COMPUTER CALCULATION OF WATER–CLAY INTERACTIONS USING ATOMIC PAIR POTENTIALS

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ABSTRACT: Existing data on interatomic potentials have been used to study the interactions between an uncharged clay sheet and a water molecule. Calculations show that most of the clay surface is relatively hydrophobic, with binding energies for a water molecule in the range 1·0–4·5 kcal mol⁻¹. There is, however, a low-energy site for an oriented water molecule above the layer OH group and within the ring of six SiO₄ tetrahedra. Using two different models for the interactions, the binding energy in this position is found to be either 13·2 or 21·8 kcal mol⁻¹. The existence of the low-energy site accounts for the formation of the hydrated ‘10 Å’ phase of talc, which is known from high-pressure experiments. Data on the PT stability of this phase can be used to estimate its energy of dehydration. This quantity is shown to be consistent with the value of 21·8 kcal mol⁻¹ for the binding energy of a water molecule and the energy associated with the expansion of the layers from the 9·35 Å phase.

An understanding of clay–water–cation interactions is directly relevant to a variety of industrial problems. Two examples may be chosen to illustrate this. The first concerns the role of clays in drilling muds. In this case one is particularly interested in the physical properties of the clay–water complexes, and the precise nature of the atomic-scale interactions which control their viscosity and non-Newtonian behaviour. A second important problem concerns the properties of clay-rich rocks, such as shales, when they come into contact with drilling fluids. Since the chemistry of the drilling fluid is generally markedly different from that of the natural pore-fluid, conditions of strong chemical non-equilibrium normally exist. This promotes the transfer by diffusion of both water and cations between the drilling fluid and rocks forming the well-bore. The concomitant change in hydration state of the clays is usually associated with a change in volume, and the resulting mechanical failure of the rock can lead to severe problems during drilling.

To solve problems relating to clay–water complexes it is necessary to have a proper understanding of their behaviour at an atomic level. It is evident that there is a great deal of local structure developed in these systems, since the water present has a wide range of binding energies depending on its proximity to either interlayer cations or special sites on the clay surface. However, conventional structural studies are made difficult by the fact that these complexes comprise particles of colloidal dimensions. The interpretation of probe data, such as nuclear magnetic resonance or inelastic neutron scattering, in terms of specific clay–cation–water configurations is therefore not possible.

Computer experiments provide one means of overcoming this problem. They can be used to explore the local structure and to characterize the transport properties of both water and cations, which are the subject of existing probe data. This information will be invaluable in
the non-equilibrium situations envisaged, where the diffusion of water and exchange cations occurs between the drilling fluid and the shale rocks of the well-bore.

The work presented in this paper forms part of a new scientific initiative in which computer experiments will be used to provide insights into the local structure and dynamics of clay–water–cation systems. The complete sequence of these computer experiments begins with the study of the interactions between uncharged clay surfaces and a single water molecule. From this static computation we obtain an energy surface in the six-dimensional space of the water–clay-sheet orientation. Subsequent steps in the overall programme will comprise:

(i) computer modelling of interlayer cation–water interactions, and the constraints exercised by the interlayer environment,

(ii) the study of interactions between charged and uncharged clay sheets,

(iii) molecular dynamics simulations of the complete clay–water–cation system.

The remainder of this paper deals in sequence with the derivation of suitable pair potentials, their application to the determination of the energy surface for a single water molecule and a talc sheet, and finally with an analysis of the energetics of water in the 10 Å phase of talc.

MODEL INTERACTION POTENTIALS

To model the interaction energy between two molecules the complete interaction potential is built out of more primitive functions. These are assumed to act between sites on each molecule, and to depend only on the distance between these sites. This approach has been used with considerable success in the study of systems as diverse as molecular crystals (Ramdas & Thomas, 1977), liquid water (Finney et al., 1986) and silicate minerals (Price et al., 1987).

Two common forms of the site–site potential, and the ones used in this work, are the Buckingham potential with an added coulombic term:

$$V(r_{ij}) = -A_{ij}/r_{ij}^6 + B_{ij} \exp (-C_{ij} r_{ij}) + q_i q_j/r_{ij},$$

and the one used by Matsuoka et al. (1976):

$$V(r_{ij}) = -B_{ij} \exp (-C_{ij} r_{ij}) + B_{ij} \exp (-C_{ij} r_{ij}) + q_i q_j/r_{ij}.$$  

The first term represents the attractive London or dispersion forces, the second the short-range repulsions, and the third is the Coulomb force between charged sites. The parameters $A_{ij}, B_{ij}, C_{ij}$ and $q_i$ describe the interactions between a particular pair of sites $i$ and $j$. They have traditionally been determined empirically by calculating various properties of the solid or liquid (e.g. structure or phonon dispersion curves) and adjusting the parameters to give a best fit to experimental data. More recently it has become possible to fit their values to ab initio quantum mechanical calculations of interaction energies.

If there is more than one component in the system there will be a distinct energy function between each pair of components. For the clay–water–cation system there are six interactions to consider. In this paper we concentrate on the clay–clay and clay–water potentials. Water–water potentials are the subject of an extensive literature; for a review see Finney et al. (1986). Cation–water, cation–cation and cation–clay interactions will be dealt with in later papers.

Clay–clay interactions for uncharged sheets have been investigated by Alcover & Giese (1986) using pair potentials. They describe two different potentials, using parameters derived
Calculation of water-clay interactions

by Huggins (1937) and by Busing (1970). This yields energy as a simple function of one variable, the layer separation. The two models give very different values for the minimum energy: $-10.9$ kcal mol$^{-1}$ and $-32.5$ kcal mol$^{-1}$ respectively for talc. However, the calculated value of the compressibility evaluated with the Busing potential (1.43 Mb$^{-1}$) is much closer to the experimental value (1.72 Mb$^{-1}$) than with the Huggins potential (2.34 Mb$^{-1}$). Though neither model is completely satisfactory, we use Busing's parameters for pyrophyllite as the best so far available. These give a compressibility of 1.90 Mb$^{-1}$ and a minimum energy of $-36.1$ kcal mol$^{-1}$ at a layer separation of 9.25 Å.

We have studied two different models for the water–clay potential. The first models the clay sheet as an assembly of discrete water molecules, with the oxygens situated at oxygen sites in the sheet, and hydrogens directed towards the silicon sites. It is based on the assumption that an oxygen atom bonded to silicon in a SiO$_2$ sheet has a similar electronic environment to an oxygen atom bonded to hydrogen in water. This is a reasonable approximation as the Pauling electronegativities of silicon and hydrogen are similar (1.8 and 2.1 respectively). The hydroxyl group is represented by 'half' a water molecule, but no account is taken of the octahedral magnesium ions. The interaction is therefore reduced to a sum of water–water interactions. For these we use the potential of Matsuoka et al. (1976), which is known as the MCY model. It has interaction sites on the oxygen and hydrogen positions and a charge site on the HOH axis (see Figs 1 and 2 and Table 1). It has been highly successful in the study of liquid water (Wojcik, 1985).

The second model uses quantum mechanical potentials based on electrons and nuclei for the water–silicate interactions, and is therefore known as QPEN (Sauer et al., 1984). The parameters $A_y$, $B_y$, $C_y$ and $q_y$ were fitted to $ab$ initio quantum mechanical calculations for the energies of a water molecule and Si(OH)$_4$ molecule in a range of configurations. Sites on the molecules were based on the QPEN model and chosen so that the potential should be transferable to other silicate structures. Electron interaction sites are placed on the Si–O and O–H bond axes, and on the oxygen 'lone pairs'. The atomic and ionic nuclei are represented as charge sites (see Figs 3 and 4 and Table 1).

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Fig. 1. Interaction sites in the MCY model of a water molecule.
The XY projection only shows the top half of the sheet

The charge sites are not shown, see figure 1.

**FIG. 2.** The interaction sites in the MCY model of a talc sheet.

One or both of these potential models will eventually be used in molecular dynamics simulations. During the course of a simulation run the energy will be evaluated many thousands of times, so the potential model must be as simple and quick to evaluate as possible. Both water–layer and water–water interactions are needed, and for consistency the same sites on the water should be used to model both. Judged by these criteria the MCY model would be preferable; it has only four sites as against the seven of QPEN. More importantly the MCY model provides a far better representation of the water–water interaction than does the QPEN. It was calculated using the more sophisticated configuration interaction (CI) technique rather than the simpler self-consistent field (SCF) approach, and is therefore much more accurate (Finney et al., 1986). However the QPEN
Calculation of water–clay interactions

Table 1. The parameters of the MCY and QPEN potentials.

<table>
<thead>
<tr>
<th></th>
<th>(\mathcal{D}_{ij}/\text{kcal mol}^{-1})</th>
<th>(\mathcal{C}_{ij}/\text{A}^{-1})</th>
<th>(\mathcal{E}_{ij}/\text{kcal mol}^{-1})</th>
<th>(\mathcal{F}_{ij}/\text{A}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>0.0</td>
<td>0.0</td>
<td>666.38</td>
<td>2.7608</td>
</tr>
<tr>
<td>O–H</td>
<td>2736.1</td>
<td>2.2333</td>
<td>1455.5</td>
<td>2.9619</td>
</tr>
<tr>
<td>O–O</td>
<td>0.0</td>
<td>0.0</td>
<td>1088300.0</td>
<td>5.1527</td>
</tr>
</tbody>
</table>

\(q_H = 0.717484 \text{ e}, \quad q_{CC} = -1.434968 \text{ e}\)
\(r_{O-H} = 0.9527 \text{ Å}, \quad r_{O-CoM} = 0.0737 \text{ Å}, \quad r_{O-CC} = 0.246 \text{ Å}\)

<table>
<thead>
<tr>
<th></th>
<th>(A_i/\text{kcal mol}^{-1})</th>
<th>(\mathcal{A}_{ij}/\text{Å}^6)</th>
<th>(\mathcal{B}_{ij}/\text{kcal mol}^{-1})</th>
<th>(\mathcal{C}_{ij}/\text{Å}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_{P_{\text{water}}} - B_{P_{\text{water}}})</td>
<td>52.717</td>
<td>12192.0</td>
<td>4.2759</td>
<td></td>
</tr>
<tr>
<td>(B_{P_{\text{water}}} - L_{P_{\text{water}}})</td>
<td>2.5319</td>
<td>14090.0</td>
<td>4.6037</td>
<td></td>
</tr>
<tr>
<td>(B_{P_{\text{SiO}} - B_{P_{\text{water}}}})</td>
<td>268.25</td>
<td>5435.4</td>
<td>3.3618</td>
<td></td>
</tr>
<tr>
<td>(B_{P_{\text{SiO}} - L_{P_{\text{water}}}})</td>
<td>12.883</td>
<td>6642.6</td>
<td>3.6931</td>
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<td>3.6931</td>
<td></td>
</tr>
</tbody>
</table>

\(q_{LP} = q_{BP} = -2.0 \text{ e}, \quad q_O = +6.0 \text{ e}, \quad q_{Si} = +4.0 \text{ e}, \quad q_H = 1.0 \text{ e}\)

In water: \(r_{O-H} = 0.9527 \text{ Å}, \quad r_{O-CoM} = 0.0737 \text{ Å}\), \(r_{O-BP} = 0.56658 \text{ Å}, \quad r_{O-LP} = 0.32561 \text{ Å}\)

In the clay: \(r_{O-BP} = 0.38862 \text{ Å}, \quad r_{O-LP} = 0.12120 \text{ Å}\)

Fig. 3. Interaction sites in the QPEN model of a water molecule.

model should clearly give a better representation of the water–silicate interactions, for which it was designed.

In this paper we evaluate both the MCY and QPEN models for the water–surface interaction. The only way to do this is to compare the results of calculation with experimental data, taken in this case from the 10 Å phase of talc (see later).
THE ENERGY OF A WATER MOLECULE NEAR TALC SHEETS

Method

The energy surface of a water molecule near one or two talc sheets was investigated, using the pair potentials of Sauer et al. (1984) and Matsuoka et al. (1976) described in the previous section. Once the potential model is given, calculation of the water–surface interaction energy is conceptually very simple. The total energy is evaluated as a sum of site–site energies over all sites in each molecule. This is done for a range of positions and orientations of the water relative to the surface.

A complication arises over the size of the clay layer to be used. Ideally it should be infinite, to avoid effects associated with the edges. The usual approach to handling long-range \((1/r)\)
Coulombic forces is to make use of the periodicity of the system via the Ewald sum technique (Berthaut, 1953; Parry, 1975). However, because there is only one water molecule, it is computationally quicker to use a large surface. The sheets should therefore be sufficiently large so that the interaction of a water molecule at the centre with sites at the edge has decayed to a negligible level.

The layers constructed contained $16 \times 16$ unit cells ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ or the equivalent), and were about 80 Å in both the $a$ and $b$ directions. The dimensions of the layers were chosen to give energies within 0.5% of the test values calculated by using a two-dimensional Ewald sum. In the case of the QPEN potentials each layer contained about 25 000 interaction sites.

The water molecule was moved over the layers in discrete steps, and its position described by the $x$, $y$ and $z$ co-ordinates of its centre of mass, relative to the centre of inversion of the layer. The angular orientation is given $\theta_x$, $\theta_y$ and $\theta_z$, which are the size of the rotations about the $x$, $y$ and $z$ axes (see Figs 1 or 3). These are zero when the molecular points with the HOH axis towards the lower layer and the HOH plane parallel to the $a$ vector.

The energy of a water molecule above a single talc sheet

The minimum energy configuration for a water molecule above a single clay sheet is directly above the hydroxyl group. The oxygen of the water faces the layer, and therefore forms a slightly distorted hydrogen bond to the hydroxyl ($\theta_x = 180, \theta_y = 0$ and $\theta_z = 0$, see Figs 5 and 6). The distance to the centre of the layer is then 3.7 Å. In this configuration energies of $-13.2$ and $-21.8$ kcal mol$^{-1}$ are obtained with the QPEN and MCY potentials respectively, as illustrated in Figs 5 and 6. In these diagrams the energy for the water molecule orientated with hydrogen atoms facing the layer ($\theta_x = 0$) is also presented.

![Graph](image)

**FIG. 5.** The binding energy of MCY water to the hydroxyl site of a single talc sheet.
FIG. 6. The binding energy of QPEN water to the hydroxyl site of a single talc sheet.

FIG. 7. The binding energy of MCY water to the oxygen or silicon site of a single talc sheet.
Calculation of water–clay interactions

Water forms a hydrogen bond to a surface oxygen site ($\theta_x = 0, \theta_y = 52$ and $\theta_z = 0$) with an energy of $-4.04$ kcal mol$^{-1}$ (QPEN) or $-1.25$ kcal mol$^{-1}$ (MCY), at a distance of 6.2 or 6.5 Å respectively from the layer centre (Figs 7 and 8). Above the silicon atoms the water orients with the oxygen facing the surface ($\theta_x = 180, \theta_y = 0$ and $\theta_z = 0$) in the case of the QPEN model, with an energy $-4.47$ kcal mol$^{-1}$ at a distance of 6.4 Å. When the MCY model is used the minimum of $-0.86$ kcal mol$^{-1}$ is obtained when the hydrogens face the layer ($\theta_x = 0, \theta_y = 0$ and $\theta_z = 0$); see Figs 7 and 8.

The energy of a water molecule between two talc sheets

To allow quantitative comparison with experimental data for the 10 Å phase of talc (next section), the energy of a water molecule between two talc sheets was calculated. The two layers were positioned so that the facing hydroxyls had the same $x$ and $y$ co-ordinates (Fig. 9). This is the same arrangement as in the natural mineral (Brindley & Brown, 1980).

With the sheets 10 Å apart the energy minima obtained for the water–layer interaction using the QPEN and MCY models are $-15.9$ and $-21.8$ kcal mol$^{-1}$ respectively (Fig. 9). As expected these minima occur when the water is placed between the hydroxyl groups, as illustrated in Fig. 9. The effect of layer separation on the water–layer interaction energy has also been investigated, and is plotted in Fig. 10. The minimum energies of $-16.3$ kcal mol$^{-1}$ (QPEN) and $-21.9$ kcal mol$^{-1}$ (MCY) occur at separations of 9.5 Å and 10.5 Å respectively. It is not possible for water to escape from the region between the two hydroxyl groups; this must therefore be the site occupied by water in the 10 Å phase of talc. To compare the current
Fig. 9. The binding energy of water in the 10 Å phase of talc as a function of distance from the lower layer.

Fig. 10. The maximum binding energy of a water molecule between two talc sheets.
Calculation of water–clay interactions

MCY model
OPEN model

FIG. 11. The sum of the water–layer and layer–layer interaction energies for a water molecule bound between two talc sheets.

data with the experimental value of the lattice c parameter, the layer–layer interaction has to be incorporated.

The sum of the pyrophyllite layer–layer interaction of Busing (1970) (Alcover & Giese, 1984) and the present water–layer energy is plotted as a function of layer separation in Fig. 11. From this graph the calculated lattice parameter c corresponding to minimum energy for hydrated talc is 9.35 Å. This value is consistent with the 9.96 Å c spacing measured at 298 K (Brindley & Brown, 1980), since the water trapped between the layers in the simulation is effectively at 0 K. Therefore no account is taken of the energy required to confine the water at a finite temperature.

THE 10 Å PHASE OF TALC

For some time it has been known that hydrated talc, with one water molecule per formula unit of Mg₃Si₄O₁₀(OH)₂, can be made at elevated temperatures and pressures. This phase has a c lattice parameter of 9.96 Å, compared to 9.35 Å in the natural form. The PT plot for the conversion of the ‘10 Å’ phase to normal talc has been determined by Yamamoto & Akimoto (1977), and is shown in Fig. 12. Note the extrapolation of this plot to lower temperatures suggests that the 10 Å phase can exist at room temperature. This is consistent with the observation that the phase can be recovered by a suitable quenching technique, and examined by X-ray powder methods in the laboratory.

The present computer results concerning the interaction between a water molecule and a talc surface have an important bearing on the existence of the 10 Å phase. In the first place
talc, unlike smectite, does not hydrate with substantial layer expansion. This, we now understand, must be associated with the fact that most of the surface of an uncharged talc layer is mildly hydrophobic. At the same time we have proposed the existence of a strongly-bound water molecule within the tetrahedral ring (p. 419). This is clearly the site occupied by a water molecule in the 10 Å phase of talc. It remains only to show that the overall energy associated with the expansion of the layer and the occupation of the low-energy site agrees with the value obtained for the heat of dehydration of the 10 Å phase using the Clapeyron relationship, $\Delta H/\Delta V = dP/dT$.

Using the plot of Fig. 12, from Yamamoto & Akimoto (1977), $\Delta H$ is found to be 6.5 kcal mol$^{-1}$. If we add to this the exothermic effect of the collapse of the layers, $E_c$ (6.5 kcal mol$^{-1}$; Alcover & Geise, 1986; Busing, 1970) and the heat of condensation of the water (8.1 kcal mol$^{-1}$) the result is 21.1 kcal mol$^{-1}$. This figure is between the two calculated values of -15.9 kcal mol$^{-1}$ (QPEN) and 21.8 kcal mol$^{-1}$ (see p. 419). These will be discussed quantitatively in the next section. The Born–Haber cycle for the hydration–dehydration process is shown in Fig. 13.

The largest uncertainty in this cycle is introduced by the theoretical model for the layer–layer interaction. The parameters of Busing (1970) used for this purpose are known to give a compressibility, $\beta$, which is about 15% larger than the measured value (see p. 421). Since $\beta$ gives a measure of $d^2 E_c/dc^2$ it is therefore likely that the 6.5 kcal mol$^{-1}$ attributed to the layer expansion is too great. For this reason the real total is probably smaller than the estimated value of 21.1 kcal mol$^{-1}$, by ~1 kcal mol$^{-1}$.

**DISCUSSION**

The success of the two sets of potentials can only be judged by comparing the calculated results with those of experiments. In the absence of any direct measurement of the heat of
adsorption of water on an uncharged clay surface, the binding energy of water in the 10 Å phase of talc will be used for this purpose.

The MCY potential

Calculation using the MCY potential gives a value of 21.8 kcal mol\(^{-1}\) for the binding energy of water in the 10 Å phase of talc. This figure is 0.7 kcal mol\(^{-1}\) larger than the estimate obtained earlier, and is probably \(\sim 1.7\) kcal mol\(^{-1}\) larger than the true value. This level of agreement is satisfactory, given the simplicity of the model.

Out of the calculated total of 21.8 kcal mol\(^{-1}\), only 8.4 kcal mol\(^{-1}\) is due to the hydrogen bond between the water and the surface hydroxyl group. The remaining 13.4 kcal mol\(^{-1}\) is a direct result of the dipolar water molecule aligning itself in the electric field of the six-membered ‘SiO\(_4\)’ ring. With this in mind it is straightforward to explain why the calculated binding energy might be slightly larger than the true value.

Water bound to the hydroxyl site of a clay sheet penetrates the layer to some extent (Figs 5 and 6). For this reason it will be influenced to some small degree by the internal magnesium ions and oxygen atoms of the layer. In the current MCY model there has been no attempt to deal with this complication. A simple method to overcome this problem, and one which is currently being tested, is to represent the octahedral cations and oxygen atoms by positive and negative point charges respectively. The additional charge distribution has a non-zero quadrupole moment (but a zero dipole moment), and is repulsive to water in the strongly bound site. This interaction decays faster than that due to the dipolar six-membered ring, and will represent a small correction for water at any larger distance from the surface. The calculations involving water placed over other parts of the clay surface can therefore be discussed with some confidence.

In the MCY model a water molecule can bind with an energy of 1.25 kcal mol\(^{-1}\) to a surface oxygen atom of an uncharged clay sheet. There are two main reasons why this value is considerably smaller than the 5.8 kcal mol\(^{-1}\) which is the energy of an ideal water–water hydrogen bond in the same model. First, the protons cannot adopt a trans geometry, because the molecule approaching the sheet would then touch one of the other surface oxygen atoms.
Secondly, the lower half of the layer acts to repel the incoming water; if it is removed the interaction energy increases to 3.0 kcal mol\(^{-1}\). Since a water molecule binds to a surface oxygen atom with less energy than it would to another molecule in the liquid, the oxygen site can be regarded as hydrophobic. The same is true for the 'silicon' site.

The 'silicon' site of an MCY clay surface is represented by the three hydrogen atoms of the nearest surface water molecules. This will only be a reasonable approximation if the water is not bound strongly to the surface at this site. The current work suggests that this is the case. Above a 'silicon' site an MCY water molecule can achieve a binding energy of only 0.86 kcal mol\(^{-1}\). The oxygen atom is then 3.0 Å from the surface and the hydrogen atoms are directed towards the layer. Because the water assumes this orientation the dominant interaction must be with the surface oxygen atoms, which carry a negative charge. This is physically reasonable, as they are the species closest to the incoming molecule. For the same reason water at large distances from the layer tends to orientate with its hydrogen atoms facing the layer \((\theta_x = 0)\). This is in marked contrast to the results for the QPEN model.

The QPEN potential

Calculations involving the QPEN potential result in a binding energy of 15.9 kcal mol\(^{-1}\) for water in the 10 Å phase of talc. It was pointed out earlier that the estimated figure of 21.1 kcal mol\(^{-1}\) is probably ~1 kcal mol\(^{-1}\) larger than the true value. The QPEN energy is therefore at least 4.2 kcal mol\(^{-1}\) too small, and it is concluded that the QPEN model does not provide a satisfactory representation of water bound to an uncharged clay surface. The reasons for this become clear when the geometry of the QPEN water molecule is considered.

The QPEN water molecule has a tetrahedral geometry, as a result of putting interaction sites on 'lone pairs'. In a predominantly tetrahedral structure, such as liquid water, this is not a serious defect—as has been demonstrated by the success of the ST2 model by Finney et al. (1986). In the current application, however, the water is being introduced into a hexagonal site. In this environment there is no reason to assume that the water will adopt a tetrahedral geometry, since this is incommensurate with that of its surroundings. A result of this mismatch is that the total energy of the system will be increased. A similar problem would be encountered if the model was used to study cation–water interactions.

The QPEN model has a further disadvantage. It is known that the strength of water–water interactions are overestimated in the QPEN model; a single water–water hydrogen bond has an energy of \(-9.16\) kcal mol\(^{-1}\) as opposed to accepted values around 6 kcal mol\(^{-1}\) (Marchese et al., 1982). A QPEN water molecule might therefore be expected to interact too strongly with some sites on clay surface. This view is supported by comparison with the results of the MCY model.

A QPEN water molecule binds to a surface oxygen site with an energy of 4.04 kcal mol\(^{-1}\). This compares with 1.25 kcal mol\(^{-1}\) for the equivalent site in the MCY system. Although it is possible that the MCY model is incorrect in this case, it is more likely that the inconsistency is a direct result of the QPEN model overestimating the strength of a hydrogen bond to the surface. A similar problem is encountered when the silicon site is considered.

Water above the silicon site of QPEN clay can achieve a binding energy of 4.5 kcal mol\(^{-1}\), if the hydrogen atoms point away from the surface \((\theta_x = 180)\). This is a surprising result because the molecule is closest to the surface oxygen atoms, which are known to carry a negative charge. From the parameters in Table 1 it can be seen that the bonding pair electrons in the QPEN model of water are placed closer to the hydrogen atoms than to the
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oxgen atom. For this reason the oxygen of the water molecule can appear to carry a positive charge, and be attractive to the oxygen atoms in the surface. The same argument applies at large distances from the sheet (Fig. 6); this behaviour is unphysical.

CONCLUSIONS

A single low-energy site has been identified above the hydroxyl group within the six-membered SiO₄ ring of an uncharged clay surface. With the water in this position calculations involving the QPEN and MCY models of clay–water interactions have resulted in values of 15.9 and 21.8 kcal mol⁻¹ respectively for the binding energy in the 10 Å phase of talc. Comparison with a semi-empirical value of 21.1 kcal mol⁻¹ suggests that the MCY model is more accurate.

Apart from the single site above the surface hydroxyl group the clay surface is found to be hydrophobic; the binding energy is typically 1 kcal mol⁻¹. This explains why uncharged clays exhibit only limited hydration.

The programme of computer experiments is now to be extended to charged sheets and the study of cation–water, clay–clay and cation–clay interactions. The use of molecular dynamics methods is envisaged. In light of the results discussed in this paper it is expected that the MCY potential will be used for this work. This potential has been used successfully to simulate the structure of water and aqueous solutions, and does not impose a tetrahedral geometry on the system.

REFERENCES


