

Adsorption of Humic Acids to Mineral Particles. 2. Polydispersity Effects with Polyelectrolyte Adsorption

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The adsorption of humic acid to mineral particles can be characterized by specific and electrostatic interactions and by adsorption fractionation. In this paper we focus on adsorption fractionation and the influence of the polydispersity (with respect to size) of humic acids on the adsorption process and the shape of the isotherms at different pH values. In the previous paper the effects of electrostatic interactions were described. The adsorption from a mixture of two humic substances, purified Aldrich humic acid (PAHA) and Laurentian fulvic acid, on nonporous hematite is studied. It is shown that, in time, the large humic acid molecules replace the readily adsorbed, small, fulvic acid molecules. Preferential adsorption of large humic molecules over small ones also affects the shape of the adsorption isotherm of a single humic acid. After a high affinity start, the adsorbed amount of PAHA gradually increases with increasing humic acid concentration. This is mainly due to an increasing adsorption fractionation. For a certain concentration in solution the effect of the fractionation increases with increasing adsorbed amounts. This explains why for PAHA the polydispersity effect is much stronger at pH 4 than at pH 9 where the adsorption is lower. To obtain a general impression of the effects of polydispersity on the adsorption of weak polyelectrolytes on a variably charged surface, calculations are presented using a self-consistent-field theory. The calculated adsorption of a mixture of two acidic polyelectrolytes, that (mainly) differ in size, onto an oppositely charged hematite type surface confirm the trends found for humics: adsorption fractionation occurs, and the effect of the fractionation on the isotherm increases with decreasing pH. The calculations also show that the area-to-volume ratio affects the isotherm and results in an adsorption/desorption hysteresis.

Introduction

The adsorption of humic substances onto the mineral soil matrix is important in relation to the speciation and mobility of contaminants present in the soil system. In general, humic substances are a polydisperse mixture of heterogeneous polyelectrolytes¹⁻³ that can be divided into several fractions, including fulvic and humic acid that each are polydisperse with respect to size.⁴⁻⁶ The humic and fulvic fractions are differentiated by their solubility at different pH.⁷ Humic acid remains in solution at pH 2 and higher and is composed of the higher molecular weight fraction of the humic matter, while fulvic acid has a relatively low molecular weight and remains in solution under all pH conditions. Furthermore fulvic acid is slightly more acidic. Under conditions that normally prevail in the natural environment, both humic and fulvic acids are mobile, unless they are bound to the mineral phase.

In general, it is known from polymer adsorption studies on nonporous surfaces that polydispersity with respect to size leads to isotherms that increase substantially with increasing polymer concentration, particle concentration or surface area-to-volume ratio effects, and hysteresis between the adsorption and the desorption upon dilution isotherms (pseudo-irreversibility).⁸⁻¹⁰ These effects can be explained by preferential adsorption of the higher molecular weight fraction over the lower molecular weight fraction within a given polymer sample.

In the case of polyelectrolyte adsorption the situation is similar, but more complex. Several authors¹¹⁻¹⁶ mention that it is more difficult to achieve equilibrium with polyelectrolytes than with uncharged polymers. This has been worked out most convincingly by De Laat et al.¹⁵ who showed that an electrostatic barrier, caused by the adsorption of the polyelectrolyte itself, retards the adsorption and that the retardation is a function of the salt concentration and the molecular weight. In practice, this can lead to preferential adsorption of the intermediate molecular weight fraction over the high molecular weight fraction.¹⁶

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Also for the adsorption of humics, polydispersity effects and (partial) irreversibility of the adsorption have been mentioned. Davis and Gloor¹⁷ have reported that the adsorption of different molecular size fractions of lake water humics onto nonporous alumina suspensions leads to preferential adsorption of the highest molecular weight fraction. However, they do not discuss the mechanism responsible for the observed phenomenon. Summers and Roberts¹⁸ have investigated the adsorption of humic substances onto activated carbon and conclude that, on the basis of the accessible surface area, the larger molecules have a greater extent of adsorption. The adsorption isotherms for different adsorbent doses result only in a unique isotherm when the surface area-to-volume ratio is taken into account.

Contrary to these studies, Kilduff et al.¹⁹ have reported that the smaller humic acid molecules adsorbed to a greater extent onto porous activated carbon than the larger molecules. However, the total adsorption was not based on the accessible surface area but on the adsorbed mass per gram. In this case, the trend is reversed because the large molecules cannot penetrate in the pores of the carbon particles.

Hysteresis effects are discussed by several authors.^{20–24} Most prominent is the work of Gu et al.^{22,24} who reported that natural organic matter adsorbed onto hematite showed adsorption/desorption hysteresis. The main explanation given for the observed hysteresis was the existence of multiple binding between the adsorbed natural organic matter and the iron oxide, so that desorption required simultaneous detachment of all bound segments. As a consequence of this only the molecules adsorbed by a few bonds are easily desorbed.

The observed hysteresis and preferential adsorption of a specific fraction (adsorption fractionation) of humic substances are certainly not specific for humics and, at least partly, they should be closely related to polydispersity (in size) effects in general. In our first paper²⁵ on the adsorption of humic acid onto hematite, the general trends in the adsorption behavior as a function of pH and salt concentration (electrostatics) were compared with calculated results. Special emphasis was given to the interaction mechanisms without paying much attention to polydispersity effects. Therefore, the objective of the present paper is to investigate the effect of adsorption fractionation of humic substances on (1) the adsorption process and the competition between humic and fulvic acid and (2) the shape of the adsorption isotherms. To this aim, the adsorption of humic and fulvic acid on nonporous hematite particles is studied. Further insight is gained in the adsorption characteristics of polydisperse polyelectrolytes through model calculations. The calculated results are based on the self-consistent-field (SCF)

theory for adsorption of weak polyelectrolytes^{26–28} onto a surface with a variable charge.²⁹

Materials and Methods

Chemicals used were p.a. quality. The water was purified by percolating tap water through a mixed bed ion exchange column followed by an activated carbon column and a microfilter. All experiments were performed in a constant temperature room at 21 °C.

Hematite. A well-aged nonporous Hematite B (α -Fe₂O₃) suspension, prepared as described by Breeuwsma and Lyklema,³⁰ with a BET (N₂) surface area of 43 m² g⁻¹ and a mean particle size of 50 nm was used. The point of zero charge of the hematite was 8.9.

Humic Substances. Two different humic substances were used, Aldrich humic acid (PAHA) purified from insoluble material²⁵ and Laurentian fulvic acid (LFA). PAHA is in its proton form and was freeze-dried and stored in a glass container. Before use, PAHA was dissolved overnight in a solution with pH = 10. Other PAHA solutions were made from this stock solution. LFA was a gift of Dr C. Langford; it was derived from a sample of a podzol collected in the Laurentian Forest Preserve of Laval University, Québec, Canada.³¹

The elemental analysis of PAHA is (wt %): C, 55.8; O, 38.9; H, 4.6; N, 0.6. The elemental analysis of LFA³² is: C, 45.14; O, 49.68; H, 4.11; N, 1.07. The H:C ratio for LFA was 1.09 and the ratio for PAHA was 0.99. These values correspond to organic matter of which the basic unit consists of an aromatic nucleus with aliphatic side chains up to 10 carbon atoms.³³ Since the H:C ratios differ only slightly, it may be assumed that both humic substances show a similar basic carbon structure. The O:C ratios for LFA and PAHA were respectively 0.83 and 0.52; the higher O:C ratio for LFA than for PAHA indicates a higher total acidity.³³ LFA has a total acidity of 11.6 mmol g⁻¹, of which 8.6 mmol are carboxylic groups and 3.0 mmol phenolic groups. For PAHA the total acidity is 5.0 mmol g⁻¹ of which 3.7 mmol g⁻¹ are carboxylic groups and 1.3 mmol g⁻¹ phenolic groups. These values were obtained from potentiometric proton titrations by fitting the bimodal NICA-DONNAN model to the charge–pH curves.³⁴ It can be concluded that (1) LFA has more reactive sites per unit mass than PAHA, (2) the ratio of carboxylic and phenolic groups in both humics is nearly the same, and (3) in both samples carboxylic sites are the most abundant. With dynamic light scattering we found that the diffusion coefficient of LFA (6×10^{-11} m² s⁻¹) is about 10 times larger than that of PAHA (4×10^{-12} m² s⁻¹). The corresponding hydrodynamic radius of LFA is about 3 nm and that of PAHA is in the order of 50 nm. The average molecular weight of PAHA was estimated by viscosity measurements and gel permeation chromatography (calibrated with proteins) and was 21 kD. That of LFA was about 9 kD. Although the acidity of LFA is somewhat higher than that of PAHA, it can be concluded that the main difference between LFA and PAHA is the molecular size.

UV and Fluorescence Spectroscopy. UV measurements² at 254 nm of both PAHA and LFA solutions and their mixtures were performed with a Hitachi U-3210 spectrophotometer. Fluorescence emission spectra of solutions of the humics were recorded with a Perkin-Elmer LS-5 luminescence spectrometer

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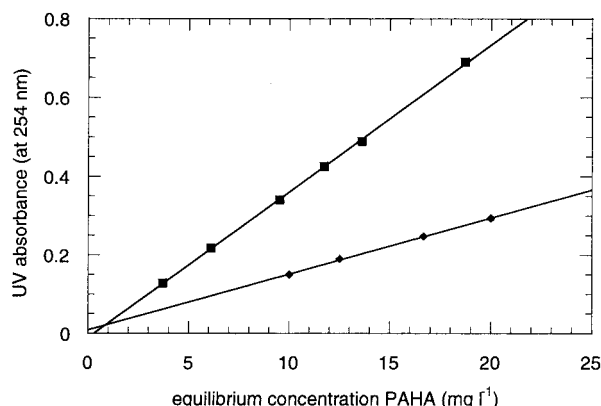


Figure 1. Calibration of the UV spectrophotometry at pH 6 and 0.01 M KNO₃ for the two humic substances: ■ = PAHA; ◆ = LFA. The lines are obtained by linear regression. The regression coefficients are shown in Table 1.

at an excitation wavelength of 340 nm, monitoring the emission over the range of 365–650 nm, following Senesi et al.³⁵ Corrections for background scattered light were made according to Ewald et al.³⁶ to be able to compare the intensities of the two humic substances.

Adsorption Kinetics and Competition. The effect of a strong polydispersity in size on the adsorption kinetics and adsorption fractionation is investigated by measuring the adsorption of PAHA and LFA from a mixture of both as a function of time at pH 6 and 0.01 M KNO₃. For these measurements a solution was used that contained 23 mg L⁻¹ natural organic matter of which 7 mg L⁻¹ was LFA and 16 mg L⁻¹ PAHA. These values were chosen to obtain about equivalent numbers of LFA and PAHA molecules in the sample. To each polyalymere tube subsequently, a suspension containing 0.13 m² hematite and 7 mL of the humic mixture was added. The pH and salt concentration were adjusted by adding HNO₃ or KOH and KNO₃, respectively. The total solution volume was 10 mL, and after the tubes were closed, the suspensions were shaken, head over head. At different incubation times the tubes were centrifuged for 15 min using a Beckman JS-7.5 centrifuge at 7500 rpm. After separation of the supernatant, the pH was checked and minor adjustments were made prior to the spectroscopic measurements to obtain the solution concentrations of both PAHA and LFA.

Adsorption Isotherms. Adsorption isotherms of single PAHA onto hematite at pH 4, 6, and 9 and 0.01 M KNO₃ were measured after an incubation time of 18 h using the depletion method, for details see Vermeer et al.^{25,37}

Experimental Results and Discussion

UV and Fluorescence Spectroscopy. Calibration curves for both PAHA and LFA using UV and fluorescence spectrometry (FS) measurements, at pH = 6 and 0.01 M KNO₃ are shown in Figure 1 and Figure 2, respectively. Figure 1 shows that the relation between the LFA or PAHA concentration and the UV absorbance at 254 nm is linear up to 20 mg L⁻¹ for both humics. Normalized fluorescence intensities at 460 nm observed for PAHA and LFA at different concentrations are shown in Figure 2. Linear relations are established for both humics in the concentration range 1 to about 15 mg L⁻¹. Regression coefficients *S* and *I* of the linear parts of the measured calibration lines are summarized in Table 1.

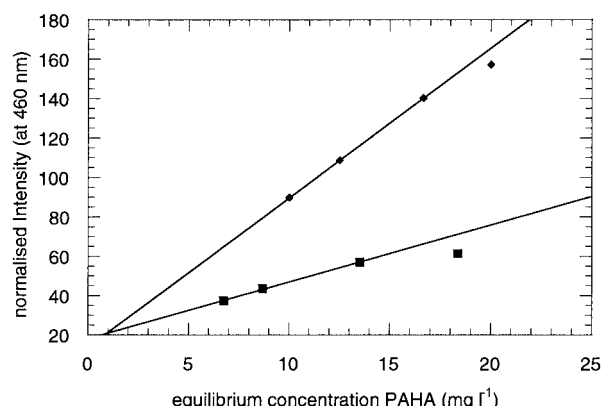


Figure 2. Fluorescence spectroscopy calibration for PAHA and LFA at pH 6 and 0.01 M KNO₃: ■ = PAHA; ◆ = LFA. The lines are obtained by linear regression through the lower concentrations only. The regression coefficients are shown in Table 1.

Table 1. Regression Coefficients of the UV and FS Calibration Lines (pH = 6, 0.01 M KNO₃)^a

	slope (<i>S</i>)	intercept (<i>I</i>)	correlation coefficient
HA _{UV}	0.037108	-0.00971	0.9998
FA _{UV}	0.014316	0.008717	0.9995
HA _{FS}	2.899351	18.15465	0.9997
FA _{FS}	7.590612	13.85867	0.999

^a UV stands for UV spectrophotometry, FS for fluorescence spectrometry.

According to the Lambert–Beer law both the UV absorbance and the FS intensity of a mixture of humic and fulvic acid are due to the contributions of the individual components. For the UV absorbance one finds

$$UV_{\text{mix}} = S_{UV}^{\text{HA}}[HA] + I_{UV}^{\text{HA}} + S_{UV}^{\text{FA}}[FA] + I_{UV}^{\text{FA}} \quad (1)$$

and for the FS intensity:

$$FS_{\text{mix}} = S_{FS}^{\text{HA}}[HA] + I_{FS}^{\text{HA}} + S_{FS}^{\text{FA}}[FA] + I_{FS}^{\text{FA}} \quad (2)$$

where the *S* and *I* parameters can be found in Table 1. By the combined use of fluorescence and UV spectroscopy it is possible to differentiate between humic and fulvic acids in a mixture. Combination of eqs 1 and 2 results in eq 3 for the humic acid concentration

$$[HA] = \frac{FS_{\text{mix}} - S_{FS}^{\text{FA}}UV_{\text{mix}} - C_1}{C_2} \quad (3)$$

where *C*₁ and *C*₂ are constants depending on the calibration coefficients shown in Table 1

$$C_1 = -I_{FS}^{\text{HA}} - I_{FS}^{\text{FA}} + S_{FS}^{\text{FA}}(I_{UV}^{\text{HA}} + I_{UV}^{\text{FA}}) \quad (4)$$

and

$$C_2 = S_{FS}^{\text{HA}} - S_{FS}^{\text{FA}}S_{UV}^{\text{HA}} \quad (5)$$

Once [HA] is found eq 1 or 2 can be used to calculate the fulvic acid concentration. The above-described procedure was tested with mixtures of known composition, ranging in mass ratio from 1:3 to 3:1. The calculated UV absorbances and FS intensities deviated less than 3% from the measured ones; see Table 2.

Adsorption Competition and Kinetics. In Figure 3 the total adsorption and the adsorption of the individual components, PAHA and LFA, are shown at pH = 6 and 0.01 M KNO₃ as a function of time. The concentrations of both components are calculated with eqs 1–5. The

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Table 2. Correlation between the Measured and the Calculated UV Absorbances and FS Intensities for PAHA/LFA Mixtures with an Overall Concentration of the Mixtures of 20 mg L⁻¹ ^a

PAHA: LFA ^a	UV _{measured} (abs at 254 nm)	FS _{measured} (I at 460 nm)	UV _{calculated} (abs at 254 nm)	FS _{calculated} (I at 460 nm)
3:1	0.598	93.2	0.583	91.5
2:1	0.558	99.2	0.550	102.3
1:1	0.500	110.7	0.484	113.8
1:2	0.427	124.4	0.418	126.2
1:3	0.376	131.8	0.385	132.5

^a The calculations are based on eqs 3 and 1 or 2, with *S* and *I* parameters as quoted in Table 1.

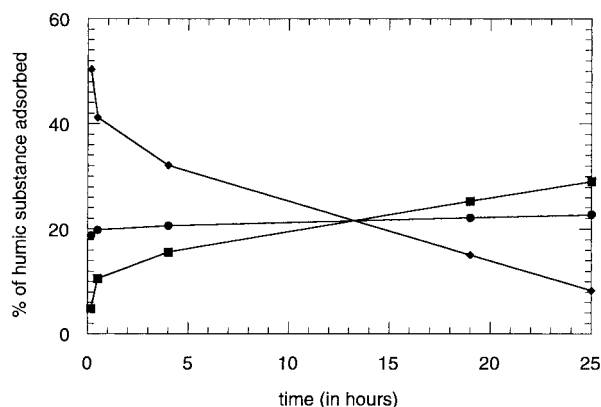


Figure 3. Adsorption kinetics for a mixture of 16 mg L⁻¹ PAHA and 7 mg L⁻¹ LFA, at pH 6 and 0.01 M KNO₃. At the y-axis the percentage adsorbed of the total amount present is given as a function of the time the suspension was allowed to equilibrate. ■ = PAHA; ◆ = LFA, and ● = the mixture of both humic substances.

results are expressed as a percentage of the total available amount of the components. Although the system is mildly shaken to speed up the adsorption, diffusion of the molecules through a stagnant layer near the surface is important. Initially LFA is preferentially withdrawn from the solution, because the diffusion rate of LFA is considerable larger than that of PAHA. For instance, after 15 min 50% of the available LFA is adsorbed, compared to 5% of PAHA. However, when the time proceeds, the adsorbed amount of PAHA increases and that of LFA decreases, clearly PAHA adsorbs preferentially and it displaces the LFA molecules from the surface. A similar preference has been reported by Davis and Gloor.¹⁷ After 13 to 14 h about 23% of each of the humics is adsorbed. However, the exchange continues, and after 25 h the adsorbed amounts of the single components still change at the same rate as after 5 h. Apparently the exchange is not slowing down the displacement process and extrapolation of the fulvic acid line indicates that the equilibrium situation will be reached after about 30 h. Contrary to the behavior of the individual components the total adsorbed amount increases only slightly after the first half hour, and although the equilibrium situation is not yet reached, the adsorbed amount is not far from its equilibrium value.

The large PAHA molecules displace the small LFA molecules mainly for entropical reasons: upon adsorption of a given amount in milligrams the loss of translational entropy is smaller for PAHA than for LFA. The experiment shows that the adsorption of LFA is reversible. For PAHA this conclusion cannot be drawn on the basis of Figure 3. However, in a separate experiment nearly complete desorption of PAHA adsorbed at pH = 4 could

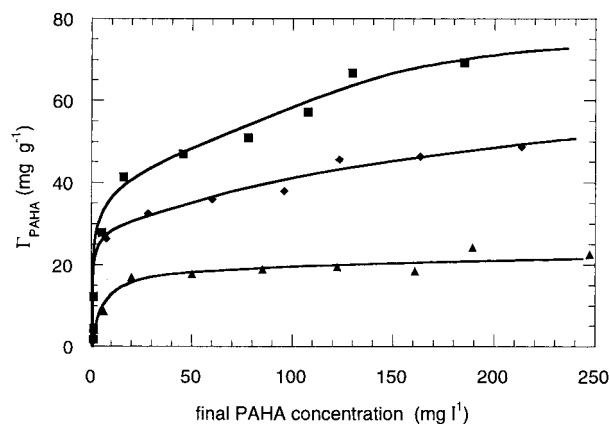


Figure 4. Adsorption isotherms of PAHA on hematite B at 0.01 M KNO₃, effect of pH on the adsorption isotherms: ■ = pH 4; ◆ = pH 6; ▲ = pH 9.

be achieved by increasing the pH to 10. A detailed study on the desorption of PAHA as a function of pH has been made by Avena and Koopal.³⁸

Generalizing the above findings we may conclude that (1) in the (near) equilibrium situation high molecular weight humics adsorb preferentially over low molecular weight humics and (2) the adsorption of humics is reversible.

Adsorption Isotherms of PAHA. In general, both humic and fulvic acids are mixtures of similar molecules with a broad molecular weight distribution.⁴⁻⁶ Above an "artificial", high polydispersity was introduced to study the adsorption fractionation and the displacement process. This method was applied because it is not possible with simple spectroscopic means to measure the concentration of the different molecular weight fractions of a single fulvic or humic acid sample directly. However, the adsorption fractionation and displacement processes observed for the extremely polydisperse mixture will also occur for a single humic acid, like PAHA, that is polydisperse in size in itself.⁶ The polydispersity effects should therefore also occur when studying the adsorption of PAHA.

Figure 4 shows the adsorption isotherms of PAHA on hematite B at pH = 4, 6, and 9 and 0.01 M KNO₃. Concentrations were measured after an incubation time of 18 h using UV spectroscopy only. Although full equilibrium is not yet reached after this period (compare Figure 3), the adsorbed amounts will be close to their final values. The increase in adsorption with decreasing pH is quite common^{22,39,40} and has been discussed extensively in part 1 of this series.²⁵ The adsorbed amount is determined by Coulombic and specific interactions and the loss of conformational entropy of the adsorbed PAHA. The considerable adsorption at pH 9, the pristine point of zero charge of hematite B, underlines the importance of surface complexation and hydrophobic effects. The simple fact that the adsorption is pH dependent shows that the Langmuir equation is far too simple to describe the adsorption.

Another phenomenon that needs consideration is the shape of the isotherms: although the isotherms are high affinity, the adsorption continues to increase upon raising the PAHA concentration. This phenomenon is common for polydisperse polymers and polyelectrolytes, whereas for monodisperse samples "flat" high affinity isotherms

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are expected.^{8-10,13} The effect depends on the pH and is most outspoken for pH 4 where the amount adsorbed is the highest. As shown in the previous section, at large incubation times, preferential adsorption of the high molecular weight fraction occurs. For a given surface-area-to-volume ratio (as in the present experiments) the fractionation effect will increase with an increasing PAHA concentration (more high molecular weight material is present). This leads to an increase in adsorption at increasing concentration and it gives the isotherms the characteristic appearance.

For a given humic acid concentration and a decreasing surface-area-to-volume ratio, a similar reasoning applies. The larger the volume is as compared to the surface area, the more high molecular weight material is present per unit area, the stronger the fractionation effect will be, and the higher is the average molecular weight of the adsorbed polyelectrolyte layer. Therefore, it is to be expected that the shape of the isotherms will depend on the surface area-to-volume ratio. For humic acid adsorption this behavior has been shown experimentally by Summers and Roberts.¹⁸ Although these results are obtained with another adsorbent and humic acid, they fully support the view that polydispersity effects are rather important for humic acid adsorption.

The effect of the pH on the shape of the isotherms is typical for polyelectrolytes. Due to the electrostatic interactions the adsorption of PAHA on hematite increases with decreasing pH. This is mainly due to a decrease in lateral electrostatic repulsion and a higher fraction of the adsorbed molecules that is not in contact with the surface. As a consequence the molecular weight dependence of the adsorption increases with decreasing pH. The more strongly the adsorbed amount depends on the molecular weight, the larger is the effect of preferential adsorption on the slope of the isotherm. For low adsorption values in the pseudoplateau region (pH = 9), also the molecular weight dependence of the adsorption is small. In this case the effect of an increasing preferential adsorption with increasing concentration will be small, and a fairly "flat" isotherm results. For high adsorption values in the pseudoplateau region (pH = 4), the molecular weight dependence of the adsorption is large and an isotherm that strongly increases with increasing concentration appears (fractionation strongly affects the adsorbed amount). The fact that the increase in adsorption with increasing polymer concentration is dependent on the pH is a phenomenon that is typical for polyelectrolytes.

We end this section by noting that, in principle, also the results of Gu et al.,^{22,24} who observed a large hysteresis between the adsorption and the desorption isotherm, can be explained by preferential adsorption.

Modeling the Adsorption of Polydisperse Polyelectrolytes. In this section it will be illustrated that the phenomena described above for humic acid adsorption are quite general. Calculations will be made for a bimodal polyelectrolyte mixture and attention will be given to the difference between the isotherms of monodisperse and polydisperse samples, the pH dependence of the shape of the isotherms, the surface-area-to-volume effect, and the adsorption/desorption hysteresis. Moreover, it will be shown that the effects of polydispersity in size are dominant when the two species are not entirely identical with respect to their chemistry or charge.

System Description and Choice of Parameters. The adsorption of weak polyelectrolytes onto a surface with a variable charge can be modeled with the extended self-consistent-field theory,²⁹ which was originally developed by Scheutjens and Fleer for the adsorption of polymers.

In principle, the theory describes the adsorption of flexible polyelectrolyte molecules, composed of different segments, to a rigid, charged, surface. Upon adsorption the polyelectrolyte molecules will change their coil conformation and form an adsorbed layer with trains of segments in direct contact with the surface and loops and tails protruding in the solution. The calculation of the conformation statistics of the polyelectrolyte molecules is based on a first-order Markov approach. The interactions between the polymer segments, the electrolyte solution, and the surface are accounted for on the basis of mean field nearest neighbor interactions. The Coulombic interactions near the surface are calculated on the basis of a multi-Stern-layer model. Basically the theory calculates, by minimizing the free energy of the system, iteratively, the equilibrium distribution of the different segments in the potential field exerted by the presence of the segments themselves. For details on the theory we refer to the review by Fleer et al.¹³ and to refs 27-29. Below we specify the system description and the parameter choice.

For the SCF calculations all components are placed in a cubic lattice consisting of M layers parallel to the surface (S) and numbered from $z = 1$ to $z = M$. The distance, d between two adjacent layers is fixed at 0.311 nm and $M = 100$ unless specified otherwise. At $z = 0$ the surface (an impenetrable wall) is placed. At the other boundary at $z = 101$, reflecting conditions are assumed. The protons present are dimensionless and determine the pH of the system. Salt ions (Na^+ , Cl^-), water molecules (W), polymer segments (U, C, P), and surface units (S) occupy the unit cells of the system. The dielectric constant ϵ_r of all units equals 80. The total amount of polyelectrolyte in the system is expressed in equivalent monolayers, θ . Each segment type x ($x = \text{U}, \text{C}, \text{P}, \text{Na}^+, \text{Cl}^-, \text{W}, \text{S}$) experiences a potential $u_x(z)$ at a distance $z \cdot d$ from the surface, $u_x(z)$ is normalized with respect to the bulk solution, and thus $u_x(M) = 0$. The potential $u_x(z)$ is a free energy composed of all energetic and entropic interactions a segment undergoes; it depends on the average surroundings, through nearest neighbor segment-segment interactions and long-range electrostatic interactions. The Flory-Huggins $\chi_{x,y}$ parameters⁴¹ describing the nearest neighbor interactions between the segments x and y are all put equal to zero. This means that the polyelectrolytes are in a good solvent. The χ parameters of all segments with the surface are also zero, except $\chi_{\text{C,S}}$, which is set to -15. This choice indicates that only the C segments have a specific affinity for the surface.

The surface is composed of two types of groups, a charged and a neutral one in the ratio of 1:1. The charged group has a pK of 9 and is titrated from 0.5 to -0.5 according to the one pK model.⁴²

The polyelectrolytes are taken to be linear with three types of segments: U, C, and segment P. Segment U is uncharged, segment C has a pK of 4, and segment P a pK of 10. The chargeable segments of the polyelectrolyte are titrated from 0 to -1.

The effect of the polydispersity on the adsorption is illustrated through calculations for a simple mixture of two monodisperse samples. For a more general approach we refer to Roefs et al.⁴³ The first polyelectrolyte (P_1) is

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(43) Roefs, S. P. F. M.; Scheutjens, J. M. H. M.; Leermakers, F. A. M. *Macromolecules* **1994**, *27*, 4811.

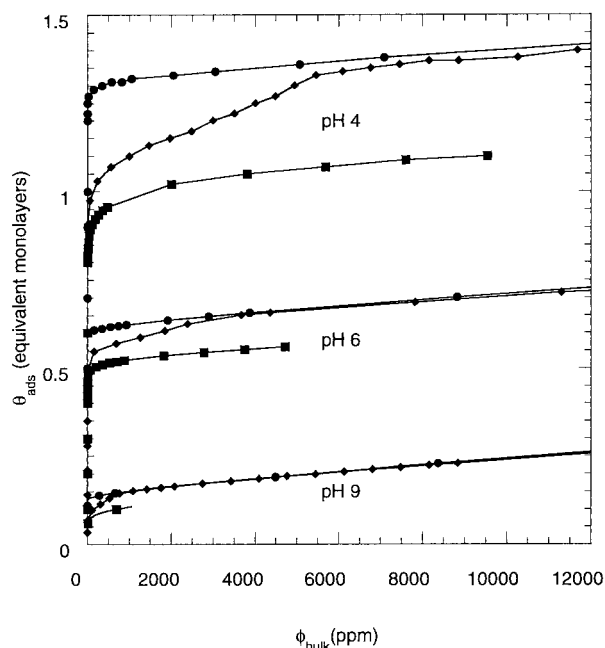
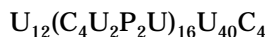
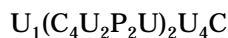


Figure 5. Calculated adsorption isotherms for P_I and P_{II} and a bimodal mixture of P_I and P_{II} at 0.01 M salt: \bullet = P_I ; \blacksquare = P_{II} ; \blacklozenge = mixture of P_I and P_{II} . The isotherms are given for three different pH values as indicated.

a chain with the following composition:



The arbitrary and complex structure of P_I is intended to mimic a simple humic acid with two types of charged segments, representing the carboxylic (C) and phenolic (P) groups, together with two blocks of uncharged segments. The composition of the second polyelectrolyte (P_{II}) is



As compared to P_I the repeating block is decreased from 16 to 2, and considerably less uncharged segments are present. P_{II} is intended to represent a fulvic acid. The number of segments, and thus its molecular weight, is about 8 times smaller than that of P_I . Moreover, the proportion of the chargeable segments C and P is relatively high.

The surface-area-to-volume ratio is given by $S/V = (Ml)^{-1}$, where l equals d . Standard calculations are made for $M = 100$; some calculations are made for higher values of M to illustrate the effect of S/V on the isotherms.

SCF Modeling Results. The adsorption isotherms of P_I and P_{II} at three different pH values and a salt concentration of 0.01 M are presented in Figure 5. The adsorption, θ_{ads} , is expressed in equivalent monolayers; the "concentration" is expressed as volume fraction, ϕ_{bulk} , in ppm. The individual isotherms are "high affinity" and relatively "flat", typical for monodisperse polyelectrolytes. The level of the adsorption is for both polyelectrolytes increasing with decreasing pH; this is mainly due to the decrease of the polyelectrolyte charge. This trend compares very well with that observed for PAHA.

In Figure 5 the three isotherms obtained for a mixture of P_I and P_{II} are also shown. The weight fraction of P_I within the mixture equals 5/7. The isotherms for the mixture show an initial high affinity part, where the surface accommodates practically speaking all available

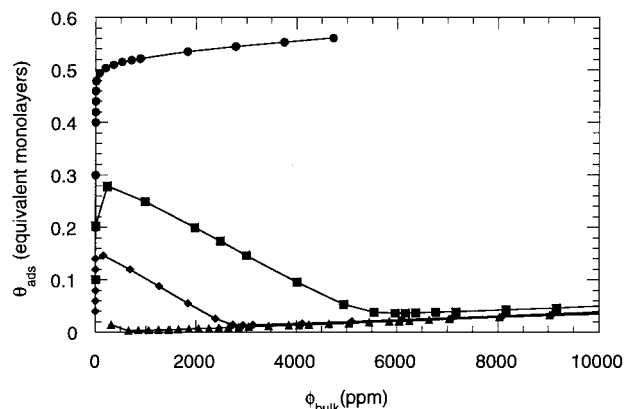


Figure 6. Calculated adsorption isotherms of P_{II} for a bimodal mixture of P_I and P_{II} at 0.01 M salt: \blacksquare = pH 4; \blacklozenge = pH 6; \blacktriangle = pH 9; \bullet = adsorption isotherm at pH 6 in the absence of P_I .

polyelectrolyte molecules. When the pseudoplateau level of P_{II} is reached, the overall polyelectrolyte volume fraction starts to build up and the isotherm increases gradually until it reaches the pseudoplateau level of P_I . The gradual increase in the low volume fraction range is due to replacement of P_{II} by P_I . When all P_{II} molecules are replaced, the adsorption level of P_I is reached. The transition from the level of the isotherm of P_I at very low ϕ_{bulk} to that of the isotherm of P_{II} at higher values of ϕ_{bulk} gives the isotherm of the mixture its specific shape. The increase of the isotherm is most profound at low pH where the adsorption values of the two components are high and relatively far apart. Due to the large difference between the isotherms complete displacement of the small molecule fraction occurs only at a relatively large equilibrium concentration. At pH 9 the difference between the two isotherms is small and hence the polydispersity effect is small. The trends observed in Figure 5 agree very well with the observed trends for PAHA; compare Figure 4.

To demonstrate the displacement of P_{II} in a very clear way, the adsorption isotherms of P_{II} from the mixture at the three pH values are presented in Figure 6. The isotherm of pure P_{II} at pH 6 is shown as reference. The adsorbed amount of P_{II} decreases with increasing overall concentration of the mixture. At high concentrations the entire adsorption of P_{II} nearly vanishes. From Figure 6 follows that the final pseudoplateau in Figure 5 does not coincide exactly with that of pure P_I . The adsorption from the mixture is always lower than that of pure P_I . This is due to the fact that the total equilibrium concentration is plotted rather than the equilibrium concentration of P_I .

From the results presented in Figure 5 and Figure 6 it also follows that desorption by dilution hardly occurs for a mixture of polyelectrolytes. This is most easily explained for the conditions that the adsorption from the mixture approximates the adsorption level of P_I . Once the adsorption has reached this level, the adsorbed layer contains practically speaking only P_I . In this case the desorption upon dilution isotherm will follow the adsorption isotherm of the high molecular weight species P_I . That is to say, the desorption isotherm of the polydisperse mixture will approximately coincide with the flat adsorption isotherm of P_I . This explains that a strong hysteresis loop will occur between the adsorption and the desorption isotherm.

Another consequence of preferential adsorption is that the appearance of the isotherm plotted as adsorption versus concentration or volume fraction of polyelectrolyte in solution becomes a function of the surface-area-to-volume ratio, S/V . The larger this ratio is, the higher the

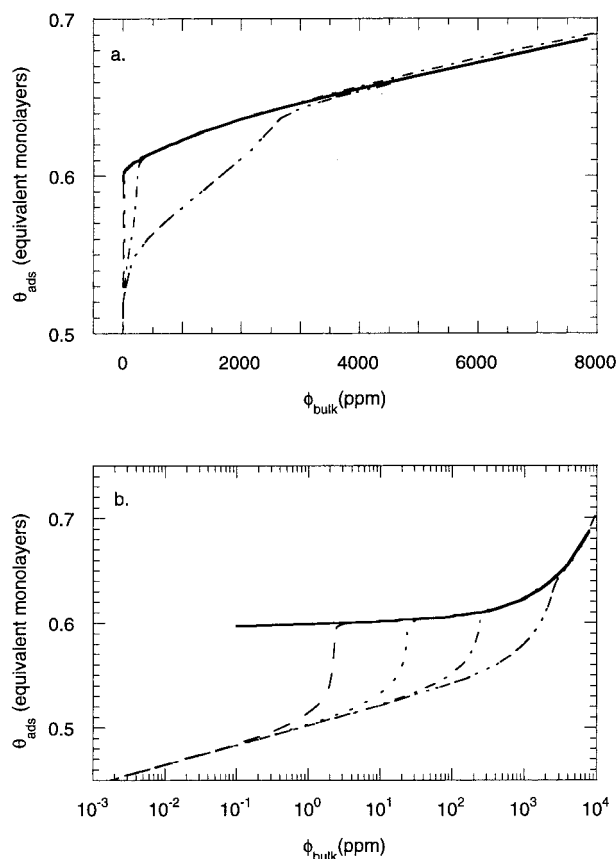


Figure 7. Four adsorption isotherms at different S/V ratios for a bimodal mixture of P_I and P_{II} at $\text{pH} = 6$ and 0.01 M salt: \cdots , $S/V = (100 \text{ l})^{-1}$; $-\cdot-$, $S/V = (1000 \text{ l})^{-1}$; \cdots , $S/V = (10000 \text{ l})^{-1}$; $---$, $S/V = (100000 \text{ l})^{-1}$; $-$, desorption isotherm. In panel a the volume fraction is plotted on a linear scale, and in panel b the volume fraction is plotted on a logarithmic scale.

overall concentration or volume fraction has to be before the surface is "saturated" with the largest molecules. This is illustrated in Figure 7 for four S/V ratios varying from $(100 \text{ l})^{-1}$ to $(100.000 \text{ l})^{-1}$. The total amount of polyelectrolyte in the system is one equivalent monolayer. In Figure 7a the volume fractions are plotted on a linear scale and in Figure 7b on a logarithmic scale. It can be observed that with increasing S/V it takes a higher overall bulk volume fraction to displace the small molecules from the surface. Therefore, for high surface-area-to-volume ratios the increase of the isotherm with increasing volume fraction in solution persists up to very high volume fractions. The final level of the adsorption reached is in all cases that of P_I , which is independent of S/V . The solid line in Figure 7 represents a desorption isotherm (lowest value for $S/V = (1.000.000 \text{ l})^{-1}$) that follows the individual isotherm of P_I .

Conclusions and Remarks

Following the adsorption of a mixture of LFA and PAHA in time it was observed that the relatively small LFA molecules adsorb quickly but that the initially adsorbed LFA is replaced in the course of time by the larger PAHA molecules. Evidently, in the (near) equilibrium situation, at a nonporous surface, larger humic molecules adsorb preferentially over the smaller ones and the adsorption of humic substances is largely reversible.

Preferential adsorption of the high molecular weight fraction within a single humic acid sample is of importance for the shape of the isotherms and for the effect of the pH. The effect of the surface-area-to-volume ratio on the humic acid adsorption as described by Summers and Roberts¹⁸ and the hysteresis between the adsorption and desorption upon dilution isotherms as found by Gu et al.^{22,24} can also be explained by polydispersity effects. As a consequence of the adsorption fractionation humic acids will be bound mainly to the immobile phase, whereas fulvic acids remain in solution. This explains that relatively high concentrations of hydrophobic contaminants that are mainly bound by the humic acid fraction are found in sediments of rivers and other waters.⁴⁴

Calculations with the SCF theory for the adsorption of a mixture of two acidic polyelectrolytes that differ mainly in molecular weight to a hematite-like surface with a variable charge show that the trends observed for humic acid are quite general. Preferential adsorption of the high molecular weight fraction over the low molecular weight fraction occurs, similarly as for uncharged polymers. This leads to an increase in adsorption with increasing polyelectrolyte concentration, only at high concentrations the isotherms level off when the largest molecules are exclusively adsorbed. Similarly the surface-area-to-volume ratio affects this concentration, the higher this ratio, the larger is the polyelectrolyte concentration where the isotherm levels off. This adsorption behavior indicates that there should be a hysteresis between the polyelectrolyte adsorption isotherm and the desorption upon dilution isotherm.

The calculations also show that the shape of the isotherms is strongly dependent on the pH. The higher the adsorbed amounts are at a given polymer concentration, the larger is the effect of preferential adsorption on the isotherms. These effects are typical for polyelectrolyte adsorption and indicate that polydispersity effects are more complicated for polyelectrolytes than for uncharged polymers.

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