

Chapter 7.3

CLAY MINERAL ORGANIC INTERACTIONS

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Clay minerals can react with different types of organic compounds in particular ways (Fig. 7.3.1). Kaolin species (kaolinite, nacrite, and dickite) adsorb particular types of neutral organic compounds between the layers. The penetration of organic molecules into the interlayer space of clay minerals is called intercalation. Intercalated guest molecules can be displaced by other suitable molecules.

A broader diversity of reactions characterises the behaviour of 2:1 clay minerals. Water molecules in the interlayer space of smectites and vermiculites can be displaced by many polar organic molecules. Neutral organic ligands can form complexes with the interlayer cations. The interlayer cations can be exchanged by various types of organic cations. Alkylammonium ions, in industrial applications mainly quaternary alkylammonium ions, are widely used in modifying bentonites. The other important group of organic compounds are cationic dyes and cationic complexes. The interaction of clay minerals with different types of polymers including polypeptides and proteins was intensely studied many decades ago and recently seems to revive.

Grafting reactions, i.e. forming covalent bonds between reactive surface groups and organic species is an important step to hydrophobise the surface of clay mineral particles. The 2:1 clay minerals provide the silanol and aluminol groups on the edge surface for grafting reactions. The hydroxyl groups on the interlayer surface of kaolinite are accessible to the grafting agents when the interlayer space is expanded by intercalation.

Clay mineral–organic reactions are used to identify kaolinites and 2:1 clay mineral, to modify the surface character of clay mineral particles and the colloidal behaviour of clay dispersions in industrial applications. The organic derivatives are suitable adsorbents and useful in pollution control. Clay mineral–dye interactions, clay mineral–hybrid film formation, and clay polymer nanocomposites are actual

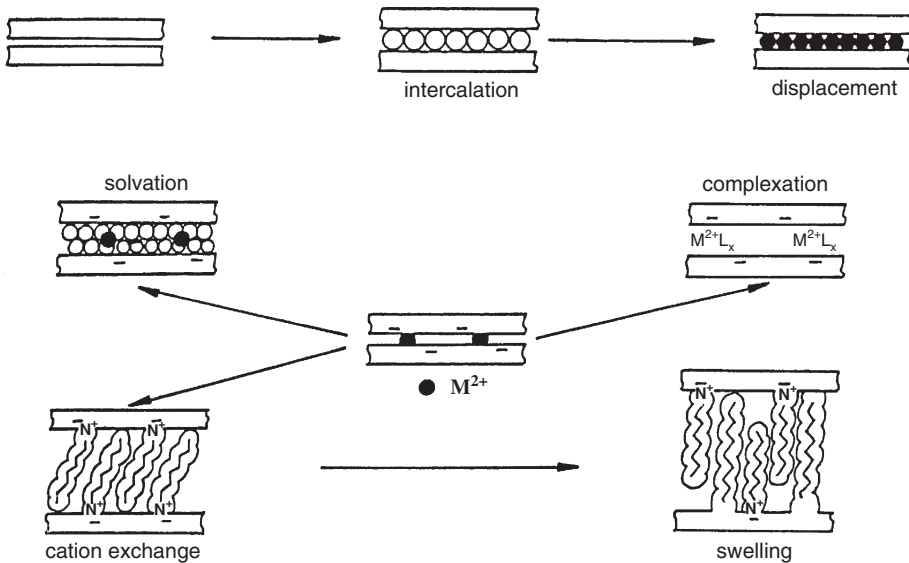


Fig. 7.3.1. Interlayer reactions of 1:1 and 2:1 clay minerals. From Jasmund and Lagaly (1993).

topics in material science. These aspects of clay–organic interaction are discussed in more detail in Chapters 5, 10.1, 10.2, 10.3, 11.1 and 11.2.

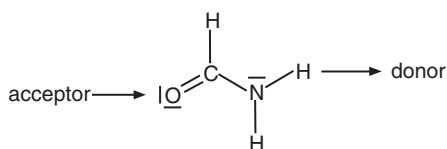
7.3.1. INTERCALATION REACTIONS OF KAOLINITES

Among 1:1 clay minerals only the kaolin species intercalate various organic molecules (Fig. 7.3.1); serpentines are non-reactive.

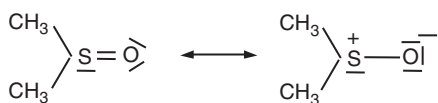
A. Type of Guest Compounds

As the layers in kaolinite and its polytypes are held together by hydrogen bonds and dipole–dipole interactions in addition to the van der Waals forces, the organic guest compounds that are directly intercalated are divided into three groups (Weiss, 1961; Weiss et al., 1963a, 1963b, 1966; Olejnik et al., 1970):

1. Compounds that form hydrogen bonds like hydrazine, urea, and formamide. To break the hydrogen bonds between the layers, the guest molecules must contain two separated groups to accept and donate hydrogen bonds, like acid, amides, and urea (Scheme I): the carbonyl group accepts and the amide group donates hydrogen bonds. Alcohol molecules are not directly intercalated because the OH group combines donor and acceptor properties.



Scheme I.



Scheme II.

2. Compounds with high-dipole moments like dimethyl sulphoxide (DMSO) and pyridine-*N*-oxide (Scheme II).

3. Potassium, rubidium, caesium, and ammonium salts of short-chain fatty acids (acetates, propionates, butyrates, and isovalerates) (Wada, 1961; Weiss et al., 1966). The reason for this reaction is still unclear. The intercalation of cadmium cysteine complexes into a low-ordered kaolinite may belong to this group of reactions (Benincasa et al., 2002).

Compounds with bulky substituents are not intercalated, but many are intercalated by displacement or entraining reactions.

Intercalation reactions were also reported for nacrite and dickite (Weiss and Orth, 1973; Weiss et al., 1973; Adams and Jefferson, 1976b; Adams 1978b; Adams, 1979; Ben Haj Amara et al., 1995).

Most intercalated guest compounds are easily desorbed by washing with water or by heating. As the state with the maximum number of intercalated molecules is only achieved in the presence of an excess of guest molecules (outside of the interlayer space), the analytical composition of many intercalates can only be approximately determined. Removing the excess of guest molecules (by washing or heating) is accompanied by desorption of a certain amount of intercalated molecules. High temperature X-ray studies of dimethyl sulphoxide–kaolinite indicated the thermal desorption of the sulphoxide occurred over several stages up to 300 °C (Franco and Ruiz-Cruz, 2002). The potassium acetate–kaolinite complex was stable up to 298 °C. At this temperature the intercalated potassium acetate melted. The following decomposition took place in two stages at 430 °C and 480 °C. Dehydroxylation occurred at a lower temperature than for the pure kaolinite (Gábor et al., 1995).

B. Mechanism of Intercalation

Intercalation compounds are usually prepared by reacting the kaolinite with the guest molecules in the form of liquids, melts, or concentrated solutions, often at about 60–80 °C. Intercalation is a slow process that often requires several days

(Table 7.3.1; Fig. 7.3.2). The reaction rate depends not only on the type of guest compound, temperature, and concentration (if solutions are used) but also on the type of kaolinite and the particle size. It can also depend on the host–guest mass ratio.

The degree of reaction is calculated from the intensities of the (00*l*) reflections of the unreacted kaolinite, I_K , and the intercalation compound, I_I :

$$\alpha = I_I / (I_K + I_I)$$

Table 7.3.1. Reaction conditions and basal spacing of a few kaolinite intercalation compounds

Guest compound	Basal spacing (nm)	Reaction conditions
None	0.71	
Formamide	1.01	4 days, 60 °C
Hydrazine hydrate	1.04	1 day, 60 °C
Urea*	1.07	8 days, 60–110 °C
<i>N</i> -methylformamide	1.08	2 days, 60 °C
Dimethyl sulphoxide	1.12	30 h, 50 °C
	1.12	20 min, 150 °C*
Potassium acetate*	1.40	1 day, 65 °C, pH = 8
Ammonium acetate*	1.41	20 days, 20 °C, pH = 8–9

From Weiss et al. (1966); Weiss and Orth (1973); Vempati et al. (1996)

*In saturated aqueous solutions.

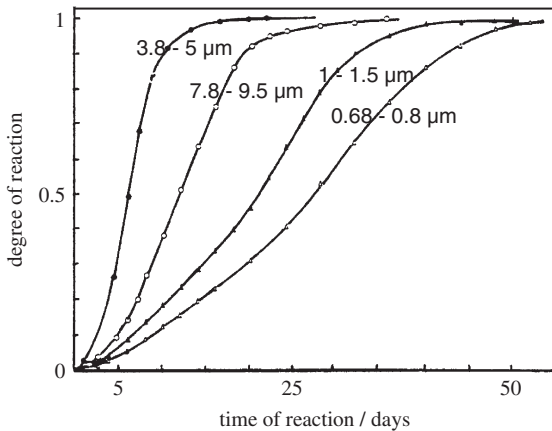


Fig. 7.3.2. Intercalation of urea (saturated aqueous solution at 65 °C) into kaolinites of different particle sizes (Weiss et al., 1970). From Jasmund and Lagaly (1993).

The degree of reaction defined in this way can differ from the effective degree of reaction because the influence of the Lorentz and Polarization factor, the possible effects of distortion of the layers (see below), and interstratification are not considered.

The degree of reaction as a function of time often increases in the form of an S-shaped curve, and the reaction rate obeys the Avrami–Erofeev equation for a two-dimensional phase boundary reaction and can eventually change into a two-dimensional diffusion controlled reaction (Fenoll Hach Ali and Weiss, 1969). Many kaolinites do not reach quantitative reaction, i.e. $\alpha = 1$.

Weiss and co-workers concluded from neutron scattering data that the reaction is started by the migration of protons or re-orientation of OH groups under the influence of the dipole moment of the guest molecules adsorbed at the external basal plane surfaces (Weiss et al., 1981; see also Lagaly, 1984, 1986a). This causes an elastic deformation of the kaolinite layer near the basal plane that opens the interlayer space. Electron resonance spectroscopy revealed that the kaolinite layer is deformed by the intercalated guest compounds (Lipsicas et al., 1986). The effect was stronger for DMSO than for *N*-methylformamide. A certain deformation and disorder of the layers was retained after desorption of the guest molecules.

After nucleation, intercalation proceeds as a co-operative process (Fenoll Hach Ali and Weiss, 1969). The first guest molecules can only penetrate between the silicate layers when one or both layers begin to curl (Fig. 7.3.3). This creates a zone of deformation the extent of which depends on the elastic properties of the silicate layer. After the nucleation step (*N* in Fig. 7.3.3) the layer rolls up and promotes the penetration of guest molecules at the neighbouring sites along the edge *N*. Thus, cooperativity is caused by the process in which a few molecules succeed in rolling up the layer so that a large number of guest molecules can rapidly penetrate between layers, and the reaction front moves to the centre of the particle. The reaction front moving

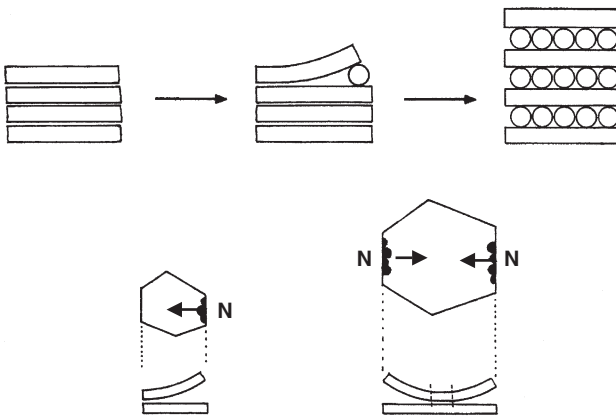


Fig. 7.3.3. Mechanism of intercalation. N nucleation sites, arrow: moving reaction front.

in the direction of the arrow (Fig. 7.3.3) exerts a geometrical constraint to nucleation at other sites. Only when the distance of edges from the reaction front starting at N exceeds a critical value (which depends on the elasticity moduli of the layer) can nucleation start at these edges simultaneously with nucleation at edge N. Thus, nucleation at any site of small crystals cannot occur independently of the nucleation at other sites. In contrast, nucleation at large crystals can start simultaneously at several edges. As a consequence, smaller particles react more slowly than larger ones, contrary to the general rule in solid-state chemistry (Fig. 7.3.2). More recently, Uwins et al. (1993) observed that the intercalation of *N*-methyl formamide into kaolinites was strongly reduced for particles < 0.4 μm and concluded that particle size is a more significant controlling factor for intercalation than defect distributions.

Cooperativity was also observed with other types of layer compounds (see also Section 7.3.8) (Lagaly, 1986a). For instance, cation-exchange reactions of micas revealed cooperative effects (Mortland and Lawton, 1961; Graf von Reichenbach and Rich, 1969; Sawhney, 1972; Graf von Reichenbach, 1973; Ross and Rich, 1973). While formation of superstructures (regular interstratification) by cation-exchange reactions can be related to (negative) cooperativity it may also be produced by unsymmetrical charge distributions (Lagaly, 1986a).

The rate of intercalation can be strongly dependent on the liquid structure of the guest molecules (Olejnik et al., 1970), for example, on the mass ratio of DMSO to kaolinite. Intercalation rate is at maximum when the amount of DMSO corresponds to a monomolecular layer on the external surface. The self-preservation of the strongly organised liquid DMSO retards the entry of the DMSO molecules between the layers. Therefore, soluble salts that change the liquid structure can influence the reaction rate (see also Section 7.3.6).

Desorption of the intercalated guest molecules can be a complex process. A two-dimensional contracting-circle mechanism was consistent with the results of the thermal desorption of dimethyl sulphoxide, provided the nucleation process was not instantaneous (Adams and Wautl, 1980). The activation rate was very high (~ 105 kJ/mol dimethyl sulphoxide), indicating that the rate-determining step is complex and cannot be interpreted by assuming that single guest molecules are desorbed as in the case of *N*-methylformamide-kaolinite (Adams, 1978a).

Intercalation into kaolin minerals can split larger particles into thinner lamellae. The extreme stability of Chinese eggshell porcelain results from delamination of the kaolinite particles by urea (Weiss, 1963a). Even weak mechanical forces can delaminate the particles of intercalated kaolinite to such an extent that the lamellae roll up forming halloysite-type structures (Weiss and Russow, 1963; Poyato-Ferrera et al., 1977; Gardolinski and Lagaly, 2005b). Colloidal dispersions of finest kaolinite particles were prepared by the reaction of kaolinite with DMSO in the presence of ammonium fluoride (Lahav, 1990; Chekin, 1992). A certain exchange of hydroxyl ions by fluoride ions reduces the number of hydrogen bonds and promotes delamination.

Kaolinitic claystones (tonsteins, flint clays) are difficult to disaggregate. Immersion in hydrazine hydrate disaggregates most claystones as a consequence of

the swelling pressure developed during intercalation. Hydrazine hydrate works more quickly and efficiently than DMSO (Weiss and Range, 1970; Triplehorn et al., 2002).

C. Structure of Intercalation Complexes

Infrared, Raman, and NMR studies are useful to derive the arrangement and orientation of guest molecules between the silicate layers (Johnston et al., 1984; Duer and Rocha, 1992; Duer et al., 1992; Hayashi, 1995, 1997; Frost et al., 1997, 1998a, 1998b). The intensity of the OH stretching modes of the inner surface hydroxyl groups might serve as a quantitative measure of the number of the interlayer OH groups interacting with the guest molecules (Frost et al., 1998c). X-ray diffraction studies and one-dimensional Fourier projections were reported for kaolinite intercalated with dimethyl sulphoxide, *N*-methylformamide, imidazole, pyridine-*N*-oxide, picoline-*N*-oxide (Weiss et al., 1963a, 1963b, 1966, 1973; Weiss and Orth, 1973). The first three-dimensional crystal structure was solved for dickite intercalated with formamide and *N*-methylformamide (Adams and Jefferson, 1976b; Adams 1978b, 1979). A neutron powder diffraction study revealed the hydrogen bonding system in formamide-kaolinite (Adams et al., 1976a).

D. Displacement Reactions

Almost all intercalated molecules can be displaced by other polar molecules, even by molecules that are not directly intercalated. A large number of intercalation compounds were prepared in this way (Weiss et al., 1966; Olejnik et al., 1970; Gardolinski et al., 2000; Kelleher and O'Dwyer, 2002). Suitable starting materials are DMSO and ammonium acetate kaolinite. For example, ammonium acetate was displaced by *N,N*-dimethyl formamide, *N,N*-dimethyl urea, and pyridine (Weiss et al., 1966). Long-chain alkylamines were intercalated by displacement of ammonium acetate, and considerably increased the basal spacing (2.2 nm for butylamine, 5.8 nm for octadecylamine) (Weiss et al., 1966). Intercalated ammonium propionate obtained by the displacement of ammonium acetate combined in the interlayer space with diaminohexane to the corresponding amide (Seto et al., 1978a, 1978b). Acrylamide intercalated by displacement of *N*-methylformamide was polymerised by heating to 300 °C for 1 h (Komori et al., 1999). Poly(β -alanine)-kaolinite was prepared by the polycondensation of intercalated β -alanine, with ammonium acetate-kaolinite as the precursor material (Itagaki et al., 2001).

The kaolinite methanol complex is a highly versatile intermediate/intermediary for displacement reactions (Komori et al., 1999). The methanol intercalate itself is prepared by displacement of *N*-methylformamide. As an example, methanol was displaced by ortho- and para-nitroaniline (not by the meta-isomer!). These intercalates may be of interest for future research because they exhibit second-harmonic generation (Takenawa et al., 2001).

Several guest molecules intercalated into kaolinite can be replaced by water molecules (basal spacing 1.0 nm), simply by washing with water (Wada, 1965). A part of the water molecules are keyed into the ditrigonal holes, while the remaining water molecules are more mobile (Costanzo et al., 1984; Lipsicas et al., 1985). The hydrates of different types of kaolinites differ in stability and not all types of kaolinites form hydrates (Range et al., 1968, 1969; Bartz and Range, 1979; Lipsicas et al., 1985). In many but not all kaolinites the water molecules can be replaced by other guest compounds (Costanzo and Giese, 1990). Wada (1959a, 1959b, 1964) earlier reported the penetration of salts into the interlayer space of halloysite.

E. Entraining Reactions

Many non-reactive compounds are intercalated in the presence of guest molecules that directly penetrate into the interlayer space. Weiss et al. (1963a) studied the intercalation of several potassium salts of organic acids. As long as hydrazine hydrate was present, the basal spacing of the kaolinite was similar to the hydrazine intercalation compound (1.04 nm). When hydrazine was removed by desorption in air, the spacing typical of the entrained compounds developed, often distinctly higher than 1.04 nm.

This type of reaction is distinguished from the displacement reaction. Entraining occurs when reactive guest molecules open the interlayer space so that non-reactive compounds simultaneously penetrate between the layers.

F. Intercalation of Alkali Halogenides

An interesting group of reactions is the intercalation of alkali halogenides (Wada, 1964). One possible way to intercalate inorganic salts is the displacement of DMSO or ammonium acetate by the salts (Weiss et al., 1966; Yariv et al., 2000). CsCl and CsBr intercalated kaolinite was also prepared by grinding the kaolinite-salt mixtures with a limited amount of water or by evaporating dispersions of kaolinite in aqueous caesium salt solutions, followed by ageing in humid air (Michaelian et al., 1991a, 1991b; Yariv et al., 1991, 1994; Thompson et al., 1993; Lapidés et al., 1994, 1995).

G. Grafting Reactions

Grafting reactions, i.e. attachment of organic groups by covalent bonds, is an important step to make clay minerals compatible with organic polymers (van Meerbeek and Ruiz-Hitzky, 1979). For practical applications, kaolinites are modified, for instance, with alkoxy aluminium acrylates and alkoxy titanium acrylates (Solomon and Hawthorne, 1983). In these cases, only the silanol groups at the crystal edges react with the organic agents.

Grafting reactions between the layers require the formation of an intercalation complex as the intermediate step (Gardolinski and Lagaly, 2005a). Dimethyl

sulphoxide–kaolinite and *N*-methylformamide–kaolinite reacted with methanol at 150–270 °C and yielded products in that every third OH group of the interlayer aluminol groups was replaced by methoxy groups (Tunney and Detellier, 1996).

Displacement of DMSO by ethylene glycol yields an ethylene glycol intercalate with a basal spacing of 1.08 nm. Refluxing the dimethyl sulphoxide–kaolinite with dry ethylene glycol yielded a well-ordered, thermally robust derivative with a basal spacing of 0.94 nm where the glycol was grafted to the interlayer aluminol groups (Tunney and Detellier, 1994).

Phenylphosphonium acid underwent a topotactic reaction with the aluminol groups of kaolinite and halloysite during refluxing in water-acetone at 70 °C (Breen et al., 2002). In an acidic medium, phosphates, especially in the presence of potassium ions, decompose clay minerals through the formation of aluminium phosphates like taranakite (Weiss et al., 1995). The reaction with several organo-phosphates like trimethyl phosphate or phenyl phosphonates did not yield the intercalation compound, but decomposed the kaolinite structure under formation of metal organo-phosphonates (Sánchez-Camazano and Sánchez-Martín, 1994; Guimarães et al., 1998; Trobajo et al., 2001; Wypych et al., 2003; Gardolinski et al., 2004).

H. Differentiation of Kaolinites

Many kaolinites do not react quantitatively with reactive guest molecules such as DMSO or hydrazine, and the (001) reflection of non-reacted kaolinite remains visible, i.e. $\alpha < 1$, even after prolonged reaction periods (Fig. 7.3.4). A possible explanation is that these kaolinites are mixtures (or zonal structures) of kaolinites of different reactivity. Three types of kaolinites are classified (Fig. 7.3.4) (Range et al., 1968, 1969; Fernandez-Gonzales et al., 1976; Lagaly, 1981a):

Type A is the most reactive species. It intercalates dimethyl sulphoxide, urea, and many other compounds.

Type B reacts with DMSO but not with urea.

Type C is non-reactive.

Measuring the degree of reaction with DMSO and urea allows the determination of the mass fractions of the three types that make up the investigated kaolin sample.

Many kaolins are in fact composed of different kaolinites (Keller and Haenni, 1978; de Luca and Slaughter, 1985; Lombardi et al., 1987; Plançon et al., 1988). However, different reactivity may be related to defects like the presence of a few interlayer cations compensating sporadically occurring charges of the silicate layers (Range et al., 1969). The difficulty of intercalation of a kaolinite from Birdwood, South Australia, was related to a highly disordered kaolinite coating the particles of highly ordered kaolinite (Frost et al., 2002). All types of kaolinites are expanded by hydrazine-DMSO after they were ground with dried CsCl (Jackson and Abdel-Kader, 1978; Calvert, 1984).

The lattice expansion with DMSO (or hydrazine hydrate), if necessary after grinding with CsCl, is used for X-ray identification of kaolinites and to distinguish

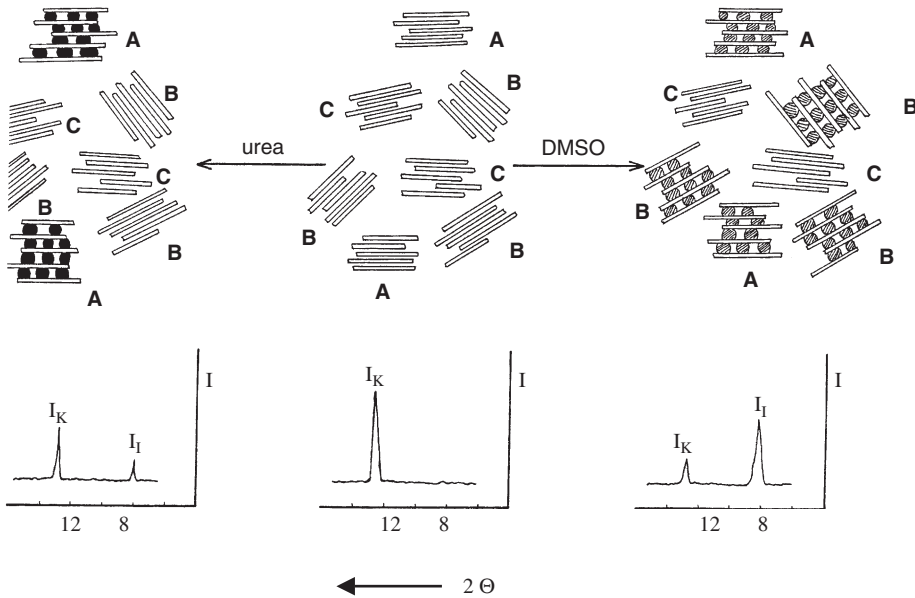


Fig. 7.3.4. Reaction of a kaolin sample consisting of three types of kaolinites (reaction types A, B, and C) with dimethyl sulphoxide (DMSO) and urea (see text). Fernandez-Gonzales et al. (1976).

them from chlorites that show the (002) reflection at 0.71 nm. Dehydrated halloysite and kaolinite are distinguished by the rate of reaction with formamide. Halloysite reacts within about 1 h, kaolinite expands after 4 hs. This reaction can also be used to determine the halloysite content (Churchman et al., 1984; Theng et al., 1984; Churchman, 1990). Halloysite may also be identified by the reaction with ethylene glycol. The response to ethylene glycol solvation involves a decrease in the intensity of the 0.72 nm reflection but an increase in the intensity of the peak at ~ 0.358 nm (MacEwan effect) and is related to an interstratification effect (Hillier and Ryan, 2002).

7.3.2. REACTIONS OF 2:1 CLAY MINERALS

The adsorption of neutral molecules on smectites is driven by various chemical interactions: hydrogen bonds, ion-dipole interaction, co-ordination bonds, acid-base reactions, charge-transfer, and van der Waals forces (Weiss, 1963b; Theng, 1974; Lagaly, 1984, 1987a; Jasmund and Lagaly, 1993; Yariv and Cross, 2002). Polar molecules such as alcohols, amines, amides, ketones, aldehydes, and nitriles form intercalation complexes with smectites. Even acids are intercalated (Brindley and Moll, 1965; Yariv and Shoval, 1982; Ogawa et al., 1992c). Guest compounds can be intercalated from the vapour, liquid, and solid state. When intercalated from solutions, solvent molecules are generally coadsorbed in the interlayer space.

Guest molecules may be intercalated in dried clay minerals or may displace the water molecules of hydrated smectites and vermiculites. The displacement of interlayer water molecules depends on the HSAB character¹ of the interlayer cations and the interacting groups of the guest molecules. Water molecules around hard cations like Na^+ , Mg^{2+} , and Ca^{2+} are displaced only by $\text{HO}-$ or $\text{O}=\text{}$ containing compounds but not by amines. In contrast, amines as soft bases displace water molecules from soft interlayer cations like Cu^{2+} and Zn^{2+} .

Intercalation of neutral compounds into dried montmorillonites and vermiculites is not necessarily accompanied by cation movement midway between the silicate layers (outer-surface complexes). The cations can remain in contact with one silicate layer, i.e. the oxygen atoms of the silicate surface occupy the coordination sites of the cations (inner-surface complexes). However, little relationship was found between the intercalation and bulk properties of the liquid guest molecules (Berkheiser and Mortland, 1975).

Many large molecules are not directly intercalated, but can be introduced by stepwise expansion of the interlayer space (propping-open procedure). For instance, the ethanol intercalation complex of Ca^{2+} montmorillonite was used as a starting material to prepare the butanol and hexanol intercalates. The hexanol complex was then used as a base to intercalate longer chain alkanols up to octadecanol (Brindley and Ray, 1964). Fatty acids up to 18 carbon atoms were intercalated into Ca^{2+} montmorillonite starting from the hexanol or octanol intercalates. Shorter chain fatty acids with less than 10 carbon atoms could be directly intercalated because they expanded only to basal spacings < 1.7 nm (Brindley and Moll, 1965).

Colour often changes when clay minerals with transition metal ions on exchange positions react with aromatic ligands. UV-Vis, IR, and ESR spectroscopic techniques are useful tools to investigate the cation-ligand interactions (Farmer and Russell, 1967; Yariv and Cross, 2002). The relationship between the infrared absorption frequency and the polarisation by the interlayer cations confirms the importance of the ion-dipole interactions. As an example, the frequency shift of the CN stretching vibration of acrylonitrile indicates the strength of the cation-nitrile interactions (Yamanaka et al., 1974). Unlike other ligands the CN stretching vibration of benzonitrile shifted to larger wave numbers when the polarising power of the interlayer cations increased (Serratosa, 1968).

The solid-solid reaction between 2,2'-bipyridine and montmorillonite yielded metal-(2,2'-bipyridine) complexes in the interlayer space. The products were identical to those prepared by cation-exchange reactions of montmorillonite with pre-formed complex cations (Ogawa et al., 1991).

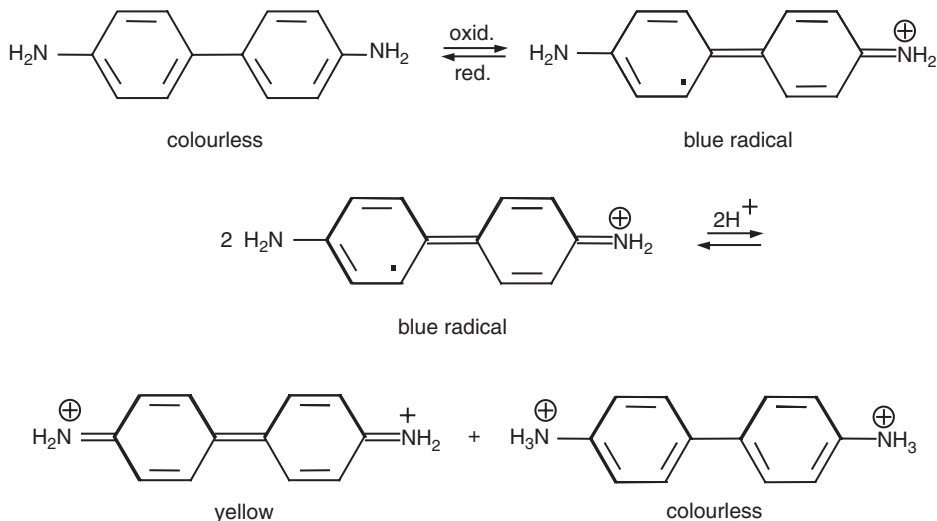
A few complexes that were not stable in homogeneous solution were found to be stable in the interlayer space. Benzene vapour reacts with copper(II)-montmorillonite and hectorite by displacing a part of the hydration water. In these yellow

¹Concept of hard and soft acid and bases, see Textbooks of Inorganic Chemistry (see also (Auboiroux et al., 1998)).

complexes, the π electrons of benzene interact with the copper ions. Complete removal of the interlayer water yields red benzene complexes by one-electron transfer from benzene to the interlayer cation, and the aromaticity of benzene is lost. Such complexes were also formed with a few other aromatic compounds and also with Fe^{3+} and VO^{2+} interlayer cations (Doner and Mortland, 1969; Pinnavaia and Mortland, 1971; Rupert, 1973; Pinnavaia et al., 1974; see also Lagaly, 1984).

Other well-known species that undergo charge transfer reactions with the clay mineral layers are benzidine and strongly electron-accepting species like tetracyanoethylene. Electron transfer from the diamine to the clay mineral produces the blue monovalent radical cation (Scheme III) (Theng, 1971). The electron acceptors are Lewis acid sites, mainly Fe^{3+} ions in structure. Octahedrally coordinated aluminium ions at the edges only act as Lewis acid sites when coordinated OH or OH_2 groups are desorbed in the form of water (see discussion below). The radical cation, which is unstable in a homogeneous solution, is stabilised by π electron interactions with the oxygen atoms of the silicate layer (Yariv et al., 1976). When pH of the dispersion is below ~ 2 , the blue radical cation disproportionates into the yellow divalent radical cation and the colourless benzidinium dication (Lahav, 1972; Furukawa and Brindley, 1973; Soma and Soma, 1988). Hendricks and Alexander (1940) proposed this colour reaction as a qualitative test of montmorillonites.

Another blue dye–clay mineral complex is the famous Maya blue. It can be prepared by a solid–state reaction between indigo and sepiolite or palygorskite with subsequent heating to 120°C (sepiolite) and 150°C (palygorskite). The indigo molecules are attached at the openings of the tunnels and are anchored by hydrogen bonds to the silanol groups projecting out from the edges of the tunnels (van Olphen,



Scheme III.

1966; Hubbard et al., 2003). The unusually radiant colour of the ancient Maya blue is probably related to the presence of iron and iron oxide nanoparticles (Polette et al., 2002).

The arrangement and orientation of the intercalated molecules depend not only on the type of bonding (un-directed for ion–dipole interactions, directed for all types of coordination bonds), the polarisation power of the cations, i.e. the size and charge of the cations, the properties of the guest molecules, but also on the association tendencies of the guest molecules and their van der Waals interaction with the silicate layer. The structure of the intercalation compounds is often derived by considering the size and shape of the guest molecules and the basal spacing. The orientation of several intercalated species was derived from anisotropic infrared spectra, for instance of pyridine (Serratosa, 1966) and benzonitrile (Serratosa, 1968). More precise information is obtained from one-dimensional electron density projections (Fourier analysis of the $(00l)$ reflections). Oriented films are often used in such studies.

Studying homologous series of adsorptives such as alkanols and alkylamines allows the arrangement of the intercalated molecules to be derived from the changes of the basal spacing with the alkyl chain length. A linear increase of the basal spacing with the alkyl chain length, for instance observed for *n*-alcohols and *n*-alkylamines, is interpreted by assuming paraffin-type mono- or bi-layer arrangements, and the mean tilting angle is derived from the increase of the basal spacing per C–C bond (Brindley and Ray, 1964; Brindley and Moll, 1965; Brindley, 1965). The derived model is correct when a good agreement between the calculated and observed basal spacings is reached by considering the position of the polar end groups and the van der Waals distance between the CH₃ groups and the silicate layer (for monolayers) or between the methyl end groups midway in the interlayer space (for bilayers). Neglecting these distances can lead to unrealistic models.

The arrangement and orientation of intercalated long chain compounds is therefore decisively dependent on the van der Waals energy between the alkyl chains (Sections 7.3.3, and 7.3.6). This strong interaction can shift the polar end groups out of the positions for optimal hydrogen bond formation. As a consequence, the orientation of guest molecules with short alkyl chains is mainly determined by the interactions of the polar groups with the silicate layer, whereas the increased van der Waals energy forces longer chain compounds into paraffin-type arrangements. An example is the transition from flat-lying fatty acids into the paraffin-type structure when the number of carbon atoms exceeds nine (Brindley and Moll, 1965).

The interlamellar adsorption of methanol on Li⁺- and Ca²⁺-montmorillonite illustrates the interplay of the ion–dipole interaction between the alcohol molecules and the interlayer cations with the association tendency of the guest molecules (Annabi-Bergaya et al., 1981). In the presence of lithium ions, the arrangement of methanol molecules in zigzag chains is similar in structure to solid methanol (Fig. 7.3.5). The strong polarising power of calcium ions impedes the association of the methanol molecules and leads to the formation of a strong solvation shell around the cations.

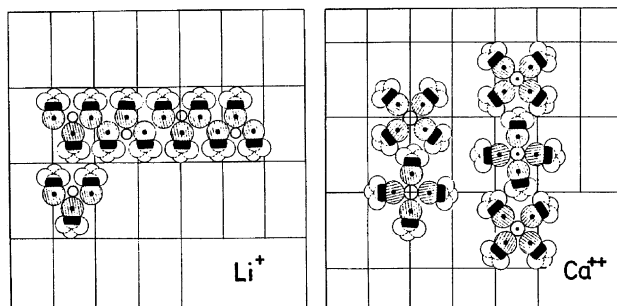


Fig. 7.3.5. Idealised arrangement of methanol molecules in the interlayer space of Li^+ -montmorillonite and Ca^{2+} -montmorillonite. From Annabi-Bergaya et al. (1981).

Intercalation of ethylene glycol (1,2-ethanediol) and glycerol (1,2,3-propanetriol) in expanding 2:1 clay minerals is widely used for routine identification of montmorillonite and vermiculite (Bradley, 1945; MacEwan, 1946; Walker 1958; Reynolds, 1965; Brindley, 1966). Smectites show basal spacings of 1.70–1.77 nm (Table 7.3.2), which correspond to the bilayer arrangement of the intercalated molecules. Vermiculite can form either mono- or bilayer complexes depending on the type of the interlayer cation and the layer charge. However, clear differentiation of montmorillonite and vermiculite is difficult and requires the determination of the layer charge, for instance by the alkylammonium method (see below). The specific surface area of montmorillonite (internal and external) was measured by glycol adsorption (Moore and Dixon, 1970; Madsen, 1977). The retention of the adsorbed molecules is dependent on the polarising power of the interlayer cations. Multivalent cations with their strong electrostatic field retain larger amounts of the organic compounds than alkali and ammonium ions (Brindley, 1966).

The intercalation of macrocyclic polyethers into smectites was investigated by Ruiz-Hitzky and co-workers (Ruiz-Hitzky and Casal, 1978; Aranda et al., 1994; Ruiz-Hitzky et al., 2001). These intercalation compounds may be used as solid-electrolytes and ion selective membranes. The interaction between the interlayer cations and the ligands caused different arrangements of the polyether molecules (Fig. 7.3.6).

Aliphatic and aromatic amines can be directly coordinated to the interlayer cations (Scheme IVa) or bound by water bridges (Scheme IVb) (Farmer and Mortland, 1966; Yariv and Heller, 1970; Heller and Yariv, 1970; Cloos et al., 1975; Laura and Cloos, 1975). The type of bonding is mainly determined by the hardness or softness of the cations due to the HSAB concept. While soft cations such as Zn^{2+} , Cd^{2+} , Cu^{2+} , and Ag^+ bind amines directly, water bridges are formed between amines and hard cations (alkali and earth alkali ions, Al^{3+}).² For instance, pyridine is directly

²These cations do not form stable amino complexes in water.

Table 7.3.2. Basal spacing (nm) of 2:1 clay minerals after solvation with ethylene glycol and glycerol (Brindley, 1966; Malla and Douglas, 1987). On the influence of humidity see Hsieh (1989)

Cation	Montmorillonite	Beidellite	Vermiculite	
	$\zeta = 0.3^*$	$\zeta = 0.45$	$\zeta = 0.55$	$\zeta \geq 0.7$
<i>Ethylene glycol</i>				
Lithium	1.69–1.71		1.62	1.60
Sodium	1.69–1.71	1.69	1.63	1.48 [†]
Potassium	1.69–1.71	1.35		1.04
Magnesium	1.69–1.71	1.69	1.63	1.40–1.43
Calcium	1.69–1.71	1.69	1.62	1.56 [†]
Strontium	1.69–1.71		1.61	1.56 [†]
Barium	1.69–1.71		1.62	1.60
<i>Glycerol</i>				
Lithium	1.68–1.78		1.42	1.43
Sodium	1.64–1.78	1.77	1.48	1.43–1.48
Potassium	1.32–1.42		~1.4	1.04
Magnesium	1.76–1.81	1.76–1.79	1.43	1.42–1.46 [‡]
Calcium	1.68–1.78	1.76–1.78	1.76	1.43
Strontium	1.70–1.78		1.76	1.43
Barium	1.72–1.78		1.76	1.43

*Mean layer charge (eq/formula unit).

[†]Non-integral (00*l*) reflections.

[‡]Dioctahedral vermiculites from soils ($\zeta \geq 0.6$) also showed basal spacings of 1.79–1.86 nm (Malla and Douglas, 1987).

coordinated to copper ions, but bound by water bridges to magnesium and calcium interlayer cations (Farmer and Mortland, 1966).

In addition to the coordination bonds, ionic bonds are often observed, especially in aqueous dispersions when the base is protonated due to acidic solution pH (Ainsworth et al., 1987; Slide et al., 1987) or to the increased acidity of interlayer water molecules (Scheme V) (see Chapter 5):

Pyridine molecules in Na⁺ montmorillonite are oriented about perpendicular to the silicate layers with the nitrogen atom pointing to the sodium ions. Three different states with basal spacings of 1.48, 1.94, and 2.33 nm were observed in the presence of water (Adams and Breen, 1982). In contrast, pyridinium cations were arranged flat between the layers (Serratosa, 1966; van Olphen, 1968). The amount of protonated base was determined by DTG or temperature programmed desorption (Ballantine et al., 1987; Breen et al., 1987).

The ratio of protonated base to unprotonated base in the interlayer space differs from the ratio in homogeneous solution (Karickhoff and Bailey, 1976). An important reason is the increased acidity of interlamellar water. In addition, protonation is

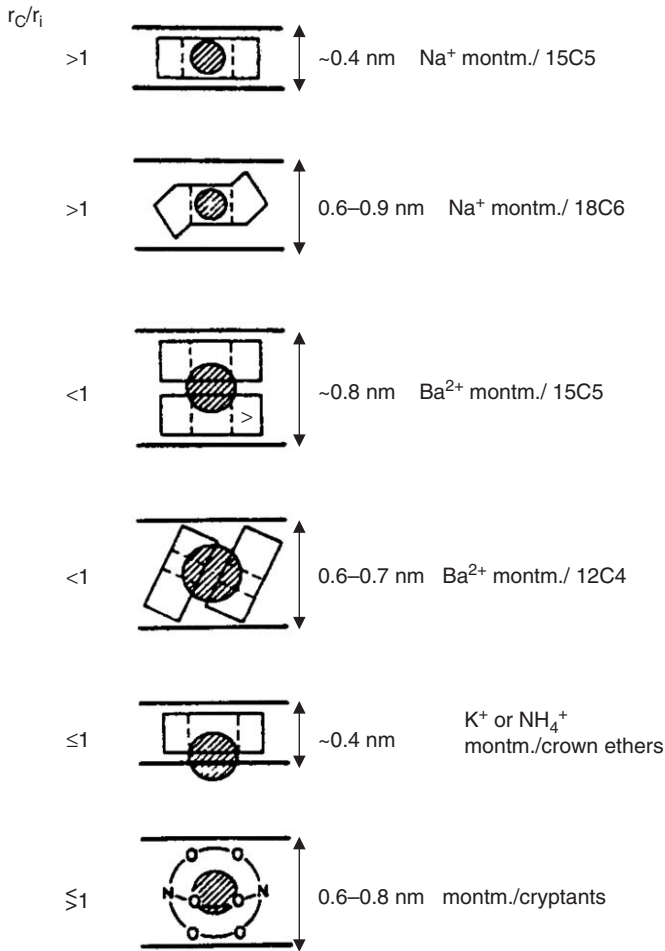
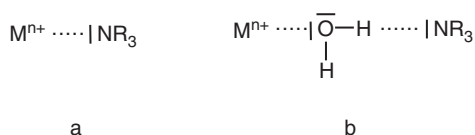


Fig. 7.3.6. Interlamellar arrangement of crown ether and cryptant molecules in homoionic smectites. From Ruiz-Hitzky et al. (2001).

enhanced by the ability of the negatively charged clay mineral surface to lower the chemical potential of the protonated form of the base relative to the neutral form (Feldkamp and White, 1979). Often, acid–base pairs (Scheme VI) are formed in a certain pH range around neutral.

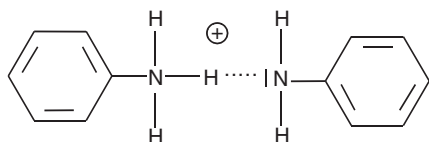
Bases are often used to measure the amount of acidic sites of clay minerals and to distinguish between Brønsted and Lewis acid sites. Brønsted acidity mainly arises from interlamellar water (see Chapter 5) (Yariv, 1992) as silanol groups at the edges are only weak-acidic centres. The simplest method for determining the Brønsted acidity strength is the use of Hammett indicators (Benesi, 1957; Benesi and Winquist,



Scheme IV.



Scheme V.



Scheme VI.

1978; Solomon and Hawthorne, 1983). However, these indicators only measure the acidity of the external surfaces. Yermiyahu et al. (2003) proposed the use of Congo red as an indicator in the study of surface acidity of smectites in aqueous dispersions.

Lewis acidic sites on clay mineral surfaces are usually coordinately unsaturated Al^{3+} ions that can accept electron pairs from donor molecules. Such sites can be formed by aluminium atoms at the edges or of adsorbed oligomeric hydroxo aluminium ions. In the presence of water the Lewis acidic species are hydrated and their Lewis acidity is masked. As the electron pair of nitrogen groups cannot displace water molecules from Al^{3+} ions, Lewis acidity of these Al^{3+} ions only develop after thermal decomposition of the water molecule, i.e. when the heated clay mineral is reacted with a base in the absence of water.

The protonated (Brønsted) and coordinated (Lewis) amines are distinguished by spectroscopic measurements, in some cases also by temperature programmed desorption (Solomon and Hawthorne, 1983; Breen et al., 1987; Carvalho et al., 2003).

Amino acids are bound by cation exchange and/or complexation (Theng, 1974, 1979; Siffert and Kessaissia, 1978). The charge of these molecules depends on the solution pH. With increasing pH the charge changes from positive to the neutral zwitter ion and, at still higher pH, to the anionic form. The isoelectric point varies between $\text{pH} = 5$ and 10 (cysteine 5.1 and glycine, alanine 6.1, histidine 7.6, and lysine 9.6).

Most studies of the adsorption of amino acids were carried out in a medium (mostly acidic) where the cationic forms of the acids were bound by cation exchange. A further mechanism is the complexation of the interlayer cations by the carboxylate groups of the zwitter ion and the anionic form. The degree of ion exchange and complexation in an acidic medium depends on the interlayer cation. Generally, the formation of complexes is stronger with transition metal cations than with alkali and

earth alkali cations. Di Leo (2000) compared the intercalation of glycine into Ca^{2+} and Cd^{2+} montmorillonite. The exchange reaction was dominant for Ca^{2+} montmorillonite. Once glycine molecules in the zwitter ionic form penetrated the interlayer space, the molecules were fully protonated due to the enhanced acidity of interlayer water molecules. Complexation was preferred by Cd^{2+} ions. The interesting observation that Cd^{2+} ions on the external surface were not complexed was related to the formation of inner-surface complexes between these Cd^{2+} ions and the surface oxygen atoms. Aspartic acid in the anionic form (isoelectric point at $\text{pH} = 3$) was weakly bound in the interlayer space of montmorillonite and easily extractable with KCl solutions (Naidja and Huang, 1994). The authors assumed the carboxylate groups were coordinated to the interlayer calcium ions by water bridges. The intercalation of several amino acids (cysteine, lysine, and proline) can be accompanied by polycondensation (Siffert and Kessaissia, 1978).

When vermiculite was reacted with γ -amino butyric acid, ω -amino caproic acid, or ornithine (Rausell-Colom and Fornés, 1974; Raupach et al., 1975; Raupach and Janik, 1976), the vermiculite particles delaminated in water and formed hydrogels (see Chapter 5). The exchange of the inorganic interlayer cations by 11-carboxy undecylammonium ions (the protonated form of ω -amino undecanoic acid) allowed the intercalation and polymerisation of ϵ -caprolactam (see Chapter 10.3).

The study of amino acid–clay mineral interactions was promoted by the possibility that a clay mineral may discriminate between optical isomers of amino acids. This possibility attracted much interest as well as controversy (see Hashizume et al., 2002). Kaolinite with other than triclinic stacking of the layers exhibits two inverse forms, and a stereoselective adsorption of optically active molecules may be understandable. The reports in the literature are contradictory (Siffert and Naidja, 1992). In contrast, montmorillonite particles do not exhibit “structural asymmetry”. However, structural chirality may be induced by the different packing modes of adsorbed enantiomers or DL pairs as proposed by Yamagishi (see Section 7.3.5). In fact, Siffert and Naidja (1992), studying the adsorption and deamination of glutaminic and aspartic acid, found a certain preference for the L forms and a higher degree of deamination of these enantiomers. More recently, Hashizume et al. (2002) reported a preference of certain allophanes for the L form of alanyl alanine, but no clear preference was developed for D- or L-alanine.

The adsorption of organic molecules with more highly complicated structures depends on the type of the clay mineral, the degree of purification (see Chapter 4), the interlayer cation, the mean layer charge, concentration (or vapour pressure) of the adsorptive, pH value, and temperature, but also on the fine structure of the clay mineral (type and degree of substitutions, especially $\text{Al}^{3+}/\text{Si}^{4+}$, layer charge distribution), particle size, degree of dispersion, ionic strength (Narine and Guy, 1981), type of salts present, and possible association equilibria in the solution. The adsorption of nuclein bases (adenine, cytosine, thymine, and uracil) on montmorillonite not only depended on the salts present and the mean layer charge but also on the charge distribution (Lagaly, 1984; Samii and Lagaly, 1987). Exchange of the sodium

and calcium ions by several diammonium cations showed a certain selectivity strongly influenced by the solvent (Mizutani et al., 1995).

Synergism effects were observed in co-adsorption experiments (Lailach and Brindley, 1969). Corresponding to the base pairing in DNA, the adsorption of thymine and uracil was enhanced in the presence of adenine (Lagaly, 1984, 1987a; Samii and Lagaly, 1987). Another example was the adsorption of adenosine monophosphate (AMP), which was increased by addition of adenosine triphosphate (ATP) whereas the adsorption of ATP was not influenced by AMP. As the adenosine phosphates are bound at the edges, their adsorption depends on the degree of dispersion (and, therefore, on the exact procedure of purification and fractionation, see Chapters 4 and 5) and the particle size (Graf and Lagaly, 1980; Herrmann and Lagaly, 1985).

Competitive adsorption (see Section 7.3.7) and co-adsorption phenomena must be considered when clays are applied as adsorbents. A model for calculating co-adsorption processes of cations was developed by Margulies et al. (1988).

7.3.3. ALKYLAMMONIUM DERIVATIVES

The interlayer cations of smectites and vermiculites can be exchanged by organic and organometallic cations in solution and in the solid state. Cation exchange reactions are performed by mixing aqueous dispersions of clay mineral and a solution of organoammonium salt. The products are separated by centrifugation or filtration and washed repeatedly. When the solubility of the guest species is low, water–alcohol mixtures are often used as solvents. Quantitative exchange requires a certain excess of alkylammonium salts in relation to the cation-exchange capacity (Lagaly, 1981a, 1994a). The alkylammonium derivatives in contact with the alkylammonium salt solutions not only intercalate water molecules but also some amounts of alkylammonium ions together with the anion, i.e. as ion pairs (Lagaly, 1981a; Klapayta et al., 2001; Lee and Kim, 2002; Kuwaharada et al., 2002; Janek and Lagaly, 2003). The pure alkylammonium derivatives needed for layer charge determination are obtained after washing and careful drying (Rühlicke and Kohler, 1981; Lagaly, 1994a). For solid-state reactions the clay mineral and solid organoammonium salt are mixed without solvent and ground in a mortar (Ogawa et al., 1990).

Thermodynamic excess functions were derived for the exchange of Laponite with primary, secondary, and ternary amines and indicated the importance of the van der Waals interaction (Vansant and Peeters, 1978).

Quantitative exchange of the interlayer cations of smectites by alkylammonium ions provides a method for characterisation of smectites and vermiculites and determination of their layer charge (Lagaly, 1981a, 1994a; Mermut and Lagaly, 2001). The arrangement of the intercalated surfactant cations depends on the layer charge and the alkyl chain length (Figs. 7.3.7 and 7.3.8). Short chain alkylammonium ions are arranged in monolayers, longer chain alkylammonium ions in bilayers with the alkyl chain axes parallel to the silicate layers. The monolayer has a basal spacing of ~ 1.4 nm, the bilayer

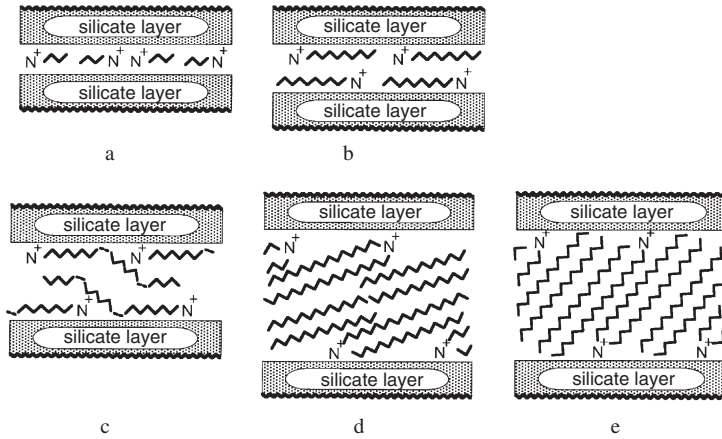


Fig. 7.3.7. Arrangement of alkylammonium ions in the interlayer space of smectites: (a) monolayers, (b) bilayers, (c) *pseudo*-trimolecular layers, and (d, e) paraffin-type arrangements of dialkylammonium ions with different tilting angles of the alkyl chains.

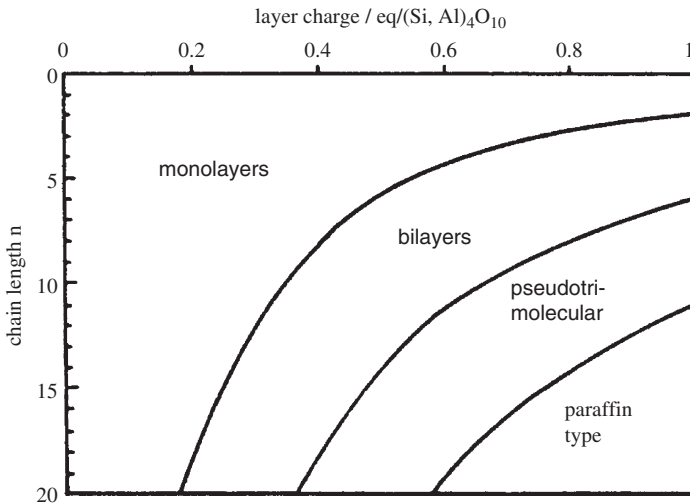


Fig. 7.3.8. Influence of layer charge and alkyl chain length on the arrangement of alkylammonium ions. n = number of carbon atoms in the n -alkyl chains. From Lagaly, (1986b).

of ~ 1.8 nm. The monolayer rearranges into the bilayer when the area of the flat-lying alkylammonium ions becomes larger than the equivalent area. The monolayer/bilayer transition is used to measure the charge distribution and the mean layer charge.

Three-layer structures of kinked alkyl chains (see Section 7.3.8) are observed with highly charged smectites and/or long surfactant cations. This pseudotrimolecular

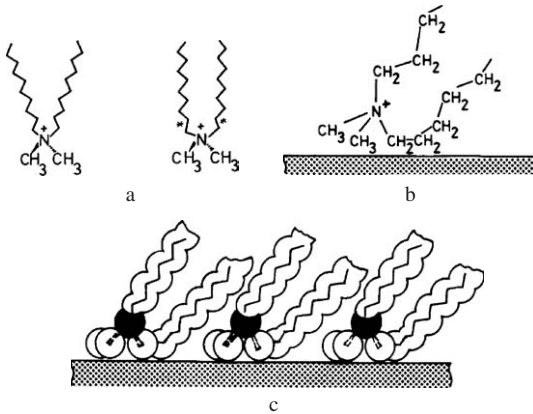


Fig. 7.3.9. (a–c) Conformation of dialkylammonium ions with and without *gauche* bonds (*) near the ammonium group.

arrangement exhibits a basal spacing of ~ 2.2 nm. The term *pseudo* is used because the positive surfactant groups are attached on the silicate layers whereas the alkyl chains assume a trimolecular arrangement by formation of kinks (Fig. 7.3.7).

Paraffin-type arrangements (Fig. 7.3.7d,e) in the interlayer space of smectites are formed by quaternary alkylammonium ions with two or more long alkyl chains. If all C–C bonds are in *trans*-conformation, the dialkylammonium ions are V-shaped. An almost parallel orientation of the chains is attained by formation of *gauche*-bonds near the ammonium group (Fig. 7.3.9). This conformation allows a denser packing of these surfactants in mono- and bimolecular films (Lagaly et al., 1975; Favre and Lagaly, 1991).

The alkylammonium ions in more highly charged vermiculites (mean layer charge ≥ 0.8 eq/(Si, Al) $_4$ O $_{10}$) form paraffin-type monolayers. The basal spacing increases linearly with the alkyl chain length and the layer charge is derived from the mean increase of the basal spacing (Lagaly, 1982; Ghabru et al., 1989; Mermut, 1994; Mermut and Lagaly, 2001). Low-charged vermiculites (mean layer charge ≤ 0.6 eq/(Si, Al) $_4$ O $_{10}$) intercalate alkylammonium ions in monolayers, bilayers, and pseudo-trimolecular arrangements, and the basal spacing increases in steps. These arrangements of flat-lying alkyl chains alternate with paraffin-type structures in medium-charged vermiculites. In these cases the layer charge is best derived by comparison with theoretical diagrams (Lagaly, 1982).

Paraffin-type arrangements are also observed in several types of layered materials with high-layer charge density such as M(IV) phosphates, niobyl phosphate, titanates, niobates, molybdates (Lagaly, 1981b; 1986b; Lagaly and Beneke, 1991).

Orientation and mobility of the intercalated organoammonium cations were examined by infrared (Stevens and Anderson, 1996a, 1996b; Parker and Frost, 1996; Yariv, 1996) and ^{13}C -nuclear magnetic resonance spectroscopy (Pratum, 1992).

High-resolution transmission electron microscopy revealed the paraffin-type arrangement of alkylammonium ions in Ba^{2+} exchanged biotites (Marcks et al., 1989). This method of investigation of alkylammonium exchanged samples is a sensitive tool to visualise the organisation of smectite particles (see Chapter 5) (Vali and Köster, 1986; Lee and Kim, 2002) and to detect different types of interlayer spaces, especially of illite/smectite mixed-layer minerals (Rühlicke and Niederbudde, 1985; Bell, 1986; Klimentidis and Mackinnon, 1986; Ghabru et al., 1989; Vali et al., 1991; Cetin and Huff, 1995).

7.3.4. INTERACTIONS WITH CATIONIC DYES

A. Aggregation of the Adsorbed Dyes

The interaction of cationic dyes with clay mineral surfaces changes the spectroscopic properties of the dye molecules (see Chapter 3). An example of the influence of surface acidity on the colour of adsorbed dyes was reported for Congo red (Yerminahu et al., 2003). The adsorbed dyes often exhibit unique spectroscopic and photochemical properties. Orientation and aggregation of the intercalated dye molecules can be derived from absorption and luminescence spectra, in steady-state mode or time-resolved. The study of photo-processes also gives information about the distribution and mobility of adsorbed photoactive species (Ogawa and Kuroda, 1995; Garfinkel-Shweky and Yariv, 1999).

Metachromasy is a deviation from Beer's law caused by the aggregation of the dye molecules. The principal band in the visible region is gradually replaced by a band at a shorter (or longer) wavelength (Ogawa and Kuroda, 1995; Garfinkel-Shweky and Yariv, 1999; Yariv and Cross, 2002).

The adsorption of methylene blue (and other cationic dyes) from aqueous solution is often used to measure the cation-exchange capacity and specific surface area of clay minerals. However, spectroscopic studies of aqueous dispersions indicated the distribution of the dye cations on the surface of smectites is determined not only by electrostatic interactions, but also by dye-dye interactions (Cenens and Schoonheydt, 1988; Bujdák et al., 1998, 2003; Jacobs and Schoonheydt, 2001). Simply measuring the maximum amount adsorbed of methylene blue provides only approximate values, and modification of this procedure is required (Hang and Brindley, 1970; Rytwo et al., 1991; Kahr and Madsen, 1995; see also Avena et al., 2001).

That methylene blue adsorption occurs initially on the external surfaces of montmorillonite particles was discussed by several researchers. The concentration of dye in this area increases considerably and induces the formation of MB aggregates (Breen and Loughlin, 1994; Breen and Rock, 1994; Neumann et al., 2002). The dye molecules then migrate from the external surface to the interlayer region. The endothermic reaction of montmorillonite with methylene blue at loadings smaller than the cation-exchange capacity (Rytwo and Ruiz-Hitzky, 2003) supports this hypothesis. The reaction changed

to exothermic at higher loadings when interactions between the methylene blue cations became more dominant. Due to the stronger aggregation of crystal violet cations the reaction of montmorillonite with this dye was exothermic even at small amounts adsorbed. The more pronounced intermolecular interactions of the crystal violet cations also caused the larger yield value of crystal violet containing montmorillonite dispersions in comparison with methylene blue (Penner and Lagaly, 2000).

If the intercalation is really a two-step process, the re-arrangement will depend on particle size and texture (see Fig. 5.1, Chapter 5), the layer charge and charge distribution. Due to the strong electrostatic interactions, formation of aggregates should be promoted by a favourable distribution of the electrostatically anchored methylene blue cations; i.e. the aggregation is influenced by the distribution of the charges in the silicate layer (Bujdák et al., 1998). Methylene blue cations competed effectively with cationic surfactants but were also solubilised in the surfactant clusters on the clay mineral surface (Breen and Loughlin, 1994).

Because of their biological, catalytic, conductive, and photoactive properties, porphyrins and phthalocyanines were intercalated. Porphyrins undergo reversible protonation–deprotonation reactions and can be used as probes for the Brønsted acidity of the interlayer environment. Cady and Pinnavaia (1978) reported on the reaction of *meso*-tetraphenylporphyrine (TPPH₂) with the interlayer cations of montmorillonite. The acidity of the hydrated interlayer cations affected the adsorption state of TPPH₂. The strongly acidic aquo complexes of Fe³⁺ and VO²⁺ protonated the porphyrines quantitatively, and the cations were arranged in monolayers in the interlayer space. Hydrated Na⁺ and Mg²⁺ yielded only trace amounts of TPPH₄²⁺. The reaction of (n-C₃H₇)₄N⁺, Co²⁺, Cu²⁺, and Zn²⁺–montmorillonite with TPPH₄²⁺ mainly yielded the proton-exchanged form of the montmorillonite, and the metalloporphyrine was displaced into solution. Formation of porphyrine from aldehyde and pyrrole was catalysed by the Brønsted acidity of the hydrated cations (Cady and Pinnavaia, 1978).

Abdo et al. (1980) described metallation–demetallation reactions of tin tetra(4-pyridyl) porphyrine in Na⁺–hectorite. The UV–Vis and luminescence spectra revealed that the adsorbed complex was demetallated, forming the tetra(4-pyridyl) porphyrine dication when the clay mineral was dehydrated. This process was reversible, indicating that the Sn⁴⁺ ions remained in the vicinity of the porphyrine after demetallation.

Photoluminescence is a powerful tool to obtain information on the composition, structure and dynamics of the surrounding medium. The luminescence parameters (decay, quantum efficiency, and polarisation) are sensitive to changes in the microenvironment of the probe. Quenching, sensitisation, and energy transfer observed by adding a second component or changing the microenvironment also provide information, especially on dynamics.

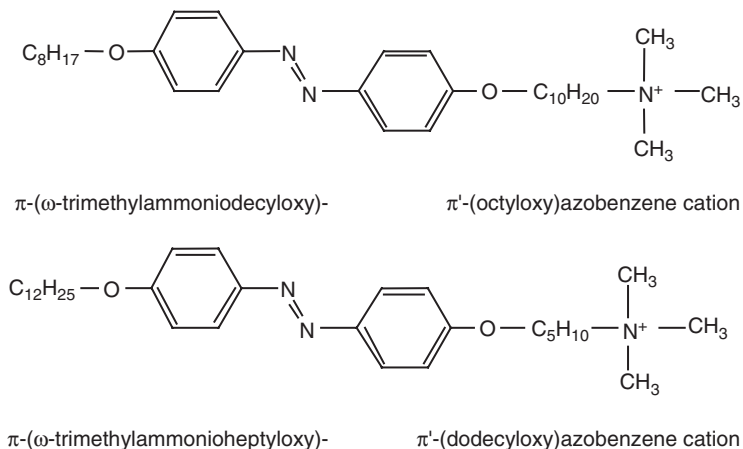
Aromatic hydrocarbons like pyrene and anthracene were applied as luminescence probes in a variety of assemblies. The vibronic fine structure of the pyrene monomer is sensitive to the polarity of the surrounding molecules. When pyrene molecules are

forced into close proximity or are present at high concentrations, excited state dimers (excimers) are observed. The intensity ratio of excimer to monomer fluorescence is often considered as a measure of pyrene mobility and proximity. The luminescence properties of cationic pyrene derivatives like (1-pyrenyl) trimethylammonium ions indicated the distribution of the adsorbed ions was determined by the surrounding medium as well as by the distribution of negative adsorption sites. The bonding between the positive probe and negative surface sites was not strong enough to inhibit diffusion of the adsorbed ions on the surface (Viane et al., 1988).

B. Orientation of Intercalated Dye Molecules

In addition to one-dimensional Fourier analysis, the orientation of intercalated dye molecules can be derived from the spectroscopic anisotropy. As an example, the orientation of cationic amphiphilic azobenzene derivatives (Scheme VII) in the interlayer space was derived from the spectral shifts and the basal spacings (Ogawa and Ishikawa, 1998). The spectral shifts reflect the orientation of the dipoles in the aggregates; smaller red shifts are expected for dipole orientations with larger tilting angles.

The orientation of Co(II) tetrakis-(1-methyl-4-pyridyl) porphyrine in the interlayer space of Na^+ hectorite and synthetic Li^+ fluorhectorite was studied by X-ray diffraction and anisotropic ESR spectroscopy of oriented thin films (Ukrainczyk et al., 1994). It depended on the layer charge. When intercalated in hectorite, the porphyrine ring was oriented with its molecular plane parallel to the silicate layer and did not coordinate water molecules in the axial direction. In the more highly charged fluorhectorite, the porphyrine ring was tilted at 27° to the silicate layer, with



Scheme VII.

water molecules coordinated to Co(II). Dehydration in vacuum decreased the basal spacing from 1.96 to 1.76 nm, causing a rearrangement of the intercalated porphyrine into a staggered bilayer with no axial water bound to Co(II).

The electric linear dichroism (ELD), which measures the change in the absorption of light linearly polarised in the directions parallel and perpendicular to the applied electric field (Fig. 7.3.10), is a further powerful tool to determine the orientation of the guest molecules. For 2- and 4-[4-(dimethylamino)styryl]-1-ethylpyridinium cations on saponite, the tilting angles were determined by the amount of the intercalated dye as well as its molecular structure (the position of cationic site within the dye) (Sasai et al., 2000b).

Regioselective photocycloaddition of stilbazolium cations intercalated in the interlayer space of saponite was reported by Usami et al. (1990). Four photochemical reaction paths have to be considered for the stilbazolium ion (Scheme VIII). During irradiation of the dispersed stilbazolium saponite by UV light, *syn*-head-to-tail dimers were predominantly formed at the expense of *cis*-*trans* isomerisation, which is the major path in homogeneous solution. The selective formation of head-to-tail dimers suggests the intercalation occurs in an anti-parallel mode (Fig. 7.3.11). As the yield of dimers was barely dependent on the amount of the guest ions added, one has to assume the cations formed aggregates with alternating anti-parallel orientation, even at very low loading (e.g. 1% of the cation-exchange capacity). The preferential formation of *syn*-head-to-tail dimers reveals the influence of the van der Waals interaction between the adsorbed ions. Co-adsorption of alkylammonium ions affected the photoreactivity of the intercalated stilbazolium ions (Usami et al.,

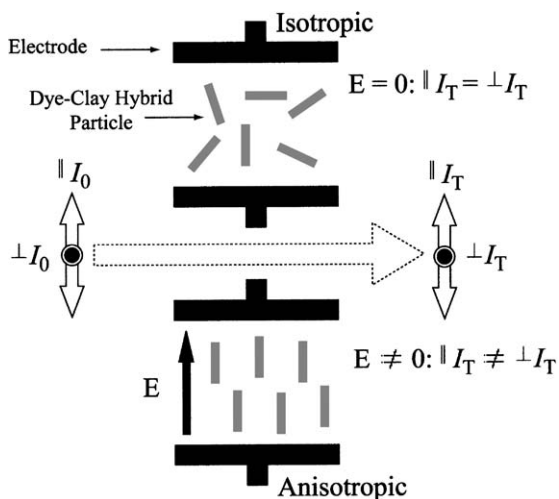
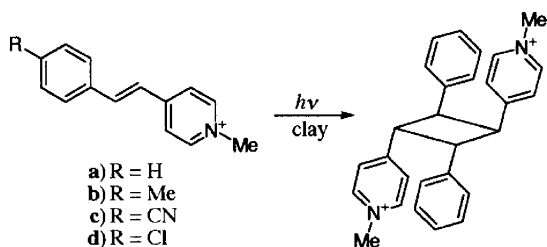


Fig. 7.3.10. Principles of electric dichroism in clay mineral-dye systems From Sasai et al. (2000b).



Scheme VIII.

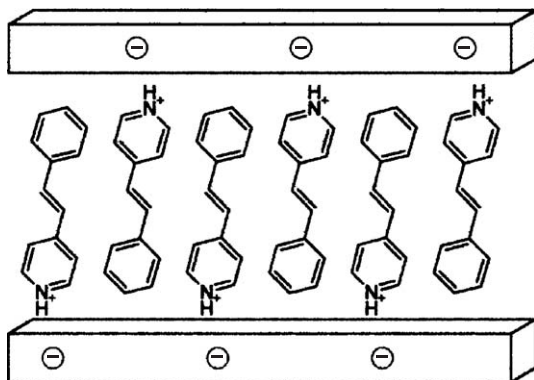


Fig. 7.3.11. Packing of stilbazolium cations in the interlayer space of saponite. From Usami et al. (1990).

1990). When the co-adsorbed alkylammonium ion was longer than the stilbazolium ion, the dominant photoreaction changed from cyclodimerization to *cis-trans* isomerization and the excimer emission of the intercalated stilbazolium ions was strongly reduced.

7.3.5. REACTION WITH CATIONIC COMPLEXES

Cationic organometallic complexes are intercalated by cation exchange or formed by in situ complexation in the interlayer space. The catalytic application of clay minerals with intercalated heavy metal complexes was studied some time ago (Pinnaivaia, 1983). The tris (2,2'-bipyridine) ruthenium(II) complex ($\text{Ru}(\text{bpy})_3^{2+}$), abbreviated as Ru(II), is widely used as a luminescence probe (Kalyanasundaram, 1992). The shift of metal-to-ligand charge transfer bands and the $\pi-\pi^*$ transitions of bipyridine as well as Raman and XPS studies indicated the bipyridine ligands were slightly distorted by the steric constraints when Ru(II) was adsorbed on montmorillonite. Partial oxidation of Ru(II) was also reported (Habti et al., 1984).

Ru(II) complexes are adsorbed at the edges, the external basal plane surfaces and between the silicate layers (DellaGuardie and Thomas, 1983; Schoonheydt et al., 1984). The occupancy of edge sites for the planar sites increased with decreasing particle size (Thomas, 1988). The Ru(II) and Na^+ ions were segregated in the interlayer space of montmorillonite, yielding high local concentrations of the complex ions in the interlayer space even when the concentration of Ru(II) added was only 1–2% of the cation-exchange capacity (Ghosh and Bard, 1984). When $(\text{Zn}(\text{bpy})_3)^{2+}$ was co-adsorbed with Ru(II) on hectorite, the effective self-quenching rate was largely reduced, presumably due to surface dilution of the Ru(II) cations. The origin of the segregation process is unclear. The non-uniform charge distribution of the silicate layers or interactions between the Ru(II) complexes may be involved.

The decay profiles indicated the quenching effect of iron ions in the clay mineral structure and the essentially immobile character of adsorbed Ru(II) cations in the time-scale of microseconds (Habti et al., 1984). The total quenching probability for a particular probe was determined by the quencher concentration in the solid and by the number of solid particles in contact with the probe.

Yamagishi (1987, 1993) observed differences in the adsorption of the enantiomers and racemic pairs of ruthenium and iron polypyridine and 1,10-phenanthroline (phen) complexes on montmorillonite. When a racemic mixture of $[\text{Fe}(\text{phen})_3]^{3+}$ was added to a montmorillonite dispersion, racemic pairs rather than optical isomers in random distribution were adsorbed. Enantiomeric $[\text{Fe}(\text{phen})_3]^{3+}$ cations were adsorbed in excess of the cation-exchange capacity. When the tris(phen) complex is oriented with its threefold symmetry axis perpendicular to the silicate surface, the base of the complex forms a regular triangle with a side length of about 0.65 nm. Since this distance is close to the distance of 0.55 nm between the centres of the hexagonal holes of the silicate layer, the three hydrogen atoms of the ligands can be buried in the silicate surface, and the chelate is rigidly fixed on the surface at a definite orientation. It was concluded from molecular model considerations that racemic adsorption by metal chelates on a solid surface is preferential when (i) the density of the adsorbed chelated cations allows lateral interactions and (ii) the surface is capable of fixing the complexes at a definite orientation. When bound by cation exchange, a divalent complex cation should have a molecular radius larger than 0.5 nm. Breu and Catlow (1995) pointed out that observed chiral recognition phenomena are related to the lateral interactions between the guest complexes that are modified by the corrugation of the silicate layer. The clay mineral controls the orientation and relative positions of the complexes in the interlayer space, i.e. the geometrical fit between host and guest shapes is important.

Cationic imine and amine complexes with 2:1 type clay minerals were used in preparing clay-modified electrodes (Fitch, 1990).

Synthetic fluorhectorites modified with $[\text{Co}(\text{en})_3]^{3+}$ cations showed pronounced differences in rates of gas uptake at 77.3 and 90.2 K. H_2 , D_2 , O_2 , and Ne were much more rapidly adsorbed than N_2 , Ar, and CH_4 . Similar effects were observed with certain zeolites (Barrer, 1986).

7.3.6. ADSORPTIVE PROPERTIES OF ALKYLAMMONIUM CLAY MINERALS

Replacement of the inorganic interlayer cations by cationic surfactants changes the hydrophilic silicate surface into hydrophobic (Jordan, 1950; Jones, 1983; Lagaly et al., 1983). The hydrophilic/hydrophobic balance depends on the length and packing density of the alkyl chains (Weiss, 1966; Lagaly, 1984, 1987b). Organophilic clays are used as rheological additives in paints, greases, and cosmetic formulations (see Chapter 10.1) (Jones, 1983).

The adsorptive properties of the organoammonium clay minerals were already been recognised (Barrer, 1978; 1989a, 1989b). Adsorption from aqueous solutions is usually studied by adding a solution of the organic compound to the dispersed clay mineral, shaking for 12–24 h, centrifuging, and determining the amount of the organic compound remaining in solution (often by ultraviolet spectroscopy and gas chromatography). Depletion of the organic compound measured in this way does not give the real amount adsorbed but rather the specific surface excess (see Section 7.3.7). Adsorption from the vapour phase is measured by gravimetric or volumetric methods.

As long as the alkylammonium ions lie flat between the silicate layers, small molecules like short chain alcohols, formamide, dimethyl sulphoxide, and water are adsorbed in the pores between the alkylammonium ions with none or only a modest increase of the basal spacing (by a few 0.01 nm). Longer alkylammonium ions $C_{n_C}H_{2n_C+1}NH_3^+$, typical $n_C > 8$ (Malberg et al., 1989) move from flat into perpendicular orientation so that the volume accessible to the adsorptive increases strongly. Short-chain alcohols $C_{n_A}H_{2n_A+1}OH$ ($n_A < 8$) fill the space between the perpendicular alkylammonium ions arranged in monolayers (Fig. 7.3.12). Longer chain alkanols form interlayer bimolecular films composed of alkanol molecules and alkylammonium ions. When $n_A = n_C$, the bilayers are densely packed but contain vacancies for $n_A \neq n_C$. These bilayers are stable in spite of relatively high amounts of vacancies (Lagaly, 1976). Too large vacant volumes are reduced by formation of kinks (see Section 7.3.8).

The numerical values of the exothermic heats of immersion decreased strongly with n_C , which illustrates the importance of the enthalpy required to move the alkyl chains from close contacts with the surface oxygen atoms in perpendicular orientation. The gain of adsorption enthalpy due to the increased adsorption volume is largely consumed to overcome the van der Waals energy between the surface and the alkyl chains lying flat in close contacts with the surface oxygen atoms. The energy required is about $+5.7 \text{ kJ/mol} - \text{CH}_2$ – for $n_C = 6$ –10 and above $+3.8 \text{ kJ/mol} - \text{CH}_2$ – for $n_C > 10$. The decrease is related to the different interlayer packing density of the alkyl chains because the flat-lying alkyl chains in bilayers ($n_C > 10$) are not as tightly fixed between the silicate layers as in monolayers (Malberg et al., 1989; Lagaly and Malberg, 1990). In the bilayer structures at $n_A \sim n_C$ the van der Waals energy between the long alkyl chains is decisive. It is about $2.5 \text{ kJ/mol} - \text{CH}_2$ – and smaller than in

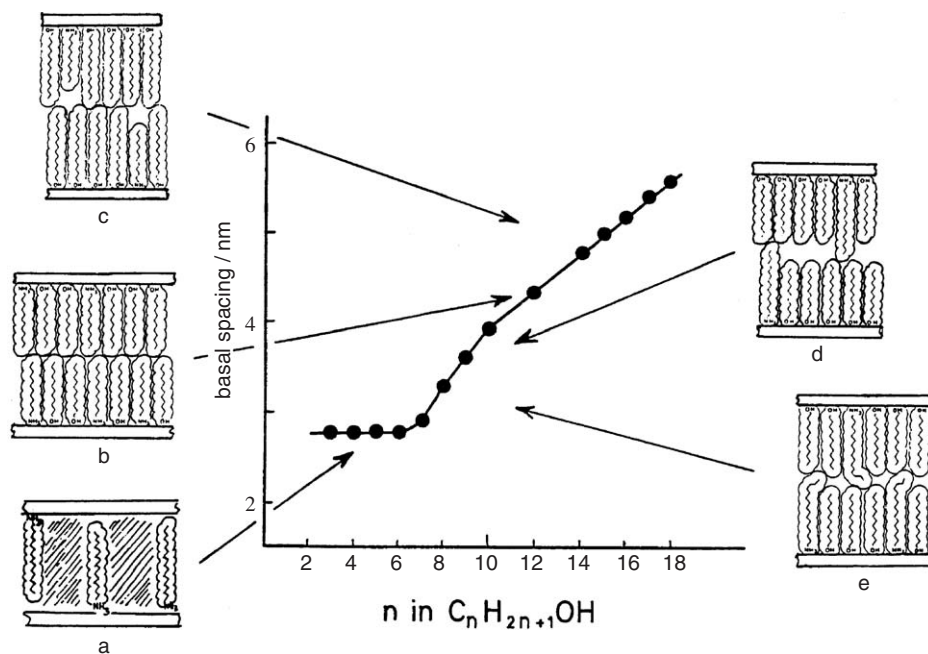


Fig. 7.3.12. Interlayer arrangements of alkylammonium ions and alkanol molecules. As an example: dodecylammonium montmorillonite and *n*-alkanols. (a) zeolitic uptake of short chain alcohol molecules, (b) dense bimolecular films for equal chain lengths, (c, d) vacancies in case of differently long chains, and (e) shortening of longer chains by kinks. From Jasmund and Lagaly (1993).

the crystalline long-chain compounds (about 5.8 kJ/mol – CH₂ –) because the chains in the interlayer space are more loosely packed (Lagaly and Weiss, 1969). Owing to the high van der Waals energy between the alkyl chains, the bilayer structures tolerate relatively large vacancies. In addition, the distribution of vacancies and, in some cases, kinks represent an important entropy contribution.

Smaller molecules like formamide, dimethyl formamide, DMSO increase the spacing of the alkylammonium montmorillonites and vermiculites at least to separations corresponding to monomolecular films of perpendicular alkyl chains. Salts soluble in the organic solvent strongly influence the adsorption of the solvent and the basal spacing. They can increase or decrease the layer separation. The effects are more strongly influenced by the salt cations, less by the anions. In comparison with water, cations in organic liquids are more strongly solvated than anions. The structure-breaking influence of potassium iodide exerted a strong effect on the swelling of tetradecylammonium montmorillonite in DMSO. Even concentrations as low as 0.01 M impeded the intercalation of solvent molecules (Lagaly et al., 1983; Lagaly, 1987b).

Swelling of the alkylammonium derivatives in polar liquids was discussed on the basis of formation of solvent clusters between the alkyl chains (Lagaly and Witter, 1982; Lagaly et al., 1983). If this were true, salts should exert a strong effect on the swelling in water. The basal spacings of alkylammonium beidellites (not of alkylammonium vermiculites) dispersed in water were distinctly below the spacings produced by the organic liquids. However, they were considerably enhanced by addition of modest amounts of salts (concentrations > 0.01 mol/L), especially by structure breaking salts like KSCN (Fig. 7.3.13) (Lagaly et al., 1983; Lagaly, 1987b).

An interesting question, even for practical applications, concerns the possibility of delamination of alkylammonium clay minerals in organic solvents. Owing to the strong van der Waals interaction between the chains and the chains and solvent molecules, basal spacings exceeding the bilayer arrangement were seldom observed. A certain but not complete disaggregation was observed in nitrobenzene (Lagaly and Malberg, 1990). The impossibility of delamination in organic liquids is a serious obstacle in preparing clay-polymer nanocomposites (see Chapter 10.3). It is therefore still surprising that the butylammonium derivative of low-charged vermiculites delaminates in water and forms hydrogels (see Chapter 7.6).

Mortland et al. (1986) determined the adsorption isotherms of phenol, 3-chlorophenol, 3,5-dichloropheno, and 3,4,5-trichlorophenol from water on hexadecyl

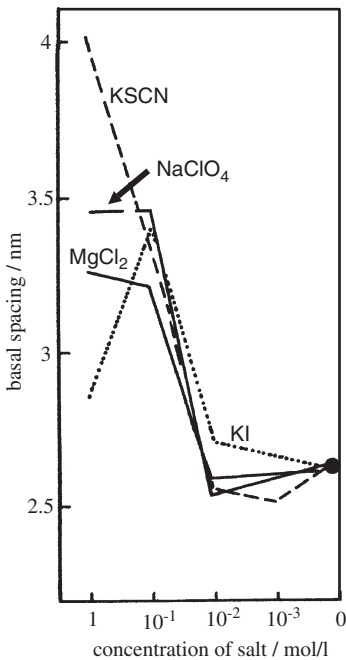


Fig. 7.3.13. Salt effects on interlayer water: basal spacing of tetradecylammonium montmorillonite in aqueous salt solutions. From Lagaly (1987b).

trimethylammonium smectite. The amount adsorbed increased with the number of chlorine atoms on the benzene ring. In contrast, similar amounts of phenol and 3,4,5-trichlorophenol were adsorbed from *n*-hexane. This different behaviour was ascribed to the influence of adsorptive-solvent and adsorptive-surface interactions on the partitioning of the adsorptive between solvent and surface (see Chapter 11.1). Compared with the long-chain derivatives, rigid interlayer cations like tetramethylammonium ions (Lee et al., 1989, 1990; Jaynes and Boyd, 1991) or tetraphenylphosphonium ions (Meier et al., 2001) can improve the adsorption properties towards certain organic compounds (see Chapter 11.1). Infrared studies of water adsorption on tetramethylammonium and triethyl phenylammonium montmorillonite revealed that water preferentially hydrates the organic ions but not the siloxane surface of montmorillonite (Stevens and Anderson, 1996a, 1996b). The orientation of the cations determines the siloxane surface area accessible to the adsorptive and whether the phenyl ring can interact with the aromatic groups of the adsorptive. A further example of the importance of the phenyl ring orientation on the adsorption of aromatic compounds was reported by Nir and co-workers (see Chapter 11.2).

In comparison with the tetramethylammonium smectite, the tetraphenylphosphonium derivative was a better adsorbent of aromatic and chlorinated hydrocarbons from water. The reason is seen in the lower degree of hydration of the tetraphenylphosphonium cations (Kukkadapu and Boyd, 1995). Compared with smectites modified with flexible organic cations, the tetraphenylphosphonium derivatives of low-charged smectites also revealed an enhanced adsorption of 2-chlorophenol, especially at low-pollutant concentrations (Meier et al., 2001).

Organo bentonites retained considerable amounts of heavy metal ions (together with the counterions) from aqueous solutions. The adsorption increased in mixtures of water with organic solvents. Synergetic effects were observed: addition of the organic solvent enhanced the heavy metal adsorption and the metal ions enhanced the adsorption of the organic component (Stockmeyer and Kruse, 1991; Lagaly, 1994b, 1995).

The adsorption of anions by alkylammonium bentonites is probably mediated by the particular arrangement of the water molecules around the alkyl chains (Lagaly, 1995). Adsorption of radioiodide by organo bentonites may be of practical interest (Bors, 1990; Bors and Gorny, 1992).

7.3.7. ADSORPTION FROM BINARY SOLUTIONS AND THE HYDROPHILIC/HYDROPHOBIC CHARACTER OF CLAY MINERAL SURFACES

Hydrophobisation of clay minerals by adsorption of surfactants and macromolecules is an important step in modifying clays. This step is needed for many technical applications when the clay minerals are dispersed in less polar solvents or polymers

or are tailored to improve gas and liquid adsorption properties (see Chapters 10.1 and 10.3). A quantitative description of the surface modification requires evaluation of the mosaic structure of the surface. Liquid sorption and immersionsal wetting experiments (mostly by microcalorimetry) open the way for a quantitative characterisation of surface hydrophobisation and for describing the effects of surface modification on the properties of the clay minerals.

The solid–liquid interaction can be derived from the adsorption excess isotherms in liquid mixtures and the heat of immersion in pure liquids, mixtures, or solutions (Everett, 1964, 1965; Kipling, 1965). Further information is obtained if the amount of liquid adsorbed on the surface is related to the heat of immersion. A further benefit of the adsorption excess isotherms is the possibility of calculating the free enthalpy of adsorption as a function of the composition (Dékány, 1992; Regdon et al., 1998).

A. Adsorption Excess Isotherms

When solid particles are immersed in a liquid medium, solid/liquid interfacial interactions lead to formation of an adsorption layer. The material content of the adsorption layer is the adsorption capacity of the solid particle and can be derived from the so-called adsorption excess isotherms of binary liquid mixtures (Everett, 1964, 1965). Adsorption changes the composition of the liquid mixture from x_1^0 to the equilibrium concentration x_1 . The value $\Delta x_1 = x_1^0 - x_1$ is analytically determined. The relationship between the specific adsorption excess amount $n_1^{\sigma(n)} = n^0(x_1^0 - x_1)$ calculated from Δx_1 and the material content of the interfacial layer is given by the Ostwald–de Izaguirre equation (Kipling, 1965):

$$n_1^{\sigma(n)} = n^0(x_1^0 - x_1) = n_1^s - n^s x_1 = n^s(x_1^s - x_1) \quad (1)$$

where n^0 is the total amount of adsorptive molecules (e.g. in mmol/g), $n^s = n_1^s + n_2^s$ is the mass content of the interfacial phase, and $x_1^s = n_1^s/n^s$ is the molar fraction of component 1 in the interfacial phase. According to Eq. (1), the excess isotherm $n_1^{\sigma(n)} = f(x_1)$ represents the combination of the individual isotherms $n_1^s = f(x_1)$ and $n_2^s = f(x_1)$.

The volume occupied by the components adsorbed on the solid surface is $V^s = n_1^s V_{m,1} + n_2^s V_{m,2}$ where n_1^s and $V_{m,1}$ are the amount and the partial molar volume of the components in the adsorption layer. The volume fraction of component 1 in the adsorption layer is calculated from the excess isotherm:

$$\phi_1^s = \frac{n_1^s}{n_{1,0}^s} = \phi_1 + \frac{r^* n_1^{\sigma(n)} V_{m,1}}{V^s(x_1 + r^* x_2)} \quad (2)$$

The adsorption capacity of the pure component 1 is $n_{1,0}^s = n_1^s + r n_2^s = n^s x_1^s + r n^s x_2^s$ where $r = V_{m,2}/V_{m,1} = n_{1,0}^s/n_{2,0}^s$. It can be determined by the Everett–Schay method

(Everett, 1964, 1965; Kipling, 1965):

$$\frac{x_1 x_2}{n_1^{\sigma(n)}} = \frac{1}{n_{1,0}^s} \left[\frac{r}{S-1} + \frac{S-r}{S-1} x_1 \right] \quad (3)$$

where S is constant for ideal adsorption from ideal solutions (Kipling, 1965). The value of $n_{1,0}^s$ is derived from the linear relation between $x_1 x_2 / n_1^{\sigma(n)}$ and x_1 .

Since in liquid adsorption processes the surface of the adsorbent is always completely covered, the equivalent specific surface area a_{eq}^s is related to the cross-sectional areas of the components, $a_{m,1}$ and $a_{m,2}$, which are calculated from the molar volumes of the components (Dékány et al., 1985a):

$$n_1^s a_{m,1} + n_2^s a_{m,2} = a_{\text{eq}}^s \quad (4)$$

Thus, the specific surface area of the adsorbent can be calculated from the adsorption capacities and the cross-sectional areas. The specific surface area determined in this way for many non-swelling and dis-aggregating adsorbents was in good agreement with the areas obtained by gas adsorption measurements (Dékány et al., 1985a).

The liquid adsorption capacity can be expressed as a function of surface modification $\Theta_2 = n_2^s a_{m,2} / a^s$, where $n_2^s a_{m,2}$ is the hydrophobic surface area and a^s is the total surface area of the adsorbent (Dékány et al., 1985a).

B. Heat of Wetting

Immersion microcalorimetry is a simple and straightforward method for quantifying the solid/liquid interfacial interaction. The solid material previously heated in vacuum is brought into contact with the pure liquid (Dékány, 1992, 1993). It is advisable to choose liquids of different polarity so that the hydrophobic/hydrophilic balance of the surface can be estimated from the heats of wetting. Wetting a hydrophilic surface by a polar liquid liberates a large enthalpy, while wetting a hydrophobic surface yields a smaller exothermic heat. When a solid adsorbent is immersed in a binary mixture, the heat of wetting is intermediate between the values $\Delta_w H_1^0$ and $\Delta_w H_2^0$ measured in the pure components. This immersion technique gives direct information on the strength of the solid/liquid interactions. According to Everett's adsorption layer model (1965; Kipling, 1965; Everett, 1964; Dékány, 1993) the heat of immersional wetting, $\Delta_w H_t$, can be calculated when the molar adsorption enthalpies of the components, $(h_1^s - h_1)$ and $(h_2^s - h_2)$, of the system are known. Introducing the volume fractions ϕ_1^s and ϕ_2^s , the heat of wetting is determined as

$$\Delta_w H_t = \phi_1^s \Delta_w H_1^0 + \phi_2^s \Delta_w H_2^0 + H^{\text{se}}(x_1^s) \quad (6)$$

$H^{\text{se}}(x_1^s)$ is an excess enthalpy of the adsorption layer due to deviation from ideality.

C. Examples

When the components of a binary mixture largely differ in polarity, for instance methanol and benzene, the shape of the excess isotherms and the azeotropic composition are related to the polarity of the surface. As an example, adsorption excess isotherms were determined on hydrophilic and partially hydrophobic illites in methanol–benzene mixtures (Fig. 7.3.14). The adsorption capacities were obtained by the Schay–Nagy extrapolation and the adsorption space-filling model. The amount of methanol in the adsorption layer, $1-\Theta_2$, decreased with increasing coverage of the illite surface by hexadecylpyridinium cations (Table 7.3.3). The free energy of adsorption $\Delta_{21}G = f(x_1)$ was derived from the excess isotherms (Fig. 7.3.15) (Dékány, 1992; Regdon et al., 1998).

The enthalpy of wetting as a function of the molar fraction of methanol in the equilibrium solution was large for Na^+ illite because of the preferential adsorption of methanol (Fig. 7.3.16). It decreased after hydrophobisation and became even endothermic at $x_1 > 0.5$. The molar wetting enthalpy decreased with increasing hydrophobicity (Table 7.3.3).

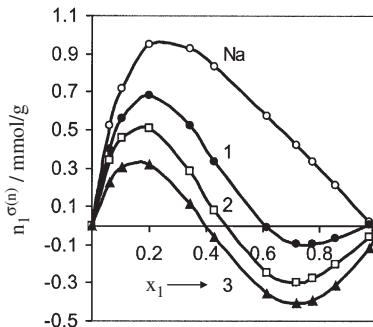


Fig. 7.3.14. Adsorption excess isotherms for Na^+ illite (Na) and hexadecylpyridinium illites (1,2,3: increasing amounts of hexadecylpyridinium ions, see Table 7.3.3) in methanol(1)-benzene(2).

Table 7.3.3. Adsorption of methanol(1)-benzene(2) mixtures on Na^+ illite and hexadecylpyridinium illites

Adsorbent	$n_{1,0}^s$ (mmol/g)	a_{eq}^s (m^2/g)	Θ_2^*	$-\Delta_{2,1}H_t$ (J/g)	$-(h_1^s - h_2^s/r)$ (kJ/mol)
Na^+ illite	0.84	51	0.11	11.10	13.65
HDP ⁺ illite 1 [†]	1.25	57	0.52	1.70	4.32
HDP ⁺ illite 2	1.30	78	0.66	1.35	3.21
HDP ⁺ illite 3	1.42	85	0.78	0.85	2.27

* $\Theta_2 = n_{1,0}^s a_{m,2} / a^s$: Surface hydrophobicity.

[†]Content of hexadecylpyridinium ions: **1** 0.097, **2** 0.139, **3** 0.233 mmol/g.

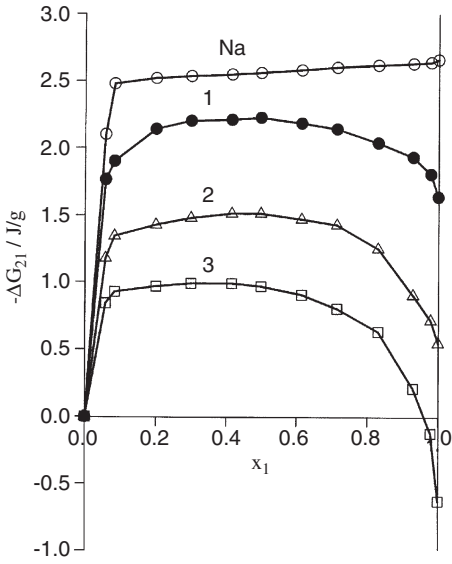


Fig. 7.3.15. Free enthalpy of adsorption, $\Delta_{21}G$, of methanol(1)-benzene(2) on Na^+ illite (Na) and hexadecylpyridinium illites (1, 2, 3; see Table 7.3.3).

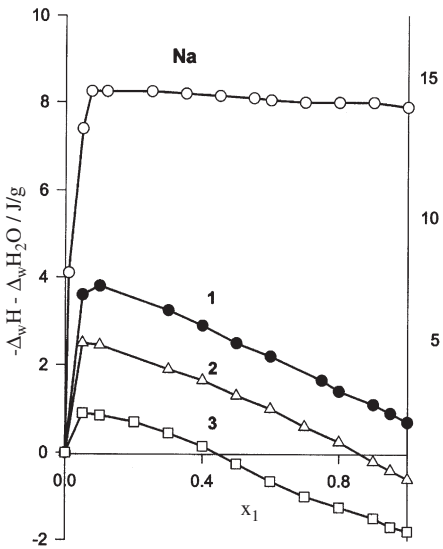


Fig. 7.3.16. Immersional wetting enthalpy of Na^+ illite (\circ) and illites modified with hexadecylpyridinium ions (\bullet 1, Δ 2; \square 3, see Table 7.3.3) in methanol (1)-benzene (2).

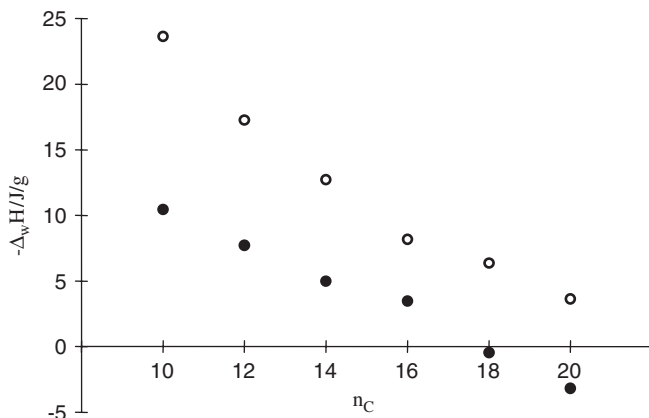


Fig. 7.3.17. Immersional wetting enthalpy as a function of the chain length of alkylammonium illites in methanol (○) and toluene (●).

The heat of immersion of hydrophobised montmorillonite in methanol decreased almost exponentially with increasing alkyl chain length (Fig. 7.3.17). The decrease in toluene was surprising because the increased organophilicity of the surface should be associated with an increase of the enthalpy of immersional wetting as measured in the case of non-swelling hexadecylpyridinium illites. The immersional wetting of hydrophobised montmorillonites in methanol, toluene, and their mixtures gave rise to three types of detector signals (Fig. 7.3.18). The heat of immersion of hexadecylpyridinium montmorillonite in methanol was exothermic, whereas in toluene a sharp endothermic signal was followed by an exothermic peak. The first endothermic signal is caused by the opening of the interlayer space. This step consumes enthalpy because the alkyl chains in bilayers move from close contacts with the surface oxygen atoms into upright positions (see Section 7.3.6), which allows the exothermic solvation of the chains and the silicate surface by toluene. The importance of the endothermic re-arrangement of the alkyl chains is illustrated in Fig. 7.3.18c. The large enthalpy required for the re-orientation of the octadecyl chains is not compensated by the solvation enthalpy of the chains (mainly by toluene) and the surface (mainly by methanol) (Dékány et al., 1985b, 1986; Regdon et al., 1998), and the total process becomes endothermic. Thus, entropy effects are very important in swelling processes of hydrophobised clay minerals. A considerable part of the entropy increase is related to the increased conformational freedom when the chains move in upright position.

7.3.8. PHASE TRANSITIONS

The interlayer bilayers composed of long-chain alkylammonium ions and alkanol molecules show a series of thermal phase transitions, indicated by basal spacings stepwise decreasing with increasing temperature (Fig. 7.3.19). The small steps of

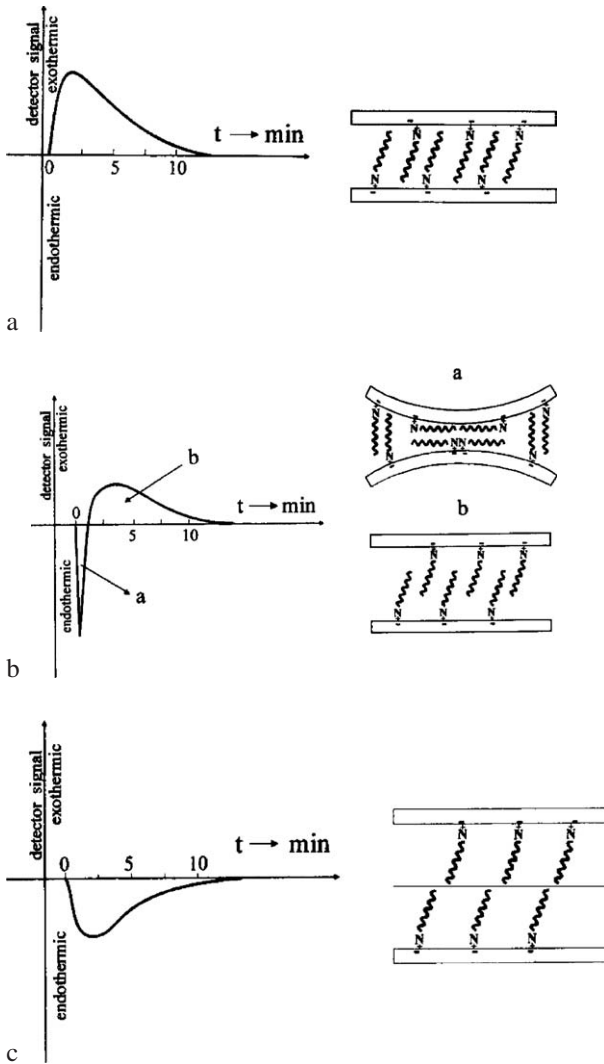


Fig. 7.3.18. Heat effects during immersion of organo montmorillonites in organic solvents (a) exothermic signals for hexadecylammonium montmorillonite in methanol (basal spacing 3.2 nm), (b) endothermic and exothermic heat effects for hexadecylammonium montmorillonite in toluene (basal spacing 3.8 nm), (c) endothermic signal for octadecylammonium montmorillonite in methanol-toluene (molar fraction of methanol 0.05, basal spacing 4.6 nm).

about 0.11 nm are related to the formation of kink-blocks, whereas the larger decrease at higher temperature (between 45 °C and 100 °C, depending on the alkyl chain lengths) is caused by the re-arrangement of the kink-blocks into gauche-blocks (Baur, 1975; Stohrer and Noack, 1975; Lagaly, 1976, 1981b; Pechhold et al., 1976).

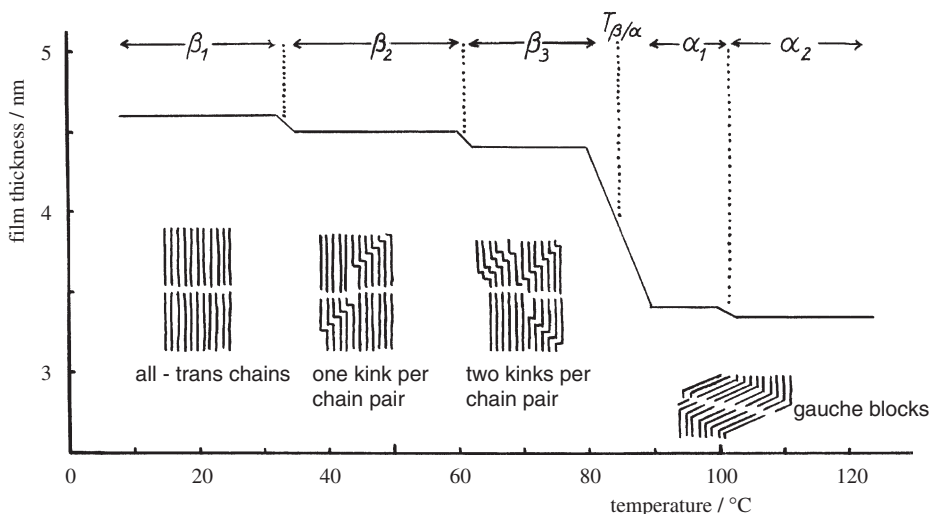


Fig. 7.3.19. Phase changes (schematic) of interlayer bimolecular films, for instance of bilayers of alkanol and alkylammonium ions in 2:1 clay minerals. From Lagaly et al. (1976).

Kink-block formation is a consequence of conformational changes of the alkyl chains. Transition of the sequence of three *trans* C–C bonds into a *gauche*(+)*–trans–gauche*(–) conformation is called a kink (Fig. 7.3.20). Gauche-blocks are formed due to the desorption of a certain amount of interlayer alcohol. The chains in these structures contain isolated gauche bonds or, more likely, *gauche*(+)*–trans–gauche*(+) conformations, and both chain sections are no longer parallel but form an angle.

Kink and gauche-block formation were also reported for alkylammonium montmorillonites with intercalated poly(ethylene oxides) (Platikanov et al., 1977) and the alkanol derivatives of alkali and earth alkali clay minerals (Pfirrmann et al., 1973). Many other layered materials with intercalated long-chain compounds show these thermal phase transitions (Lagaly et al., 1975; Lagaly, 1981b; Rösner and Lagaly, 1984).

Kinks are typical defects in films of self-aggregating long chain compounds. In a lamella of alkyl chains the probability of kink formation in a chain depends on the state of neighbouring chains. Steric effects play a fundamental role in this process. The geometric conditions in the alkanol-alkylammonium smectites and vermiculites appear to be optimal for kink-block formation. If a kink is formed in one alkyl chain (nucleation step), the displaced part of the chain thrusts against the neighbouring chains, which give way in a formation of kinks (growth step), and an ordered kink-block forms (Fig. 7.3.21). If the packing density is too high (as in the uranyl vanadate uvanite), the nucleation of kinks is rendered more difficult and the basal spacing remains constant up to the transition into gauche-blocks. The different lateral symmetry in uranium micas leads to random formation of kinks (Lagaly, 1981b).

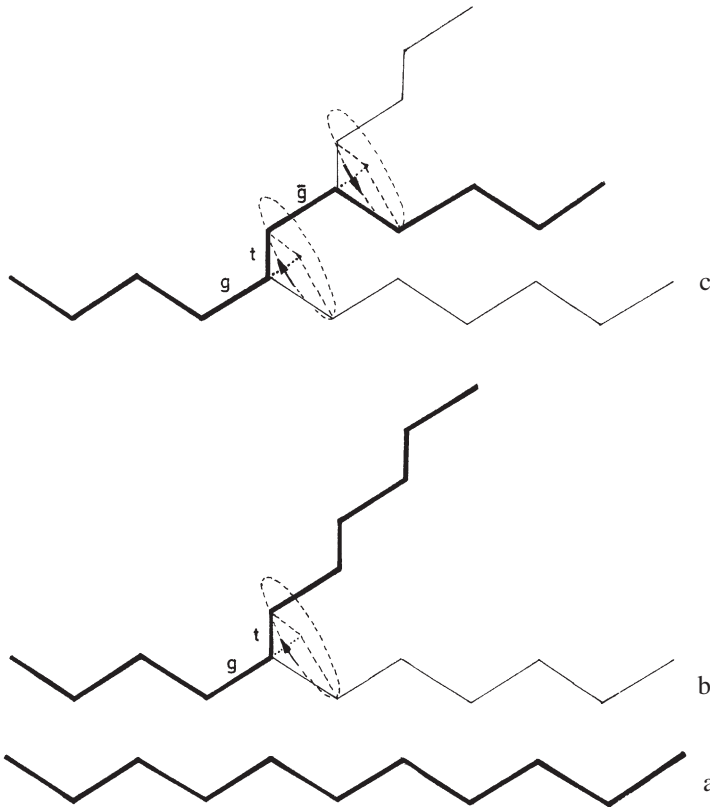


Fig. 7.3.20. Formation of kinks in alkyl chains (a) all-trans chain, (b) insertion of one *gauche* bond, (c) insertion of a second *gauche* bond and formation of the kink. From Lagaly (1976).

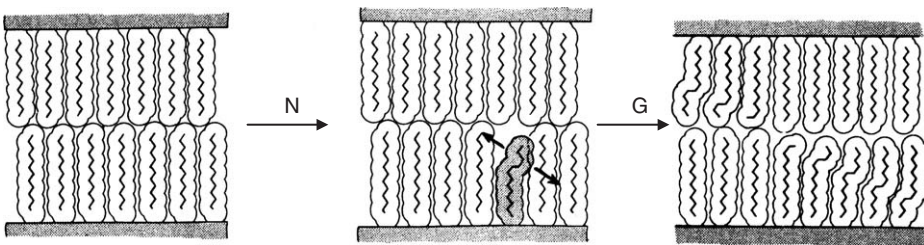


Fig. 7.3.21. Formation of kink-blocks as a co-operative reaction. N, G nucleation and growth step. From Lagaly (1976).

The alkanol-alkylammonium clay minerals and their phase transitions provide useful models of possible conformational changes of alkyl chains in mono- and bi-layer films. Unsaturated chains with *cis*- double bonds are important components in biomembranes. It was shown that they can be incorporated in lipid films when the

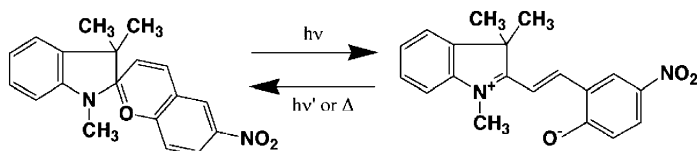
chains assume conformations like *cis-trans-gauche* (Lagaly, 1976; Lagaly et al., 1976). The transition into *gauche*-blocks is related to the “chain melting” or crystalline/liquid-crystalline phase transitions of lipids. The possibility of conformational changes of interlayer alkyl chains is an important condition in preparing nanocomposites.

Phase transitions induced by conformational changes of the alkyl chains were also observed for dialkyl dimethylammonium clay minerals (Okahata and Shimizu, 1989). The phase transition affects the permeation properties and intra- and intermolecular reaction kinetics of the adsorbed species. An example is the photoinduced thermal isomerisation of merocyanine (MC) into spiropyran (SP) (Scheme IX) in dioctadecyl dimethylammonium montmorillonite (Seki and Ichimura, 1990). The decoloration reaction rate is dependent on the mobility of the surrounding chains and is influenced by the phase transition. The reaction rate abruptly increased near the gel to liquid-crystal phase transition temperature at 54 °C.

The phase transition was also investigated by luminescence measurements with 1,3-di(1-pyrenyl)propane and pyrene (Ahmadi and Rusling, 1995). The first molecule provided a better probe molecule than pyrene because of the two pyrene groups and formed intramolecular excimers at extremely low concentrations. In the gel state at lower temperature, the hydrocarbon chains in *trans* conformation were more rigid than in the liquid crystalline state when the alkyl chains contained many *gauche* conformations and kinks. Above the phase transition the relative intensity of the excimer peak increased gradually with increasing temperature and indicated the increased mobility of the alkyl chains. The phase transitions of the dialkyl dimethylammonium silicates were also indicated by the temperature dependence of the pyrene fluorescence as well as by the photochromism of azobenzene. The phase transition temperatures reported for the dioctadecyl dimethylammonium clay minerals are listed in Table 7.3.4 (Ogawa et al., 1999).

7.3.9. INTERCALATION OF POLYMERS AND PROTEINS

The interaction of clay minerals with organic macromolecules received a considerable amount of attention because of the use of clays and polymers in many industrial applications and in soil conditioning (see Chapter 10) (Theng, 1970, 1979, 1982). In many cases the polymers are adsorbed on the external surface and are not intercalated. The adsorption of macromolecules and the influence of polymers on the



Scheme IX.

Table 7.3.4. Basal spacings and phase transition temperatures of silicates modified with dioctadecyl dimethylammonium ions

Silicate	Phase transition temperature (K)	Basal spacing (nm)	Technique	Reference
Montmorillonite*	327	4.24	Thermal decoloration of photomerocyanine to spiropyran	Seki and Ichimura (1990)
Montmorillonite*	327	4.83	Permeation of a fluorescence probe [‡] and DSC	Okahata and Shimizu (1989)
Bentonite	326	4.3	Pyrene luminescence	Ahmadi and Rusling (1995)
Bentonite	327		Electrochemical reduction of trichloro acetic acid	Hu and Rusling (1991)
TSM [†]	328	3.4	Photochromism of azobenzene	Ogawa et al. (1999)

*Kunipia G, Kunimine Industries Co.

[†]Sodium fluorotetrasilicic mica, ideal composition $\text{NaMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$, Topy Industries Co.

[‡]1-(1,3,4,5-Tetrahydroxy cyclohexane carboxyamido) naphthalene.

colloidal properties of clay dispersions are described in Chapter 5. The discussion in this chapter refers to the intercalation of polymers.

Many linear non-ionic polymers penetrate into the interlayer space when the clay mineral is dispersed in aqueous or organic solvents of the polymers. Several types of macromolecules of technical importance are intercalated from aqueous solutions (Table 7.3.5). Even alkylammonium montmorillonites intercalate poly(ethylene oxides) from aqueous solutions.

Many polymers are intercalated in extended conformation and in strong contact with one (bilayers of macromolecules) or two silicate layers (monolayers) (Table 7.3.5). The unfolding of polylysine and polyglutamic acid during intercalation into montmorillonite was recently described by Gougeon et al. (2003). The reason for the preference of trains over loops is the van der Waals interaction between the polymer segments and the surface oxygen atoms and the reduced importance of the solvent in the interlayer space. A good geometrical fit is often achieved between the macromolecules and the surface, which increases the van der Waals interaction considerably. As a result, the amount of solvent in the interlayer space is determined by the volume available between the macromolecules constrained between the silicate layers. Loops as a consequence of good solvency are generally not formed and the expansion

Table 7.3.5. Intercalation of neutral polymers into Na⁺ and Ca²⁺-montmorillonite

Polymer	Cation	Basal spacing (nm)		Reference
		in solution	dried	
Poly(vinyl alcohol)	Na ⁺	Diffuse	1.36, at 65 °C	Lagaly, 1986a
	Ca ²⁺	1.9–2.0	1.48, at 70 °C	Greenland, 1963
Poly(vinyl alcohol)*	Na ⁺	Diffuse	4.0, at 65 °C	Lagaly, 1986a
Poly(ethylene oxide)	Na ⁺		1.74, Air-dried	Parfitt and Greenland, 1970a, 1970b
	Ca ²⁺	1.7–2.2	1.73, 10% R. H.	Parfitt and Greenland, 1970a, 1970b
	Na ⁺	1.46 + 1.86		Billingham et al., 1997
	Na ⁺		1.75, at 70 °C	Aranda and Ruiz-Hitzky, 1999
	Na ⁺ †	1.78–1.87		Bujdák et al., 2000
Poly(ethylene-propylene oxide)	Na ⁺	1.83‡	1.37, at 200 °C	Breen et al., 1998
Poly(ethylene oxide)-10-cetyl ether (Brij 56)	Ca ²⁺		1.73, Air-dried	Deng et al., 2003
Poly(ethylene oxide)-12-nonylphenyl ether (Igepal CO 720)	Ca ²⁺		1.65, Air-dried	Deng et al., 2003
Poly(vinyl pyrrolidone)	Na ⁺	Diffuse§	2.45–2.85, Air-dried	Levy and Francis, 1975a, 1975b
	Ca ²⁺	1.88–1.96§	1.70–1.92, Air-dried	Levy and Francis, 1975a, 1975b
Dextran	Na ⁺		1.76, Air-dried	Olness and Clapp, 1973
	Ca ²⁺		1.43, Air-dried	Olness and Clapp, 1973
Polysaccharides	Na ⁺	1.6	1.47, P ₄ O ₁₀	Parfitt and Greenland, 1970c
	Ca ²⁺	1.4	1.37, P ₄ O ₁₀	Parfitt and Greenland, 1970c

*In the presence of boric acid.

†With reduced charge montmorillonites.

‡Stable up to 150 °C.

§In contact with 1% PVP ethanol solutions and different amounts of water.

||Reflections rather diffuse.

of the interlayer space is modest, often corresponding to the thickness of the linear macromolecules (for monolayers) or twice this value (for bilayers). Thus, large basal spacings up to delamination are generally not observed. This structure distinguishes intercalated polymers from polymers adsorbed on freely accessible surfaces.

In contrast to polymer adsorption on external surfaces, interlayer adsorption can lead to a preference for smaller macromolecules. Simon et al. (2002) observed the preference of montmorillonite for hydroxyethyl cellulose molecules of lower molecular weight.

The single silicate layers often aggregate when a polymer is added to highly dispersed and delaminated sodium smectites. Examples are poly(vinyl pyrrolidone) (PVP) (Levy and Francis, 1975a, 1975b), poly(ethylene oxides) (Ogata et al., 1997a), and poly(L-lactide) (Ogata et al., 1997b). In other cases, e.g. with non-ionic polyacrylamide, the colloidal distribution of the silicate layers is retained but the tactoid size increases (Bottero et al., 1988). Larger amounts of macromolecules can impede parallel orientation of the silicate layers as observed for sodium montmorillonite and poly(vinyl alcohol). When this polymer is added to a sodium montmorillonite dispersion, the silicate layers remain in colloidal distribution (Ogata et al., 1997a). During the desorption of water by drying, steric constraints by some macromolecules attached to the silicate layers impede re-aggregation of a certain number of layers so that not all silicate layers can re-aggregate forming ordered domains (Fig. 7.3.22) (Lagaly, 1986a). Wide-angle X-ray powder diffraction diagrams pretend fully ordered materials but small-angle scattering reveals the presence of additional disordered domains.

A few macromolecules assume helical conformations in the interlayer space: poly(vinyl alcohol) intercalated in sodium montmorillonite in the presence of boric acid (Table 7.3.5) (Lagaly, 1986a) and poly(ethylene oxides) intercalated in clay

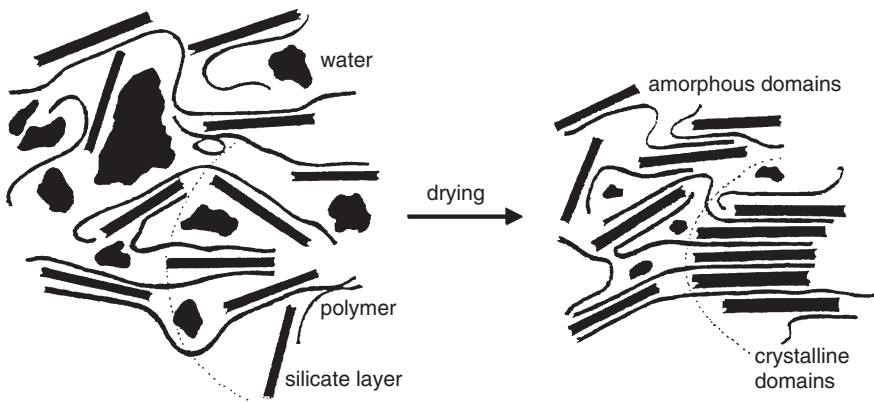


Fig. 7.3.22. Single silicate layers embedded in poly(vinyl alcohol)-water. The geometrical constraint exerted by a part of the macromolecules impedes re-aggregation of a certain number of silicate layers into ordered domains during drying. From Jasmund and Lagaly (1993).

minerals (Aranda and Ruiz-Hitzky, 1999) and layered dichalcogenides (Hernán et al., 1998).

The effect of the nanometer confinement on the short-time dynamics of intercalated polymers was studied by molecular dynamics simulation for poly(ethylene oxides) (Kuppa and Manias, 2003).

Strawhecker and Manias (2003) studied the crystallisation of poly(ethylene oxides) in the presence of sodium montmorillonite with differential scanning calorimetry and cross-polarisation optical microscopy. The coordination of poly(ethylene oxide) to the surface sodium ions promoted the miscibility of montmorillonite and polymer, but favoured the amorphous structure of poly(ethylene oxide) on the montmorillonite surface so that formation of crystal nuclei in the vicinity of the clay mineral was inhibited.

Complex macromolecules cannot penetrate into the interlayer space. One possible way to enhance polymer adsorption is the propping-open procedure (see Section 7.3.1). Observations during the alkylammonium exchange of Andalusian black soils were explained by the presence of natural macromolecules (of unknown identity) that penetrated into the interlayer space when it was opened by alkylammonium ions (Fernandez-Gonzales et al., 1976). The disaggregation–reaggregation mechanism provides a further way of enhanced polymer adsorption (Larsson and Siffert, 1983). When clay mineral particles came into contact with the protein lysozyme, they aggregated forming an interlayer space filled with the protein (Fig. 7.3.23a). Stirring this dispersion created fresh surfaces that again adsorbed lysozyme molecules and aggregated. In this way complete saturation with lysozyme was achieved by alternating disaggregation and reaggregation processes. In a similar way, sodium montmorillonite reacted with polyvanadic acid forming montmorillonite–vanadium oxide hydrogels. Drying yielded non-dispersible xerogels of the lamellar solids (Anaissi et al., 2001).

The particles may not require to be split under mechanical forces. As described for polycations (see Chapter 5), the strong interaction between a polymer-coated face and the bare face of two particles can peel off one silicate layer of each particle so that two fresh surfaces can again adsorb the macromolecules. Eventually, all layers are aggregated and separated by the polymer (Fig. 7.3.23b) (Breen et al., 1996; Billingham et al., 1997).

Cationic polymers strongly interact with clay minerals and penetrate between the layers if their segments are not too bulky. Displacement of the interlayer cations and covering of the internal surface are often not quantitative. As penetration proceeds, the increasing number of contacts reduces the mobility of the polycations so they cannot occupy the whole interlayer space, but accumulate near the edges.

The adsorption of polycations reduces the cation-exchange capacity of the clay mineral and can provide the clay mineral a certain anion-exchange capacity as a consequence of positive charges not balanced by surface charges (Ueda and Harada, 1968). These authors attributed the anion-exchange capacity to the loops and tails of the polycations. With denser surface coverage, the proportion of loops and tails increased relative to the train segments and the anion-exchange capacity gradually raised while the cation-exchange capacity was reduced. However, this effect was

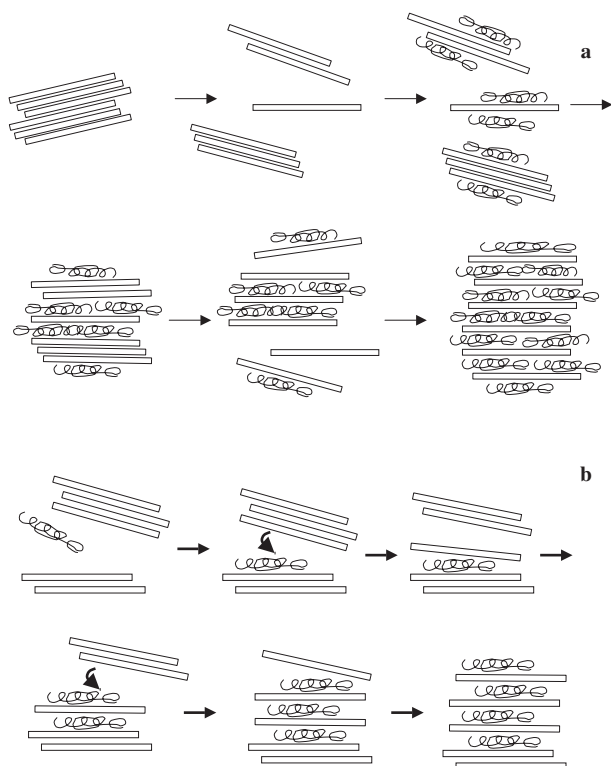
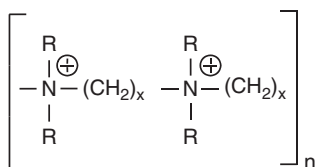


Fig. 7.3.23. Formation of intercalated montmorillonite-polymer hybrids by the dis-aggregation/re-aggregation mechanism proposed for lysozyme intercalation (Larsson and Siffert, 1983) (a) and (b) the “peal-off mechanism” proposed for polycations (Breen et al., 1996; Billingham et al., 1997).



Scheme X.

scarcely been studied. A recent study revealed the anion-exchange capacity of chitosane-montmorillonite (Ruiz-Hitzky et al., 2001).

The adsorption of polyionenes (Scheme X) was studied in detail and illustrated the combined effects of electrostatic interaction and steric factors (Lagaly, 1986a). The electrostatic interaction of the charges is important but by no means exclusively

decisive. An optimal geometrical fit between the macromolecules and the surface atoms has great influence and can overcome the electrostatic interactions. The high van der Waals energy at optimum geometrical fit can even lead to the adsorption of macroions at surfaces with the same sign of charges (Norde, 1983, 1986).

Polyimines are important technical products, for example used in paper making as retention aids. The technical polyimines are not simple linear polycations but are branched and cross-linked polymers. Nevertheless, they penetrate to some extent into the interlayer space of montmorillonite. The interplay between disaggregation and reaggregation of montmorillonite particles by polyimines or other polymers may be useful in optimising retention aids in the paper industry (see Chapter 5).

Polyanions do not penetrate into the interlayer space but considerable amounts can be enriched at the edges of clay mineral particles. The edges provide strong adsorption sites for many polyanions so that these compounds are very useful as flocculants (see Chapter 5).

The pronounced aggregation of delaminated smectites in the presence of polymers is a serious obstacle in preparing clay-polymer nanocomposites (see Chapter 10.3). A promising way is intercalation of melted polymers, for instance poly(ethylene oxides) (Vaia et al., 1993, 1995, 1997) or polystyrene (Vaia et al., 1993, 1996). When melted poly(ethylene oxide) was intercalated, the macromolecules penetrated completely between the layers whereas poly(ethylene oxide) molecules from aqueous solutions penetrated only to some extent between the silicate layers, a consequence of the good solvency of water for poly(ethylene oxides) (better-than-theta condition).

The study of protein adsorption began many decades ago. Proteins of minor complexity that can unfold penetrate between the silicate layers (Ensminger and Gieseking, 1939; Talibudeen, 1954; Weiss, 1963b; Armstrong and Chesters, 1964). Large size and high complexity (inability to unfold) prevent most proteins from penetrating between the silicate layers. However, many proteins are tightly adsorbed at the edges. The wedge-shaped opening of the interlayer spaces favours the adsorption of complex molecules.

Protein adsorption often goes through a maximum near the isoelectric point of the protein. The adsorption maximum indicates the protonation of the protein is not the only effect of pH changes. Progressive unfolding with increasing distance from the isoelectric point can decrease the adsorption. The protein is still adsorbed at higher pH where the net protein charge is negative. As mentioned above, strong van der Waals interactions can overcome the electrostatic repulsion (an effect well-known to colloid scientists).

Adsorption and activity of enzymes were studied in detail by Quiquampoix and co-workers using β -D-glucosidase and bovine serum albumin (Quiquampoix, 1987a, 1987b; Quiquampoix and Ratcliffe, 1992; Quiquampoix et al., 1989, 1993). Owing to the irreversible adsorption of these enzymes, the activity of an adsorbed enzyme at a given pH depended on the pH at which adsorption took place. Three domains are distinguishable:

- At pH below the isoelectric point, the electrostatic interaction between the enzyme and the surface is strong and causes conformational changes of the enzyme with a reduction or loss of the catalytic activity.

- At pH near the isoelectric point, the enzyme is adsorbed by non-electrostatic forces (hydrogen bonds, van der Waals forces, and hydrophobic interaction), which in many cases are too weak to modify the protein structure.
- At pH above the isoelectric point, adsorption of the enzyme at low-ionic strength is reduced or absent but occurs at high-ionic strength.

In displacement reactions, Quiquampoix (1987b) observed small cations like pentylammonium were displaced by β -D-glucosidase regardless of the enzyme charge. Adsorbed poly(ethylene oxides) were displaced when the enzyme was positively charged. Positively charged lysozyme was not displaced by glucosidase.

As a consequence of the clay mineral–enzyme interaction, the effect of pH on the activity of an enzyme in soils differs from that in solution. In other words, at a given pH in the soil, enzymes excreted by microorganisms or plant roots can show an activity different from that in solution (Quiquampoix and Ratcliffe, 1992; Quiquampoix et al., 1993).

Recently, Baron et al. (1999) studied the interaction of α -chymotrysin with montmorillonite (in D₂O). At pD = 4.5–10 (pD = pH + 0.4) adsorption only perturbed some peripheral domains of the protein compared to the solution. The inactivation of the catalytic activity of the adsorbed enzyme at pD = 5–7 was due mainly to the steric hindrance when three essential imino/amino groups were oriented to the clay mineral surface. When these functional groups lost their positive charge at higher pD values, the enzyme changed the orientation and recovered an activity similar to that in solution at equivalent pH.

7.3.10. POLYMERISATION IN THE INTERLAYER SPACE

Interlayer polymerisation and polycondensation reactions were described for many monomers. The reaction is usually started by initiator molecules, e.g. polymerisation of acrylonitrile by initiation with benzoyl peroxide (Kato et al., 1979a, 1979b; Bergaya and Kooli, 1991), or by enhanced temperature, e.g. ϵ -caprolactam into poly 6-amide at 250 °C (Fukushima et al., 1988) and acrylonitrile in kaolinite (Sugahara et al., 1988). In a few cases, e.g. diazomethane (Bart et al., 1979) or 4-vinylpyridine (Friedlander, 1963), spontaneous polymerisation was observed, probably initiated by the enhanced acidity of the interlayer water molecules. Potential initiation sites are also Lewis acid sites and redox centres (Solomon and Loft, 1968). Polymerisation of benzene to poly(*p*-phenylene) on Cu²⁺-smectites is initiated by the loss of aromaticity of benzene by charge transfer from benzene to the Cu²⁺ ions (Stoessel et al., 1977; Walter et al., 1990; Eastman et al., 1996).

If the monomers are hydrophobic molecules such as styrene, the clay mineral has to be made hydrophobic by the reaction with alkylammonium ions (Kato et al., 1981). Fukushima and Inagaki (1987) and Fukushima et al. (1988) modified montmorillonite with 11-carboxy undecylammonium cations (protonated ω -amino undecanoic acid) before ϵ -caprolactam was intercalated and polymerised into poly 6-amide: the study of clay mineral–polymer nanocomposites came into vogue.

Polyimide clay hybrids were prepared by interlayer polymerisation of diamino diphenyl ether and pyromellitic dianhydride yielding of poly(amic acid) which was transformed into the polyimide by decomposition of water at 300 °C (Yano et al., 1997).

Weimer et al. (1999) described the anchoring of living polymerisation initiator molecules inside the interlayer space.

As discussed in Section 7.3.8, adsorption of polymers by clay minerals, even after modification, usually does not lead to delamination, which is a basic requirement for preparing clay mineral–polymer nanocomposites for technical applications. The most promising way is the interlayer polymerisation. The enthalpy evolved during the interlayer polymerisation provides an essential contribution to the exfoliation (Lan et al., 1995). A variety of interlayer polymerisation or polycondensation reactions were studied (Kelly et al., 1994; Lan and Pinnavaia, 1994; Messersmith and Giannelis, 1994; Lan et al., 1995; LeBaron et al., 1999; Triantafillidis et al., 2002). Interlayer polycondensation of polyols and diisocyanates yielded polyurethane–clay mineral nanocomposites (Wang and Pinnavaia, 1998; LeBaron et al., 1999; Zilg et al., 1999).

7.3.11. ADVANCED APPLICATIONS OF CLAY MINERAL-ORGANIC COMPLEXES

Organic modification of clay minerals is a decisive step in preparing very different types of advanced materials. Actual interests are directed to the tailoring of clay minerals for the use of adsorbents, thickening and thixotropic agents, for preparing nanocomposites (see Chapter 10.3), and to create new materials with catalytic (Hu and Rusling, 1991), optical (Ogawa and Kuroda, 1997), and electronic functions (switches and sensors) (Fitch, 1990; Fitch et al., 1998; Fendler, 2001). Bentonites modified by organic cations provide colloidal adsorbents for improved pesticide formulations with reduced leaching (see Chapter 11.2). The dispersion of organoammonium clays in organic solvents and polymers is an important step in many practical applications (see Chapters 5, 10.1, and 10.3). The enhanced thermal stability of the organo phosphonium derivatives compared with the alkylammonium derivatives may be of advantage for melting processing of clay mineral nanocomposites (Xie et al., 2002). Preparation of pellets of clays and clay–organic intercalation compounds for chromatographic applications was reported by several authors (Bondarenko et al., 1982, Nakamura et al., 1988, Klopogge et al., 1997).

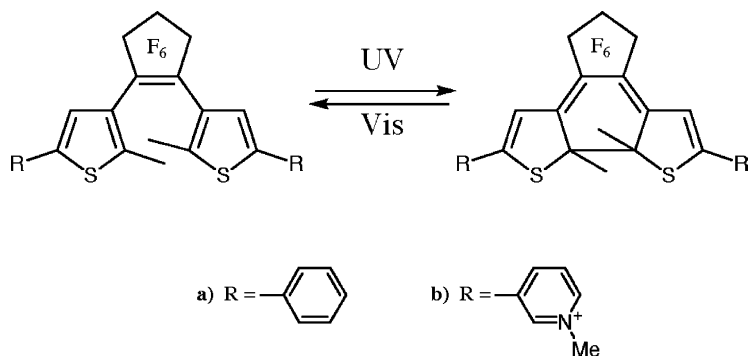
The organoammonium ions not only provide hydrophobic interlayer spaces but also control the states of the adsorbed species. An example is the intercalation of aromatic molecules in long-chain quaternary alkylammonium smectites by solid-state reactions (Ogawa et al., 1992a, 1993). Fluorescence spectra of the intercalated arenes and X-ray diffraction indicated the influence of the arrangement of the alkylammonium ions on the adsorption state of the guest species. When, for instance,

the alkylammonium ions were arranged parallel to the silicate layers, the intercalated pyrene molecules were aggregated, but were more evenly distributed when the interlayer alkylammonium ions assumed a paraffin-type arrangement. Thus, one can create various reaction environments by selecting alkylammonium ions of different size and differently charged clay minerals.

To develop advanced materials, a wide variety of photochromic reactions in clay-organic systems were studied (Seki and Ichimura, 1990; Takagi et al., 1991; Tomioka and Itoh, 1991; Ogawa and Ishikawa 1998; Ogawa et al., 1999). The photochromism of an intercalated cationic diarylethene, 1,2-bis(2-methyl-3thiophenyl) perfluorocyclopentene bearing two pyridinium substituents at each thiophenyl ring, was recently reported (Scheme XI) (Sasai et al., 2000a). Oriented films of the intercalation compound were prepared by casting so that the dye orientation could be derived from the basal spacing and the spectra of polarised light. The photochromic reaction was efficient and smooth but efficiency decreased with repeated irradiation. The decrease was attributed to the formation of photoinactive species. Degradation was suppressed by co-adsorption of dodecylpyridinium cations.

The optical properties of pseudoisocyanine dyes are under extensive investigation. Important properties of molecular assemblies of these dyes in head-to-tail arrangement (J-type aggregates) are non-linear optical behaviour and spectral hole burning, which is potentially used as a new type of memory storage. The pseudoisocyanine dyes mostly form H-aggregates (head-to-head aggregation) in aqueous solutions. Formation of J- and H-aggregates was observed in dispersions of montmorillonite. Evidently, the cationic dyes formed domains with J- or H-type aggregation. Spectral bleaching of the dyes was also observed in these systems (Bujdák et al., 2002).

Ogawa et al. (1992b) described the photochemical hole burning (PHB) of tetramethylammonium saponite with intercalated quinizarine. PHB was induced by resonant laser light irradiation at cryogenic temperatures. The site-selective and persistent photobleaching was indicated by the decreased absorption (hole) at the wavelength of the laser within the broadened absorption band. PHB attracted



Scheme XI.

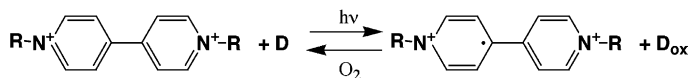
increasing attention due to its possible application for optical storage at the high-density frequency domain. The PHB characteristics depend significantly on the nature of host–guest interactions. The PHB reaction of quinizarine is related to the break of one or more internal hydrogen bonds and the subsequent formation of external hydrogen bonds to proton acceptors in the matrix. The quinizarine molecules were incorporated into the tetramethylammonium saponite at monomolecular level without aggregation, a pre-requisite for effective PHB.

Miyata *et al.* (1987) reported the photochromism of viologens (1,1'-dialkyl-4,4'-bipyridinium ions) intercalated into montmorillonite together with PVP. The viologens were reversibly photoreduced in the presence of an electron donor, forming blue radical cations with absorption bands at 610 and 400 nm (Scheme XII). The co-intercalated PVP was assumed to act as an electron donor for the reduction of the viologens. Colour-fading of the blue radical cations required a longer time period than in the matrix of pure PVP because the contacts between the viologen radical cations and the oxidising agents were reduced.

Stabilisation of dyes by intercalation was applied in the production of carbon-less copying paper and for thermal dye transfer printing (Ito *et al.*, 1996). During this type of printing, the dye migrates from an ink layer (a colour ribbon) to the clay particles dispersed in a receiver layer. Tetra-*n*-decylammonium or dioctadecyl dimethylammonium montmorillonite was used as a component in the receiving layer for cationic dyes like Rhodamine 6G and an oxazine dye. The image fixation occurred by cation exchange. The counter anions of the dye in the ink layer and the interlayer cations of the clay mineral in the receiving layer influenced the printing speed.

Preparation of ultraviolet radiation filters was based on the absorption properties of dye–clay mineral hybrids (Vicente *et al.*, 1989; Del Hoyo *et al.*, 2001). Further studies are needed to optimise the UV absorption and to reduce desorption of the intercalated dye molecules.

Application of clay minerals in advanced materials will increasingly require oriented films. Smectites can be fabricated as thin films on substrates or self-supporting films by casting the aqueous dispersions. Long-chain alkylammonium smectites swell in organic solvents, while the tetramethylammonium smectites swell in water. By simply casting the dispersions in organic solvents or water, thin films are formed with the *ab* planes of elementary platelets oriented parallel to the substrate. The driving force for the orientation is gravity. Spin and dip coating of clay dispersions on substrates are further ways to prepare thin films with thicknesses of ~10 nm to a few hundreds of nm. Films with precisely controlled thickness are prepared by the Langmuir–Blodgett technique (see Chapter 5).



Scheme XII.

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