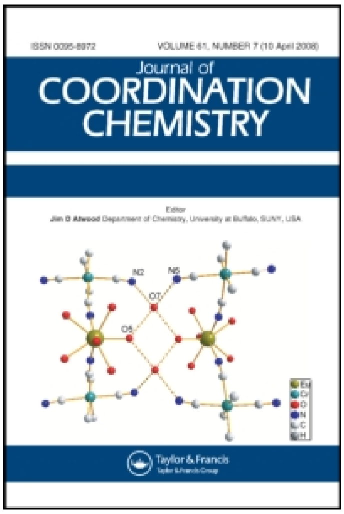

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Kinetics and equilibrium of surface complexation reactions: the adsorption of polycarboxylic acids on titanium dioxide§

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A Fourier transform infrared attenuated total reflectance (FT-IR-ATR) study on the adsorption equilibria of several polycarboxylic acids, citric acid, ethylenediaminetetraacetic acid (EDTA), and triethylenetetramine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexaacetic acid (TTHA), on titanium dioxide (TiO_2) in the concentration range from 3×10^{-7} to 6×10^{-4} mol, is reported. The phenomenon involved is the heterogenous complexation of surface Ti ions by the adsorbing ligand. The adsorption of citric acid, EDTA, and TTHA is compared with that of acetic and oxalic acids. The IR spectra were analyzed by singular value decomposition, showing that the only one basis spectrum contributed significantly to the experimental spectra for all the cases. Adsorption isotherms were fitted to two Langmuirian equations. Langmuir constants (K_L) were interpreted in terms of the molecular structure and a number of carboxylic groups. The highest K_L characterizes the citric acid adsorption ($7.1 \pm 0.3 \times 10^6\,\text{mol}^{-1}$), followed by oxalic acid and TTHA ($2.1 \pm 0.1 \times 10^6\,\text{mol}^{-1}$). Surprisingly, EDTA has the smallest Langmuir constant of the group (except for acetic acid that adsorbs negligibly), $4.06 \pm 0.7 \times 10^5\,\text{mol}^{-1}$. Structures for the most important surface complexes of each of the studied ligands are proposed based on the previous studies on related systems. We propose that the most stable adsorption mode corresponds to fully deprotonated ligands interacting with Ti ions through all the carboxylates.

Keywords: Adsorption; Surface complexation; TiO_2; Carboxylic acid; FT-IR-ATR

1. Introduction

It has been well established that the chemisorption of carboxylates onto metal oxides immersed in water is a true heterogeneous complexation reaction, yielding surface complexes that can be considered as true chemical entities [1]. Surface complexation models accept that adsorption is a substitution reaction, where the organic adsorbate (usually an anion) substitutes for water (or their protolysis products) in the first coordination sphere of the surface metal ions.

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§Dedicated to Prof Rudi van Eldik on the occasion of his 65th birthday.

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Adsorption of organic substances on metal oxides is relevant to oxide dissolution [1], biosorption, pollutant removal [2], etc. Titanium dioxide (TiO_2) has a particular importance due to its use for water remediation through heterogeneous photocatalysis [3]. All these processes are mediated by the formation of surface complexes [1].

Several studies have been published on surface complexation equilibria, using two different approaches. The traditional one involves conventional adsorption studies *in batch* [4, 5]: a suspension of a certain amount of metal oxide is equilibrated with a solution of known ligand concentration, the supernatant solution is then analyzed to obtain the equilibrium concentrations and the surface speciation is derived from them. Different adsorption isotherms may be used to interpret the data, the simplest (and most common) one being the Langmuir isotherm.

The second approach involves the use of the Fourier transform infrared attenuated total reflectance (FT-IR-ATR): a total reflecting crystal (ZnSe or Ge) is coated with a film of the adsorbent and allowed to reach equilibrium with a solution of the ligand [6–9]. This technique senses selectively the adsorbed species, since the penetration depth of the IR beam is of the order of 1 µm and the species present in the bulk solution do not interfere when they are at sufficiently low concentrations ($<1\,\mathrm{mmol\,L^{-1}}$). This technique allows the spectroscopic (IR) characterization of the adsorbed species, i.e., different adsorption modes can be observed. For this purpose, the singular value decomposition (SVD) has become a very powerful tool [6–11]. This mathematical procedure permits decomposition into three matrices, wherein the matrix contains one spectrum in each column obtained under a certain given condition (concentration, pH, time, etc.). The columns of the first matrix contain the basis spectra or eigenvectors; real spectra are linear combinations of them. The diagonal elements in the second matrix are the singular values or eigenvalues; the squares of the eigenvalues give the relative weight of each eigenvector. The third matrix describes the composition of the real spectra in terms of the eigenvectors or basis spectra. An analysis of the eigenvalues allows us to discriminate the signals from noise and to know the number of components in the system, i.e., chemical species. Finally, the real spectra of the surface complexes and characteristic constants of the system (i.e., Langmuir constants) can be derived from the eigenvectors or basis spectra using a chemical model (e.g., Langmuir isotherm). *Ex situ* transmission IR spectroscopy has also been used recently to characterize adsorption kinetics and the transformation of adsorbed species on TiO_2 films supported on glass or other substrates [12].

Using the traditional approach, many kinetic studies of the adsorption of different substances have also been done [13, 14], although studies of a series of compounds are very scarce [12]. Several empirical models were used to describe the results; later on, theoretical justifications for their use have been provided [15, 16]. Some FT-IR-ATR kinetic studies have been reported more recently [17]; the dynamics of adsorption for different carboxylic acids on TiO_2 including oxalic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), and triethylenetetramine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexaacetic acid (TTHA) have been reported [18]. The adsorption mechanism bears similarities with the bulk complexation processes; the latter are well known to be described by the Eigen–Wilkins mechanism [1]. This mechanism was able to interpret the results obtained for the kinetics of the complex formation of a wide range of metal ions in solution. However, in heterogeneous systems, diffusion phenomena must also be taken into account, especially when oxide films are studied.

Surface complexation models suggest that chemisorption follows the same mechanism as ligand exchange in dissolved metal ions, i.e., Eigen–Wilkins mechanism [1]. Equations (1) and (2) describe the heterogeneous version of this mechanism.

$$\equiv\mathrm{M{-}OH} + \mathrm{HL} \rightleftarrows \equiv \mathrm{M{-}OH;\ HL} \tag{1}$$

$$\equiv\mathrm{M{-}OH;\ HL} \rightleftarrows \equiv \mathrm{M{-}L} + \mathrm{H_2O} \tag{2}$$

In these equations, ≡M represents a surface metal ion, HL is a complexing weak organic acid, usually bi- or poly-dentate (oxalic or citric acids, EDTA). Bound surface –OH groups can also protonate; this well-known feature is not discussed here [1]. MOH; HL represents an outer sphere complex and ML an inner sphere one.

The study of heterogeneous affinity trends has been very limited until now. The study of the stability behavior of a series of related adsorbates is relatively straightforward, and some examples are found in the literature [1, 8, 11, 19]. Comparison of a series of related adsorbents and one ligand is more difficult because of the many uncertainties involved in the history of different solid samples. Stability trends have been used to establish the similarities between the complexation of surface Ti and dissolved Ti (IV) [7, 11]. The adsorption of oxalic acid on TiO_2 is one of the most thoroughly studied systems. Both two and three different adsorption modes have been reported and their proposed structures have been analyzed by theoretical calculations [20].

Oxalic, citric, and EDTA acids are widely used as chelating agents in solution and in surfaces [1, 21]. Both thermodynamic (adsorption isotherms) and structural (spectral) information have been reported on the adsorption of these ligands onto metal (iron) oxides [22–29]. In this article, we report an FT-IR-ATR study of the adsorption of citric acid, EDTA, and TTHA on TiO_2, in order to study the influence of the number of carboxylic groups on the isotherms, Langmuir constants, and spectra.

2. Experimental

Citric acid (Riedel de Haen), EDTA acid (disodium salt, dihydrated, Mallinckrodt), and TTHA acid (Sigma) were of analytical grade and used without purification. The structures of the ligands studied in this article are shown in figure 1. De-ionized water was doubly distilled from a quartz apparatus. TiO_2 Degussa P 25 was purified by dialysis against distilled water.

FT-IR-ATR measurements were performed in a Nicolet Magna IR 560 spectrometer equipped with a MCT-A detector cooled by liquid N_2. The spectrometer was operated by the OMNIC 5.0 program from Nicolet A 12 reflection. Trapezoidal ZnSe ATR crystal (0.3 × 7.2 × 1.0 cm) was placed inside a horizontal ATR flow cell Spectratech attenuated total reflectance kits (ARK) 0056-303. The ATR flow cell was mounted on a Spectratech ARK accessory. The spectrometer and the last accessory were purged with dry air generated in a Whatman FT-IR purge gas generator. The ATR flow cell was connected by two Teflon tubes to a 300 mL cylindrical glass cell, which was thermostated at 25.0°C and deaereated by continuous slow N_2 bubbling. A Hewlett Packard 89052B peristaltic pump was used to flow the solution from the glass cell

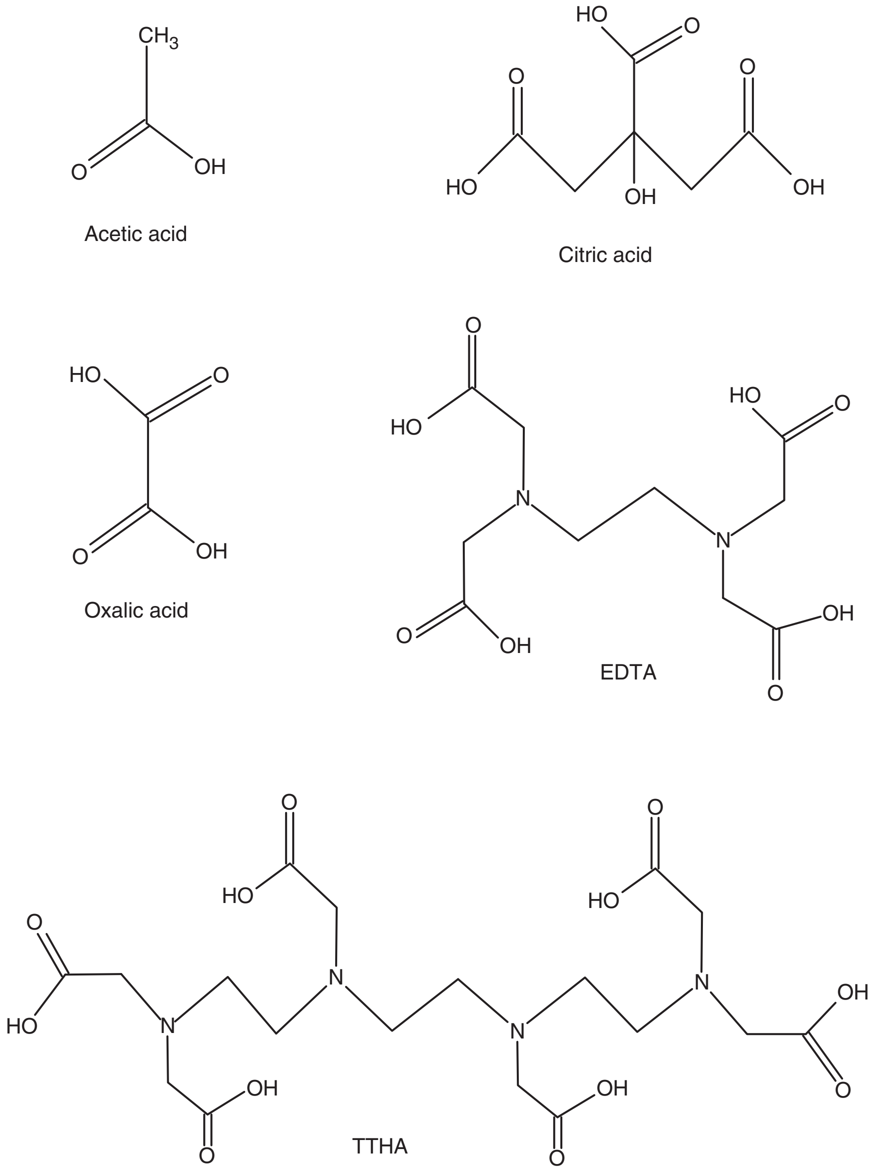

Figure 1. Structures of the studied ligands.

through the ATR cell and back to the glass cell. The flow of the peristaltic pump was 8.1 mL min^{-1}.

Dilute NaOH or HCl solutions (Merck) were used to adjust the pH at 4.0, and NaCl (Merck) was used to control ionic strength, 0.01 mol.

For the preparation of TiO_2 thin films, 200 µL of a water suspension of TiO_2 Degussa P 25 (60 mg 10 mL^{-1}) was spread on one of the faces of the ATR crystal (7.2 × 1.0 cm) and allowed to evaporate overnight. From the previous reports, we have that the thin film has a thickness of *ca* 1.7 µm [6]. The coated crystal was placed in the ATR flow cell and at least 100 mL of water was flowed through it in order to remove the impurities and equilibrate the surface, before connecting the glass cell that contained 300 mL NaCl solution (0.01 mol) at pH 4.0.

Carboxylic acid (0.01 mol) solution was prepared without the addition of NaCl and the pH was adjusted to 4.0. Increasing aliquots of the carboxylic acid solution were added to the glass cell (10, 20, 30, 50, 100, 200, 300, 500, 1000, 2000, 5000, and 10,000 µL), and after homogenization the solution was made to flow through the cell. Spectra were recorded from 900 to 2000 cm^{-1}, (512 scans, resolution 2 cm^{-1}). When the spectra showed no further appreciable changes (up to 5 h were required to achieve this condition for the lowest concentrations), a new aliquot of the carboxylic acid solution was added to the glass cell. These experiments allowed recording spectra in the concentration range from 3×10^{-7} to 6×10^{-4} mol L^{-1}.

In processing spectra obtained at each carboxylic acid concentration, we assumed that the total absorbance at a given wavenumber is the sum of the Lambert–Beer absorbances of all species adsorbed on the surface. The spectra were baseline corrected, using the *spline* mode of the OMNIC 5.0 program, and smoothed (5 points, 10 cm^{-1}, and 25 points, 50 cm^{-1} in the range of 1600–1670 cm^{-1}) with the same program. The baseline were corrected, and smoothed spectra were analyzed with Specfit [30, 31] in the range of 1800–1100 cm^{-1}. SVD of the spectra [6] done by this program was employed to identify different species taking part during the adsorption process. In all the cases, the eigenvalue of the first species was around three orders of magnitude higher than the others. Thus, only the first eigenvector or basis spectrum was relevant and all the spectra were approximately proportional to this basis spectrum. Fitting of the contribution of this eigenvector to each spectrum (at each concentration; third matrix, *vide supra*, A) required the use of two Langmuirian components (equation (3)), where K_1 and K_2 are the Langmuir constants of the two identified adsorption modes. Non-linear fits were done with Origin 6.0. This procedure, conceptually equivalent to fitting the absorbance at the most relevant wavenumbers, has the advantage of using all the data from 1800 to 1100 cm^{-1}. Simulated spectra (Microsoft Excel) and the residuals (i.e., difference between the experimental spectra and the simulated ones at each concentration) were obtained. In the figures, data of absorbance *versus* concentration at a particular wavenumber are fitted as follows:

$$\mathrm{A} = \frac{\mathrm{A}_{1\,\mathrm{max}} K_1[\mathrm{L}]}{1 + K_1[\mathrm{L}]} + \frac{\mathrm{A}_{2\,\mathrm{max}} K_2[\mathrm{L}]}{1 + K_2[\mathrm{L}]} \tag{3}$$

3. Results and discussion

The IR spectrum of adsorbed EDTA at pH 4.0 on TiO_2 is shown in figure 2(a); the spectra of adsorbed TTHA and citric acids are included in the "Supplementary material." All spectra show two broad bands centered around 1400 and 1600 cm^{-1} with several shoulders (table 1). These two bands have been assigned to the symmetric and asymmetric stretching modes of the CO groups [9, 24, 25] (ν^{s}(C–O) and ν^{as}(C–O)), respectively, although contributions from other modes may be present. SVD analysis revealed that the first singular value or eigenvalue was approximately three orders of

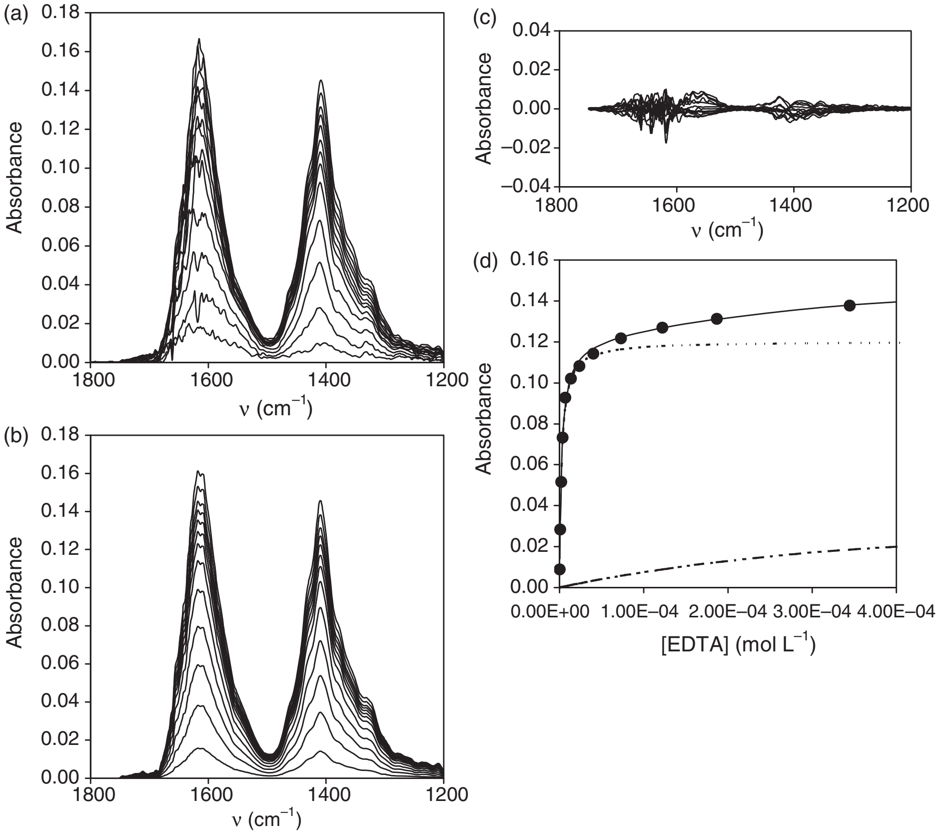

Figure 2. (a) FTIR-ATR spectra of EDTA adsorbed on TiO_2, concentration range from 3×10^{-7} to $6 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$, pH 4.0, $T = 25.0°\mathrm{C}$, $I = 0.01\,\mathrm{mol\,L^{-1}}$. (b) Simulated spectra from SVD analysis. Singular values 6.54, 6.27×10^{-3}, 1.69×10^{-3}. (c) Residual data from SVD analysis, considering only one basis spectrum. (d) Absorbance at $1410\,\mathrm{cm^{-1}}$, (●) experimental data, dashed lines: contributions of the two Langmuir isotherms, $K_1 = (4.06 \pm 0.7) \times 10^5\,(\mathrm{mol\,L^{-1}})^{-1}$ and $K_2 = (1.9 \pm 0.3) \times 10^3\,(\mathrm{mol\,L^{-1}})^{-1}$, solid line: sum of the two contributions.

magnitude larger than the others. However, the Langmuir equation was not adequate as a chemical model to fit all the spectra as a function of concentration. The drift in intensity at high concentrations required the introduction of a second Langmuirian adsorption mode, as described in equation (3) and shown in figure 2(c). For EDTA, this analysis afforded $K_1 = (4.06 \pm 0.7) \times 10^5\,(\mathrm{mol\,L^{-1}})^{-1}$ and $K_2 = (1.9 \pm 0.3) \times 10^3\,(\mathrm{mol\,L^{-1}})^{-1}$, implying the existence of two different [6, 8, 9], albeit spectrally undistinguishable, adsorption modes. The simulated spectra using the data obtained from the fit with equation (1) are shown in figure 2(b) for EDTA. The residuals, i.e., difference of the spectra in figure 2(a) and (b), are shown in figure 2(c). The spectra of the residuals are small compared to the experimental or simulated spectra, thus it can be concluded that the model is reasonably accurate. Simulated spectra and adsorption isotherms are also shown for TTHA and citric acids in the “Supplementary material.” Attempts to include another basis spectrum in the analysis of the three ligands studied in this report were unsuccessful due to the small contribution of the second spectrally different component.

Table 1. IR spectroscopic data and Langmuir constants for the studied carboxylic acids adsorbed on TiO_2.

Ligand		ν_{as}(C–O) (cm^{-1})	ν_s(C–O) (cm^{-1})	log K_L
Acetic[a]		1550	1410	2.1
Oxalic[b]	Mode 1	1692, 1712 (sh)	1415	6.38
	Mode 2	1719	1405	4.48
	Mode 3	1726	1409	3.48
Citric[c]		1575; 1712 (sh)	1400; 1430 (sh), 1295 (sh); 1250 (sh)	6.9; 4.1
EDTA[c]		1610	1410, 1430 (sh), 1380 (sh); 1327 (sh)	5.6; 3.3
TTHA[c]		1610	1410; 1438 (sh); 1385 (sh), 1335(sh)	6.3; *ca* 3.0

For IR data, apparent positions of the bands and shoulders are reported; assignments are based on previous works [6, 7, 11, 24–28].

[a] From Ref. [6].

[b] From Refs. [6–9, 11].

[c] This work, concentration range from 3×10^{-7} to 6×10^{-4} mol L^{-1}, pH 4.0, $T = 25.0°C$, $I = 0.01$ mol L^{-1}.

The interpretation chosen to model the results is not unique. The deviation from Langmuir behavior may be simply due to changes in the electrostatic contribution to the complexation Gibbs energy, or to the operation of lateral interactions between adsorbed ligands. Both effects result in changes of affinity with the degree of surface coverage, and a difficult approach to saturation [1, 21]. However, it is important to recognize that more than one surface complex may be present even if not characterized by distinct spectral signatures. Classical adsorption studies of EDTA onto magnetite showed the formation of a second species at high ligand concentration [23].

The adsorption of EDTA on different metal oxides has been studied, and IR spectra of the complexes formed with various metal oxides have been reported [24, 25]. However, we are not aware of the reports on the interaction of EDTA with TiO_2, except for our recent report on the kinetics of surface complexation [18]. In a recent paper on the adsorption of EDTA on goethite, assignment of the IR bands are offered based on the density functional theory (DFT) calculations and IR studies in solution at different pHs [25]. The conclusion was that two different species were also present on goethite: $HEDTA^{3-}$ (HEDTA, hydroxyethyl EDTA) and H_2EDTA^{2-}. The only subtle indication of a second species in our spectra is a small shoulder at *ca* 1575 cm^{-1}, most apparent at the two lowest concentrations (figure 1a), but probably still present at higher ones. We propose, alternatively, that $EDTA^{4-}$ is responsible for the shoulder at *ca* 1575 cm^{-1}. The ν^s(C–O) are insensitive to protonation due to coupling with other molecular vibrations. On the other hand, adsorption of $EDTA^{4-}$ would maximize the interaction with the surface (i.e., the four carboxylic groups coordinated to the surface) and H_2EDTA^{2-} (responsible for the band at 1610 cm^{-1}) would maximize surface concentration (i.e., two carboxylic groups coordinated and the other uncoordinated).From the kinetic data, $\log K_L = 6.2$ can be estimated [18] in reasonable agreement with the value of 5.6 ($K_1 = (4.06 \pm 0.7) \times 10^5$ mol^{-1}) (table 1) for the most stable complex.

Citric acid is widely used and present in biological fluids [1]. Adsorption on different substrates, particularly goethite, has been studied by several authors [26–28]. It has been proposed that citric acid adsorbs through inner sphere complexes, where the three carboxylic groups are deprotonated [27]. Other authors proposed that at low pH, i.e., 3–4, one or more of these groups could be protonated [26]. Analysis of the spectra shown in the "Supplementary material" affords the two Langmuir constants,

$K_1 = (7.1 \pm 0.3) \times 10^6\,\mathrm{mol}^{-1}$ and $K_2 = (1.2 \pm 0.2) \times 10^4\,\mathrm{mol}^{-1}$. A broad band centered at $1575\,\mathrm{cm}^{-1}$ can be assigned to ν^{as}(C–O), similar to the one observed previously on goethite and at high pH in solution [26]. At higher concentrations a small shoulder at $1712\,\mathrm{cm}^{-1}$ is observed, which was not accurately fitted by our model, probably due to its small contribution. From its wavenumber, we assign this shoulder to an adsorption mode where one of the carboxylic groups is protonated and non-coordinated [6, 9, 26]. Usually, protonated carboxylic groups show intense bands. The low intensity of this band suggests that the surface concentration of this complex is low. Interestingly, EDTA shows no bands at wavenumbers higher than $1680\,\mathrm{cm}^{-1}$, although adsorption modes leaving pendant uncoordinated carboxylic groups are proposed. A possible explanation for this lies on the $\mathrm{p}K_\mathrm{a}$ values of EDTA (0.0, 1.5, 2.0, and 2.66 for the carboxylic groups, and 6.16 and 10.24 for the amine groups) that define the prevalence of zwitter ionic species [10]. Thus, at pH 4.0, pendant carboxylates would remain deprotonated, and the amine groups would provide any required charge compensation through protonation. In fact, aqueous EDTA shows a band near $1700\,\mathrm{cm}^{-1}$ at pH lower than 3.0 [25]. For this reason, small spectral changes would be expected upon coordination on the TiO_2 surface. For citric acid, in contrast, no zwitter ions are possible, and the carboxylate $\mathrm{p}K_\mathrm{a}$ values are 3.13, 4.76, and 6.40 [10]. The IR aqueous spectrum at pH 4.8 shows a band at $1724\,\mathrm{cm}^{-1}$ [27]. According to this value, when carboxylic groups are uncoordinated to the TiO_2 surface, they would be partially protonated, showing the characteristic IR stretching mode at $1712\,\mathrm{cm}^{-1}$. Similar arguments should hold for TTHA (*vide infra*). Following all these arguments, we propose that the main adsorption mode involves a deprotonated triply coordinated bridging ligand, as previously proposed by other authors for the goethite system [28]. The Langmuir constant $K_1 = (7.1 \pm 0.3) \times 10^6\,\mathrm{mol}^{-1}$ ($\log K_\mathrm{L} = 6.9$) obtained for this adsorption mode is in good agreement with the estimation from the kinetic data [18], i.e., $\log K_\mathrm{L}$ 6.5.

TTHA offers six carboxylic groups available for coordination. In the "Supplementary material," spectra at different ligand concentration, the isotherm fitted to equation (3), simulated spectra, and the residuals are shown. The spectra are very similar to the ones of EDTA. The first spectrum shows a small shoulder *ca* $1575\,\mathrm{cm}^{-1}$ probably due to a second adsorption mode, similar to EDTA. Like EDTA, but in contrast to citric acid, TTHA does not give rise to bands or shoulder *ca* $1700\,\mathrm{cm}^{-1}$. The obtained Langmuir constants were $K_1 = (2.1 \pm 0.1) \times 10^6\,(\mathrm{mol\,L}^{-1})^{-1}$ and K_2 $1000\,(\mathrm{mol\,L}^{-1})^{-1}$. Again, reasonable agreement is found for $\log K_1$ from equilibrium (6.3) and kinetic (6.6) data [18]. Probably, the same type of surface coordination as in EDTA is involved, the main species being formed by a completely deprotonated and polydentate ligand. Again, in the presence of excess ligand, the denticity may decrease to permit the adsorption of further ligands.

A final comment on the trends in the values of K_L: As already stated, mono-carboxylic acids, like acetic or benzoic acids, do not form stable surface complexes [6, 8, 11]. Higher denticity, whether or not accompanied by higher nuclearity, is required to form stable surface complexes. However, EDTA and TTHA, which are tetradentate and hexadentate, do not have the highest K_L values in table 1. Citric and oxalic acids are stronger surface complexants. There are several factors that may operate to explain this observation. First, the protolytic equilibria of the ligands may influence the sequence observed at pH 4 [7, 11]. Also, the increase in denticity is probably accompanied by an increase in nuclearity, and hence no direct comparisons can be made. Finally, it seems to emerge from all available data that aminocarboxylic acids (as EDTA and TTHA) are less strong surface complexants than carboxylic acids (oxalic and citric acids), probably because protonated pendant amino groups decrease the electrostatic contribution to the overall complexation Gibbs energy. In agreement with our results, it has been reported that glycine does not bind to TiO_2 [29], although scanning tunneling microscopy (STM) studies of glycine on TiO2 (1 1 0) single crystal surfaces [32] conclude that glycine adsorbs as glycinate. The low affinity is reasonable for a ligand with only one carboxylic group and one amino group.

4. Conclusions

The spectral study of the surface complexation equilibria of several polycarboxylic acids on TiO_2 shows that citric acid, EDTA, and TTHA have high affinities for surface Ti (IV) ions. As the solution chemistry of Ti (IV) is rather limited, the heterogeneous systems provide a good tool to explore this affinity and the spectral features of the complexes. The IR spectra can be modeled using only a single basis spectrum for each ligand, but the adsorption isotherm fitting requires two Langmuirian equations. Langmuir constants (K_L) can be interpreted in terms of the molecular structure and the number of carboxylic groups. The highest K_L holds for citric acid, followed by oxalic acid and TTHA. EDTA has the smallest Langmuir constant of the group, $K_L = (4.06 \pm 0.7) \times 10^5\,(\text{mol}\,L^{-1})^{-1}$. Structures for the most important adsorption modes of each of the ligands are proposed based on the previous studies on related systems. We suggest that the most stable adsorption mode corresponds to the fully deprotonated ligands and with all the carboxylic groups coordinated to Ti ions.

Supplementary material

FT-IR-ATR spectra of citric acid and TTHA adsorbed on TiO_2; simulated spectra from SVD analysis; residual data; plots of absorbance *versus* ligand concentration: experimental data and contributions of the two Langmuir isotherms.

Acknowledgments

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