

Interaction of Catechol and Gallic Acid with Titanium Dioxide in Aqueous Suspensions. 1. Equilibrium Studies

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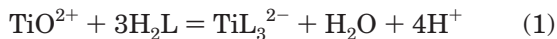
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The adsorption isotherms of catechol (1,2-dihydroxybenzene) and gallic acid (3,4,5-trihydroxybenzoic acid) onto titanium dioxide (Degussa P-25) were measured at various pH values and room temperature using attenuated total reflection Fourier transform infrared (FTIR-ATR) data, processed by singular value decomposition. The affinity is largely pH independent, although the deprotonation of the carboxylic group in gallic acid might produce a slight increase in the affinity. Catechol was shown to form two complexes, with Langmuir stability constants $\log K$ of 4.66 (strong mode) and 3.65 (weak mode). Both complexes have the same spectral signature, and mononuclear and binuclear chelate structures are proposed for them. Gallic acid chemisorbs by complexation through two $-\text{OH}$ groups and forms one complex only, $\log K = 4.70$. The third $-\text{OH}$ and the pendant carboxylate do not influence much the stability of the surface complex. Comparison with literature data demonstrates that the affinity of 4-chlorocatechol is also similar, whereas 2,3-dihydroxynaphthalene and 4-nitrocatechol form more stable complexes, probably because of the solvation contribution to the overall Gibbs adsorption energy. All quoted constants refer to the surface complexation equilibria written as follows: $(\equiv\text{Ti}-\text{OH})_2 + \text{H}_2\text{L} = (\equiv\text{Ti})_2-\text{L} + 2\text{H}_2\text{O}$, i.e., as electroneutral processes. The FTIR-ATR spectra of the surface complexes are also discussed.

1. Introduction

In this paper, we present an experimental study of the surface complexation reactions of catechol and gallic acid onto titanium dioxide (Degussa P25, mainly composed of anatase). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is used to characterize the surface under equilibrium (dark) conditions, thus providing both structural and thermodynamic (stability constants) information on the surface complexes formed by adsorption. In a previous paper¹ the use of ATR-FTIR to study the kinetics of photochemical degradation of catechol was described. A future paper shall deal with the illuminated gallic acid/ TiO_2 interface.

Hydroxyaromatic compounds interact strongly with Ti(IV) ; this ion is able to displace the proton from the $-\text{OH}$ group, forming an inner sphere complex. This reaction is particularly important with dihydroxyaromatic compounds, the simplest of which is catechol, 1,2-dihydroxybenzene. A five member ring chelate is formed, conferring special stability to the complex. For the complexation reaction written as in eq 1 where H_2L stands for catechol, $\log K = 5.1$ is calculated using data from ref 2. Thus, already at pH 3, and a concentration of free catechol of $0.001 \text{ mol dm}^{-3}$, $[\text{TiL}_3^{2-}]/[\text{TiO}_2^{2+}] \approx 10^8$.



Ti(IV) is also able to interact with carboxylates; again, the formation of chelated species favors the stability of

the complex. A combination of bonds with $-\text{O}^-$ and $-\text{COO}^-$ explains the formation of Ti(IV) salicylate (2-hydroxybenzoate).^{3,4,5}

Titanium dioxide particles immersed in aqueous solutions are also able to interact with these classes of compounds, forming well-characterized surface complexes. The interaction of TiO_2 with catechol^{6,7} and 4-chlorocatechol⁸ has been described; use of the FTIR-ATR technique permitted description of the chemisorbed species as specific surface complexes, for which Langmuir-type stability constants were derived. It is well documented that the two $-\text{OH}$ groups participate in the formation of coordinate bonds with surface Ti atoms, in a fashion that resembles Ti(IV) solution chemistry. Conventional measurements of the adsorption isotherm were also used to derive stability constants using the triple layer model for the interfacial region;⁶ again, the formation of surface chelate species was postulated. The interaction of salicylic acid with TiO_2 has also been characterized and modeled in terms of the surface complexation approach. Species involving mononuclear and binuclear chelate rings have been proposed, both $-\text{COO}^-$ and $-\text{O}^-$ being involved in surface coordination.⁵ Oxalate and salicylate surface complexes have also been characterized spectroscopically using ATR-FTIR

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spectroscopy.^{9–11} Conventional adsorption isotherms have also been measured in most cases, including catechol. The compatibility of affinity data derived from conventional and from FTIR measurements is still an open question; conventional isotherm characterization is limited at low concentrations by the sensitivity of analytical technique and at high concentrations by the availability of surface sites for adsorption. FTIR data, on the other hand, are usually modeled with the simple Langmuir equation, on the assumption that the species that can be spectroscopically seen must be formed by an electroneutral process.^{3,9} The difference is clearly seen by comparison of the available Langmuir constants for catechol, using conventional measurements ($K_L = 8.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$)⁶ and for 4-chlorocatechol, derived from FTIR data ($K_L = 9.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$).⁸

Natural organic matter (NOM) contains the so-called humic and fulvic acids, oligomers or polymers containing hydroxyaromatic building blocks. One of the simplest possible models for NOM is gallic acid, 3,4,5-trihydroxybenzoic acid. Soluble NOM is therefore expected to exhibit a large adsorption affinity onto titanium dioxide. This characteristic, added to the well-known photocatalytic properties of titanium dioxide for heterogeneous oxidation of organic substances, makes it of interest to understand the nature of the interaction of catechol and gallic acid with titanium dioxide, both in the dark, under equilibrium conditions, and under light in the presence of dissolved oxygen. In the latter case, an efficient catalytic photo-oxidation is expected, leading in the limit to carbon dioxide and water.

For large organic compounds, even if carboxylate and other potentially complexing groups are present, it has been pointed out that outer sphere complexation may account for a large fraction of the observed adsorption. Thus, Yoon et al.¹² have interpreted similarities in the ATR-FTIR spectra of dissolved and adsorbed (on aluminum oxohydroxide) Suwannee River fulvic acid as indicative of outer sphere complexation predominance. Similarly, the adsorption of benzene tri-, tetra-, and hexacarboxylate on goethite^{13–15} is dominated by outer sphere complexation. Thus, careful evaluation of FTIR data is a powerful tool to elucidate adsorption modes of NOM on metal oxides.

2. Experimental Section

2.1. Materials. Titanium dioxide was Degussa P-25. It is composed mainly of anatase, with a rutile content of ca. 15%. The modal particle size is ca. 25 nm, and its BET specific area was $51.4 \text{ m}^2 \text{ g}^{-1}$. Degussa P-25 was used without further purification. All other reagents were analytical grade and were used as received. All solutions were prepared with deionized water from an E-pure equipment (resistance = $18 \text{ M}\Omega$).

2.2. Methods. A typical experiment was performed as described in ref 2. Successive TiO_2 layers were deposited on the ATR crystal surface by placing 0.150 cm^3 of TiO_2 suspension (20 g dm^{-3}) and evaporating to dryness at room temperature. The calculated final layer thickness was of the order of $1 \mu\text{m}$. Prior to use, the TiO_2 layer was rinsed with water to eliminate loosely deposited particles. Fresh gallic acid or catechol solutions of

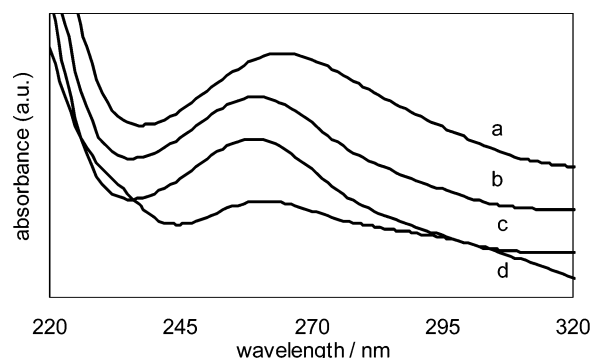


Figure 1. Gallic acid solution UV spectra at selected pH values: (a) 4.35; (b) 5.28; (c) 6.11; (d) 8.11. Above $\text{pH} \approx 5$, a maximum is seen at 260 nm. At pH 8.11 the spectrum demonstrates the onset of further deprotonation and/or decomposition processes. The spectra are displaced vertically for clarity.

predetermined pH and ionic strength (10 mM KCl) were placed on the TiO_2 film and successive FTIR spectra were recorded, until no further changes were detected. Typically, equilibration times were of the order of 30 min. FTIR spectra were recorded in a NICOLET MAGNA 560 instrument equipped with a liquid N_2 cooled MCT-A detector. The incidence angle of the Spectra Tech horizontal Zn Se-ATR unit (area = $10 \times 72 \text{ mm}^2$) was 45° , and the total number of reflections was 11. Spectra were taken with 200 scans and 4 cm^{-1} resolution, the background was subtracted, and baseline correction was made due to instrumental instabilities. At the end of each experiment the UV-vis spectrum of the remnant solution was recorded in a diode array Hewlett-Packard 8453 apparatus.

The FTIR spectra of solid catechol and gallic acid, and of their aqueous solution (FTIR-ATR), were obtained for comparative purposes. The signal was negligible when the solution concentration was below 0.001 and $0.0001 \text{ mol dm}^{-3}$ for gallic acid and catechol, respectively. Adsorption was studied at several pH values, between 3.65 and 6.5. The lower limit was set to protect the integrity of the ATR crystal, and the upper limit was set to avoid adsorbate decomposition.

3. Results and Discussion

3.1. UV Spectra. The UV solution spectrum of catechol (not shown) is pH insensitive in the range $3.83 < \text{pH} < 7.23$. For identification and analytical determinations, the band maximum at 275 nm was used.

Figure 1 shows the UV solution spectra of $0.0001 \text{ mol dm}^{-3}$ gallic acid at selected pH values. The spectral changes with pH in the range below pH 8 can be ascribed to the presence of two components, linked by an acid–base equilibrium with $\text{pK}_a = 4.2 \pm 0.2$ (cf. spectra at pH 4.35 and 5.38 in Figure 1; other recorded low pH spectra are not shown). These results agree with the known acidity of gallic acid, associated with the deprotonation of the carboxylic acid group, for which $\text{pK}_a = 4.3$ has been reported at $I = 0.1 \text{ mol dm}^{-3}$.² Upon protonation, the band maximum shifts from 260 to 271 nm. The incipient spectral changes observed at pH 8.11 become more important at higher pH values and indicate further deprotonation and/or decomposition.

3.2. FTIR Spectra. The FTIR spectrum of aqueous catechol solution at pH 3.8 is shown in Figure 2; no spectral changes are observed in the pH range $3.8 \leq \text{pH} \leq 6.5$. Band assignment can be done by analogy with 4-chlorocatechol.⁸ The 1037 and 1103 cm^{-1} bands are attributed to in-plane C–H bending, the 1201 cm^{-1} band to in plane O–H vibration (with probable contribution of in plane C–H bending), absorption in the region between 1263 and 1278 cm^{-1} to radial stretching vibrations of the C–O group, and the region between 1440 and 1504 cm^{-1} to

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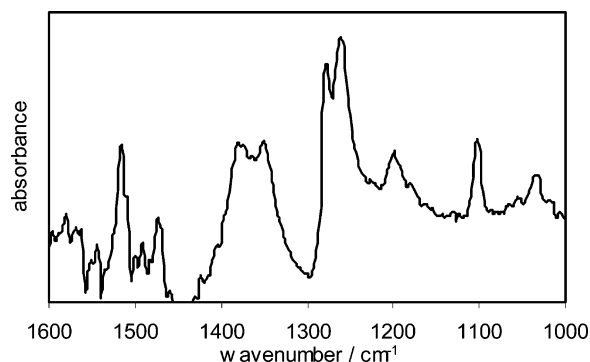


Figure 2. FTIR spectrum of 0.01 mol dm⁻³ aqueous catechol at pH 3.8.

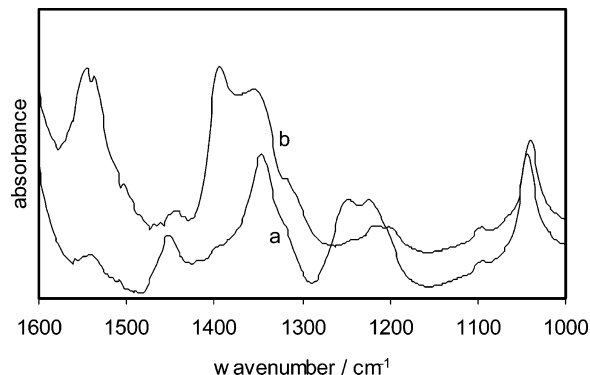


Figure 3. FTIR spectra of 0.01 mol dm⁻³ aqueous gallic acid at (a) pH 3.37 and (b) pH 7.32. The spectra are displaced vertically for clarity.

tangential C–C normal modes of the aromatic ring. The peaks at 1353 and at 1380 cm⁻¹ can be attributed to in-plane OH bending, and the peak at 1515 cm⁻¹ can be assigned to ring C=C stretching.^{16,17}

The FTIR spectrum of protonated gallic acid in aqueous solution (Figure 3a) is dominated by the peaks due to in-plane OH bending, at 1346 cm⁻¹,¹⁶ Ph–O stretching⁹ and C–O stretching at 1234 cm⁻¹ (with probable contribution of in-plane O–H vibration) and 1251 cm⁻¹, and aromatic C–H deformation vibration at 1098 and 1045 cm⁻¹. The C=O stretching, expected in the region 1740–1710 cm⁻¹, is blurred by water absorption.¹⁷ The spectrum of the monoanion (Figure 3b) presents additional bands due to ν_s and ν_a of the –COO⁻ moiety, at 1396 and 1545 cm⁻¹, respectively.⁹ The peak due to in-plane OH bending is seen at 1360 cm⁻¹,¹⁶ Ph–O stretching⁹ and C–O stretching at 1205 cm⁻¹ (with contribution of in-plane O–H vibration) and 1222 cm⁻¹, and aromatic C–H deformation vibration at 1107 and 1041 cm⁻¹.

The ATR-FTIR spectra of catechol on titanium dioxide has been presented earlier.¹ The main bands, and their assignment,⁸ are as follows: 1486 cm⁻¹, stretching (C–C); 1450 cm⁻¹, stretching (C=C); 1263 cm⁻¹, stretching (C–O); 1215 and 1105 cm⁻¹, bending (C–H). The vibrations associated with the –OH groups are appreciably different from those in aqueous solution, indicating deprotonation and surface complexation: the 1201 cm⁻¹ in-plane –OH vibration and the 1353 cm⁻¹ in-plane OH bending are not seen in the surface complex (only a weak and broad feature, centered at 1215 cm⁻¹, is seen and

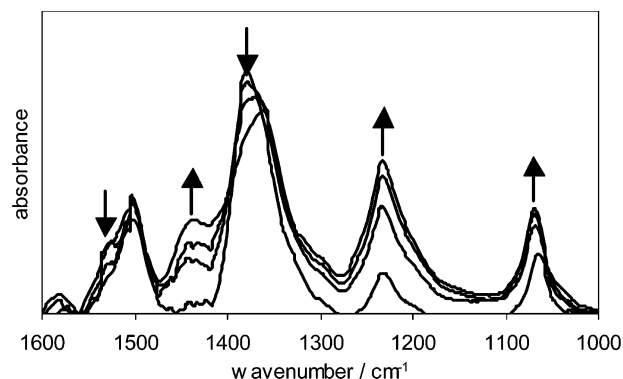


Figure 4. ATR-FTIR spectra of gallic acid adsorbed onto TiO₂ in the dark from a 1.0 × 10⁻⁴ M aqueous solution at pH 6.35, 5.34, 4.51, and 3.65. The arrows indicate the direction of increasing pH.

Table 1. FTIR Band Assignment for Gallate and Catecholate/TiO₂ Surface Complexes

surface complex	pH = 3.75	pH = 6.15	assignment
gallic acid		1530	$\nu_s(\text{CO}_2^-)$
	1503	1502	$\nu(-\text{C}=\text{C}-)/\nu(-\text{C}-\text{C}-)$
		1380	$\nu_s(\text{CO}_2^-)$
	1442	1445–1425	C–O str + O–H def in the dimer?
	1366	1363	$\delta(\text{Ph}-\text{O}-\text{H}/\text{C}-\text{O})$ str comb ¹⁷
	1234	1234	$\nu(\text{Ph}-\text{O})/\text{OH}$ def vib (COOH monomer)
catechol	1070	1068	$\delta(\text{C}-\text{H})$ in plane
		1486	$\nu(-\text{C}-\text{C}-)$
		1450	$\nu(-\text{C}=\text{C}-)$
		1263	$\nu(\text{C}-\text{O})$
		1215; 1105	$\delta(\text{C}-\text{H})$ in plane

assigned to C–H vibrations), and the splitting of stretching(C–O) in aqueous catechol disappears in the surface species.

Figure 4 shows the FTIR-ATR spectra of the TiO₂ film deposited onto the ATR crystal, in contact with 0.0001 mol dm⁻³ gallic acid aqueous solutions of various pH values. The changes with pH suggest the presence of two species linked by a protolytic equilibrium.

Parts A and B of Figure 5 show the FTIR-ATR spectra of the TiO₂ film deposited onto the ATR crystal, in contact with gallic acid aqueous solutions of increasing concentration, at pH 6.15 and 3.75, respectively.

Peak assignments, done by comparison with the literature,^{8,16–23} are given in Table 1. In the region around 1380 cm⁻¹, ν_s is seen at pH 6.15, overlapping on the strong OH deformation vibration seen at both pH values. In agreement, ν_a is also seen at pH 6.15, as a shoulder at 1530 cm⁻¹. Thus, the surface gallate may undergo protolytic equilibria at the –COOH moiety, suggesting that this group is not involved in complexation of Ti atoms. A similar case has been reported for the adsorption of *N*-(phosphonomethyl)glycine on goethite: the interaction with the surface takes place through the phosphonate group, and the pendant carboxylate is free and exposed to solution.^{24,25}

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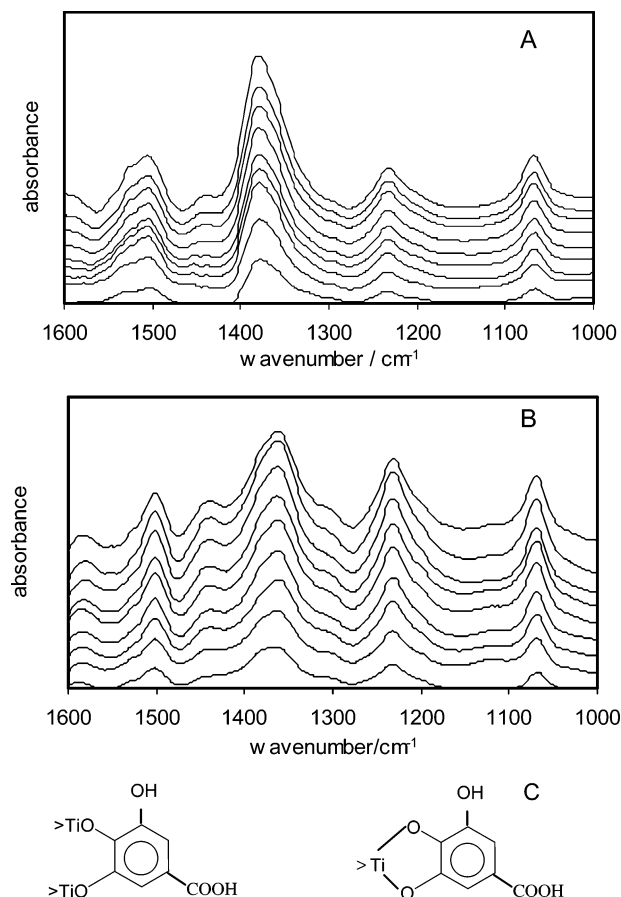


Figure 5. ATR-FTIR spectra of gallic acid adsorbed onto TiO₂ in the dark at pH 6.15 (A) and 3.75 (B) for various gallic acid concentrations. From bottom to top: 1×10^{-5} , 1.5×10^{-5} , 2×10^{-5} , 2.5×10^{-5} , 3.5×10^{-5} , 5×10^{-5} , 7.5×10^{-5} , 1.0×10^{-4} , and 2.0×10^{-4} . (C) Possible structures of the surface complexes formed by chemisorption of gallic acid on TiO₂. The actual charge borne by the complexes depends on the description of the anatase surface; irrespective of the assumptions, however, any negative charge on the complexes must be compensated by positive charges on vicinal sites.

As discussed above, binding of catechol via the two deprotonated $-OH$ groups is indicated by the spectral data. Spectral comparison (see Table 1) also supports the proposed structure of the gallate complex, with both compounds bound through two adjacent $-OH$ groups (see Figure 5C).

In contrast, it has been proposed that the adsorption of fulvic acid onto γ -AlOOH and of benzene di-, tetra-, and hexacarboxylate onto α -FeOOH involve mainly the formation of outer sphere complexes.^{12–14} The difference may be traced to the differing complexation properties Ti(IV), as compared to Fe(III) and Al(III). In support, Roddick-Lanzilotta and McQuillan propose the formation of inner sphere complexes between glutamic or aspartic acid and TiO₂.²⁶ However, the spectral changes are not very large, and structural assignment is in neither case straightforward. Nonspecific interactions may indeed play an important role in the stability of the inner sphere surface complexes, especially when large organic molecules are involved; stability trends are useful to probe this possibility (see below).

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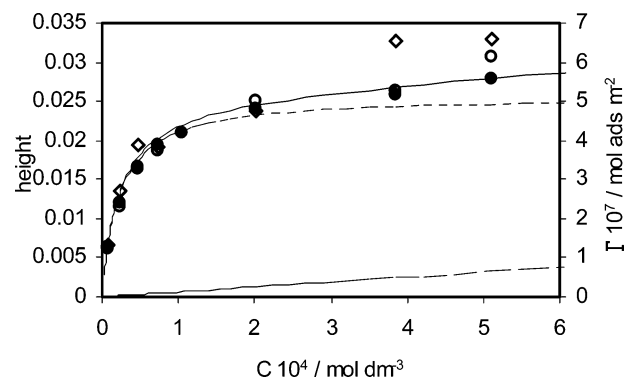


Figure 6. Catechol adsorption onto TiO₂ at pH 6.15. ATR-FTIR data by SVD: (---) Langmuir contribution; (- · -) linear contribution; (—) total adsorption. UV measurements of remnant solution concentration, (\diamond) (right-hand y-axis). For comparison, normalized intensities of the 1484 cm⁻¹ (\circ) and the 1263 cm⁻¹ bands (\bullet) are also shown.

3.3. Adsorption Isotherms. The adsorption isotherm of catechol at pH 6.15 derived from the SVD treatment of the spectra is seen in Figure 6. SVD does not yield absolute surface excess Γ values, but only degrees of coverage, θ . The values in the right y axis were calculated that the operative available surface area was one-fourth of the area calculated on the basis of the total mass and the specific surface area; this assumption was required to make FTIR and suspension adsorption data⁶ compatible. SVD treatment indicates the existence of one spectral component only. The chemical model of the concentration dependence however requires the use of two contributions for adequate fitting: a Langmuirian contribution, $\log(K_L/M) = 4.66$, and a minor linear one. Using the value $\Gamma_{\max} = 5.28 \times 10^{-7}$ mol m⁻² derived above, the slope of the line is found to be 1.25×10^{-4} dm³ m⁻², as shown in Figure 6; for comparison, normalized intensities of the peaks at 1484 and 1263 cm⁻¹ (FTIR data) and experimental data by UV are also shown.

The linear contribution might correspond to a second, weak surface complex or, alternatively, to increasing availability of inner film surface at larger concentrations (i.e., an experimental artifact). In either case, both complexes have identical spectra, thus ruling out the possibility that the second contribution is due to dissolved catechol. Assuming a Langmuirian behavior for the weak mode, the slope of the line is $K_L^w \Gamma_{\max}^w$. Using the maximum adsorption density from the previous work,⁶ and interpreting it as the sum of $\Gamma_{\max} + \Gamma_{\max}^w$, the values $K_L^w = 5.0 \times 10^2$ dm³ mol⁻¹ and $\Gamma_{\max}^w = 7.0 \times 10^{-7}$ mol m⁻² are derived.

In our previous study at higher adsorbate concentrations,⁶ a single Langmuir isotherm was found to fit the data, with $K_L = 8.2 \times 10^3$ dm³ mol⁻¹ and $\Gamma_{\max} = 1.25 \times 10^{-6}$ mol m⁻². The overlap of the data described in this paper and those reported in ref 6 is very restricted, and at higher concentrations, the more complex behavior now described could be smeared out.

It is tempting to conclude that the two surface complexes detected by the changes in FTIR peak intensities with concentration, correspond to the two modes discussed in ref 6. Both modes have expectedly similar spectral signatures, and their affinities are both pH independent.

The adsorption isotherms of gallic acid were obtained at pH 3.75 and 6.15 both from measurements of remnant concentration in solution (UV) and from surface (FTIR-ATR) spectral data. Solution UV data indicate that the affinity does not change appreciably with pH; a single Langmuir equation with $K_L = 7.2 \times 10^4$ dm³ mol⁻¹ and $\Gamma_{\max} = 9.40 \times 10^{-7}$ mol m⁻² suffices to describe the data

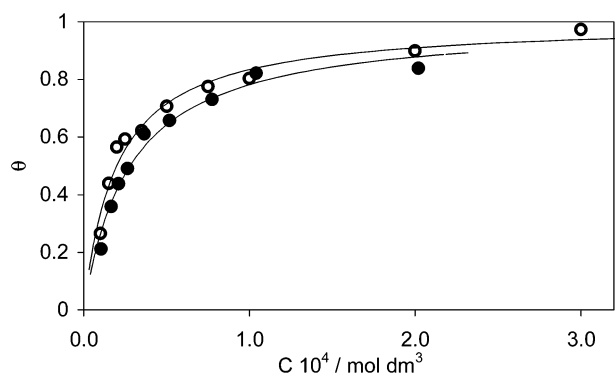
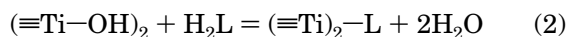


Figure 7. Gallic acid adsorption isotherms onto TiO_2 from ATR-FTIR data processed by SVD, showing $\theta = \Gamma/\Gamma_{\text{max}}$ as a function of solution concentration: (—) pH 6.15; (---) pH 3.75. The measured values at each concentration, corrected by the SVD program, are also shown: (○) pH 6.15; (●) pH 3.75.

at both pH values. SVD treatment of the whole FTIR spectra also identifies only one component at each pH. However, the Langmuir affinity constant is lower at pH 3.75. It decreases by ca.30% in going from pH 6.15 ($K_L = 5.04 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$) to pH 3.75 ($K_L = 3.59 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$). Figure 7 shows the SVD results; the lines describe the isotherm corresponding to the optimized fitting, and the dots are the relative areas, corrected by SVD, for each concentration. As opposed to remnant solution concentration (UV) data, the FTIR data have the advantage of using the whole spectral signal, and we believe that the slight decrease of affinity at lower pH is real. It is thus concluded that carboxylic group deprotonation may lead to an increase in the affinity in the range $3.2 < \text{pH} < 5.2$, due to an increased Lewis basicity of the anion.

4. Stability Trends

Table 2 shows in column 3 the Langmuir-type constants $K_{\text{H}_2\text{L}}$ calculated for equilibrium 2, from the measured Langmuir constants at a given pH value and the acidity constants of the ligand.



Alternatively, the affinity can be calculated for the reaction written as eq 3 (column 4, Table 2):

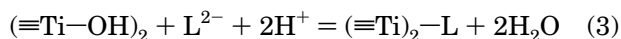


Table 2. Langmuir Stability Constants for Selected Catecholate–Titanium Surface Complexes Formed upon Chemisorption on Titanium Dioxide

ligand	$\text{p}K_{\text{a}1},^a \text{p}K_{\text{a}2}^a$	$\log K_{\text{H}_2\text{L}}^c$	$\log K_{\text{L}^{2-}}^c$	reference
catechol	9.4, 12.8	4.9 4.66 3.65	27.1 26.9 25.8	<i>b, e</i> this work ref 6 ^{b+} this work
4-chlorocatechol	8.77, 12.73	5.0 4.98	26.5 26.5	ref 7 ^b ref 8
(gallate) [−]	8.69, 11.45	4.70	24.84	this work
gallic acid	4.26, 8.69, 11.45 ^d	4.56	24.70	this work
2,3-dihydroxy-naphthalene	8.89, 12.93	6.0	27.8	ref 7 ^b
4-nitrocatechol	6.88, 11.24	6.3	24.4	ref 7 ^b

^a $\text{p}K_{\text{a}1}$, $\text{p}K_{\text{a}2}$ values from ref 2. ^b Conventional adsorption measurements. ^c $K_{\text{H}_2\text{L}}$ values calculated for the equilibrium $(\equiv\text{Ti}-\text{OH})_2 + \text{H}_2\text{L} = (\equiv\text{Ti})_2-\text{L} + 2\text{H}_2\text{O}$ from the measured Langmuir constants at a given pH value and the acidity constants of the ligand. ^d In the analysis of possible correlations between $\log K_{\text{H}_2\text{L}}$ and the acidity of the phenolic groups, an independent assessment of the acidity of these groups in the presence of protonated carboxylate would be required. ^e From: Moser, J.; Punchedewa, S.; Infelta, P. P.; Grätzel, M. *Langmuir* **1991**, 7, 3012.

The analysis of the $K_{\text{H}_2\text{L}}$ values demonstrates that catechol (strong mode), 4-chlorocatechol, and gallate ion have practically the same affinity for the surface, whereas 4-nitrocatechol and 2,3-dihydroxynaphthalene form more stable complexes. As written, eq 2 represents the replacement of two protons in the dissolved ligand by two surface Ti atoms.

The constancy of $K_{\text{H}_2\text{L}}$ for the first three ligands demonstrates that the affinity for the surface of the totally deprotonated ligands ($K_{\text{L}^{2-}}$) run parallel with the Brønsted acidity. The changes seen upon deprotonation of gallic acid are very minor in the log scale and reinforce the idea of a close balance between Brønsted and Lewis acidities. The last two ligands, on the other hand, exhibit a comparatively enhanced affinity for the surface, a fact that can be attributed to solvation effects.

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