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Integrating Structural and Thermodynamic Mechanisms for Sorption of PCBs by Montmorillonite

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Abstract

Strong sorption of planar nonionic organic chemicals by clay minerals has been observed for important classes of organic contaminants including polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dioxins, and such affinity was hypothesized to relate to the interlayer hydrophobicity of smectite clays. In batch sorption experiments of two trichlorobiphenyls on homoionic Na-, K-, Cs-montmorillonites, considerably greater sorption coefficient (K_w) was observed for coplanar 3,3',5-trichlorobiphenyl (PCB 36); $\log K_w$ for Na-, K-, and Cs-montmorillonite were 3.69, 3.72, and 4.53 for coplanar PCB 36 vs 1.21, 1.46, and 0.87 for the nonplanar 2,2',6-trichlorobiphenyl (PCB 19). MD simulations were conducted utilizing X-ray diffraction determined clay interlayer distances (d -spacing). The trajectory, density distribution, and radial distribution function of interlayer cation, water, and PCBs collectively indicated that the hydrophobic nature of the interlayer regions was determined by the hydration status of exchangeable cations and the associated d -spacing. The sorption free energies calculated for both coplanar and nonplanar PCB molecules by adaptive biasing force (ABF) method with an extended

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Supporting Information

Description of chemicals, sorption, and XRD experiments, MD simulation setups, snapshots of MD models: SWy-2, PYRO and interlayer-micropore two-phase model, tables of linear isotherm parameters in mixed solvents, chemical properties of PCBs, and calculated hydrogen bond numbers in clay interlayers, figures showing calculated free energy profile associated with dihedral angle of PCBs, calculated free energy profile for transfer of PCBs from water into 1-octanol ($\log K_{OW}$), sampling quality and convergence of ABF simulations, density profiles, and radial distribution functions of interlayer species, overlays of intercalated PCBs trajectories, and the explicit forcefield energy expression and parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>

Notes

The authors declare no competing financial interest.

interlayer–micropore two-phase model consisting of cleaved clay hydrates and “bulk water” are consistent with the Gibbs free energies derived from the measured $\log K_w$, manifesting enhanced sorption of coplanar PCBs was attributed to shape selectivity and hydrophobic interactions.

Graphical abstract

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a family of toxic organic compounds consisting of 209 congeners, and can bioaccumulate in food chains because of their recalcitrant and lipophilic nature.^{1–3} Due to their extensive use between the 1930s and 1970s, significant levels of PCBs have been detected in the environment.^{4–7} It has been estimated that about 7709 t of PCBs have been released into the environment based on the calculations of global PCB mass balance.⁸ Soil is a major reservoir for environmental PCBs, and can function as a source of atmospheric PCBs.^{9–11}

To better understand the environmental fate and transport of PCBs, it is important to study sorption process of PCBs with different geosorbents present in soil including soil organic matter (SOM) and clay minerals. Because PCBs are sparingly soluble, they tend to be strongly sorbed by soils, and residual PCB concentrations in aqueous phase are typically very low. To accurately quantify sorption a method utilizing cosolvents has been developed in which mixtures of water and miscible organic solvents, e.g., methanol, are used at varying ratios.^{12–14} The sorption coefficient in pure water is derived from the following:

$$\log(K_m/K_w) = -\alpha\sigma f_c \quad (1)$$

where K_m and K_w are sorption coefficients in cosolvent and in pure water systems, α is an empirical constant related to the interaction between solvent and sorbent; σ represents the cosolvency power; f_c is the volume fraction of cosolvent. According to this cosolvency model, sorption coefficient K_m increases log linearly as the fraction of cosolvent decreases, and sorption in pure water (K_w) can be estimated by extrapolating the sorption data to $f_c = 0$.^{12–14}

SOM is considered the major sorptive compartment in soils for PCBs, and partitioning is regarded as the primary mechanism.^{15,16} Recent studies have shown that clay minerals may also play an important role for sorption of many neutral organic chemicals (NOCs), such as dioxins, nitroaromatic compounds (NACs), trichloroethene (TCE), and atrazine.^{17–22} The interaction between NOCs and clay minerals is strongly dependent on exchangeable interlayer cations and structural characteristics of NOCs.^{20,21,23} Sorption of semipolar NACs and nonpolar TCE from water by homoionic montmorillonite clays showed that sorption by Cs- or K-saturated montmorillonite was 10–100 times greater than that by Na- or Ca-saturated montmorillonite.^{21,24} Hydration of interlayer cations is a major determinant of sorption of NOCs by clays. Exchangeable cations with lower hydration energy such as K^+ and Cs^+ , manifest smaller hydration radii, and result in larger siloxane surface area not obfuscated by water; these surfaces are, in general, relatively hydrophobic in nature.²⁵ Weakly hydrated exchangeable cations also manifest an optimal interlayer spacing that corresponds to the approximate thickness of the sorbed molecule, and those hydrophobic slits act as sorption domains. Movement of NOCs from bulk water to these domains enables partial dehydration of the sorbate, which is an energetically favorable process.^{19,25} The formation of complexes between weakly hydrated cations and negatively charged moieties of the molecules (e.g., $-NO_2$ of NACs and bridge-O of dioxins) or π -electrons has also been observed, which further promotes the sorption of NOCs by smectite clays.^{18,20,21} Steric effects of organic molecules with bulky substituents or with nonplanar structures can inhibit intercalation, since the nonplanar molecules cannot maximally interact with the opposing clay sheets of expandable 2:1 clay minerals.^{20–24,26} However, the contributions of such non-bonded interactions, hydrophobic, and steric effects to the overall sorption are difficult to be elucidated or quantified by macroscopic experiments.

Molecular dynamics (MD) simulations have been used successfully for quantitatively characterizing interlayer structure of hydrated clay minerals and mechanistic interactions between organic molecules and clay minerals.^{27–31} Trajectory analysis from MD simulation of hydrated Cs-montmorillonite interlayers showed that a larger portion of relatively hydrophobic siloxane surface was not occupied by water in the stable Cs-clay as compared to Na- or K-clays.³² Complexation of interlayer cations with organic molecules at the functional groups or atoms possessing negative charge character was confirmed by pair distribution function analysis.³³ Free energy perturbation and thermodynamic integration techniques were applied to calculate the free energies of cation exchange processes for hydrated clay minerals with different exchangeable cations; these methods successfully interpreted the thermodynamic origin of interlayer hydrophobicity.^{34,35} Qualitative sorption enthalpies for the interactions between hydrated clay minerals and organic molecules such as NACs and dioxin were computed by thermodynamic cycles, and agreed favorably with experimental observations.^{33,36} However, simulations with sufficient accuracy to characterize the energetic properties of dynamic sorption processes, i.e., transport of sorbate molecules from bulk solution to interlayer surfaces, require the system sizes and simulation time scale beyond the capability of traditional MD techniques. Also, estimating the component free energy of cavity formation in the thermodynamic cycle integration may introduce significant errors for larger complex systems.³⁶ Recent developments in accelerated MD techniques such as metadynamics and adaptive biasing force methods

substantially speed up MD simulations by enhancing the conformational space sampling, and are capable of accurately describing the free energy surface of processes of large systems at longer time scale.^{37,38} Rotenburg et al., constructed a clay–water interface system, used accelerated MD techniques, and successfully simulated the exchange process of water and alkali cation across the interface.³⁹ The sorption of organic contaminants from “bulk water” by clay minerals may also be amenable to these new accelerated MD simulations, yet few such studies exist.⁴⁰

In this study, the mechanistic interaction of two representative PCB congeners, coplanar 3,3',5- and ortho-substituted nonplanar 2,2',6-trichlorobiphenyl (PCB 36 and PCB 19, respectively) by montmorillonite saturated with different exchangeable cations (Na^+ , K^+ , and Cs^+) was examined using macroscopic sorption data obtained from water/methanol cosolvent mixtures, XRD, and accelerated MD simulations. The mechanistic effect of molecular planarity on sorption of PCBs by clays was elucidated.

MATERIALS AND METHODS

Chemicals, Sorption Isotherm, and X-ray Diffraction Experiments

Details of chemicals, clay preparation, measurement of sorption isotherms, and X-ray diffraction (XRD) experiments are detailed in the Supporting Information (SI) Text S1.

Computational Methods

MD simulations of different cation-saturated montmorillonite hydrate systems with or without sorbed PCBs were performed to explore molecular-scale interactions among PCBs, exchangeable cations, and water in montmorillonite interlayer region. Periodic models for Na-, K-, and Cs- exchanged montmorillonite (SWy-2) and noncharged montmorillonite (the surface isomorphous substitution and the interlayer cations were removed to make pyrophyllite-like sheets, PYRO) hydrates (SI Figure S1) were constructed following the procedure described by Aggarwal et al.³⁶ The supercells ($8 \times 6 \times 1$ unit cells) of the clays have the composition $(\text{M}_{28})[\text{Al}_{168}\text{Mg}_{24}][\text{Si}_{380}\text{Al}_4]\text{O}_{960}(\text{OH})_{192}$ possessing 24 octahedral charges and four tetrahedral charges which are compensated by 28 interlayer cations for SWy-2, and $[\text{Al}_{192}][\text{Si}_{384}]\text{O}_{960}(\text{OH})_{192}$ for PYRO. Twenty-eight Na^+ , K^+ , or Cs^+ cations were placed randomly within the interlayer regions for SWy-2, and one molecule of PCB was then added for both SWy-2 and PYRO. Various amounts of water were added to swell the clay minerals to their stable or metastable states corresponding to one, two, and three interlayer water layers, in which d -spacings correspond to 12.5, 15.5, and 18.5 Å, respectively. The trajectories of equilibrium systems were collected for dynamic and structural analyses.

An extended interlayer-micropore two-phase periodic system was constructed as shown in SI Figure S1, where the noncharged montmorillonite structure (a supercell consisting of $8 \times 6 \times 1$ unit cells) was cleaved along the 010 plane, and the broken edges were compensated with OH groups to keep the layer charge neutral. A water slab with a width of ~ 50 Å was inserted between the cleaved edges to make an interlayer–micropore two-phase unit cell that could be interrogated by periodic methods. The effects of interlayer hydration status on

thermodynamic energetics were studied using the adaptive biasing force accelerated MD method (ABF).⁴¹ The free energy of the sorption process, that is, a PCB molecule reversibly moving from the clay mineral interlayer to the aqueous micropore (representing the bulk water) was investigated: The reaction coordinate was designated as the z-axis, with its origin located at the z-position of surface protons on the cleaved clay edge. Sorption free energy profiles were calculated from trajectories for three equilibrium hydration states of the clay interlayer, with *d*-spacings of 12.5, 15.5, and 18.5 Å, representing the interlayer hydration properties of Cs-, K-, and Na- exchanged montmorillonite systems, respectively.

The molecular dynamics package LAMMPS (Sandia National Laboratory, ver. Aug-2013) was used to run the all-atom molecular simulations with extended PCFF force field and the clay mineral structure and hydroxyl edge groups are kept flexible.⁴² More details of the simulation setup including the force field, MD parameters and protocol can be found in SI Text S2. Validation of the force field was conducted by calculations of free energy profiles associated with (a) the dihedral angles of the PCBs, and (b) transfer of each PCB from water to 1-octanol, and the sampling quality and convergence of the ABF method was tested by a series of simulations for PCB 36 transfer between bulk water and 15.5 Å clay hydrates (SI Text S2, Figures S2–S4).

RESULTS AND DISCUSSION

Sorption isotherms of PCB 36 and PCB 19 by homoionic Na-, K-, and Cs-montmorillonite (SWy-2) at different methanol volume fractions are shown in Figure 1a–c and Figure 1d–f, respectively. The isotherm data were all fit to linear sorption isotherm model:

$$q_e = K_m \times C_e \quad (2)$$

where q_e (mg/kg) is the sorbed PCB concentration, C_e (mg/L) is the equilibrium aqueous concentration, and K_m (L/kg) is the linear sorption coefficient. Sorption parameters are shown in SI Table S1 for the mixtures of methanol and water. The linear sorption coefficients (K_w) in pure water were extrapolated to $f_c = 0$ based on the relationship between $\log K_m$ and the corresponding methanol volume fraction (eq 1). The intercepts, i.e., $\log K_w$ values, were 3.69, 3.72, and 4.53 for PCB 36 sorption by Na-, K-, and Cs-montmorillonite, respectively. In comparison, the nonplanar PCB 19 yielded much lower $\log K_w$ values of 1.21, 1.46, and 0.87 for Na-, K-, and Cs-montmorillonite, respectively (Table 1). The Gibbs free energies (ΔG_w) of sorption (from pure water) were calculated using eq 3:

$$\Delta G_w = -RT \ln K_w \quad (3)$$

The sorption of PCB 36 from water by montmorillonite was substantially affected by the exchangeable cation (Figure 1a–c), with the linear sorption coefficients decreasing in the order $\text{Cs}^+ \gg \text{K}^+ > \text{Na}^+$ (SI Table S1). This is consistent with our previous results for dioxin sorption on various smectites.³³ The hydration of exchangeable cations is a major determinant of sorption affinities of the clay for aqueous phase NOCs, as it determines the

interlayer distance, and the portion of unobscured hydrophobic clay siloxane surfaces between exchangeable cations that function as adsorption domains.^{17,18,20,43} Weaker cation hydration produces a smaller hydration sphere surrounding the cation (such as Cs⁺), thereby manifesting larger hydrophobic siloxane surfaces available for sorption.^{44,45} Large hydration spheres and strongly held hydration water (such as Na⁺) would also prohibit the direct interactions between sorbed NOCs and interlayer cations. These concepts help explain the greater PCB 36 sorption by Cs-saturated montmorillonite compared with K- and Na-montmorillonite, and indicate that the clay interlayer is the predominant locale for sorption of PCB 36. As shown in Figure 1a–c, sorption of PCB 36 significantly decreased with increasing cosolvent fraction, and log K_m decreased linearly with increasing f_c in accordance with eq 1 with $r^2 = 0.99$ (SI Table S1). The K_w values (Table 1) are comparable or greater than sorption of phenanthrene by high organic-carbon soil in a similar study, or the estimated sorption of PCB 36 by SOM (K_{om}) calculated from empirical correlations of K_{om} with octanol–water partitioning coefficient (K_{ow}).¹⁵ This indicates that SOM is generally the dominant partitioning phase in soils for hydrophobic compounds as expected, while soil clay fractions might constitute a non-negligible contribution in sorption of NOCs with planar structures dependent on the abundance of clay minerals in the soil matrices.⁴⁶

Sorption of PCB 19 by montmorillonite is much lower compared with PCB 36 despite the fact that both PCBs have similar log K_{ow} values (or hydrophobicity) 5.04 for PCB 19 vs 5.81 for PCB 36 (SI Table S2). For example, the K_m values quantifying sorption of PCB 36 by Cs-montmorillonite is ~20 times greater than that of PCB 19, at $f_c = 0.3$. This remarkable difference in sorption affinities can be explained by steric effects. For PCB 19, the presence of two ortho-Cl substituents results in a dihedral angle between the two aromatic rings of ~90.8°, and an internal energy barrier of rotation of 42.3 kcal/mol (SI Table S2). Hence, it is very unfavorable energetically to rotate the two rings into a coplanar position. The nonplanarity of PCB 19 could inhibit its intercalation in clay interlayers and interactions with both opposing clay siloxane surfaces.²⁵ Interestingly, sorption of PCB 19 by montmorillonite clays did not decrease in the order Cs⁺ > K⁺ > Na⁺ (Figure 1), as the hydration enthalphy increases, which is typically observed for NOCs.¹⁸ This could be due to the size limitation of PCB 19 molecule to fit into the clay mineral interlayer.

The transmission XRD patterns of montmorillonite clay suspensions were recorded in water–methanol mixtures at different volume ratios to evaluate the size of the clay mineral interlayer gallery (Figure 2). The d -spacings of Cs-SWy-2 within the cosolvent range (0–50%) were ~12.5 Å, and expanded slightly to 13.1 Å in 100% methanol. The thickness of a montmorillonite sheet is ~9.6 Å leaving an interlayer distance of ~3 Å which exactly fits the thickness of coplanar PCB 36 molecule (~3 Å). These data demonstrate a parallel orientation of PCB 36 on the planar clay layers of Cs-SWy-2 where it could simultaneously interact with the opposing siloxane surfaces without the intermediation of water. This structure allows the dehydration of PCB 36, and is believed to be responsible for the great sorption (Figure 1).⁴⁷ In contrast, the nonplanar PCB 19 molecule is too bulky (~8 Å thick) to be intercalated by Cs-SWy-2, manifesting comparatively low sorption. The XRD patterns for K- and Na-montmorillonite showed larger d -spacings (001 peaks at 15.5 and 16.8 Å, respectively) in 100% methanol. No significant peak was observed for K-montmorillonite in the low 2θ range at lower methanol ratios (0–50%), while the 001 peak for Na-

montmorillonite shifted to 20.2 Å in 50% methanol and disappeared in 30% and 0% methanol. The disappearance of 001 peaks for Na-montmorillonite at lower methanol ratios (<50%) suggested that Na-montmorillonite would expand to the distance equivalent to three or more layers of water, or even delaminate. In these clays, the PCB 19 molecule could be intercalated into the interlayer or onto the external surface of Na-SWy-2 without shape deformation, however the interlayer regions or external surface are fully hydrated hence preventing direct interaction of PCB 19 with interlayer cations or siloxane surfaces. Therefore, insignificant sorption of PCB 19 by Na-montmorillonite was observed. Hydrated K-montmorillonite can be considered as intermediate between Cs- and Na-SWy-2. In this and previous studies,^{20,24,48} K-SWy-2 likely exists as two-layer hydrate in pure water which allows the access of PCB 19 to the interlayer domains without substantial deformation. In the mixed solvent systems described here, no apparent difference in the XRD patterns was observed for clay controls and PCB-loaded clays due to that the highest PCB sorption was <100 mg/kg, which would not cause the changes of XRD patterns (data not shown). However, on the basis of the XRD results presented here and in previous studies of SWy-2 in pure water,^{20,24,48} we could assume that in aqueous suspension the idealized interlayer spacing for Cs-SWy-2 is 12.5 Å corresponding to one-layer hydrates, 18.5 Å for Na-SWy-2 corresponding to three-layer (or more) hydrates, and 15.5 Å for K-SWy-2 corresponding to two-layer hydrates, which reconciles the observed sorption trends for both PCB 36 and PCB 19 (as listed in Table 1).³³ Such idealized clay systems were utilized in the following MD simulations.

To further investigate the underlying molecular-scale mechanism leading to the observations described above, a series of MD simulations of PCBs intercalated in hydrated montmorillonite clays was performed. The influence of the key variables including the type of interlayer cations (i.e., Na⁺, K⁺, and Cs⁺), water structure, *d*-spacing, and PCB structures on the sorption were investigated by following dynamic and structural analyses.

Trajectories of interlayer Na⁺, K⁺, and Cs⁺ in SWy-2 hydrates (Figure 3) show that interlayer Cs⁺ oscillated in comparatively small vicinities above surface tetrahedra or hexagonal cavity sites, experiencing strong electrostatic interactions with surface oxygen atoms in one-layer hydrate (Figure 3a). The mean residence time of Cs⁺ before migrating to different sites was on the order of 1 ns, with longer residence time and shorter subsequent migration distance for cations near surface Al-substitution sites. At each time scale, cation-free surface siloxane domains were observed whose size would be sufficient to accommodate planar PCBs. Furthermore, the movement of Cs⁺ was relatively synchronized (presumably due to cation–cation repulsions and only two dimensions of translational freedom in one-layer hydrate), so the large cation-free surface siloxane domains observed in the 1 ns Cs⁺ trajectory are shifting but relatively constant feature of the entire simulation. This yields a molecular-scale structural hypothesis for the strong sorption affinities of Cs-clay minerals for NOCs including PCBs.

In contrast, interlayer Na⁺ within three-layer hydrate formed weaker, outer-sphere complexes with basal surface oxygens, resulting in Na⁺ moved much more freely over the siloxane surfaces, with their trajectories spreading almost completely over the basal plane (Figure 3c), and hence hindering direct contacts between sorbed NOCs and basal surfaces.

^{18–26} For the intermediate case, i.e., the two-layer hydrates, K^+ close to noncharged sites moved freely like Na^+ , whereas the mobility of K^+ near surface Al-substitution sites was much constricted; the formed inner-sphere K^+ complexes rarely jumped from one site to another during the course of simulation (Figure 3b).

Noncharged montmorillonite (PYRO) model was constructed to mimic the interlayer regions of Cs-, K-, and Na-SWy-2 with one, two, and three layers of water, except that the structural negative charges hence the interlayer cations were not present. The purpose of PYRO model is to examine the effects of interlayer hydration status on PCB sorption by comparing the dynamic properties of PCB sorption in the interlayers of the two systems, viz., SWy-2 and PYRO. As discussed above, our hypothesis is that PCBs sorb into cationfree surface siloxane domains in SWy-2, and the PYRO model is the limiting case in which the entire interlayer region is a cation-free surface siloxane domain.

The density distributions of interlayer water (i.e., oxygen and hydrogen atoms of water) between the opposing siloxane surfaces (the surface oxygen layers) behaved similarly in both SWy-2 and PYRO systems (SI Figure S5): in the one-layer hydrates, water molecules reside at the midplane; in the two-layer hydrates water molecules were distributed equally in two planes (equidistant from the opposing siloxane surfaces), and in the three-layer hydrates three planes of water molecules were clustered parallel to the midplane with decreased relative densities. However, in SWy-2 systems the H atoms in water tended to correlate more strongly with the oxygens on clay basal surfaces, as the near-surface peaks became asymmetric with elevated shoulders toward clay surfaces in all three hydrates. Stronger interactions between interlayer water and surface oxygens for SWy-2 were also observed in hydrogen bond analysis (SI Table S3). The average number of hydrogen bonds between water and surface oxygen was 0.06 per surface oxygen for all three PYRO hydrates, but 0.19 to 0.25 for SWy-2 one- to three-layer hydrates. This is to be expected since the negative charges of SWy-2 surfaces function as better hydrogenbond acceptors than PYRO. The average number of intermolecular hydrogen bonds per interlayer water was 3.2 for all three PYRO hydrates, less than the value (3.8) for water in bulk solution. SWy-2 hydrates manifested lower values (1.9–2.6) because the hydration of interlayer cations apparently interrupts the interactions among water molecules.⁴⁹ The weaker hydrogen bonding between interlayer water and PYRO basal surfaces, suggest that the cation-free siloxane surfaces could be more hydrophobic than SWy-2 surfaces. The poorly hydrated basal surfaces could plausibly provide favorable domains for NOC adsorption.

MD simulations were also performed for the three different hydrates of SWy-2 and PYRO each containing a PCB molecule (SI Text S2 and Figure S1). The radial distribution functions (RDFs) were calculated to examine the interactions of PCB with water and clay surfaces (SI Figure S6). Unlike the strong direct complexation found between interlayer cations and negatively charged groups on NACs, the correlations between interlayer cations and PCB chlorines were not significant, as the first weak correlation peaks were not observed until 4.8–5.4 Å.¹⁹ Even for Cs-SWy-2 one-layer hydrate, only a weak peak was observed at 3.6 Å for the Cs^+-Cl pairs. Since chlorine atoms on the PCBs were assigned partial charges of $-0.102 e$,^{21,36} only weak interactions between chlorine groups and interlayer cations could be expected. The interlayer cations were mostly complexed by water

and surface oxygens, while the PCB molecules were driven to relatively hydrophobic regions, where presumably only minimal numbers of weaker hydrogen bonds were forced to break for loading PCB molecules, and the overall sorption energy gain was mainly originated from the decrease in water surface area in desolvation of PCB from the solution phase.

The distributions of dihedral angles between PCB aromatic rings and clay basal surfaces as a function of simulation time were plotted in Figure 4. Interestingly, the PCB aromatic ring with two chlorines (ring 1) remained almost parallel to the clay basal plane for both PCB 36 and PCB 19 in all clay hydrates. For PCB 36, the aromatic ring containing one chlorine (ring 2) was also oriented parallel to the basal plane in all hydrates with a dihedral angle between the two aromatic rings less than 10° , while ring 2 of PCB 19 retained a dihedral angle deviated little from 90° to ring 1 in two- and three-layer hydrates, and the angle was forced to about 30° in the interlayer of one-layer hydrates. A lower frequency of ring 1 lying parallel to the basal plane was observed for SWy-2 than the corresponding PYRO; the PCB conformations were apparently jostled by the hydrated cations (Figure 3) in SWy-2. The preferred configurations of PCBs in the clay interlayer were also observed from the overlay of 10 ns trajectories of PCB molecules in the interlayer of PYRO and SWy-2 hydrates as shown in SI Figures S7 and S8, where PCB 36 adopted a coplanar conformation with both rings laying almost exclusively on one clay basal surface, while PCB 19 rotated more freely in the interlayer region to maximize its torsion angle and to minimize the energy penalty. These observations support our hypothesis that interlayer regions near uncharged clay basal surfaces could be relatively hydrophobic, since a low density of hydrogen bonds between siloxane surface and interlayer water was observed for all three montmorillonite hydrates in the MD simulations (SI Table S3). Such surface regions are believed to be the energetically favorable domains for PCB sorption, and PCBs could achieve the highest sorption affinity when the molecule could be orientated parallel to and in direct contact with the basal surfaces. That is, PCB molecules are highly hydrophobic; directly laying on clay basal surfaces favors the whole sorption by obscuring both or one side PCB molecule from water phase.²⁰

The above dynamic analyses together suggest that the hydrophobicity of the interlayer region is controlled by the hydration status of the exchangeable cation and the local layer charges, which are the determinants of PCB sorption affinity on montmorillonite. The relatively strong sorption for PCB 36 on SWy-2 with all cations (Figure 1) could be due to coplanar structure, where we hypothesize the energetics would be optimal since PCB 36 lies directly on clay basal plane. The highest sorption affinity of PCB 36 for Cs-montmorillonite was observed because in the one-layer hydrated Cs-SWy-2 (Figure 2) *both* sides of the planary PCB 36 molecule could directly contact the opposing clay basal planes; at this scenario the PCB 36 molecule could be almost fully dehydrated. But this cannot occur in the two- or three-layer hydrates, thereby sorption affinity for PCB 36 was significantly reduced in K- and Na-smectites. The weak sorption of PCB 19 by montmorillonites may be due to the thermodynamic penalty of its steric restrictions. For Cs-montmorillonite, PCB 19 could not enter the interlayer gallery, so presumably most PCB 19 could be adsorbed on external surfaces which only account for 10% to 20% of the total surface area of smectites. PCB 19 might be able to enter the interlayer galleries of K and Na-montmorillonites, but the two

aromatic rings could not simultaneously contact the basal planes, which led to the significant decrease of sorption affinity.

As another test of these hypotheses, the sorption free energies were directly estimated with ABF method,⁴⁰ using a PYRO model in contact with a micropore of “bulk water” (SI Figure S1). Conceptually, this free energy corresponds to the transfer of PCB molecules between bulk water and interlayer cation-free siloxane surface domain (see above discussion regarding Figure 3). The free energies along the reaction coordinate defined as PCB molecules moving from clay interlayer into “bulk water” show that the calculated free energy was always lower with the PCB in clay interlayer (Figure 5). The free energies for sorption of PCB 36 were ~3 kcal/mol more favorable than those for PCB 19 in corresponding clay hydrates, which are in agreement with the observed sorption trends (Figure 1). The consistency between the Gibbs free energies calculated from experimental isotherms and ABF-MD (G_W vs G_{ABF} in Table 1) was remarkably good, even though the ABF-calculated values were slightly more negative. As discussed above, the removal of layer charges to construct the PYRO model for ABF simulations could cause the interlayer to be more hydrophobic due to weaker hydrogen bonding of water with the basal surfaces, so the interlayer became more favorable for PCB sorption, therefore, the ABF-estimated sorption free energies were somewhat overestimated.

The ABF-calculated free energy for PCB 36 sorption into 12.5 Å PYRO was -14.4 kcal/mol, which was much more negative than the experimentally derived value. Close agreement of the other free energy estimates begs the question of the possible origins of this discrepancy. Note that the free energy estimated for PCB 36 transfer from water to 12.5 Å PYRO is more favorable than the transfer from water to 1-octanol (SI Figure S3). Again, though, the calculated free energy for PCB 36 transfer from water to octanol is -6.8 kcal/mol, in decent agreement with the value of -7.9 kcal/mol derived from the experimental log K_{ow} (SI Table S2).

We pointed out earlier that the PYRO system is rare case in which the entire interlayer region is free of exchangeable cation, which could serve as the hydrophobic end of the spectrum favoring PCB sorption. For Cs-SWy-2, the hypothesized cationfree surface siloxane domains (Figure 3) should be *much* smaller, so we would expect the corresponding PYRO model to overestimate PCB sorption affinity. Thus, the excellent agreement of some sorption energies in Table 1 may be fortuitous. Another potential source of discrepancy is that, in real Cs-SWy-2, some of the interlayers were found to completely collapse to ~10 Å and hence be unavailable for PCB sorption.²¹ This could lower the sorption per unit mass of clay and thus the perceived free energy of sorption.

The ABF calculation for PCB 19 into 12.5 Å PYRO failed to complete, since the formation of coplanar PCB 19 in the one-layer hydrate was highly energetically unfavorable (42.3 kcal/mol, SI Table S2). As a result, the nonplanar thickness of PCB 19 (~8 Å) was not able to diffuse into the ~3 Å interlayer of the 12.5 Å hydrates; the PCB 19 rings poked into the hexagonal cavities of the clay and PCB 19 diffusion through the 12.5 Å PYRO interlayer could not even be forced. Therefore, it is suggested that PCB 19 would only be sorbed on

external surface of the Cs-SWy-2, and the lowest sorption in the conducted series of experiments was observed (Figure 1d,e).

By a combination of experimental and MD studies of coplanar and nonplanar PCBs, the preferential sorption mechanisms of coplanar over nonplanar PCBs by montmorillonite were investigated, and the results support the hypothesis²⁵ that the relative hydrophobicity of less hydrated interlayers of clay minerals is the domain for PCB sorption. The steric hindrance of nonplanar PCB molecules restricted their access to the interlayer surfaces of montmorillonite, thus their sorption affinities could be significantly diminished. The sorption free energies of PCBs on clay minerals with different d -spacing were directly calculated by the extended interlayer-micropore two-phase model and ABF method for the first time with sufficient accuracy. This study could extend to other key geosorbents that determine the transport and fate of PCBs in the environment. For example, similar preferential sorption of coplanar PCBs has also been found for black carbon, char materials in sediments, etc., in which the surfaces might be dominated by slit-like nanopores, similar to those in montmorillonite.⁵⁰ A molecular mechanism involving hydrophobic driving force and steric selectivity would be expected in these geosorbents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Sorption isotherms of PCB 36 by montmorillonite (SWy-2) saturated with Na⁺, K⁺, or Cs⁺ at methanol volume fractions (a) 30%, (b) 40%, (c) 50%, and sorption isotherms of PCB 19 by montmorillonite (SWy-2) saturated with Na⁺, K⁺, or Cs⁺ at methanol volume fractions of (d) 15%, (e) 20%, and (f) 30%.

Figure 2.

Transmission XRD patterns of Na⁺, K⁺ and Cs⁺-saturated montmorillonite suspensions in water-methanol mixtures with methanol content from 0 to 100%. The 001 peaks were labeled with calculated *d*-spacings in the unit of Å.

Figure 3.

Trajectories of interlayer cations, plotted from viewpoints perpendicular to the SWy-2 clay basal plane. Surface siloxane tetrahedra are yellow and surface Al-substitution sites are purple. Cation positions were recorded each 5 ps to build trajectories of 1, 5, and 10 ns duration, with each cation drawn in a different color.

Figure 4.

Distributions of dihedral angles between PCB aromatic rings and the clay basal surface of SWy-2 and PYRO as a function of simulation time. The aromatic ring containing two chlorines was denoted as ring1 and the other as ring2. The dihedral angles between the pairs of planes (ring1–basal surface, ring2–basal surface, and ring1–ring2) were plotted in red, blue, and cyan, respectively.

Figure 5. Schematic results of the extended interlayer-micropore two-phase system (SI Figure S1) used for the direct calculation of sorption free energies by ABF method. Snapshots along the reaction coordinate are shown (top), with the PCB molecule colored by time during the transfer process. The corresponding free energy profiles are plotted (bottom) for PCB 36 and PCB 19 transfer between “bulk water” and 12.5, 15.5, and 18.5 Å clay hydrates. Total ~125 ns trajectory was collected for each profile. The ABF simulation of PCB 19 sorption into the 12.5 Å clay hydrate failed due to steric hindrance.

Sorption Coefficients in Aqueous Phase K_w and Corresponding Sorption Free Energies G_w were Derived from Eqs 1 and 3 in Compared with ABF-Calculated G_{ABF}

Table 1

PCB	montmorillonite	$\alpha\sigma^b$	$\log K_w^b$	G_w kcal/mol ^c	simulated d -spacing Å	calculated G_{ABF} kcal/mol ^d
PCB36	Na-SWy-2	-7.50	3.68 ± 0.26	-5.01 ± 0.35	18.5	-5.40
	K-SWy-2	-6.65	3.73 ± 0.25	-5.09 ± 0.34	15.5	-5.91
	Cs-SWy-2	-7.25	4.53 ± 0.11	-6.18 ± 0.14	12.5	-14.43
PCB19	estimated SOM ^a		4.47	-6.10		
	Na-SWy-2	-0.97	1.21 ± 0.04	-1.65 ± 0.06	18.5	-1.84
	K-SWy-2	-1.34	1.46 ± 0.15	-2.00 ± 0.20	15.5	-2.82
	Cs-SWy-2	0.40	0.87 ± 0.16	-1.19 ± 0.21	12.5	NA
	estimated SOM ^a		3.78	-5.15		

^a K_{SOM} was estimated sorption coefficients on SOM, calculated by linear equation $\log K_{SOM} = 0.904 \log K_{OW} - 0.779$.⁴⁶

^b $\alpha\sigma$ and K_w were calculated by fitting eq 1 from $\log K_m$ in SI Table S1 using linear least-squares method, and the mean values were shown with standard errors.

^c G_w Free energies of sorption in aqueous phase were calculated by eq 3, and the mean values were shown with standard errors.

^d G_{ABF} was calculated by ABF MD method from the interlayer-micropore two-phase model to estimate the adsorption free energy. The values from $-15 \sim -7.5$ Å were averaged for evaluating the energy state of PCB intercalated in the interlayer.