

Influence of Solution pH on Pyrene Binding to Sorption-Fractionated and Kaolinite-Bound Humic Substance

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ABSTRACT

Changes in pyrene binding by dissolved and kaolinite-associated humic substances (HS) due to HS adsorptive fractionation processes were examined using purified Aldrich humic acid (PAHA) at different pH (4, 7 and 9). Irrespective of solution pH, molecular weight (MW) fractionation occurred upon adsorption of PAHA onto kaolinite, resulting in the deviation of residual PAHA MW from the original MW prior to sorption. Variation in K_{oc} by bulk PAHA was observed at different pH due to relative contributions of partitioning and size exclusion effects (i.e., specific interactions). For all pH conditions investigated, carbon-normalized pyrene binding coefficients for nonadsorbed, residual fractions ($K_{oc}(res)$) were different from the original dissolved PAHA K_{oc} value ($K_{oc}(orig)$) prior to contact with the kaolinite suspensions. Positive correlations between pyrene $K_{oc}(res)$ and weight-average molecular weight (MW_w) for residual PAHA fractions were observed for pH 7 and 9. However, such a positive correlation was not found at pH 4 due to the absence of the dramatic fractionation observed for high pH conditions (i.e., exclusive fractionation with respect to higher MW), suggesting that actual MW distribution pattern is more important for sorption-fractionated HS than the composite MW value. For adsorbed PAHA, conformational changes of PAHA upon adsorption seem to be important for the extent of pyrene binding. At relatively high pH (7 and 9), lower extent of pyrene binding was observed for adsorbed PAHA versus nonadsorbed PAHA. The conformation effects were more pronounced at higher pH.

Key word : Humic substances (HS), Hydrophobic organic contaminants (HOCs), Organic carbon normalized binding coefficient (K_{oc}), Adsorptive fractionation; kaolinite

요 약 문

다양한 pH 조건하에서 휴믹물질 흡착적 분획현상에 의해 변화하는 용존 및 kaolinite에 흡착된 휴믹물질(Aldrich 휴믹산)과의 pyrene의 결합변화를 조사하였다. 먼저 흡착효과를 배제한 흡착 전 상태에서 bulk 휴믹산은, pH에 따른 분배(partitioning)과 크기별 배제효과 영향 차이에 의해 유기탄소 결합계수의 변화를 보였다. 모든 용액 pH 조건에서 Aldrich 휴믹산은 kaolinite에 흡착하는 과정에서 분자량별 분획이 일어났으며 용존 휴믹산의 분자량은 흡착전의 분자량과는 달랐다. 그에 따라 흡착 후 남은 휴믹산과의 pyrene 결합계수는 흡착 전의 경우와 달랐다. pH 7과 9 조건에서 흡착 후 남은 휴믹산은 그 분자량과 pyrene 결합계수 사이에 양성 상관관계를 보였으나 그러한 상관관계가 pH 4의 조건하에서는 관찰되지 않았다. 이러한 차이는 흡착적 분획과정에서 pH 4인 경우 고분자에 대한 독점적 분획현상이 없었고 분자량에 대해 다소 균일한 분획이 일어났다는 점으로 설명할 수 있었다. 또한 관찰되는 분획현상 차이는 pH 조건에 따라 달라지는 흡착포화 정도 차이 때문인 것으로 사료된다. 흡착된 PAHA의 경우, 형태변화(conformational changes)가 pyrene 결합에 중요한 것으로 나타났다. pH 7과 9 조건 하에서, 흡착전의 휴믹산의 경우 더 낮은 pyrene 결합계수를 보였고 이러한 형태변화효과는 pH가 높을수록 더 크게 나타났다.

주제어 : 휴믹물질, 소수성 유기오염물, 유기탄소 결합계수, 흡착적 분획, kaolinite

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1. Introduction

Apparent aqueous concentrations and transport of hydrophobic organic contaminants (HOCs) are greatly affected by the presence of humic substance (HS) (Thurman, 1985). The mobility of HOCs is facilitated by dissolved HS in an aqueous phase, whereas their transport is retarded by binding with adsorbed HS on inorganic surfaces (McCarthy and Zachara, 1989; Liu and Amy, 1993). Understanding the sorption behavior of HS onto minerals is a prerequisite for evaluating the fate and distribution of HOC in many aquatic environments. Solution pH influences HS sorption behavior by changing the surface chemistry of minerals and the degree of the ionization of acidic functional groups in HS. Numerous studies have reported that HS sorption on minerals is pH-dependent. The pH dependence of HS adsorption has been reported to be the most likely due to several mechanisms: 1) increased ligand exchange between the acidic functional groups on HS and protonated surface hydroxyl groups at lower pH, 2) increased electrostatic attraction between mineral surfaces and charged HS at a pH value below the point of zero charge (PZC) of minerals, and 3) changes in macromolecular conformation of HS (Sposito, 1984; Schlautman and Morgan, 1994; Kretzschmar *et al.*, 1997).

Size or molecular weight (MW) fractionation of HS occurs via mineral sorption, and the fractionation pattern is dependent on solution chemistry as well as the type of mineral and HS used (Zhou *et al.*, 2001; Hur and Schlautman, 2003a; Hur and Schlautman, 2004a). For example, Zhou *et al.* (2001) observed preferential adsorption of high molecular weight fractions of an aquatic fulvic acid on goethite at low pH and of medium size fractions at higher pH. They explained that, at the higher pH, increasing repulsion between neighboring negatively charged molecules adsorbed on goethite could limit further adsorption of larger and highly charged HS molecules. More recently, Hur and Schlautman (2004a) observed a greater extent of preferential adsorption of higher MW fraction of Aldrich humic acid with higher pH, demonstrating that adsorption

selectivity for particular molecular weight components is influenced by solution pH.

Many prior studies suggest that HS adsorptive fractionation with respect to MW may influence HOC binding in mineral surfaces-abundant systems such as contaminated soil or groundwater. For example, positive relations between HS MW and the extent of HOC binding have been reported for fractionated HS as well as bulk HS (Chin *et al.*, 1997; Hur and Schlautman, 2003a). More recently, Hur and Schlautman (2003b) reported that a positive relationship between MW of HS and the extent of pyrene binding still remained even after HS fractionated via mineral sorption, indicating that MW of HS plays a critical role in binding HOC in aqueous phase regardless of structural loss of HS from sorption onto mineral surfaces.

There were only a few studies of solution pH effects on the ability of mineral-bound HS to bind HOC. Schlautman and Morgan (1993a), using humic and fulvic acids, investigated perylene binding with HS-coated aluminum oxide surfaces at varying solution chemistry (pH and solution composition) and compared the results with K_{oc} obtained from dissolved HS. Loar *et al.* (1998) studied phenanthrene sorption to goethite coated with Aldrich humic acid at pH 5 and 7. Schlautman and Morgan (1993a), under the condition that characteristics of adsorbed HS are principally identical to the original HS except for structural change upon adsorption, focused the magnitude of the conformational change at different pH for explaining the variations in the perylene K_{oc} with adsorbed HS. However, all of these studies neglected HS adsorptive fractionation effects and they never interpreted their results in terms of HS MW.

To the author's knowledge, there was no effort made to investigate solution pH effects on HOC binding in HOC-HS-mineral systems from a standpoint of HS adsorptive fractionation and the relationship between HS MW and the extent of binding. The objective of this study was to evaluate the adsorptive fractionation effect of HS on the extent of pyrene binding to dissolved HS and kaolinite-bound HS at different pH (4, 7 and 9).

2. Materials and Methods

2.1. Materials

Purified Aldrich humic acid (PAHA) was used for HS. Pyrene was selected as the model HOC. Commercially available kaolinite (Sigma) was used for the model mineral adsorbent without further treatment. The treatment and basic characteristics of the materials have been previously reported (Hur and Schlautman, 2003a, 2003b).

2.2. Analytical Methods

A total organic carbon (TOC) analyzer equipped with an autosampler (Shimadzu model 5050) was used to quantify PAHA concentrations in the aqueous phase. A UV-vis spectrophotometer (Beckman model DU640) was used to consider inner-filter correction of pyrene samples (Gauthier *et al.*, 1987). Pyrene concentrations in aqueous solutions or hexane extracts were quantified by a luminescence spectrophotometer (Perkin-Elmer, LS-5B) using external standards. The excitation/emission wavelengths (nm/nm) for pyrene were 336/373, and the slits were set for bandwidths of 3 nm for excitation and 5 nm (in aqueous solutions) or 20 nm (in hexane extracts) for emission. Relative precisions of 1 and 3% were routinely obtained for absorbance/fluorescence and TOC measurements, respectively.

Size exclusion chromatography (SEC) was used to determine weight-average molecular weights (MW_w) of PAHA samples, generally following a methodology based on the work of Zhou *et al.* (2000). Prior to SEC measurements, the pH values of residual PAHA samples from adsorption experiments conducted at pH 4 and 9 were adjusted to be around 6.8 using 0.01N of HCl or NaOH solution to avoid potential non-size exclusion effects derived from pH difference between PAHA sample and the mobile phase (pH 6.8) (Hur and Schlautman, 2004a). In addition, the adjustment of pH made it easier to compare HS adsorptive fractionation observed at different pH without considering the changes of structural configurations with pH. All PAHA samples were filtered through prewashed 0.45-mm PVDF membrane filters prior to sample injection

to the SEC system. The details for the SEC system and MW calculation were provided in Hur and Schlautman (2003b).

2.3. Pyrene binding to residual PAHA

Detailed experimental procedures for HS adsorption by kaolinite is described elsewhere (Hur and Schlautman, 2004a). Pyrene K_{oc} values with the residual HS, designated here as $K_{oc(res)}$, were determined using the supernatant HS solutions resulting from the HS adsorption experiments. A fixed concentration (80 $\mu\text{g/L}$) of pyrene was spiked into each residual HS sample. Due to the limited concentrations and volumes of residual HS samples, a modified fluorescence quenching technique was utilized to determine $K_{oc(res)}$ instead of the more typical Stern-Volmer analysis (Hur and Schlautman, 2004b). All samples were mixed on a reciprocating shaker at low speed for 20 min to attain equilibrium before removing aliquots for fluorescence and absorbance measurements.

For the modified fluorescence quenching technique, residual HS-associated pyrene, freely dissolved pyrene and residual HS concentrations were all quantified separately to determine $K_{oc(res)}$ values with the following equation (Hur and Schlautman, 2003a):

$$K_{oc(res)} = \frac{[\text{pyr-HS}]}{[\text{pyr}]_{\text{free}} \cdot [\text{HS}]} \times 10^{-6} \quad (1)$$

where $[\text{pyr-HS}]$ is the HS-associated pyrene concentration ($\mu\text{g/L}$), $[\text{pyr}]_{\text{free}}$ is the freely dissolved pyrene concentration ($\mu\text{g/L}$), and $[\text{HS}]$ is the dissolved residual HS concentration (mg/L). For this study, concentrations of freely dissolved pyrene in HS samples were determined by fluorescence using external standards, and pyrene concentrations associated with the residual dissolved HS were calculated by mass balance.

2.4. Pyrene binding to kaolinite-bound PAHA

This experiment was very similar to the HS adsorption experiments, except for the spiking of pyrene (100 $\mu\text{g/L}$) into centrifuge tubes that contained appropriate concentrations of HS and minerals. First, the same HS concentrations as used in HS adsorption

experiments were added to centrifuge tube that containing a fixed mineral suspension and solution composition (i.e., 0.1 M NaCl, pH 7, 50 or 10 g/L of kaolinite or hematite, respectively). All samples were equilibrated on the shaker for 72 hours, based on preliminary rate studies. After centrifuging (3,000 rpm, 30 min) each sample to separate the solid phase, the total concentration of dissolved pyrene (i.e., = freely dissolved pyrene + pyrene associated with residual dissolved HS) was quantified by hexane extraction and subsequent fluorescence measurement. The pyrene concentration adsorbed to the mineral-associated HS was then determined by mass balance. Details of the procedure were illustrated in a figure included in a previous report (Hur and Schlautman, 2004b). Although Johnson and Amy (1995) reported successful quantification of pyrene in HS samples using hexane extraction and fluorescence measurement, a slight increase was observed for this study in the fluorescence of HS-equilibrated hexane control solutions. Therefore, a modified hexane extraction method was developed and utilized to quantify total dissolved pyrene concentrations (Hur and Schlautman, 2004b). Briefly, the background fluorescence of hexane solutions after equilibration with residual HS in the absence of pyrene was measured and used to make fluorescence corrections. Preliminary studies showed pyrene recovery percentages of 100.5 (± 1.3) and 99.1 (± 2.8) in the presence of 10 and 50 mg C/L, respectively, HS solutions.

3. Results and Discussion

3.1. PAHA adsorption by kaolinite at different pH

Fig. 1 shows PAHA sorption isotherms on kaolinite at different pH. All the sorption isotherms were fit well with the Langmuir isotherm model ($R^2 > 0.97$), indicating that site-limiting mechanisms may be responsible for PAHA sorption on kaolinite regardless of the pH conditions. Greater adsorption was observed at lower pH, which is in a good agreement with prior reports (Schlautman and Morgan, 1993b; Gu et al., 1994; Hur and Schlautman, 2004a). The maximum sorption density of the isotherm obtained at pH 4 is

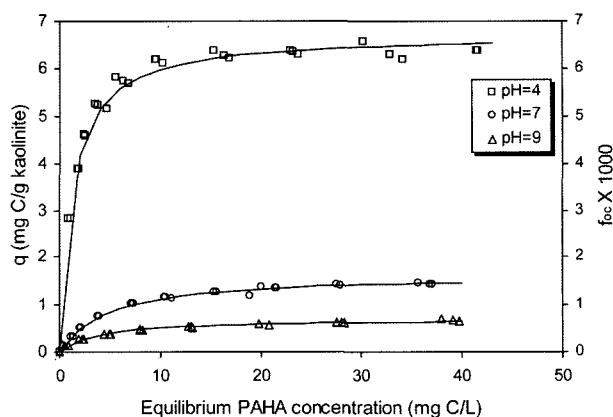


Fig. 1. Adsorption isotherms of PAHA on kaolinite at pH 4, 7 and 9 (0.1 M NaCl). The adsorption data were adopted from Hur and Schlautman [9].

four-fold higher than that observed at pH 7, and ten-fold, at pH 9. It appears that the site-dependent sorption mechanisms such as ligand exchange and electrostatic attraction are more strongly involved and the contributions become greater for PAHA sorption to kaolinite at lower pH.

3.2 Pyrene Binding by Dissolved Bulk PAHA at Different pH

Pyrene K_{oc} binding to bulk PAHA, $K_{oc}(\text{bulk})$, at different pH was investigated (Fig. 2). A consistent trend of K_{oc} was not observed with pH. Instead, relatively low K_{oc} was achieved at the neutral pH (7.0) versus pH 4 and 9. The higher K_{oc} values at pH 4 versus pH 7 may be attributed to the increase in hydrophobic regions of PAHA because of neutralization of the charged acidic functional groups in PAHA at lower pH. However, a single mechanism of partitioning cannot explain the increased K_{oc} at pH 9. Schlautman and Morgan (1993b) found that a Flory-Huggins partitioning model failed to predict HOC binding by Suwannee River humic and fulvic acids at varying solution chemistry. They hypothesized that hydrophobic cavities might play a role in binding HOC as secondary structures of HS. Xing and Pignatello (1997) incorporated the size exclusion effect into the dual-mode model (glassy/rubbery model), and suggested that two mechanisms, partitioning and hole-filling mechanism, control HOC binding by HS. In the glassy/rubbery

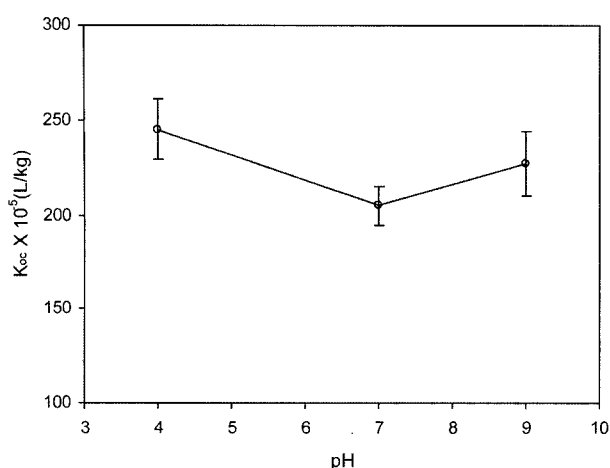


Fig. 2. Pyrene K_{oc} by dissolved bulk PAHA at different pH (0.1M NaCl solutions). The values were estimated by the modified fluorescence technique.

model, HS were depicted as having two domains—rubbery and glassy domain. Partitioning occurs in both domains, however, the glassy domain also has holes where specific interactions occur. If solution pH changed the hole environments of the glassy domains by contracting or expanding HS structure, the relative contributions of both partitioning and hole-filling mechanism could influence the extent of binding.

At lower pH, HS may adopt more a constricted conformation because of weak repulsive forces between negatively charged functional groups in HS and, possibly, more H-bonding. The more compact conformation of HS may restrict pyrene accessible to HS attachment sites, and there may not be a sufficient number of holes to fit pyrene and size exclusion effects may not operate in the overall binding. In this case, hydrophobicity of HS is expected to determine the extent of binding. As pH increases, however, a greater number of acidic functional groups dissociate and the hole-filling mechanism participates more effectively in the overall binding. The results shown in Fig. 2 suggest that a “threshold” pH, after which the specific mechanism becomes more important than partitioning, may be greater than 7.0 for this particular case.

Previous investigations of pH effects on HOC binding to dissolved bulk aquatic HS have shown a decrease in K_{oc} values for higher pH (Carter and

Suffet, 1982; Schlautman and Morgan, 1993b). In contrast, an increasing trend of K_{oc} with pH has been reported with terrestrial HS (Clapp *et al.*, 1997; John and Tiller, 1999; Hur and Schlautman, 2004c). For example, Clapp *et al.* (1997), using a soil-derived HS, observed an increase in the extent of binding of a slightly soluble herbicide, napropamide, with pH increasing from 4 and 8. More recently, Jones and Tiller (1999) observed increasing trends of phenanthrene K_{oc} with pH (4-10) by a soil-derived HS in different concentrations of NaNO_3 aqueous solutions. The apparent contrasting results for aquatic vs. terrestrial HS indicate that the trend of K_{oc} with pH may depend on the type of HS. Jones and Tiller (1999) suggested larger molecular sizes of a soil-derived humic acid versus aquatic HS as a possible explanation for the conflicting observation with aquatic HS.

It is noteworthy that the molecular size of either phenanthrene or napropamide is smaller than pyrene. Due to the smaller molecular size of these solutes versus pyrene, the size exclusion effect may begin at a pH lower than the “threshold” pH of this study, which could explain the increasing trend of K_{oc} over the pH ranges they investigated. Moreover, the relative contribution of the size exclusion effect (by specific interactions) versus partitioning may be greater than the case of pyrene due to the higher aqueous solubilities of the solutes. In this sense, the result of this study seems to generally agree with the two previous studies. The trend of K_{oc} values with pH for this study is more consistent with a recent report of Hur (2004c), who demonstrated using the same humic acid (i.e., PAHA) that size exclusion effects play a secondary role in determining the extent of binding pyrene and naphthalene for HS.

3.3. Pyrene binding to residual PAHA at different pH

MW_w values of residual PAHA after sorption are plotted as a function of equilibrium PAHA concentrations in Fig. 3a. Deviations of these values from their corresponding original MW_w value indicate that MW fractionation of PAHA occurred upon adsorption to kaolinite. Apparently, the extent of the fractionation

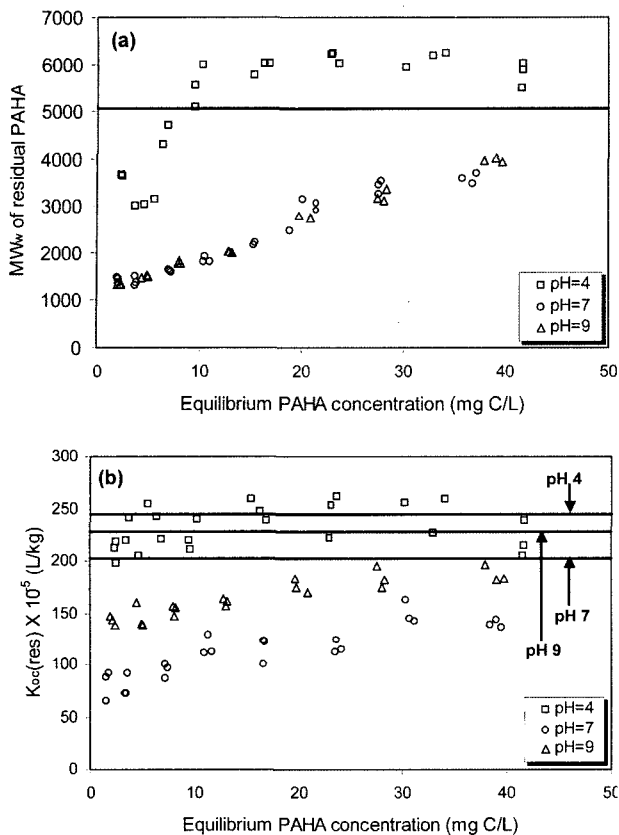


Fig. 3. (a) MW_w of residual PAHA after adsorption on kaolinite (adopted from ref 18) (b) $K_{oc}(res)$ (L/g-OC), pyrene K_{oc} with the residual PAHA, as a function of equilibrium PAHA concentrations after sorption at different pH. The horizontal lines represent the original values before adsorption. The molecular weight data were adopted from Hur and Schlautman [9].

at pH 7 is very similar to that observed at pH 9 at comparable equilibrium PAHA concentrations. However, it should be kept in mind that more fractionation occurred at pH 9 when the residual MW_w data were compared as a function of percent carbon adsorption (Hur and Schlautman, 2004a). The detailed discussion and explanations for the adsorptive fractionation results shown in Fig. 3a have been provided in a previous report (Hur and Schlautman, 2004a). For example, at lower percent carbon adsorption, which corresponds to the plateau regions of the sorption isotherms, available sorption sites become limiting and competition among PAHA components for adsorption sites is highest. In this case, strongly-adsorbing PAHA components (i.e., lower MW_w fractions), which are likely governed by ligand exchange or electrostatic

attraction, are expected to be more competitive. In contrast, at high percent carbon adsorption (i.e., low surface excess concentration), competition is less important and hydrophobic interactions likely lead to nonadsorbed PAHA fractions of lower MW_w remaining in solution versus the original MW_w .

$K_{oc}(res)$ values were compared with the original K_{oc} values obtained from bulk PAHA in Fig. 3b. All $K_{oc}(res)$ values at pH 7 and 9 were lower than the original values, consistent with the lower MW_w of residual PAHA versus the original MW_w . This suggests that the extent of pyrene binding depends on the MW_w of the residual PAHA for pH 7 and 9. However, $K_{oc}(res)$ values at pH 4 do not deviate much from the original value, indicating that the adsorptive fractionation occurring at pH 4 does not change the extent of binding (Fig. 3b). Therefore, changes in pyrene binding due to adsorptive fractionation was observed at high pH (7 and 9).

The relative impacts of adsorptive fractionation on pyrene binding can be evaluated by plotting the $K_{oc}(res)$ values as a function of the MW_w of the residual PAHA at different pH (Fig. 4). Positive correlations between K_{oc} and MW_w of residual PAHA were observed for pH 7 and 9 conditions, which is consistent with a prior study (Hur and Schlautman, 2004b). The positive relationship was more pronounced for pH 9 versus pH 7, as demonstrated by the higher R^2 value of the linear regression equations (Fig. 4). However, such a positive correlation was not found for pH 4. The lack of the positive relationship is possibly explained by a wider range of adsorption selectivity of kaolinite with respect to PAHA MW for pH 4 versus other pH conditions (Hur and Schlautman, 2004a). In other words, despite the apparent difference in the measured MW_w values, residual PAHA is likely to have a wide range of MW after sorption at pH 4 because hydrophobic interactions and site-limiting HS sorption mechanisms, which were responsible for preferential adsorption of higher MW and lower MW fractions, respectively, do operate simultaneously under the condition. The different fractionation pattern also explains the higher degree of the positive correlation

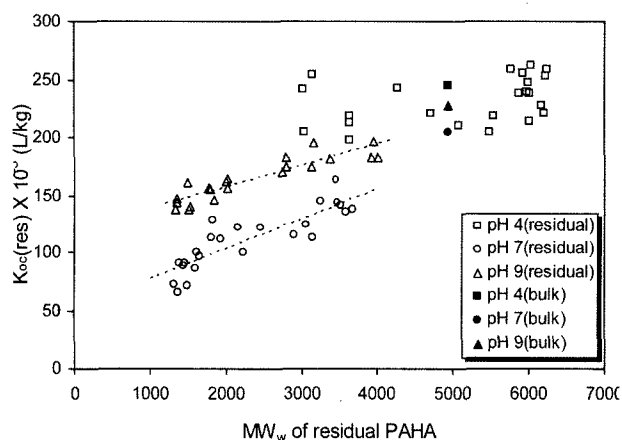


Fig. 4. Relationship between K_{oc} and MW_w of nonadsorbed PAHA fractions. The dotted lines represent the regression equations for pH 7 ($K_{oc} = 0.026 \cdot MW_w + 51.4$; $R^2 = 0.743$) and pH 9 ($K_{oc} = 0.018 \cdot MW_w + 121.3$; $R^2 = 0.827$). Note that no apparent linear relationship was found for pH 4.

observed for pH 9 versus pH 7 because hydrophobic interactions, which are responsible for preferential of higher PAHA MW_w fractions, are more dominant at pH 9 versus pH 7 (Hur and Schlautman, 2004a). The observation suggests that an actual MW_w distribution of HS may be more important in determining the extent of pyrene binding to dissolved HS than is the apparent composite MW_w value. Despite large scatter of pH 4 data, the relatively higher $K_{oc}(res)$ values were still observed in the declining order of pH 4 > pH 9 > pH 7 on the overlapped MW_w range as for the case of bulk PAHA.

3.4. Pyrene binding to kaolinite-bound PAHA at different pH

Apparent MW_w values of the adsorbed PAHA fractions in low (<0.002) f_{oc} systems were calculated following the ideal mixture approach described in Hur and Schlautman (2003a). The approach is based on the concepts of mass balance and adherence to the Beer-Lambert law for UV absorbance, and calculates adsorbed MW_w values from their corresponding residual MW_w values, corresponding relative fractions of residual UV absorbing components, and the original bulk HS MW_w value. In general, MW_w of adsorbed PAHA increased with carbon fractional coverage on kaolinite surfaces ($f_{oc} = 0-0.0015$) at pH 7 and 9 (Fig. 5a). Higher

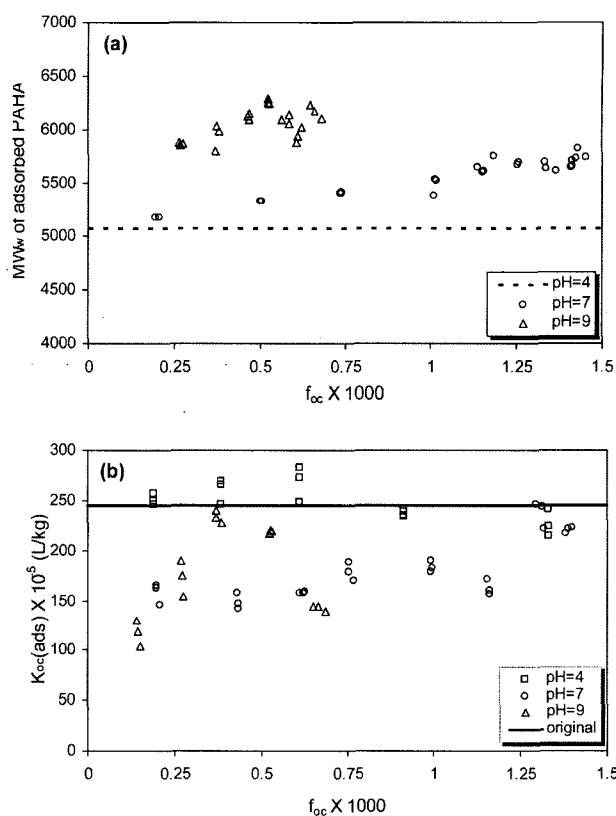


Fig. 5. (a) MW_w of adsorbed PAHA on kaolinite after adsorption with f_{oc} (b) pyrene $K_{oc}(ads)$, pyrene K_{oc} , with adsorbed PAHA, as a function of f_{oc} .

MW_w of adsorbed PAHA versus bulk PAHA reflects preferential adsorption of higher MW_w fractions. Note that MW_w of adsorbed PAHA is the same as the original MW_w at pH 4 because no residual PAHA was detected from the adsorption isotherms at the range of f_{oc} investigated.

Estimating the contribution of bare kaolinite to pyrene sorption is well described in a previous study (Hur and Schlautman, 2004b). $K_{oc}(ads)$ values were calculated using the following equation.

$$K_d = \frac{[PYR]_{solid}}{[PYR]_{aq}} = f_{io} \cdot K_{io} + f_{oc} K_{oc}(ads) \quad (2)$$

where $[PYR]_{aq}$ is the free pyrene concentration dissolved in water and $[PYR]_{solid}$ is the adsorbed pyrene concentration, K_{io} and f_{io} are the partition coefficient of pyrene with inorganic surfaces and the fraction of inorganic surface area available for pyrene sorption (0-1), respectively. In this study, f_{io} was

estimated under an assumption that the maximum available kaolinite surface area for PAHA is 0.272.

$K_{oc}(ads)$ values obtained from kaolinite-bound PAHA under different pH conditions were plotted as a function of f_{oc} in Fig. 5b. Compared to the original bulk K_{oc} values, $K_{oc}(ads)$ values at pH 7 and 9 were lower across most of the f_{oc} range investigated, whereas the values at pH 4 are nearly constant over the f_{oc} range without major deviation from the original K_{oc} . $K_{oc}(ads)$ values were lower at pH 7 and 9 than their respective bulk K_{oc} values despite the higher apparent MW_w for adsorbed PAHA components. This observation demonstrates that MW_w is not the sole controlling factor for pyrene binding at pH 7 and 9.

Schlautman and Morgan (1993a), in a study of perylene binding to an alumina-bound aquatic humic acid at varying solution chemistry (pH 4, 7 and 10, and different concentrations of NaCl), observed no perylene binding at neutral to high pH (pH 7 and 10) for all NaCl aqueous solutions. Perylene binding was found at only a low pH (pH=4) through their investigation. They explained that ligand exchange became more dominant at high pH due to higher polarity of HS, whereas hydrophobic interaction significantly contributes to HS sorption at low pH as a result of increasing protonation of carboxyl groups on HS. It was also inferred therein that HS adsorption by ligand exchange at high pH severely restricts conformational changes of the adsorbed HS necessary to bind perylene because HS are bound tightly at the mineral surface by inner-sphere complexes. In contrast, weakly-adsorbed HS at low pH (e.g., through hydrophobic interaction) were thought to be able to change their conformation at the surface if necessary to bind perylene.

Although the apparent $K_{oc}(ads)$ trend with pH agrees with the result of this study, some caution must be exercised because 1) Schlautman and Morgan (1993a) used an aquatic HS and different mineral, and 2) they did not consider HS adsorptive fractionation. Therefore, the trend they reported could be less pronounced if higher MW_w fraction of the HS were preferentially adsorbed. In addition, the explanations

they offered are not consistent with those provided for the results of this study (i.e., sorption mechanisms for different pH). For this study, ligand exchange and/or electrostatic interactions were considered as more important sorption mechanisms at a lower pH.

It was reported that apparent pK_a range of HS is rather broad and also that the value decreases at higher ionic strength of a solution (Stevenson, 1994). Since a high ionic strength (0.1 M) was used in this study, an appreciable fraction of carboxyl groups on PAHA probably still remains dissociated and electrostatic interactions is expected to still operate at a low pH. Therefore, different combination of orientation and arrangement of adsorbed PAHA may better explain the changes in K_{oc} values with pH rather than the degree of the tightness in binding between HS and minerals described by Schlautman and Morgan (1993a). At lower pH, more hydrophilic regions may be attached to mineral surfaces due to electrostatic attraction formed between negatively charged acidic functional groups of HS and positively charged kaolinite surfaces. In this case, more hydrophobic regions of HS, exposed toward to a solution, is expected to enhance pyrene binding.

4. Conclusions

Irrespective of solution pH, MW fractionation occurred upon adsorption of PAHA onto kaolinite, resulting in the deviation of residual PAHA MW from the original MW prior to sorption. The adsorptive fractionation changed the extent of pyrene binding. Positive correlations between pyrene K_{oc} and MW_w values for PAHA were achieved for pH 7 and 9, but not for pH 4. No positive correlation at pH 4 was explained by relatively a wide range of MW components present in solution due to less selective adsorptive fractionation with respect to MW for the particular pH. Variation in K_{oc} by bulk dissolved PAHA at different pH was observed, which was explained by relative contributions of partitioning and size exclusion effects (i.e., specific interactions). For adsorbed PAHA, conformational changes of PAHA

upon adsorption seem to be more important for the extent of pyrene binding than does HS MW. At relatively high pH (7 and 9), lower extent of pyrene binding was observed for adsorbed PAHA versus nonadsorbed PAHA. The conformation effects were more pronounced at higher pH.

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