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# Molecular dynamics investigation into the adsorption of organic compounds on kaolinite surfaces

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## Abstract

Molecular dynamics simulations have been performed to determine the partitioning behaviour of organic compounds between water phases and inorganic surfaces. In the first of these sets of simulations the heat of adsorption of a single benzocarbazole molecule on water-wet kaolinite surfaces was determined. The results from these simulations show that the benzocarbazole isomers have a slight preference for being adsorbed on the water-wet kaolinite mineral surfaces over being desorbed in the water phase (about  $-1.5$  kcal/mol for the kaolinite alumina surfaces and about  $-4$  kcal/mol for the kaolinite silica surface). No significant differences between the adsorption behaviour of benzo[a]- or benzo[c]carbazole were found. In a second set of simulations the stabilities of four different configurations of a three-phase water/cyclohexane/kaolinite system were determined. The results from these simulations show that a fully water-wet kaolinite is thermodynamically preferred over a fully cyclohexane-wet kaolinite system and that the silica-surface of kaolinite has a higher affinity for the water-phase than the alumina surface. The contrasting results from these two sets of simulations show that the phase behaviour of a single organic molecule in a water/mineral surface system is not necessarily related to the behaviour of an equivalent organic phase in the same system. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Molecular dynamics; Benzocarbazoles; Kaolinite; Wettability

## 1. Introduction

The distribution of organic compounds in subsurface sediments is controlled by a complex interplay of chemical and physical processes. Of these physical processes, partitioning of compounds between solid and fluid organic, aqueous and solid inorganic phases is of prime importance in controlling organic phase composition in a variety of settings relevant to environmental and industrial interests. Sorption of hydrophobic organic compounds to minerals is especially important in controlling the wettability of permeable rocks (Anderson, 1986) and as a potential

factor affecting the composition of migrating petroleum (Nagy, 1960; Krooss et al., 1991). In a previous paper (van Duin and Larter, 1998) we have reported on the application of molecular dynamics calculations (MD; Allen and Tildesley, 1987; Frenkel and Smit, 1996) in predicting the differences in oil/water partitioning behaviour of benzocarbazole isomers (benzo[a]- and benzo[c]-carbazole, Fig. 1). These calculations indicated a relative preference for the benzo[a]isomer to partition into the water-phase, compared with the benzo[c]isomer, which could potentially explain the observed changes in benzo[a]-carbazole/benzo[c]carbazole ratios observed in migrating petroleum (Larter et al., 1996). To elaborate on these results we have expanded our investigation into the phase behaviour of the benzocarbazole isomers in sediment systems by using MD to determine the affinity of the benzocarbazole isomers for adsorption on a kaolinite

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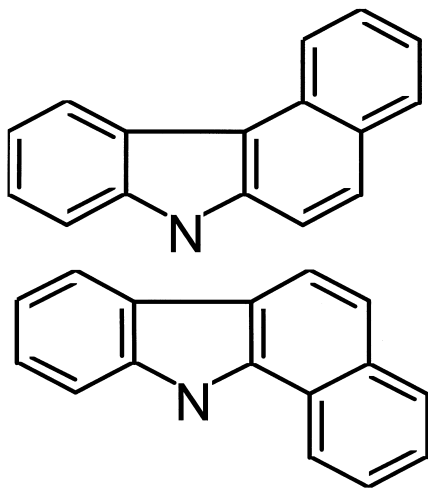


Fig. 1. Molecular structures of benzo[a] (bottom) and benzo[c]carbazole (top).

surface. As a major constituent of the inorganic matrices found in sediments, kaolinite is an important case to study from the geochemical perspective. From the computational chemical perspective, kaolinite has two advantages compared to other mineral systems. First, it has a well-defined layered clay structure, allowing for a straightforward definition of the crystal surfaces and, secondly, it has the advantage over other clay minerals that it has a neutral crystal lattice, which means that simulations are not complicated by the presence of counterions. Furthermore, kaolinite provides two distinctly different potential adsorption surfaces (Fig. 2), an alumina surface characterised by surface hydroxyl groups and a silica surface characterised by oxygen-bridged silica atoms. As has been observed in previous computational studies regarding water/organic/kaolinite systems (Teppen et al., 1998; Murgich and Rodríguez, 1998; Smirnov and Bougeard, 1999) these two surfaces have different affinities for organic and water phases, making kaolinite an interesting case to study.

Compared to other clay surfaces, in particular illite, kaolinite has a high affinity for organic compounds (Saada et al., 1995a,b; Bantignies et al., 1997). This can probably be attributed to the charge-neutrality of the kaolinite lattice; the presence of charge-counterbalancing ions near the illite-surfaces making the water-layer more polar and decreasing its affinity for less polar organic compounds. This is seen in the higher oil/water partition coefficients for phenol compounds in oil/water systems of increasing salinity (Bennett and Larter, 1997). However, in comparison with other charge-neutral mineral systems like calcite, silica and pyrite kaolinite has been described as being highly hydrophilic (Czernichowski et al., 1987; Trabelsi, 1987). In the absence of highly-polar organic compounds, like low molecular mass acids or phenols, which migrate through water films to adsorb

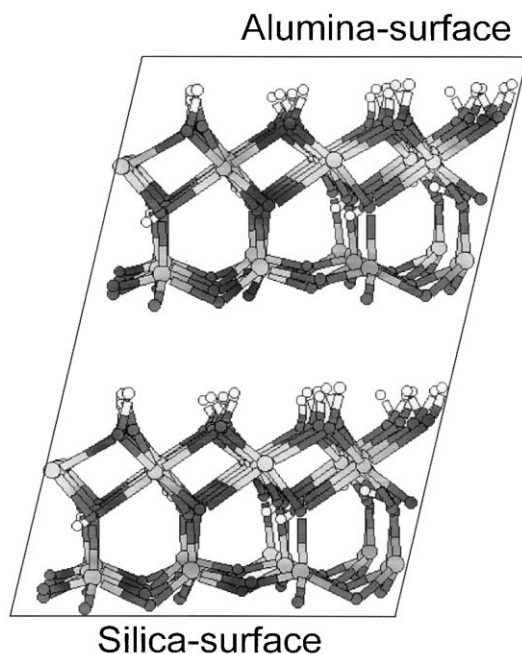


Fig. 2. Structure of kaolinite and definition of silica- and alumina surface.

on the mineral surfaces and act as surfactants, making the surface more accessible for the adsorption of less polar organic compounds, kaolinite is therefore likely to be water-wet (Larter et al., 1994; Anderson, 1986; Huang et al. 1995). For this reason, and because rock surfaces initially are likely to be wetted by water, we have chosen to initially study the adsorption of the benzocarbazole isomers on a water-wet, rather than an oil-wet, kaolinite surface.

To further justify this choice, and to investigate the potential application of MD-simulation in mineral surface wettability studies in general, we have also performed a series of simulations of kaolinite in contact with water/cyclohexane mixtures. Cyclohexane was chosen as an organic phase in these MD-simulations over an *n*-alkane, which might be more representative of an oil-phase, due to the fact that, especially compared to the longer *n*-alkanes, the relative lack of conformational freedom in cyclohexane facilitates the simulations. Despite the differences between a cyclohexane and an oil phase, observations derived from cyclohexane/water studies should still be indicative for the wetting behaviour of mineral surfaces in oil/water environments. In the kaolinite/cyclohexane/water simulations four different initial configurations of a water/cyclohexane mixture were used (Fig. 3), (1) a water-wet kaolinite alumina surface and a cyclohexane-wet silica surface, (2) a water-wet kaolinite silica surface and a cyclohexane-wet alumina surface, (3) both surfaces water-wet with a cyclohexane-phase between

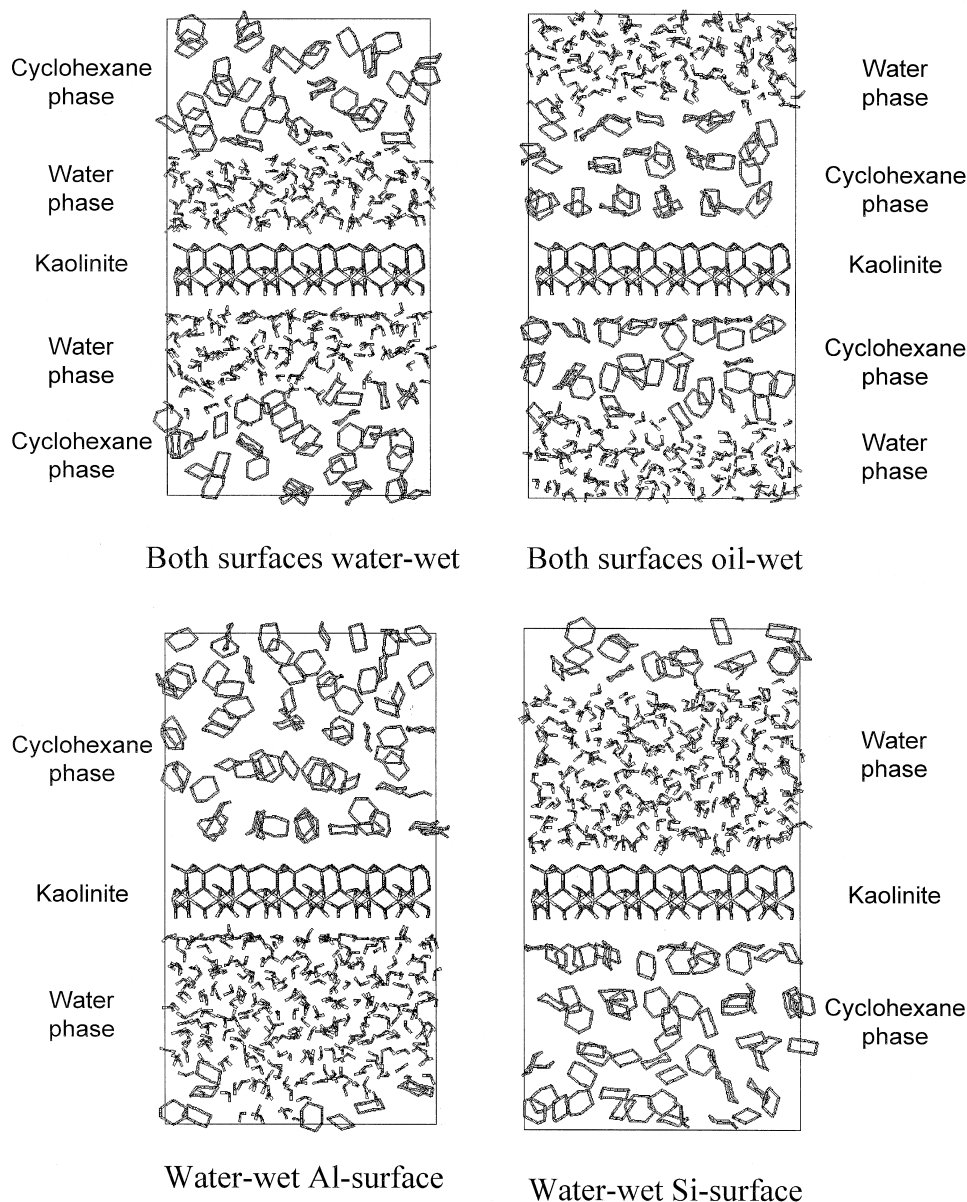


Fig. 3. Water/cyclohexane system configurations used to determine the wetting behaviour of the kaolinite surfaces.

the water layers and (4) both surfaces cyclohexane-wet with a water-phase between the organic phases. These computational studies were performed using a periodic box model with both clay surfaces exposed to the fluids. A periodic box allows passage of the molecules from one end of the box directly to the other end (this is a standard computational chemical approach). By comparing the thermodynamic stability of configurations (1)–(4) we aim to obtain information regarding the wetting behaviour of the two kaolinite surfaces. To investigate whether the thermodynamic driving forces, as determined

by the MD-simulations on configurations (1)–(4), can control the phase behaviour on the short time-scales necessarily employed in MD-simulations we also performed a simulation in which the kaolinite-surfaces were contacted with a randomly-orientated water/cyclohexane mixture. During the MD-simulation this initially randomly configured mixture should separate into two phases with an orientation towards the kaolinite surfaces which should comply with the thermodynamic driving forces identified in the pre-ordered phase simulations with configurations (1)–(4).

## 2. Methods

### 2.1. Force fields

During the simulation the atoms in the kaolinite layer were kept fixed at their crystallographic positions as determined by Bish (1993). Atomic charges on the atoms in the kaolinite layer were taken from Teppen et al. (1997). The Lennard-Jones parameters of the Dreiding force field (Mayo et al., 1990) were used to describe the kaolinite atoms. The water molecules were simulated using the transferable intermolecular potential 3 (TIP3P)-water force field from Jorgensen et al. (1983). For the benzocarbazoles the force field derived in our earlier oil/water partition coefficient studies was used (van Duin and Larter, 1998). For the cyclohexane molecules in the water/cyclohexane/kaolinite simulations a united atom approach was used, describing each CH<sub>2</sub>-unit as a single atom, with the composite parameters as described by DeBolt and Kollman (1995).

### 2.2. Molecular dynamics simulations

To determine the heat of adsorption of the two benzocarbazole isomers on the water-wet kaolinite surfaces a periodic box (dimensions: 20.5988×26.8053×28.000 Å), containing the kaolinite layer and 333 water molecules, was equilibrated at  $T=298$  K. During this equilibration run, which lasted 50,000 MD-iterations, the water molecules orientated themselves towards the kaolinite mineral surfaces. Near the silica-surface an orientational preference similar to that reported by Smirnov and Bougeard (1999) was observed, with the hydrogens of the water molecules pointing towards the mineral surface-oxygens. The 333 water molecules generate a water phase with sufficient volume to display bulk water properties away from the mineral surfaces, allowing for

the determination of the energies of the desorbed benzocarbazole isomers unbiased by the orientating effect of the kaolinite surfaces on the adsorbed water layers.

For each benzocarbazole isomers three starting configurations were generated from this equilibrated water/kaolinite system by introducing the benzocarbazole at positions near the alumina surface, near the silica surface and about 9 Å away from both surfaces (Fig. 4). The 8 water molecules nearest to the introduced benzocarbazole isomer were removed from the system. To remove remaining short water-benzocarbazole contacts a short MD-simulation at low (8 K) temperature was performed for each system. By this means, three kaolinite/water/benzocarbazole systems with comparably orientated water molecules were generated for each benzocarbazole isomer. All these systems were subsequently equilibrated for 25,000 MD-iterations. Hereafter, the stability of each system was determined by monitoring its running average energy for 950,000 MD-iterations at a temperature of 298 K. By comparing the three different system stabilities the affinity of both benzocarbazole isomers for adsorption on the kaolinite surfaces was determined. On the computer system primarily used in these simulations (a Sun Ultra-1 computer) each iteration takes 2.4 s to complete, which means that the full simulation for each of these systems (975,000 iterations, from which 25,000 for equilibration) took 650 h of computer time.

For the water/cyclohexane/kaolinite simulations five systems were prepared, each containing 80 cyclohexane molecules, 320 water molecules and 1 kaolinite layer (dimensions: 20.5988×26.8053×49.660 Å) (Figs. 3 and 5a). The systems in Fig. 3 were equilibrated for 10,000 MD-iterations. Hereafter, the stabilities of these systems were determined by monitoring their running average energies for 25,000 MD-iterations. The demixing of the randomly orientated water/cyclohexane phase in Fig. 5a was simulated for 150,000 iterations.

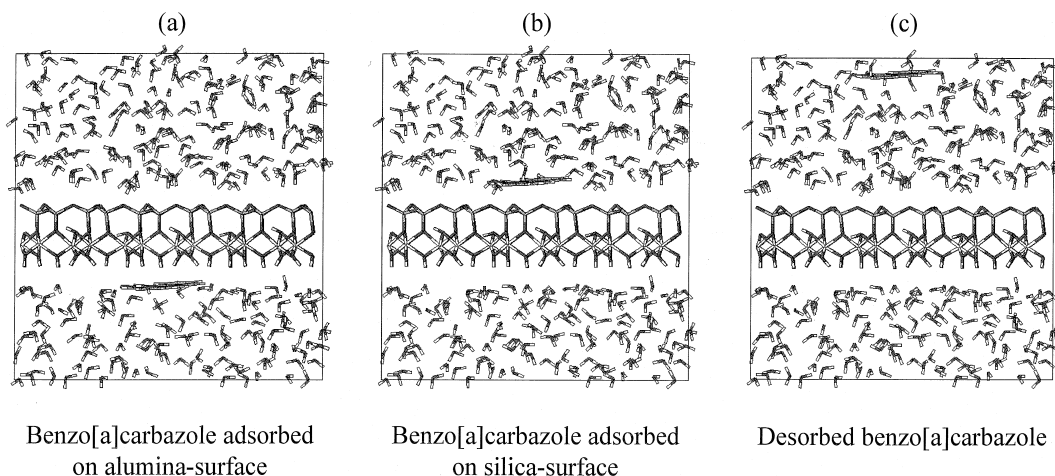


Fig. 4. System configurations used to determine the heat of adsorption of individual benzocarbazole isomers on water-wet kaolinite surfaces.

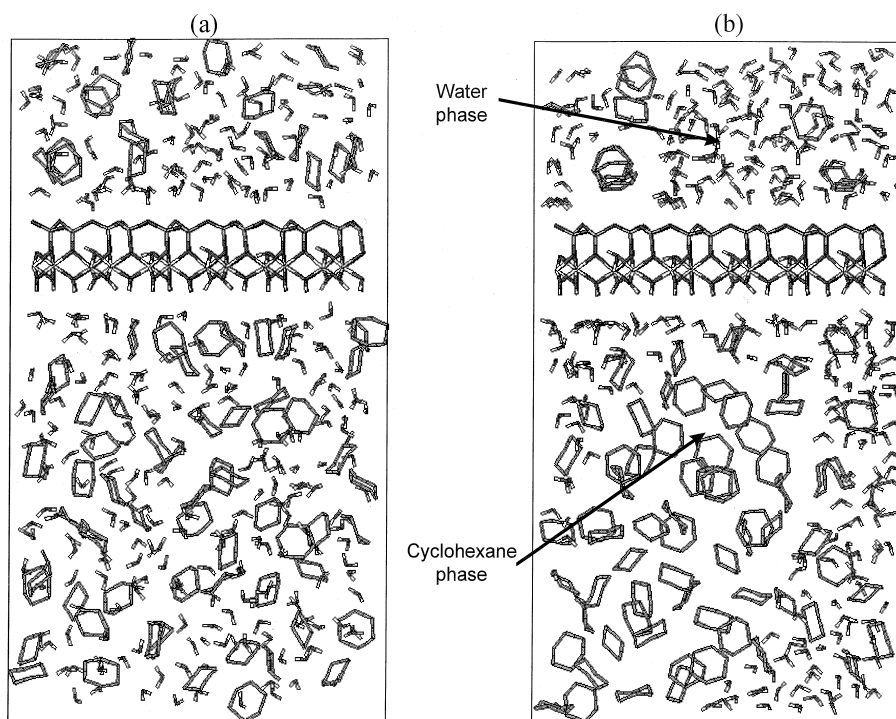


Fig. 5. System containing a kaolinite layer in contact with a randomly configured water/cyclohexane mixture (a) and the same system with demixed water and cyclohexane phases after 150,000 MD-iterations (b).

In all simulations MD-time steps of 1 femtosecond and a MD-temperature of 298 K were used. The temperature was held constant using the algorithm described by Berendsen et al. (1984) with a very weak temperature-coupling, making these virtually NVE-simulations (constant number of atoms, constant volume and constant total [potential + kinetic] energy). A cutoff radius of 8.5 Å was used in all simulations and the system energy was corrected for van der Waals interactions beyond the cut-off radius range (Allen and Tildesley, 1987). The value of this cutoff radius is dictated by the dimensions of the periodic cell used in the simulations as the maximum allowed value for the cut-off radius equals half the size of the smallest dimension of the periodic cell. To ensure a stable simulation of the Coulomb interactions a 7th order taper function was applied as described by de Vos Burchart (1992). Molecular bonds and bond angles were constrained during the simulations using the approach described by Andersen (1983).

### 3. Results and discussion

#### 3.1. Benzocarbazole adsorption on water-wet kaolinite

Table 1 shows the results from the simulations on the benzocarbazole/water/kaolinite systems depicted in Fig.

4. For both benzocarbazole isomers the desorbed system (Fig. 4c) is calculated to be thermodynamically unfavourable compared to adsorption on either kaolinite surface. This indicates that in water/kaolinite systems both benzocarbazole isomers will partition to the mineral surfaces. Furthermore, both isomers prefer adsorption on the silica surface over adsorption on the alumina surface. The partition coefficient data in Table 1 show that at lower temperatures the benzocarbazole concentration at the kaolinite silica surface should be significantly higher than in the water phase or at the alumina surface.

The results from the simulations do not show any significant difference between the partitioning behaviour of either benzocarbazole isomer in the water/kaolinite system. This indicates that water/rock partitioning may be of less importance to changes in benzo[a]/benzo[c]-carbazole ratios than oil/water partitioning in water-wet systems.

The calculated energies associated with adsorption of the benzocarbazoles from the water phase onto the kaolinite surfaces are small (about  $-1.5$  kcal/mol for the alumina surface and about  $-4$  kcal/mol for the silica surface). This makes good sense, as both the water-phase and the two kaolinite surfaces are polar media and should, for that reason, not show a greatly different affinity for the comparatively apolar benzocarbazole

Table 1

Average system energies and derived heats of adsorption and partition coefficients of benzo[a]- and benzo[c]carbazole on water-wet kaolinite surfaces<sup>a</sup>

	Benzo[a]carbazole	Benzo[c]carbazole
Desorbed in water phase	-3643.9±1.4	-3653.1±2.1
Adsorbed on alumina surface	-3645.7±1.8	-3654.5±1.4
Adsorbed on silica surface	-3647.4±1.2	-3657.9±1.6
$\Delta H_{\text{ads}}$ (water phase to alumina surface)	-1.8±1.1	-1.3±2.2
$\Delta H_{\text{ads}}$ (water phase to silica surface)	-3.5±1.7	-4.8±1.7
$K_{\text{alumina surface/water}}$ (25°C)	$2.1 \times 10^1$	$9.0 \times 10^0$
$K_{\text{silica surface/water}}$ (25°C)	$3.7 \times 10^2$	$3.3 \times 10^3$
$K_{\text{alumina surface/water}}$ (200°C)	$6.8 \times 10^0$	$4.0 \times 10^0$
$K_{\text{silica surface/water}}$ (200°C)	$4.1 \times 10^1$	$1.7 \times 10^2$

<sup>a</sup> Error margins reflect the standard deviation of the system energies averaged over 950,000 MD-iterations. Data are given in kcal/mol. Partition coefficient data were calculated from the heats of adsorption as described by van Duin and Larter (1998). The MD-derived heat of adsorption data, determined at a temperature of 25°C, were used as an estimate for heat of adsorption data at 200°C to determine the partition coefficients at 200°C.

isomers. Simulations using the same configurations as depicted in Fig. 4 but without the water-phase indicate that the gas-phase heats of adsorption of both benzocarbazole isomers on the kaolinite silica and the alumina surfaces have values of about -21 kcal/mol and -23 kcal/mol, respectively. Introduction of the water phase reduces the heats of adsorption considerably by competing with the benzocarbazole isomers for the kaolinite surface adsorption sites. Interestingly, but not surprising given the somewhat polar nature of the benzocarbazoles, the water-phase preference of the benzocarbazole isomers for the silica surface over the alumina surface is reversed in the gas-phase.

### 3.2. Cyclohexane/water/kaolinite simulations

Fig. 3 shows four system configurations used in the cyclohexane/water/kaolinite simulations. A clear difference in thermodynamic stability is observed between these four systems (Fig. 6). The system with a water-wet silica surface and a cyclohexane-wet alumina surface is thermodynamically the most stable (running average energy at the end of the simulation  $[E]_{\text{final}} = -3033.4 \pm 2.5$  kcal/mol), followed by the system with water-wet silica and alumina surfaces ( $[E]_{\text{final}} = -2976 \pm 2.3$  kcal/mol), followed by the water-wet alumina/cyclohexane-wet silica system ( $[E]_{\text{final}} = -2927.9 \pm 5.1$  kcal/mol). The system with cyclohexane-wet alumina and silica surfaces is calculated to be by far the least stable ( $[E]_{\text{final}} = -2743 \pm 1.8$  kcal/mol). The higher thermodynamic stability of the completely water-wet system, compared to the completely cyclohexane-wet system, shows that, in the presence of a mixture of a highly apolar organic and a water phase, kaolinite is likely to be water-wet. However, if the volume of the water phase is not large enough to form substantial water-phases near the kaolinite surfaces, which could be the case in, for example, nanometer scale

rudstone pore systems, the formation of one large water-phase near the silica surface is preferred over the formation of smaller water-phases near both surfaces. In this case, the alumina-surface could become cyclohexane-wet.

The preference of the water-phase for wetting the kaolinite silica-surface is also reflected in the results from the simulations on the demixing of a random water/cyclohexane mixture near the kaolinite surface (Fig. 5). After 150,000 MD-iterations the random water/cyclohexane mixture (Fig. 5a) demixes into roughly two water-phases, one near the silica-surface and one near the alumina surface, separated by a cyclohexane phase (Fig. 5b). The water-phase near the silica surface is far more substantial than that near the alumina surface, which agrees with the results obtained for the systems depicted in Fig. 3.

### 3.3. Comparison of the benzocarbazole adsorption and the cyclohexane/water/kaolinite simulations

The main difference between the benzocarbazole adsorption and the cyclohexane/water/kaolinite simulations is that in the latter a complete phase, rather than just a single molecule, of an apolar organic compound is present. As the results show, this difference has a profound impact on the simulation results. While a single organic compound is found to prefer adsorption on both kaolinite surfaces over being dissolved in the water phase, an extended organic phase shows exactly the opposite behaviour, resulting in a thermodynamic preference for water-wet mineral surfaces over cyclohexane-wet mineral surfaces. While benzocarbazole and cyclohexane have different properties they are similarly apolar in comparison with water. For this reason, a comparison of their behaviour in the water/kaolinite system is valid.

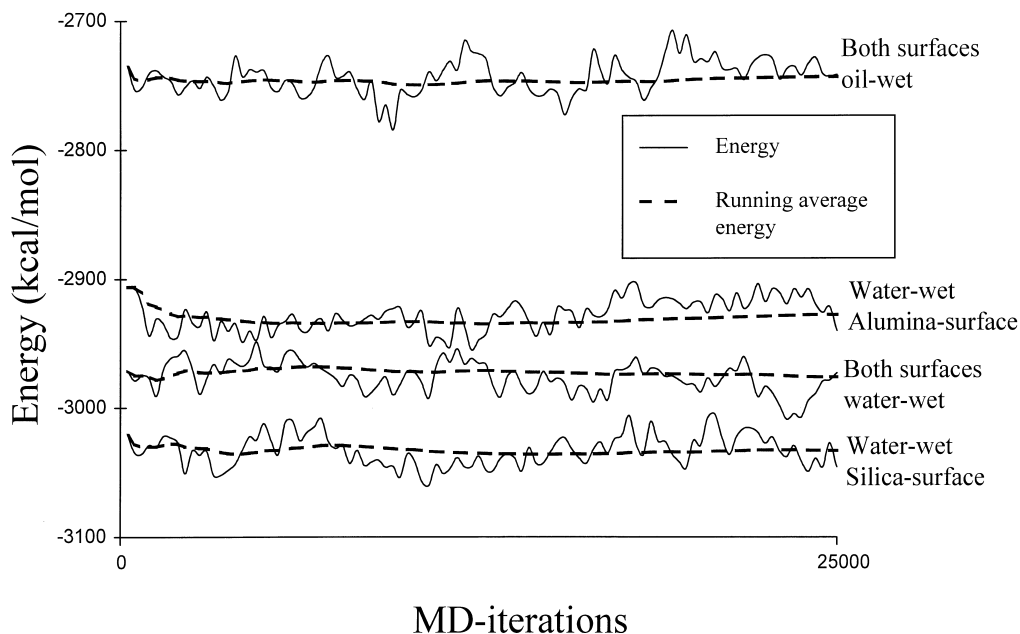


Fig. 6. Results from the cyclohexane/water/kaolinite simulations.

The differences in stability between an adsorbed and a desorbed benzocarbazole isomers (ranging from about 1.5 kcal/mol for the alumina surface to about 4 kcal/mol for the silica surface) are small compared to the energy differences between the various cyclohexane/water/kaolinite configurations (about 250 kcal/mol between a completely water-wet and a completely oil-wet kaolinite). Although these numbers are not directly comparable due to differences in the molecular composition of the systems, this still indicates that the driving force for the formation of a separate organic phase is much larger than the forces resulting from differences in affinity of organic compounds for either water phase or polar mineral surfaces.

#### 4. Conclusions

Simulations of single benzocarbazole molecules in water/kaolinite systems have showed that these compounds will partition to the mineral surfaces rather than being desorbed in the water phase. Calculated heats of adsorption from the water phase are about  $-4$  kcal/mol for the kaolinite silica-surface and about  $-1.5$  kcal/mol for the kaolinite alumina surface. No significant differences between the adsorption behaviour of benzo[a]- and benzo[c]carbazole were observed, indicating that oil/water partitioning may be of more importance to changes in benzocarbazole isomer ratios with migration distance than water/rock partitioning. When the organic phase is

expanded from a single molecule to a full apolar organic phase (80 cyclohexane molecules) a completely different phase behaviour is observed. In these three-phase simulations a water-wet kaolinite system is favoured over a cyclohexane-wet kaolinite, which indicates that kaolinite is water-wet in the presence of continuous apolar organic and aqueous phases. Furthermore, these simulations show that the water-phase has a higher affinity for the silica surface than for the alumina surface, which means that when contacted with relatively small volumes of water the alumina surface is most likely to become oil-wet. These observations are confirmed by the results from a simulation on the demixing of a randomly orientated water/cyclohexane mixture near the kaolinite surfaces as the most substantial water phase in this simulation is formed near the silica-surface.

Obviously, the systems studied here reflect idealised situations. In sediments the water/oil phase behaviour will be complicated by the presence of polar organic molecules, able to partition through water-films and act as surfactant molecules once adsorbed on the mineral surfaces. Furthermore, factors like salinity and pH (especially pH-gradients near mineral surfaces) will have a major impact on wettability. However, identification of the thermodynamic driving forces in the 'ideal' systems studied here is of vital importance for beginning to understand (and predict) wettability in complex matrices such as sediment systems. As this work indicates, computational chemical techniques like molecular dynamics can provide useful tools for studying these driving forces.

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*Associate Editor—C.E. Snape*

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