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Interaction of Hydrophobic Organic Compounds with Mineral-Bound Humic Substances

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The sorption of hydrophobic organic compounds (HOC) on mineral-associated peat humic acid (PHA) was evaluated under different pH and electrolyte regimes. Relative size distribution measurements indicated that PHA was "coiled" in solution at high ionic strength (I) and elongated at low I . The sorption of PHA to hematite and kaolinite varied with I and electrolyte cation, suggesting that the configuration of the humic acid in solution influenced its structure on the mineral surface. The sorption maxima for PHA on kaolinite indicated that PHA occupies twice the mineral surface area at low I (0.005) as that observed at high I (0.1). HOC sorption to mineral-bound PHA in Na^+ electrolyte was greater at lower I , indicating that humate structure was a plausible determinant of HOC sorption. Freundlich isotherms of dibenzothiophene on the PHA-coated kaolinite did not display unit slope, regardless of pH, I , or cation. Carbazole and anthracene displayed competitive behavior for sorption onto PHA-coated kaolinite. Collectively, the experimental observations indicate that hydrophobic adsorption rather than phase partitioning was the dominant mode of HOC binding.

Introduction

The aqueous concentrations and transport of hydrophobic organic compounds (HOC) in subsurface systems are influenced by sorption to organic matter (1-5) and binding to dissolved humic substances (6-13). Natural dissolved/colloidal organic material binds to a variety of aluminum and iron oxides and layer silicate surfaces that are common in aquifers (14-22). Thus, dissolved humic substances may form organic coatings on aquifer sediments that may in turn facilitate the sorption of HOC.

The sorption of HOC to mineral-bound organic matter is influenced by the chemical properties of the humic material (23-29). The structural orientation of sorbed humic substances may be controlled by the distribution of hydroxyl groups on the mineral surface, and this structure can also influence HOC sorption (2, 3). Furthermore, the surface structure of mineral-bound humic substances may be controlled by their solution conformation, as has been observed for polyelectrolytes (30-33).

The structure of dissolved humic substances is affected by pH, ionic strength (I), and electrolyte cation valence (17, 18, 34-36). The configuration and sorption behavior of humic substances are analogous to those of polyelectrolytes, which have received more research attention. At high I and low pH, the charge repulsion between adjacent carboxyl or hydroxyl groups on the humic substance is neutralized by solvating cations, resulting in a coiled configuration (18, 34, 35). The sorption of the "coiled" humic substance may be similar to that of an uncharged polymer that displays a loop and tail formation (37) with

few attachment points to the mineral surface (18, 32, 33). At low I and high pH, the humic substance may adopt a more open configuration in solution as a result of charge repulsion between ionized functional groups (37-39). This extended configuration may create more points of attachment to the mineral surface (39).

Electrolyte cation valence also affects the configuration of humic acid in solution. Calcium increases the sorption of humic substances to goethite, presumably by the interaction of Ca^{2+} with carboxyl groups on the humic acid (18, 37, 40, 41) and decreases the negative electrophoretic mobility of the humic oxide complex. Calcium increases sorption and the initial slope of the isotherm of polyacrylic acids (average MW 4000, 2000, and 700) to TiO_2 and decreases the dependence of sorption on molecular weight (37). Calcium is believed to form a binuclear complex with polyacrylic acid (37, 42), internally bridging carboxyl groups that affect the dimension and rigidity of the polyacrylic acid structure (43).

Although research has focused on the effects of I , pH, and cation valence on the configuration of humic substances and polyelectrolytes in aqueous solutions, it is not known whether these same variables influence the configuration and structure of mineral-bound humic substances. Given that natural waters show a wide range in chemical composition, it is important to establish the influence of aqueous chemical variables on the sorptivity of organic matter coatings. In this study, we evaluated the effects of I , pH, and cation valence on HOC sorption to humic-coated mineral solids to determine whether HOC sorption trends indicate structural differences in the sorbed humic coating. In addition, the sorption of HOC to the mineral-bound organic matter was evaluated for its consistency with phase partitioning or hydrophobic adsorption.

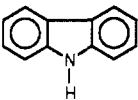
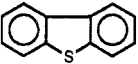
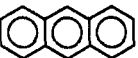
Experimental Procedures

Materials. A well-crystallized kaolinite (KGA-1, Clay Minerals Society Source Clay) was prepared according to the methods of Johnston et al. (44) and Zachara et al. (45). This involved the separation of the 0.2-2.0- μm fraction of kaolinite and its extraction to remove oxide and hydroxide coatings. Both Na^+ - and Ca^{2+} -saturated kaolinites were prepared. Electrolytes used in the experiments encompassed high and low I (0.1 or 0.005), pH 4.5 or 6.5, and mono- or divalent cations [NaClO_4 or $\text{Ca}(\text{ClO}_4)_2$]. Immediately before use, the kaolinite was treated with H_2O_2 to remove oxidizable organic material (46). Hematite was purchased from J. T. Baker Chemical Co. Trace organic contaminants were removed by heating the hematite at 500 °C overnight prior to the sorption experiments. The BET surface areas determined by triple-point $\text{N}_2(\text{g})$ adsorption were 12.5 and 5.4 m^2/g for kaolinite and hematite, respectively (Table 1).

Peat humic acid (PHA), a well-characterized terrestrial humic substance from the International Humic Substances

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Table 1. Properties of Mineral Sorbents, Peat Humic Acid, and Hydrophobic Organic Compounds

Properties of Mineral Sorbents							
		kaolinite	hematite				
surface area (m ² /g) ^a		12.5	5.41				
sites (mol of OH ⁻ /g) ^b		1.56 × 10 ⁻⁵	8.98 × 10 ⁻⁵				
expt surface area (m ² /L) ^c		1600	400				
pH _{zpc}		7.3 ^d	8.5 ^e				
Properties of Peat Humic Acid ^f							
atomic (110-165)	aliphatic (0-90)	carboxyl (165-190)	C	H	O	N	Ash
47	24	20	56.82	4.06	34.91	3.74	1.92
Properties of Hydrophobic Compounds							
		MW	solubility (mg/L)	log K _{ow}			
carbazole		167.2	1.88	3.29			
dibenzothiophene		184.3	1.47	4.38			
anthracene		178.2	0.075	4.45			

^a Surface area was measured by triple-point N₂(g) adsorption and calculated using BET equation. ^b Kaolinite (45, 47); hematite (48, 49). ^c Sorbent concentration used in the HOC experiments. ^d Apparent pH_{zpc} of the kaolinite edge (50, 51). ^e Refs 48 and 49. ^f The distribution in percent of carbon functional groups was determined by liquid-state ¹³C NMR (ppm range shown in parentheses) (52). Elemental analyses (ppm) were performed by Huffman Laboratories, and oxygen was measured directly (R. L. Malcolm, personal communication, 1990, U.S. Geological Survey, Golden, CO).

Society (IHSS), was used as a representative humic substance that would be associated with soils and sediments (Table 1). Buried peat deposits are often found in deep formations and may provide a source of humic substances to groundwater (53, 54). However, more importantly, PHA is representative of the type of humic substances likely to be associated with the solid phase rather than the aqueous phase in groundwater systems.

Uniformly ¹⁴C-ring-labeled carbazole (Pathfinders Laboratory Inc.), dibenzothiophene, and anthracene (Sigma Chemical Co.) were dissolved in HPLC-grade acetone and stored in light-excluding containers at 4 °C. The integrity of the labeled compounds was verified by HPLC. The radiochemical purity of carbazole was determined to be greater than 99% with a specific activity of 9.2 Ci/mol. Dibenzothiophene had a purity greater than 98% with a specific activity of 1.1 Ci/mol, and anthracene had a purity greater than 99% with a specific activity of 20 Ci/mol. A solution of unlabeled anthracene (Aldrich Gold Label) was also prepared using HPLC-grade acetone. The physical properties of these compounds are shown in Table 1.

High-Performance Size Exclusion Chromatography. High-performance size exclusion chromatography (HPSEC) was used to determine the relative molecular sizes of PHA in solutions with different pH, *I*, and cation valence. The HPSEC system consisted of a Waters 6000A pump equipped with a Rheodyne 7125 manual injection valve, a 1-mL injection loop, a Bio-Sil SEC 250 preparative column (21.5 × 600 mm) (Bio-Rad Labs, Richmond, CA),

a SpectroMonitor 3100 UV-vis detector (absorbance = 254 nm) (Rainin Instruments, Woburn, MA), an HP 1046A programmable fluorescence detector (E_x = 230 nm, E_m = 401 nm), and an HP 3396 Series II integrator (Hewlett Packard, Corvallis, OR). The samples were run at ambient temperature at a flow rate of 6 mL/min in either sodium acetate or calcium acetate eluent. Aliquots of a concentrated solution of PHA, dissolved in distilled water, were adjusted in either sodium or calcium acetate at *I* ranging from 0.1 to 0.001 and at pH 4.5 or 6.5 prior to injection. Therefore, the pH and *I* of PHA sample injection volume matched those of the eluent.

Sorption Experiments. The kaolinite and hematite were coated with PHA for the HOC sorption experiments by equilibrating the sorbents for 20 h with varying amounts of dissolved PHA (0–90 mg/L) in NaClO₄ (0.1 or 0.005 mol/L at pH 4.5) or in Ca(ClO₄)₂ (0.035 or 0.0017 mol/L at pH 4.5 or 6.5). A time-course study showed that the sorption equilibrium of humic acid with hematite occurs within the first hour and within 8–10 h on kaolinite. The pH was maintained with a titrator/pH stat during the equilibration. The suspension was then centrifuged (3000g for 20 min), and the humic acid in the supernatant was analyzed by measurement of the dissolved organic carbon (DOC). The coated sorbent was washed once with DOC-free electrolyte and centrifuged, after which the DOC of the supernatant was analyzed. The suspension was then concentrated ~4 times by decanting the supernatant and resuspending the sorbent in a smaller volume of DOC-free electrolyte. Aliquots of the sorbent suspension were transferred to tared, 8.5-mL, glass centrifuge tubes to measure HOC sorption (described below). The mass fraction organic carbon (*f*_{oc}) contributed by the sorbed humic substances ranged from ~0.01 to 0.5% (calculated by difference accounting for the mass of DOC at each step of the preparation).

The radiolabeled carbazole, dibenzothiophene, or anthracene solutions were added to the concentrated sorbent suspensions to reach a concentration of 25% of the compound's water solubility. Large sorbent concentrations were required for statistically valid sorption measurements. The surface area concentrations of kaolinite and hematite were 1600 and 400 m²/L (128 and 74 g/L), respectively. Headspace in the 8.5-cm³ centrifuge tube was 0.5 cm³ to minimize HOC volatilization, and the tube caps were lined with aluminum foil. Light was excluded from the anthracene experiments to prevent photodegradation. The suspensions were equilibrated with slow end-over-end mixing for 20 h at 25 °C and centrifuged at 3000g; then 1-mL aliquots of the supernatant were transferred to tared vials containing 12 mL of scintillation cocktail. Each experiment was repeated with a mineral blank containing the sorbent with no humic coating and a "no-HOC" blank containing only the coated mineral to determine the extent of desorption of the bound humic substances. The pH of the supernatant was determined, and the no-HOC blank was analyzed for DOC. Desorption of the humic coating was insignificant (i.e., DOC was not measurable) over the course of these experiments.

The sorbed fraction of HOC was calculated by difference based on the ¹⁴C counts remaining in solution. In a previous study (2), the experimental procedures were tested by desorbing the ¹⁴C-labeled HOC and counting the bound fraction. An average of 92% of the sorbed HOC was recovered, which showed good agreement with the

values for fractional HOC sorption calculated by difference.

Dibenzothiophene Sorption Isotherms at Constant f_{oc} . Isotherms for dibenzothiophene were determined for kaolinite (800 m²/L) with a PHA- f_{oc} of 0.05% at pH 6.5 and 0.08% at pH 4.5. Four-point isotherms were measured (in triplicate) over the concentration range of 0.22–0.80 mg/L at pH 4.5 and 6.5 in low I (0.005) Ca(ClO₄)₂ or NaClO₄ electrolytes. Equilibration and sampling were performed as described above.

Competition Experiments. Kaolinite was transferred to tared 25-mL Corex tubes to yield 800 m²/L, cleaned (H₂O₂), and rinsed three times in 0.0017 mol/L Ca(ClO₄)₂ at pH 6.0. The kaolinite was then coated with PHA (f_{oc} = 0.05%) as described above and rinsed two times in DOC-free 0.0017 mol/L Ca(ClO₄)₂ electrolyte. Six stock solutions were prepared containing 220 nmol/L ¹⁴C-labeled carbazole and variable amounts of unlabeled anthracene, ranging from 0 to 280 nmol/L. Individual HOC stock solutions were added to duplicate PHA-coated kaolinite samples and an organic-free kaolinite blank. A no-HOC blank containing the coated mineral only was used to determine the extent of desorption of the bound PHA.

The suspensions were equilibrated and sampled as described previously. The supernatants were analyzed for pH, DOC, carbazole (by scintillation counting and high-performance liquid chromatography, HPLC), and anthracene (by HPLC). A C-18 (ODS) column was used with a Waters Associates WISP 710B HPLC. The mobile phase was 85:15 (v:v) acetonitrile:water. An HP 1046A fluorescence detector was used to detect the carbazole and anthracene with an excitation wavelength of 237 nm and an emission wavelength of 401 nm. The retention times for carbazole and anthracene were 4.8 and 7.7 min, respectively. The fractions of HOC sorbed were determined by difference, as described above. In the case where the carbazole concentration was determined by the two analytical methods (i.e., ¹⁴C counts and HPLC), both methods gave similar values.

Results and Discussion

In this paper, hydrophobic sorption is used as a general term which encompasses two primary mechanisms: phase partitioning and hydrophobic adsorption. Phase partitioning is the transfer of a solute from the aqueous phase to an organic phase. The transferred solute is "solvated" by the organic material, which surrounds it in a three-dimensional orientation. Hydrophobic adsorption (also referred to as "specific hydrophobic adsorption" in the literature) is a surface reaction that occurs in competition with water on a region of the surface (either organic or inorganic) that exhibits low hydration energy. The free energy of the sorbed complex is controlled by one- or two-dimensional contact with the surface. Both of these mechanisms are believed to be environmentally significant for different types of materials. We note that ambiguity exists with respect to this terminology, and controversy does exist regarding the mechanisms of "hydrophobic" sorption on different environmental substrates.

Configuration of Humic Substances in Solution. The effect of solution chemistry on the molecular size of humic substances has been determined by viscosity and surface pressure measurements (34, 55), sedimentation and diffusion measurements (36, 56), and size exclusion chromatography (13, 35, 57, 58). Although each method

has limitations, all of these studies have suggested that humic macromolecules behave like polyelectrolytes and that the configuration of the macromolecule in solution will influence its structure when bound to a solid surface (30–33).

Solute retention in HPSEC depends on differential migration of molecules between the mobile phase and the pore space on the stationary phase (an entropy-driven process). Recent HPSEC studies of humic substances have used surface-modified porous silica as a column packing (13, 35, 57, 58) which minimizes enthalpy-driven or nonexclusion processes (charge repulsion and adsorption). Evidence that enthalpy-driven processes are minimal is based on whether the eluted peaks fall between V_o (void volume) and V_p (total permeation volume). The largest molecules are excluded from the pores and elute as nonretained molecules. The amount of mobile phase that is required for a nonretained molecule to elute is the V_o (defined using dextran, MW = 162 000). Smaller molecules have longer retention times. The volume of mobile phase that is required for the smallest molecules to elute is called the V_p (defined using acetone). Regardless of the electrolyte, the PHA peaks were never out of the working range of the column (before V_o or after V_p), indicating that peak shift under different chemical regimes was not significantly affected by nonexclusion phenomena (13, 59). Molecular weights were not calculated from the chromatograms because humic substances have a multimodal distribution that is dependent on I , pH, and cation valence.

The HPSEC results (Figure 1) were consistent with that reported for polyelectrolytes (30–33, 37, 42, 43). At a given pH, the relative size of PHA increases with decreasing I (denoted by the shift in PHA mass toward shorter retention times). Others have observed this phenomenon with humic substances using HPSEC (13, 35, 59) and have evoked the random coil model (34, 56). At low I or high pH, the electrostatic repulsion between adjacent functional groups (e.g., carboxyl, hydroxyl groups) is maximized, expanding the structure of PHA and increasing its apparent molecular size. Comparison of the chromatograms in the presence of the sodium electrolyte (Figure 1a,b; pH 6.5 and 4.5, respectively) illustrates a shift to smaller relative sizes (denoted by longer retention times) at low pH. The smallest, or perhaps most coiled, configuration occurred at pH 4.5 and I = 0.1 Na⁺.

In calcium electrolyte (Figure 1c,d), the peaks also shifted to smaller relative sizes at higher I . However, the elution peaks were more coalesced in the calcium electrolyte than in sodium. Bridging between ionized sites by Ca²⁺ may aggregate components within PHA so that they elute as combined peaks that would otherwise show up as distinct peaks in the sodium electrolyte. These aggregate peaks have slightly longer retention times than their sodium electrolyte counterparts, indicating smaller apparent molecular sizes (or greater coiling).

PHA Sorption to Mineral Surfaces. The different combinations of pH, cation, and I used in these experiments along with their possible effects on the structure of PHA are shown in Figure 2. This conceptual diagram was compiled from HPSEC information on the relative size of PHA in solution; the sorbed humic structures are speculative, as direct observations do not exist. The structure of the sorbed humic substance is controlled (1) by the configuration of the humic substance in solution (32, 33, 60), (2) by the number of attachment points and degree

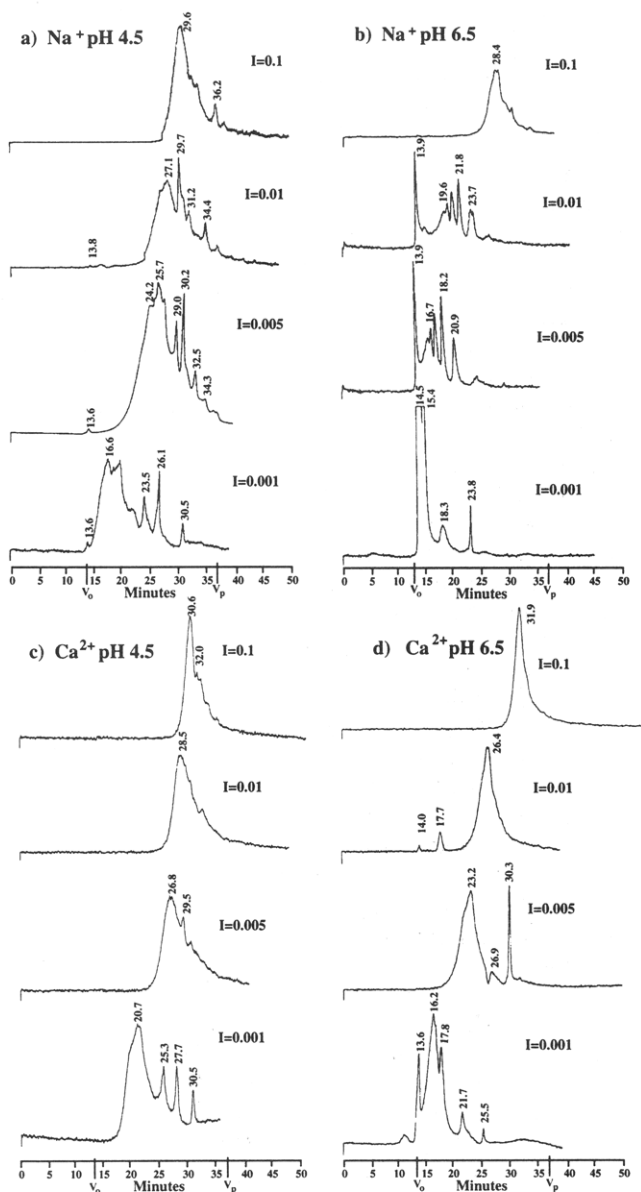


Figure 1. High-performance size exclusion chromatography of PHA (50- μ g sample size) under different pH, I , and solvating cation conditions. (a) Na^+ , pH 4.5; (b) Na^+ , pH 6.5; (c) Ca^{2+} , pH 4.5; (d) Ca^{2+} , pH 6.5. V_0 is the void volume, and V_p is the total permeation volume.

of ionization of carboxylate and hydroxyl sites on the humic substance, and (3) by the density, distribution, and reactivity (i.e., pK_a) of hydroxyl sites and other microtopographic features of the surface. Evidence suggests that the aqueous configuration of the humic substances may be a primary determinant of its surface structure (30–33). The PHA was adsorbed to kaolinite and hematite under the pH and electrolyte conditions shown in Figure 2, with one exception. To enhance the sorption of PHA to kaolinite in Na^+ electrolyte for the experiments conducted at pH 6.5, it was necessary first to adsorb the PHA to kaolinite at pH 4.5 and then raise the pH to 6.5.

At low pH (4.5), ligand exchange will be the primary binding mechanism of humic substances to hydroxylated mineral surfaces (i.e., iron and aluminum oxides; layer silicate edges) (14, 16–18, 61). Evidence for organic carboxylate ligand exchange is indirect, often following the lines of evidence established for inorganic oxyanion ligand exchange (47). Sorption of humic substances by ligand exchange is believed to occur in three steps: (1)

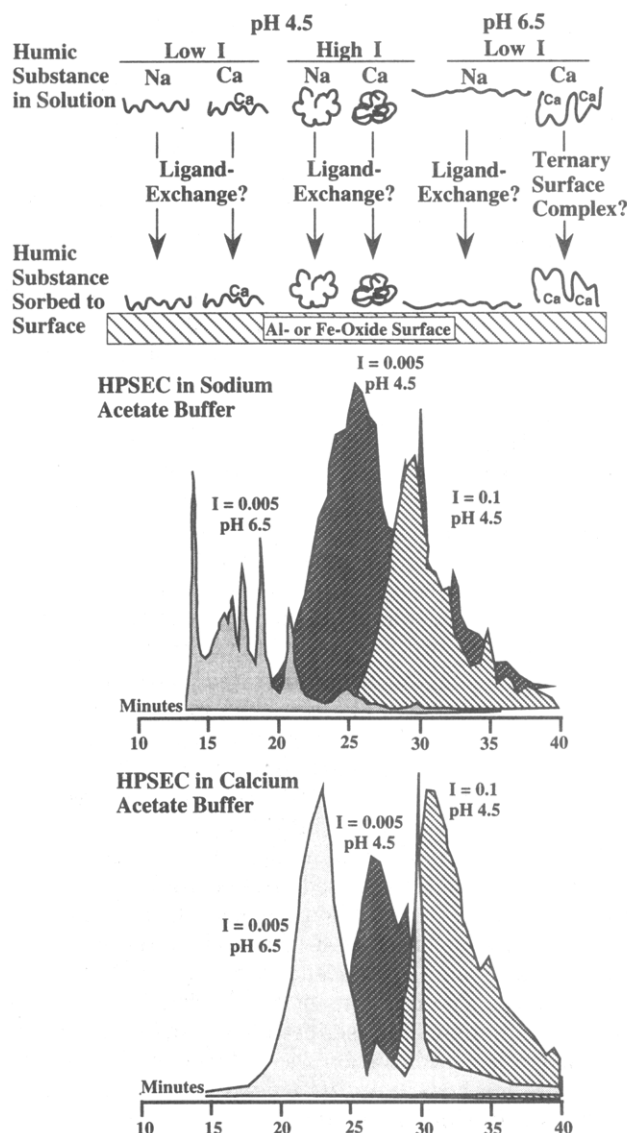


Figure 2. Combinations of pH, I , and cations used in these experiments and their effects on the conformation of PHA in solution based on size exclusion chromatography and the hypothetical conformation of PHA adsorbed to an oxide surface.

protonation of the surface hydroxyl ($\text{SOH} + \text{H}^+ = \text{SOH}_2^+$), rendering it more exchangeable (47, 62); (2) outer-sphere complexation of the carboxylate group with the protonated hydroxyl group; and (3) ligand exchange (OH_2 for Hu-COO^-) to yield an inner-sphere complex. The release of hydroxyl ion during the adsorption of humic substances to hematite in the sodium electrolyte (pH = 4.5) has been taken as direct evidence for the ligand exchange mechanism (3, 61) and has been previously measured in our laboratory (3).

At high pH (6.5) and in the presence of di- and trivalent cations, a ternary surface complex may form between the hydroxyl site, the electrolyte cation, and ionized groups in the humic substance (47, 60, 63). Among these ternary surface complexes, a distinction can be made between solvated cations (water-bridging) and unsolvated cations (cation-bridging) (47, 64, 65). Water-bridging implies that the cation remains solvated, as would occur with Ca^{2+} and other hard Lewis acids (47, 60). In the presence of monovalent cations, the solvating water molecule may be displaced yielding an inner-sphere complex. In this study, kaolinite was the only sorbent used with calcium electrolyte

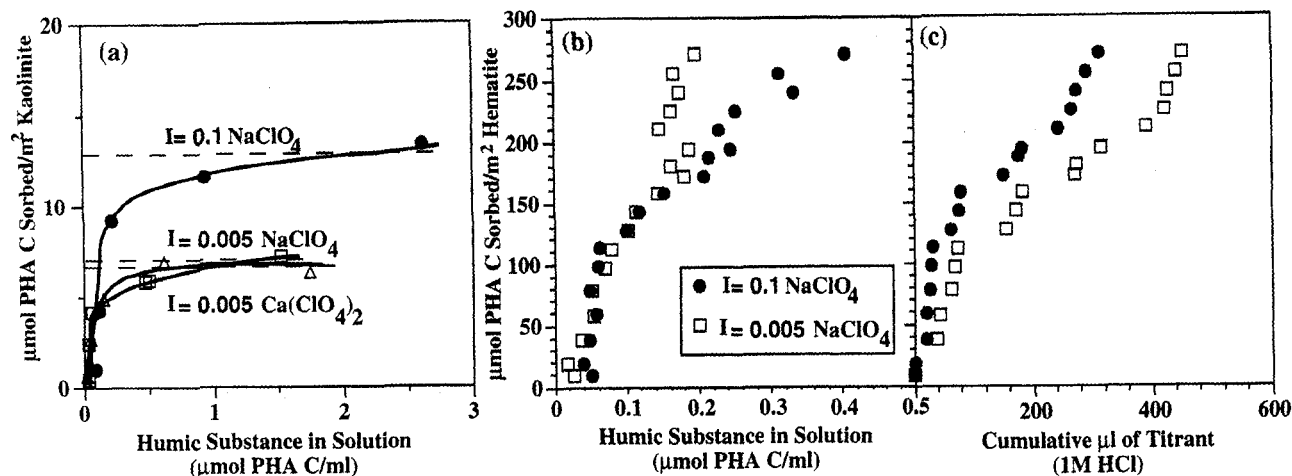


Figure 3. (a) Sorption isotherms of PHA on kaolinite in NaClO_4 electrolyte at $I = 0.1$ (●) and 0.005 (□) at pH 4.5 and in $\text{Ca}(\text{ClO}_4)_2$ electrolyte at $I = 0.005$ (Δ), pH 6.5. Dashed lines define approximate sorption maxima. (b) Sorption isotherms of PHA on hematite at pH 4.5 in NaClO_4 electrolyte at $I = 0.1$ (●) and 0.005 (□). (c) Cumulative hydroxyl release from sorption isotherms of PHA on hematite (shown in b) as measured by titrant addition to maintain constant pH at $I = 0.1$ (●) and 0.005 (□).

at pH 6.5. A ternary surface complex is plausible for this system at pH 6.5 (Figure 2) because a measurable cation-exchange capacity (CEC) exists for kaolinite (0.0973 mol/g at pH 6.5 for KGa-1).

The adsorption of PHA to kaolinite followed a Langmuir-type isotherm (Figure 3a) similar to those reported by others (2, 16, 61). The plateau or adsorption maximum of the Langmuir isotherm can be used to estimate the monolayer coverage of the solid by the polymer (2, 14). However, monolayer formation does not necessarily imply saturation of surface hydroxyls. Langmuir isotherms of PHA on kaolinite in Na^+ electrolyte varied with I (Figure 3a). At $I = 0.005$, the sorption maximum of PHA occurred at approximately $6.5 \mu\text{mol of C/m}^2$ as opposed to almost $13 \mu\text{mol of C/m}^2$ at $I = 0.1$. On a mole-carbon basis, this implied that the PHA occupied approximately twice ($2.31 \times 10^{-19} \text{ m}^2$) the surface area at low I as compared to high I . The adsorptive maxima were consistent with the relative sizes of PHA in solution (Figure 2; 34, 35). At low I , the adsorption maximum in the Ca^{2+} electrolyte was similar to that in the Na^+ electrolyte (Figure 3a). The HPSEC chromatograms for PHA under these electrolyte conditions were also similar (Figure 1), suggesting that the PHA was constrained to the same size range.

The mass of PHA sorbed to hematite was ~ 1 order of magnitude higher than that sorbed to kaolinite (Figure 3b) reflecting differences in (1) the distribution, concentration, and electrostatic environment of hydroxyl sites on the two sorbents and (2) the intrinsic selectivity of coordinating metal ion centers for carboxylate groups. Ionic strength effects were not observed until a sorption density of approximately $150 \mu\text{mol of PHA C/m}^2$ of hematite was reached. At high concentrations, PHA sorption displayed non-Langmuirian behavior possibly resulting from multiple-layer adsorption or lateral interactions. At low I , hydroxyl release was greatest at low sorption densities (Figure 3c) suggesting that in the elongated PHA configuration there were more attachment points between the PHA carboxyls and the iron-hydroxyls. In contrast, at high I , hydroxyl release was less at low sorption densities, consistent with a coiled structure (less exposure of carboxyls on the PHA) and fewer attachment points.

Sorption of HOC to Humic-Coated Minerals in Na Electrolyte. Previous studies of HOC binding to humate-coated sorbents indicated that sorption was more con-

sistent with an adsorption process rather than a phase partitioning process (2). Given these observations and the results of the isotherm experiments in the previous section, we speculated that HOC sorption would be greatest at low I where a maximum amount of humic surface area (34–36), and therefore hydrophobic sites, on the PHA would be exposed.

Experimental data with the Na electrolyte seemed to confirm this hypothesis; HOC sorption was greater at $I = 0.005$ than at $I = 0.1$ (Figure 4). This trend is opposite to a salting-out effect. The effect of I was greater for PHA bound to kaolinite than for PHA bound to hematite. However, and consistent with previous work (2), the sorption of HOC was greater on PHA associated with hematite than on that associated with kaolinite. This effect of I contrasts with that expected for partitioning, where increasing I reduces the aqueous solubility of HOC and increases partitioning to organic phases (66, 67).

PHA should display its most linear, elongated structure at high pH and low I (Figure 1 and refs 34–36) as a result of charge repulsion between ionized functional groups. If the solution configuration is a determinant of surface structure and hydrophobic adsorption is the dominant process, then HOC sorption to the mineral-bound PHA should be maximized under these conditions. Kaolinite was used to test this hypothesis. Because PHA sorption was low at pH 6.5, PHA was bound to the kaolinite at pH 4.5 to achieve the requisite adsorption density. After coating, the pH was raised to 6.5 for the HOC sorption experiment. Similar to the results at pH 4.5, the sorption of dibenzothiophene was enhanced at low I at pH 6.5 (inset of Figure 4). However, there was no significant difference in the sorption of dibenzothiophene at pH 4.5 and pH 6.5. Apparently, the surface structure of the humic substance, as it affects dibenzothiophene sorption, was determined by the pH at which the PHA was bound.

Comparative Effects of Ca^{2+} Electrolyte. In the calcium electrolyte, the mineral-bound PHA may adopt a condensed structure that is promoted by intrasite cation-bridging resembling a hydrophobic phase (rather than a hydrophobic surface). If this is the case, then the likelihood of a phase-partitioning mechanism should be maximized in the presence of the calcium electrolyte. Conversely, it may be hypothesized that calcium facilitates the exposure of hydrophobic binding sites to the solution phase by

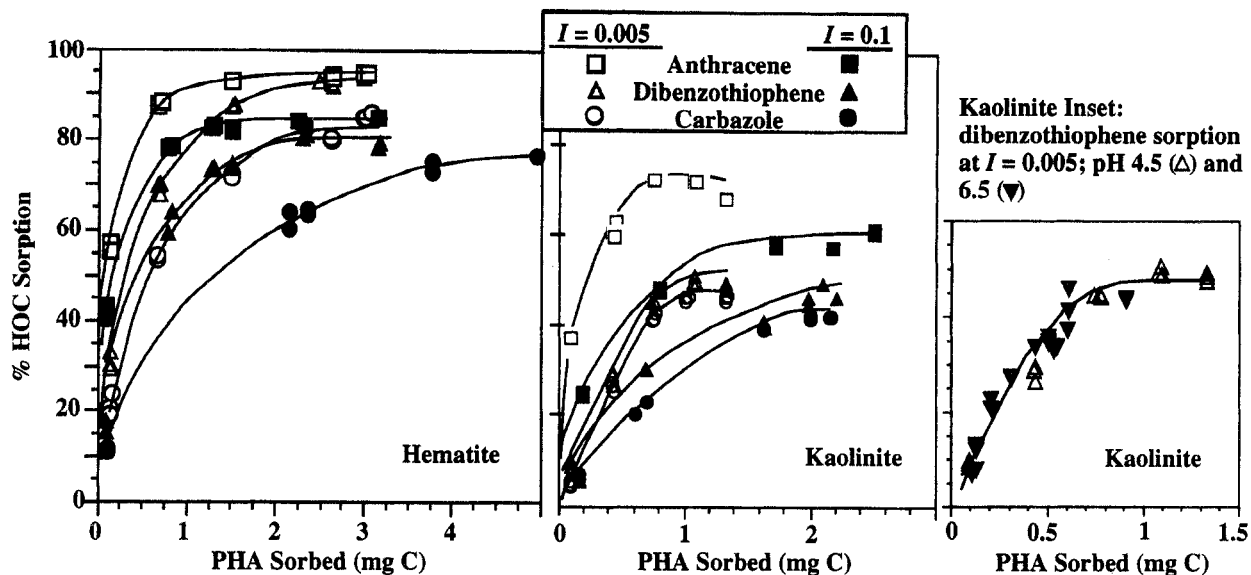


Figure 4. Comparison of the fractional sorption of HOC on kaolinite and hematite coated with PHA in NaClO_4 electrolyte at $I = 0.1$ and 0.005 at pH 4.5. Kaolinite inset of dibenzothiophene sorption at constant I but varying pH.

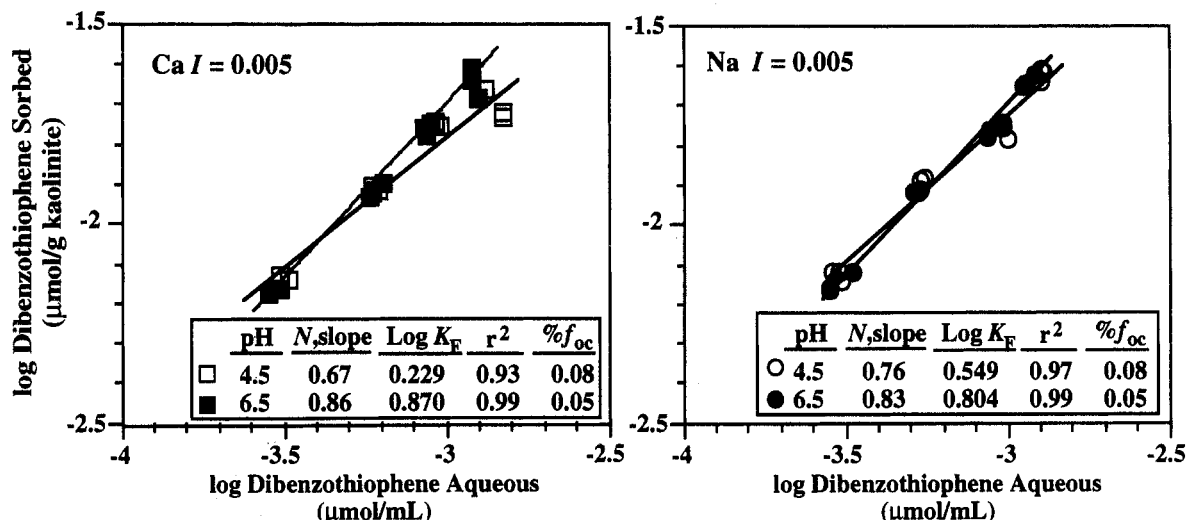


Figure 5. Sorption isotherms of dibenzothiophene on kaolinite coated with PHA in Ca^{2+} or Na^+ electrolyte at pH 4.5 and 6.5; $I = 0.005$. The inset tables show the Freundlich isotherm constants.

bridging (18, 37, 42, 43) or neutralizing ionized sites on the PHA (18, 37, 40, 41). The existence of a phase-partitioning mechanism for HOC sorption would be supported by HOC sorption isotherms exhibiting unit slope and by a lack of competition between like sorbates.

Sorption isotherms for dibenzothiophene on kaolinite coated with PHA were linear on a log-log basis (Figure 5) and conformed to the Freundlich equation:

$$\log S = \log K_F + N \log C_e \quad (1)$$

where K_F and N are constants specific to the coated sorbent, S equals micromoles of HOC adsorbed per gram of solid, and C_e equals micromoles of HOC per milliliter of solution. The log-log isotherms did not exhibit unit slope (i.e., Freundlich $N \neq 1$) regardless of electrolyte. A previous evaluation (2) showed that nonunit slopes were observed regardless of whether sorption was measured by aqueous-phase difference or by direct analysis of the sorbent phase. The isotherm slopes were farthest from unity at lower pH. Hydrophobic adsorption may yield a linear (i.e., $N = 1$) or a nonlinear (i.e., $N \neq 1$) isotherm; however, phase partitioning generally yields a linear

isotherm (24, 66, 68). The slopes of the dibenzothiophene isotherms on the kaolinite/PHA mixture suggested that the sorbed humic substance behaved as a hydrophobic surface toward the HOC, characterized by hydrophobic adsorption.

The HPSEC analyses (i.e., coalesced peaks in Figure 1) suggested that the disordered configuration of the humic macromolecule may be constrained in the presence of calcium. Unlike the Na^+ electrolyte, I had little effect on dibenzothiophene sorption in the calcium electrolyte at comparable PHA carbon concentrations (Figure 6). Apparently, dibenzothiophene sorption was insensitive to shifts in the relative size of PHA over this range of I in the Ca^{2+} electrolyte (Figure 1). We suggest that the configuration of PHA in the presence of Ca^{2+} may differ from that of PHA in high I Na^+ . The HPSEC chromatograms in Figure 1a,c showed that the PHA peaks in Ca^{2+} and Na^+ at $I = 0.1$ coalesce into one major peak, but that the relative size of PHA in Ca^{2+} is smaller (indicated by a longer retention time). However, the sorption of dibenzothiophene is enhanced in Ca^{2+} (Figure 7), and given the HPSEC results, the enhanced sorption cannot be

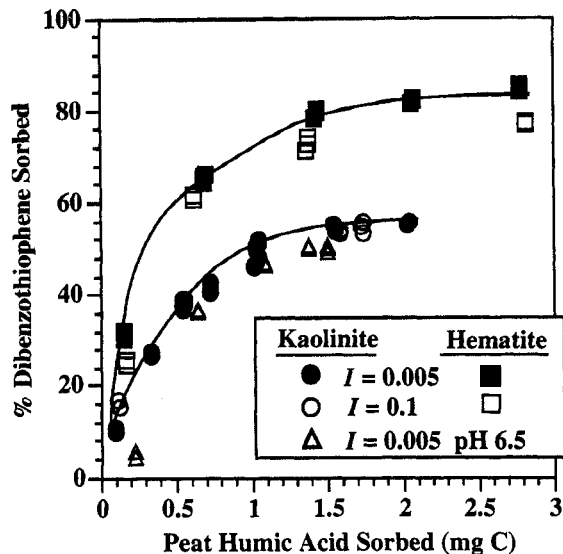


Figure 6. Fractional sorption of dibenzothiophene on kaolinite and hematite coated with PHA in $\text{Ca}(\text{ClO}_4)_2$ electrolyte at pH 4.5 and $I = 0.1$ and 0.005 . The sorption of dibenzothiophene on humic-coated kaolinite at pH 6.5 and $I = 0.005$ is shown for comparison.

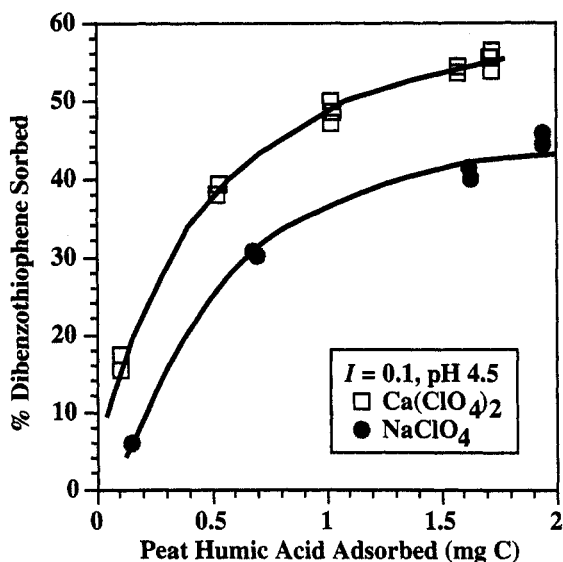


Figure 7. Comparison of dibenzothiophene sorption on kaolinite coated with PHA in high I (0.1) Ca^{2+} or Na^+ electrolyte at pH 4.5.

attributed to differences in PHA size under the two different cations. Therefore, the calcium may be facilitating the exposure of hydrophobic regions on the PHA, enhancing HOC sorption.

If hydrophobic adsorption is important, then in accordance with mass action laws, HOC with different K_{ow} should display competitive adsorption behavior as site saturation is approached. By analogy, the absence of competition is often taken as evidence of a partitioning mechanism (7, 24). Multisorbate experiments were performed by holding the carbazole concentration constant and varying the anthracene concentration over a range in molar ratios from 0 to over 1. Because anthracene is more strongly sorbed than carbazole, it should suppress carbazole sorption if the sorbates indeed compete for a common set of surface sites on the mineral-bound PHA.

The HOC single-point K_d 's for the sorbed humic phase were calculated according to the method of Murphy et al. (2). Calculation of the mineral contribution to sorption

requires that the surface area of the mineral sorbent exposed to the HOC be known (69); that is

$$S_{\min} = K_{d(s)} C \hat{s} \quad (2)$$

where S_{\min} is the sorbed HOC concentration (mol/g) attributed to the mineral surface, $K_{d(s)}$ is the mineral surface-binding constant (mL/m^2) as calculated from a sorption experiment with clean mineral surface, C is the HOC concentration in solution (mol/mL), and \hat{s} is the exposed surface area of the mineral (m^2/g). Sorption of the HOC was very low on the bare mineral surfaces because they had been pretreated to remove any small amounts of organic carbon. Sorption was nonetheless measurable because the mineral surface areas used in the sorption experiments were large ($1600 \text{ m}^2/\text{L}$ for kaolinite and $400 \text{ m}^2/\text{L}$ for hematite). At an initial sorbate concentration of 25% water solubility, the percent sorption of carbazole, dibenzothiophene, and anthracene was 3, 6, and 8%, respectively, for hematite and 6, 19, and 25%, respectively, for kaolinite.

Using S_{\min} from eq 2, a value for the organic-only contribution to S , S_{org} , can then be calculated:

$$S_{\text{org}} = S - S_{\min} \quad (3)$$

The exposed surface area of the mineral, \hat{s} , was calculated by assuming that the plateau in the adsorption density in the humic/mineral isotherms (e.g., Figure 3) corresponded to monolayer coverage. Based on this assumption, the surface area occupied by 1 mol of humic acid carbon was calculated, and this parameter was used to determine the fractional coverage of the mineral surface by PHA at lower adsorption densities. The complexation of humic substances to kaolinite occurs at the edge where Lewis acid aluminol groups are exposed. We surmise, but cannot substantiate, that the gibbsite basal plane on kaolinite with its doubly coordinated hydroxyls would be uncovered by the humic substance. Lockhart (70) similarly concluded that the basal plane of kaolinite was free of organic substances in a humate-clay association with 6% organic carbon.

Single-point sorption constants (K_d) were calculated according to the relation

$$K_d = [S - S_{\min}] / C \quad (4)$$

where S is total adsorbed HOC (in mol/g), S_{\min} is HOC adsorbed to the mineral surface in the absence of the humic substance, and C is the equilibrium concentration (in mol/mL).

The competition experiment was performed in low ionic strength ($I = 0.005$) calcium electrolyte to facilitate the potential formation of hydrophobic domains with the PHA. Chiou et al. (7) suggested that the inability of polyacrylic acid to enhance HOC solubility may relate to the frequent and orderly attachment of carboxyl groups that prevent the formation of a sizable hydrophobic domain, a constraint that was not observed with the natural humic substances used in their experiments. The calcium concentration in our experiments was low enough to avoid flocculation of the PHA, but high enough to facilitate sorption of the PHA to the mineral surface at the higher pH (presumably by forming a ternary surface complex). A suppression in the K_d of carbazole in the presence of anthracene (Figure 8) was indeed noted. The carbazole K_d decreased as it

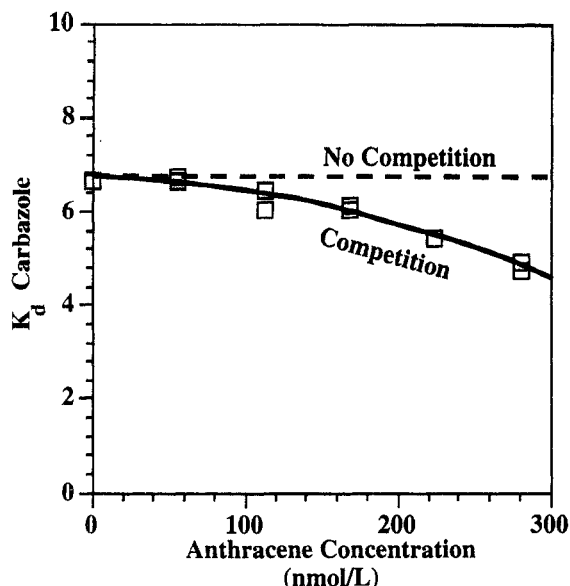


Figure 8. Sorption distribution coefficient, K_d , of carbazole with varying concentrations of anthracene on kaolinite coated with PHA at pH 6.0 in low I (0.005) Ca^{2+} electrolyte.

would if the carbazole was competing with anthracene for hydrophobic adsorption sites on the mineral-bound PHA. In a system where partitioning is occurring and the amount of carbon sorbent is not limiting, carbazole sorption should not be affected by a changing concentration in anthracene (7, 24). On a mole-carbon basis, the concentration of sorbent (PHA) was 100 times greater than the highest combined concentration of carbazole and anthracene. An analysis of variance showed that an average error for the triplicate carbazole K_d values was ± 0.2 , yielding narrow error bars corresponding to the width of the symbol boxes. Thus, the reduction in the K_d of carbazole was statistically significant.

Conclusions

Ionic strength, pH, and electrolyte cation valence were varied to maximize structural differences in the dissolved humic acid, which would also influence the structure of the sorbed humic coating. On a micromole-carbon basis, PHA occupies approximately twice as much surface area on kaolinite when adsorbed in sodium electrolyte at low I than at high I . In sodium electrolyte, the sorption of HOC to humic-coated minerals is enhanced at low I , suggesting that the linear or open configuration of the humic acid at low I facilitated the exposure of hydrophobic adsorption sites.

In both calcium and sodium electrolytes, the distribution of hydroxyl groups on the solid surfaces apparently affects the structure of the sorbed humic acid in ways that are important to HOC sorption. Hematite coated with PHA always showed greater HOC sorption enhancement than a comparable amount of PHA coated with kaolinite, regardless of the cation or I . The hydroxyl groups on kaolinite exist on the crystallite edge, while active hydroxyl sites on hematite exist on all exposed crystallographic faces. These differences in the distribution of hydroxyl sites apparently affect the sorbed configuration of the PHA and HOC sorption. The hematite surface may promote a more open or elongated structure to the PHA that, like the low I Na^+ electrolyte, is favorable to HOC sorption.

The strength of the calcium-carboxylate interaction negates apparent I effects on HOC sorption. Changes in I ranging from 0.1 to 0.005 had little effect on HOC sorption in the calcium electrolyte. It is possible that, over the range of I used in these experiments, sufficient calcium ion is present to set the structure of the PHA in solution that is preserved when the PHA is adsorbed to the mineral surface.

In these experiments, HOC sorption was most consistent with a hydrophobic adsorption mechanism. HOC sorption isotherms on humic-coated minerals were nonlinear regardless of cation, pH, or I . Carbazole and anthracene displayed competitive sorption behavior on PHA-coated kaolinite in low I calcium electrolyte, further supporting the suggestion that hydrophobic adsorption rather than phase partitioning is occurring on these natural coatings.

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