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Nonideal Binding between Dissolved Humic Acids and Polyaromatic Hydrocarbons

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Interactions between hydrophobic organic chemicals (HOCs) and dissolved organic matter (DOM) are of environmental significance due to their influence on mobility and bioavailability of HOCs. The linear dissolution concept has been widely used to describe the interactions between HOCs and DOM, but it may not be correct. To date there is no systematic evaluation of nonideal interactions between HOCs and DOM. Therefore, this study employed a dialysis method to investigate sorption, desorption, and competition of two polyaromatic hydrocarbons (PAHs), phenanthrene (PHE) and pyrene (PYR), by two DOMs at pHs of 4, 7, and 11. Nonlinear interactions between PAHs and DOM and desorption hysteresis were consistently observed. The isotherm nonlinearity factor, *n* value, increased significantly after the addition of cosolutes, indicating the occupation of specific binding sites by the cosolute molecules. Significant influence of pH on PAHs-DOM interaction was also observed (higher binding coefficients, stronger desorption hysteresis, and increased nonlinearity at lower pH). This study for the first time systematically showed the nonideal binding behavior of PAHs by DOM. A more complete model rather than linear distribution is required to describe the interactions between HOCs and DOM. Conformation changes of DOM molecules were proposed to explain the interactions between HOCs and DOM.

Introduction

Dissolved organic matter (DOM) is known for its great influence on mobility and bioavailability of hydrophobic organic compounds (HOCs) in the environment. The HOC-DOM interaction has been widely considered to be non-specific partitioning of HOCs between water and DOM (*1*). According to the partitioning concept, contaminant distribution coefficient, K_{DOC}, is independent of free solute concentration. Therefore, most of the studies on HOC-DOM interactions were based on single-concentration experiments, such as studies on HOC solubility enhancement by DOM (*1*), or neglected the concentration effect, such as the application of a linear Stern–Volmer equation to process the HOC-DOM binding data (*2*). The linear concept of the HOC-DOM interaction has also been often used in HOC fate (*3*, *4*) and risk predictive models (*5*). Most previous investigations focused on establishing the relationship between binding coefficients (K_{DOC}) and DOM properties, such as

aromaticity and polarity (*6*). For example, Thomsen et al. (*7*) conducted one-concentration experiments based on linear binding concept, and they observed large uncertainties of the relationship between K_{DOC} and DOM properties. They stated that different predictive models were needed for DOMs from different origins. Hur and Schlautman (*8*) also failed to establish a general correlation of ultraviolet absorbance or molecular weight with the K_{DOC} of several dissolved humic substances.

Several recent studies implied nonideal interactions between HOCs and DOM. For example, Schlebaum at al. (*9*) and Akkanen et al. (*10*) observed a two-stage desorption of HOCs from DOM, indicating the existence of different binding sites in DOM. Nonlinear association between total TNT (sum of 2,4,6-trinitrotoluene and its degradation products) and DOM was reported but was attributed to the DOM ionic character (*11*). In addition, nonlinear interactions for apolar compounds such as polyaromatic hydrocarbons (PAHs) have been also reported after excluding possible artifacts, such as dynamic quenching caused by oxygen, photodegradation caused by UV radiation, and inner filter effect (*12*, *13*).

Based on the above brief review, it is clear that different views exist in describing HOC-DOM interactions in the literature. If the nonlinear interaction is true, then the influence of DOM on HOCs mobility and bioavailability should be examined differently from linear partitioning, especially in exposure and risk modeling. However, very few studies are focused on nonlinear binding of HOCs with DOM so far (*12*, *13*). In addition, to our knowledge, all studies on HOC-DOM interactions are based on single-solute sorption experiments, but mixtures of HOCs are common for polluted waters and soils. A systematic examination on HOC-DOM nonideal interactions will provide more accurate data for HOC risk assessment.

Theoretically, isotherm nonlinearity indicates a heterogeneous energy distribution of sorption (binding) sites, and the related phenomena include competition and sorption/desorption hysteresis. Therefore, this study was designed to take one step further to systematically understand nonlinear HOC-DOM interactions. Pyrene (PYR)-DOM and phenanthrene (PHE)-DOM interaction was investigated on two dissolved humic acids (DHA) at pHs of 4, 7, and 11 for both sorption and desorption. The competition between PHE and PYR on DOM was also examined in bisolute sorption experiments.

Experimental Section

Chemicals. [14]C Labeled and unlabeled phenanthrene (PHE) and pyrene (PYR) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO) and used without further purification. These chemicals were dissolved in methanol separately as stock solutions. All other chemicals and solvents were better than analytical grade. NaN_3 (200 mg L^{-1}) was dissolved in deionized water as background solution, and the pH of this solution was adjusted to 4, 7, and 11 using 0.1 M HCl or 0.1 M NaOH.

Humic Acid (HA) Purification and Characterization. Two HAs were investigated in this study. One was Amherst HA (extracted from Amherst peat) and the other was from Aldrich Chemical Co. Both HAs were extracted and purified from the original matrix after Pan et al. (*14*). Briefly, a solution containing 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ was mixed with Amherst peat or Aldrich HA (50:1, v:w) to extract HA and fulvic acid. The supernatants were filtered and collected, and the HA was precipitated with HCl. The precipitated HAs were washed using distilled water until a negative test of chloride

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sample	aliphatic	carbohydrate	aromatic	carboxylic	C (%)	H (%)	O (%)	N (%)	ash (%)
Aldrich HA	33.4	6	45.1	15.6	60.0	4.47	34.5	0.96	0.1
peat HA	15.8	21.6	34.1	28.6	51.9	4.35	40.9	2.54	0.3

[a] Aliphatic, carbohydrate, aromatic, and carboxylic carbons are chemical shifts of 0−50, 50−108, 108−162, and 162−220 ppm from NMR spectra, respectively.

using $AgNO_3$, freeze-dried and ground to <500 μm particles. The C, H, and N contents were determined using an elemental analyzer (Elementar Vario EL, Germany). Functional groups were determined by solid-state ^{13}C NMR (Bruker DSX-300) (15). The parameters used on NMR were set as follows: contact time, 1 ms; spinning speed, 5 kHz; 90° [1]H pulse, 5 μs; acquisition delay, 4 s; and the number of scans, 10 000. Within the 0−220 ppm chemical shift range, C atoms were assigned to alkyl C (0−50 ppm), O-alkyl C (50−108 ppm), aromatic C (108−168 ppm), carboxyl C (168−192 ppm), and carbonyl C (192−220 ppm). The results are listed in Table 1.

Preparation of Dissolved Humic Acid (DHA). An aliquot of each HA (0.1 g) was dissolved overnight in 2 mL of NaOH (0.5 M) and mixed with 100 mL of 200 mg L^{-1} NaN_3 solution. The HA solution was enclosed in a dialysis membrane (Snakeskin 3500 Da, Pierce) and was soaked in the background solution (200 mg L^{-1} NaN_3). The background solution outside the bag (membrane) was refreshed everyday for 1 week until no leakage was observed on a TOC analyzer (5000A, Shimadzu, Kyoto) to discard molecules smaller than 3500 Da. The solution inside the bag was measured for its TOC content and used as DHA. The pH of DHA was adjusted using 0.1 M HCl or 0.1 M NaOH to 4, 7, or 11. No precipitation of DHA was observed at any pH during the experiment. The DHA made from Amherst peat HA is noted as PDHA, and the one from Aldrich HA is noted as ADHA. The concentration of the stock solution was 520 mgOC L^{-1} for ADHA and 480 mgOC L^{-1} for PDHA.

Batch Sorption Experiment Using Dialysis Bags. The dialysis membrane was soaked in 1 M $NaHCO_3$ for 30 min and in 1 M Na_2CO_3 for 30 min sequentially and then washed using distilled water. The membrane was tied at one end and put inside a 40 mL vial. The DHA solution and the PAH solution were added into the bag to reach a volume of 20 mL. DHA was added to reach 40 mgOC L^{-1} inside the bag. Both ^{14}C labeled and unlabeled PAHs were added into the bags to achieve a seven-concentration gradient ranging from 5 to 120 μg L^{-1} for PYR or from 8 to 800 μg L^{-1} for PHE based on the total solution volume in the vial. NaN_3 (200 mg L^{-1}) solution was added to fill the vial volume external to the dialysis bag (around 20 mL), and the headspace was kept minimal to avoid vapor loss. The vials were closed using Teflon lined caps immediately. The open end of the bag was tightly pressed under the cap with Teflon-lined silicone septum, and thus the bag was sealed. According to preliminary experiments, the interaction between PYR and DHA reached the apparent equilibrium before 24 h (Figure S1, see the Supporting Information). After shaking the vials in the dark for 2 days, the vials were opened, and samples were taken from both sides of the bags. The samples of about 1.0 mL were mixed with 7.0 mL of cocktail (Ultima Gold, Perkin-Elmer, Boston) for liquid scintillation counting. PAH concentration outside the bag stands for free solute, while concentration inside the bag is the sum of free and bound PAH. The concentration of bound PAH was calculated by the concentration difference between both sides and was normalized by DHA concentration based on organic carbon content. Since water molecules can pass through the membrane by diffusion during the equilibration, the actual volume of the solution outside the bag was measured at the end of equilibration. The actual DHA concentration inside

the bag was also recalculated. DHA concentration varied less than 5%.

Competition and Desorption Experiments. Unlabeled PYR was added to the PHE-DHA sorption system at a concentration of 100 μg L^{-1}, and unlabeled PHE was added to the PYR-DHA sorption system at a concentration of 1000 μg L^{-1} to investigate competition between PHE and PYR on DHA. Other experimental conditions were kept the same as in the single solute experiments.

In desorption experiment, solution outside of the dialysis bags was poured out and refilled with the fresh background solution. The removed solution was weighed and recorded to calculate the aqueous volume and TOC content inside the bag. The equilibration time was 2 days for each desorption cycle, and the procedure was repeated three times. Thus, four points (one from sorption and three from desorption procedure) were used to obtain a desorption isotherm.

Data Analysis. The supercooled aqueous solubility reduced Freundlich equation was used to fit the binding data. The equation was expressed as

$$C_b = K_{FOC} \times (C_i/C_{scl})^n \qquad (1)$$

where C_b is the concentration of bound PAH (μg kgOC^{-1}), C_i represents free concentration of PAH (μg L^{-1}), and C_{scl} is the supercooled liquid state solubility of PAH (5970 μg L^{-1} for PHE and 2170 μg L^{-1} for PYR (14)). K_{FOC} (μg kgOC^{-1}) and n (dimensionless) are the Freundlich sorption parameters.

The single point binding coefficient, K_{DOC}, was also calculated for comparing with literature values (16)

$$K_{DOC} = C_b/C_i = K_{FOC} \times C_i^{n-1}/C_{scl}^n \qquad (2)$$

where C_i is a given solute equilibration concentration. In this study, K_{DOC} is calculated at $C_i = 0.01\ C_s$, and 0.1 C_s. C_s is the PAH solubility in water at 25 °C.

The thermodynamic index of irreversibility (TII) was proposed by Sander et al. (17) to evaluate sorption/desorption hysteresis. This study adopted a Freundlich form of TII from their paper

$$TII_{Freundlich} = 1 - n_{desorb}/n_{sorb} \qquad (3)$$

where n_{desorb} and n_{sorb} are the nonlinear factors for sorption and desorption isotherms, respectively. TII is 0 when the system is completely reversible and is approaching 1 when the system tends to be completely irreversible.

Results and Discussion

Nonlinear Binding between PAHs and DHA. PYR-ADHA isotherms at pHs 4, 7, and 11 were plotted in Figure 1 in log scale. All n values were significantly smaller than 1 ($P <$ 0.05) and varied from 0.87 to 0.89. The same nonlinear behavior was also observed in both PHE-ADHA (Figure S2) and PYR-PDHA systems (Figure S3). The overall fitting results are listed in Table 2.

Since the partitioning model has been widely reported to describe the interaction between HOCs and DOM, investigators, who observed nonlinear behavior, discussed extensively to exclude any possible artifact (12, 13). The possible
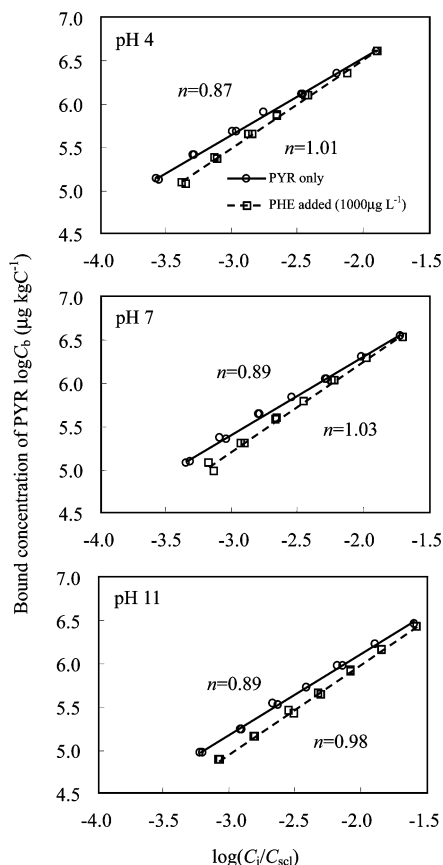
FIGURE 1. Nonlinear isotherms of PYR on ADHA and competitive effect after the addition of PHE (1000 μg L^{-1}) at pH 4, 7, and 11. The open circles are the measured sorption points for PYR only, and the open squares are those with PHE added as cosolute. The fitting results were listed in Table 2.

artifacts in this study are different from those in the literature. Because the smaller molecules (<3500 Da) of HA were discarded during our sample preparation (see the Experimental Section), no DHA leakage was observed during the experiment. According to solute mass balance calculations, about 10% of PAHs was not recovered, mainly due to sorption by the dialysis membrane. However, this sorption will not affect the equilibrium distribution of PAHs between water and DHAs, because we did not use solute mass balance to calculate binding coefficients. As indicated in Figure S4, the presence of DHA of up to 80 mgOC L^{-1} in solution did not affect the final detection of ^{14}C labeled PAHs using liquid scintillation counting. Therefore, the free and bound concentrations were determined separately in this study instead of the calculation based on total mass balance. Hence, the observed nonlinear binding was real for the interaction between PAHs and DHAs because any artifact was ruled out easily in our experiment design.

Laor et al. (*12*) also used the Aldrich HA to investigate the interaction between PHE and DOM. The nonlinearity they observed is stronger than that in our study, with a low n value of 0.73, but they used a complexation-flocculation method (CF). It should be noted that they reported greater n values when using a fluorescence quenching (FQ) method than their CF method. Although they argued that the addition of alum in CF method did not alter the equilibrium, the conformation of DOM may have changed to a more condensed configuration (*18*). The K_{DOC} values of this study are comparable to the results reported by Laor et al. (*12*) and Marschner et al. (*19*).

Competition between PHE and PYR on DHA. If nonlinear binding is true for the interaction between PAH and DOM,

the sites on DOM should be varied in energy for binding with PAH molecules, which will result in preferential sorption on high-energy sites and consequently causes competition between chemicals with similar properties. This hypothesis is supported well in our competition experiments. In our first competition experiment, PHE was added at 1000 μg L^{-1} to investigate the cosolute effect on PYR-ADHA interaction. Binding isotherms of the bisolute system and the fitting results are shown in Figure 1 and Table 2. Consistent with nonlinear binding, distinct competition between PHE and PYR was observed (Figure 1). Compared to a single solute system, the overall sorption was decreased, and the linearity increased significantly ($P < 0.05$) for bisolute system at pHs of 4, 7, and 11. The n values were between 0.98 and 1.03, not significantly different from 1 ($P < 0.05$). Similar competition was also observed in the PYR-PDHA system (Figure S3). Although the n values for the PHE-ADHA system did not statistically increase after the addition of PYR ($P < 0.05$), they showed an increasing trend (Table 2 and Figure S2). The weaker competition for the PHE-ADHA system could have resulted from a much partitionlike sorption (as indicated by relatively high n values from 0.91 to 0.95, Table 2) and lower cosolute concentration (100 μg L^{-1} of PYR due to its solubility).

As discussed earlier, 10% of PAHs was sorbed by the dialysis membrane. If competition came only from the sorption sites on the membrane, the amount of solute molecules available for DHA binding would have been increased. The equilibrated point would be shifted slightly to the upright on the isotherm comparing to the system without cosolute and should stay on the same isotherm. However, this is not the case in this study. The isotherm with cosolute distinctly departed from the original isotherm. Moreover, the dialysis membrane is made of regenerated cellulose. As indicated by several studies (*20*, *21*), the sorption by cellulose is linear without competition. Therefore, the competition observed in this study would be directly from the specific sorption of PAHs on DOMs.

As seen in all the competition curves (Figures 1, S2, and S3), at low concentrations, the sorption points after adding cosolute were below the original ones, indicating more competition. As the concentration of cosolute increased, the two isotherm curves approached each other (Figure 1). Previous researchers have reported similar competition for solid organic matter (*20*). According to the dual mode model for HOCs sorption on solid organic matter, the sorption mechanism of partitioning and adsorption exist simultaneously (*22*). The partition is a linear, concentration-independent process, while adsorption is a nonlinear, concentration-dependent process. Because adsorption domain contains mostly high energy sorption sites, sorbate molecules tend to occupy these sites at lower concentrations, and thus adsorption predominates the overall uptake at low concentrations (*23*).

This concept is applicable for the PAH-DHA interaction observed in this study. DOM has been proved to contain semimicelle or pseudomicelle structures (*24*). Although it is argued that the micelle concentration of DOM is far higher than the concentration in solute enhancement or fluorescence quenching experiments (*12*), there may be some micellelike regions present because of the cross-linking of DOM molecules (*24*).

Chien et al. (*25*) investigated the paramagnetic relaxation of two probes in atrazine solubilization by humic acid. They observed a rapid paramagnetic relaxation for the hydrophobic probe which was sorbed by humic micelles but no relaxation for the hydrophilic probe which remains in aqueous solution. Their results confirmed the presence of hydrophobic region in DOM matrix, and HOCs (e.g., atrazine) can reside in the hydrophobic interior of DOM. Partitioning concept has been applied to describe the distribution of HOCs in hydrophobic

TABLE 2. Fitting Results of the Sorption Isotherms in Single Solute and Bisolute Systems[a]

	pH	single solute system					bisolute system				
					logK$_{oc}$ (mL g^{-1})					logK$_{oc}$ (mL g^{-1})	
		n	logK$_{Foc}$ (µg kgC^{-1})	r^2	C$_i$ = 0.1C$_s$	C$_i$ = 0.01C$_s$	n	logK$_{Foc}$ (µg kg C^{-1})	r^2	C$_i$ = 0.1C$_s$	C$_i$ = 0.01C$_s$
PHE	4	0.95 ± 0.02	8.01 ± 0.04	0.995	4.31	4.35	0.95 ± 0.02	7.97 ± 0.04	0.997	4.27	4.32
ADHA	7	0.91 ± 0.01	7.67 ± 0.02	0.997	4.04	4.13	0.96 ± 0.01	7.71 ± 0.03	0.998	4.00	4.04
	11	0.92 ± 0.02	7.68 ± 0.04	0.997	4.03	4.10	0.97 ± 0.02	7.79 ± 0.04	0.997	4.05	4.08
PYR	4	0.87 ± 0.01	8.28 ± 0.04	0.998	5.22	5.34	1.01 ± 0.02	8.52 ± 0.05	0.997	5.16	5.15
ADHA	7	0.89 ± 0.02	8.08 ± 0.04	0.997	4.98	5.09	1.03 ± 0.02	8.29 ± 0.06	0.995	4.89	4.87
	11	0.89 ± 0.01	7.92 ± 0.04	0.998	4.81	4.92	0.98 ± 0.01	7.97 ± 0.03	0.998	4.68	4.69
PYR	4	0.76 ± 0.01	7.68 ± 0.03	0.997	4.87	5.11	0.91 ± 0.04	7.86 ± 0.09	0.985	4.72	4.81
PDHA	7	0.83 ± 0.02	7.61 ± 0.04	0.997	4.65	4.82	0.97 ± 0.03	7.84 ± 0.07	0.990	4.58	4.61
	11	0.86 ± 0.02	7.24 ± 0.04	0.997	4.22	4.36	1.01 ± 0.04	7.48 ± 0.09	0.987	4.11	4.10

[a] For the bisolute system, PYR (100 µg L^{-1}) was added as cosolute in PHE sorption experiments, and PHE (1000 µg L^{-1}) was added as cosolute in PYR sorption experiments. K_{OC} was calculated as $K_{FOC} \times C_i^{n-1} \times C_{scl}^{-n}$. C_s is the solubility of PHE (1290 µg L^{-1}) or PYR (134 µg L^{-1}) in water at 25 °C. ADHA is dissolved Aldrich humic acid. PDHA is dissolved Amherst peat humic acid.

regions. However, the hydrophobic domain in a three-dimensional matrix of DOM is not a uniform continuous phase but a discrete microenvironment (1). The dimension and compactness of the hydrophobic region could be affected by DOM molecular structures, size, concentration, and solution chemistry. Therefore, partitioning and site-specific sorption most likely take place simultaneously. Literature data support this idea, e.g., Schlebaum et al. (9) and Borisover et al. (13) reported saturation of DOM by pentachlorobenzene and PYR, respectively. Since the specific sites normally have higher energies and are limited in number, a higher percentage of solute molecules are adsorbed on those specific sites at low concentrations than at high solute concentration, which results in an obvious decrease of sorption after the addition of cosolute due to competition for these sites. All n values were not significantly different from 1 after the addition of cosolutes (Table 1), again indicating competition on the specific sorption sites. Cosolute molecules would block or occupy the specific sites but not affect the partitioning domain.

Therefore, for the first time, we directly observed competition between PAHs on DHAs. Because competition between different chemicals is due to occupation of the same type of adsorption sites, this study provides further support for site specific sorption of HOCs on DOM, leading to nonlinear isotherms.

Desorption Hysteresis. Desorption curves were plotted for the PYR-ADHS system at pHs of 4, 7, and 11 (Figure 2). Only selected desorption curves are presented to avoid clustering on these graphs. Clearly, desorption isotherms deviated from the sorption isotherms, with a general up-left shift in direction, which means that the solute molecules tend to bind more with DHA during desorption. The TII values were calculated according to eq 3 and were plotted in Figure 3c. The TII values were in the range of 0.46 to 0.79 at pH 4, 0.18 to 0.53 at pH 7, and 0.16 to 0.32 at pH 11, indicating a significant hysteresis for all concentrations ranging from 5 to 120 µg L^{-1}. Hysteresis was also confirmed in the PHE-ADHA (Figure S5) and PYR-PDHA (Figure S6) systems.

Sorption hysteresis has been reported for solid organic matter. The irreversibility of sorption of HOCs by solid organic matter was explained by the formation of meta stable states of adsorbate in fixed mesopores and irreversible deformation of the sorbent by the sorbate (17, 26). Using atomic force microscopy, Ge et al. (27) investigated the adsorption and aggregation of humic substances on mica. They observed a more compact conformation of humic substance assemblies after the sorption of naphthalene. Therefore, it is possible that the conformation of DOM was changed after binding with solute, which resulted in the pathway of desorption
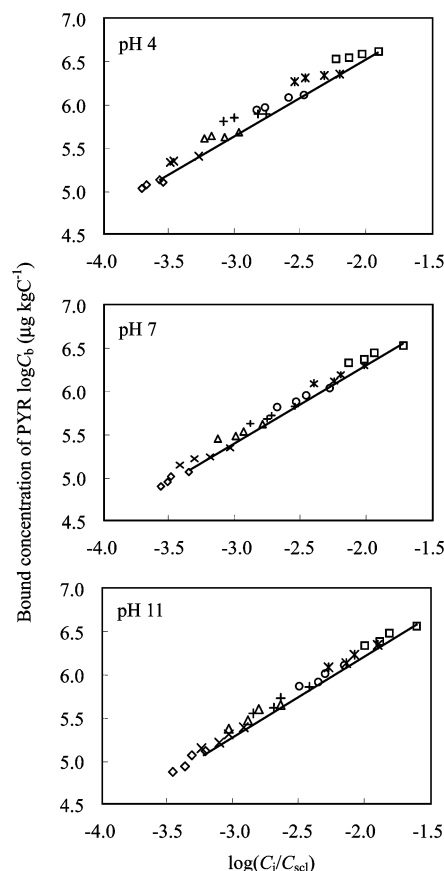

FIGURE 2. Desorption isotherms of PYR from ADHA at pH 4, 7, and 11 showing hysteresis. The solid lines are the original sorption isotherms. The same symbol indicates the successive desorption from a single sorption point.

being different from that of sorption. Further investigation is needed to determine the exact hysteretic mechanism for PAH desorption from DOM.

For the PYR-ADHA system, after three times desorption, 45−53% of PYR was still retained in the system. According to a theoretical calculation (Figure S7), the hysteresis resulted in a 16% higher bound-concentration and an 18% lower free-concentration compared to a completely reversible desorption after three times successive desorption in our dialysis system. Compared to a partitioning process, three times successive desorption in a hysteretic system could bring 21% higher bound-concentration and 21% lower free-concentra-
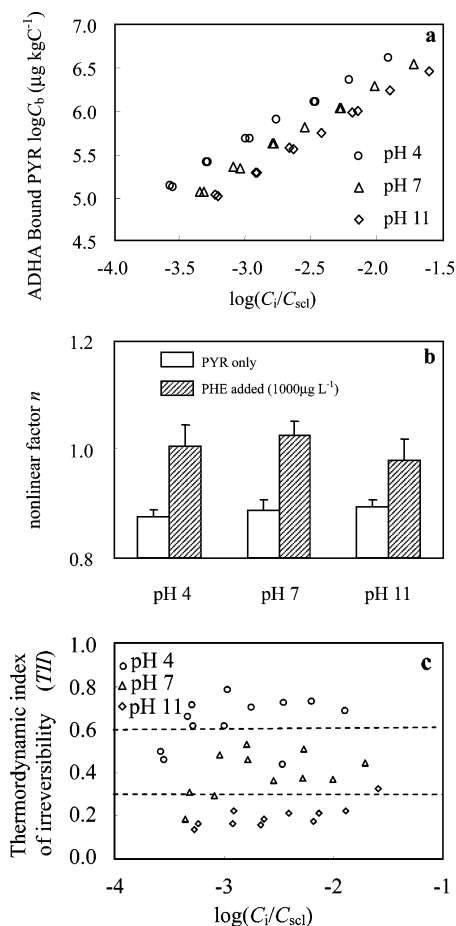
FIGURE 3. pH influence on sorption/desorption characteristics of the PYR-ADHA system. Sorption isotherms (a), nonlinearity comparison between single solute and bisolute systems (b) and thermodynamic index of irreversibility (c) at different pHs.

tion. If the prediction of bound concentration is only based on the free concentration, a calculation based on reversible desorption could make a 39% underestimation of bound-concentration, and that based on a linear concept could result in a 52% underestimation of bound-concentration. Thus, it is of great importance to apply an appropriate model to predict the behavior and availability of HOCs in the presence of DOM.

Previous studies have indicated that only free dissolved chemicals could pass through the biological membrane and become bioavailable (*28*). If partition is the only mechanism for the interaction of HOCs and DOM, the DOM-bound chemicals could release into the aqueous phase continuously as the free dissolved chemicals are absorbed by organisms. In that case, since the equilibrium of HOCs between DOM and water could be established within 3−5 min in a well mixed system (*2*), the partitioning of HOCs in DOM would hardly influence the accumulation of chemicals by organisms. However, numerous studies have reported the significant influence of DOM (increase or decrease) on bioaccumulation of HOCs (*29, 30*). Although the discussions on the influence of DOM on HOC bioavailability were mainly focused on binding of HOCs by DOM, it is the irreversible desorption of bound HOCs affecting uptake and bioaccumulation. Because nonlinearity, competition, and irreversibility were consistently observed in this study, the influence of DOM on the fate and environmental risk of HOCs has to be evaluated using a more complete model rather than simple, reversible linear ones.

Comparison of PAH-DHA Interactions at Different pHs. The effect of pHs on sorption/desorption characteristics of the PYR-ADHA system is shown in Figure 3. Similar information was also obtained for PHE-ADHA and PYR-PDHA systems (Table 2, Figures S2, S3, S5, and S6). Sorption was generally increased as pH decreased (Figure 3a and Table 2), and the irreversibility index (TII) increased as pH decreased (Figures 3c, S5, and S6). An increasing trend of n values due to the increase of pH could be also seen for the PYR-PDHA
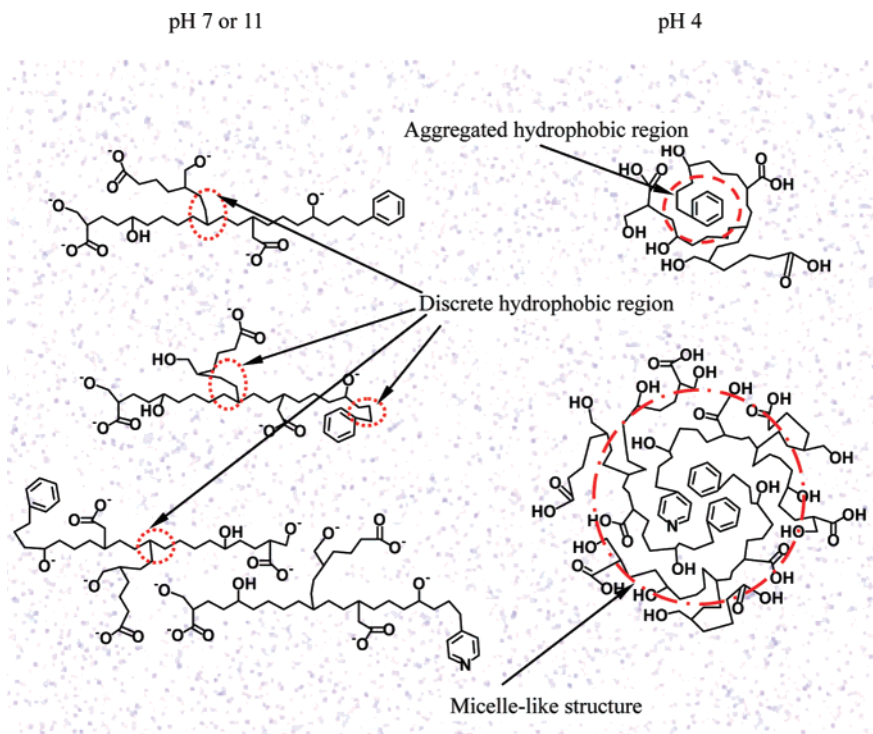

FIGURE 4. Schematic diagram of possible conformation changes of DOM at different pHs. Discrete hydrophobic region (circle with dots), aggregated hydrophobic region (circle with dashes), and micellelike structure (circle with dots and dashes) are the possible sorption region for HOCs. The area in color is the water molecules.

system. However, the nonlinearity did not change significantly for the other systems.

Since the composition of DOM did not change at different pHs, only DOM property affecting sorption characteristics would be its conformation, i.e., reorganization of DOM molecules at different pHs. A schematic diagram of speculated DOM molecular conformation is displayed in Figure 4. For apolar organic compounds such as PAHs, hydrophobic interaction is mainly responsible for binding with DOM. At alkaline and neutral conditions (pH 7 and 11), carboxyl and hydroxyl functional groups of DOM are deprotonated, and the molecules are overall negatively charged. The molecules are stretched and opened because of the inter- or intramolecular repulsion. But loosely coiled structures and a nonpolar microenvironment may still exist as hydrophobic regions. Some of the hydrophobic microenvironment may be too small to act as binding sites for PAHs or may be surrounded by polar groups and not accessible by PAHs (1). Other regions may be relatively compact and have higher energy for sorption. Therefore, the overall sorption shows a nonlinear isotherm because of the unevenly distributed hydrophobic regions. Hence, we postulate the discrete hydrophobic sites for pH 7 and 11 (Figure 4). On the other hand, at acidic pH (pH 4), the carboxyl and hydroxyl groups can be protonated and the surface charge of the DOM molecules are neutralized, and thus the self-coiling and aggregation of DOM molecules are facilitated. The discrete hydrophobic microenvironment could be aggregated together to form large hydrophobic regions, and the loosely coiled structure could form a more compact structure (Figure 4). When several molecules come together to form bigger aggregates, a micellelike conformation could be formed, and the binding with PAH could be enhanced at low pH (Figure 4). Furthermore, as discussed by Zhu et al. (31), the $\pi-\pi$ electron donor−acceptor interactions are favored in an acidic environment. Although they argued that alteration of hydrophobic character of solid humic substances cannot be attributed to the pH effect, the conformation of DOM could be changed significantly in different pHs, leading to a more favorable $\pi-\pi$ interaction environment at low pH.

This study consistently observed nonlinear sorption, desorption hysteresis, and competition of PHE and PYR on DHA at pHs of 4, 7, and 11. Our results provide a solid support for site-specific binding of PAHs on DOM. True bioavailability of DOM-bound HOCs could be lower than that predicted from reversible desorption and higher than that assuming nonbioavailable for DOM-bound chemicals. This study emphasizes the requirement of reevaluation on binding mechanisms between HOCs and DOM and their impact on fate and bioavailability of HOCs. Systematic studies are required in order to establish reliable risk assessment models including the nonideal HOC-DOM interactions, especially the desorption hysteresis.

Acknowledgments

Supporting Information Available

PYR-ADHA interaction kinetics (Figure S1); nonlinear sorption, competition, and desorption in PHE-ADHA and PYR-PDHA systems (Figures S2, S3, S5, and S6); DHA effect on liquid scintillation counting (Figure S4); and a mathematical modeling of three-time successive desorption based on different models (Figure S7). This material is available free of charge via the Internet at http://pubs.ac.org.

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