external surface induce a rearrangement of structural OH groups which causes the layers to bend in such a way that the interlayer space opens.

The nucleation processes depend on the chemical nature and the elastic properties of the layers. The last parameter is difficult to measure and may serve as a welcome pretext in explaining the non-reactivity of certain host compounds. Votinsky and Benes [67] obtained a measure of the flexibility of

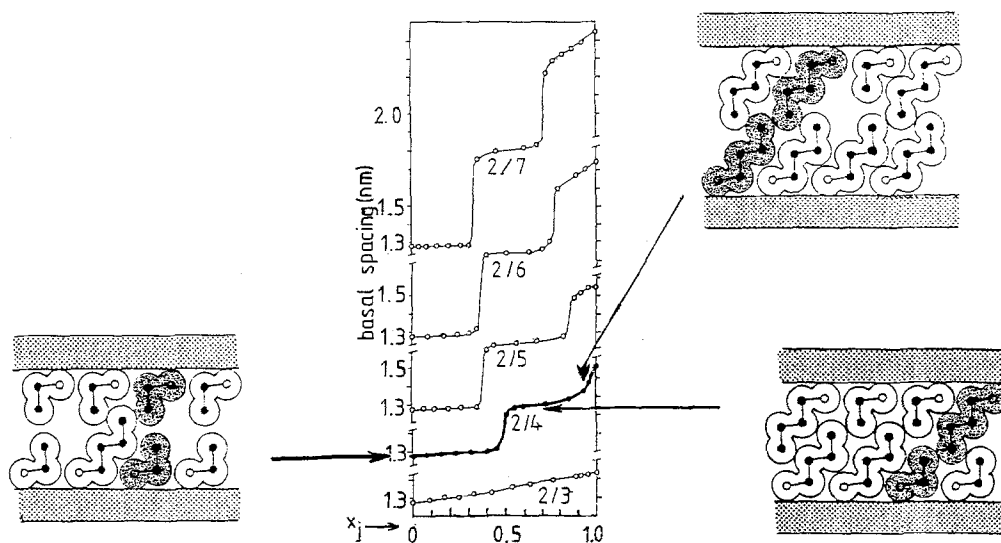


Fig. 8. Intercalation of mixtures of alcohols into vanadyl sulfate VOSO_4 ; basal spacings of mixtures of ethanol with propanol, butanol . . . heptanol as a function of mole fraction, x_j , of the longer-chain alcohol (from [62])

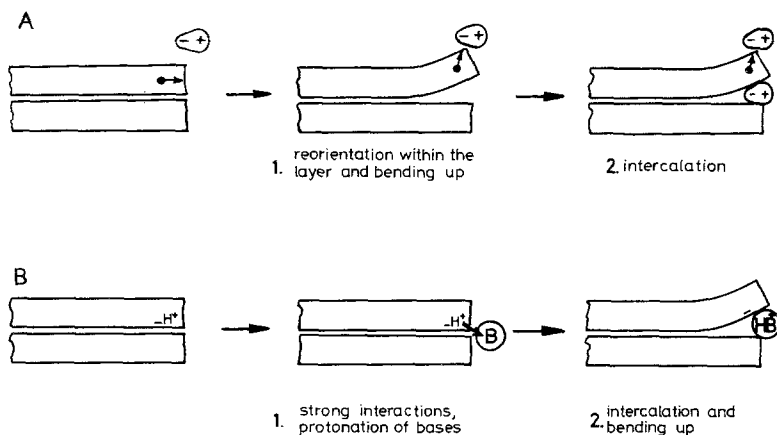
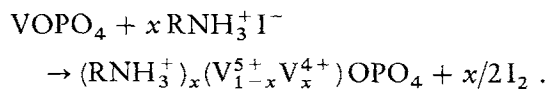


Fig. 9. Two mechanisms of initiation of intercalation processes: A) reorientation of structural groups under the influence of adsorbed guest molecules opens the interlayer space; B) strong interactions between the guest molecules and the host force the molecules to squeeze into the interlayer space and push up the layers

the layers by assuming that flexibility is related to the lengthening or shortening of the bonds within the layer when the layer is bent. Without true consideration of the force constants (which are unknown), calculated flexibility parameters are in qualitative agreement with the reactivity of a series of host compounds.

The most probable sites for nucleation of an intercalation process are the terminal interlayer spaces. Opening of an interlayer space within a packet of unreacted layers is much more difficult to nucleate. Thus, the reaction rate will also be governed by the way the intercalation proceeds from one interlayer space to the succeeding one. The reaction is stopped or strongly retarded when the entry of an interlayer space is blocked. The reaction rate for intercalating DMSO in zirconium phosphate is reduced in the presence of certain salts. Exchange of protons ($\text{>P-OH} + \text{Na}^+ \rightarrow \text{>P-O}^- \text{Na}^+ + \text{H}^+$) creates edge charges which impede intercalation [38]. Another instructive example is reported for the intercalation of alkylammonium iodide into $\alpha\text{-VOPO}_4 \cdot 2\text{H}_2\text{O}$ [58]. These salts are intercalated by a redox process:



The shortest alkylammonium salts (methyl-, ethyl-, and propyl-ammonium iodide) are not intercalated, but are adsorbed parallel to the host layers at the crystal edges, thereby blocking the diffusion of further alkylammonium iodide. Longer-chain salts adopting different arrangements at the opening of

the interlayer spaces push up the layers and open the diffusion path into the crystals.

The unusual dependence of the rate of reaction on particle size as described for kaolinite could not be observed for other lamellar oxidic host compounds. Also, staging effects which are typical of intercalation into graphite and several sulfides [8], occur very seldom. An example of the manifestation of cooperative effects is the stepwise transformation of $\text{H}_2\text{Si}_2\text{O}_5$ into the sodium salt [12].

Cation exchange

The study of cation exchange reactions of non-clay layer compounds was instituted by Weiss and coworkers [68–71]. This group of compounds comprises titanates, vanadates, niobates, molybdates, wolframates, uranates, uranyl phosphates, and several other compounds [5, 72] (Table 1). The interlayer cations in most compounds lie unhydrated between the negatively charged layers, as do the potassium ions between mica layers. Generally, the charge density is high and comparable to that in micas or even brittle micas. For both reasons the interlayer cations are not (or only at very peculiar conditions) exchanged by other inorganic cations; they can be replaced, at least partially, by alkylammonium ions. Large alkylammonium ions displace inorganic cations at the external regions, open the interlayer space, and push up the layers within a certain domain. Several interlayer cations lose contact to one of the layers, and exchange is promoted.

Table 1. Layered host materials with intracrystalline reactivity (oxidic compounds) (see also [5, 72])

Class	Neutral layers	Charged layers
Silicates	kaolinite crystalline silicic acids	2/1 clay minerals hydrated alkali silicates
Titanates	see Table 2	$\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_4\text{O}_9$, $\text{KTiNbO}_5 \dots$
Phosphates	$\text{H}_2\{M^{\text{IV}}(\text{PO}_4)_2\} \cdot x\text{H}_2\text{O}$, $\text{CaPO}_4\text{R} \cdot \text{H}_2\text{O}$ ($\text{R} = \text{CH}_3$, C_2H_5), $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NbOPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{H}\{\text{SnCl}(\text{OH})\text{PO}_4\} \cdot 2\text{H}_2\text{O}$	$M_2\{M^{\text{IV}}(\text{PO}_4)_2\} \cdot x\text{H}_2\text{O}$
Arsenates	$\text{H}_2\{M^{\text{IV}}(\text{AsO}_4)_2\} \cdot x\text{H}_2\text{O}$, $\text{H}\{\text{MnAsO}_4\} \cdot \text{H}_2\text{O}$ (krautite), $\text{H}\{\text{SnCl}(\text{OH})\text{AsO}_4\} \cdot 2\text{H}_2\text{O}$	$M_2\{M^{\text{IV}}(\text{AsO}_4)_2\} \cdot x\text{H}_2\text{O}$ KNiAsO_4 , NaNiAsO_4
Vanadates	$\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$	KV_3O_8 , hewetite
Niobates	see Table 2	KNb_3O_8 , $\text{K}_4\text{Nb}_6\text{O}_{17} \dots$
Molybdates	$\text{MoO}_3(\text{OH})_2$ H_xMoO_3	$\text{Ag}_6\text{Mo}_{10}\text{O}_{33} \dots$
Manganates		buserite
Uranyl compounds	$\text{H}\{\text{UO}_2\text{PO}_4\} \cdot 4\text{H}_2\text{O}$ $\text{H}\{\text{UO}_2\text{AsO}_4\} \cdot 4\text{H}_2\text{O}$	uranium mica, sabugalite, uvanite

The exchange of large polyoxo cations of aluminum for potassium ions in $\text{K}_2\text{Ti}_4\text{O}_9$ is facilitated when the aluminum chloride solution is hydrolyzed by alkylamine so that alkylammonium ions open the interlayer space [73]. Several compounds, when reacted with protons, are transformed into solid acids (Table 2). Most of these acids reveal only a modest intercalation capability which often is restricted to the sorption of amines.

Alkylammonium derivatives

In many layered compounds the exchange only proceeds to a degree that the interlamellar alkylammonium ions can aggregate to stable mono- or bimolecular films. The stability is then of kinetic and not of thermodynamic nature. A typical example is KNiAsO_4 [74, 75] which forms mica-like yellow-green crystals and has a tetrahedral-octahedral-tetrahedral structure (Fig. 10) [76]. The surface charge density ($74.3 \mu\text{Ccm}^{-2}$) and equivalent area ($0.108 \text{ nm}^2/\text{charge}$) correspond to brittle micas ($\approx 69 \mu\text{Ccm}^{-2}$, $0.11\text{--}0.13 \text{ nm}^2/\text{charge}$).

KNiAsO_4 easily exchanges alkylammonium ions, but exchange is strongly retarded when about two-thirds of the potassium ions are replaced by alkylammonium ions. The alkylammonium ions are in a monolayer paraffin-type arrangement with

Table 2. Examples of intracrystalline-reactive lamellar protonic oxides obtained from layered titanates and niobates

Protonic oxide	Parent compound	References
$\text{H}_2\text{Ti}_3\text{O}_7$	$\text{Na}_2\text{Ti}_3\text{O}_7$	[80]
$\text{H}_2\text{Ti}_4\text{O}_9 \cdot x\text{H}_2\text{O}$	$\text{K}_2\text{Ti}_4\text{O}_9$	[80]
$\text{H}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$	$\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$	[98]
HTiNbO_5	KTiNbO_5	[99]
$\text{HTi}_2\text{NbO}_7 \cdot \text{H}_2\text{O}$	$\text{CsTi}_2\text{NbO}_7$	[99]
$\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$	$\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ (Ln = La or rare earth)	[100]
$\text{H}_3\text{Ti}_5\text{NbO}_{14}$	$\text{A}_3\text{Ti}_5\text{NbO}_{14}$ (A = Li, Na, K, Rb, Cs, Tl)	[99]
$\text{HNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$	KNb_3O_8	[83]
$\text{H}_4\text{Nb}_6\text{O}_{17}$	$\text{K}_4\text{Nb}_6\text{O}_{17}$	[101]
$\text{HCa}_2\text{Nb}_3\text{O}_{10}$	$\text{ACa}_2\text{Nb}_3\text{O}_{10}$ (A = K, Rb, Cs)	[102]

the alkyl chains tilted at 64° ($n_c = \text{even}$) or 61° ($n_c = \text{odd}$) to the layer. A well developed even-odd alternation (Fig. 11) indicates a high degree of regularity of the interlayer arrangement. Even-odd alternation occurs when the chains are tilted and are in mutual contacts in such a way that they interlock properly. This geometrical constraint can only be fulfilled for certain combinations of angles of tilt and chain-packing densities [74, 77].

Potassium titanoniobate KTiNbO_5 [78] may serve as a further example. The degree of exchange

reaches a plateau when about 70% of the potassium ions are exchanged by alkylammonium ions (Fig. 12). The plateau indicates that a relatively stable interlayer structure is formed. The equivalent area of KTiNbO_5 is 0.122 nm^2 . When 70% of potassium ions are replaced by alkylammonium ions in bilayers, the area per chain is $2 \cdot 0.122 / 0.7 = 0.349 \text{ nm}^2$ and comparable to that in the alkylammonium vermiculites. The basal spacing of dried and washed samples increases linearly with the chain length. The chains are tilted

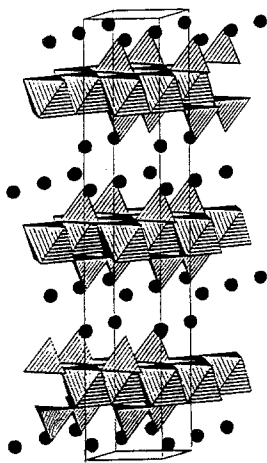


Fig. 10. The $[\text{AsO}_4]$ tetrahedral- $[\text{NiO}_6]$ octahedral- $[\text{AsO}_4]$ tetrahedral sheet structure of KNiAsO_4 (from [76])

at 52° to the layer. Lambert et al. [79] discussed several models of interlamellar alkyl chain arrangements.

The degree of exchange of potassium ions in KNb_3O_8 increases continuously with time (Fig. 13). The reaction product is a mixture of KNb_3O_8 and the alkylammonium derivative; the proportion of the alkylammonium derivative increases with reaction time. Micas react with alkylammonium ions in the same way, but with much decreased reaction rate. One cannot decide whether the potassium ions in the alkylammonium derivative are completely displaced by alkylammonium ions. The degree of exchange within the individual crystals can only be determined when the period of reaction is prolonged until a plateau is reached or by separation of the alkylammonium derivative from the mixture (which seems to be possible because of its hydrophobic surface).

In some cases, exchange of alkylammonium ions may be accompanied by the exchange of protons for the inorganic ions, in particular when the compound is easily transformed into the acid (for instance, $\text{K}_2\text{Ti}_4\text{O}_9$ [80]).

It is often difficult to explain the basal spacings of the alkyl ammonium derivatives by layers of completely extended alkyl chains (all-trans conformation). More likely, the chains contain gauche-bonds or kinks and are aggregated to gauche- or kink-blocks (Fig. 14) [5]. The area per chain in

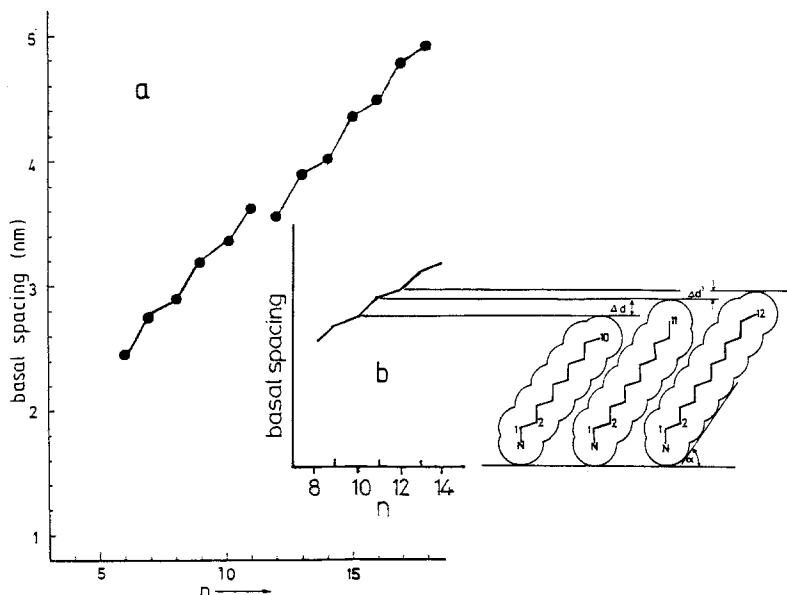


Fig. 11. The even/odd-alternation of the basal spacings: a) basal spacing of the alkylamin derivatives of KNiAsO_4 ; n is the number of carbon atoms in the primary n -alkylammonium ion $\text{C}_n\text{H}_{2n+1}\text{NH}_3^+$. At $n = 12$ the interlamellar structure changes; b) even-odd alteration as caused by the different orientation of the methyl end group to the layers

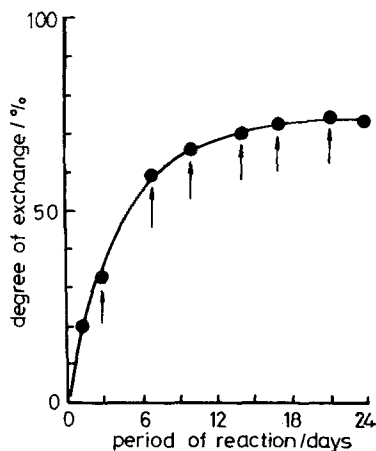


Fig. 12. Exchange of hexadecylammonium ions for potassium ions of KTiNbO_5 . Arrows indicate renewal of 0.05 M hexadecylammonium chloride solution

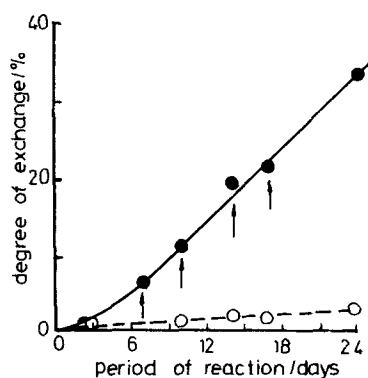


Fig. 13. Reaction of hexadecylammonium ions with KNb_3O_8 : (—) 0.05 M hexadecylammonium chloride solution several times (arrows) replaced by a fresh solution; (---) solution not replaced

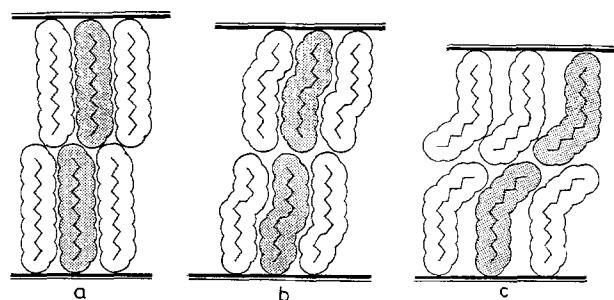


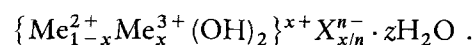
Fig. 14. Aggregation of alkyl chains: chains in all-trans conformation (a), kink-blocks (b), and gauche-blocks (c)

gauche-blocks ($\geq 0.33 \text{ nm}^2$) is distinctly larger than in kink-blocks ($\leq 0.25 \text{ nm}^2$). Gauche-blocks of densely packed chains (area per chain $\approx 0.35 \text{ nm}^2$) are relatively stable in the sense that the basal spacings change only slightly during washing and drying of the samples. In compounds, with the area per alkyl chain being larger, considerable amounts of water are enclosed between the alkyl chains and the basal spacing decreases during drying.

Formation of gauche-blocks was postulated, for instance, for alkylammonium exchanged silver molybdate [5, 65], alkylammonium iodide in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ [58], and alkylamine in $\text{HMnAsO}_4 \cdot \text{H}_2\text{O}$ [81]. In synthetic sabugalites where a part of the interlayer $[\text{Al}(\text{OH})_x(\text{H}_2\text{O})_{6-x}]^{(3-x)+}$ cations are exchanged by alkylammonium ions insertion of gauche-bonds in the alkyl chains allows a geometrical fit of the chains to the $[\text{Al}(\text{OH}, \text{H}_2\text{O})_6]$ -octahedra remaining in the interlayer space and decreases the rate of exchange [82]. In other systems, formation of gauche-bonds near the chain ends enables the polar end groups to dip into the cavities of the host layer. An example is the intercalation of primary alkyl-diamines into $\text{HNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ [83] or HTiNbO_5 [84], whereas the primary alkylamines of the bilayers in $\text{HNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ are in all-trans conformation [85] (Fig. 15). Gauche-bonds at the chain ends to allow for the alignment of the chains were deduced from electron density maps of alkylammonium perovskite-type compounds like $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{CdCl}_4$ [86, 87].

Layered double hydroxides

Layered double hydroxides may be considered as antitypes of clay minerals (Fig. 16). Some of the Me^{2+} ions of hydroxide layers $\{\text{Me}^{2+}(\text{OH})_2\}$ are replaced by Me^{3+} ions, and the total charge of the layers becomes positive:



Besides several minerals (hydrotalcite, manasseite, pyroaurite, sjögrenite, etc.) a variety of compounds (M^{2+} : Ca^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} ; M^{3+} : Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+}) can easily be synthesized [88, 89]. The inorganic interlayer anions X^- are exchangeable by other inorganic and organic anions.

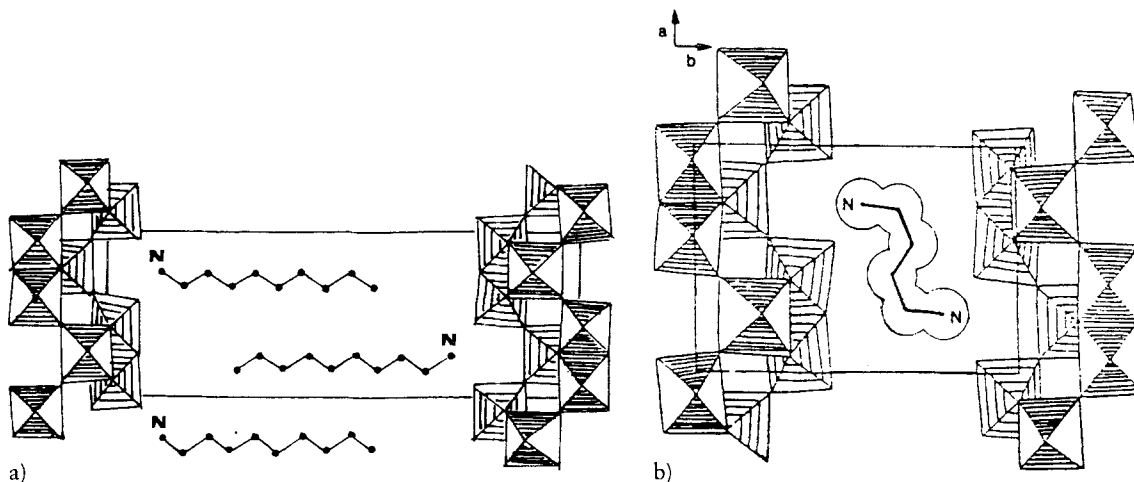


Fig. 15. Alkylamine molecules intercalated into $\text{HNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ (from [83, 85]): a) primary alkylamines in all-trans conformation; b) primary alkyldiamines with gauche-bonds near the chain ends

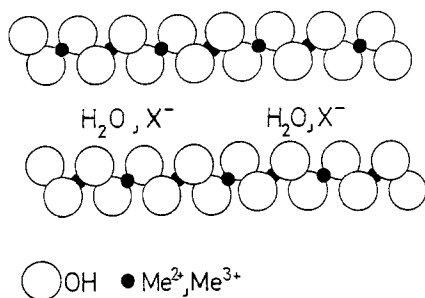


Fig. 16. The layer structure of layered double hydroxides: $M = \text{Ca}^{2+}$, Mg^{2+} , Zn^{2+} etc.; $M^{3+} = \text{Al}^{3+}$, Fe^{3+} , Cr^{3+} etc., $X =$ interlayer anion (Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-} , etc.)

One reason for the importance of this class of compounds is that they are the only intracrystalline-reactive layered materials consisting of positively charged layers. They can serve as models of the binding of anionic surface active agents on solid surfaces [64, 90]. Of particular interest are the results with secondary alkanesulfonates of technical quality. In these surfactants the sulfonate group is distributed over the length of the chain with some preference to the middle part. Though these surfactants are mixtures of different isomers, the x-ray powder patterns show sharp (001) reflections of several orders. The basal spacing derived from these reflections can be explained by assuming that the alkanesulfonates are U-shaped and arranged in bilayers (Fig. 17). The bilayers must be of constant thickness throughout the crystal, in spite of the fact

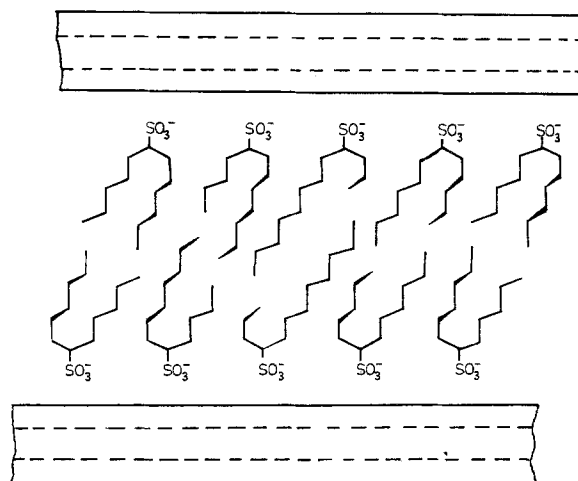


Fig. 17. Formation of bilayers consisting of isomers of secondary alkanesulfonates between the hydroxide layers (from [90])

that they consist of anions with different long branches. Thus, the differently shaped alkanesulfonate ions are paired in a way that a constant layer separation throughout the crystal is attained (Fig. 17). Two typical properties of interlamellar films [63] contribute to the high regularity of the interlayer distances: the high conformational freedom of the aggregated surfactant ions and the fact that bimolecular films can bear considerable amounts of holes which are formed between the ions not exactly fitting one to another.

Magnesium aluminium oxide powders prepared by thermal decomposition of hydrotalcite-like compounds rapidly rehydrate and adsorb various anions to reconstruct the hydrotalcite structure [91, 92]. The oxides may find practical application in removing sulfur oxo anions (SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$) [93]. All sulfur oxo anions bound in the interlayer space are transformed to SO_4^{2-} by heating at 100–300 °C. This reaction is particularly useful for decomposing dithionate anions, $\text{S}_2\text{O}_6^{2-}$, which are difficult to oxidize or reduce in solution.

A strong interest in double hydroxides results from possible uses as catalysts [88]. It is not unexpected that preparation of pillared hydroxides is also reported [94]. An interesting composite material of silicic acid and double hydroxides was obtained by intercalation of silicate anions in $\{\text{Mg}_3\text{Al}(\text{OH})_8\}\text{Cl}$ and $\{\text{Al}_2\text{Li}(\text{OH})_6\}\text{Cl}$ [95]. Magnesium aluminum hydroxides can serve as precursors for AlN production by carbothermal reactions. When the interlayer space is expanded by ion exchange with dodecylsulfate anions, acrylonitrile monomers can be intercalated and polymerized. Decomposition at 1600 °C produces submicron AlN grains [96].

Comparison with clay minerals

The interlayer cation density of many titanates, niobates, molybdates, and several other layer compounds is as high as in micas or even brittle micas. Like micas these layered materials do not exchange inorganic cations for the interlayer cations but often react with alkylammonium ions. Typically, x-ray powder patterns with sharp and integral basal reflections are obtained, although the exchange is by no means quantitative. In many cases the rate of reaction decreases considerably when a certain level of exchange is attained.

The intracrystalline reactivity of layered materials with hydrated interlayer cations (zirconium phosphate, uranium micas, uranyl phosphates like sabugalite, hydrated alkali silicates) is comparable to the reactivity of vermiculites and even montmorillonites. Generally, a high degree of exchange is rapidly attained with alkylammonium ions and several inorganic ions. In certain cases, the interlamellar water molecules can be replaced by other polar solvent molecules. The most reactive hydrated compounds with charged layers are zirconium

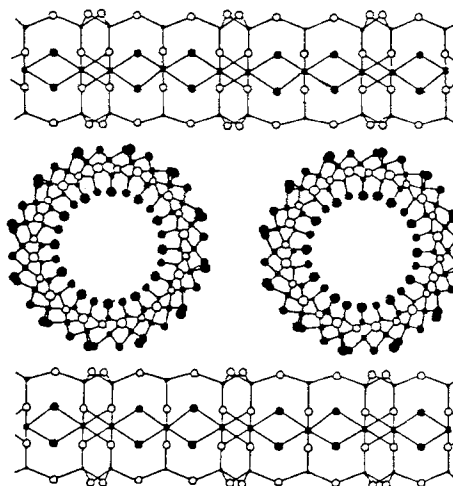


Fig. 18. Tubes of aluminosilicate (imogolite) between the layers of montmorillonite (from [97])

phosphate (and other M^{IV} phosphates and arsenates), hydrated alkali silicates (in particular two potassium silicates, [23]) and layered double hydroxides. The acid forms of uranium mica, the crystalline silicic acids, and zirconium phosphates are much more stable than the hydronium form of three-layer clay minerals.

However, there is no doubt that the reactivity of smectites and the variety of possible reactions cannot be exceeded by any other material. This may be illustrated by a reaction recently reported by Johnson et al. [97]. Smectites can even intercalate a tubular aluminosilicate (imogolite) so that silicate tubes run parallel with the silicate layer (Fig. 18).

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