



PII S0016-7037(99)00228-8

The relationship between molecular structure and ion adsorption on variable charge minerals

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(Received October 15, 1998; accepted in revised form April 29, 1999)

Abstract—Ion adsorption modeling is influenced by the presumed binding structure of surface complexes. Ideally, surface complexes determined by modeling should correspond with those derived from spectroscopy, thereby assuring that the mechanistic description of ion binding scales from the nanoscopic molecular structure to the macroscopic adsorption behavior. Here we show that the structure of adsorbed species is a major factor controlling the pH dependency of adsorption. An important aspect of the pH dependency is the macroscopic proton-ion adsorption stoichiometry. A simple and accurate experimental method was developed to determine this stoichiometry. With this method, proton-ion stoichiometry ratios for vanadate, phosphate, arsenate, chromate, molybdate, tungstate, selenate and sulfate have been characterized at 1 or 2 pH values. Modeling of these data shows that the macroscopic proton-ion adsorption stoichiometry is almost solely determined by the interfacial charge distribution of adsorbed complexes. The bond valence concept of Pauling can be used to estimate this charge distribution from spectroscopic data. Conversely, the experimentally determined proton-ion adsorption stoichiometry allows us to successfully predict the spectroscopically identified structures of, for example, selenite and arsenate on goethite. Consequently, we have demonstrated a direct relationship between molecular surface structure and macroscopic adsorption phenomena. *Copyright* © 1999 Elsevier Science Ltd

1. INTRODUCTION

Geochemists are challenged to translate the knowledge of surface species coordination gained from in situ spectroscopic techniques such as EXAFS, ATR-FTIR and CIR-FTIR into models for the calculation of chemical equilibria in soils, sediments and natural waters (Stumm and Morgan, 1996; Brown, 1990). Ideally, a mechanistic ion adsorption model can describe adsorption data using physically realistic surface structures. In other words, the model should properly scale from the nanoscopic molecular level to the macroscopic level of an adsorption experiment (Van Riemsdijk and Hiemstra, 1999).

The structure of minerals can be interpreted with great accuracy using bond valence theory (Brown, 1978), which is a refinement of the classical Pauling bond valence concept. This concept can also be applied to interfaces. The MUSIC (MUltiSite Ion Complexation) model is a framework that illustrates how one can use the bond valence concept to develop and parameterize models that describe the basic charging of minerals (Hiemstra et al., 1989a; b, (original model); Hiemstra et al., 1996 (refined model); Rustad et al., 1998; Felmy and Rustad, 1998).

Ion adsorption models should not only account for surface structure, but also for the structure of adsorbed ions. Extending the bond valence concept to describe inner and outer sphere surface complexes immediately leads to the notion that the charge of the adsorbing species is partly effective at the surface plane, and partly resides at a greater distance from the surface.

This concept led to the development of the CD-MUSIC model (Hiemstra and Van Riemsdijk, 1996), where CD stands for Charge Distribution.

In this paper we will study the relation between the microscopic distribution of adsorbed charge and an important macroscopic property of ion adsorption, (i.e., the pH dependency). The pH dependence of adsorption is classically studied either by measuring a series of adsorption isotherms at different, but constant pH values, or by measuring the change in adsorption with pH for various total solid and ion concentrations. This last procedure is commonly known as the 'adsorption edge' method. Here we follow another procedure to characterize the pH dependency of adsorption, (i.e., the determination of the proton-ion adsorption stoichiometry). It has been shown by Perona and Leckie (1985) and Cernik et al. (1996) that the macroscopic proton-ion adsorption stoichiometry is related to the pH dependence of ion adsorption via the thermodynamic consistency relationship. The ratio between the proton co-adsorption/desorption and the amount of ion adsorbed is generally non-stoichiometric, and varies with pH, ionic strength and surface coverage (Rajan, 1978; Perona and Leckie, 1985; Fokkink et al., 1987; Machesky et al., 1989; Hiemstra and Van Riemsdijk, 1996; Robertson and Leckie, 1998).

We have studied the co-adsorption of protons as a function of the oxyanion adsorption on goethite at constant pH, for conditions where almost 100% of the anion of interest was adsorbed. This condition has the advantage that the adsorbed amount directly follows from the added amount of ions. It also has the advantage that the added amount of protons will yield the co-adsorption of protons since almost no protons are consumed by the solution. We define the macroscopic proton-ion adsorption stoichiometry as the amount of acid consumed upon addition of an oxyanion in the unprotonated form, divided by

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the amount of oxyanion adsorbed at constant pH. Note that this stoichiometry is not necessarily expressing the ion binding pH dependence directly because the degree of protonation in solution must also be accounted for.

The relation between the macroscopic proton-ion adsorption stoichiometry and the structure of surface complexes can be studied for ions with a known surface structure. For goethite, the surface complexes of sulfate, arsenate and selenite seem to be best known from spectroscopy (Hug, 1997 and pers. comm.; Waychunas et al., 1993; Hayes et al., 1987). In the present study the macroscopic proton-ion adsorption stoichiometry for the above species has been determined for pH conditions that have also been used in the spectroscopic studies mentioned above. We will also present and evaluate data for phosphate, vanadate, chromate, tungstate, molybdate and selenate.

In the data analysis we assume that only one surface species per adsorbed ion is dominant. This seems reasonable given the spectroscopic results for sulfate (Hug, 1997), selenite (Hayes et al., 1987; Manceau and Charlet, 1994), and phosphate (Tejedor and Anderson, 1990) for experimental conditions similar to those of this study (pH 4 to 6, ion adsorption below 1.5 (mol/m²). Under the experimental conditions used, the surface is expected to will remain positively charged, which prevents protonation of the adsorbed oxyanion. The positive repulsive electrostatic potential is expected to strongly diminish the affinity of the adsorbed oxyanion for proton binding. This assumption is reasonable for most oxyanions. For example, phosphate ions exhibit very high affinity for proton binding in solution. However, protonation of the adsorbed complex on goethite occurs at low pH only at relatively high surface coverages because under these conditions the particle charge (surface plus adsorbed phosphate) is near neutral or negative (Tejedor-Tejedor and Anderson, 1990; Hiemstra and Van Riemsdijk, 1996).

The proton-ion stoichiometry has not been determined at high solution concentrations because analysis of surface species is more complicated because more than one surface species can exist (Tejedor-Tejedor and Anderson, 1990; Hiemstra and van Riemsdijk, 1996; 1999) and the system is problematic experimentally, as explained below.

2. MATERIALS AND METHODS

2.1. Preparation of Goethite

Goethite was prepared by slow neutralization of Fe(NO₃)₃ (Merck) with NaOH. The resulting precipitate was aged at 60°C for 3 days and subsequently dialyzed (Hiemstra et al., 1989b). The suspension has been stored in the dark at 4°C for 4 years. The BET specific surface area (96.4 m²/g) and acid-base characteristics were similar to other goethite preparations from our laboratory (Hiemstra and van Riemsdijk, 1996; Venema et al., 1996a).

2.2. Proton-Ion Titration Experiments

Vessels containing approximately 60 ml of 10 g/l (i.e., ≈ 1000 m²/L) goethite in 0.01 M NaNO₃ were kept under a N₂ atmosphere at pH 5.5 for at least two days to desorb and remove (bi)carbonate. Goethite was titrated by an automated titration system (Kinniburgh et al., 1995) with sodium salt solutions of vanadate, phosphate, arsenate, selenite, chromate, molybdate, tungstate, sulfate and selenate (Table 1). Under the experimental conditions the solution concentrations remained negligible compared to adsorbed amounts because of the high reactive surface area. The pH was kept constant by titration with standard-

Table 1. Sodium solutions of anions in this study. The solutions without additional acid were kept under N₂ atmosphere to prevent decreasing pH, which might otherwise result in polymerization.

1	Vanadate	0.007 M Na ₃ VO ₄
2	Phosphate	0.01 M Na ₂ HPO ₄ + 0.006 M HNO ₃
3	Arsenate	0.01 M Na ₂ HA ₃ O ₄ + 0.006 M HNO ₃
4	Selenite	0.01 M Na ₂ SeO ₃
5	Chromate	0.01 M Na ₂ CrO ₄
6	Molybdate	0.01 M Na ₂ MoO ₄
7	Tungstate	0.01 M Na ₂ WO ₄
8	Sulfate	0.01 M Na ₂ SO ₄
9	Selenate	0.01 M Na ₂ SO ₄

ized 0.01 M HNO₃ (Merck). The duration of each titration was 4–12 hr. Electrode drift was monitored in suspensions that were not titrated and was determined to be negligible. Stock solutions (Table 1) were calibrated against known standards with ICP-AES or ICP-MS. Differences between replicates were negligible.

The experimental proton co-adsorption (Γ_{H}) is found from the difference between the number of protons added to the suspension (H_{added}) and the change in the number of protons in solution (ΔH_{sol}): $\Gamma_{\text{H}} = H_{\text{added}} - \Delta H_{\text{sol}}$ (Hiemstra and van Riemsdijk, 1996). In our experiments protons are added using only a 0.01 M HNO₃ titrant solution, or via a 0.01 M HNO₃ titrant solution in combination with partly acidified oxyanion stock solutions. H_{added} can then be calculated with $H_{\text{added}} = 0.01 \text{ M } V_{\text{acid}}$ and, in case of phosphate and arsenate, with $H_{\text{added}} = 0.01 \text{ M } V_{\text{acid}} + 0.016 V_{\text{ion}}$. In principle the amount of added protons left in solution can be calculated with, for example, $\Delta H_{\text{sol}} = V_{\text{t}}(3[\text{H}_3\text{AO}_x] + 2[\text{H}_2\text{AO}_x] + 1[\text{HAO}_x]) + \Delta V(\text{H}^+ - \text{OH}^-)$, but these terms are negligible in our experiments because nearly 100% of the anion of interest is adsorbed and (V is small (V_{t} is the total volume after addition of a volume (V) of acid and ion solution). The value of H_{sol} has to be taken into account, as was done by Hiemstra and van Riemsdijk (1996), if the ion concentration in solution is non-negligible.

2.3. CD-MUSIC Model Approach

A description of the most relevant characteristics of the CD-MUSIC model of Hiemstra and van Riemsdijk (1996) is given here. The concept of charge distribution is based on the bond valence concept of Pauling (1929). The Pauling bond valence (ν) expresses the charge per bond and equals the valence (z) of the ion-center divided by its coordination number (CN): $\nu = z/\text{CN}$. Application of Pauling's bond valence concept to the protonation reaction of a singly coordinated surface hydroxyl at the surface of goethite leads to the formulation, $\text{FeOH}^{-0.5} + \text{H}^+ \rightleftharpoons \text{FeOH}_2^{+0.5}$, because Fe contributes 0.5 valence units per Fe-O bond. The bond valence concept can also be applied to the formation of an inner sphere ion such as selenite. The charges of the oxygen ligands of selenite (SeO_3^{2-}) are estimated from the Se-O bond valence $z/\text{CN} = 4/3 = 1.33$. EXAFS shows (Hayes et al., 1987) that adsorbed selenite shares two of its ligands with the surface and one ligand is directed to the solution. This causes a spatial charge distribution at the mineral-solution interface (Hiemstra and van Riemsdijk, 1999).

The simplest way to incorporate the spatial charge distribution of adsorbed species in surface-chemical equilibria is the partitioning of the charges over two electrostatic planes (i.e., the use of an electrostatic double layer model with at least two electrostatic planes. One electrostatic plane contains the surface groups together with the oxygens shared between the surface and the chemisorbed ion). The second plane contains the solution-oriented oxygens of the adsorbed ions. Outer sphere electrolyte ions are located at the outermost electrostatic plane. If the outermost electrostatic plane and the second plane are the same, it is a Basic Stern (BS) model (Westall and Hohl, 1980). Otherwise it is a Three Plane (TP) model (Hiemstra and Van Riemsdijk, 1996). The choice between these models is studied in a forthcoming paper (Rietra et al., 1999). The capacity (C) of the compact part of the double layer in the TP model is related to the capacitances of the individual layers by: $C^{-1} = C_1^{-1} + C_2^{-1}$. Both the BS model and the TP model include a Gouy-Chapman layer to account for the potential

profile of the diffuse part of the electrostatic double layer. The Basic Stern model is the simplest that is able to incorporate information from a variety of experimental and theoretical approaches (Hiemstra and Van Riemsdijk, 1996; Hiemstra et al., 1996; Borkovec, 1997; Felmy and Rustad, 1998; Lützenkirchen, 1998; Machesky, 1998; Schudel et al., 1998). Our experiments were performed under conditions where the total particle was always positively charged. The total charge follows from the initial charge (at pH 4.2, $\Gamma_H \approx 2 \mu\text{mol}/\text{m}^2$, at pH 6.1, $\Gamma_H \approx 1 \mu\text{mol}/\text{m}^2$ in 0.01 M NaNO_3), the adsorbed ion charge (ion charge times ion adsorption: $z_{\text{ion}}\Gamma_{\text{ion}}$) and the co-adsorbed protons ($\Delta\Gamma_H$). Thus the total particle charge, $\Gamma_H + z_{\text{ion}}\Gamma_{\text{ion}} + \Delta\Gamma_H$, is always positive.

In this paper we have used monodentate and bidentate complex formation. The corresponding affinity constants can be defined as:

$$K_{\text{mono}} = \{\text{FeO}^{+0.5+z_0}\text{AO}_{y-1}^{z_1}\} / \{\{\text{FeOH}_2^{+0.5}\} (\text{AO}_y^{z_{\text{ion}}})\} \quad (1)$$

and

$$K_{\text{bi}} = \{\text{Fe}_2\text{O}_2^{+1+z_0}\text{AO}_{y-2}^{z_1}\} / \{\{\text{FeOH}_2^{+0.5}\}^2 (\text{AO}_y^{z_{\text{ion}}})\}, \quad (2)$$

in which z_0 and z_1 are respectively the charge allocated to the 0-plane and the 1-plane ($z_0 + z_1 = z_{\text{ion}}$). The charges attributed to the planes are calculated with the Pauling bond valence concept: $z_i = n_i (\nu - 2)$, where n_i is the number of ligands per electrostatic plane, and ν is the Pauling bond valence (valence of the central ion divided by coordination number). The value -2 is the charge of the oxygen. Note that the charge attribution to the surface (z_0) for the given examples can also be calculated from the overall charge ($-2, -3$) and the number of ligands that form a bond with the surface ($z_0 = z_{\text{ion}} n/\text{CN}$). The coefficients z_0 and z_1 are used in the calculation of the electrostatic contribution to the overall affinity for the ion adsorption equilibrium according to $\ln K_i = \ln K_{\text{intrinsic}} - (z_0\psi_0 + z_1\psi_1)F/(RT)$, in which $K_{\text{intrinsic}}$ is the chemical component of the affinity.

2.4. Model Parameters

The CD-MUSIC model distinguishes between various types of surface groups. The site density of proton reactive groups (6.15 sites nm^{-2}) was estimated previously on the basis of the goethite structure (Hiemstra and van Riemsdijk, 1996). The acid-base behavior of the goethite used in this study could be described well with a capacitance of 0.91 (C/m^2), which is similar to that used in previous studies (0.90 C/m^2 , Hiemstra and van Riemsdijk, 1996; 0.85 C/m^2 , Venema et al., 1996). The log K for ion pair complexation is set to -1 as in previous studies. The acid-base behavior can only be modeled within a small range of different log K values for the ion pairs (approximately $-1.5 < \log K < -0.5$), different capacitances and site densities.

As will be discussed later, modeling of our proton-ion adsorption data is almost independent of site density (if site density of proton reactive sites > 4 sites/ nm^2), and also independent of the chosen ion pair complexation constant and capacitance, if the combination of parameters leads to a reasonable description of the experimental acid-base behavior. The maximum experimental ion adsorption used in this study is $1 \mu\text{mol}/\text{m}^2$. This is much lower than the estimated amount of singly coordinated surface groups, which are the most reactive (Hiemstra and Van Riemsdijk, 1996). Therefore, the protonation and adsorption equilibria are rather independent of the chosen site densities of 3.45 site/ nm^2 for singly coordinated and 2.7 sites/ nm^2 for triply coordinated surface groups (Hiemstra and Van Riemsdijk 1996).

3. RESULTS AND DISCUSSION

3.1. The Macroscopic Proton-Ion Adsorption Stoichiometry

The measured co-adsorption of protons as a function of the amount of oxyanion adsorbed on goethite is given in Fig. 1 for conditions where the total particle charge is still positive. The data for chromate, molybdate and tungstate follow almost exactly the same trajectory (Fig. 1). Vanadate, phosphate, and arsenate form another group of oxyanions, which are almost indistinguishable from each other with respect to the relation-

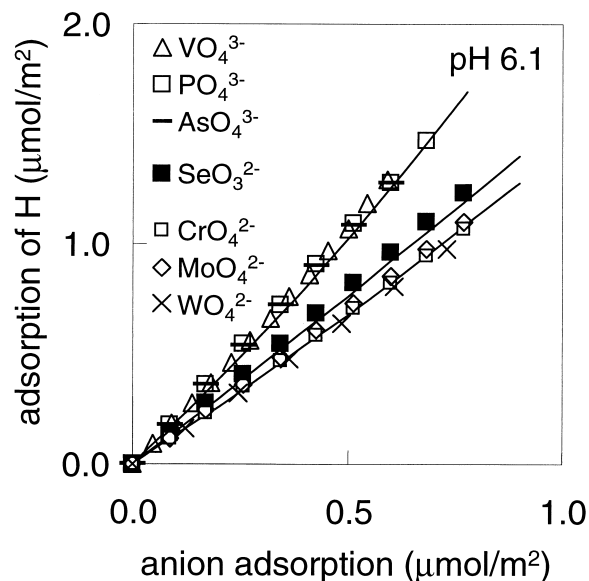


Fig. 1. Proton consumption as a function of ion adsorption at constant pH: pH 6.1 (0.01 M NaNO_3). The curves show the CD-MUSIC predictions based on the charge distributions from the surface complex structures of Fig. 3, which are calculated by applying the Pauling bond valence concept assuming bidentate complexes. Note that these predicted curves are not linear because the macroscopic proton-ion adsorption stoichiometry is not constant.

ship between proton co-adsorption and oxyanion adsorption. The data show that the group of trivalent anions (VO_4 , PO_4 and AsO_4) results in a considerably higher number of protons co-adsorbed per oxyanion than the group of bivalent anions.

The differences in co-adsorption of protons can be understood by considering the electrostatic interaction between the anionic charge and the surface. Maximum interaction occurs if the charge of an oxyanion is located at the surface plane where the protons are bound. If the relationship between surface potential and pH is Nernstian, it can be shown that a stoichiometric co-adsorption of protons results. Stoichiometric co-adsorption implies the adsorption of two protons per adsorbed bivalent anion, and the adsorption of three protons per trivalent anion. The macroscopic proton-ion adsorption ratio is less than stoichiometric. This might be rationalized by placing the adsorbed charge at a finite distance from the surface, leading to a weaker interaction (Fokkink et al., 1987; Venema et al., 1996b). Although the macroscopic proton-ion adsorption is non-stoichiometric for all ions, it is interesting that the quotient of the stoichiometries for the group of trivalent ions (vanadate, phosphate and arsenate) and the group of bivalent ions (chromate, molybdate and tungstate) is nearly equal to the quotient of the ionic charge of these ions (3/2). We will show later that this occurs if both groups of ions have the same coordination with the surface.

Not all oxyanions with a -2 charge show the same behavior. Selenite (SeO_3) has a higher number of co-adsorbed protons per oxyanion than chromate, molybdate and tungstate. This suggests a stronger interaction between the anion charge and surface protons, which can be caused by the lower coordination number of selenite compared to chromate, molybdate and tungstate (CN = 3 versus 4). In case of selenite, 2/3 of the ligands

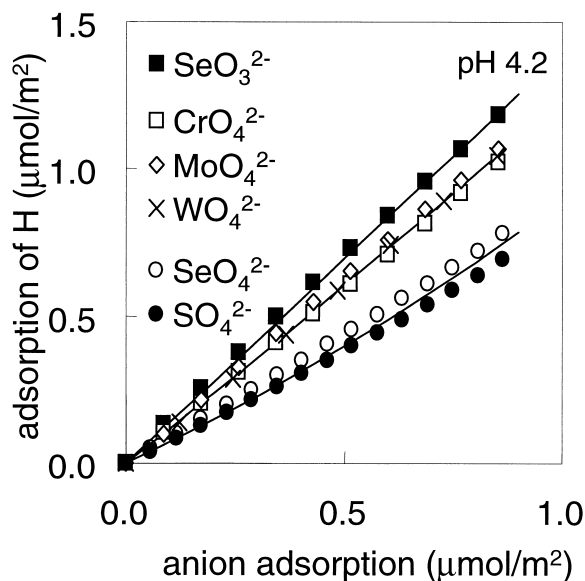


Fig. 2. Proton consumption as a function of ion adsorption at constant pH: pH 4.2 (0.01 M NaNO₃). The curves show the CD-MUSIC predictions based on the charge distributions from the surface complex structures of Fig. 3, which are calculated by applying the Pauling bond valence concept assuming bidentate complexes except for the lowest curve (monodentate).

interact with the surface in forming a bidentate surface complex. This contrasts with chromate, molybdate and tungstate, where we expect a maximum of 2/4 of the ligands (in case of bidentate complexes) to be directly involved in complexation with the surface. The relatively higher interaction of selenite with the surface leads to a higher macroscopic proton-ion adsorption stoichiometry.

We have also measured the macroscopic proton-ion adsorption stoichiometry of two other divalent ions, sulfate and selenate (Fig. 2). The stoichiometry is determined at a lower pH (pH 4.2) to ensure sufficient ion adsorption. For comparative purposes the macroscopic proton-ion adsorption stoichiometry of selenite, chromate, tungstate, molybdate have also been measured at this lower pH. Trivalent anion adsorption was not studied at this lower pH because protonation of the adsorbed species might occur. Sulfate and selenate have a much lower co-adsorption of protons compared with chromate, molybdate and tungstate, suggesting a considerably lower interaction with the surface. A lower interaction can result from a lower number of ligands being involved in ligand exchange with the surface (monodentate versus bidentate binding). A low charge attribution to the surface is also expected for outer sphere adsorption (to be discussed below).

3.2. Modeling

The co-adsorption of protons can be quantified by using the CD-MUSIC approach that relates the interfacial charge distribution to the structure of the adsorbed complex. The charge distribution concept is illustrated in Fig. 3, for relevant inner sphere structures of various ions. The charge distribution in the interface (expressed in z_0 , z_1) is calculated using the Pauling bond valence concept (Pauling, 1929), in which the central

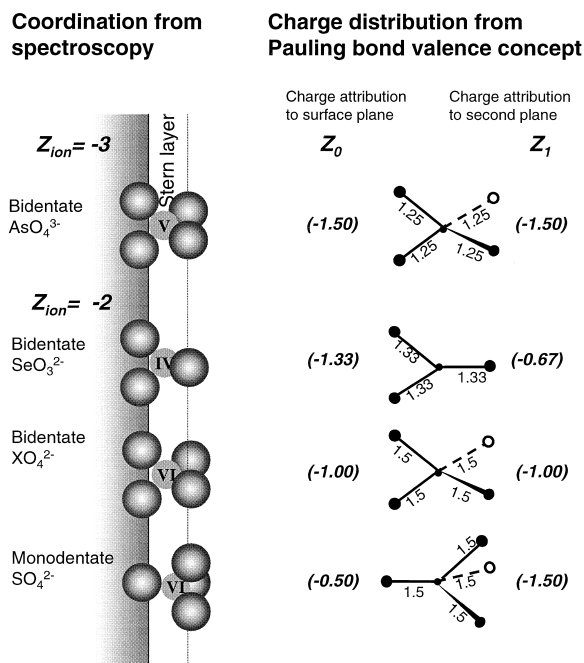


Fig. 3. Schematic representation of the surface-coordination of ions and the allocation of the charge of the ion ($z_0 + z_1 = z_{\text{ion}}$) over the two electrostatic planes. Charge attribution to the planes is calculated with the Pauling bond valence concept: $z_1 = n_i (\nu - 2)$, where n_i represents the number of ligands, and ν , the Pauling bond valence (valence of the central ion divided by coordination number). The value -2 is the charge of the oxygen atom. Note that the charge attribution to the surface (z_0) for the given examples can also be calculated from the overall charge ($-2, -3$) and the number of ligands that form a bond with the surface ($z_0 = z_{\text{ion}} n/\text{CN}$). The coefficients, z_0 and z_1 , are used in determining of the electrostatic contribution to the overall affinity for the ion adsorption equilibrium. XO_4^{2-} is used to represent ions such as CrO_4^{2-} , MoO_4^{2-} , and WO_4^{2-} .

“cationic” charge is equally distributed over the surrounding oxygen ligands. The details of the calculations are given in the Figure caption. It follows from Fig. 3 that the portion of the charge attributed to the surface (z_0) depends on the structure and can vary from -0.50 to -1.33 for bivalent oxyanions. The co-adsorption of protons is higher if the negative charge attribution to the surface plane is higher.

The structures given in Fig. 3 for arsenate (Waychunas et al., 1993; Waychunas et al., 1996; Sun and Doner, 1996; Fendorf et al., 1997) and selenite (Hayes et al., 1987) correspond with the spectroscopically found structures for pH values and surface coverages comparable to the ones used in our experiments. The structure of sulfate adsorbed onto hematite was studied recently by Hug (1997) with in situ ATR-FTIR. Only one type of adsorbed sulfate complex is found to be dominant over a wide range of pH and surface coverage. Hug (Hug, 1997; Eggleston et al., 1998) interpreted the spectrum as resulting from a monodentate innersphere complex. Similar spectra have also been observed for sulfate on goethite (Hug, personal communication).

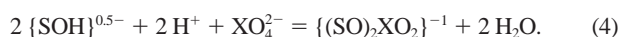
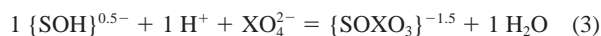
There is disagreement between spectroscopic studies concerning the coordination of phosphate by goethite (Parfitt et al., 1976; Persson et al., 1995; Tejedor-Tejedor and Anderson, 1990). Tejedor-Tejedor and Anderson assert that phosphate is

adsorbed as a non-protonated bidentate surface complex at low coverage and $\text{pH} > 5$, whereas Persson and colleagues advocate the formation of a monodentate complex. We found very similar macroscopic proton-ion adsorption stoichiometries for phosphate and arsenate, which suggests a common bonding mechanism for both anions (see also Hiemstra and Van Riemsdijk, 1999). Consequently, if arsenate is adsorbed as a bidentate complex under the conditions used (as suggested by EXAFS), the same is true for phosphate.

3.3. Modeling Results

Systematic study of the macroscopic proton-ion adsorption stoichiometry has resulted in several new insights. We have found that the macroscopic proton-ion adsorption stoichiometry, which can be calculated with a given model, is independent of the intrinsic binding constant of the adsorbing species provided there is only one kind of adsorbed species. For a given variable charge model, the number of co-adsorbed protons at constant pH and ionic strength is only determined by the amount of the adsorbed oxyanion. The solution concentration and speciation corresponding to a certain oxyanion adsorption loading has no influence. Thus, we are clearly looking at surface properties. This observation has not been noted before as far as we know, and it has important implications for the characterization of ion adsorption (as discussed below). Of course, the intrinsic affinity is a very important parameter for determining the relationship between the concentration in solution and the adsorbed amount, but not for the resulting macroscopic proton-ion adsorption stoichiometry (for the conditions of our experiments).

One may argue that the macroscopic proton-ion adsorption stoichiometry is not only determined by the charge distribution over the interface, but also by the formulation of the adsorption reaction and the protons that are involved in the reaction equation, i.e., the microscopic reaction stoichiometry. Consider the following reactions for the formation of a monodentate or a bidentate surface complex:



These equations suggest a strong difference between monodentate formation and bidentate formation with respect to the macroscopic proton-ion adsorption stoichiometry. This difference would be crucial if electrostatics were not important. However calculations show that for the model we have used, if one uses the same charge distribution, there is almost no difference between the calculated macroscopic proton-ion adsorption stoichiometry applicable to monodentate or bidentate surface complexation. In other words, the macroscopic proton-ion adsorption stoichiometry is determined dominantly by the charge distribution and not by the formulation of the reaction equation.

To illustrate this more clearly, we have calculated the proton co-adsorption for an oxyanion adsorption density of $0.5 \mu\text{mol}/\text{m}^2$ while varying the charge attribution to the surface, for an oxyanion with a -2 charge at pH 4.2, and a -3 charge at pH 6.1. The results are shown as lines in Fig. 4. The calculations were made using the Basic Stern model for both monodentate and bidentate coordination. The lines for both the monodentate

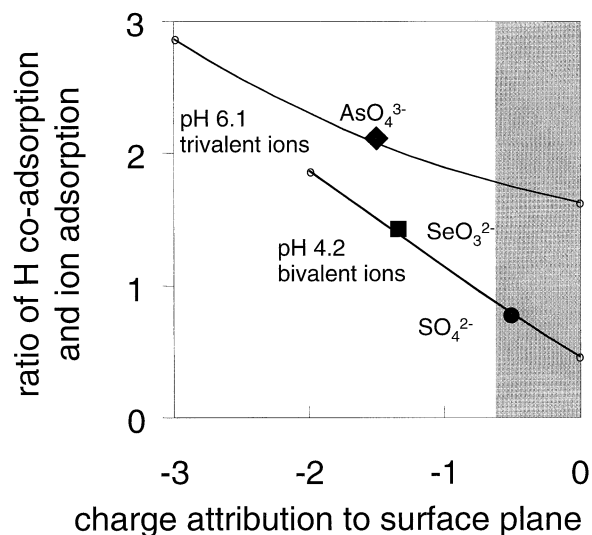


Fig. 4. The co-adsorption of H^+ , at $0.5 \mu\text{mol}/\text{m}^2$ ion adsorbed, as a function of the adsorbed ion charge attributed to the surface plane. The lines show the calculated relation for bivalent (pH 4.2) and trivalent ions (pH 6.1). Differences between monodentate and bidentate adsorption complexes are negligible. The points give the experimental proton-ion adsorption stoichiometry for arsenate, selenite and sulfate from Figs. 1 and 2 for a calculated charge distribution which is calculated by applying the Pauling bond valence concept to the structure of an adsorbed complex (see Fig. 3). The small open circles (ends of the lines) refer to the predicted proton co-adsorption by treating the adsorbed charge as a point charge: the minimum and maximum H^+ coadsorption are calculated for when the charge is located at the surface and on outermost electrostatic plane, respectively.

and bidentate coordination coincide within the scale of the graph. We have found that the calculated lines are also not affected if we change the site density, the ion pair complexation constants or the Stern layer capacitance, provided that we use a combination of parameters that still describes the acid-base characteristics of goethite in the presence of a simple electrolyte at various concentrations. These parameters influence the shape of the adsorption isotherms, but not the macroscopic proton-ion adsorption stoichiometry for the conditions of the experiments. From this, we conclude that the experimental proton-ion adsorption stoichiometry can be directly interpreted in terms of the charge distribution.

On Fig. 4 are also plotted points (black symbols) representing the oxyanions whose bonding structure is known from spectroscopy (sulfate, selenite and arsenate). Values on the vertical axis are taken from our experiments (Figs. 1 and 2), and the positions of the points on the horizontal axis are derived from the calculated charge distribution using the structure of the adsorbed complex and the Pauling concept as illustrated in Fig. 3.

A shaded area is drawn in Fig. 4 to indicate the estimated conditions where the charge distribution can potentially result from charge transfer of hydrogen bridges in outer sphere complexes (Filius et al., 1998). The maximum effect of this charge distribution from changes in hydrogen bonding is estimated to be 0.2 charge units per bond in case of strong hydrogen bond formation. If we assume that at maximum, three of the oxygens of an oxyanion can be involved in hydrogen bonding with the surface to form an outer sphere complex, the maximum charge

attribution to the surface is about 0.6 charge units. In the shaded area, a similar charge distribution can result either from inner sphere (monodentate) or outer sphere complexes. Although macroscopic proton-ion adsorption stoichiometries for sulfate and selenate are similar (Fig. 2), sulfate was interpreted to be a monodentate innersphere complex (Hug, 1997; Eggleston et al., 1998), and selenate was interpreted to be either outer sphere (Hayes et al., 1987) or a bidentate inner sphere complex (Manceau and Charlet, 1994). Our results for sulfate and selenate can be interpreted as either monodentate innersphere or as outersphere complexes, but a bidentate innersphere complex is in conflict with our results. Because of the uncertain contribution of hydrogen bridges to the charge distribution, we cannot distinguish between monodentate inner sphere and outer sphere complexes from macroscopic measurements. The results for arsenate and selenite are close to the calculated lines, demonstrating that the CD-MUSIC concept for these ions indeed scales from molecular to macroscopic levels.

3.4. Application

Since the new method in combination with the CD-MUSIC model gives results for adsorbed species of a presumed surface structure that are compatible with the experiment, we can use the approach to predict the surface structure of other oxyanions from the experimental proton-ion stoichiometry. This is done by applying the Pauling charge distributions of the adsorbed complexes, defined in Fig. 3, in the BS model. The modeling leads to the predicted curves shown in Figs. 1 and 2. The correspondence between the data points and the predicted lines is remarkably good. The model satisfactorily predicts the effect of pH (see Figs. 1 and 2). Moreover, the observed effect of ion adsorption loading (a slight bending of the curves) on the macroscopic proton-ion stoichiometry is also predicted. The charge distribution estimated from the Pauling bond valence principal is, in some cases, accurate enough to discriminate between surface structures. This is not so surprising because the difference between the calculated charge distribution for a monodentate, compared to a bidentate structure, is rather large (Fig. 3). Our results lead to a prediction of bidentate complexes for vanadate, chromate, molybdate and tungstate, and favor the bidentate interpretation of Tejedor-Tejedor and Anderson (1990) for phosphate because of its similarity to arsenate. Fine tuning of the charge distribution as predicted by a first order approach using the Pauling concept is probably required if one wants to give a more accurate description of adsorption data. For example, the macroscopic proton-ion stoichiometry for selenate and sulfate is not perfectly predicted in Fig. 2.

On Fig. 4, we have also indicated (small circles) the calculated results if the adsorbing ion is treated as a point charge (as is usually done). The values of $z_0 = -2$ and $z_0 = -3$ correspond to, respectively, bivalent and trivalent point charges located in the surface. The predicted macroscopic proton-ion stoichiometry is slightly less than 2 or 3, respectively. Consequently, placing the full anion charge at the surface leads to an overestimation of the number of co-adsorbed protons. Conversely, placing the full charge at the outermost electrostatic plane results in an underestimation of the macroscopic proton-ion stoichiometry.

Other modeling efforts to rationalize sulfate adsorption on

iron hydroxides, using the point charge concept in combination with triple layer or diffuse layer models, require two or three hypothetical surface species (Dzombak and Morel, 1990; Ali and Dzombak, 1996; Hoins et al., 1993). The model of Bowden and colleagues (1980) allows the point charge to vary position near the surface without considering ligand exchange. These approaches can give a relatively good description of data, but there is no relation to any spectroscopic information.

Our results clearly show that the charge distribution concept is an essential feature of ion adsorption models that aim to use physically realistic surface species. The relation between the charge distribution needed in the model, and the physical structure of the adsorbed complex is the key concept linking spectroscopy to adsorption models. The simple Pauling charge distribution concept is a reasonable first order approach for ions with a relatively large macroscopic proton-ion adsorption stoichiometry. Hiemstra and Van Riemsdijk (1999) have shown that the Pauling charge distribution concept leads to a very good description of selenite adsorption behavior. For ions with a relatively low macroscopic proton-ion adsorption stoichiometry, such as sulfate and selenate, more spectroscopic information is necessary to reach a conclusion about the relation between structure and charge distribution.

4. CONCLUSIONS

The macroscopic proton-ion adsorption stoichiometry is determined primarily by the electrostatic interaction of an ion with the surface. The experimental proton-ion adsorption stoichiometry for vanadate, phosphate and arsenate is very similar, as it is for chromate, molybdate and tungstate. The difference between these two groups can be explained by the difference in ionic charge (-2 , -3). Within these groups, a similar stoichiometry can only be explained by an identical ion-surface interaction. The macroscopic proton-ion adsorption stoichiometry varies within the group of bivalent ions. Selenite has the highest stoichiometry, sulfate and selenate have the lowest stoichiometry, and chromate, molybdate and tungstate are intermediate. This variation can be explained by the different structures of the adsorbed complexes.

The macroscopic proton-ion adsorption stoichiometry is independent of the affinity of the adsorbing species and of most other model parameters. It implies that in the model, charge distribution follows directly from the proton-ion adsorption stoichiometry, provided only one adsorption complex is present.

The simple Pauling bond valence concept can be used as a first order estimate in relating the charge distribution needed in the model to the structure of the adsorbing ion. The approach seems to give the correct prediction for the structure of adsorbed ions with a relatively large macroscopic proton-ion adsorption stoichiometry.

The measured proton-ion adsorption stoichiometry can be directly translated to the pH dependency of ion adsorption, using the thermodynamic consistency relationship (Perona and Leckie, 1985; Cernik et al., 1996) in combination with the well known protonation of species in solution. This implies that for a given ion solution chemistry, the pH dependence of adsorption depends primarily on the charge distribution over the

interface and therefore on the structure of the adsorbed complex (i.e., independent of the affinity constant).

The structure of the surface, the structure of the adsorbed species, and the electrostatic potential profile near the surface are all essential features of an adsorption model if the aim is to model adsorption behavior using physically realistic surface species.

Acknowledgments—We thank Stephan Hug for determining the sulfate coordination on the goethite used in this study and Anton Korteweg for the BET surface area measurements. We also thank Mike Machesky and the other anonymous reviewers for their valuable comments.

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