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Clay-Organic Interactions [and Discussion]

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Clay–organic interactions

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Clay minerals interact with organic materials by adsorption, intercalation and cation exchange.

Basic principles of intercalation reactions were obtained with kaolinite which intercalates a limited number of neutral organic compounds.

The interaction of neutral organic compounds with mica-type layer silicates (2/1 clay minerals) is of quite different type. As illustrated for the interaction with nuclein bases, the adsorption can be strikingly dependent on the layer charge and the concentration of salts and co-adsorption phenomena can occur.

Various organic materials are bound by cation exchange. Besides some other examples, the reaction with alkylammonium ions is of interest because of widespread practical applications. From a more scientific point of view, the interactions of alkylammonium ions with clays provide models for studying surfactant aggregations on solid surfaces and possible conformational changes in aggregates of long chain compounds (mono- and bimolecular films, as in biomembranes).

Negatively charged organic ions can also be bound by clays. The main mechanisms are binding by positive edge charges or exchanging structural OH-groups.

INTRODUCTION

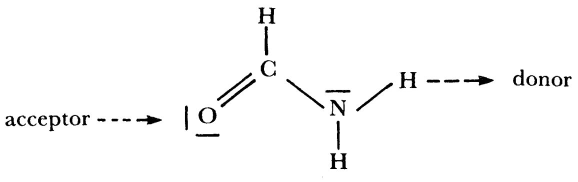
The alteration of clay properties by adsorbed organic materials has been known from the earliest use of clays by man about 7000 B.C. The Greeks profited by the interaction of clays with vegetable tannins. They probably used tannins besides potash for peptization of clays because they needed a very careful fractionation to obtain distinct clay fractions for red–black decors (Hofmann 1962). The likely use of urea for preparing very thin-walled porcelain during the Sung period in China (see below) is a further striking example of the practical application of clay–organic interactions.

INTERCALATION INTO KAOLINITE MINERALS

Type of guest molecules

Kaolinite (and also dickite, nacrite and halloysite) intercalate distinct organic compounds (Wada 1962; Weiss 1962). The guest molecules enter the interlayer spaces and prise apart the silicate layers. The reactive guest molecules were classified by Weiss *et al.* (1966) as follows:

(i) Compounds forming strong hydrogen bonds to the silicate layers: urea, formamide, acetamide, hydrazine. Suitable organic molecules have to have acceptor *and* donator sites for hydrogen bonds, for example, formamide:



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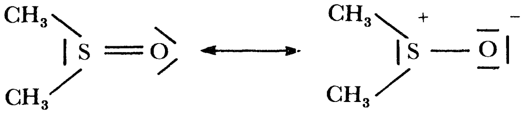
(ii) Compounds with pronounced betaine-like character with the possibility of strong dipole interactions with the silicate layers, for example, dimethyl sulphoxide (DMSO):



(iii) Alkali salts (K$^+$, NH$_4^+$, Rb$^+$, Cs$^+$, not Li$^+$, Na$^+$) of short chain fatty acids, in particular acetic and propionic acid.

Table 1. Preparation of kaolinite intercalation compounds

(Weiss *et al.* 1966; Weiss *et al.* 1970; Weiss & Orth 1973.)

guest compound	reaction time and temperature	basal spacing 10^{-10} m
hydrazine hydrate	1d, 60 °C	10.4
urea†	8d, 60–110 °C	10.7
formamide	4d, 60 °C	10.1
N-methylformamide	2d, 60 °C	10.8
acetamide	30d, 100 °C	10.9
dimethyl sulphoxide	30h, 50 °C	11.2
pyridine-N-oxide†	12d, 50 °C	12.6
imidazole†	3d, 60 °C	11.4
ammonium acetate† (pH = 8–9)	20d, 20 °C	14.1
potassium acetate† (pH = 8)	1d, 65 °C	14.0
N,N-dimethyl formamide	8d, 50 °C‡	12.0
N,N-dimethylurea	8d, 50 °C‡	10.9; 12.2
pyridine	20d, 50 °C‡	12.0
2-picoline-N-oxide	20d, 25 °C‡	12.9
alkali chlorides, bromides and iodides	5d, 25 °C‡	11.1–11.7

† Concentrated aqueous solution.
‡ From ammonium acetate kaolinite.

A large variety of organic molecules are intercalated by the displacement procedure. For example, ammonium acetate is first intercalated, then displaced by alkylamines. In a similar way ammonium acetate can be displaced by ammonium propionate and then ammonium propionate by glycol. Diaminohexane instead of glycol combines with the acid anion to the corresponding amide in the interlayer space (Seto *et al.* 1978*a*, *b*).

A different mechanism is the 'Schleppreaktion' (the entraining reaction, Weiss *et al.* 1966). Non-reacting compounds are entrained between the layers by reactive guest molecules.

In table 1 are listed some experimental conditions for preparing kaolinite-intercalation products.

Structure of kaolinite intercalates

The structure of kaolinite intercalates is now established by several X-ray diffraction studies (DMSO, NMFA, imidazole, pyridine-N-oxide, picoline-N-oxide, Weiss *et al.* 1966; Weiss & Orth 1973; Weiss *et al.* 1973). The first three-dimensional crystal structure analysis was made of a NMFA–dickite complex (Adams 1978*a*). A neutron powder diffraction study allowed insight into the hydrogen bonding scheme in the formamide–kaolinite complex (Adams *et al.* 1976).

Crystallographically ordered structures are only expected in cases where there are functional groups capable of hydrogen bond formation to the silicate oxygen atoms. Dipole and van der Waals interactions may not be strong enough to maintain a well-ordered structure with sharp (*hkl*)-reflections.

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Kinetics of intercalation

The degree of reaction increases with time in an S-shaped curve starting after a more or less pronounced induction period. According to recent neutron scattering experiments (Weiss *et al.* 1981) the adsorption on the external surfaces causes a reorientation of the OH-groups or a migration of protons during the induction period. This initiates the elastic deformation of the layers and the opening of interlayer space. In the next step the molecules enter the interlayer space. The reaction rate obeys the Avrami–Erofeev equation (two-dimensional phase boundary reaction, Fenoll & Weiss 1969) and can eventually change to a two-dimensional diffusion controlled reaction.

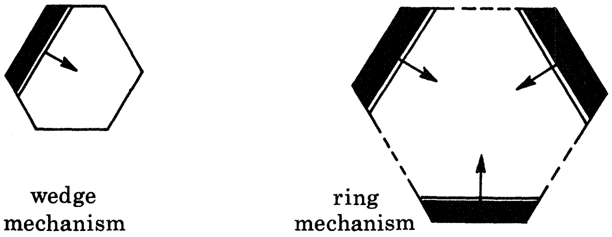

FIGURE 1. Intercalation mechanism for small and large particles according to A. Weiss.

The reaction rate as a function of particle-size has a maximum for 3.8–5.0 μm particles (Weiss *et al.* 1970). The penetration of the guest molecules between the layers requires an elastic deformation of the silicate layers. Owing to the polarity of the kaolinite layer the decisive steps of deformation proceed in one direction. This kind of deformation leads to different reaction mechanisms for small and large particles. In the case of small particles the guest molecules enter the interlayer space only at one site. The neighbouring zones are blocked, because their opening would strongly increase the energy of deformation. Large particles can react at different sites, so that the reaction rate exceeds that of somewhat smaller crystals (figure 1). The movement of the reaction front from the edge to the interior is stopped by larger defects. The reaction rate was thus found to increase with increasing crystallization index (Weiss *et al.* 1970).

The reaction rate, surprisingly, depends on the ratio of DMSO to kaolinite. A maximum appears at a very low ratio which almost corresponds to a monomolecular covering of the surface by DMSO. The formation of the liquid structure (association of the DMSO molecules) apparently retards the entry of DMSO between the layers. The tendency for 'self-preservation' of the liquid structure is evident.

The desorption of intercalated guest molecules apparently is more complex than originally thought. In an attempt to follow the thermal decomposition of DMSO–kaolinite, Adams & Waltl (1980) found a two-dimensional contracting-circle type of mechanism to be consistent with the thermogravimetric result provided that the nucleation process is exponential rather than instantaneous. The high activation energy of 105 kJ mol^{-1} DMSO, however, is inconsistent with the assumption (as in the case of NMFA–kaolinite, Adams 1978*b*) that the rate-determinant step is the desorption of single organic molecules from the silicate layer.

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Applications

Intercalation of long chain alkylamines by displacement reactions drastically changes the crystal shape. Without any mechanical treatment the plates are split into thinner layers which roll up forming halloysite-like tubes or grooves and troughs. The driving force is the misfit between the dimensions of the octahedral and tetrahedral sheet which is suppressed in thicker crystals by the superposition of the layers (Weiss & Russow 1963; Poyato-Ferrera *et al.* 1977).

The disaggregation of the kaolinite platelets by intercalation strongly increases the dry strength. Very likely the Chinese ceramists manufacturing thin-walled porcelain ('egg-shell porcelain', particular in the Sung period) took advantage of the increased dry strength of urea-treated kaolins (Weiss 1963*a*).

The maximum degree of reaction of many kaolins remains below 100 %, even after very long reaction times. Weiss and coworkers (Range *et al.* 1970) concluded that kaolins generally are mixtures of three or four types which differ by their chemical reactivity. Based on these observations a method was evaluated for estimating the composition of kaolins from the degree of reaction with DMSO and urea (Lagaly 1981*a*). Kaolins are indeed commonly and intimately intermixed in microdimensions (Keller & Haenni 1978). The experiments are still outstanding to prove this concept. It also seems likely that a relation exists between the technical applicability and the chemical reactivity of the kaolins (Fernandez-Gonzales *et al.* 1976).

Finally, the reactivity of kaolins towards DMSO and hydrazine can be used to identify even small amounts of kaolinites and halloysites (Range *et al.* 1970; Wilson & Tait 1977; Jackson & Abdel-Kader 1978). The procedure is also recommended for disintegrating flint clays and related kaolinite containing rocks (Weiss & Range 1970).

SMECTITES WITH NEUTRAL ORGANIC MOLECULES

Interlamellar solvates

The interlayer water molecules can be replaced by a variety of neutral organic molecules. A part of the organic molecules more or less strongly solvate the interlayer cations, the others are associated between the solvation shells. Like the solvation of ions in solution the bonding strength between the interlayer cations and the solvent molecules covers the range from loose aggregates to complex bonding.

Many organic molecules displace the water molecules from the interlayer cations more or less quantitatively (short chain alcohols, ethylene glycol, carbohydrates; Brindley 1966; Bissada *et al.* 1967; Dowdy & Mortland 1967; Stul & Uytterhoeven 1975; Chassin 1976). These interlayer solvates can thus be prepared by reacting air-dried smectites with the organic liquids. Other guest compounds such as nitriles have to be introduced in the interlayers by reaction with the dried smectites (Serratosa 1968; Yamanaka *et al.* 1975).

Widely applied is the use of ethylene glycol and glycerol for identifying smectites and vermiculites and for estimating the interlamellar surface area (Brindley 1966; Lagaly 1981*a*).

A basic question is that of the localization of the interlayer cations. If the interaction with the organic molecules is strong, the cations are completely solvated and solvent molecules are between the cations and the surface oxygen atoms. For weak interactions the cations may reside at the surface of the silicate layers so that only a few of their coordination sites are occupied by the solvent molecules. Berkheiser & Mortland (1975) obtained information about solvent-

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dependent cation positions from the intensity of the high field Fe(III) electron spin resonances ($g = 3.6$). The intensity varies with the degree to which the ion is removed from the smectite surface by solvation and is related to the Gutmann donor number of the solvent. For Na-smectite a Gutmann number of 14 is required for complete solvation. On the other hand, multivalent cations can retain water molecules in the presence of solvents with a low Gutmann number and are precluded from close contacts to the surface.

The problem of the interlamellar structure can also be discussed from another point of view. Liquids of highly polar molecules show a pronounced tendency to maintain the molecular association on the solid surface. The 'self-preservation' tendency competes with the forces that are introduced by the field arising from the surface charges and the gegen ions and that tend to destroy the association (Lagaly & Witter 1982). An instructive example is reported by Annabi-Bergaya *et al.* (1981). Methanol molecules on smectite surfaces tend to maintain the typical zig-zag chain aggregation with strong hydrogen bonds between the molecules. Lithium as interlayer cation does not disturb this continuous network of adsorbed species, rather it fits in the holes between the aggregated methanol molecules. Calcium ions, owing to their stronger electrical field, disturb the association completely. In the case of sodium and barium ions the chains are broken into smaller fragments.

Long chain compounds

Interlamellar long chain compounds exhibit a strong tendency to aggregation in bimolecular films. The formation of these structures in most cases requires the propping-open procedure of Brindley & Ray (1964). These authors also observed a phase transition with increasing temperature (see also Pfirrmann *et al.* 1973). One or more temperature dependent phase transitions are very characteristic of interlamellar bimolecular films and are also observed for interlamellar triglycerides (Roloff & Weiss 1966), fatty acids (Brindley & Moll 1965) and primary amines (Brindley 1965; G. Lagaly and G. Söffing, unpublished). The transitions result from trans-gauche isomerization of the alkyl chains (see below).

Besides high-spacing structures long chain compounds often form complexes with very low spacings in which the alkyl chains are parallel to the silicate surface. This arrangement favours the interactions with the interlayer cations (for fatty acids: Yariv & Shoval 1982).

It stands to reason that interlamellar long chain compounds, in particular glycerides and fatty acids, are possible precursors of petroleum.

Interlamellar complexes

Many complex-forming ligands are strongly coordinated to the interlayer cations and form complexes identical with or similar to those in solution. Examples of ligands are diacetyl dioxime (Weiss & Hofmann 1951), oxime (Yamamoto *et al.* 1969), thiourea (Pleysier & Cremers 1975), acetylacetone (Parfitt & Mortland 1968), bipyridyl (Taylor *et al.* 1978), porphyrines (Cady & Pinnavaia 1978).

Recently special rhodium phosphonium interlayer complexes like $Rh(PPh_3)_2^+$ were developed as a new class of selective heterogeneous catalysts. A typical authentic metal complex catalysed reaction is the hydrogenation of terminal olefins (Pinnavaia 1983; Farzaneh & Pinnavaia 1983).

Resolution of optically active compounds by stereoselective adsorption was reported by Yamagishi (1983). Several Co-III-chelates were resolved at least partially into two

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configurational isomers, using the montmorillonite (Δ-tris (1,10-phenanthroline)nickel-II complex as column material).

An interesting group of complexes was obtained when arenes were reacted with Cu^{2+}-montmorillonite (table 2). In the yellow benzene complex the interlayer water has been partly displaced by benzene molecules which interact by their π-electrons with the Cu^{2+} ions (type I complexes). Complete removal of water (for instance in a desiccator over P_4O_{10}) leads to the red type II complexes in which the aromaticity of the ligands is lost. The organic radical cations $C_6H_6^+$, formed by one electron transfer from the benzene molecules to the Cu^{2+} ions are probably coupling themselves (Pinnavaia & Mortland 1971; Rupert 1973; Pinnavaia *et al.* 1974).

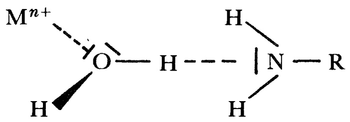
TABLE 2. AROMATIC COMPLEXES OF Cu^{2+}-MONTMORILLONITE AND Ag^+, Fe^{3+}, VO_2^+-HECTORITE

type I	Cu^{2+}:	benzene	phenol	
(ring planar, aromaticity retained)		toluene‡ xylenes mesitylene	anisole† phenyl ether benzyle methyl ether	
	Fe^{3+}:	toluene‡		
	Ag^+:		phenol anisole	
type II				
(ring distorted, aromaticity lost)	Cu^2:	benzene thiophene	anisole† butyl phenyl ether	biphenyl naphthalene anthracene
	Fe^{3+}:	benzene thiophene	anisole†‡	
	VO_2^+:	thiophene	anisole	

† Oxidation to 4.4′-dimethoxy biphenyl. ‡ Polymeric materials observed.

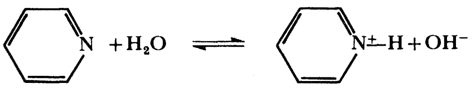
Reaction with bases

Aliphatic and aromatic amines do not coordinate alkali- and alkaline-earth ions in aqueous solutions. This may also be true for interlamellar solvates. These bases are indeed predominantly bound to the cations by H_2O bridges (pyridine: Farmer & Mortland 1966; aniline, cyclohexylamine: Heller & Yariv 1970; ethylene diamine: Laura & Cloos 1972, 1975):



The type of coordination (directly or by H_2O-bridges) should depend on the Pearson–Schwarzenbach hardness and softness of the cations. Pyridine is directly coordinated to Cu^{2+} but bound by H_2O bridges to Mg^{2+} and Ca^{2+}-interlayer cations. A direct bonding, however, seems also to be possible, even for alkali ions, or at least is tentatively suggested in recent papers (Adams & Breen 1982).

The interlayer adsorption of bases, in particular amines, from aqueous solutions is accompanied by a cation exchange (Vansant & Uytterhoeven 1973). The protonated species



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exchange interlayer cations. The interlayer ratio between the protonated and unprotonated base increases with decreasing solution pH but certainly deviates from that in solution (Karickhoff & Bailey 1976; Feldkamp & White 1979).

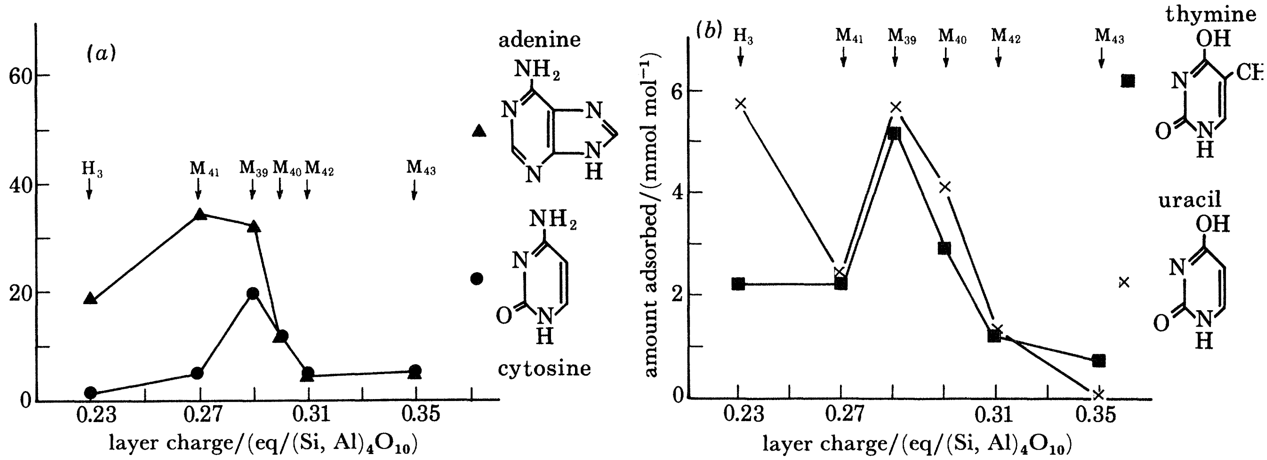
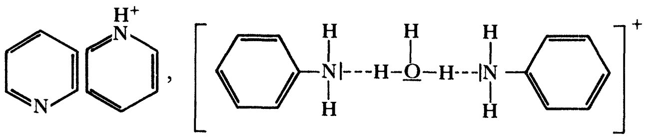


FIGURE 2. Adsorption of nuclein bases from 10^{-3} M solutions (pH = 5) on various smectites as a function of layer charge.

TABLE 3. ADSORPTION OF NUCLEIN BASES (FROM 1×10^{-3} M AQUEOUS SOLUTIONS)

montmorillonite	bases	ratio of bases adsorption from mixtures	 adsorption from pure solution
Bavaria M 39	thymine/adenine	0.49	0.17
	uracil/adenine	0.24	0.19
	thymine/cytosine	0.29	0.28
	uracil/cytosine	0.17	0.31
Wyoming M 41	thymine/adenine	0.49	0.07
	uracil/adenine	0.38	0.08
	thymine/cytosine	0.63	0.46
	uracil/cytosine	0.35	0.54

The total adsorption as a function of pH often shows a maximum because protons compete with the acid form, or acid-base pairs such as



are predominantly adsorbed (Yariv & Heller-Kallai 1975).

The adsorption of nuclein bases exhibit interesting features. Not only does it depend on the type of clay mineral (Lailach *et al.* 1968; Thompson & Brindley 1969) but also on the kind of montmorillonite and its layer charge (figure 2, Samii 1981). The adsorption from 10^{-3} M solution is maximal at a layer charge of 0.27–0.29 eq/(Si, Al)$_4$O$_{10}$. Adenine and cytosine are adsorbed in markedly higher amounts than thymine and uracil. At layer charges above 0.30 eq/(Si, Al)$_4$O$_{10}$ the adsorption is generally very low.

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The co-adsorption of nuclein bases described by Lailach & Brindley (1969) again depends on the kind of montmorillonite (table 3, Samii 1981). The presence of adenine increases the adsorption of thymine and uracil, in particular with montmorillonite from Wyoming, but the adsorption of uracil is decreased by cytosine. From a theoretical point of view the association between two different bases in solution by hydrogen bonds can decrease or increase their ratio

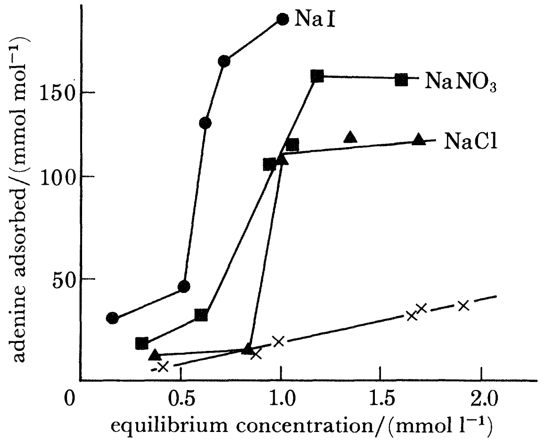

FIGURE 3. Salt effects on the adsorption of adenine on montmorillonite (from Wyoming M 41), salt concentration 0.2 M, pH = 5. ×, Without salt.

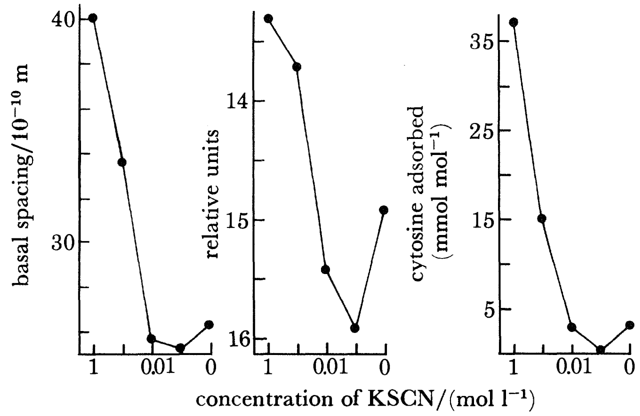

FIGURE 4. Salt dependent properties: basal spacings of tetra-decylammonium beidellite in salt solutions, water vapour pressure, cytosine adsorption on Ca-montmorillonite (from 10^{-3} M cytosine solution, pH = 5, montmorillonite: 'Greenbond' Wyoming, M 40).

in the adsorbed layer. One gets the impression that the base-pairing as in DNA plays a role, that is, besides adenine molecules pairs adenine–thymine are adsorbed. Consequently, preliminary adsorption of adenine or cytosine changes the adsorption properties of the smectite towards thymine and uracil.

The adsorption of nuclein bases is sensitively influenced by salts (figure 3). In particular the adsorption of adenine is greatly enhanced by sodium salts. (The influence of the Ca^{2+}/Na^{+} exchange on the smectite is moderate.) The effect of the anions often follows the Hofmeister series indicating the adsorption to be influenced by the water structure. The directing influence of the water structure is also evident from figure 4. The adsorption of cytosine from KSCN

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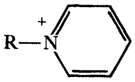
solutions has a small minimum at 0.01 M KSCN, then sharply increases with the KSCN concentration. In a similar way the structure-breaking effect of the SCN^- anion influences the water vapour pressure (figure 4) and the swelling of tetradecylammonium beidellite in water (figure 4). One arrives to the same conclusion as stated by Fripiat and coworkers (Annabi-Bergaya *et al.* 1981) that 'the intermolecular forces between adsorbed species have been generally underestimated in studies of sorption processes by smectites'.

TABLE 4. EXCHANGE OF INTERLAYER CATIONS BY CATIONIC SURFACTANTS

ξ layer charge (eq/(Si, Al)$_4$O$_{10}$)

surfactant ion	formula $R = C_nH_{2n+1}$	montmorillonites $\xi = 0.3$–0.4	beidellite $\xi = 0.4$–0.5	reactivity vermiculites $\xi \leqslant 0.7$	vermiculites $\xi \geqslant 0.7$	mica
alkylammonium	RNH_3^+	+	+	+	+	slowly
trimethyl alkylammonium	$RN(CH_3)_3^+$	+	+	+	−	−
dimethyl dialkylammonium	$R_2N(CH_3)_2^+$	+	+	+	−	−
N-alkyl pyridinium		+	+	±	−	−

The discussion of the interaction of clays with other biologically important bases and related compounds would be very fascinating but is outside the scope of this paper. For completeness some references may be listed: amino acids, peptides (Weiss 1963*b*; Fripiat *et al.* 1960; Rausell-Colom & Salvador 1971; Raussel-Colom & Fornes 1974; Slade *et al.* 1976; Raupach & Janik 1976; Siffert & Kessaissia 1978); codeine (Rupprecht *et al.* 1975); porphyrins (van Damme *et al.* 1978; see also Theng 1974 and Mortland 1970).

The present concern about pollution control will activate studies of biocide-clay interactions. The principal interaction mechanisms are known (Mortland 1970; Weber & Weed 1974; White 1976). The protonation of the molecules and their binding as interlayer cations decrease the immediate efficacy and the pollution of the environment. On the other hand, if the protonated and adsorbed species resist hydrolysis and microbial decomposition, the compound shows biological activity when it is desorbed. The bound residues pose a possible threat for the environment as they can be released over a long time.

INTERACTIONS WITH CATIONIC SURFACTANTS

Cation exchange

Cationic surfactants (table 4) are exchanged for the inorganic interlayer cations from aqueous solutions at pH 5–7. Suitable surfactant concentrations are, for example, for alkylammonium ions $C_nH_{2n+1}NH_3^+$: 0.5–2 M for $n < 10$; 0.1 M for $n = 10$–15; 0.05 M for $n > 15$. Depending on concentration, pH, kind of surfactant, alkyl chain length, and layer charge the cation exchange is accompanied by intercalation of ionic pairs: surfactant cation plus gegen ion. The total amount of interlayer surfactant in contact with the equilibrium surfactant solution can thus greatly exceed the cation exchange capacity (c.e.c.). With alkylammonium ions $C_nH_{2n+1}NH_3^+$ alkylamine molecules $C_nH_{2n+1}NH_2$ are also adsorbed, in particular at pH > 6. Most of the ionic pairs or the alkylamine molecules are removed by short washing; the fully

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quantitative removal (without showing any change in the X-ray diagram) requires intense washing of the samples.

Smectites bind very different kinds of surfactants. Selectivity arises with increasing layer charge (table 4). Highly charged vermiculites (the reaction of higher charged vermiculites is promoted when the vermiculite is in the Li form (Slade *et al.* 1978)) are expected to select distinct surfactants from surfactant mixtures. Micas and illites react very slowly with alkylammonium ions. A nearly complete reaction requires months or even years depending on the particle size (Weiss *et al.* 1956). Micas may first be treated with $BaCl_2$-solution at about 120 °C to exchange the K^+ ions by the Ba^{2+} ions (Reichenbach & Rich 1968). The Ba^{2+} ions are then easily exchanged by alkylammonium ions (Beneke & Lagaly 1982).

Application of alkylammonium exchanges

The reaction with alkylammonium ions is the simplest possibility for identifying even very small amounts of smectites and vermiculites in bentonites, kaolins, rocks and soils. It further provides the most reliable method for determining the layer charge and charge distribution of smectites, vermiculites and regular interstratified materials. Combined with carbon content determination (by combustion) the alkylammonium ion exchange further allows a rapid and reliable quantitative estimation of the smectite content in bentonites. The estimation is based on the assumption that the interlayer c.e.c. (derived from the layer charge) of most smectites is about 80% of the total c.e.c. (derived from the carbon content) (Lagaly 1981*a*).

The modification of the clay surface by surfactants changes the adsorption properties towards organic gases and liquids (Barrer & Millington 1967; Slabaugh & Hanson 1969; Stul *et al.* 1983*a*, *b*; chromatographic behaviour: Barrer & Hampton 1957; Taramasso *et al.* 1971; McAtee & Robbins 1980).

The concept of pillared clays was first used by Barrer & MacLeod (1955) to induce interlayer porosity in montmorillonites by an exchange with tetraalkylammonium ions. Other organic cations that have been used include bicyclic ammonium cations, such as triethylene diammonium ions $HN^+(CH_2CH_2)_3N^+H$ and metal chelate cations. The pillared clays offer new possibilities for heterogeneous catalysis, but sufficient temperature stability often requires pillars other than organic cations. The first pillared clays with poly-condensed Al-ions as pillars and high thermal stability were prepared by Brindley & Sempels (1977). Other inorganic pillared clays can be prepared by hydrolysis of silicon acetylacetonate and niobium and tantalum metal cluster cations (Pinnavaia 1983).

The increased hydrophobicity with increasing loading by surfactants and its effect on the adsorption from binary solutions is illustrated by the following example. The excess isotherm for the binary mixture methanol–benzene on hexadecyl pyridinium montmorillonite (figure 5) is a type IV isotherm that results from the superposition of the individual methanol and benzene isotherms, with distinct plateaux. Both compounds are adsorbed but the amount of benzene almost linearly increases with the extent of surface modification by hexadecylpyridium ions (Dekany *et al.* 1978).

The binding of surfactants by cation exchange on clay surfaces provides a simple possibility for studying hydrophobic interactions from a different point of view. The hydrophobic interactions, particularly effective in biological systems, is based on a distinct association of polar molecules, especially water molecules, in the contact area to alkyl chains or low dielectric

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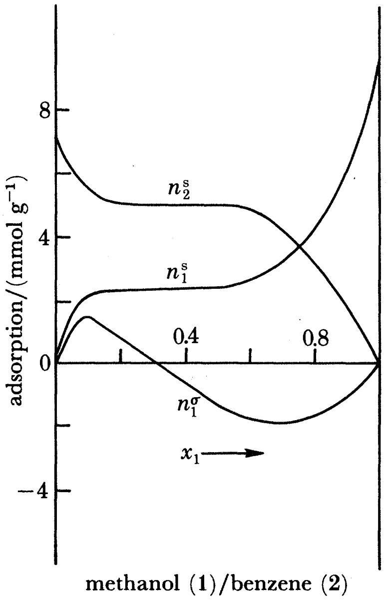

FIGURE 5. Adsorption of methanol (n_1^s) and benzene (n_2^s) from the binary mixture (X_1: mol fraction methanol) on hexadecylpyridinium montmorillonite: n_1^σ: surface excess (composite isotherm), n_1^s, n_2^s: individual adsorption isotherms of methanol (1) and benzene (2) (Dekany *et al.* 1975).

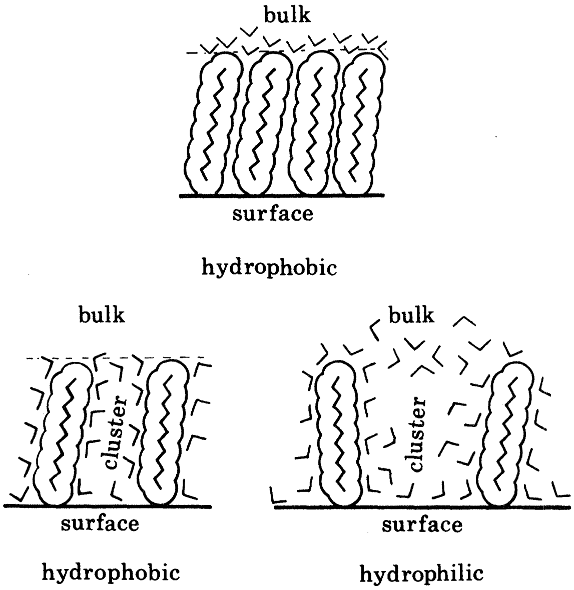

FIGURE 6. Surface hydrophobicity and hydrophilicity.

materials. Polar molecules between alkyl chains on the surface of clay minerals indeed associate to clusters (Lagaly & Witter 1982). The cluster formation of water is even enhanced by influence of the silicate surface. (The uncharged silicate surface is in principle hydrophobic. The hydrophilicity of the clay surface originates from the surface charges and the corresponding gegen ions.) A model was deduced which may explain whether an alkyl chain primed surface is hydrophobic or hydrophilic (figure 6, Lagaly *et al.* 1983). Hydrophobicity does not require the chains to be close-packed, but their distance should not exceed a critical value. Under this

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condition almost all water molecules form clusters between the chains. A discontinuity may be created to the bulk water phase. If the chains are primed more distantly from each other, the discontinuity disappears because the bulk water phase and disordered water molecules penetrate between the water clusters around the chains and the discontinuity disappears.

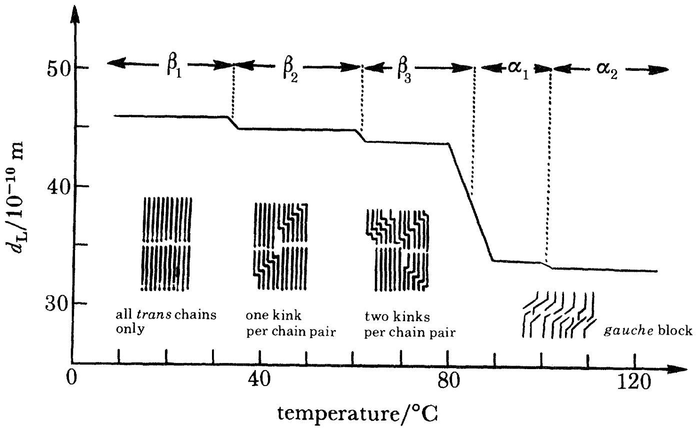

FIGURE 7. Basal spacing changes of alkylammonium Alkanol complexes (schematic) and the corresponding kink block and *gauche* block structures.

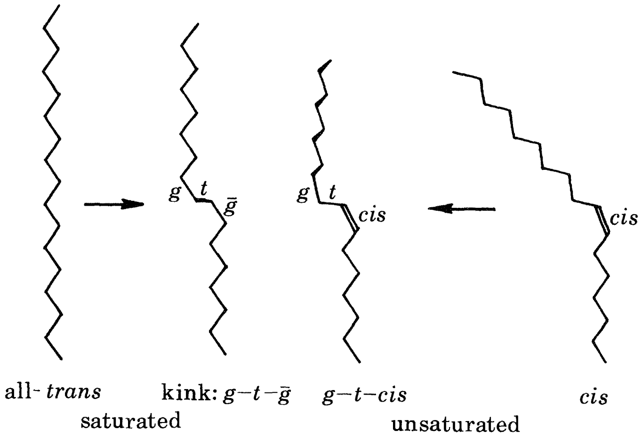

FIGURE 8. Formation of kinks (*gauche*(+)–*trans*–*gauche*(–) conformation) in saturated chains and kink-like *gauche*–*trans*–*cis* conformations in unsaturated chains with *cis*-double bonds.

The liquid clusters on the alkyl chain bearing surface are sensitively influenced by structure-breaking and structure-making ions (figure 4). The structure-breaking power of ions can increase (for example, tetradecylammonium beidellite in water) or decrease the basal spacing (tetradecylammonium vermiculite in DMSO, tetradecylammonium beidellite in ethanol, Lagaly *et al.* 1983). Consequently, the viscosity of organic dispersions of alkylammonium montmorillonites can be strongly influenced by inorganic salts (Sander & Lagaly 1983).

Technical uses

For technical uses organic-activated bentonites are usually prepared from diluted dispersions of sodium bentonite ('alkaline activated bentonite') by addition of alkylammonium salts, for instance dialkyldimethylammonium salts. Depending on the application the salts can also be incorporated in bentonite pastes.

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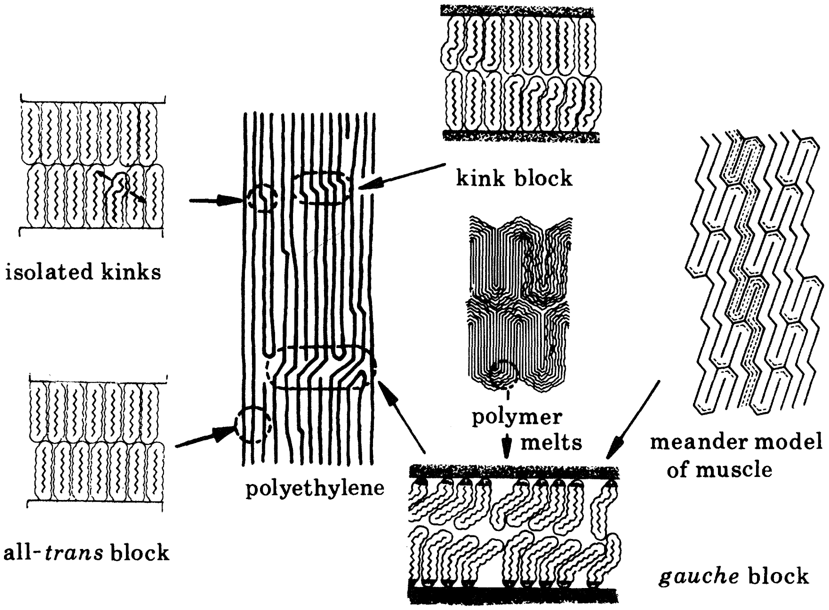

FIGURE 9. Structural elements of crystalline and melted polymers related to the alkylammonium Alkanol silicate complexes.

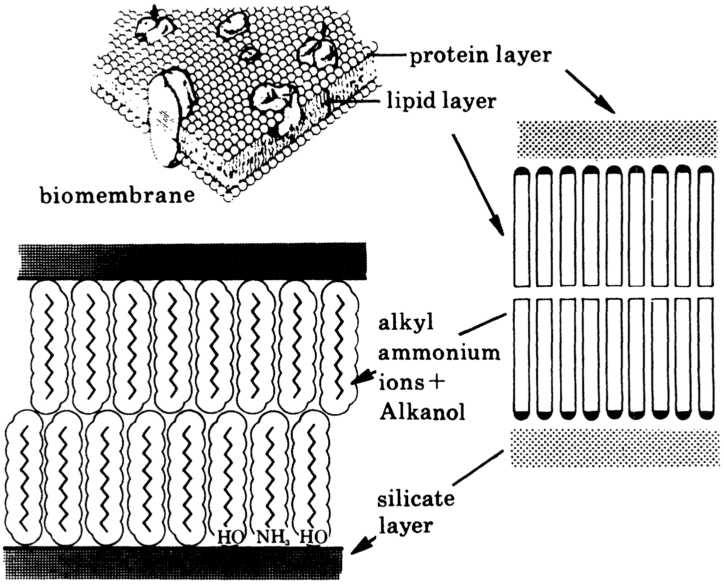

FIGURE 10. Alkylammonium Alkanol silicate complexes as models of the chain aggregation in biomembrane lipid layers.

Hydrophobic bentonites are used purely as thickeners or to produce or improve thixotropic properties (for instance of paints and waxes). Other uses are in the field of gelling agents for lubricants, as binders for water-free foundry sands and as additives in tar, asphalts and bituminous emulsions or in mastics, lutes, putties, waxes, ointments and cosmetic preparation. As fillers and strengthening agents in plastics polymeric compounds are preferred over monomeric surfactants (Lagaly 1984).

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ALKYLAMMONIUM ALKANOL COMPLEXES

The study of interlamellar bimolecular films of alkylammonium ions and long chain alcohol molecules contributed to the present knowledge on conformational changes of lamellar-aggregated alkyl chains. The films are easily prepared by adding long chain alcohols to the alkylammonium derivatives. They undergo a series of phase transitions with rising temperature (Lagaly 1981 *b*). The phase changes are recognized by the stepwise decrease of the basal spacing (figure 7) and are caused by the cooperative formation of kinks in the alkyl chains. The basic reaction is the rotational isomerization of *trans* C–C bonds into *gauche* C–C bonds (figure 8).

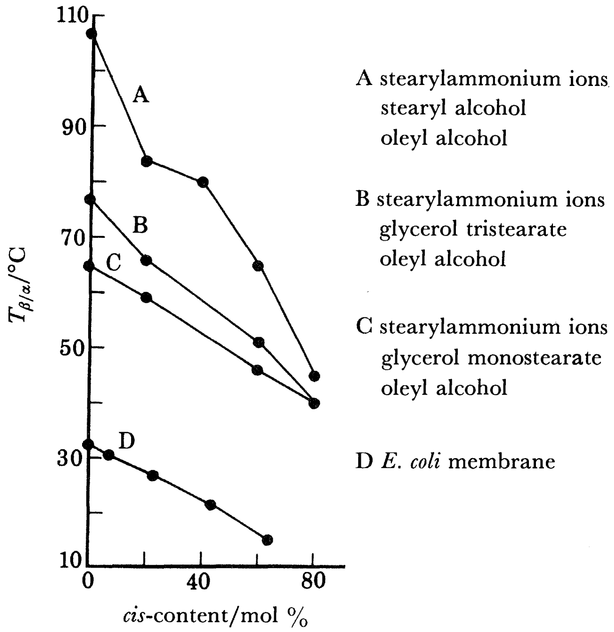

FIGURE 11. Transition temperatures of interlamellar bimolecular films (β–α transition) and of *Escherichia coli* membranes (Overath *et al.* 1971) as a function of unsaturation.

The sequence of kink blocks finally transforms to a sequence of *gauche* blocks. The corresponding changes of entropy and enthalpy make evident that the phase transitions in lamellar aggregations of alkyl chains are sensitively related to the interchain interaction parameters (Lagaly 1976, 1981 *a*; Pechhold *et al.* 1976; Baur 1975).

Figures 9 and 10 illustrate how the bimolecular alkylammonium–alcohol films are modelling the chain aggregation in polymers and in the lipid layer of PLP-biomembranes.

In partially crystalline polymers kinks and kink blocks occur as defects. Gauche blocks are elements of the meander structure postulated for amorphous and melted polymers and the filaments in muscles (Pechhold & Grossmann 1979; Pechhold *et al.* 1973).

Certainly, alkylammonium–alcohol silicate complexes are not models of biomembranes but some properties of the chain aggregation in the lipid layer can be studied. One of the problems rencountered in the studies of PLP-membranes was the stuctural effect of the high amounts of unsaturated alkyl chains with *cis*-configuration. It could be shown (Lagaly *et al.* 1977) that the *cis*-compounds adopt kink-like *cis-trans-gauche*-conformations (figure 8) and in this way are incorporated in the bimolecular film. The temperature of transition $T_{\beta/\alpha}$ from kink blocks to

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gauche blocks decreases with increasing content of *cis*-chains (figure 11). The decrease is similar to that occurring in *Escherichia coli* membranes and similarity increases when stearyl alcohol is replaced by glycerol monostearate.

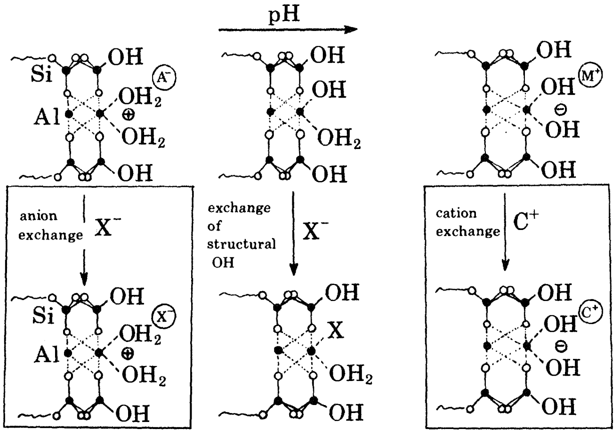
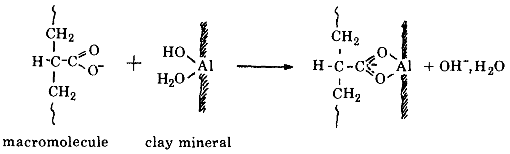
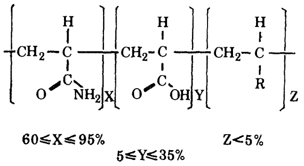


Figure 12. pH-dependent reactions on the edge surfaces.



binding carboxylate groups on the edge surface



hydrolysed polyacrylamide

Figure 13. Binding of polyacrylamide by exchange of structural OH-groups on the edge surfaces (Siffert & Espinasse 1980).

A hypothetical model for information transfer within the lipid layer by cooperative phase transitions was suggested by Lagaly *et al.* (1977). It seems that *gauche*-conformations play a role as orientation defects on the protein–lipid contacts within the lipid layer and on splay deformations in ripple membrane structures.

INTERACTIONS WITH EDGE SURFACES

The interaction of organic compounds with the edge surface is presently not understood in full detail. The difficulties arise from the pH-dependent variation of the surface structure (figure 12). The charge of the surface changes from positive to negative within the pH range 4–5 (Rand *et al.* 1980) and consequently anion exchange changes to cation exchange.

Cationic and anionic surfactants are thus adsorbed in different ranges of pH (Hower 1970).

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The corresponding changes of the zeta-potential and the type of particle–particle interactions (peptization, coagulation, sediment volumes) of kaolinite were studied by Welzen *et al.* (1981).

Besides the binding as gegen ions organic compounds can also be bound by exchanging structural OH-groups (Siffert & Espinasse 1980). The exchange of structural OH-groups likely becomes effective near the point of zero charge (p.z.c.), that is, when the charge density of the surface is low. The expected pH-dependency with adsorption maxima around the p.z.c. were indeed observed for the adsorption of the nucleotide ATP on smectites (Herrmann & Lagaly 1984).

Exchange of structural OH-groups by chelated carboxylate groups seems to be the main mechanism for binding polyanions like partially hydrolysed polyacrylamide on the edge surface (figure 13, Espinasse & Siffert 1979). Polyanions are widely used as flocculation agents and are more effective than polycations and neutral macromolecules.

The interaction of clays with polymers shows very special features and is discussed in a separate paper (Lagaly 1984).

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Discussion

R. M. BARRER, F.R.S. (*Chemistry Department, Imperial College, London SW7, U.K.*). In connection with the uptake of polymers by smectites does Professor Lagaly know whether it has proved possible first to disperse the lamellae of the mineral in water and then, by quickly adding a polymer solution, to catch the lamellae in their dispersed state and so to augment both rate and amount of uptake?

G. LAGALY. This is indeed possible and has recently been proved by an interesting paper of N. Larsson and B. Siffert (*J. Colloid Interface Sci.* **93**, 424–431 (1983)). Lysoszyme molecules are adsorbed by this disaggregation–reaggregation mechanism without any diffusion in lateral direction. So, a complete saturation is achieved which very likely would not be attained by lateral diffusion.

K. GOULDING (*Soils and Plant Nutrition Department, Rothamsted Experimental Station, Harpenden, Hertfordshire, AL5 2JQ, U.K.*). Are the intercalated charged organic molecules easily replaced by inorganic cations?

G. LAGALY. They cannot be replaced. Even uncharged molecules are often displaced with difficulty, particularly if they are polymeric molecules. There are very few studies concerning the desorption of intercalated organic materials.