Handbook of Clay Science
Edited by F. Bergaya, B.K.G. Theng and G. Lagaly
Developments in Clay Science, Vol. 1

Chapter 3

SURFACE AND INTERFACE CHEMISTRY OF CLAY MINERALS

R.A. SCHOONHEYDT[a] AND C.T. JOHNSTON[b]

[a]*Center for Surface Chemistry and Catalysis, Kuleuven, B-3001 Leuven, Belgium*
[b]*Department of Soil and Environmental Sciences, Purdue University, West Lafayette, IN 47907-1150, USA*

The surface properties of clay minerals depend on many factors including chemical composition, nature of the surface atoms (mainly oxygen and hydrogen), extent and type of defect sites, layer charge and the type of exchangeable cation(s) (see Chapter 2). One distinguishes between the edge surface and the planar surface, edges being usually associated with defect sites and pH-dependent charges (see also Chapter 5). Here we start with a description of the surface atoms and surfaces of clay minerals and continue with the interaction between the surface atoms and adsorbed molecules with special attention to water. This is followed by a discussion of the surface chemistry of smectites in aqueous suspension, leading to the exciting recent research on clay mineral nanofilms. The general principles are given and illustrated with specific examples. Experimental data are mainly derived from spectroscopic studies.

3.1. SURFACE ATOMS

The basal surface atoms of a 2:1 clay mineral are the oxygen atoms of the Si-tetrahedra; for 1:1 minerals the surface is constituted by the same type of oxygen atoms on the Si-side of the layer and by OH groups from Al-octahedra (kaolinite) and Mg-octahedra (serpentine) on the Al- or Mg-side of the layer. These basal surface oxygen atoms and hydrogen atoms are chemically similar but are crystallographically different.

Permanent charge is introduced onto the siloxane surface of clay minerals as a result of isomorphous substitution. Common examples are Al for Si in the tetrahedral sheet and Mg for Al in the octahedral sheet. When Al substitutes for Si in the tetrahedral sheet, local distortions occur because of the difference between the Si–O and Al–O bond lengths, respectively, 0.162 and 0.177 nm (Nemecz, 1981). The bridging oxygen, Si–O–Al, is similar to the bridging oxygen in zeolites (Sauer, 1989).

DOI: 10.1016/S1572-4352(05)01003-2

The most important structural-chemical information about the surface oxygens can be obtained from simple considerations of the Pauling electronegativity of the atoms of the crystallographic unit cell (Table 3.1).

As the ionicity of a bond is proportional to the difference in electronegativities of the atoms, involved in the bond, it follows that the ionicity of the bonds in clay minerals follows the order:

$$\mathrm{H{-}O} < \mathrm{Si{-}O} < \mathrm{Alsubind:{-}O} < \mathrm{Mgsubind:{-}O} < \mathrm{Li{-}O}$$

As a consequence, the charge on the oxygen is expected to increase in the same order (i.e., Si < Al < Mg < Li). Although these considerations are oversimplified because they do not take into account the structure and chemical composition of the clay mineral, nor the coordination of the cations, they provide the correct qualitative differences between these structural cations. Sanderson's (1976) electronegativity equalisation principle states that the electron flow in a molecule or solid in the ground state is such that, at equilibrium, the electronegativities of all the atoms are equal. The electronegativity of molecules and solids is then calculated as the geometric mean of the electronegativities of the constituent atoms (Table 3.1). The calculated electronegativity values of selected clay minerals are given in Table 3.2.

Table 3.1. Electronegativity of the most common atoms in clay minerals[a]

Atom	χ (Pauling)	χ (Sanderson)
O	3.44	3.46
Si	1.90	1.74
Al	1.61	1.54
Mg	1.31	1.42
Li	0.98	0.86
H	2.2	2.31

[a] From Huheey (1978).

Table 3.2. Sanderson's electronegativity values of typical clay minerals

Clay	Idealised chemical formula	χ (Sanderson)	χ (EEM)
Hectorite	$Si_8Mg_{5.25}Li_{0.75}\ O_{20}(OH)_4$	2.760	
Beidellite	$Si_{7.25}Al_{0.75}Al_4\ O_{20}(OH)_4$	2.928	
Montmorillonite	$Si_8Al_{3.5}Mg_{0.5}\ O_{20}(OH)_4$	2.927	5.11
Kaolinite	$Si_4Al_4\ O_{10}(OH)_8$	2.895	3.27

Table 3.3. Charges on surface atoms, obtained by EEM

Structure	Atom	Electronic charge
Kaolinite	H(inner)	0.152
	H(surface)	0.219
Montmorillonite	O(no cation)	−0.522 to −0.741[a]
	O(K^+)	−0.800 to −0.867[a]

[a] The charge depends on the crystallographic position.

Using the semi-empirical electronegativity equalisation method (EEM), (Mortier, 1987) the structure of the clay minerals can also be taken into account in the calculations. This has been done for kaolinite and K^+-montmorillonite (Nulens et al., 1998). These numbers are also given in Table 3.2.

The data show that beidellite with tetrahedral Al in the structure is the most electronegative 2:1 clay mineral and is predicted to have the most reactive surface.

Besides these overall chemical properties of clay minerals, special attention must be given to the surface atoms: oxygen and hydrogen. When one compares the charges on the atoms calculated with the EEM method (Nulens et al., 1998), two trends are immediately clear. The charge on the surface hydrogen atoms of kaolinite is higher than on the inner hydrogen atoms; and the charge on the oxygen atoms in contact with an exchangeable cation is higher than in the absence of exchangeable cations. In other words, the cations (represented as point charges) polarise the oxygen atoms with which they are in contact (Table 3.3).

One comes then to the following general conclusions about the surface properties of clay minerals. In the absence of isomorphous substitution and defect sites, the clay–mineral surface is composed of oxygen atoms involved in Si–O bonds. The latter have considerable covalent character and the surface is hydrophobic. Hydrophilicity is introduced by isomorphous substitution inducing the presence of exchangeable cations, which are hydrophilic and which polarise the surface oxygen atoms (Nulens et al., 1998). Hydrophilicity may also arise from the presence of hydroxyl groups at the surface such as in kaolinite and from defect sites.

3.2. SURFACE STRUCTURES AND PROPERTIES

3.2.1. The Neutral Siloxane Surface

The least reactive surface found on clay minerals under ambient conditions is the neutral siloxane surface that occurs on 2:1 phyllosilicates where no isomorphous substitution has occurred (e.g., talc and pyrophyllite), and on the Si-tetrahedral side of 1:1 kaolin group (Yariv, 1992; Giese and van Oss, 1993; Michot et al., 1994; Charnay et al., 2001).

The external oxygen atoms on the siloxane surface are relatively weak electron donors (Lewis bases) and are not capable of having strong interactions with water molecules. Minerals dominated by the neutral siloxane surface (e.g., talc and pyrophyllite) are hydrophobic as evidenced by contact angle and flotation measurements (Giese et al., 1990; Schrader and Yariv, 1990; Michot et al., 1994; Malandrini et al., 1997). These surfaces are non-polar and are not capable of forming hydrogen bonds with water molecules. Recent theoretical studies have shown that the neutral siloxane surface interacts only weakly with water molecules (Nulens et al., 1998). With this type of surface, the water molecules interact predominantly with each other and not with the surface. Additional support comes from a recent ab initio molecular dynamics study of the water–siloxane surface interactions (Tunega et al., 2002) where very weak hydrogen bonds are spontaneously broken and created by the movement of water molecules.

3.2.2. Constant Charge Sites (Siloxane Surface with Permanent Charge)

Many of the chemical and physical surface properties of 2:1 phyllosilicates are influenced by the extent and location of isomorphous substitution in the clay mineral structure. When substitution occurs in the octahedral sheet, the negative charge is more delocalised and the Lewis base character of the siloxane surface is enhanced (Sposito, 1984).

Depending on the extent of isomorphous substitution, these negatively charged sites are separated by distances ranging from 0.7 to 2 nm on the basal surface.The negative charge that results from isomorphous substitution is balanced by the presence of exchangeable cations of which Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} ions are the most common. The chemical nature of these exchangeable cations (i.e., effective ionic radius, hydration energy, hydrolysis constant) determines many of the important chemical and physical properties of clay minerals. A common feature to these cations is that they all have appreciable enthalpies of hydration, with values ranging from -300 to $-1500\,\mathrm{kJ\,mol^{-1}}$ (Atkins and de Paula, 2002). As a result, these cations are capable of acquiring complete or partial hydration shells, the effect of which is to impart an overall hydrophilic nature to the clay mineral. Furthermore, the water molecules surrounding these cations have chemical and physical properties that are distinct from those of bulk water because of their close proximity to the metal cation. Their mobility is more restricted due to polarisation effects by the cation and depends on the nature of the interlayer cation. The water molecules coordinated to the cations can be considerably more acidic than the bulk water. There is increased interest in the swelling mechanisms of clay minerals and the interplay between the hydrophobic and hydrophilic character of clay minerals (Chang et al., 1998; Greathouse and Sposito, 1998; Swenson et al., 2000; Sutton and Sposito, 2001; Hensen and Smit, 2002).

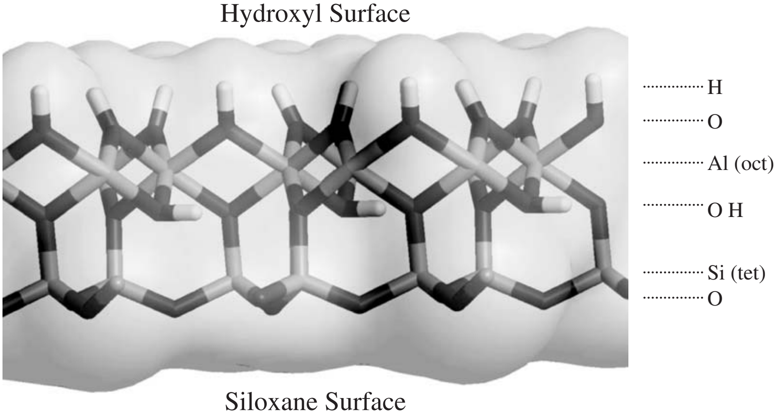

Fig. 3.1. Hydroxyl and siloxane surface of kaolinite.

3.2.3. The Hydroxyl Surface

Another type of surface that clay minerals and related hydroxides possess is the hydroxyl surface. An example is the Al-octahedral surface of kaolinite, shown in Fig. 3.1. This surface is found on 1:1 (kaolin group minerals, halloysite, serpentine) and 2:1:1 (e.g., chlorite) phyllosilicates and also on hydroxides such as gibbsite and brucite.

In the case of kaolinite, the two surfaces (hydroxyl and siloxane) have very different structures and corresponding surface chemistries. This was shown recently in an ab initio molecular dynamics study of water interacting with both types of surfaces (Tunega et al., 2002). Unlike the siloxane surface, which interacts very weakly with interfacial water molecules, the hydroxyl surface interacts strongly with water. This is shown in Figs. 3.2 and 3.3 where the closest $O_{surface}$ to O_{water} distances are plotted over the time course of the molecular dynamics study. The average O...O distances for two different surface oxygen atoms in the tetrahedral sheet are 0.445 and 0.427 nm, respectively. In contrast, the corresponding $O_{surface}$ to O_{water} distances for the oxygen atoms in the hydroxyl plane are 0.263 nm. The considerably shorter distance for the octahedral oxygen atoms reflects the fact that water molecules are hydrogen bonded to the hydroxyl surface. The hydroxyl groups on the basal surfaces of gibbsite and 1:1 phyllosilicates, as well as goethite and other oxides, are coordinated to metal atoms whose coordination environment is complete, and hence are considered to have minimal chemical reactivity.

Hydroxyl groups located at broken edges, steps and related defects of clay minerals and oxides are different, however, and are called ‘terminal OH groups’. These OH groups are under-coordinated and carry either a positive or negative charge depending on the type of metal ion and the pH of the ambient aqueous solution (Fig. 3.4). The pH value where the net surface charge is zero is referred to as the

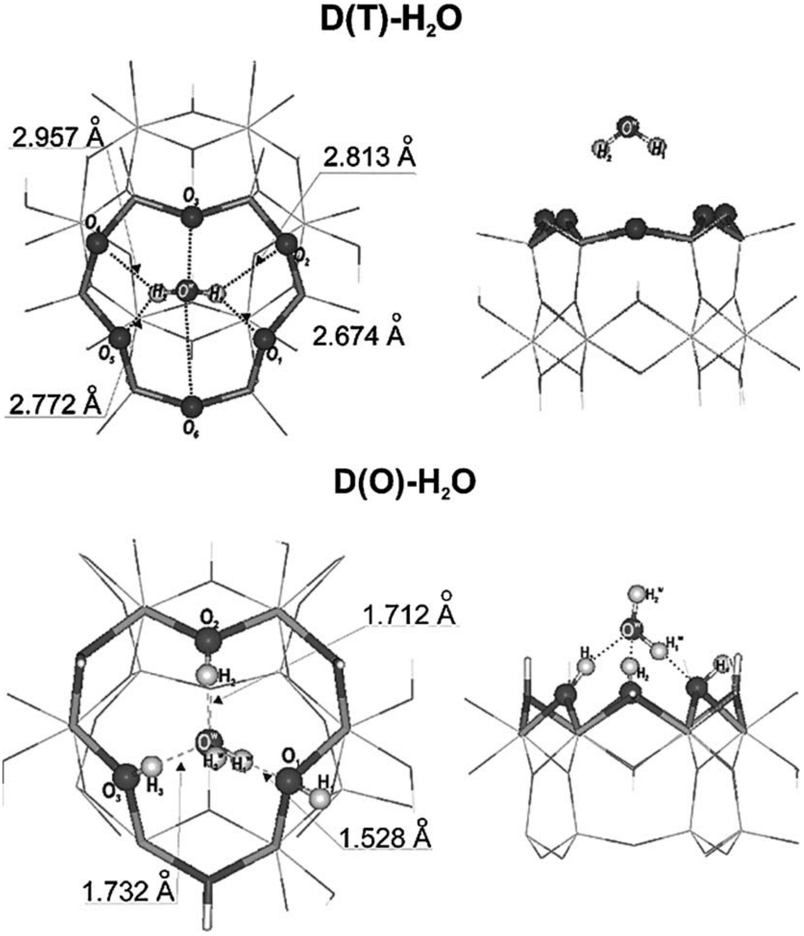

Fig. 3.2. Two views on the H_2O molecule interacting with the octahedral side of the kaolinite layer. The lengths of hydrogen bonds obtained from static relaxations are given in the figure.

point of zero charge (p.z.c.). At pH values higher than the p.z.c of a mineral, the surface will have a net negative charge and will tend to accumulate cationic species. Similarly, the edge surface will have a net positive charge when the ambient pH is lower than the p.z.c. These terminal OH groups also have the potential to chemisorb (also referred to as specific adsorption) certain types of ions, regardless of the pH value. An example is the high affinity of both terminal Al–OH and Fe–OH groups for the phosphate ion. Because these (under-coordinated) terminal OH groups have either a partial positive or partial negative charge, these sites are more reactive than the charge-neutral OH groups on basal surfaces.

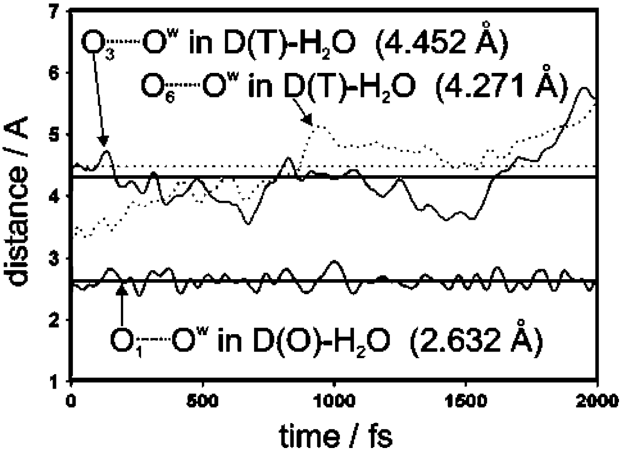

Fig. 3.3. The time evolution of the distances between the water oxygen atom and two-basal surface atoms (O_3 and O_6) in the D(T)–H_2O system (two upper curves). The bottom curve represents the time evolution of the $O_1 \ldots O_w$ distance in the D(O)–H_2O system. Horizontal lines indicate mean values and correspond to the numbers given in the figure.

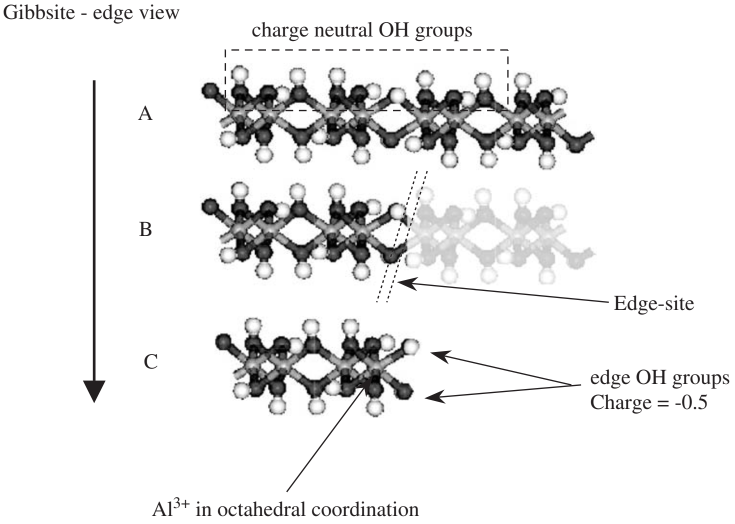

Fig. 3.4. Edge sites of kaolinite.

3.2.4. Hydrophobic–Hydrophilic Character of Clay Mineral Surfaces

The neutral siloxane surfaces found on kaolinite, talc and pyrophyllite have an overall hydrophobic character (Yariv, 1992; Giese and van Oss, 1993; Michot et al., 1994; Charnay et al., 2001). These clay minerals have little, if any, isomorphous substitution, and there is no permanent charge or dipole moment associated with their basal surfaces. Although polar molecules, including water and aqueous electrolytes have a low affinity for the neutral siloxane surface (Michot et al., 1994), non-polar organic solutes (van Oss et al., 1992; Giese and van Oss, 1993), and the non-polar portion of larger biological molecules, such as proteins and enzymes (Servagent-Noinville et al., 2000), can interact with the siloxane-type of surface.

On a more restricted spatial scale, this type of surface also occurs between hydrated cations sites on the basal surface of smectites and vermiculites (Fig. 3.5). The accessibility of non-polar compounds to these sites is controlled by the surface charge density of the clay mineral, and the nature of the exchangeable cation and its

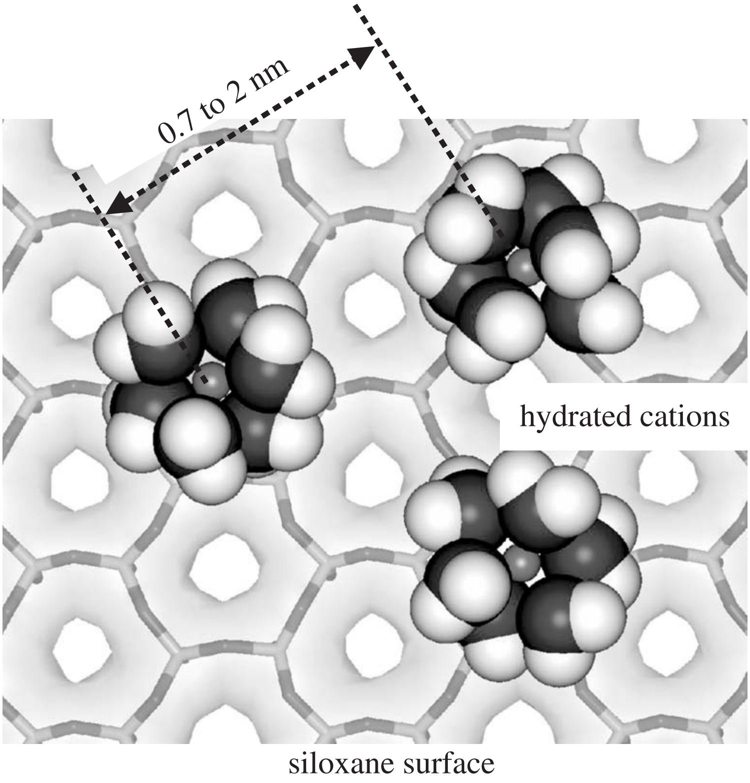

Fig. 3.5. Sites at siloxane surface.

corresponding enthalpy of hydration. For smectites with relatively low surface charge density and containing weakly hydrated exchangeable inorganic cations (e.g., K^+ and Cs^+), the interaction of organic molecules with these surface sites can be significant. Current evidence has shown that these non-polar regions between isomorphous substitution sites have some hydrophobic character. Jaynes and Boyd (1991) and Boyd and Jaynes (1994) have examined the hydrophobicity of clay minerals containing these types of surface sites by measuring the adsorption of aromatic hydrocarbons from water by smectites exchanged with inorganic and organic cations. When alkali and alkaline earth cations are present at exchange sites, little, if any, hydrocarbon sorption occurs because the hydrated cations obscure the hydrophobic regions. However, when the inorganic cations are replaced by the relatively small trimethyl phenylammonium (TMPA) cation, significant sorption takes place. Since the 'footprint' (i.e., cross-sectional area) of this cation is relatively small, a portion of the siloxane surface is accessible to organic solutes. The sharp increase in organic sorption for these organically modified smectites is attributed, in part, to hydrophobic surface interactions between the organic solute and the siloxane surface.

Additional evidence comes from the work by Laird et al. (1992) on the sorption of atrazine from water on 13 different types of Ca^{2+}-exchanged smectites, ranging from low- to high-layer charge. As shown in Fig. 3.6, the Freundlich sorption coefficients range from <0.01 to 1330. This is remarkable since all of the sorbents are Ca^{2+}-smectites. With smectites of low-charge densities, surface charge density of the clay is

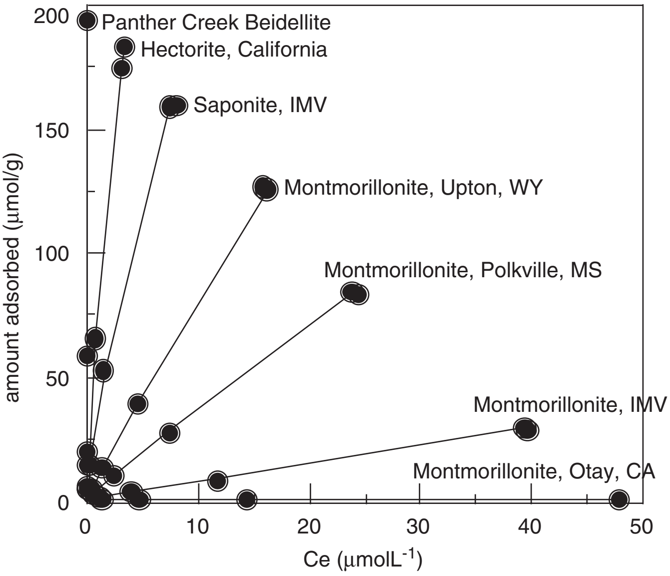

Fig. 3.6. Adsorption of atrazine by Ca^{2+}-smectites.

the most important determinant of its affinity for atrazine. In both examples, as charge density decreases, the size of the adsorptive region between neighbouring exchangeable cations increases. As a result, the siloxane surface becomes more accessible to atrazine (and other aromatic hydrocarbons). In the case of Ca^{2+}-smectites, the greater separation of exchangeable cations allowed atrazine sorption (up to 100% of that added) even though the presence of hydration water around Ca^{2+} would obscure some of the siloxane surface. These studies clearly established the importance of surface charge density to the adsorptive capabilities of smectites for non-polar organic compounds (NOCs). These experimental findings are supported by theoretical studies. For example, in a theoretical study of water molecules clustered near the siloxane surface of kaolinite, the water molecules had a tendency to avoid this surface consistent with its hydrophobic character (Nulens et al., 1998).

In contrast, the presence of hydrated cations, such as Na^+, K^+, Mg^{2+} and Ca^{2+}, in the interlayer region of smectites and vermiculites impart an overall hydrophilic nature to these clay minerals. The hydration dynamics of these cations, and the interaction of water with these metal ions underlie many of the important processes associated with clay minerals including their ability to swell in water. Expandable clay minerals are known to be strongly hydrophilic and this is largely attributed to the hydration of certain inorganic cations (Sposito and Prost, 1982; Jouany and Chassin, 1987; Johnston et al., 1992; Xu et al., 2000). In addition, the hydroxylated surface of gibbsite, and the gibbsite-like surface of kaolinite have some hydrophilic character (Nulens et al., 1998). Central to these processes are the clay–water interactions and this will be reviewed in the next section.

3.3. CLAY–WATER INTERACTIONS

Since the first reported infrared study of clay–water interactions by Buswell et al. (1937), water has been used to probe the clay–water interface. The chemical and physical properties of clay minerals are integrally linked to some aspect of how water interacts with the clay surface. Examples include essentially all of the adsorptive, catalytic and cationic exchange reactions. In fact, many of the interesting features of clay–water interactions are observable at the macroscopic level, including such properties as shrink–swell phenomena, water sorption, plasticity and catalysis.

Smectites, for example, have exceptional water sorption characteristics. Mooney et al. (1952a, 1952b) were among the first authors to show that smectites were able to sorb up to half of their mass in water and that the water sorption behaviour is strongly dependent on the nature of the exchangeable cation. The mechanisms underlying these interactions have been the subject of intense studies in recent years using a broad spectrum of sophisticated experimental and computational approaches. Examples include infrared and Raman spectroscopy, a wide range of nuclear magnetic resonance (e.g., ^{2}H, ^{29}Si, ^{27}Al, ^{23}Na, ^{7}Li), electron spin resonance, neutron scattering, neutron and X-ray diffraction and dielectric relaxation. Recognising that each of these experimental methods has a time scale associated with it, the structural information was grouped into two categories: vibrationally averaged structure ('V structure') is measured at a short-time scale, while diffusionally averaged structure ('D structure') is obtained over a long-time scale, both contributing to our knowledge about the structure and behaviour of water. For example, the time scale associated with nuclear magnetic resonance spectroscopy is generally between 10^{-10} and 10^{-3} s, whereas infrared and Raman spectroscopies measure vibrational transitions that occur over a much shorter time frame of 10^{-15} to 10^{-12} s (see Chapter 12.6).

For the purposes of our discussion, we will consider clay–water interactions from two different perspectives. First, the influence of the clay surface on the structure and properties of water will be examined. Most of the work on clay–water interactions has focused on this topic and has been the subject of several reviews (e.g. Sposito and Prost, 1982). Second, recent studies have demonstrated that the clay structure itself is influenced by changes in water content. Also, appropriate experimental methods have to be selected to provide information about the exchangeable cation itself.

3.3.1. Structure and Properties of Water Sorbed to Clay Mineral Surfaces

Because of their unique expansive nature, smectites and vermiculites are the most important clay minerals related to clay–water interactions. For these clay minerals, the initial sorption of water and related polar solvents, such as methanol, is influenced mainly by the hydration of exchangeable cations. These cations have substantial single-ion enthalpies and serve as strong hydrophilic sites for water and solvent sorption (Annabi-Bergaya et al., 1980a, 1980b; Cancela et al., 1997). Numerous spectroscopic studies have shown that the properties of sorbed water are different from those of bulk water, especially when less than three layers of water are present in the interlayer region. Water sorption on clay surfaces often shows significant hysteresis because of differences in water adsorption and desorption mechanisms. Adsorption of water proceeds by initial solvation of the exchangeable cations, followed by the occupancy of remaining interlayer space. In the case of desorption, physisorbed water molecules in interparticle or interaggregate pores, and sorbed on external surfaces, are removed first followed by the desorption of the more strongly bonded water molecules coordinated to the exchangeable cations.

Water molecules coordinated to exchangeable cations have chemical and physical properties that are different from those of bulk water. NMR and dielectric relaxation studies have shown that these water molecules have fewer intermolecular interactions and actually rotate faster about the C_2 axis as compared with bulk water. Infrared spectroscopy provides a direct means of studying water molecules and their interaction with other water molecules, solutes and surfaces. Russell and Farmer (1964) were among the first to show that water molecules coordinated to exchangeable cations were more strongly polarised than bulk water. More recently, Johnston et al.

(1992) measured the molar absorptivity of water molecules coordinated to different exchangeable cations in smectites as a function of water content. They found that the molar absorptivity of the v_2 mode of water (i.e., the H–O–H bending mode) was up to three times greater than that of bulk water. Upon lowering the water content of the clay–water system, the position of the v_2 band shifted to lower energy, indicating that the water molecules coordinated to exchangeable cations were less strongly hydrogen bonded compared with bulk water (Pimentel and McClellan, 1960; Poinsignon et al., 1978; Xu et al., 2000). By contrast, water molecules on polar surfaces tend to be more strongly hydrogen bonded at low water content.

The combined spectral data reveal that water molecules coordinated to exchangeable cations in the interlayer region are clustered around, and strongly polarised by, the exchangeable cation (Sposito and Prost, 1982). These water molecules apparently interact more strongly with the exchangeable cation and less strongly with each other. A similar behaviour has been reported for methanol interactions with montmorillonite exchanged with different cations (Annabi-Bergaya et al., 1980a, 1980b). One of the advantages of using a solvent molecule such as methanol is that it contains only one hydroxyl group, which simplifies spectral interpretation. A study of water sorption on talc suggested that the siloxane surface has some local hydrophilic character although the overall surface is strongly hydrophobic (Michot et al., 1994). Exchangeable cations control the sorption of water on clay surfaces at low water content but the influence of siloxane surfaces on water cannot be neglected, especially at high water content.

3.3.2. Influence of Water on Clay Mineral Structure

For many years, the presence of guest species, including water, in the interlayer space of 1:1 clay minerals (kaolin group of minerals) has been known to influence the inner-surface OH groups (Theng, 1974) and not only the surface hydroxyl groups.

Halloysite is a naturally occurring hydrated form of kaolinite intercalated with a monolayer of water molecules, giving a basal (d_{001}) spacing of 1.0 nm (~0.7 nm for kaolinite plus ~0.3 nm for water). Its structural formula is $Si_4Al_4O_{10}(OH)_8\ 4H_2O$. Costanzo et al. (1980, 1982) and Costanzo and Giese (1990) prepared partially hydrated kaolinite complexes with *d*-spacings of 0.84 and 0.92 nm. Infrared studies of these hydrated kaolinite complexes have shown that the inner OH groups of kaolinite are perturbed because of the partial collapse of the hydrated structure and keying of water molecules into the kaolinite structure (Costanzo et al., 1982). In addition to water, other small, polar molecules (e.g., hydrazine) could penetrate the ditrigonal cavities of the kaolinite and perturb the inner OH groups (Johnston and Stone, 1990; Johnston et al., 2000).

Similar mechanisms have also been shown to occur on expandable 2:1 clay minerals. For example, the v(OH) band of trioctahedral vermiculite was perturbed by the presence of interlayer cations at different water contents (Fernandez et al., 1970). When Na^+-vermiculite is dehydrated, the interlayer cations migrate from the centre of the interlayer space into the siloxane ditrigonal cavity and perturb the hydroxyl groups located at the base of this cavity. This has also been shown for other cations, including butylammonium (Serratosa et al., 1984). In an infrared study of reduced-charged smectites, the intensity of the hydroxyl deformation bands (e.g., Al–O(OH)–Al bending) is strongly reduced at low water content. This is attributed to the dehydration-induced movement of the exchangeable cations into the ditrigonal cavities (Sposito et al., 1983). Xu et al. (2000) have shown that the molar absorptivities of both the ν(OH) and δ(MOH) bands decrease upon lowering the water content.

There has been some speculation that in smectites the oxygen atoms of the siloxane surface interact directly with water molecules. In support of this hypothesis, the ν(Si–O) modes are coupled to the vibrational modes of water (Yan et al., 1996). In an aqueous suspension of smectite, this coupling is due to a change in particle orientation as the water content decreases (Johnston and Premachandra, 2001).

3.4. SURFACE CHEMISTRY IN AQUEOUS DISPERSIONS

Clay minerals often occur in an aqueous environment. Depending on the conditions they may be present as single layers, particles or aggregates (see Fig. 1.1). The ideal dispersion consists of individual layers that are randomly oriented and constantly moving. In 2:1 phyllosilicates, the surface consists of the planar siloxane surfaces and the edge surfaces.

To achieve this condition, very dilute aqueous dispersions of smectites, exchanged with small monovalent cations such as Li^+ and Na^+, have to be prepared. A very sensitive molecule is used to probe these clay surfaces in an aqueous environment when there is an excess of water. Such a molecule must be selectively adsorbed, and be easily detectable at trace amounts by a spectroscopic technique, for example. Cationic dyes fulfil this requirement because they are very selectively ion-exchanged. At the same time, they are easily detected in trace amounts by visible spectroscopy due to their large extinction coefficients. This subject has been recently reviewed by Yariv and Cross (2002). Only the fundamental principles are considered in the following section.

3.4.1. Preliminary Considerations

Table 3.4 lists the absorption maxima of the monomers of the most commonly used dyes on the clay mineral surface.

When these cationic dyes are ion-exchanged on the surface of smectites in dilute aqueous suspension, the clay mineral particles become hydrophobic. The clay–dye complexes form flocs and precipitate. To avoid this precipitation, the loading cannot exceed some threshold value, usually 10–15% of the cation exchange capacity (CEC) of the smectite. This loading can be increased using a very small size fraction

Table 3.4. Band positions of monomers of dye molecules in water and on the clay mineral surface

Cationic dye	$\lambda_{\max}$ (nm) in water	$\lambda_{\max}$ (nm) on clay mineral surface
Methylene blue	664	670, 652
Rhodamine 6G	526	533
Rhodamine B	555	562
Crystal violet	595	610
Thionine	595	621
Acridine orange	490	500

of the clay mineral ($<0.5\,\mu m$). With Laponite with an average size of 20 nm (Thompson and Butterworth, 1992) loadings of up to 100% of the CEC can be achieved without precipitation.

In the absence of any other specific interactions, the ion exchange of cationic dyes leads to a concentration of the dye molecules around the elementary clay layers. Similarly, increasing the concentration of dyes in aqueous solution gives rise to dimers and aggregates, which have their own spectroscopic signatures. The same behaviour occurs in the clay mineral suspension.

However, the environment of the dye molecules at the clay surface is different from that in pure water. Two situations can be envisaged. Firstly, the dye molecule is adsorbed and as a result, the water molecules in the first coordination sphere of the dye are partially replaced by oxygen atoms of the clay mineral surface. Secondly, the adsorbed dye molecule remains completely surrounded by water molecules and there is no replacement of water molecules by surface oxygen atoms. In both cases, the environment of the adsorbed dye molecules is different from that of its counterpart in bulk water. Therefore, the absorption maxima of the dye molecules adsorbed on the clay mineral surfaces are expected to shift from those in water. These shifts can be towards longer wavelengths or towards shorter wavelengths, as explained below.

3.4.2. Spectroscopy

All dye molecules of Table 3.4 have a dipole moment of the ground state and a dipole moment of the electronically excited state. These dipoles interact with the solvent molecules (water) and with surface oxygen atoms. The position of the band maximum of the electronic transition is then influenced by these interactions. This is schematically shown in Fig. 3.7. Thus, if the solvent–molecule interaction is stronger in the excited state than in the ground state a red shift of the band position of the monomer is expected and the reverse is true for a weaker solvent–molecule interaction in the excited state. In most cases a red shift is observed, indicating a stronger interaction of the excited dye molecules with water and surface oxygen atoms than

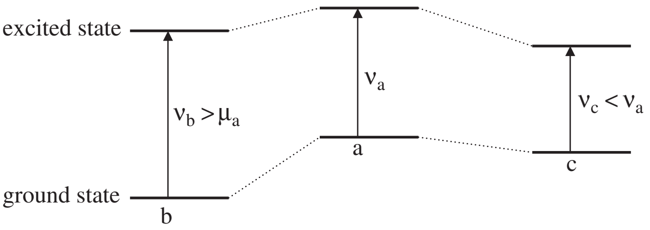

Fig. 3.7. Ground state and excited state of a dye molecule (a) in vacuo; (b) the solvent interacts more strongly with the ground state than with the excited state and (c) the solvent interacts more strongly with the excited state than with the ground state.

the dye molecules in their ground state. If the solvent is more polar than water a red shift of the band maximum of the electronic transition will be observed and a blue shift for a less polar solvent than water.

A. Monomers, Dimers and Aggregates

One observes a red shift for the dyes upon transfer from aqueous solution to aqueous clay suspension, indicating that the environment of the clay-adsorbed dye is more polar than that of the dye in aqueous solution (Table 3.4). In the case of methylene blue (MB) and very small loadings (0.1% of the CEC) two monomer bands are observed, one is blue shifted (652 nm) and the other red-shifted (670 nm) with respect to the band position in aqueous suspension (664 nm). The relative intensity of these bands depends on the type of clay mineral, as shown in Fig. 3.8. This is indicative of two different environments for the MB molecules: one is less polar (652 nm), while the other is more polar (670 nm), than water (Cenens and Schoonheydt, 1988). The time of contact as well as the type of clay, and more specifically the site of isomorphous substitution, are important factors influencing the band position of the monomer (Jacobs and Schoonheydt, 1999). Isomorphous substitution in the tetrahedral sheet gives rise to localised charges at the clay mineral surface and this results in a strong MB–surface interaction. The dye molecule is predominantly in direct contact with the surface and the absorption maximum of the monomer is at 670 nm. For clay minerals with isomorphous substitution in the octahedral sheet, the negative layer charge is diffuse and the MB–surface interaction is weak. The dye molecule remains in the water phase near the siloxane surface. The band maximum of the monomer is at 652 nm.

Fig. 3.8 also shows a third type of monomer, the protonated MB (MBH^{2+}) with its main absorption band at 760 nm. It is the only species present in the Barasym suspension at a loading of 0.1% of the CEC and it is present in trace amounts in the other clay suspensions. Thus all clay minerals in aqueous suspension contain trace concentrations of acid sites (ranging from about 0.1 to 0.5 $\mu mol\,g^{-1}$), probably located at the edges and strong enough to protonate MB (pKa is about zero).

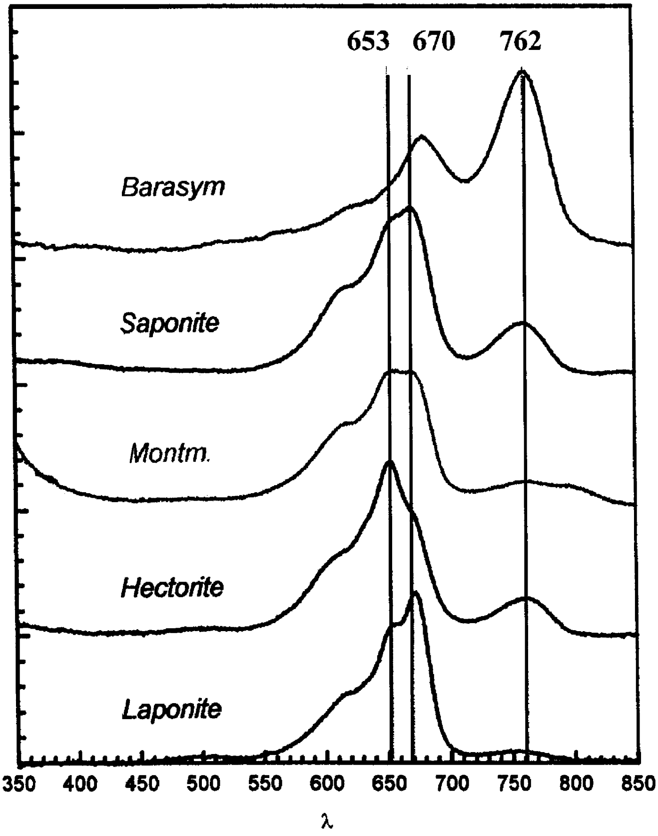

Fig. 3.8. Spectra of MB on smectites in aqueous suspension; the loading of MB is 0.1% of the CEC at 0.1 wt% clay in the suspension.

As the loading increases, more MB molecules reach the surface of the clay minerals and the dominant absorption maximum of the monomer is at 670 nm, irrespective of the type of smectite. In addition, the dye molecules are not randomly distributed over the surface. They preferentially form dimers and aggregates: the H-dimer is characterised by parallel transition dipole moments and absorbs around 600 nm; the J-dimer has antiparallel transition dipole moments and absorbs at 720 nm; and the H-aggregates absorb around 575 nm. Typical spectra of MB are given in Fig. 3.9. The relative intensity of these dimer and aggregate bands depends on the loading (the higher the loading the more intense the band of the H-aggregates); the type of exchangeable cation (Cs^+-smectites have more monomers than aggregates than Na^+-smectites); the type of clay mineral (particle size, CEC, isomorphous substitution) and time (indeed, clay–dye suspensions are not

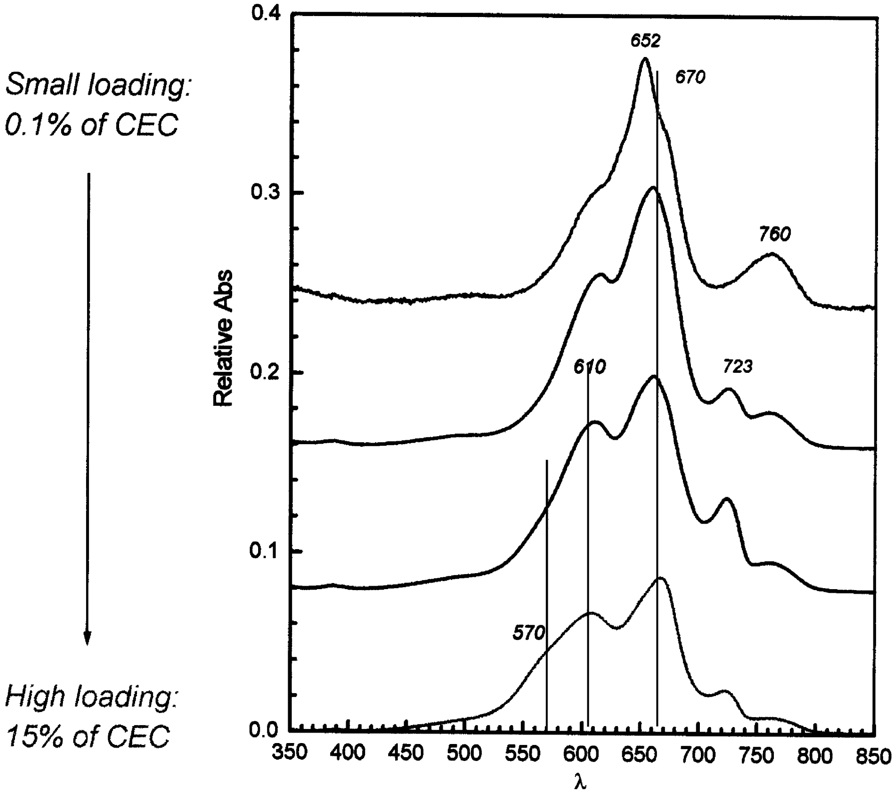

Fig. 3.9. Spectra of MB on hectorite in aqueous suspension; the amount of hectorite in the suspension is 0.1 wt%.

in a thermodynamic equilibrium, but may change slightly with time over weeks and months) (Jacobs and Schoonheydt, 2001).

In any case, clay–dye suspensions are complex systems, resulting from the balance of different interacting forces. The main forces are the dye–dye and dye–surface interactions.

In this discussion we have not specified interactions between the dye molecules and the surface oxygen atoms. Yariv and Cross (2002) have suggested that the π-electrons of the dye interact with the hybridised orbitals of the surface oxygen atoms, leading to a stabilisation of the π-orbitals and destabilisation of the π^*-orbitals. This gives rise to a blue shift of the absorption band of the adsorbed monomer.

When Al^{3+} substitutes for Si^{4+} in the tetrahedral sheet, the basicity of the surface oxygen atoms increases and so is the interaction with the π-orbitals. Thus, the blue shift of the monomer band of the adsorbed dye with respect to the monomer band in aqueous solution, due to the dye–surface interaction, reflects the basicity of the surface oxygen atoms.

This alternative explanation meets several difficulties. Indeed, as explained above, it is not evident that the monomer in an aqueous suspension, is in direct contact with the surface, in order to have the surface–dye interaction. In the case of MB, monomers in direct contact with the surface oxygen atoms absorb at 670 nm. This is a red shift of 8 nm with respect to the monomer absorption maximum in water, and contrary to the blue shift expected on the basis of the theory of Yariv and Cross (2002). Also, the removal of water (e.g., by air-drying) increases the interaction between the siloxane surface and the MB molecules and leads to a breakdown of the aggregates into monomers.

In summary, the organisation of the dye molecules at the clay mineral surface in aqueous suspensions is subjected to a sensitive balance of forces: molecule–molecule interactions, molecule–surface interactions, molecule–solvent and solvent–surface interactions. One would like to have control over the system, i.e., organise the molecules at the surface in the way we want. This requires quantitative knowledge of the different types of interactions. We are still far from that. In the mean time, the problem can be tackled experimentally and this is the subject of the next section.

3.5. ORGANISATION OF CLAY MINERAL PARTICLES AND MOLECULES

There are several ways of organising clay mineral particles: casting, spin coating, self-assembling, also called fuzzy-assembling or layer-by-layer deposition and application of the Langmuir–Blodgett (LB) technique. With all these techniques the goal is to obtain films, formed by continuous non-overlapping clay mineral layers. This ultimate goal can be attained to a large extent by self-assembling and by the LB technique. We limit the discussion to these techniques. These nanofilms are ideal samples for crystal-chemical studies of clay minerals, for studies of the adsorbed molecules and their organisation at the clay mineral surface, and for development of high-tech devices.

3.5.1. Self-Assembling

Self-assembling, fuzzy-assembling or layer-by-layer deposition refers to the alternate deposition of sheets of positively charged molecules and layers of smectite on a suitable substrate, such as glass and mica. The deposition is done from dilute aqueous solutions of cationic polymers and from dilute aqueous clay dispersions. After each deposition the excess material is washed away, and the films are gently dried before a new deposition is made. The process of film formation has been studied by van Duffel et al. (1999) and Kotov (2001).

Atomic force microscopy (AFM) shows that each clay layer is not fully covered with clay mineral particles and contains appreciable amounts of empty spaces between the particles. It is therefore a sub-monolayer of randomly oriented partially overlapping clay layers. Although a linear increase of film thickness with number of depositions has been observed, the partial overlap of randomly oriented clay layers in the film has two consequences: the extrapolation of film thickness to zero layers does not go exactly through the origin and the roughness of the films (measured as the standard deviation of the film height from the average along a straight line over the film) increases with the number of layers, and is proportional to the concentration of cationic polymer. For film thicknesses of approximately 80 nm the roughness attains values of 4−5 nm in the case of Laponite and 10−12 nm in the case of hectorite. If the cationic polymer is deposited in large amounts, it induces aggregation of clay mineral particles in the film and roughness is increased. A simple model has been developed describing the development of roughness as a function of the degree of coverage of each clay layer by the clay particles. Since Laponite has very small layer sizes, overlapping of layers in a particle does not occur. Surface coverages of 90% or more can be attained, leading to relatively smooth films. Being composed of particles with different sizes and shapes, hectorite gives surface coverages of 60−65% and more pronounced roughness than Laponite (van Duffel et al., 1999).

If functional films are to be prepared, the desired functionality has to be introduced. Several attempts have been published in the open literature. Thus, Kleinfeld and Ferguson (1994) have developed films with water-sensing properties, based on the layer-by-layer deposition of polydimethyl diallyl (PDDA) and smectite layers. van Duffel et al. (2001) have prepared films of smectite/PDDA/NAMO on glass substrate, with non-linear optical properties where NAMO is 4-[4-(*n*-allyl, *N*-metylamino) phenylazo] benzenesulphonic acid. When this film is illuminated with a Nd:YAG laser at 1064 nm, light at 532 nm is generated, the intensity of which depends on the type of clay mineral and the amount of PDDA in the film. The organisation of the positively charged PDDA polymers determines the organisation of the NAMO anions and in this case, an optimum configuration for the second harmonic light generation is obtained.

Films with magnetic properties have been prepared by Mamedov and Kotov (2000) and Mamedov et al. (2000). Here Fe_2O_3 nanoparticles are organised in films together with the cationic polymer PDDA and smectite layers. The latter clearly serve for strengthening the films. Finally, the development of clay-based biosensors must be mentioned such as urease (de Melo et al., 2002) and polyphenol oxidase (Coche-Guérente et al., 1999) on Laponite; layer-by-layer deposition of clay mineral–polymer–protein (Lvov et al., 1996) and hydrogenase biosensor (Qian et al., 2002). Heme–protein–clay mineral films have also been used for electrochemical catalysis (Zhou et al., 2002). This field is under intense investigation and major developments can be expected in the future.

3.5.2. Langmuir–Blodgett Technique

A highly organised layer-by-layer deposition of elementary clay mineral particles can be achieved with the LB technique. In the early days of development, hydrophobic clay minerals are dispersed in a volatile organophilic solvent such as chloroform.

This dilute suspension is spread over the water surface in a LB trough, the chloroform evaporates, and the film of hydrophobic clay minerals is compressed and transferred on to a substrate (Kotov et al., 1994; Hotta et al., 1997a, 1997b).

A more elegant method is to spread the amphiphilic cations on the water surface of a dilute aqueous dispersion. The dispersion has been prepared at least 24 h before use so as to ensure complete swelling and delamination. The amphiphilic cations, dissolved in chloroform or chloroform–methanol mixture, are spread over the air–water interface of the dilute clay suspension in the LB trough. An instantaneous ion-exchange reaction with the amphiphilic cations takes place at the air–water interface, giving a monolayer of elementary clay layers covered with amphiphilic cations. The monolayer can be compressed and then transferred to a substrate by vertical upstroke or horizontal deposition. If the substrate is hydrophilic, vertical deposition is preferred; if it is hydrophobic, one can perform the horizontal deposition. In the first case the sequence is substrate/clay/amphiphilic cation; in the second case it is substrate/amphiphilic cation/clay. By repetition of the procedure multilayers are obtained. The film thickness and the amount of amphiphiles have been checked in the case of horizontal deposition. Both have been found to increase linearly with the number of layers deposited, indicating that the overall composition of the layers is identical (Umemura et al., 2001a, 2001b).

From the scientific point of view the LB films are also useful for crystal-chemical studies of the elementary clay mineral layers and for studies on the organisation of the amphiphilic cations at the clay mineral surface. Molecules with desired functionality have to be used for the fabrication of functional films.

Atomic force microscopy reveals beyond any doubt that the LB films contain elementary clay mineral layers. Further, if deposition is performed at a low surface pressure (in any case below the critical pressure of film destruction), a monolayer is formed, covering more than 90% of the surface of the substrate. Occasionally, particles of elementary clay mineral layers are found. Spectroscopy with polarised light is used to study the films that are horizontally deposited. Fig. 3.10 shows the spectra of the Si–O vibrations and the structural O–H vibrations of saponite. The band positions and dichroic ratios are given in Table 3.5.

These data confirm that the elementary clay mineral layers are lying flat on the surface of the ZnSe substrate, used to deposit the film. For the first time highly resolved spectra of the in-plane and out-of-plane Si–O vibrations have been obtained. It is confirmed that the structural OH groups of the trioctahedral saponite are vibrating almost perpendicular to the planar surface and those of the dioctahedral Wyoming bentonite almost horizontally to the surface of the clay minerals. The OH bending vibrations of Wyoming bentonite have slightly different dichroic ratios, suggesting that the orientation of these OH groups depends on the cationic composition of the octahedral sheet: AlAlOH (919 cm^{-1}), AlFeOH (885 cm^{-1}) and AlMgOH (846 cm^{-1}) (Ras et al., 2003).

There are several spectroscopic techniques available to study the amphiphilic molecules adsorbed in mono- and multilayers, the most popular being FTIR and

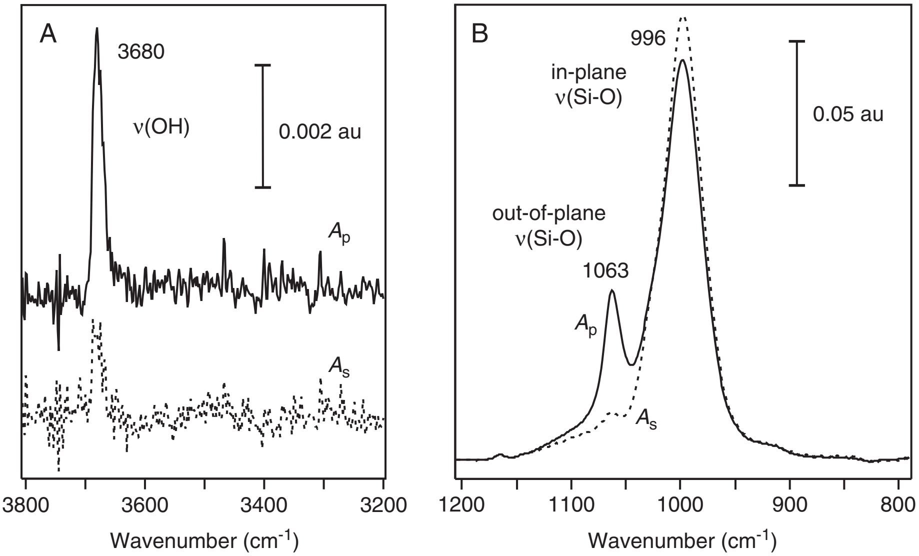

Fig. 3.10. Polarised ATR–FTIR spectra of a hybrid LB monolayer of SapCa-1 saponite and dioctadecyl thiacyanine surfactant prepared on a 50 mg dm^{-3} clay dispersion, deposited on ZnSe at a surface pressure of 5 mN m^{-1}: (A) ν(OH) region and (B) ν(Si–O) region.

Table 3.5. Band positions (cm^{-1}) and dichroic ratios R (A_s/A_p)[a] of Si–O and O–H vibrations

Vibration	Saponite	Dichroic ratio	Wyoming bentonite	Dichroic ratio
In plane Si–O	996	1.11	1024	1.11
Out-of-plane Si–O	1063	0.23	1085	0.12
Stretching O–H	3680	0.33	3628	1.08
Bending O–H	[b]		919	1.18
			885	1.13
			846	1.31

[a] A_s and A_p are, respectively, the absorption of in-plane and out-of-plane polarised light.
[b] Not detectable with ZnSe as substrate.

UV-VIS spectroscopy. With octadecylammonium (ODA) as the amphiphilic cation, the organisation of the alkyl chains is dependent on the concentration of the clay mineral in the suspension of the LB trough. At low concentration (< 10 ppm) the alkyl chains are highly ordered, similar to a crystalline ordering. This is reflected in the position of the CH_2 stretching vibration at 2925 cm^{-1}. At higher clay concentration (> 10 ppm) the alkyl chains are disordered as evidenced from the 2917 cm^{-1} position of the CH_2 stretch (Ras, 2003).

This difference in ordering has also been observed by Umemura et al. (2003). It indicates that at low clay concentration the ODA cations are organised at the air–water interface of the LB trough into two-dimensional crystalline aggregates to which the clay mineral particles are attached. At high clay concentration the clay mineral particles are attached to the ODA cations at the air–water interface before the latter have time to form the two-dimensional crystalline aggregates. In any case, the alkyl chains are oriented largely perpendicular to the surface (Ras, 2003; Umemura et al., 2003). In multilayered films the amount of ODA cations per layer is the same. This can be deduced from the linear increase of the intensity of the antisymmetric CH_2 vibrations with the number of layers (Umemura et al., 2001a, 2001b). This observation has also been made for other amphiphilic cations such as [Ru(phen)$_2$(dcC12bpy)] where phen is 1,10-phenanthroline and dcC12bpy is 4,4′-carboxyl-2,2′-bipyridyl didodecyl ester (Umemura et al., 2002). The monolayer films of clay mineral particles and ODA cations, deposited on ZnSe by upstroke vertical deposition, do not contain water (Ras, 2003). This means that in the configuration of ZnSe/clay/ODA there is no water at both ZnSe/clay mineral and clay mineral/ODA interfaces, indicating that there are no residual Na^+ cations and that the dense ODA layer is completely hydrophobic.

We end this discussion of the ODA-clay films with two remarks: (1) the ammonium group of the molecule is oxidised to the corresponding carbamate in the presence of dissolved CO_2 and methanol. The latter is present in the chloroform solution, used to spread ODA cations on the surface of water (Ras, 2003); and (2) short-chain, water-soluble alkylammonium cations can also be used for construction of hybrid clay mineral/alkylammonium films (Umemura et al., 2001a, 2001b). This means that under suitable conditions the alkylammonium cations are captured by the clay particles at the air–water interface before they are solubilised in the water of the sub-phase.

Research has been started to produce functional LB films with clay minerals. Thus, films with non-linear optical properties have been produced (Umemura et al., 2002) with the above mentioned [Ru((phen)2(dcC12bpy)] complex, which is non-centrosymmetric and chiral. A second harmonic generation (SHG) signal is produced only in the presence of ODA cations. The configuration of the films is then hydrophobic glass/[Ru(phen)$_2$ (dcC12bpy)]/clay mineral/ODA/[Ru(phen)$_2$ (dcC12bpy). It is suggested that in the presence of ODA, the Ru complexes are all oriented in the same direction in the film. This is not the case in the absence of ODA, i.e., when the Ru complexes are in direct contact with the hydrophilic surface of the clay mineral. In other words, the organisation of amphiphilic cations may be controlled by the hydrophobic/hydrophilic balance of the surface.

A hybrid film hydrophobic glass/ODA/clay mineral/Fe(phen)$_3^{2+}$ has also been assembled by Umemura (2002) that generates a SHG signal. This indicates again that the Fe(phen)$_3^{2+}$ complexes are organised at the clay surface in a non-centrosymmetric fashion. However, prior deposition of ODA cations is not necessary to give the required hydrophobic/hydrophilic balance at the clay mineral surface, whereas this is the case for Ru. Both the Ru- and Fe-complexes are supposed to be adsorbed on the clay mineral surfaces by cation exchange, possibly leaving some residual Na^+ ions. This is contrary to the conclusion drawn from the ODA/clay mineral films. These results raise several questions: (i) what is the mobility of the amphiphilic cations at the clay mineral particle surface; (ii) can they diffuse from one siloxane surface to the opposite siloxane surface of the same particle or between particles and (iii) what is the dependence of the orientation of these cations on the hydrophobic/hydrophilic balance of the clay mineral surface? Further research is needed to resolve these questions, and clarify other points of discussion.

REFERENCES

Annabi-Bergaya, F., Cruz, M.I., Gatineau, L., Fripiat, J.J., 1980a. Adsorption of alcohols by smectites. 2. Role of the exchangeable cations. Clay Minerals 15, 219–223.

Annabi-Bergaya, F., Cruz, M.I., Gatineau, L., Fripiat, J.J., 1980b. Adsorption of alcohols by smectites. 3. Nature of the bonds. Clay Minerals 15, 225–237.

Atkins, P., de Paula, J., 2002. Physical Chemistry, 7th edition. Oxford University Press, Oxford, p. 1084.

Boyd, S.A., Jaynes, W.F., 1994. Role of layer charge in organic contaminant sorption by organo-clays. In: Mermut, A.R. (Ed.), Layer Charge Characteristics of 2:1 Silicate Clay Minerals. CMS Workshop Lectures, vol. 6. Clay Minerals Society, Boulder, CO, pp. 48–77.

Buswell, A.M., Krebs, K., Rodebush, W.H., 1937. Infrared studies. III. Absorption bands of hydrogels between 2.5 and 3.5 micrometers. Journal of the American Chemical Society 59, 2603–2605.

Cancela, G.D., Huertas, F.J., Taboada, E.R., Sanchez Rasero, F., Laguna, A.H., 1997. Adsorption of water vapor by homoionic montmorillonites. Heats of adsorption and desorption. Journal of Colloid and Interface Science 185, 343–354.

Cenens, J., Schoonheydt, R.A., 1988. Visible spectroscopy of methylene blue on hectorite, Laponite B and barasym. Clays and Clay Minerals 36, 214–224.

Chang, F.C., Skipper, N.T., Sposito, G., 1998. Monte Carlo and molecular dynamics simulations of electrical double-layer structure in potassium-montmorillonite hydrates. Langmuir 14, 1201–1207.

Charnay, C., Lagerge, S., Partyka, S., 2001. Assessment of the surface heterogeneity of talc materials. Journal of Colloid and Interface Science 233, 250–258.

Coche-Guérente, L., Desprez, V., Labbé, P., Therias, S., 1999. Amplification of amperometric biosensor responses by electrochemical substrate recycling. Part II. Experimental study of the catechol–polyphenol oxidase system immobilized in a laponite clay matrix. Journal of Electroanalytical Chemistry 470, 61–69.

Costanzo, P.M., Clemency, C.V., Giese, R.F., 1980. Low temperature synthesis of a 10-Å hydrate of kaolinite using dimethylsulfoxide and ammonium fluoride. Clays and Clay Minerals 28, 155–156.

Costanzo, P.M., Giese, R.F., 1990. Ordered and disordered organic intercalates of 8.4-Å synthetically hydrated kaolinite. Clays and Clay Minerals 38, 160–170.

Costanzo, P.M., Giese, R.F., Lipsicas, M., Straley, C., 1982. Synthesis of a quasi-stable kaolinite and heat-capacity of interlayer water. Nature 296, 549–551.

de Melo, P.M., Cosnier, S., Mousty, C., Martelet, C., Jaffrezic-Renault, N., 2002. Urea biosensors based on immobilization of urease into two oppositely charged clays (Laponite and Zn-Al layered double hydroxides). Analytical Chemistry 74, 4037–4043.

Fernandez, M., Serratosa, J.M., Johns, W.D., 1970. Perturbation of the stretching vibration of OH groups in phyllosilicates by the interlayer cations. Reunion Hispano-Belga de Minerales de la Arcilla 163−167.

Giese, R.F., van Oss, C.J., 1993. The surface thermodynamic properties of silicates and their interactions with biological materials. In: Guthrie, C.D., Mossman, B.T. (Eds.), Health Effects of Mineral Dusts. Reviews in Mineralogy, vol. 28. Mineralogical Society of America, Washington, DC, pp. 327–346.

Giese, R.F., van Oss, C.J., Norris, J., Costanzo, P.M., 1990. Surface energies of some smectite clay minerals. In: Farmer, V.C., Tardy, Y. (Eds.), Proceedings of the 9th International Clay Conference, Strasbourg, 1989. Sciences Géologiques, Mémoire No. 86, pp. 33–41.

Greathouse, J., Sposito, G., 1998. Monte-Carlo and molecular dynamics studies of interlayer structure in $Li(H_2O)_3$-smectites. The Journal of Physical Chemistry B 120, 2406–2414.

Hensen, E.J.M., Smit, B., 2002. Why clays swell. The Journal of Physical Chemistry B 106, 12664–12667.

Hotta, Y., Inukai, K., Taniguchi, M., Yamagishi, A., 1997a. Electrochemical behaviour of hexa-ammineruthenium(II) cations in clay-modified electrodes prepared by the Langmuir–Blodgett method. Journal of Electroanalytical Chemistry 429, 107–114.

Hotta, Y., Taniguchi, M., Yamagishi, A., 1997b. A clay self-assembled on a gold surface as studied by atomic force microscopy. Journal of Colloid and Interface Science 188, 404–408.

Huheey, J.E., 1978. Inorganic Chemistry: Principles of Structure and Reactivity, 2nd edition. Harper & Row, New York.

Jacobs, K.Y., Schoonheydt, R.A., 1999. Spectroscopy of methylene blue-smectite suspensions. Journal of Colloid and Interface Science 220, 103–111.

Jacobs, K.Y., Schoonheydt, R.A., 2001. Time dependence of the spectra of methylene blue-clay mineral suspensions. Langmuir 17, 5150–5155.

Jaynes, W.F., Boyd, S.A., 1991. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. Clays and Clay Minerals 39, 428–436.

Johnston, C.T., Bish, D.L., Eckert, J., Brown, L.A., 2000. Infrared and inelastic neutron scattering study of the 1.03- and 0.95-nm kaolinite-hydrazine intercalation complexes. The Journal of Physical Chemistry B 104, 8080–8088.

Johnston, C.T., Premachandra, G.S., 2001. Polarized ATR-FTIR study of smectite in aqueous suspension. Langmuir 17, 3712–3718.

Johnston, C.T., Sposito, G., Erickson, C., 1992. Vibrational probe studies of water interactions with montmorillonite. Clays and Clay Minerals 40, 722–730.

Johnston, C.T., Stone, D.A., 1990. Influence of hydrazine on the vibrational modes of kaolinite. Clays and Clay Minerals 38, 121–128.

Jouany, C., Chassin, P., 1987. Determination of the surface-energy of clay-organic complexes by contact-angle measurements. Colloids and Surfaces 27, 289–303.

Kleinfeld, E.R., Ferguson, G.S., 1994. Stepwise formation of multilayered nanostructural films from macromolecular precursors. Science 265, 370–373.

Kotov, N.A., 2001. Ordered layered assemblies of nanoparticles. Materials Research Bulletin 26, 992–997.

Kotov, N.A., Meldrum, F., Wu, C., Fendler, J.H., 1994. Monoparticulate layer and Langmuir–Blodgett type multiparticulate layers of size-quantized cadmium sulfide clusters—a colloid-chemical approach to superlattice construction. The Journal of Physical Chemistry 98, 2735–2738.

Laird, D.A., Barriuso, E., Dowdy, R.H., Koskinen, W.C., 1992. Adsorption of atrazine on smectites. Soil Science Society of America Journal 56, 62–67.

Lvov, Y., Arija, K., Ichinose, I., Tunitake, T., 1996. Molecular film assembly via layer-by-layer adsorption of oppositely charged molecules (biopolymer, protein, clay) and concanavalin A and glycogen. Thin Solid Films 284, 797–801.

Malandrini, H., Clauss, F., Partyka, S., Douillard, J.M., 1997. Interactions between talc particles and water and organic solvents. Journal of Colloid and Interface Science 194, 183–193.

Mamedov, A.A., Kotov, N.A., 2000. Free standing layer-by-layer assembled films of magnetite nanoparticles. Langmuir 16, 5530–5533.

Mamedov, A.A., Ostrander, J., Aliev, F., Kotov, N.A., 2000. Stratified assemblies of magnetite nanoparticles and montmorillonite prepared by the layer-by-layer assembly. Langmuir 16, 3941–3949.

Michot, L.J., Villieras, F., Francois, M., Yvon, J., LeDred, R., Cases, J.M., 1994. The structural microscopic hydrophilicity of talc. Langmuir 10, 3765–3773.

Mooney, R.W., Keenan, A.G., Wood, L.A., 1952a. Adsorption of water vapor by montmorillonite. I. Heat of desorption and application of BET theory. Journal of the American Chemical Society 74, 1367–1374.

Mooney, R.W., Keenan, A.G., Wood, L.A., 1952b. Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction. Journal of the American Chemical Society 74, 1371–1374.

Mortier, W.J., 1987. Electronegativity equalization and its applications. Structure and Bonding 66, 125–143.

Nemecz, E., 1981. Clay Minerals. Akademiai Kiado, Budapest.

Nulens, K.H.L., Toufar, H., Janssens, G.O.A., Schoonheydt, R.A., Johnston, C.T., 1998. Clay minerals and clay mineral–water interactions: a combined EEM–Monte Carlo study. In: Yamagishi, A., Aramata, A., Taniguchi, M. (Eds.), The Latest Frontiers of the Clay Chemistry. Proceedings of the Sapporo Conference on the Chemistry of Clays and Clay Minerals, 1996. The Smectite Forum of Japan, Sendai, pp. 116–133.

Pimentel, G.C., McClellan, A.B., 1960. The Hydrogen Bond, 1st edition. W.H. Freeman, San Fransisco.

Poinsignon, C., Cases, J.M., Fripiat, J.J., 1978. Electrical-polarization of water molecules adsorbed by smectites. An infrared study. The Journal of Physical Chemistry 82, 1855–1860.

Qian, D.-J., Nakamura, C., Wenk, S.-O., Ishikawa, H., Zorin, N., Miyake, J., 2002. A hydrogen biosensor made of clay, poly(butylviologen) and hydrogenase sandwiched on a glass carbon electrode. Biosensors and Bioelectronics 17, 789–796.

Ras, R.H.A., 2003. Molecular and Particulate Organization in Organo-Clay Monolayers. Ph.D. thesis. K.U. Leuven, p. 139.

Ras, R.H.A., Johnston, C.T., Franses, E.I., Ramaekers, R., Maes, G., Foubert, P., De Schryver, F.C., Schoonheydt, R.A., 2003. Polarized infrared study of hybrid Langmuir–Blodgett monolayers containing clay mineral nanoparticles. Langmuir 19, 4295–4302.

Russell, J.D., Farmer, V.C., 1964. Infra-red spectroscopic study of the dehydration of montmorillonite and saponite. Clay Minerals Bulletin 5, 443–464.

Sanderson, R.T., 1976. Chemical Bonds and Bond Energy, 2nd edition. Academic Press, New York.

Sauer, J., 1989. Molecular models in ab initio studies of solids and surfaces: from ionic crystals and semiconductors to catalysts. Chemical Reviews 89, 199–255.

Schrader, M.E., Yariv, S., 1990. Wettability of clay minerals. Journal of Colloid and Interface Science 136, 85–94.

Serratosa, J.M., Rausell-Colom, J.A., Sanz, J., 1984. Charge density and its distribution in phyllosilicates: effect on the arrangement and reactivity of adsorbed species. Journal of Molecular Catalysis 27, 225–234.

Servagent-Noinville, S., Revault, M., Quiquampoix, H., Baron, M.H., 2000. Conformational changes of bovine serum albumin induced by adsorption on different clay surfaces: FTIR analysis. Journal of Colloid and Interface Science 221, 273–283.

Sposito, G., 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

Sposito, G., Prost, R., 1982. Structure of water adsorbed on smectites. Chemical Reviews 82, 553–573.

Sposito, G., Prost, R., Gaultier, J.P., 1983. Infrared spectroscopic study of adsorbed water on reduced-charge Na/Li montmorillonites. Clays and Clay Minerals 31, 9–16.

Sutton, R., Sposito, G., 2001. Molecular simulation of interlayer structure and dynamics in 12.4 angstrom Cs-smectite hydrates. Journal of Colloid and Interface Science 237, 174–184.

Swenson, J., Bergman, R., Howells, W.S., 2000. Quasielastic neutron scattering of two-dimensional water in a vermiculite clay. Journal of Chemical Physics 113, 2873–2879.

Theng, B.K.G., 1974. The Chemistry of Clay-Organic Reactions. Wiley, New York.

Thompson, D.W., Butterworth, J.T., 1992. The nature of laponite and its aqueous dispersions. Journal of Colloid and Interface Science 151, 236–243.

Tunega, D., Benco, L., Haberhauer, G., Gerzabek, M.H., Lischka, H., 2002. Ab initio molecular dynamics study of adsorption sites on the (0 0 1) surfaces of 1:1 dioctahedral clay minerals. The Journal of Physical Chemistry B 106, 11515–11525.

Umemura, Y., 2002. Hybrid films of a clay mineral and an iron(II) complex cation prepared by a combined method of the Langmuir–Blodgett and self-assembly techniques. The Journal of Physical Chemistry B 106, 11168–11171.

Umemura, Y., Onodera, Y., Yamagishi, A., 2003. Layered structure of hybrid films of an alkylammonium cation and a clay mineral as prepared by the Langmuir–Blodgett method. Thin Solid Films 426, 216–220.

Umemura, Y., Yamagishi, A., Schoonheydt, R.A., Persoons, A., De Schryver, F.C., 2001a. Fabrication of hybrid films of alkylammonium cations ($C_nH_{2n} + 1NH_3 +$; $n = 4-18$) and a smectite clay by the Langmuir–Blodgett method. Langmuir 17, 449–455.

Umemura, Y., Yamagishi, A., Schoonheydt, R.A., Persoons, A., De Schryver, F.C., 2001b. Formation of hybrid monolayers of alkylammonium cations and a clay mineral at the air-water interface: clay as an inorganic stabilizer for water-soluble amphiphiles. Thin Solid Films 388, 5–8.

Umemura, Y., Yamagishi, A., Schoonheydt, R.A., Persoons, A., De Schryver, F.C., 2002. Langmuir–Blodgett films of a clay mineral and ruthenium(II) complexes with a non-centrosymmetric structure. Journal of the American Chemical Society 124, 992–997.

van Duffel, B., Schoonheydt, R.A., Grim, C.P.M., De Schryver, F.C., 1999. Multilayered clay films: atomic force microscopy study and molecular modeling. Langmuir 15, 7520–7529.

van Duffel, B., Verbiest, T., Van Elshocht, T., Persoons, A., Schoonheydt, R.A., 2001. Fuzzy assembly and second harmonic generation of clay-polymer-dye monolayer films. Langmuir 17, 1243–1249.

van Oss, C.J., Giese, R.F., Li, Z., Murphy, K., Norris, J., Charudhury, M.K., Good, R.J., 1992. Determination of contact angles and pore sizes of porous-media by column and thin-layer wicking. Journal of Adhesion Science and Technology 6, 413–428.

Xu, W., Johnston, C.T., Parker, P., Agnew, S.F., 2000. Infrared study of water sorption on Na-, Li-, Ca- and Mg-exchanged (SWy-1 and SAz-1) montmorillonite. Clays and Clay Minerals 48, 120–131.

Yan, L., Roth, C.B., Low, P.F., 1996. Changes in the Si-O vibrations of smectite layers accompanying the sorption of interlayer water. Langmuir 12, 4421–4429.

Yariv, S., 1992. Wettability of clay minerals. In: Schrader, M.E., Loeb, G. (Eds.), Modern Approaches to Wettability: Theory and Applications. Plenum Press, New York, pp. 279–326.

Yariv, S., Cross, H. (Eds.) 2002. Organo-Clay Complexes and Interactions. Marcel Dekker, New York.

Zhou, Y., Hu, N., Zeng, Y., Rusling, J.F., 2002. Heme-protein-clay films: direct electrochemistry and electrochemical catalysis. Langmuir 18, 211–219.