Adsorption and Radical Stabilization of Humic-Acid Analogues and Pb$^{2+}$ on Restricted Phyllosmorphous Clay

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Huminic substances can significantly alter the characteristics of mineral surfaces,1−5 particularly trace metal sorption.6,7 Organic coatings by humic acids significantly affect the surface electrostatic properties of clays and, hence, influence clay sorption characteristics and flocculation behavior.8,9 Furthermore, there is evidence that organic acids may play a decisive role in catalyzing the dissolution of minerals since metal−organic complex formation might increase the solubility of metals.10−12

The physicochemical mechanisms of the sorption of humics on mineral surfaces are the subject of intensive investigation.1−7,13 Although significant progress has been achieved in this front,14 many cases are not well understood, and our ability to model it is limited. The main difficulties encountered with microscopic modeling stem from the structural heterogeneity and complexity of humic acids.15 Another important factor is that both the humic macromolecules and the mineral oxide surfaces have variable charges, which are determined by H$^+$ ions, that is, pH, and the metal species present.14,15

A viable approach is to examine appropriate small organic molecules as models of the humic macromolecules.16−21 While simple organic acids do not approach the structural and functional complexity of real humic acids, detailed studies have demonstrated that certain important features can be remarkably similar.16−21 In this context, Evanko and Dzombak in a paradigmatic complete survey20,21 showed that small organic acids bearing both carboxy and phenolic groups are appropriate structural models for humic substances mimicking adsorption on goethite.20,21 Analogous studies shed light on more complicated systems concerning the coadsorption of small organic molecules and metal cations, that is, Cu$^{2+}$ and Ca$^+$ on goethite$^{2+}$ or Pb$^{2+}$ on corundum.20 Recently, we demonstrated that some of these simple organic acids such as gallic (3,4,5-trihydroxybenzoic) acid or protocatechuic (3,4-dihydroxybenzoic) acid (see Figure 1) can be appropriate models for the radical properties of humic and fulvic acids.24 Electron paramagnetic resonance (EPR) spectroscopy showed that, at alkaline pH greater than 8, gallic acid (GA) can form stable

Introduction

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Figure 1. Molecular structure of the organic acids used in this work.

needed to describe sorption, and (c) ultimately provide physicochemical insight on the radical formation and stabilization due to sorption onto Laponite.

Materials and Methods

Chemicals. All solutions were prepared with analytical-grade chemicals and purified water (Milli-Q Academic system) with a conductivity of demineralized water of 18.2 μS cm⁻¹ and degassed prior to use. A Pb(NO₃)₂ (Aldrich, >99.5%) stock solution was prepared at a concentration of 500 μM and kept in a polyethylene container at pH <2. A stock solution of gallic acid (Aldrich, >99%), protocatechuic acid (Aldrich, >97%), and 4-hydroxybenzoic acid (Aldrich, >98%) was prepared at concentrations of 2 mM and 200 μM at pH values of 4.85, 4.80, and 4.60, respectively. Ionic strength was maintained at 1 mM with KNO₃ (Aldrich, >99.9%).

A buffer system of 10 mM N-morpholino-ethanesulfonic acid, 4-(2-hydroxyethyl) piperazine-1-ethanesulfonic acid, and tri-s-hydroxyethyl-aminomethane was used for all of the samples, which presented a significant buffer capacity at a PH range of 5–9, with an average value deviation from the adjusted initial value of up to 5%. The pH values were adjusted with small volumes of NaOH or HNO₃ (concentrations of 0.1 and 0.05 N). Screening experiments indicated that, under the conditions of our experiments, the buffer molecules caused no interferences on the adsorption or radical phenomena.

Laponite. Na⁺–Laponite, obtained from Laporte Industries Ltd., has a structural formula of Na₈₃[(Mg₆₋₉)Li₁₋₉Si₄O₁₀(OH)₄]·6H₂O,²⁶ similar to that of the natural clay hectorite. Our sample had a cation exchange capacity (CEC) of 48.1 mequiv/100 g of clay and a Brunauer–Emmet–Teller (BET) surface area of 300 m²/g.²⁷ Stability of Laponite Suspensions. The stability of Laponite in aqueous suspensions has been discussed and analyzed in several publications.³³–³⁵ Under prolonged incubation, that is, up to some weeks in the presence of CO₂, the clay is unstable.³⁴ This effect is severely pronounced at acidic pH lower than 7.³⁴,³⁵ Lair et al.,³⁵ in a careful study, demonstrated that, under controlled conditions, that is, short incubation times (<60 min) and low Laponite concentrations (1 g/L), Laponite degradation is minimal (i.e., <5%, even at acidic pH).³⁵ In our experiments, special care was taken to minimize the possible dissolution of Laponite. To assess the possible dissolution of Laponite clay, Mg²⁺ release was measured by graphite furnace-atomic absorption spectroscopy (Perkin-Elmer AA700). All incubation experiments were performed in CO₂-free solutions made from ultrapure Milli-Q water and exhaustively degassed with pure N₂ (99.999%) gas. Stock solutions of 1 g/L of Laponite were prepared in CO₂-free solutions at a pH >10 and stored at 4 °C. At this pH, which is near the point of zero net proton charge (PZNPC), the Laponite suspension remained in liquid phase, that is, did not form gel, for more than a week. This is in agreement with the revised state diagram for aqueous suspensions of Laponite.³³,³⁶ On the basis of detailed measurements of Mg²⁺ release, we conclude that, under our experimental conditions, the dissolution of Laponite did not exceed 5%, in agreement with Lair et al.³⁵ This amount was taken as an error percentage in the theoretical modeling of the adsorption and surface reaction phenomena.

Analytical Determination of Pb and Organic Anions. Stripping Voltammetry. The concentrations of Pb in the aqueous phase were determined by anodic stripping voltammetry by using a Trace Master-5-MD150 polarograph by Radiometer Analytica. The measuring cells were borosilicate glass cells from Radiometer. The working electrode was a hanging mercury drop electrode, with a Hg drop with 0.4 mm diameter generated by a 70 μm capillary. The reference electrode was an Ag/AgCl electrode with a double liquid

junction. The counter electrode was a Pt electrode. Initially, before the stripping step, N₂ gas (99.999% purity) was passed from the measuring solutions to remove any trace O₂. During this step, the solution was under continuous stirring at 525 rpm. During the stripping step, the solution was not stirred. Square wave (SW) measurements were performed in the anodic direction, that is, square wave anodic stripping voltammetry was used, to quantify Pb²⁺ ions. Typically, under our experimental conditions, 10⁻⁶ M Pb(NO₃)₂ in 0.01 M KNO₃ resulted in a current of Ip = 0.7 μA, Ep = −340 mV at pH 5.4 because of Pb²⁺ ions, while, at pH 8.5, a typical signal was Ip = 0.3 μA, Ep = −390 mV because of Pb(OH)²⁺ ions.²⁹,³⁸

In certain experiments, cathodic stripping voltammetry, that is, SW-CSV, was used to determine the concentration of gallic acid. Typically, 25 × 10⁻⁶ M GA in 0.01 M KNO₃ resulted in a current of Ip = 2.4 μA, Ep = −540 mV at pH 8.5. while, at pH 5.7, a typical signal was Ip = 1.7 μA, Ep = −410 mV.

**UV–Vis Spectroscopy.** Aqueous-phase concentrations of the organic acids were measured with UV–vis spectroscopy with a Perkin-Elmer Lamda 35 double beam UV–vis instrument. For each organic acid, a dilute solution (typically 0.01 mM) was analyzed across the UV–vis spectrum to determine an appropriate wavelength for analysis. Samples where brought to the same pH value for measuring solutions to remove any trace O₂. During this step, the solution was continuously stirred and purged by nitrogen gas. When the pH of the solution reached the range of interest, were prepared and analyzed with each batch experiments were performed for selected compounds and conditions. On the basis of these experiments, no significant losses were observed. The preparation of the blank samples was similar to that of the sorption samples, except that Laponite was not added to the blanks. For the initial experiments with each organic acid, the supernatants were analyzed for dissolved Mg²⁺ to determine whether significant dissolution of the solid occurred in the presence of the organic acid. We underline the importance of the exclusion of O₂ in the adsorption experiments described in this section to prevent the formation and polymerization of radicals.²⁴ In a separate set of adsorption experiments, the samples were deliberately exposed to O₂ to study, by EPR, the radical formation and stabilization properties. The EPR data is discussed in the next section of this paper.

**Surface Charge Properties of Laponite.** The surface charge properties of Laponite suspensions were evaluated by two methods: potentiometric acid–base titration and mass titration.²⁴

**Potentiometric Titration of Organic Acids.** Potentiometric titrations for gallic, 4-hydrobenzoic, and 3,4-dihydroxybenzoic acid were performed by using a Metrohm 794 Basic Titrino as described previously.²⁴ The concentration of gallic acid, 4-hydrobenzoic acid, and 3,4-dihydroxybenzoic acid were 20 mM in 25 mL of Milli-Q water. The solution was exhaustively stirred and purged by pure N₂ gas to deplete O₂ to avoid the formation of radicals.²⁴

**Adsorption Experiments at Low Concentrations.** A fixed amount of Laponite suspension and sorbate spike, along with varying amounts of HNO₃ or NaOH, were added to 20 mL polyethylene tubes to yield a range of pH values. For ternary experiments, preliminary tests showed that, within our experimental errors, the sequence of organic and Pb addition did not alter the adsorption edge. Stock solutions were maintained strictly O₂−free by purging with nitrogen to exclude uncontrolled radical formation phenomena.²⁴ The reaction tubes were capped (after headspace was purged with N₂), and stirred for 60 min, an amount of time found to be adequate for adsorption equilibrium to be established. After the equilibration period, the pH of the solution was measured with a Metrohm microelectrode. Replicate sorption experiments were performed for selected compounds and conditions. The X-ray diffraction (XRD) data showed significant intercalation. The XRD data show that (a) for a ratio of up to 6 mM gallic acid and 1 g/L Laponite, the clay retains its periodic phyllophorous structure, and (b), under these conditions, the presence of Pb ions does not disrupt the structure. On the basis of these observations, we proceed in the following in a more detailed study of the surface charge properties and the adsorption edge of hydroxybenzoic acids and Pb. Taking into account the XRD data, the adsorption experiments were performed at low concentrations, that is, in the micromolar (10⁻⁶ M) range to ensure the absence of surface precipitation or the formation of polynuclear Pb(OH)₆ species. This protocol allowed us to analyze the pH-dependent adsorption experimental data by surface complexation modeling with the underlying assumption that the clay structure is kept intact. An ionic strength of IS = 0.001 (10⁻³ M KNO₃) was used in the adsorption experiments.
mixture for 12 h, the Lap–GA aggregates were separated by centrifugation, washed with water, and air-dried by spreading on glass plates. In addition, 100 mg of a Lap–GA sample (with \( R = 6 \) mM gallic acid/g Lap) were dispersed in water, and the resulting suspension was reacted with 5 mL of an aqueous 0.01 M \( \text{Pb(NO}_3\text{)}_2 \) solution (1.2 times the CEC). The sample was then stirred for 12 h, and the final sample was obtained in powder form as above (Lap–GA + \( \text{Pb}^{2+} \)). Similarly, 10 mL of a 1.0 wt% aqueous lead–Laponite (\( \text{Pb}^{2+} \)–Lap) suspension was reacted with 5 mL of an aqueous 0.006 M gallic acid solution (\( \text{Pb}^{2+} \)–GA) in 1.1, 1.2, and 1.3 molar ratios were prepared by reacting aqueous solutions of \( \text{Pb(NO}_3\text{)}_2 (\text{0.0375 M}) \) and gallic acid (0.025 M). The 1.1 \( \text{Pb}^{2+} \)–GA complex (40 mg, 1.5 times the CEC) was then reacted under stirring with an aqueous clay suspension (1.0 wt%), centrifuged, washed twice with distilled water, and finally air-dried (Lap + \( \text{Pb}^{2+} \)–GA).

**XRD Experiments.** X-ray powder diffraction data were collected on a D8 Advance Bruker diffractometer by using \( \text{CuK}_α (40 \text{ kV}, 40 \text{ mA}) \) radiation and a secondary beam graphite monochromator. The patterns were recorded in the 2\( θ \) range from 2 to 80\(^°\), in steps of 0.02\(^°\) and a counting time of 2 s per step.

**Electron Paramagnetic Resonance.** Continuous-wave EPR spectra were recorded at liquid helium temperatures with a Bruker ER 200D X-band spectrometer equipped with an Oxford Instruments cryostat. The microwave frequency and the magnetic field were monitored by a counting time of 2 s per step.

**Adsorption Modeling.** Surface complexation models (SCMs) can successfully model the adsorption of ions on charged surfaces by assuming that the adsorption involves both a coordination reaction at specific surface sites and an electrostatic interaction between adsorbing ions and the charged surface. The true physical meaning of the surface species and the limitations of the model-derived parameters have been discussed in the literature. At the molecular level, the true molecular identity of the surface species derived by SCMs have to be verified by appropriate in situ physicochemical methods. Nevertheless, the surface species information derived by phenomenological SCMs can serve as comparative studies since they relate to measurable physicochemical parameters, that is, pH and charge, which determine the observed trends. In the present case, the aim of the modeling was (a) to provide a physicochemical basis for understanding the observed phenomena, (b) to derive a consistent set of equilibrium parameters that can be used for a comparative discussion with other pertinent systems, and (c) to ultimately understand the radicals’ formation and stabilization within this speciation formalism. Several reasonable reactions have been tested, including (a) ligand exchange (e.g., the ligation of an organic anion onto surface sites accompanied by an OH\(^−\) release), (b) electrostatic adsorption at the variable charge sites, or (c) electrostatic adsorption at permanent charge sites. Because of the low concentration of \( \text{Pb(NO}_3\text{)}_2 \) (10\(^−6\) M), on the basis of speciation calculations according to the hydrolysis properties of Pb in aqueous solutions, polymeric \( \text{Pb(OH)}_n \) species were not expected to form. In this context, surface the precipitation of Pb was not considered in the modeling of the adsorption, in accordance with previous extended X-ray absorption fine structure (EXAFS) studies for Pb adsorption on other clays such as montmorillonite. Ligand exchange reactions were discarded on the basis of the unacceptable fit obtained if OH\(^−\)/organic exchange was included, as well as the experimental observation of a slight pH decrease, indicating H\(^+\) release upon adsorption of Pb or organics in unbuffered Laponite solutions. The equilibrium constants of Pb\(^{2+}\) reacting with the surface

### Table 1. Summary of Laponite Properties

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>BET surface area (m(^2)/g) *</th>
<th>CEC (mequiv/100 g)</th>
<th>pH(_{\text{PZNPC}}) *</th>
<th>Surface site density, ( N'_s ) (sites/nm(^2)) = mol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>20(^+)</td>
<td>300(^+)</td>
<td>48.1(^+)</td>
<td>10.05 ± 0.3 IS</td>
<td>3.2 IS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.5 ± 0.3 IS</td>
<td>1.1 IS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( p\text{K}_a\text{int} = 10.4 ± 0.3 IS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( p\text{K}_a\text{int} = -9.7 ± 0.3 IS)</td>
<td></td>
</tr>
</tbody>
</table>

* Reference 27. This work.

**X-ray Diffraction.** The effect of gallic acid loading to the d\(_{001}\) spacing of Laponite clay was studied by means of X-ray powder

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Gallic Acid and Pb\(^{2+}\) Adsorption on Laponite Clay

![Figure 2](image_url)

Figure 2. XRD patterns of Laponite films loaded with gallic acid at different ratios R.

**Table 2.** \(d_{001}\) Values and Basal Spacing of Laponite Clay Composites

<table>
<thead>
<tr>
<th>sample</th>
<th>(d_{001}) (Å)</th>
<th>interlayer space (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})–Lap</td>
<td>13.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Lap–GA</td>
<td>15.4</td>
<td>5.8</td>
</tr>
<tr>
<td>[Pb(^{2+})–Lap] + GA</td>
<td>15.5</td>
<td>5.9</td>
</tr>
<tr>
<td>[Lap–GA] + Pb(^{2+})</td>
<td>15.5</td>
<td>5.9</td>
</tr>
<tr>
<td>Cu(^{2+})–Lap</td>
<td>13.8(^a)</td>
<td></td>
</tr>
<tr>
<td>[bis(oxazoline)Cu–Cl(_2)]–Lap</td>
<td>18.4(^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Reference 29.

diffraction. Figure 2 shows the XRD patterns of Laponite loaded with gallic acid at different ratios \(R\) ([mM gallic acid]/[gram of clay]). Basal spacing (interlayer distances) of the clay composites obtained from the \(d_{001}\) peak position of the corresponding XRD patterns are shown in Table 2. The \(d_{001}\) spacing of Laponite gradually increases for \(R\) ratios up to 0.75, and, from this ratio on, it remains stable at 14.1 Å. This value corresponds to an interlayer gallery height of 14.1 – 9.6 = 4.5 Å, where 9.6 Å is the thickness of the clay sheet. The increase in the interlayer spacing may be taken as evidence of the formation of the organoclay by intercalation of the organic molecules in the interlayer space.

Intercalation of gallic acid molecules into a Pb-homoionic Laponite (13.9 Å) gives a \(d_{001}\) spacing of 15.5 Å. Finally, similar \(d_{001}\) spacing (15.4 Å) was observed after the intercalation of Pb\(^{2+}\)–GA complexes into Laponite clay. These data show that the interlayer spacing of Laponite in the final composites (Lap–Pb\(^{2+}\)–GA) is stable (5.8–5.9 Å) and independent from the route and sequence of the addition of the three reactants. This Lap–Pb\(^{2+}\)–GA spacing is smaller than that observed for other metal–organic complexes intercalated into Laponite sheets [e.g., (bis(oxazoline)Cu–Cl\(_2\)]–Lap].\(^{29}\) On the other hand, the spacing of 5.9 Å is comparable with the shorter dimension of the van der Waals cloud for the GA/Pb complex calculated by density functional theory (DFT).\(^{24}\) In this context, the XRD data may be taken as an indication that the GA–Pb complex is intercalated, with its longer dimension being parallel to the Laponite sheets.

**Surface Charge of Laponite.** The mass titration experiments for Laponite are shown in Figure 3A,B for two values of ionic strength. In nonbuffered solution, the pH gradually changes with the addition of solid and asymptotically approaches a limiting value. The direction of the pH depends on the starting pH of the solution. Therefore, the pH where solid addition does not produce any change in the pH can be estimated by interpolation. This value can be taken as a good approximation of the PZNC.\(^{41,43}\) For Laponite, the data in Figure 3A,B give pH\(_{PZNPC}\) = 9.8 for IS = 0 and pH\(_{PZNPC}\) = 9.5 for IS = 0.1M KNO\(_3\). In the following, the value pH\(_{PZNPC}\) = 9.8 for IS = 0 is used together with eq 1 to consistently fit the acid–base potentiometric titration data for Laponite, which are shown in Figure 3C. The best fit is obtained by using the intrinsic protonation constants:

\[
\equiv\text{SOH} \rightleftharpoons \equiv\text{SO}^- + \text{H}^+ \log K_{\text{intrinsıc}} = -9.7 \pm 0.3 \quad (2)
\]

\[
\equiv\text{SOH} + \text{H}^+ \rightleftharpoons \equiv\text{SOH}_2^+ \log K_{2\text{intrinsıc}} = 10.4 \pm 0.3 \quad (3)
\]

which are also listed in Table 3 (reactions 6a and 6b). To verify the consistency between these values and the mass-titration data, we see that

\[
\text{pH}_{\text{PZNPC}} = \frac{1}{2} (|pK_{\text{intrinsıc}}| + |pK_{2\text{intrinsıc}}|) = 10.0 \pm 0.3 \quad (4)
\]

which is consistent with the value of 9.8 from the mass-titration data. This value for Laponite is similar to the point of zero charge (PZC) value of ~10 for hectorite.\(^{54}\) On the basis of these experiments, we conclude that, at pH < 10, where all of our adsorption experiments where performed, the surface of Laponite is positively charged since it is dominated by the \(\equiv\text{SOH}_2^+\) surface sites. The X\(^-\)–site concentration shown in this plot was calculated from the fit of the Pb\(^{2+}\) adsorption data that we discuss in the following. The very low concentration of the X\(^-\) sites as, shown in Figure 3D, is intimately related to the low CEC of Laponite (48 mequiv/100 g), and it results in low values of permanent charge density \(\sigma_0 = f[X^{-}]/s = -1.5 \times 10^{-3} \text{C/m}^2\), for s = 300 m\(^2\)/g. Including this \(\sigma_0\) value in the calculation of the zero point charge, the formula of Kraepiel and Morel\(^{22}\) for \(pK_1 = -9.7, pK_2 = 10.4\) gives a PZC of 10.31 for IS = 0.001, and 10.14 for IS = 0.01, which is within the ±0.3 units given in Table 1 for the PZNPC of Laponite. Thus, the permanent charge has a limited, although nonzero, effect on the PZC of Laponite. Given that a more detailed investigation of this topic is out of the scope of the present work, to keep the present discussion to a tractable level, we hereafter use the parameters listed in Table 1.

Laponite is a trioctahedral silicate clay with each layer consisting of two outer tetrahedral sites and one central octahedral site. It is a small particle size clay, that is, 0.02 \(\mu\)m in diameter.\(^{25,27}\) The layer negative charge arises from the isomorphous substitution of some Mg\(^{2+}\) in the octahedral sheet by Li\(^+\) cations. The small particle size of Laponite leads to relatively more edge area than face area compared to larger particle clays. In hectorite, the main octahedral surface sites for proton adsorption should be the Mg\(^{2+}\)–O–Si, then the Mg\(^{2+}\) and Mg\(^{2+}\)–O–Mg sites.\(^{54}\) The protonation–deprotonation of the Mg\(^{2+}\)–O–Mg sites is controlling the hectorite clay charge near the PZC which is near pH 10.\(^{54}\) This is very close to the PZC, that is, 9.8, we find for Laponite. Accordingly, on the basis of the structural similarity between hectorite and Laponite, we may postulate that the Mg\(^{2+}\)–O–Mg sites control the pH-dependent surface charge on Laponite.

**Adsorption Experiments.** Laponite–Organic Anions. The adsorption edge of protocatechuic and gallic acid on Laponite is displayed in Figure 4A,B, respectively. The adsorption of

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hydroxybenzoic acid under comparable conditions was negligible, that is, below 10% (not shown). For both protocatechuic and gallic acid, strong pH-dependent adsorption occurs. At acidic pH values, an ~10% adsorption is observed (see Figure 4), while a steep increase in adsorption occurs at pH > 7. Qualitatively, this adsorption profile can be understood as the convolution of the pH-dependent surface charge of the clay and the pH-dependent deprotonation of the organic acids, for example, according to their pKs values. The pKs values of the organic acids (see Table 3) have been calculated by fitting the potentiometric titration data shown in Figure S1 of the Supporting Information. In the pH range span in the experiment of Figure 4, the clay surface is positive since it is at pH > PZNPC. At pH < 6, only the carboxy groups of the organic acids are negatively charged.

The FITEQL speciation shown by the dashed-dotted lines in Figure 4A provides evidence that the adsorption of the species PrH2O+ at the positively charged surface sites (≡SOH$_2^+$) can account for the observed ~10% adsorption at this pH range. An analogous conclusion can be drawn for gallic acid (Figure 4B). In this case, ≡SOH$_3^+$GAH$_3^-$ is the formed surface species. At pH > 7, the phenolic oxygens of the organics start to deprotonate. In the case of protocatechuic acid, the speciation cannot distinguish between the two deprotonated phenolic oxygens with pKs 8.7 and 9.2, therefore the observed adsorption can be operationally attributed to the formation of the [≡SOH$_2$Pr]$^{-1}$ surface species of the fully deprotonated protocatechuic acid.

In the case of gallic acid, the three phenolic oxygens have a more widespread set of pKs values, that is, between 8.7 and 11.4. Accordingly, the adsorption of the charged gallic acid anions is due to the combined contribution from three surfaces species, namely, the dominant [≡SOH$_2$GAH]$^{-2}$ species together with [≡SOH$_2$GAH]$^{-2}$ and [≡SOH$_2$GA]$^{-1}$ (see Figure 4B). Thus, it is apparent that the pH dependence of the adsorption of the organic anions can be attributed to the positively charged clay sites (e.g., those modeled as ≡SOH$_2^+$). At pH > 9, the number of ≡SOH$_2^+$ sites rapidly diminishes (see Figure 3D), hence the sharp adsorption drop seen in Figure 4B at pH > PZNPC.

The absence of noticeable adsorption for hydroxybenzoic acid is in clear contrast with the adsorption of gallic and protocatechuic acid. Given that, in the pH range of 5–8, hydroxybenzoic acid is in anionic form, structural factors other than electrostatics might be responsible for this effect. On the basis of the structures of the three molecules (see Figure 1) it may be suggested that two adjacent OH groups on the ring are required in order to be adsorbed on the Laponite surface, in addition to the proper charge sign. An analogous effect and similar explanation has been reported for the adsorption of gallic, protocatechuic, and hydroxybenzoic acid on goethite. Similarly, in a more recent attenuated total reflection Fourier transform infrared study, it was shown that the two adjacent OH groups of gallic acid are involved in its binding on TiO$_2$ surface, with the carboxy group playing a secondary role.

Previous adsorption studies on Laponite referred mainly to the adsorption of surfactants. For example, it is found that the level of adsorption of a nonionic surfactant dimethyldodecylamine-N-oxide (DDAO) (~1 g DDAO/g Laponite) at pH 7, 8, and 9 and at various NaCl concentrations is found to be much higher than that of its cationic homologue, dodecyltrimethylammonium. The intercalation of uncharged polar organic molecules such as alcohols and amines by clay minerals is essentially a process in which the organic molecules penetrate the interlamellar space and replace the water associated with the exchangeable interlayer cations. In the case of surfactants, the surface interaction mechanism involves hydrophobic interactions and surface tension phenomena. All these mechanisms are radically different than the low-loading adsorption phenomena studied here, that is, electrostatic interactions at variable charge sites.

Figure 3. Estimation of the surface charge properties for Laponite clay. The arrows mark the PZNPC: (A,B) mass-titration data for IS = 0 (A) and IS = 0.1 KNO$_3$ (B). (C) Potentiometric acid—base titration (symbols) and theoretical fit (solid line) by using surface reactions 6a and 6b in Table 3 and the parameters listed in Table 1. (D) Speciation analysis of the surfaces species derived by using the parameters in Table 1.

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(56) Strawn, D. G.; Sparks, D. J. Colloid Interface Sci. 1999, 216, 257–269.
Table 3. Reactions and the Corresponding Stability Constants (log \( K \)) Used to Fit the Experimental Adsorption Data

<table>
<thead>
<tr>
<th>#</th>
<th>solution reactions</th>
<th>log ( K )</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>( \text{GA}^{4+} + \text{H}^+ \leftrightarrow \text{GAH}^{3+} )</td>
<td>10.92 ± 0.3</td>
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<td>1b</td>
<td>( \text{GA}^{4+} + 2\text{H}^+ \leftrightarrow \text{GAH}_2^{2+} )</td>
<td>22.4 ± 0.3</td>
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<tr>
<td>1c</td>
<td>( \text{GA}^{4+} + 3\text{H}^+ \leftrightarrow \text{GAH}_3^{1+} )</td>
<td>32.2 ± 0.3</td>
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<td>1d</td>
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<td>2a</td>
<td>( \text{PrC}^{3+} + \text{H}^+ \leftrightarrow \text{PrCH}^{2-} )</td>
<td>9.3 ± 0.3</td>
<td>this work</td>
</tr>
<tr>
<td>2b</td>
<td>( \text{PrC}^{3+} + 2\text{H}^+ \leftrightarrow \text{PrCH}_2^{1-} )</td>
<td>17.5 ± 0.3</td>
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<tr>
<td>2c</td>
<td>( \text{PrC}^{3+} + 3\text{H}^+ \leftrightarrow \text{PrCH}_3^0 )</td>
<td>22.0 ± 0.3</td>
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<td>3a</td>
<td>( 4\text{HB}^{2+} + \text{H}^+ \leftrightarrow 4\text{HBH}^{-1} )</td>
<td>9.35 ± 0.2</td>
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<td>3b</td>
<td>( 4\text{HB}^{2+} + 2\text{H}^+ \leftrightarrow 4\text{HBH}_0^0 )</td>
<td>13.9 ± 0.2</td>
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<td>4a</td>
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<td>7.7</td>
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<td>4b</td>
<td>( \text{Pb}^{2+} \leftrightarrow \text{Pb(OH)}_2 + 2\text{H}^+ )</td>
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<td>5a</td>
<td>( \text{GA}^{4+} + 3\text{H}^+ + \text{Pb}^{2+} \leftrightarrow \text{GAH}_3^{2+} \text{Pb}^{0} )</td>
<td>10.0 ± 0.2</td>
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<tr>
<td>5b</td>
<td>( \text{GA}^{4+} + 2\text{H}^+ + \text{Pb}^{2+} \leftrightarrow \text{GAH}_2^{1+} \text{Pb}^{0} )</td>
<td>25.0 ± 0.4</td>
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<td>5c</td>
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<td>5e</td>
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<td>5f</td>
<td>( \text{GA}^{4+} + \text{Pb}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{GAHPbOH}^{2+} + \text{H}^+ )</td>
<td>22.0 ± 0.4</td>
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<tr>
<td>5g</td>
<td>( \text{GA}^{4+} + \text{Pb}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{GAH}_2\text{PbOH}^{3-} )</td>
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<td>6a</td>
<td>( \equiv \text{SOH} \leftrightarrow \equiv \text{SO}^- + \text{H}^+ )</td>
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<td>6b</td>
<td>( \equiv \text{SOH} + \text{H}^+ \leftrightarrow \equiv \text{SOH}^+ )</td>
<td>10.4 ± 0.3</td>
<td>this work</td>
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<td>7a</td>
<td>( \equiv \text{SOH} + \text{Pb}^{2+} \leftrightarrow [\equiv \text{SO}^- \text{Pb}^+ + \text{H}^+] )</td>
<td>6.20 ± 0.4</td>
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<tr>
<td>7b</td>
<td>( \equiv \text{SOH} + \text{Pb}^{2+} \leftrightarrow [\equiv \text{SO}^- \text{Pb}^+ \text{OH}^- + 2\text{H}^+] )</td>
<td>−6.15 ± 0.4</td>
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<tr>
<td>7c</td>
<td>( 2\text{XNa} + \text{Pb}^{2+} \leftrightarrow \equiv \text{X} + \text{Pb}^+ )</td>
<td>8.50 ± 0.4</td>
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<table>
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<td>8a</td>
<td>( \equiv \text{SOH}_2^+ + \text{GA}^{4+} \leftrightarrow \equiv \text{SO}^- \text{GA}^2+ )</td>
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<td>8b</td>
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<td>21.8 ± 1.0</td>
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<td>8d</td>
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<tr>
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<td>30.0 ± 1.0</td>
<td>this work</td>
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<tr>
<td>9c</td>
<td>( \equiv \text{SOH}_2^+ + \text{PrCH}_2^{1-} \leftrightarrow \equiv \text{SO}^- \text{PrCH}_2^0 )</td>
<td>42.0 ± 1.0</td>
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\( a \) The convention used for cation exchange is that of Gaines and Thomas (ref 62).

**Pb–Laponite.** An adsorption edge of Pb on Laponite is shown in Figure 5. At acidic pH, the Pb uptake is quite low. Taking into account the \( pK_a \) values of the variable charge surface sites, it is apparent that the prevailing positively charged surfaces sites at acidic pH are not favorable for \( \text{Pb}^{2+} \) adsorption. Assuming that the observed low adsorption of Pb involves the permanently charged \( \equiv \text{X}^- \) sites, we have the speciation scheme shown in Figure 5. This has been obtained by assuming the cation exchange reaction\(^{41,48–50} \)

\[ \text{Pb}^{2+} + 2\text{XNa} \leftrightarrow \equiv \text{X} + \text{Pb}^+ + 2\text{Na}^+ \]  

The operational stability constant derived from the fit is 8.5 (see Table 3). This value is comparable to that reported by Barbier et al.\(^{41} \) for Pb exchange for Na–SWy-2 montmorillonite and a commercial Na–bentonite. However, a distinctive feature in the case of Laponite is that the concentration of the permanently charged sites is on the order of 10\(^{-1}\) M, which is 2 orders of magnitude lower than the concentration (10\(^{-6}\)M) of the variable charge sites \([\equiv \text{SOH}].\) Including the formation of the species \( \equiv \text{SOH} \text{Pb} \) in the modeling explains the appearance of a plateau at pH < 5.4, which is seen as a small adsorption, that is, 5%, in the experimental data in Figure 5. On the basis of the CEC of Laponite...
concentrations of the formed species: 10^{-6} M Pb^{2+} ions that are present in this sample. Thus, the present data show that, under low Pb loading, the cation exchange sites do not compete efficiently with the variable-charge edge sites. Overall, both the experimental data and the theoretical analysis show that the permanent charge sites play a minor role in the adsorption of Pb on Laponite. This is in contrast to the characteristic role played by the permanently charged sites on metal sorption in montmorillonite.41,50,57 Barbier et al.41 reported that the sorption Pb ions by Na--montmorillonite is primarily via cation exchange, that is, at ion exchange sites XNa, while surface complexation soil organic matter, that is, at amphoteric surface hydroxyl groups Al(OH)(OH2), seems to play a secondary role. In the case of Na--Laponite, the large adsorption increase observed at pH > 6 shows that adsorption at variable charge sites is the dominant adsorption mechanism. This may be attributed to the more fractionated structure of Laponite platelets (CEC = 48 mequiv/100 g clay; particle size clay ~20 nm in diameter).27,58 The small particle size of Laponite leads to relatively more edge area than face area compared to larger particle clays such as montmorillonite, that is, with typical particle sizes of ~200 nm, resulting in a higher percentage of edges exposed to the solvent.

Previous EXAFS studies for Pb adsorption on montmorillonite56 show that, at low ionic strength and pH, Pb adsorption is pH independent and takes place at the basal planes existing in the interlayer regions of the clay. Pb forms outer sphere complexes having H2O molecules intervening between the metal and the clay phase. As pH and ionic strength are increased, Pb adsorption is occurring on the edges of the montmorillonite. Adsorption is pH dependent as a result of the formation of inner sphere complexes between Pb and the oxygen atoms of the negatively charged amphoteric sites.

According to the speciation in Figure 5, in the case of Laponite, the main adsorbed species is Pb^{2+} as well as PbOH^+, which is sorbed onto the SO^− sites. This can be contrasted with the high Pb loading conditions (e.g., see the XRD data), where the Pb ions are intercalated into the interlayer sites. Ternary System: [Pb--GA--Lap]. In Figure 6 the adsorption edge for gallic acid in the presence of Pb is shown for two GA/Pb ratios (i.e., GA/Pb = 4, Figure 6A; and GA/Pb = 25, Figure 6B).

An important observation is that the Pb uptake is severely promoted by the presence of the organic acid (e.g., compare Figure 6 with Figure 5). In Figure 5, 500 mg/L of Laponite achieves a maximum adsorption of ~80% of 10^{-5} M Pb, which corresponds to ~1.6 μM Pb per gram of Lap. In Figure 6, the maximum adsorption of GA/Pb is ~60% of 1 μM Pb by 200 mg Laponite, that is, 3.0 μM Pb per gram of Laponite. An analogous promotive effect has been observed for Pb uptake by kaolinite in the presence of hexanoic acid.49 In kaolinite the Pb uptake occurs mainly at the variable charge sites such as in the case of Laponite. Moreover, Schroth and Sposito showed that Pb binding at variable charged sites, occurs electrostatically with no ligand exchange.49 It appears that a similar mechanism is operative in the case of Pb--GA adsorption on Laponite.

The coadsorption of Pb and GA can be analyzed according to the adsorption edge of ternary complexes, as described by Schindler.44 This is verified by the speciation results of the FITSEQL analysis presented in Figure 6 where it is shown that adsorption can be operationally attributed to the positively charged (SOH2^+) sites. The total adsorption edge is the superposition of the adsorption edges from the various Pb--GA species.

Figure 4. Adsorption edge for (A) protocatechuic (PrC) or (B) gallic (GA) acid onto Laponite (solid circles) experimental data. Solid line: theoretical fit obtained by assuming the reaction and stability constants listed in Table 1. Dashed--dotted lines: theoretical concentrations of the formed species: 10^{-2} M organic acid, 10^{-3} M KNO_{3}, and 500 \times 10^{-3} g/L Laponite.

Figure 5. Adsorption edge for Pb(II) onto Laponite (solid circles) experimental data. Solid line: theoretical fit obtained by assuming the reaction and stability constants listed in Table 1. Dashed lines: theoretical concentrations of the formed species: 10^{-6} M Pb(NO_3)_2, 10^{-3} M KNO_{3}, and 20 \times 10^{-3} g/L Laponite.

(48 mequiv/100 g clay) which was used as the fixed total concentration for the X^− sites, we estimate a max of 0.96 \times 10^{-6} equiv of CEC sites to be available in the adsorption experiment in Figure 5. This is almost 1/2 of the charge equivalents of the 10^{-6} M Pb^{2+} ions that are present in this sample. Thus, the present data show that, under low Pb loading, the cation exchange sites do not compete efficiently with the variable-charge edge sites. Overall, both the experimental data and the theoretical analysis show that the permanent charge sites play a minor role in the adsorption of Pb on Laponite. This is in contrast to the characteristic role played by the permanently charged sites on metal sorption in montmorillonite.41,50,57 Barbier et al.41 reported that the sorption Pb ions by Na--montmorillonite is primarily via cation exchange, that is, at ion exchange sites XNa, while surface complexation soil organic matter, that is, at amphoteric surface hydroxyl groups Al(OH)(OH2), seems to play a secondary role. In the case of Na--Laponite, the large adsorption increase observed at pH > 6 shows that adsorption at variable charge sites is the dominant adsorption mechanism. This may be attributed to the more fractionated structure of Laponite platelets (CEC = 48 mequiv/100 g clay; particle size clay ~20 nm in diameter).27,58 The small particle size of Laponite leads to relatively more edge area than face area compared to larger particle clays such as montmorillonite, that is, with typical particle sizes of ~200 nm, resulting in a higher percentage of edges exposed to the solvent.

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These findings are in qualitative agreement with the conceptual scheme by Murphy and Zachara\textsuperscript{57} who proposed that anionic organic ligands will enhance trace metal adsorption at pH values below the intersection of the ligand envelope (see Figure 4) with the free-metal adsorption edge (just above pH 6 in Figure 5 for Pb\textsuperscript{2+}), whereas they will diminish trace metal adsorption above this pH value. An analogous effect has been observed for adsorption of Pb on goethite in the presence of desferrioxamine\textsuperscript{58} adsorption of Pb on goethite in the presence of desferrioxamine derivatives.\textsuperscript{58}

Although a detailed structural scheme at the atomic level is out of the scope of the present work, it is useful to discuss some reasonable structural options. According to our DFT calculations\textsuperscript{24} show that, in solution, the lead cations would be coordinated via the carboxy and the deprotonated OH. Given the weak, electrostatic nature of the adsorption on Laponite it is reasonable to assume that analogous geometry can be retained in the surface species.

In summary, the analysis of the adsorption edges for the organic molecules and Pb provides a descriptive basis of the charged species involved. On this basis, we proceed in the following in the study of the radical stabilization properties and the implicated mechanisms.

**EPR Spectroscopy.** GA–Lap. Figure 7A shows EPR spectra from GA in solution (trace a) and when adsorbed onto Laponite (trace b) at pH 9.3. Under O\textsubscript{2}–free conditions, no EPR signal is detected (not shown). The EPR signals of significant intensity appear only after exposure of the adsorption samples to ambient O\textsubscript{2}.

The origin and physicochemical characteristics of the EPR signal for GA in solution “a” have been analyzed in detail.\textsuperscript{24} In brief, in alkaline pH (\(pH > 9\)) and in the presence of O\textsubscript{2}, GA in solution forms stable anionic radicals. The EPR signal of GA in frozen solution is a radical singlet with \(g = 2.0039\) and \(\Delta H = 4.5\) G.\textsuperscript{24} The signal is inhomogeneously broadened by unresolved hyperfine couplings. In the presence of Laponite, the adsorbed gallic acid easily generates radicals after exposure to ambient O\textsubscript{2} for 30 min (see Figure 7, trace b). The EPR signal of the adsorbed gallic acid radical onto Laponite is characteristic of a monomeric radical singlet with \(g = 2.0035\). The \(g\) value is lower than the \(g\) value for gallic acid in solution (\(g = 2.0039\)). According to the speciation analysis (Figure 4), at pH 9.3, the prevailing surface species are mainly [\(\text{SOHGAH}_{2}\)]\textsuperscript{−} (\(\sim 60\%\)) and some 30% [\(\text{SOHGAH}_{2}\)]. These observations are discussed in more detail in the following.

**Resolution Enhancement.** A significant resolution enhancement is observed for the adsorbed GA radicals relative to the frozen solution spectrum (see Figure 7, trace b). The improved resolution can be assigned to the spatial separation of the adsorbed radicals, which removes random dipole–dipole interactions between neighboring spins. An analogous improved resolution has also been observed for well-separated tyrosine radicals immobilized on Laponite clay.\textsuperscript{26}

**Radical Stabilization.** The double integral of the EPR signal under nonsaturating conditions is analogous to the concentration of the radicals. A detailed analysis of the radical concentration shows that the radical concentration formed by adsorbed GA is...
The GA/Pb radical. The Pb complex, the spin density is mainly localized on the Pb atom. 24 This unusual electron density onto the Pb atom. In Figure 7, the observed signal has been analyzed previously. 24 The most characteristic feature of the GA/Pb complex. Here, it may be used as a fingerprint for one Pb atom. 

To examine the influence of adventitious Mg 2+ ions, that is, from the possible dissolution of Laponite, on the radical properties, we performed EPR measurements on aqueous samples containing Mg(NO3)2 and gallic acid. The EPR measurements showed that, for an equimolar GA/Mg ratio, Mg2+ ions do not have any resolvable effect on the gallic acid EPR radical signals. As we have discussed previously 24 only at higher concentrations (GA/Mg > 2), the magnesium ions slightly increase the radical concentration with a lowering of the g value to g = 2.0036. Thus, we conclude that, under the conditions of the present adsorption experiments, Laponite dissolution has no effect on the properties of gallic acid radicals.

The EPR signal for gallic acid adsorbed onto Laponite has a g value of g = 2.0035, which is lower in comparison with that of gallic acid in solution (g = 2.0039). To examine the possible role of coordination on the purported Mg−O−Mg sites of the clay, we performed EPR experiments for gallic acid in the presence on Mg2+ ions in solution. Indeed it is verified that the GA/Mg radicals have a g value of 2.0037 (not shown). Thus, taking into account these observations, it is reasonable to assume that both the observed g-lowering, as well as the radical stabilization, can be attributed to the ionic interaction between the gallic acid anion radical and the clay structural Mg2+ ion. 

GA/Pb/Lap. Exposure of the GA/Pb/Lap samples to ambient O2 leads to the facile formation of strong EPR signals. The dotted signal in Figure 8A is the EPR signal for GA/Pb in solution. This signal has been analyzed previously. 24 The most characteristic feature is the g value of g = 1.9999, that is, below the free-electron g value of 2.0023, due to the delocalization of the spin density onto the Pb atom. 24 This unusual g value is a unique feature of the GA/Pb complex. Here, it may be used as a fingerprint for the identification of this species.

In Figure 8, the solid lines are EPR signals for GA/Pb/Lap. In Figure 8A, the signals have been recorded under EPR conditions for the detection of narrow radical signals, that is, those low in microwave power (1.2 mW) and modulation amplitude (2 Gpp). In Figure 8B, the signals for the same sample have been recorded at high microwave power (32 mW) and a 10 Gpp modulation amplitude to detect broad signals with fast relaxation properties.

In Figure 8A, a narrow EPR signal, g = 1.9999, ΔH = 12 G, is recorded for GA/Pb/Lap after a 60 min exposure to ambient O2 at pH 9.5. Its g value and line width are characteristic of the GA/Pb radical. The g value indicates that, in this adsorbed GA/Pb complex, the spin density is mainly localized on the Pb atom.

The concentration of this radical becomes a maximum after a 3 h exposure to ambient O2. However, after prolonged exposure to O2, a very broad EPR signal, that is, ΔH = 250 G, is detected...
O2 is shown in Figure 9. A detailed analysis of the formation of the polymeric broad signal reveals the following: (a) this polymeric signal is not detected for gallic acid in the absence of Pb, and (b) gallic acid in the presence of Pb generates this signal only after adsorption onto Laponite. Thus, the present data demonstrate that, at low-loading, Laponite promotes the polymerization of GA/Pb radicals.

The polymeric EPR signal is also detected in the high-load GA/Pb/Lap samples used for the XRD data (not shown). Because of the higher concentration in the samples used for XRD, the EPR signals are even broader, that is, they attain a line width of $\Delta H = 350$ G. At this point, the XRD information recorded for the samples giving the broad EPR signals is of relevance. According to the XRD data in the high-load GA/Pb/Lap sample, the GA/Pb complexes are intercalated at a $d_{001}$ spacing of 5.8 Å (see Table 2). Taking into account the geometrical dimensions of the GA/Pb complex calculated by DFT, we may conclude that the complex should be intercalated in a slightly tilted orientation. After formation of the polymeric species, the $d_{001}$ is not changed, that is, it remains 5.8 Å. This can be envisaged if we assume that the polymeric GA/Pb species are arranged in chains, which are arranged horizontally in the interlayer space. This arrangement is an efficient sequestration scheme, and this concurs with the extreme stability of the polymeric radicals. An analogous stabilization has been observed for tyrosine radicals after intercalation into Laponite sheets.

The properties of radicals incorporated into Laponite have been the subject of various investigations. The noncovalent assembly of the nitroxide spin label 2,2,6,6-tetramethyl-1-piperidinyloxy1 of Laponite films resulted in the formation of a one-dimensional Heisenberg antiferromagnet. This was assigned to islands of spin label stacks embedded in the Laponite matrix. XRD data showed that some spin labels were intercalated parallel to the interlayer sheets with $d_{001}$ spacing of 0.9 nm. The stacked spin labels gave a singlet EPR line with angle-dependent line width between 15 and 30 G, determined by the one-dimensional Heisenberg exchange.

In the case of GA/Pb/Lap the observed EPR spectrum is of different origin: the large line width, the detection of the semiforbidden transition $\Delta m_S = 2$ at $g = 4$, and the EPR power saturation properties are indicative of a dominant dipolar interaction instead of an exchange between GA/Pb radicals. On the other hand, a similarity between the GA/Pb radicals and the spin-label films in ref 31 is the long-term stability.

**Conclusion**

The present data show that the association of gallic acid with Laponite results in a significant stabilization of radicals, similar to that observed previously for tyrosine radicals. In all cases, the formed organoclay shows enhanced stability against acid dissolution. The structural details of the association of gallic acid with Laponite depend on the GA/Lap loading.

At low GA/Lap ratios ($\sim 10^{-6}$ M gallic acid per gram of clay), gallic acid is adsorbed at the variable charge sites of Laponite. The adsorption can be adequately described by surface complexation modeling.

At higher GA/Lap ratios ($\sim 10^{-3}$ M gallic acid per gram of clay), gallic acid is intercalated at the interlamellar sites of Laponite in a perpendicular orientation.

The GA/Pb/Lap complex is associated with Laponite in an analogous structural manner, that is, adsorption at variable charge sites or intercalation at the interlamellar sites of Laponite, depending on the loading.

Laponite stabilizes the GA/Pb radicals. At prolonged exposure to ambient O2, Laponite promotes the formation of stable polymeric GA/Pb species, which are intercalated into interlamellar sites, probably in the form of dimers or oligomeric chains.

**Supporting Information Available:** Figure S1 showing potentiometric titration data and the fit of the organics. Figure S2 showing the dissolution of Laponite in the presence of gallic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

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