

Computational chemical investigation into the partitioning of organic compounds in the subsurface

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1. Introduction

Partitioning between organic, water and mineral phases is one of the main processes controlling the transport properties of organic compounds in sediments. The measurement and prediction of these transport properties are central topics in various fields of organic geochemical research. Important geochemical issues, ranging from the changes in petroleum composition during migration to the bioavailability of carcinogenic polyaromatic hydrocarbon (PAH) compounds in urban environment sites, are all directly controlled by organic compound partitioning.

One of the central problems of geochemical research concerns the chemical complexity of sediment systems; most of the time this research is focusing on mixtures of a wide variety of organic compounds (oil, for example, has a composition ranging from highly polar organic acids and alcohol compounds to apolar, wax-like C_{40+} -alkanes) in contact with a variety of mineral facies. For this reason, characterisation of the sediment systems is of prime importance in the investigation of partitioning processes. This need for good characterisation indicates the potential of computational chemical techniques for obtaining partitioning data on geochemically relevant compounds, as computational chemical techniques allow for an exact definition of the composition of the system under investigation. Until so far, geochemical applications of computational chemical techniques have mainly been limited to the determination of the thermodynamic stabilities of so-called biomarker compounds [1-2] (organic compounds, observed in the geosphere, whose chemical structure can be related to biogenic sedimentary input) whose relative concentrations can be used to determine, for example, sediment maturity (time/temperature history) and in oil/source rock correlations [3]. In these studies molecular mechanics (MM), a computational chemical technique using a set of empirical potential functions to relate molecular structure to thermodynamic stability [4], was used. MM is generally employed to determine the most stable conformation for a given molecular structure, from which subsequently its gas-phase thermodynamic stability can be obtained. Such gas-phase stability data can be applied to explain observed molecular transformations in sediments [5-7]. As such, MM can be used to predict the chemical fate of sedimentary organic compounds. To predict their

physical fate, *i.e.* the effects of partitioning and diffusive processes on their distribution in the geosphere, the MM-predicted gas phase stability data are generally insufficient as environmental influences, like the solvent matrix or mineral surface adsorption site, need to be taken into account. The static picture, as sketched by the MM minimum energy determination, works as long as a single compound is investigated; for more realistic and complex systems, like a molecule dissolved in a solvent phase (Figure 1), a dynamical approach is required, taking the effects of molecular movement on system stability into account.

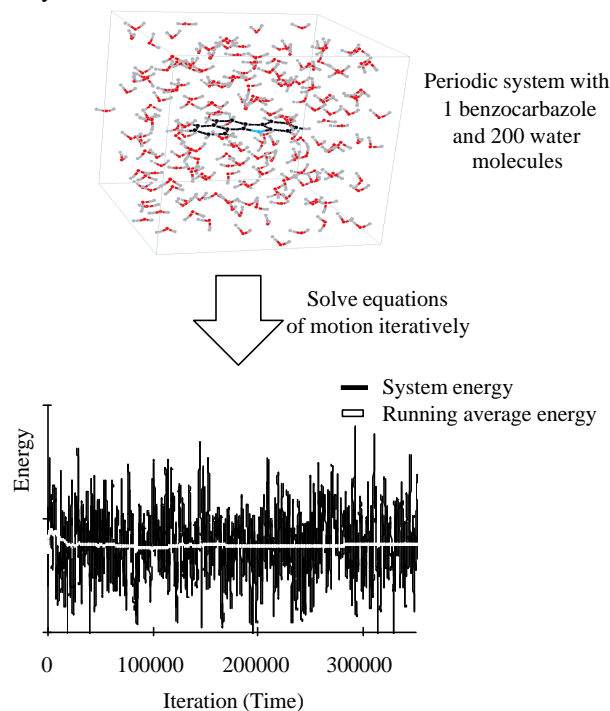


Figure 1. Molecular dynamics scheme for determining the stability of a water-solvated benzocarbazole molecule.

One computational chemical technique able to perform such dynamical simulations is molecular dynamics (MD; see [8-9]) in which, similar to MM, an empirical set of potential functions is used to determine the inter- and intramolecular forces in multimolecular systems. These forces are used in MD to iteratively solve the equation of motion for the atoms in the system. Based on the atomic positions derived from these movements, the thermodynamic stability of the entire system can be determined at each iterative time-step. These system energies fluctuate with time; by

averaging these system energies for a large amount of time steps (the running average energy in Figure 1) a reliable estimate for the thermodynamic stability of the complete system, rather than that of a single compound as is done in MM simulations, can be obtained. As indicated in Figure 1, MD-simulations usually employ periodic systems, which means that molecules leaving the periodic box on the right side get reintroduced on the left and molecules leaving the periodic box at the bottom get reintroduced on the top (and vice versa). This means that MD-simulations are performed on semi-infinite systems.

To demonstrate and utilise the geochemical potential of MD in geochemical research we used this technique to investigate the partitioning behaviour of two specific compounds found in the oil phase, benzo[a]- and benzo[c]carbazole (Figure 2), between organic, water and mineral phase.

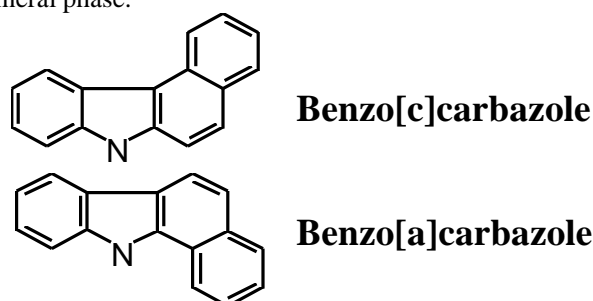


Figure 2. Molecular structure of benzo[a]- and benzo[c]carbazole.

Sedimentary evidence suggests that, compared to the benzo[c]-isomer, benzo[a]carbazole is preferentially removed from petroleum during its migration from the source rock to the reservoir [10]. This preferential removal is probably related to differences in phase behaviour between these isomers. During the migration from source to reservoir oil comes in contact with water and mineral phases (Figure 3). Because of this, compounds with a higher affinity for either the water phase or the inorganic surfaces will decrease in relative abundance in the oil phase.

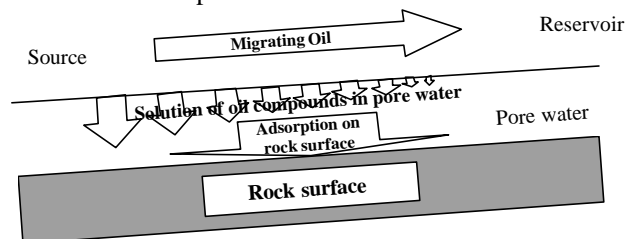


Figure 3. Partitioning processes responsible for oil composition changes during migration from source rock to reservoir.

To determine whether differences in partitioning behaviour are indeed responsible for the observed changes in benzo[a]/benzo[c] ratio with migration distance the oil/water partition coefficient and the affinity for adsorption on the rock surface need to be

determined for both benzocarbazole isomers. However, the extremely low solubility of these benzocarbazole isomers in the water phase severely restrict the accuracy of experimental measurements of their oil/water and water/rock partitioning behaviour. For this reason we have performed a series of molecular dynamics calculations to determine the relative thermodynamic stability of the benzocarbazole isomers in, respectively, an aqueous and an organic (cyclohexane) phase. This difference in phase stability can be directly correlated to the oil/water partition coefficient of these compounds.

To examine the influence of adsorption on mineral surfaces on benzocarbazole distributions we also determined the adsorption energy of both benzocarbazole isomers on a water-wet kaolinite surface. Kaolinite was chosen as inorganic phase because it is an ubiquitous mineral in sediment systems. Furthermore, kaolinite has a layered clay structure with two well-defined surfaces (Figure 4) which facilitates computational simulation. Using molecular dynamics we can determine the affinity for both the silica and the alumina kaolinite surfaces.

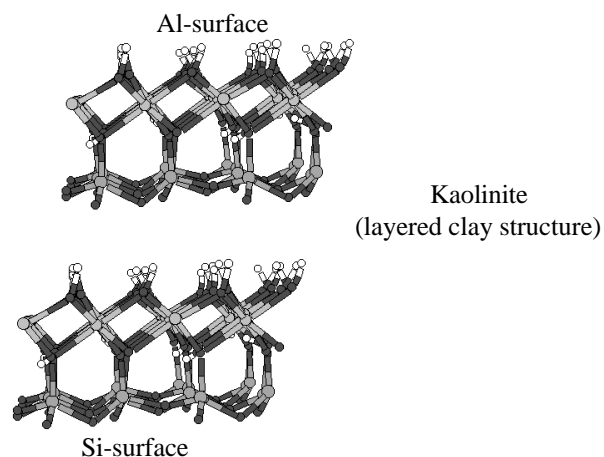


Figure 4. Kaolinite structure and surfaces.

By combining the oil/water benzocarbazole partitioning data with the benzocarbazole affinities for adsorption on the kaolinite surfaces we can begin to sketch a picture of the relative importance of these partitioning processes on oil composition in sediments.

2. Methods

2.1 Oil/water partitioning coefficients. To determine the benzocarbazole oil/water partitioning coefficients, molecular dynamics simulations were performed using the Delphi-program [11]. For each benzocarbazole the stability in both the water and the cyclohexane phase were calculated by immersing them in these solvent phases and averaging the energy of these systems for 1,000,000 iterations. Cyclohexane was used as a proxy for the oil phase, having a density and boiling point (778.55 kg/m³ and 81°C, respectively) comparable to that of oils. Cyclohexane is probably more apolar than

most oils, but qualitative differences between cyclohexane/water and oil/water partition coefficients should be similar, since the water phase is far more polar than both the oil and cyclohexane phases. The oil/water partition coefficients were subsequently calculated from the difference between these system energies (Figure 5). This computational scheme was tested by performing these calculations, in addition to the two benzocarbazole isomers, for phenol, o- and m-cresol and carbazole. For these four compounds reliable octanol/water partition coefficients have been measured, allowing evaluating of the quality of the computational data.

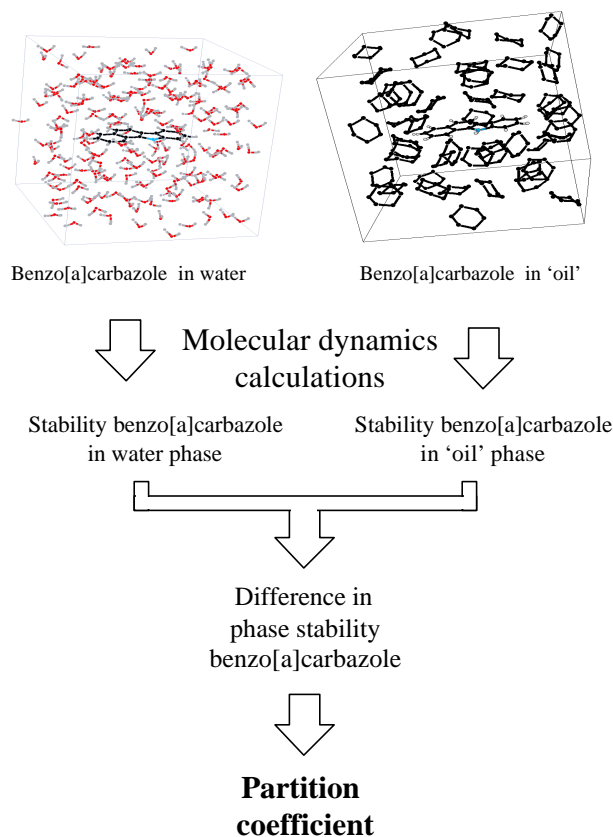


Figure 5. Scheme used for determining the oil/water partitioning coefficients of benzo[a]- and benzo[c]carbazole.

For the water phase, the TIP3P-force field of Jorgensen *et al.* was used [12]. For the cyclohexane phase an united-atom approach was used (lumping together the CH₂-groups in one superatom to reduce the amount of atoms in the simulation) with the parameters described by DeBolt *et al.* [13]. For carbazole, o-cresol, m-cresol, phenol, benzo[a]- and benzo[c]carbazole a force field was developed [14] using the EEM-approach [15] to calculate the molecular charge-distribution. This force field was based on literature data and molecular data calculated using the MM3-force field [16].

2.2 Benzocarbazole adsorption on water-wet kaolinite surfaces. To determine the influence of kaolinite mineral surfaces on the benzocarbazole distribution in sediment systems three MD-simulations were performed for each benzocarbazole isomer. These simulations consisted of (1) the benzocarbazole adsorbed on the kaolinite silica surface, (2) the benzocarbazole adsorbed in the kaolinite alumina surface and (3) the benzocarbazole suspended in the water-phase between the two mineral surfaces (Figure 6). By subtracting the system stability of simulation (3) from those obtained from simulation (1) and (2) the affinity of the benzocarbazole for the kaolinite silica and alumina surfaces could be determined.

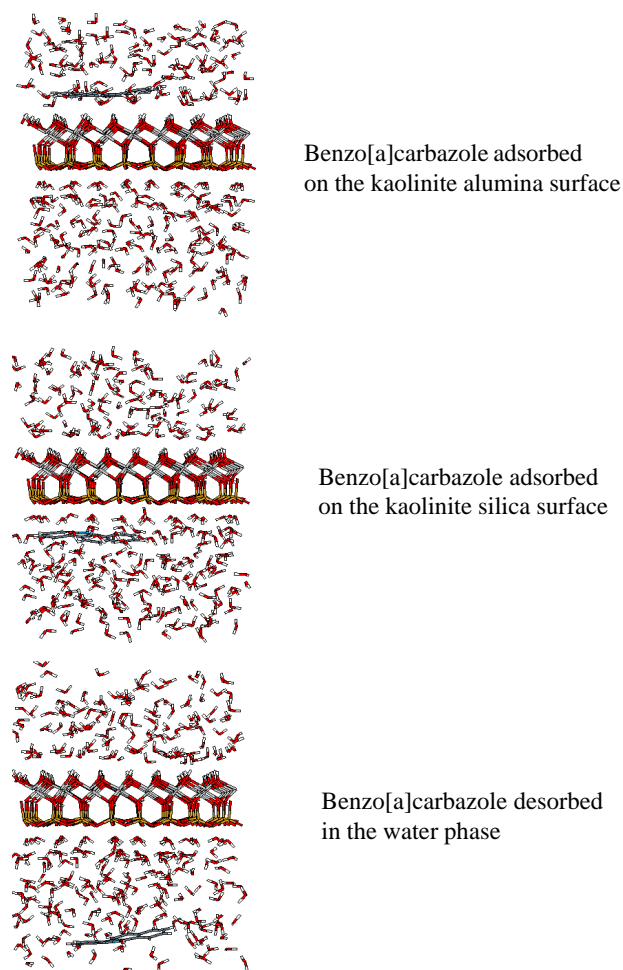


Figure 6. Periodic systems used in the benzocarbazole/kaolinite MD-simulations.

The kaolinite atom positions were taken from Bish [17]. These positions were kept fixed during the simulations. The atomic charges in the kaolinite layer were taken from Teppen *et al.* [18] and the van der Waals parameters for the atoms in the kaolinite layer from the Dreiding force field [19]. Mild distance restraints, perpendicular to the mineral surfaces, were used to ensure that the benzocarbazole isomers did not accidentally migrate to the kaolinite surfaces in the

desorbed benzocarbazole simulation. The energy associated with these distance restraints were not taken into account in calculating the system energy.

3. Results and Discussion

3.1 Oil/water partitioning coefficients. Table 1 shows the results from the oil/water partition coefficient calculations for phenol, o- and m-cresol and carbazole. A good correlation, both qualitatively as well as quantitatively, is observed between the MD-derived cyclohexane ('oil')/water partition coefficients for phenol, o- and m-cresol and carbazole and their experimentally observed octanol/water partition coefficients, indicating that the computational scheme should be able to predict reliable partition coefficients for the benzocarbazole isomers.

Table 1. Oil/water partition coefficients derived from the MD-simulations.

Compound	$\Delta\Delta G_{oil'/water}$	K_{calc}	K_{exp}
Phenol	7153.0	1	1
o-Cresol	7147.9	8	3.1
m-Cresol	7145.4	21	3.2
Carbazole	7140.4	1.6×10^2	1.8×10^2
Benzo[a]carbazole	7126.6	4.2×10^4	-
Benzo[c]carbazole	7123.3	1.6×10^5	-

$\Delta\Delta G_{oil'/water}$ is the difference in stability for the compound in the cyclohexane ('oil') phase and the water phase in kJ/mol. K_{calc} is the partition coefficient, relative to that of phenol, calculated from $\Delta\Delta G_{oil'/water}$.

K_{exp} is the experimentally observed octanol/water coefficient [20] taken relative to the phenol octanol/water partition coefficient (1.46) to allow direct comparison with the MD data.

The results in Table 1 show that both benzocarbazole isomers have high oil/water partition coefficients, which agrees well with their observed low concentrations in the water phase. Furthermore, the benzo[a]carbazole is calculated to have a slightly higher affinity for the water phase than its benzo[c]-isomer. These results fit very well, and potentially explain, the preferential removal of the benzo[a]carbazole from migration oils.

3.2 Benzocarbazole adsorption on water-wet kaolinite surfaces. Figure 7 shows the running average energies obtained from the MD-simulations using the periodic systems depicted in Figure 6 for the benzo[a]- and benzo[c]carbazole isomers. As shown previously in Figure 1, these running average energy values fluctuate strongly at the beginning of the simulation but become more reliable when increasing amounts of MD-iterations are taken into account. As these results from these MD-simulations indicate, both benzocarbazole isomers will prefer adsorption on the kaolinite alumina surface over being desorbed in the water phase by about 10 kJ/mol.

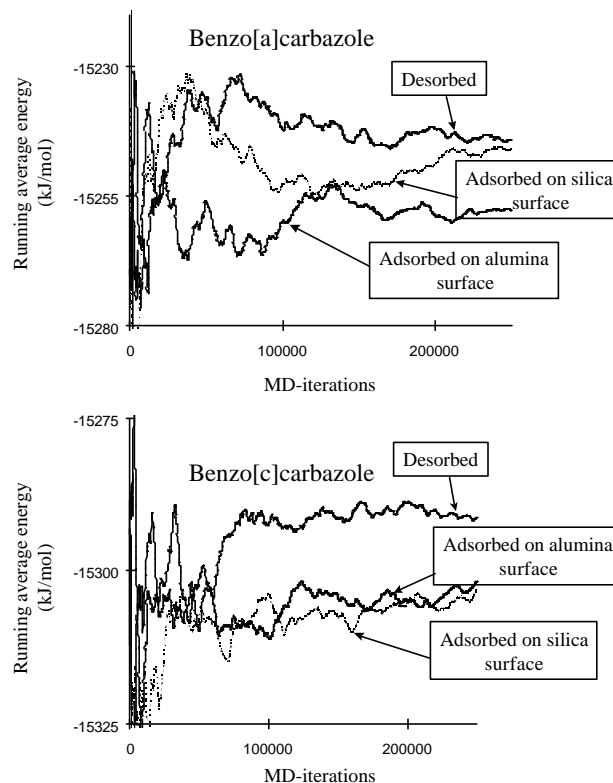


Figure 7. Running average energies obtained from the MD-simulations on benzo[a]- and benzo[c]carbazole adsorbed on the kaolinite silica and alumina surfaces and desorbed in the water phase.

For the kaolinite silica surface the current results from the MD-simulations are more difficult to interpret. Current results seem to suggest that the benzo[a]carbazole has a low affinity for this surface, comparable to its affinity for the water phase, while the benzo[c]carbazole has a higher affinity for this surface, comparable to its affinity for the alumina surface. However, the error margin in the running average energy data for the interaction of the benzocarbazole isomers with the kaolinite silica surface are still fairly high and more MD-iteration will be required to confirm these observations.

Combined with the oil/water partition coefficient data for the benzocarbazole data these adsorption data allow us to sketch a general picture of the partitioning behaviour of the benzocarbazole isomers in sediments. Due to their high oil/water partitioning coefficients these isomers will be slowly removed from the oil phase during migration, the benzo[a]carbazole slightly faster than its benzo[c]isomer. Once partitioned in the water phase both isomers will migrate to the mineral surface, provided that a suitable inorganic phase, like kaolinite, is present. This picture is obviously incomplete, as it does not fully take the complexity of sediment systems into account. For example, this explanation assumes that the oil phase is always separated from the inorganic surfaces

by a water film ('water-wet mineral surfaces', see [21]). Furthermore, although sediment systems can roughly be divided in the three phases (organic, aqueous and inorganic) used in our MD-simulations, these individual phases are far more complex in sediments, compared to the single compound-phases used in the simulations. Despite these shortcomings, however, this study has demonstrated that MD can be used to identify the general thermodynamic driving forces responsible for the distribution of organic compounds in the subsurface.

4. Conclusions

MD-simulations on benzo[a]- and benzo[c]carbazole dissolved in a water and a cyclohexane phase have indicated that the benzo[a]-isomer has a slightly higher affinity for the water phase. For both isomers, however, the calculated oil/water partition coefficient are large, indicating that their concentrations in the water phase will be minimal. These observations could explain the preferential removal of the benzo[a]carbazole, compared to its benzo[c]-isomer, from the oil phase during its migration from source rock to reservoir.

Additional simulations on the adsorption of these benzocarbazole isomers from the water phase to kaolinite mineral surfaces show that both isomers will preferentially migrate to these surfaces once they get partitioned into the water-phase.

The results from this study show the potential of computational chemical techniques in predicting the physical fate of organic compounds in the subsurface. Computational chemical techniques allow one to exactly define the molecular composition of the system under investigation. Because of this, the methods described here should be applicable to a wide range of geoscientific topics.

Acknowledgments - This work was supported by TMR grant no. ERBFMBICT971871. Computational support from Dr. J.M.A. Baas from the Delft University of Technology, the Netherlands, the Department of Petrol Engineering, Heriot-Watt University, Edinburgh, Scotland and Prof. W.A. Goddard III for the California Institute of Technology, USA, is gratefully acknowledged.

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