Stability of Surface Complexes Formed at the TiO$_2$/Water Interface*

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Keywords
adsorption
surface complexation
titanium dioxide
carboxylic acids
affinity trends

TiO$_2$ surface complexation by bidentate organic ligands is analysed in terms of the ligand Brønstead and Lewis basicities. The complexation and basicity constants comply with linear Gibbs Energy relationships (LGERs). For dicarboxylic acids, the surface chelate bond makes an approximately constant contribution to the stability. The proton transfer to the surface modulates the pH dependence of stability. A correlation exists between the surface complexation constant of the neutral acid H$_2$L and the ligand first acidity constant. On the other hand, the surface complexation constants of dianions L^{2-} of cathecols and aminophenols are positively correlated with the ligand second acidity constant. Apparent stability is determined by the competition of H$^+$ and surface metal ions for the ligand. Stability trends are strongly influenced by the Brønstead acid base reaction between the acid ligands H$_2$L and the surface, whereas the stability of the surface chelate contributes to the overall stability.

INTRODUCTION

The surface complexation approach has been very successful in describing the factors that influence the extent of chemisorption of complexing ligands onto oxidic surfaces placed in aqueous media. In this approach, »stability constants« of surface complexes are derived from experimental adsorption isotherms, assuming valid the basic tenet that a surface complex is a *quasichemical entity, largely decoupled from the rest of the solid framework*; oxide groups binding this entity to the rest of the solid are simply regarded as pendant ligands.[1] If this point of view were totally correct, surface complexes could be, in principle, characterised as precisely as their equivalent dissolved analogues; in practise, this idea needs to be validated experimentally.

Even accepting this approach, several factors must be recognised that make surface complexes appreciably different from aqueous species: (i) depending on the detailed characteristics of the charge distribution across the solid/liquid interface, non-zero macropotentials may result in the locus of adsorption even under zero surface charge conditions; indeed, many common electrical double layer (edl) models, such as the triple layer model, place adsorbing ligands in planes that differ from those of proton adsorption; (ii) solvation effects may be appreciably

different at the interface and in bulk solution; (iii) the electronic structure of the surface complex may in fact be strongly influenced by the solid lattice; for example, in the case of n-type semiconductors such as TiO$_2$, surface complexes may act as electron traps, *i.e.,* they may behave as localised surface states with peculiar electronic structures.

The classical road to understanding the stability of dissolved complexes involved the analysis of stability trends within series of related complexes. This approach is limited in the case of surface complexes because of a restricted amount of experimental data, and also because surface complexation stability constants are model-dependent: the assumptions made about the edl structure influence drastically the values of the derived 'constant'. There is no unique accepted model, and data derived using the diffuse layer, the constant capacitance and the triple layer models are frequently presented in the literature.[1] The problem of trends in a series of allegedly similar surface complexes is compounded when the analysis is focused on a series of complexes formed by the same ligand with a series of solid oxides. Here, all factors affecting the surface structure of each solid due to their histories may completely blur any 'intrinsic' trend. It is, however, still possible to analyse trends based on data collected with a single sample of a given metal oxide and a series of related ligands, recognising that other samples of the same solid may yield different absolute values of stability constants but, hopefully, identical trends.

In this paper, we compile and discuss a series of stability constants for the adsorption of carboxylate- and phenolate-bound ligands onto TiO$_2$. Adsorption of carboxylates onto metal oxides has been frequently dealt with in the literature, including the very detailed studies of adsorption onto iron oxides by Kallay.[2–6] In what follows, we shall assume that adsorption is electroneutral. This assumption allows using a simple Langmuirian model for adsorption, disregarding the possible influence of macropotential variations on the stability. Such simplified approach is adequate to analyse trends; a detailed analysis of the edl structure is of course necessary to describe electrokinetic properties.[2–8]
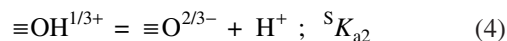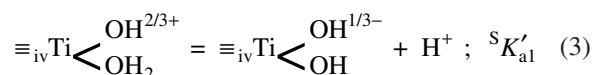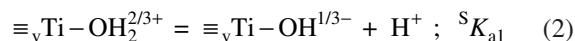
The Model

For any diprotic acid that complexes metal ions exposed on the TiO$_2$ surface, we assume that n complexation modes can operate, each being described by specific values of a and b in the general stoichiometric equation of the form:

$$\equiv Ti_a(OH)_2 + H_2L =$$
$$\equiv Ti_a\text{-}L(H_2O)_b + (2-b)H_2O; \; {}^SK(H_2L) \quad (1)$$
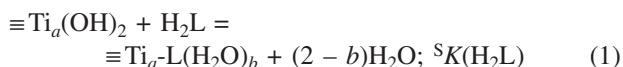
In a previous paper,[9] we identified three types of surface sites on TiO$_2$, called *A*, *B* and *C*. These sites are

schematically shown in Figure 1; the number of coordination positions of surface Ti ions occupied by lattice O^{2-} ions is 5 and 4 for sites *A* and *C*, respectively. Surface complexation involves sites *A* and *C*; thus Eq. (1) recognises different adsorption modes, depending on the values of a (1 or 2) and b (0 or 1).

Surface complexation is always coupled to the acid--base surface equilibria. In fact, the metal centres on the TiO$_2$ surface are charged, as described by Eqs. (2) and (3). Counterion adsorption (essentially H$^+$) compensates most of the charge borne by the Ti surface complexes, but the state of charge of the surface changes somewhat with increasing substitution, mainly because of a decrease in the number of *A* sites involved in the protolytic equilibrium (2), and the indirect effect on the protolytic equilibria of *B* sites, Eq. (4); the influence of *C* site protolytic equilibria is minor because of its lower surface density. If these changes do not affect to any important extent the affinity of the surface for the ligand, a reasonable assumption in view of the electroneutral nature of Eq. (1), it can also be assumed that pH influences the affinity only through the changes in solution speciation of the ligand. Insofar as the degree of protonation of the surface is low, its effect is indeed expectedly low. This approximation breaks down in very acidic media.

$$\equiv_v Ti-OH_2^{2/3+} = \equiv_v Ti-OH^{1/3-} + H^+ ; \; {}^SK_{a1} \quad (2)$$

$$\equiv_{iv}Ti{<}^{OH^{2/3+}}_{OH_2} = \equiv_{iv}Ti{<}^{OH^{1/3-}}_{OH} + H^+ ; \; {}^SK'_{a1} \quad (3)$$

$$\equiv OH^{1/3+} = \equiv O^{2/3-} + H^+ ; \; {}^SK_{a2} \quad (4)$$

Most of the reported surface stability constants are in fact Langmuirian, derived either from classical adsorption experiments or from the concentration dependence of *in situ* FTIR-ATR spectra, both types of experiments being carried out at constant pH. As such, the reported constants (hereafter K^{ap}) are conditional and pH dependent. However, on the basis of the above assumptions, they can be converted into ${}^SK(H_2L)$ (Eq. (5)), the constants used in this paper to characterise the stability of different surface complexes, through Eq. (6)

$$^SK(H_2L) = \frac{\{\equiv Ti_a\text{-}L(H_2O)_b\}}{\{\equiv Ti_a(OH)_2\}[H_2L]} \quad (5)$$

$$K^{ap} = {}^SK(H_2L)\frac{[H_2L]}{[H_2L]_T} \quad (6)$$

where { } represents surface concentrations (mol m^{-2}) and [] concentrations in solution (mol dm^{-3}), and [H$_2$L] is the ligand concentration at the explored pH, and [H$_2$L]$_T$ is the total (analytical) concentration of the ligand in the equilibrated solution.
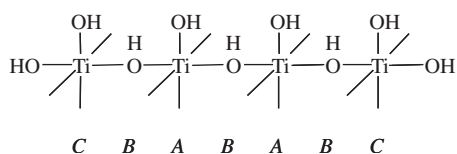
Figure 1. Representation of the different sites formed upon hydroxylation of the surfaces of low Miller indexes of anatase; *C* sites belong to the surface edge.
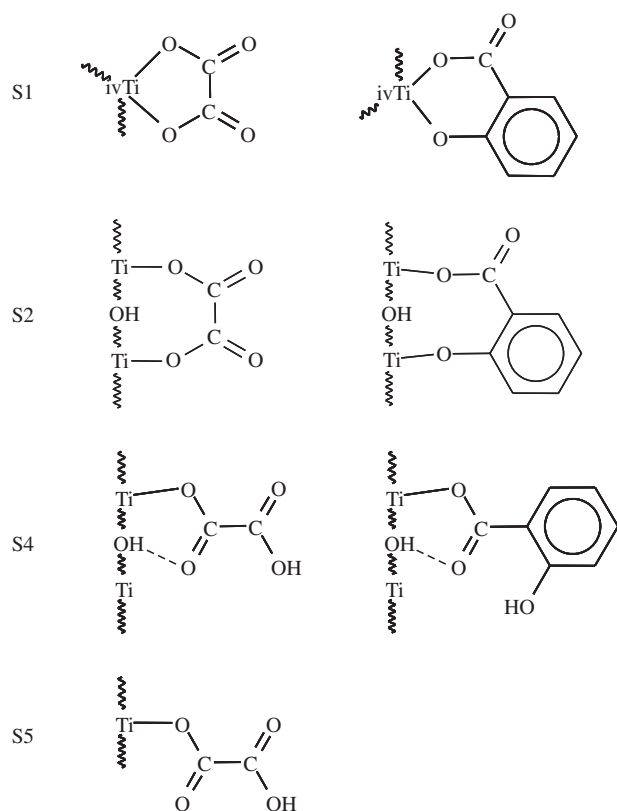

Figure 2. Structure of the surface complexes formed by chemisorption of oxalate and salicylate onto TiO₂, as derived by analysis of the FTIR-ATR changes upon changes in the concentration of the ligand (from Ref. 12).

Structural Characterisation and Stability of Surface Complexes

Eq. (1) describes the complexation of surface Ti ions *A* and *C* in terms of the values of *a* (1 or 2) and *b* (0 or 1). For *b* = 0, the value of *a* defines the participation of a single (*C*) or two metal (*A*) sites in the complexation reaction. The complexes thus formed are, respectively, a chelate and a bridged binuclear complex. Eq. (1) represents a ligand exchange reaction, L^{2-} substituting for two OH⁻, and describes an electroneutral process. For *b* = 1, a monodentate complex is formed at site *C*, and site *B* participates, together with site *A*, through a hydrogen bond or a proton transfer reaction with the pendant complexing group; again, the process is electroneutral. Structures of individual surface complexes formed by oxalate and salicylate on TiO₂ are shown in Figure 2.

The postulated structures interpret adequately the FTIR-ATR spectral features observed when a TiO₂ film is equilibrated with an aqueous solution of a given ligand, in particular the bands attributed to the carboxylate ν_a and ν_s vibrations.[10–15] The most stable ones (S1 in Figure 2) are chelates formed according to Eq. (1) with *a* = 1 and *b* = 0. For further details, see Refs. 11 and 12. Recent MSINDO[16] calculations have however suggested that the most stable surface species formed by dicarboxylates may be the binuclear complex (S2), in which each carboxylate group is bound to a different surface Ti ion.[17–19] For our purposes, the difference between mononuclear and binuclear chelates is not important. The analysis will be focused on the stability of the most stable species.

Table I lists the values of the Langmuir-type stability constants of a whole series of complexes formed on the surface of TiO₂ P-25. Except in the case of monocarboxylic acids, all of them are chelates. The constants for carboxylic acids and carboxypyridines were derived by modelling the dependence of the relative intensities of the IR bands on ligand concentration,[11,12,20] or from adsorption isotherms.[21] Those for aminophenols and catechols also correspond to adsorption isotherms,[22] but from pH envelopes. Despite these ^{S}K values being derived using the diffuse layer model, they are included because complexes formed by aminophenols are described as neutral species, in line with the premises of Eq. (1); the negatively charged complexes formed by catechols are also included. Hopefully, this very simple structure of the edl does not blur the comparison of the constants. Data reported for salicylic acid[9] catechol[8] and 4-chlorocatechol,[23] derived using the more elaborated triple layer model, were excluded from the present analysis.

Linear Gibbs Energy Relationships (LGERs)

Trends in Homogeneous Complexation in Aqueous Solution. – In solution, the values of pK_{a1} and pK_{a2} of weak diprotic acids (Eqs. (7) and (8)) increase as the Brønstead basicity of L^{2-} anions increases.

$$H_2L = HL^- + H^+ \tag{7}$$

$$HL^- = L^{2-} + H^+ \tag{8}$$

The stability of the complexes formed by L^{2-} and M^{2+} cations (stability constant *K*) depends on the Lewis basicity of L^{2-}. Figure 3 shows the correlation between the stability constants $K(H_2L)$ and $K(L^{2-})$ of the Co^{II} complexes, defined by Eqs. (9) and (10), and the pK_{a1} values for a series of dicarboxylate ligands (oxalate, malonate, succinate, glutarate and chinolinate). The data show reasonably good LGERs, with slopes – 2.2 and – 0.99, respectively, for $K(H_2L)$ and $K(L^{2-})$. These two constants are related through Eq. (11); hence the slopes in Figure 3 are linked through Eq. (12). In the plot, for the linear rela-

TABLE I. Dissociation constants of selected ligands and Langmuirian stability constants of the most stable surface complexes formed on titanium dioxide (P-25)

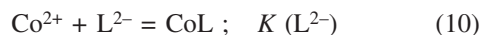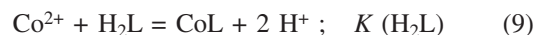| Protonated ligand	pK_{a1}[a]	pK_{a2}[a]	log K^{ap} [b]	log $^SK(H_2L)$[c]	log $^SK(L^{2-})$[d]	Ref.[e]
Acetic acid	4.75		2.3 (4.5)	2.44	7.19	20
Benzoic acid	4.20		3.3 (3.6)	3.40	7.60	21
Oxalic acid	1.25	4.27	6.5 (3.6)	8.93	14.46	11
			6.6 (3.0)	8.38	13.90	20
Malonic acid	2.85	5.70	6.1 (3.5)	6.84	15.39	11
Phthalic acid	2.95	5.40	4.7 (3.6)	5.44	13.79	21
Isophthalic acid	3.50	4.50	4.3 (3.6)	4.68	12.68	21
Terephthalic acid	3.61	4.50	5.3 (3.6)	5.62	13.73	21
Salicylic acid	2.97	13.74	5.1 (4.1)	6.26	22.97	11
Picolinic acid	1.01	5.39	5.8 (3.5)	8.30	14.70	11
Nicotinic acid	2.03	4.83	6.3 (3.5)	7.80	14.66	11
Dipicolinic acid	2.27	5.07	5.4 (3.5)	6.67	14.01	11
Cinchomeronic acid	2.70	4.90	6.1 (3.5)	6.98	14.58	11
2-aminophenol	3.90	9.30		−1.69	11.51	22
4-methyl-2-aminophenol	3.10	7.60		0.19	10.89	22
4-phenyl-2-aminophenol	4.40	9.70		−1.41	12.69	22
4-chloro-2-aminophenol	4.70	9.90		−2.53	12.07	22
4-nitro-2-aminophenol	4.30	10.00		−2.07	12.23	22
4-chlorocatechol	8.77	12.73		−0.98	20.52	22
4-nitrocatechol	6.88	11.24		0.26	18.38	22

[a] From Ref. 24
[b] Values within parentheses correspond to experimental pH
[c] See Eq. (6)
[d] *cf.* Eq. (11)
[e] Values reported in Ref. 22 correspond to $^SK(L^{2-})$
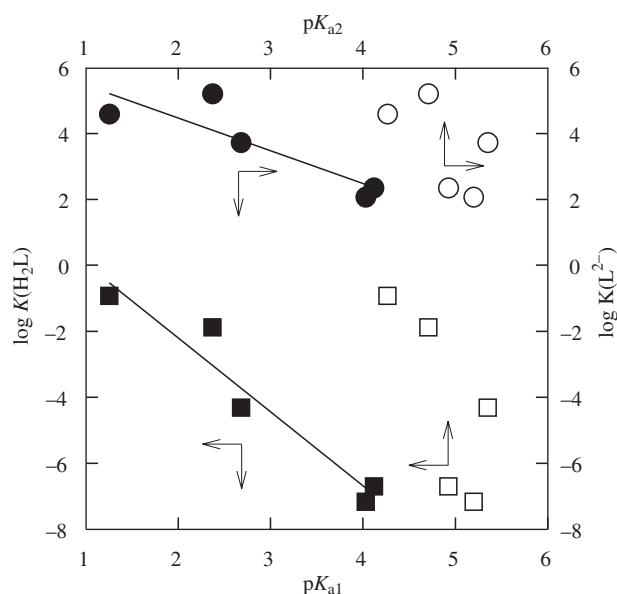
Figure 3. LGER between log $K(H_2L)$ (■, lower line) or log $K(L^{2-})$ (●, upper line) and pK_{a1}; stability constants of CoL aqueous complexes were taken from Ref. 24. Also included are (□) log $K(H_2L)$ and (○) log $K(L^{2-})$ values plotted as a function of pK_{a2}.

tionships to be intrinsically consistent, a constant pK_{a2} value should be equal to the difference in the ordinate at the origin, *i.e.,* ≈ 4.9. The deviations are due to fluctuations in pK_{a2} values, which do not follow any definite trend when the ligands are ordered according to their pK_{a1} values.[a] The values (log $K(H_2L)$; pK_{a2}) and (log $K(L^{2-})$; pK_{a2}) are also shown in Figure 3.

$$Co^{2+} + H_2L = CoL + 2\,H^+ ; \quad K\,(H_2L) \quad (9)$$

$$Co^{2+} + L^{2-} = CoL ; \quad K\,(L^{2-}) \quad (10)$$

$$K\,(H_2L) = K\,(L^{2-})\,K_{a1}\,K_{a2} \quad (11)$$

$$\frac{\partial \log K(H_2L)}{\partial pK_{a1}} = \frac{\partial \log K(L^{2-})}{\partial pK_{a1}} - 1 - \frac{\partial pK_{a2}}{\partial pK_{a1}} \quad (12)$$

The less basic anions L^{2-}, as measured by (pK_{a1} + pK_{a2}) or simply by pK_{a1}, form the less stable CoL complexes. The values of pK_{a1} for the explored dicarboxylic acids span three orders of magnitude, reflecting the different stabilisation of the monoanion HL^- by forma-

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[a] The relation between pK_{a1} and pK_{a2} is also shown below (see Figure 6).

tion of an inner hydrogen bond; this effect is responsible for the high acidity of oxalic acid. Stabilisation of complex ML by chelation runs parallel to this trend, and explains the observed inverse LGER. The vicinity of two carboxylate groups defines the high Brønstead acidity (pK_{a1}) and high Lewis basicity ($-pK(L^{2-})$). The values of pK_{a2} change less along the series and affect less the stability of the complexes.

The analysis of the stability of aqueous $Ti^{IV}L$ complexes is precluded by the dearth of data.

Surface Complexation. – As illustrated in Figure 2, the studied ligands form two or three different surface complexes on TiO₂. The dissolved complexes discussed above are mononuclear chelates, similar to those postulated as the most stable surface complexes. We shall therefore focus on these most stable complexes. The Langmuir type stability constants $^SK(H_2L)$ of these complexes (Eq. (1), for $a = 1$, $b = 0$) are shown in Table I.

Figure 4A shows the LGERs for log $^SK(H_2L)$ with pK_{a1}. For dicarboxylic acids, the slope of the straight line is –1.8. Again, an inverse relationship exists between the Brønsted (pK_{a1}) and the Lewis (log $^SK(H_2L)$) basicity of the ligands (*cf.* Figure 3). An interesting feature is that simple monocarboxylic acids and monocarboxylic pyridines also comply with the LGER.

Aminophenols also show an inverse log $^SK(H_2L)$ *vs.* pK_{a1} relationship, the slope not being very different, but with lower values of $^SK(H_2L)$. Whether this is a consequence of electrostatic correction implicit in the diffuse model is an open question. The figures as reported indicate that, for a given Brønsted basicity, the Lewis basicity of aminophenolates is lower than that of dicarboxylates. It should be noted that pK_{a1} in this case refers to the protolysis of the $^+H_3N-$ group.

The few available data on complexation by catechols demonstrate, as expected, higher affinity. The lower slope suggests a weak correlation between surface complexation and Brønsted basicity.

Equilibrium (1) can be analysed also in terms of the equivalent Eq. (13). $^SK(L^{2-})$ constants, corresponding to $a = 1$ and $b = 0$, are also listed in Table I; relationships (11) and (12) still hold for ^SK constants. As opposed to the case of aqueous complexes (see Figure 3), for which both log $^SK(H_2L)$ and log $^SK(L^{2-})$ depict similar trends with pK_{a1}, Figure 4B shows that log $^SK(L^{2-})$ values corresponding to dicarboxylates and carboxypyridines are not influenced by pK_{a1}, the slope of the plot being null.

$$\equiv Ti_a(OH)_2 + L^{2-} + 2H^+ =$$

$$\equiv Ti_a\text{-}L(H_2O)_b + (2-b)H_2O ; \quad ^SK(L^{2-}) \quad (13)$$
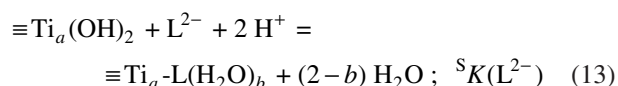
Comparison of Eqs. (1) and (13) shows that the base accepting the protons from H_2L is in the first case a surface OH group, and the solvent H_2O in the second. It is thus reasonable to infer that the stability of surface complexes is governed by the ease of proton transfer from the ligand to the surface. Figure 5 compares the experimental data for dicarboxylic acids with the simple expression (14), which implies a constant log $^SK(L^{2-})$ value of 14.2 for the whole series of ligands.

$$\log {}^SK(H_2L) = 14.2 - pK_{a1} - pK_{a2} \quad (14)$$

Eq. (14) represents a simple case in which the tendencies in affinity of a series of related ligands are defin-
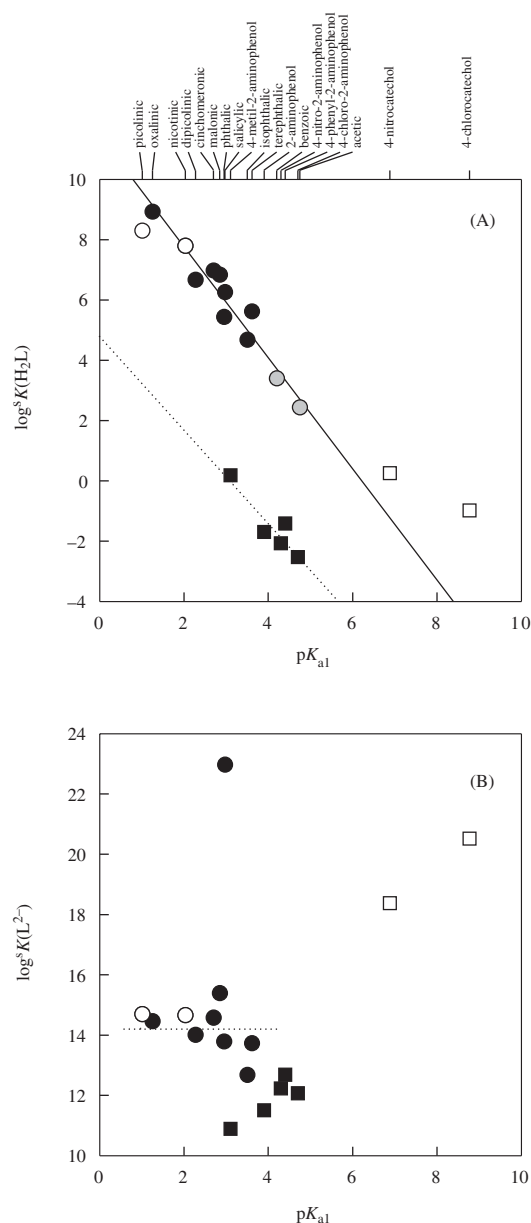

Figure 4. (A) Dependence of log $^SK(H_2L)$ on pK_{a1} for dicarboxylates (full circles), monocarboxylates (grey circles), monocarboxypyridines (open circles), aminophenols (full squares) and cathecols (open squares). (B) Dependence of log $^SK(L^{2-})$ on pK_{a1}; monocarboxylates are not included in this plot.
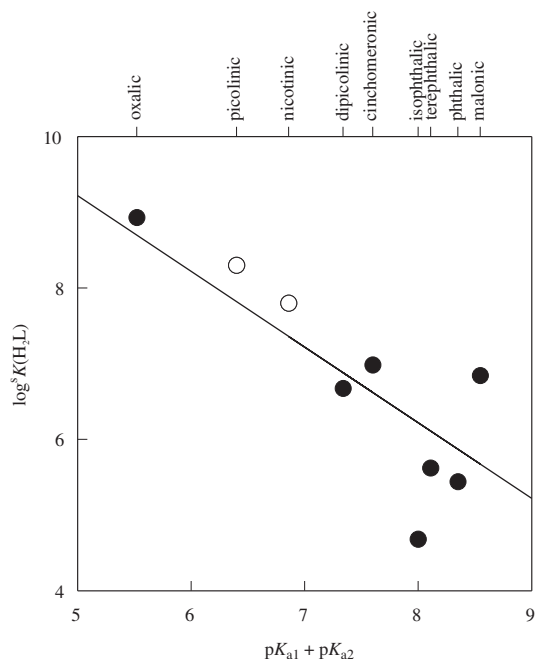
Figure 5. Log $^SK(H_2L)$ values plotted as a function of the sum $(pK_{a1} + pK_{a2})$.
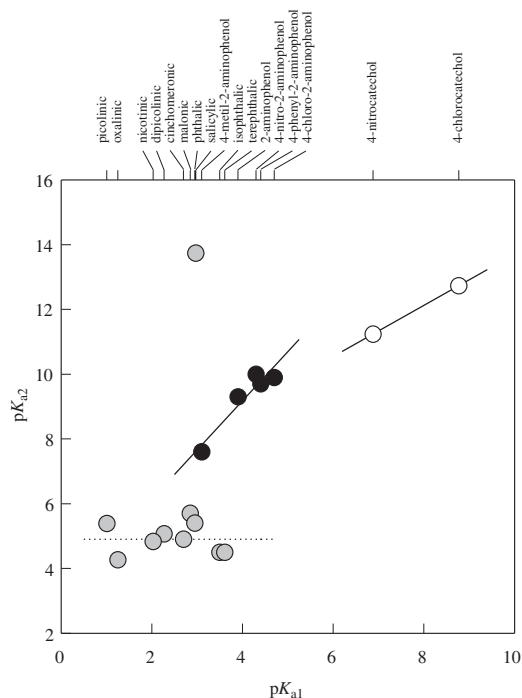

Figure 6. LGER between pK_{a2} and pK_{a1} for aminophenols (full symbols), cathecols (open symbols). Data for carboxylates (grey symbols) are also shown.

the actual coordinative bonding of the dianion to the surface Ti atoms.

In the case of cathecols and aminophenols, the acidity of the ligands is appreciably lower than that of carboxylates. Furthermore, in these cases there is a good correlation between pK_{a1} and pK_{a2}, as shown in Figure 6. The LGERs are given by Eqs. (15) and (16) for aminophenols and cathecols, respectively.

$$pK_{a2} = 3.1 + 1.5 \ pK_{a1} \qquad (15)$$

$$pK_{a2} = 5.8 + 0.8 \ pK_{a1} \qquad (16)$$

As opposed to the case of carboxylates, log $^SK(L^{2-})$ values for aminophenols and cathecols show now a positive correlation with pK_{a1} (Figure 4B, square points) and pK_{a2} (Figure 7). For aminophenols, ∂log $^SK(L^{2-})/\partial pK_{a2}$ equals 0.60, whereas ∂log $^SK(L^{2-})/\partial pK_{a1}$ is 0.98. For cathecols, the slopes are 1.5 and 1.1, respectively. These figures are consistent with the LGERs represented in Eqs. (15) and (16). In these cases, where the Brønsted and Lewis basicities are positively correlated, the more basic ligands L^{2-} form more stable complexes, and the stability of the coordinative bond responds to the same structural factors as the affinity for H^+. Different stabilities of these sets of ligands are related to the donor ability of the more acidic group.[22] For aminophenols, K_{a2} corresponds to the ionisation of the only OH group, thus rendering it comparable to the pK_{a1} of cathecols; the charge borne by the
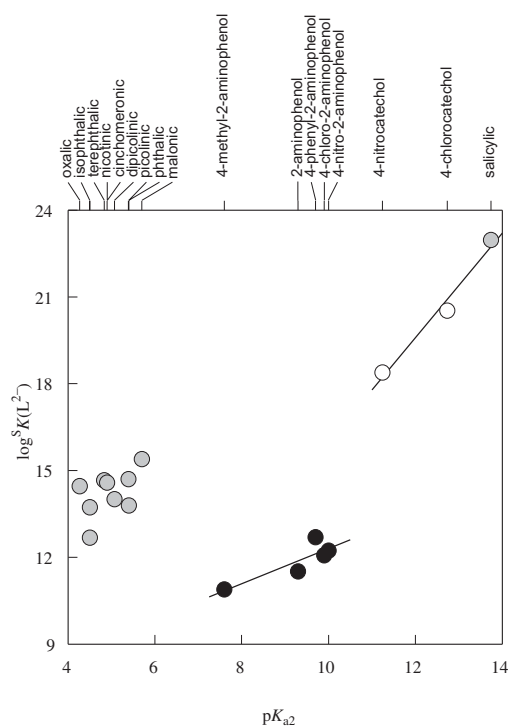

Figure 7. Dependence of log $^SK(L^{2-})$ on pK_{a2} for aminophenols (full symbols) and cathecols (open symbols). Data for carboxylates (grey symbols) are also shown.

ed solely by the Gibbs energy of the transfer of the two protons from the neutral ligand to the surface. It is obvious that actual data do not comply exactly with Eq. (14), but it is also clear that proton transfer is more important to define the stability trends of the surface complexes than

anion is however –1; hence, a much lower affinity for the surface is observed. Interestingly, salicylate compares with catechols if the stability trend is cast in terms of log $^SK(L^{2-})$ *vs.* pK_{a2}, but behaves like a carboxylate when the log $^SK(H_2L)$ *vs.* pK_{a1} LGER is examined.

In summary, whereas surface dicarboxylate complexes are more stable when the dicarboxylic acid loses readily its first proton, the stability of surface catecholates and surface aminophenolates parallels their Brønsted basicity.

CONCLUSIONS

Both in solution and on the surface of metal oxides, complexation by the anion of weak acids involves the competition of H^+ and the metal centre for the anion. Whereas in the former case protons are transferred to the solvent (water), in the latter case they are transferred to surface OH groups, which are just as important as the metal centres in defining the stability of the surface complexes. Strongly basic surface OH groups are therefore essential to stabilise surface complexes. Surface complexation by anions cannot be isolated from surface protonation in any thermodynamic or structural account of anion chemisorption on the surface of metal oxides.

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SAŽETAK

Stabilnost površinskih kompleksa na međupovršini TiO₂/voda

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Kompleksiranje bidentantnih organskih liganada na površini TiO$_2$ analizirano je na temelju Brønstead/Lewisove teorije kiselina i baza. Ravnotežne konstante kompleksiranja i protonacije linearno su ovisne o Gibbsovoj energiji. Stabilnost nastalih kompleksa dikarboksilnih kiselina ovisi o površinskim helatnim vezama i o pH otopine. Utvrđena je korelacija ravnotežne konstante površinskog kompleksiranja neutralne diprotonske kiseline (H$_2$A) i ravnotežne konstante disocijacije prvog protona s liganda. Ravnotežne konstante kompleksiranja aniona (L^{2-}) katehola i aminofenola korelirane su s ravnotežnom konstantom disocijacije drugog protona s liganda. Stabilnost je određena natjecanjem protona i površinskih kovinskih iona za ligand. Također je pokazano, da je stabilnost pod jakim utjecajem Brønsteadove kiselo-bazne reakcije između liganda kiseline H$_2$L i površine, dok stabilnost površinskog helata doprinosi ukupnoj stabilnosti.