INTERACTION OF ALKYLAMINES WITH DIFFERENT TYPES OF LAYERED COMPOUNDS

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Long chain alkylamines $C_nH_{2n+1}NH_2$ can be successfully used as guest molecules to test an intracrystalline reactivity of layered materials. A large variety of host compounds consisting of neutral layers intercalate alkylamines. Generally the alkylamines between the layers aggregate to paraffin-type structures. If the successive layers are negatively charged and separated by an interlayer region containing exchangeable cations, alkylammonium ions can be bound by cation exchange. The alkylammonium ions between the solid surfaces aggregate in a diversity of structures. Besides paraffin-type structures of the chains in all-trans conformation (exemplified by $KNiAsO_4$), aggregates of chains containing gauche-conformations are commonly formed. Typical are gauche-block structures as in alkylammonium silver decamolybdate. The exchangeable cations in the interlayer region of many non-silicatic compounds are not quantitatively exchanged. The exchange proceeds to such an extent that distinct types of alkyl chain arrays can be formed. In many cases, the required packing density of the chains is obtained by an additional uptake of alkylamine during exchange of the alkylammonium ions. Under very distinct conditions crystals of several alkylammonium derivates disintegrate into individual layers or thin packets of a few of such layers, so that colloidal dispersions form.

1. Introduction

Long chain alkylamines can be introduced into the interlayer spaces of layered compounds as (i) neutral molecules by intercalation, (ii) alkylammonium ions by cation exchange. Layered materials consisting of neutral layers bind alkylamines by intercalation . Several types of host compounds and some selected examples are listed in tables 1 and 3. If the successive layers are negatively charged and separated by an interlayer region containing exchangeable cations (table 2), exchange of these cations by alkylammonium

Table 1
Intracrystalline reactive host materials with neutral layers [a]

Group	Examples
oxides, hydroxides	see table 3
chlorides, oxychlorides	$ReCl_3$, $FeOCl$
chalcogenides	TiS_2, MPS_3
cyanides	$Ni(CN)_2$
	$Mg_3((CH_2)_6N_4)_4(Fe(CN)_6)_2 \cdot 24H_2O$ [b]
graphite	

[a] Ref. [1].
[b] Magnesium hexamethylene-tetramine hexacyano ferrate (III), ref. [2].

Table 2
Layered host materials with interlayer cations exchangeable by alkylammonium ions.

Group	Examples
2/1 clay minerals	smectites, vermiculites, (micas)
hydrated alkali silicates	magadiite $Na_2Si_{14}O_{29} \cdot xH_2O$, kenyaite $Na_2Si_{20}O_{41} \cdot xH_2O$, $K_2Si_{20}O_{41} \cdot xH_2O$
titanates	$Na_2Ti_3O_7$, $K_2Ti_4O_9$, $KTiNbO_5$
phosphates	$M_2\{M^{IV}(PO_4)_2\} \cdot xH_2O$ [a]
arsenates	$M_2\{M^{IV}(AsO_4)_2\} \cdot xH_2O$ [a] $KNiAsO_4$, $NaNiAsO_4$
vanadates	hewetite: $Ca\{V_6O_{16}\} \cdot xH_2O$ KV_3O_8
niobates	KNb_3O_8, $K_4Nb_6O_{17}$
molybdates	$Ag_6Mo_{10}O_{33}$, $Cs_2Mo_5O_{16}$, $Cs_2Mo_7O_{22}$
manganates	Na-buserite, $Na_4\{Mn_8^{4+}Mn_6^{3+}O_{27}\} \cdot 21H_2O$
uranyl compounds	uranium micas: $M\{UO_2PO_4\} \cdot xH_2O$, $M\{UO_2AsO_4\} \cdot xH_2O$ uvanite: $M\{UO_2V_3O_9\} \cdot xH_2O$ $Na_2U_2O_7$, $K_2U_2O_7$

[a] M^{IV} = Zr, Ti, Sn ... .

ions is the reaction mostly preferred. In addition, several of these host lattices intercalate neutral alkyl-amines, so that two types of derivatives can be prepared. For instance, silver decamolybdate exchanges alkylammonium ions for silver ions when alkylammonium nitrates are added to aqueous dispersions of the decamolybdate. If samples of decamolybdate are placed in contact with liquid or molten alkylamines or ethanolic solutions, alkylamine molecules are intercalated.

In some cases the reaction between alkylamines and neutral layer compounds proceeds as intercalation but the final products are alkylammonium derivatives. This occurs when the surface OH groups are acidic enough that protons can be transferred to the amine group. Typical examples are M-IV phosphates like zirconium phosphate $\{Zr(HPO_4)_2\}$, refs. [3—5] and H-uranyl phosphates $H\{UO_2PO_4\} \cdot 4H_2O$ [6,7]. Alkylamine molecules in the interlayer region are protonated even at surface acidities $H_0 \approx 5-7$ as found, for instance, in krautite $\{MnHAsO_4 \cdot H_2O\}$ [8].

2. Intercalation of alkylamines

2.1. Alkylamines as guest molecules

Long chain alkylamines are outstanding guest molecules which are easily intercalated by numerous layered oxides (table 3). They are excellent agents for testing the intracrystalline reactivity. Other guest compounds like urea and DMSO frequently used in intercalation chemistry react with a limited number of layered compounds only (table 3).

The behaviour of kaolinite differs from all other host compounds (table 3). Kaolinite intercalates urea and DMSO but is the only layered material that does not intercalate alkylamines in a direct way. Alkylamines are only intercalated by displacement reactions [10,11].

The cause may be found in different nucleation processes [12,13]. In most cases, the reaction may be initiated by guest molecules which squeeze between the layers and, subsequently, cause an elastic deformation of the layers. This process requires strong inter-

Table 3
Intracrystalline reactivity of layered oxidic compounds.

Group	Examples	Reaction with guest molecules		
		urea	DMSO	alkylamines
silicates	kaolinite	+	+	−
crystalline silicic acids	$H_2Si_2O_5-I$	−	+	+
	$H_2Si_{14}O_{29} \cdot xH_2O$	+	+	+
oxides, hydroxides	$V_2O_5 \cdot xH_2O$		+	+
	$HTiNbO_5$	−	−	+
	$MoO_3(OH_2)$, $WO_3(OH_2)$, $UO_2(OH)_2$	−	−	+
H-oxide bronzes	H_xMoO_3	−	−	+
phosphates	$VOPO_4 \cdot 2H_2O$		+	+
	$NbOPO_4 \cdot 3H_2O$	−	−	+
	$\{M^{IV}(HPO_4)_2\} \cdot 2H_2O$, M^{IV} = Zr, Ti, Sn...	+	+	+
	$H\{UO_2PO_4\} \cdot 4H_2O$	−	−	+
	$CaPO_4R \cdot H_2O$, R = CH_3, C_2H_5	−		+
arsenates	$\{MnHAsO_4 \cdot H_2O\}$, $H\{UO_2AsO_4\} \cdot 4H_2O$	−	−	+
	$\{M^{IV}(HAsO_4)_2\} \cdot 2H_2O$, M^{IV} = Zr, Ti, Sn...	+	+	+
molybdates	$Ag_6Mo_{10}O_{33}$	−	−	+

a) Ca mono methyl (ethyl) phosphoric acid ester, ref. [9].

actions between guest molecules and internal surface groups or interlayer ions. In many cases, the intercalation of alkylamines and other bases is initiated by proton transfer from acidic surface OH-groups to the amine groups. Intercalation of alkylamines into silver molybdate is initiated by complex formation between silver ions and alkylamine molecules.

The surface acidity of kaolinite is too low to protonate alkylamine molecules. In contrast, the polar character of the layer enables a different type of nucleation when guest molecules like DMSO possess high dipole moments. As proposed by Weiss the reaction starts with adsorption of the polar molecules on the external surface which induces a rearrangement of OH groups within the layer (cf. Lagaly [11]). This re-orientation causes an elastic deformation of the layers; the layers curl, the interlayer spaces open, and the guest molecules "walk in".

The difference between both mechanisms is a hen-and-egg problem. In one case, the initiating step is squeezing in of guest molecules into the interlayer region, and elastic deformation of the layers follows. In the other case, intercalation is initiated when the layers bend up after adsorption of dipole molecules on the external surface.

The ubiquitous applicability of alkylamines as guest molecules is certainly related to their basic character which enables nucleation by interactions with surface OH groups or interlayer ions. The intercalation may be further facilitated by the ease with which long chain alkylamine molecules change their conformation. During penetration between the layers and migration within the interlayer space, the molecules can adopt conformations distinctly different from the extended conformation assumed in the final product.

2.2. Interlamellar structure

Alkylamine molecules in the interlayer space commonly aggregate to simple mono- or bimolecular, structures. The molecules assume upright positions, radiating away from the surface (fig. 1). Often, the tilting angle α increases with the alkyl chain length. As the chain length and the van der Waals interactions increase, the chains gradually move from a tilted orientation into the perpendicular direction [14–18]. A decreasing chain tilt is indicated by basal spacing
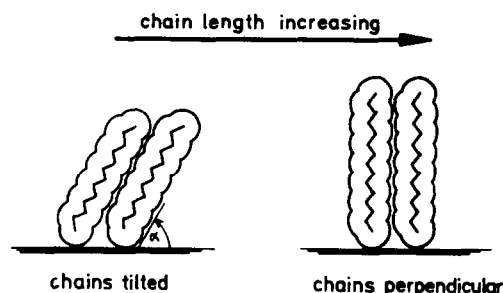

Fig. 1. Orientation of alkylammonium ions (all-trans conformation) in paraffin-type structures; α = tilting angle.

increments which exceed 1.27 Å (for alkyl chain monolayers) or 2.54 Å (for bilayers). As the chain length increases, the spacings approximate the line calculated for perpendicular chains (fig. 2).

The ease with which alkylamine molecules change conformation facilitates the interaction of the end groups with the surface geometry and the close-packing of the chains. For instance, a gauche bond near the amine group can improve the fit to the surface "roughness" (fig. 3) [19].
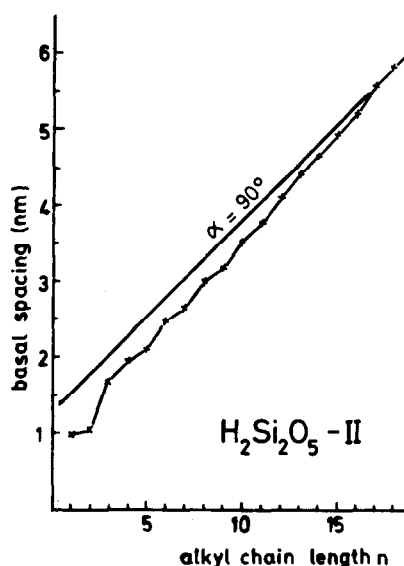

Fig. 2. Paraffin-type aggregation of alkylamine molecules in the crystalline silicic acid $H_2Si_2O_5$–II, tilting angle increasing with the alkyl chain length; straight line calculated for perpendicular chains (α = 90°) [17].
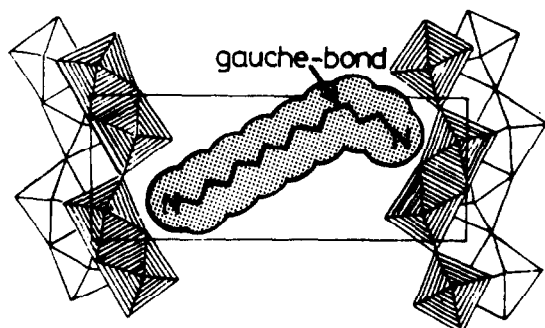
Fig. 3. Formation of a gauche bond near the amine group of alkyldiamines allowing a better fit on the surface geometry (HTiNbO$_5$ (Grandin et al. [19]).

2.3. Colloidal dispersions

A fascinating aspect of intercalation chemistry is formation of colloidal dispersions under conditions that the layers become completely separated. Well known is the disintegration of crystals of smectite in very dilute dispersions when the interlayer cations have been replaced by sodium or lithium ions (fig. 4a). Colloidal dispersions of this type can also be obtained from layered sulfides and H$_x$RuCl$_3$ [20–22]. Only a few examples of alkylamine derivatives are known which disintegrate during dispersion. In water, two conditions must be fulfilled:

(i) the alkylamine molecules should not be too long, because the strong interchain van der Waals en-
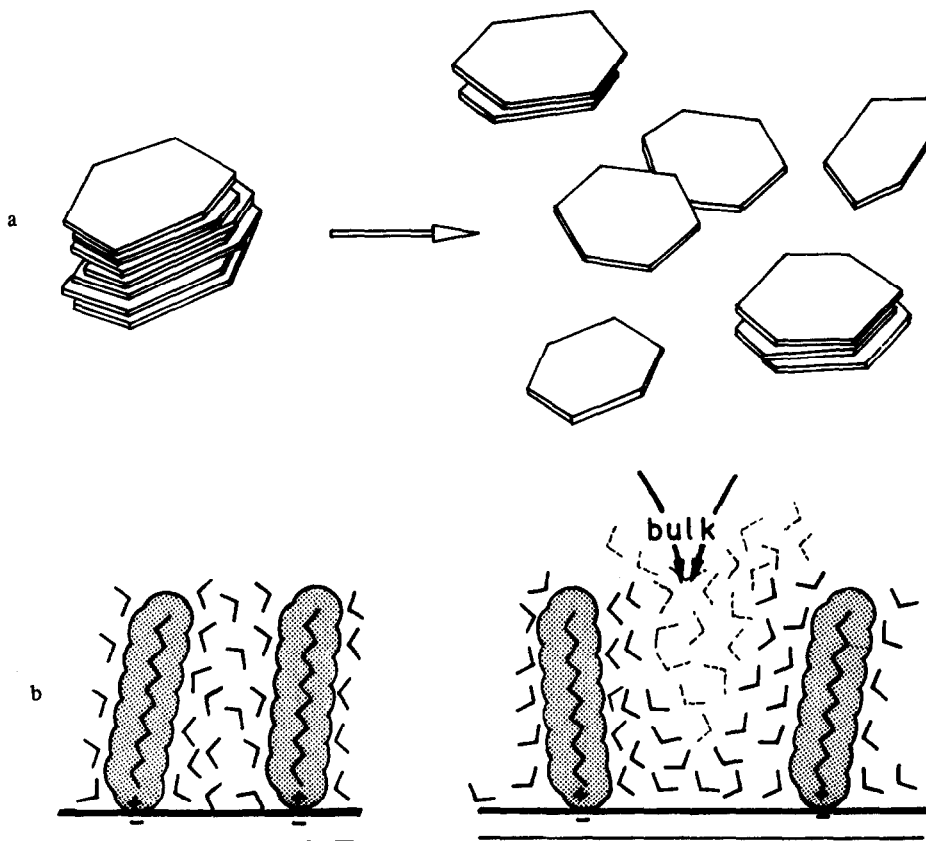

Fig. 4. (a) Formation of colloidal dispersions when crystals of the layered host materials disintegrate into individual layers and packets of a few of such layers; (b) Condition for complete separation of the layers in the presence of alkylamines: the chains are surrounded by clusters of water molecules (indicated by ∨). Disintegration occurs when bulk water (∨) can penetrate between the chains and the surrounding clusters.

ergy would prevent separation of the layers;

(ii) the alkylamine molecules should not be close-packed but also not too far from each other; intermediate distances are required.

The second condition is derived from the behavior of water molecules near solid surfaces primed with alkyl chains [11,23]. Dispersion and separation of the layers occur when the distance between the chains is so large that bulk water can penetrate between the water clusters around the alkyl chains (fig. 5). Butyl-ammonium vermiculite completely disperses in water, and the dispersion contains individual butylammonium silicate layers or packets of a few of such layers [24]. The same reaction was observed with vermiculite and γ-aminobutyric acid [25]. Recently, Alberti et al. [26] reported formation of such dispersions from α-zirconium phosphate after adsorption of distinct amounts of propylamine ("pellicular" zirconium phosphate).

3. Exchange reactions with alkylammonium ions

3.1. Pecularities of alkylammonium exchange

Alkylammonium derivatives obtained by cation exchange are distinguished by a great diversity of interlayer structures. Packing density and type of aggregation depend on the density of the negative layer charges, the geometry of the surface, and the degree of exchange.

The alkylammonium ions in 2/1 clay minerals (smectites, vermiculites, micas) lie flat on the silicate surface in mono- and bilayers or form paraffin-type arrangements with the chains radiating away from the surface (fig. 5). In the pseudo trimolecular arrangement [27,28], some chain ends are shifted above one another, so that the spacing is determined by the thickness of three alkyl chains. The chains assume
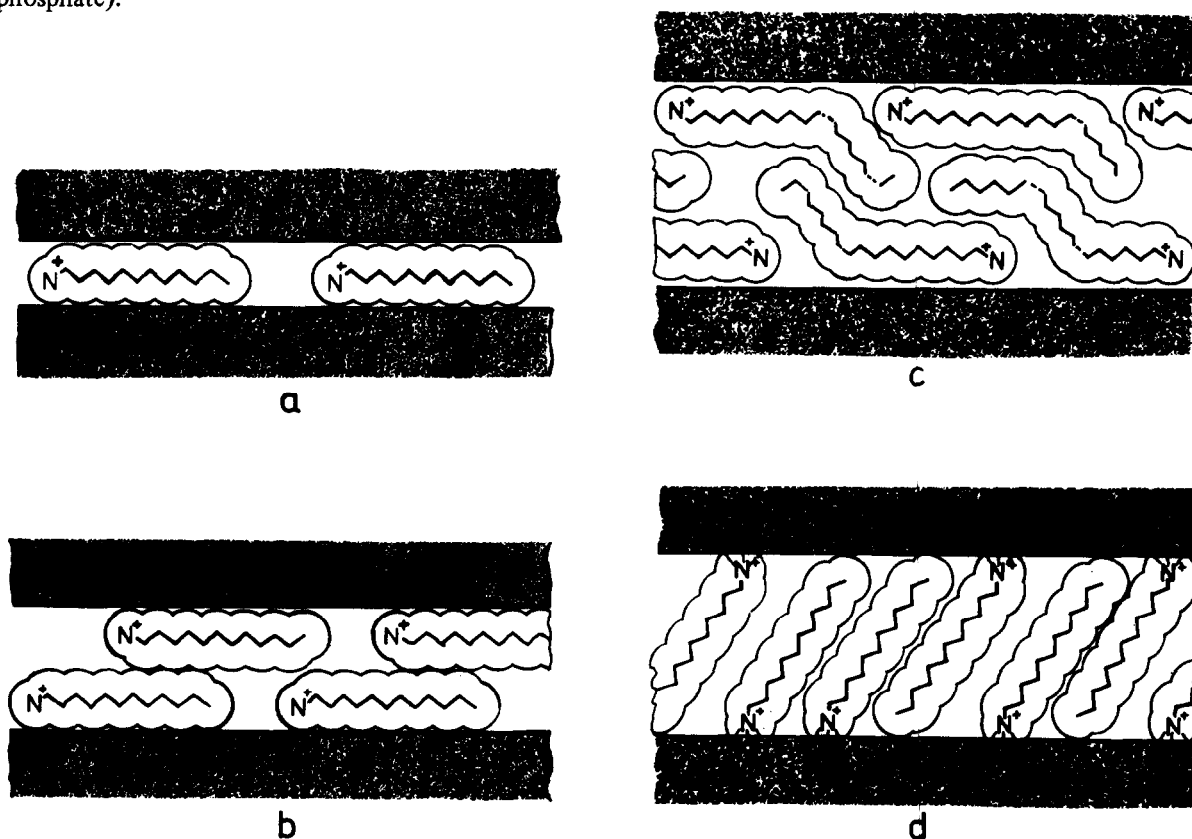

Fig. 5. Alkyl chain aggregations in 2/1 clay minerals: monolayers (a), bilayers (b), and pseudotrimolecular layers (c) of chains lying flat on the surface, and paraffin-type monolayers (d).
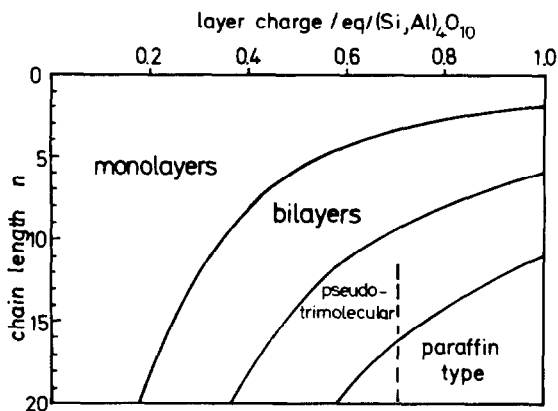
Fig. 6. Dependence of alkylammonium derivatives on the layer charge of 2/1 clay minerals and the alkyl chain length (calculated as indicated in ref. [27]).

the required conformation by kinking (fig. 8b, [29]). The interlamellar structure depends on the alkyl chain length and the packing density which is determined by the layer charge (fig. 6). In some cases, the alkyl chains form paraffin-type structures rather than pseudo trimolecular layers. The paraffin-type aggregation allows a better fit of the ammonium groups

to the surface oxygen atoms than it is the case for close-packed chains in pseudo trimolecular layers.

The alkylammonium exchange in non-silicatic systems [30,31] shows some remarkable facts. The interlayer cations of many host structures are not quantitatively exchanged by alkylammonium ions. Generally, the reaction proceeds to such levels of exchange that distinct interlayer structures can form. Typically, the chains do not aggregate in simple mono- or bilayer structures (as in smectites) or paraffin-type structures (as in vermiculites and $KNiAsO_4$) but abandon the all-trans conformation and aggregate to gauche blocks.

3.2. Paraffin-type arrangements in alkylammonium nickel arsenate

Alkylammonium ions displace about 65% of the potassium interlayer cations in nickel arsenate $KNiAsO_4$ [32]. The alkyl chains are arranged in paraffin-type bilayers with a tilting angle of about 60°. A feature of note is the even/odd alternation of the basal spacings. As explained in fig. 7 the spacing increases by 1.54 Å (chain tilt $\alpha = 56°$) from n = even to n = odd, and by 0.54 Å from n = odd to n = even.
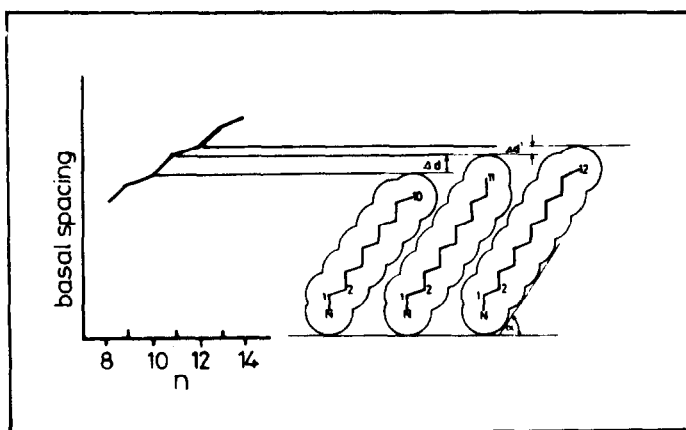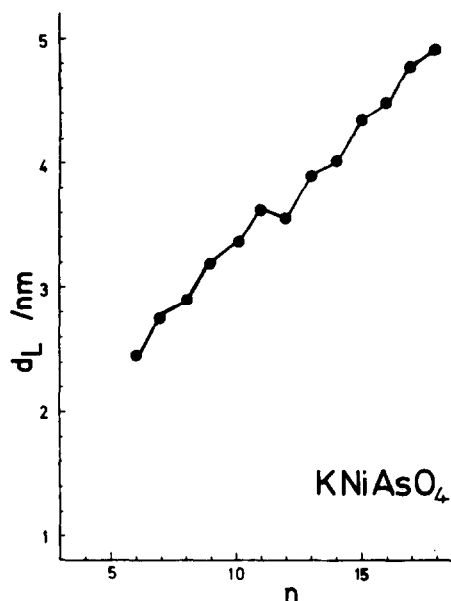

Fig. 7. (a) Alkylammonium derivatives of $KNiAsO_4$ with pronounced even/odd alternation of the basal spacing d_L; (b) The explanation of even/odd alternation.

Alternating spacings should be generally observed when the chains of paraffin-type mono- or bilayers are tilted towards the layer. However, alternation only occurs in some favored cases because the chains must be arranged in a sufficiently regular pattern. Several geometrical conditions have to be fulfilled [32]. The chains must interlock, but close-packing is not required. The packing of neighboring chains has to meet an additional geometrical constraint [33], so that a CH_2 group of one chain points between two such groups of the neighboring chains. Thus, it depends on the geometry of the layers of the host compound whether these conditions can be fulfilled. The lattice dimensions of $KNiAsO_4$ enable a high degree of order of the alkyl chains and even/odd alternation is observed. A misfit between the aggregation pattern of the alkylammonium ions in vermiculites and the a_0, b_0-lattice dimensions disorders the interlayer structure and even/odd alternation is suppressed [28].

3.3. Alkylammonium exchange of silver molybdate

Silver decamolybdate $Ag_6Mo_{10}O_{33}$ forms a layer structure which contains silver ions within and between the layers [34]. Surprisingly, only a small quantity (up to 17%) of silver ions is replaced by alkylammonium ions when the molybdate is reacted with aqueous solutions of alkylammonium nitrate [35]. However, the packing density of the alkyl chains is increased by neutral alkylamine molecules which are also taken up during the exchange. Evidently, it is not essential whether the alkyl chains in

the interlayer space belong to alkylammonium ions (that have displaced silver ions) or to intercalated alkylamine molecules. This explains observations that samples with different degrees of exchange sometimes show identical basal spacings. A lower content of alkylammonium ions can be compensated by an increased uptake of alkylamine molecules.

3.4. Gauche-blocks in alkylammonium silver molybdate

The basal spacings of alkylammonium exchanged silver decamolybdate under different conditions (cf. table 4) cannot be explained by simple paraffin-type aggregations of all-trans alkyl chains. Fig. 8 shows aggregates of alkyl chains in all-trans conformation and with kinks (gtḡ conformation [29]). Alkyl chains with isolated gauche bonds or gtg conformations can aggregate in different ways, so that structures with different packing densities and end-group distances can be realized [29,31]. Gauche blocks as in fig. 8c are distinguished by close contacts between the chains and, thus, high van der Waals interactions. They can be formed when the geometry of the layer allows the required close-packing of the polar end groups. In looser-packed gauche blocks (as in fig. 8d) a better fit of the end groups to the surface geometry may be attained of the expense of interchain van der Waals energy, in particular when the layers are puckered. The close-packing between the sections of tilted chains is then important as a criterion of stability.

Table 4
Different types of gauche-blocks in alkylammonium/alkylamine silver decamolybdate.

	A[a]		B, C		D		E	
chain length n	8	→ 16	11	→ 18	10	→ 18	12	→ 18
basal spacing (A)	27.4	→ 51.5	29.4	→ 42.8	25.2	→ 35.4	39.0	→ 50.9
n_t [b]	16	→ 32	22	→ 36	20	→ 36	24	→ 36
n_p	10	→ 26	8	→ 14	2	→ 4	18	→ 26
$n_t - n_p$	6	→ 6	14	→ 22	18	→ 32	6	→ 10
n_n/n_t	0.63 →	0.81	0.36 →	0.39	0.10 →	0.11	0.75 →	0.72

[a] A: intercalation of $C_nH_{2n+1}NH_2$; B: A, washed, air-dried; C: Exchange with $C_nH_{2n+1}NH_3^+$, under equilibrium solution; D: C, washed, air-dried; E: D + intercalation of alkanol $C_nH_{2n+1}OH$.

[b] n_t: total number of carbon atoms in a chain pair, n_p, $n_t - n_p$: number of carbon atoms in the perpendicular and tilted sections of the chains.
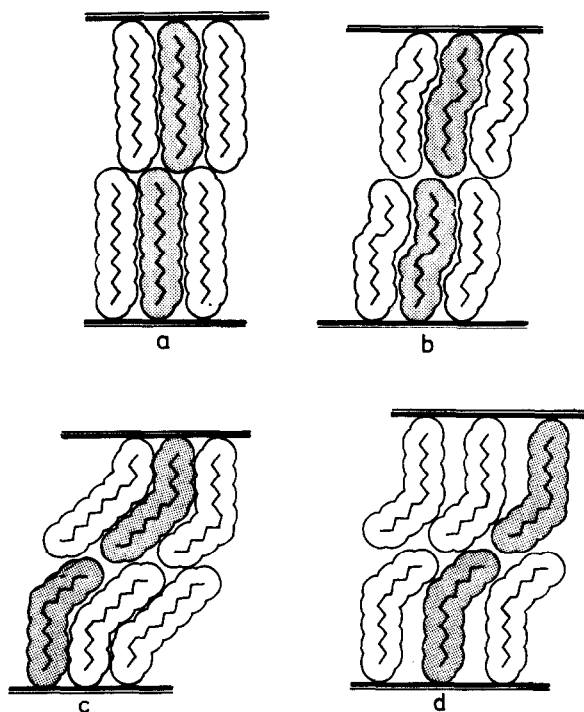
Fig. 8. Aggregation of chains in all-trans conformation to all-trans blocks (a), with gtg̅ conformation to kink blocks (b) and with g (or gtg conformations) to gauche blocks (c, d).

Presently, it is less likely that experimental evidence of the exact structure of gauche-blocks can be obtained; figs. 8c, d give two limiting cases. Generally, the gauche-blocks are not close-packed because the area per chain usually is $33-36$ Å^2 or even larger. In extreme cases (for instance, alkylammonium silver decamolybdate and alkyl chains $n < 10$) the packing density is extremely low (area/chain > 50 Å^2). One has to assume that the chains are no more uniformly distributed but aggregate to groups which, as pillars, prize apart the layers. If the host layers are rigid enough, a few pillars on a large area can maintain a regular distance between the layers.

Gauche blocks are described by selecting two opposite chains (a chain pair, dotted in fig. 8) and counting the C–C bonds in the perpendicular section (n_p) and relating n_p to $n_t = 2n$, the total number of C–C-bonds of the chain pair [31].

That the basal spacings of the alkylammonium silver molybdates under different conditions (cf. fig. 3, [35]) can assume distinct values only, indicates the

preference of distinct gauche blocks. With increasing chain length the gauche bond shifts to the terminal methyl group (n_p increasing) so that either the difference $n_t - n_p$ (number of C–C bonds in the tilted chain) or the ratio n_p/n_t is constant (table 4). Table 4 also includes data of the alkylammonium silver decamolybdates after swelling in alkanols $C_nH_{2n+1}OH$ (n is the same as in the alkylammonium ion). During the alkanol uptake the gauche bond shifts to the terminal methyl group and, again, gauche blocks with $n_p/n_t = 0.7-0.8$ are formed.

The alkylammonium silver molybdate exhibits an interesting behavior towards hydrocarbons. Alkanes, alkenes and alkynes are intercalated if particular relations between the chain lengths of the hydrocarbons and the alkylammonium ions are fulfilled (fig. 9). For instance, the dodecylammonium derivative intercalates decane but not octane and dodecane. Likely, the driving force for intercalation is formation of distinct gauche-block structures.

Initially, gauche-block structures were observed as high-temperature forms of alkanol–alkylammonium smectites and vermiculites [29,31] and were believed to be typical high-temperature phases. Extensive studies with non-silicatic host materials (titanates, niobates, molybdates, uranates etc.) now reveal that gauche-block structures are more common than originally assumed. Typically, they are observed as room temperature phases of the alkylammonium derivatives of many layered materials. They are particularly favored above all-trans and kink-blocks when the host materials contain puckered layers. The flexibility of
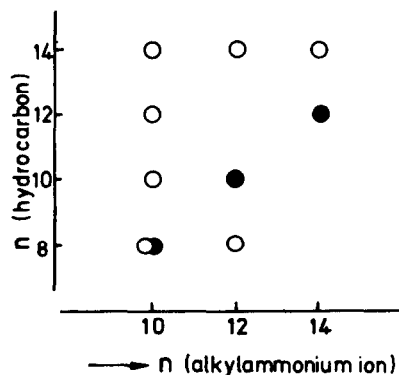

Fig. 9. Intercalation of hydrocarbons by alkylammonium silver decamolybdate: (●) alkanes, (○) 1-alkenes intercalated.

monolayers or bilayers of alkyl chains with gauche bonds allows a better fit on the surface structure of the host layers. Formation of gauche blocks is promoted by entropic terms which are related to the less regular arrangements of the chains and the relatively high proportion of gauche-bonds and gtg conformations. This explains why alkylammonium ion exchange is often restricted to the formation of gauche blocks and does not proceed further on to higher packing densities and formation of more regular all-trans blocks.

4. Applications

The alkylammonium exchange provides a very simple and the most reliable method for determining the layer charge of 2/1 clay minerals (smectites, vermiculites; [27,28]). Alkylammonium bentonites are widely used in practical applications [36], and are produced on large scales. Alkylammonium exchange can be advantageously used to hydrophobize inorganic materials when they have to be dispersed in organic liquids. Preliminary results show that several alkylammonium derivatives of inorganic layer compounds may be used as phase transfer catalysts. Alkylamine intercalation and alkylammonium exchange are useful test reactions to prove the layer structure of new layered materials and to examine the intracrystalline reactivity.

Studies of the alkanol–alkylammonium films between solid surfaces show many interdisciplinary aspects which, for instance, are related to the structure of polymers and lipid layers in biomembranes [11,12,31].

References

[1] M.S. Whittingham and A.J. Jacobson, Intercalation chemistry (Academic Press, London, 1982) p. 595.

[2] A. Weiss, A. Weiss and U. Hofmann, Z. Anorg. Allgem. Chem. 273 (1953) 129.

[3] J.P. Goupta and D.V. Nowell, J. Chem. Soc. Dalton Trans. (1979) 1178.

[4] G. Alberti and U. Costantino, J. Mol. Catal. 27 (1984) 235.

[5] R.M. Tindwa, D.K. Ellis, G.-Z. Peng and A. Clearfield, J. Chem. Soc. Faraday Trans. I 85 (1985) 545.

[6] E. Michel and A. Weiss, Z. Naturforsch. 20b (1965) 1307.

[7] M. Fernández-Gonzáles, A. Weiss, K. Beneke and G. Lagaly, Z. Naturforsch. 31b (1976) 1205.

[8] K. Beneke and G. Lagaly, Am. Mineral. 66 (1981) 432.

[9] K. Hartl and A. Weiss, Z. Naturforsch. 17b (1962) 11.

[10] J. Poyato-Ferrera, H.O. Becker and A. Weiss, Proc. 3rd. European Clay Conf. (Oslo, 1977) p. 148.

[11] G. Lagaly, Phil. Trans. Roy. Soc. (London) A 31 (1984) 315.

[12] G. Lagaly, in: Developments in ionic polymers, eds. A.D. Wilson and H.J. Prosser, Vol. 2 (Elsevier, Amsterdam, 1986) p. 77.

[13] G. Lagaly, H.-M. Riekert and H.H. Kruse, in: Chemical reactions in organic and inorganic constrained systems, ed. R. Setton (Reidel, Dordrecht, 1986) p. 361.

[14] A. Weiss and R. Ruthardt, Z. Naturforsch. 28b (1973) 249.

[15] R. Schöllhorn, E. Sick and A. Weiss, Z. Naturforsch. 28b (1973) 168.

[16] G. Lagaly, K. Beneke, P. Dietz and A. Weiss, Angew. Chem. [Int. Ed. Engl.] 13 (1974) 819.

[17] G. Lagaly, Colloid Interface Sci. 11 (1979) 105.

[18] A. Weiss and J.H. Choy, Z. Naturforsch. 39b (1984) 1193.

[19] A. Grandin, M.M. Borel and B. Raveau, J. Solid State Chem. 60 (1985) 366.

[20] A. Lerf and R. Schöllhorn, Inorg. Chem. 16 (1977) 2950.

[21] R. Schöllhorn, in: Chemical reactions in organic and inorganic constrained systems, ed. R. Setton (Reidel, Dordrecht, 1968) p. 323.

[22] R. Schöllhorn, Pure Appl. Chem. 56 (1984) 1739.

[23] G. Lagaly, R. Witter and H. Sander, in: Water on hydrophobic surfaces: Adsorption from solution, eds. R.H. Ottewill, C.H. Rochester and A.L. Smith (Academic Press, London, 1983) p. 65.

[24] J.A. Rausell-Colom, Trans. Faraday Soc. 60 (1964) 190.

[25] J.A. Rausell-Colom and P.S. Salvador, Clay Miner. 9 (1971) 193.

[26] G. Alberti, M. Casciola and U. Costantino, J. Colloid Interf. Sci. 107 (1985) 256.

[27] G. Lagaly, Clay Miner. 16 (1981) 1.

[28] G. Lagaly, Clays Clay Miner. 30 (1982) 215.

[29] G. Lagaly, Angew. Chem. [Int. Ed. Engl.] 15 (1976) 575.

[30] K. Beneke and G. Lagaly, Z. Naturforsch. 33b (1978) 564.

[31] G. Lagaly, Naturwissenschaften 68 (1981) 82.

[32] K. Beneke and G. Lagaly, Clay Miner. 17 (1982) 175.

[33] G.W. Brindley and W.F. Moll, Clay Miner. 6 (1965) 91.

[34] B.M. Gatehouse and P. Leverett, Chem. Commun. (1969) 1093.

[35] C. Rössner and G. Lagaly, J. Solid State Chem. 53 (1984) 92.

[36] T.R. Jones, Clay Miner. 18 (1983) 399.

[37] G. Lagaly, K. Beneke and A. Weiss, Am. Mineral 60 (1975) 650.