

## Physical chemical interpretation of primary charging behaviour of metal (hydr)oxides\*

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### Abstract

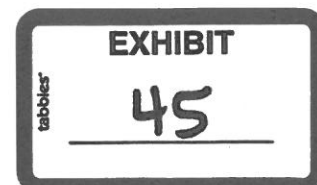
The primary charging behaviour of metal (hydr)oxides is of great practical and theoretical importance. It has been shown in the literature that it is possible to describe this charging behaviour with widely different models. This ability to describe the experimental observations has not contributed to a consensus with respect to the physical interpretation. The most popular models for interpretation are, in essence, all a combination of a description for adsorption of protons ("site-binding model") with a double layer model. The classical one- and two-pK site-binding models assume that the surface can be treated as chemically homogeneous. Recently, a multisite complexation model has been formulated (MUSIC model) that allows for a priori estimation of the proton affinity constants for various types of reactive groups present on metal (hydr)oxides. Large differences between experimental capacitance ( $d\sigma_0/dpH$ ) as well as model constants for the Stern layer capacitance ( $0.2-4 \text{ F m}^{-2}$ ) can be found for different metal (hydr)oxides, and are discussed.

A physical model for the compact part of the double layer on metal (hydr)oxides is derived and compared with that for AgI. From the model it follows that for well crystallized non-porous metal (hydr)oxides the Stern layer capacitance is expected to be smaller than or equal to around  $1.7 \text{ F m}^{-2}$ . Analysis of primary charging curves of non-porous colloids like gibbsite ( $\text{Al}(\text{OH})_3$ ), rutile ( $\text{TiO}_2$ ) and goethite ( $\text{FeOOH}$ ) in combination with the MUSIC model approach leads to a Stern layer capacitance of  $1.2 \pm 0.4 \text{ F m}^{-2}$ , in agreement with the proposed double layer structure. Salt dependency of the charging curves as well as the value of the capacitance support the assumption of ion-pair formation. For silica a higher capacitance is derived which can easily be interpreted in the light of the surface structure since the reactive groups are not confined to a layer of densely packed reactive surface groups. Goethites with a specific surface area of less than  $50 \text{ m}^2 \text{ g}^{-1}$ , prepared by rapid neutralization of an iron salt, charge significantly better. This is interpreted as being due to the presence of other crystal faces and/or porosity.

### INTRODUCTION

Metal (hydr)oxides are characterized by a pH-dependent surface charge as a result of the adsorption or desorption of protons. During the last two decades

\*In honour of Professor Dr. Hans Lyklema on the occasion of his 60th birthday, 23 November 1990.



much research has been devoted towards the understanding of the complex primary charging of metal (hydr)oxides in inert electrolyte solutions. In the following discussion the term charging behaviour will be shorthand for the primary charging behaviour. The understanding of the charging behaviour is of great practical importance in various disciplines.

A wide variety of models has been used to describe the charging behaviour. This ability to describe the experimental observations with widely different models has not contributed to a consensus with respect to the physical interpretation. Starting from the well established charging of AgI, the general opinion was that metal (Me) (hydr)oxides were in many respects quite different. The constituent ions of Me oxides do not govern the surface potential, but rather the H and OH ions. For many Me (hydr)oxides the experimental capacitance is much higher than for AgI and the surfaces seemed to be typically non-Nernstian surfaces [1–4]. More recently it has become the prevailing opinion of some authors that metal (hydr)oxides often show a (near) Nernstian behaviour for the relationship between the surface potential and the pH [5,6], comparable with the classical idea for AgI. This similarity between AgI and Me (hydr)oxide is not found for the double layer capacitance. The double layer capacitance of the Stern layer of the classical AgI is low ( $C=0.2 \text{ F m}^{-2}$ ). For metal (hydr)oxides very different capacitances for the compact part of the double layer have been reported, ranging from values of  $0.26$  [7], to values around  $1.5 \text{ F m}^{-2}$  [8,9] and even very high values of  $3\text{--}4 \text{ F m}^{-2}$  can be found [5,10]. The physical interpretation of capacitances is strongly related to the structure of the double layer. Widely different interpretations, which may vary from a purely diffuse double layer (DDL) only [11,12] to a triple layer model (TL) [13], are found in the literature.

Although it is possible to describe the charging behaviour of Me (hydr)oxides as a function of  $\Delta\text{pH}$  using Nernstian behaviour in combination with an assumption about the double layer structure [5], most authors have used models where site binding of protons is combined with an assumption about the double layer structure. Several groups have contributed to the early concepts of this latter approach [14–19]. The affinity of protons for the surface sites determines the point of zero charge (PZC). These values can be related to properties of the solid phase [20,21].

The extensive sets of experimental observations reported in the literature clearly show a large variety in PZC and experimental capacitances [10]. Serious problems may arise when both the measured charging curves and the measured zeta potentials are to be modelled using the site-binding concept in conjunction with the assumption that the zeta potential equals the potential at the head end of the diffuse part of the double layer [11,12,22,23]. This has cast some doubt about the validity of the site-binding approach combined with a smeared-out potential [22,23]. Nevertheless, an extended site-binding model version is used in this paper in combination with the generally used approxi-

mation of a smeared-out potential. Emphasis will be on the description of the charging behaviour using a priori predicted proton affinity constants for the various types of surface groups. Attention is also given to a simplified picture of the structure of the double layer in order to get an impression of the value of the Stern layer capacitance that may be expected for metal (hydr)oxides. In the last section we shall discuss the charging behaviour of some Me (hydr)oxides in terms of the physical concepts presented in the earlier sections.

#### PROTON BINDING AT A METAL (HYDR)OXIDE SURFACE

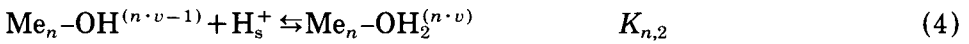
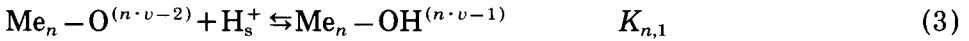
The early site-binding models all assume that the surfaces of Me (hydr)oxides could be treated as being chemically homogeneous with the presence of one type of reactive oxygen surface group that may adsorb zero, one or two protons. This concept leads to the so-called two-p*K* model, characterized by the following reactions



To obtain intrinsic affinity constants, the proton concentration near the interface,  $\text{H}_s^+$ , is used in the definition of  $K_{\text{H1}}$  and  $K_{\text{H2}}$ . A difference between the local proton concentration and the proton concentration in solution is due to the presence of an electrostatic field. In this model approach two intrinsic proton affinity constants must be derived from the experimental information. It has been shown that this is not an easy task since for one and the same set of experimental data widely different constants for  $K_{\text{H1}}$  and  $K_{\text{H2}}$  are reported [24]. In the so called one-p*K* model [7,18,19] only one proton affinity constant is needed, which follows directly from the experimental PZC of the metal (hydr)oxide in inert electrolyte solutions. Neither the one- nor the two-p*K* model explains why there are differences in PZC values between the metal (hydr)oxides ranging from as low as 2 to above 10.

Both the one- and the two-p*K* models assume that a metal (hydr)oxide can be treated as a homogeneous surface. However, it is well known that at least three types of surface oxygen groups may occur on a metal (hydr)oxide surface, namely an oxygen that is singly, doubly or triply coordinated to the underlying Me ion(s) of the solid [3,25]. It is to be expected that the proton affinity of these various groups may differ considerably. Each of these types of surface oxygen groups may adsorb in principle one or two protons. Recently a model, which was called the MUSIC (multisite complexation) model, has been presented that allows for a priori estimation of the value of the proton affinity constants of these different groups and for different metal (hydr)oxides [21]. The model predicts that the affinity constants for adsorption of the first and the second proton on one type of surface group differ by approximately 14

log  $K$  units. This large difference in log  $K$  has as a consequence that in general only one of the two protonation steps is of relevance with respect to the charge development in titration experiments, where the pH range is seldom higher than 6 pH units. The predictive model is based on the concept of local neutralization of charge as introduced by Pauling [26]. The charge of the metal ion in the solid is distributed over the surrounding ligands and can be expressed per bond, leading to the definition of the bond valence  $\nu$  as the charge  $z$  of the Me ion divided by its coordination number  $CN$ . In this way a formal charge for a surface group can be calculated. The general formulation of the protonation reaction now becomes:



where  $n$  equals the number of Me ions in the solid that coordinate to a specific type of reactive surface group. The formal charge of a reactive surface group, imposed by the crystal structure of the Me (hydr)oxides, may influence the resulting charging curves strongly.

Most surfaces are heterogeneous. Two important types of heterogeneity may be distinguished on a metal (hydr)oxide, namely the presence of different types of surface groups on one crystal face and the presence of clearly developed different crystal faces on Me (hydr)oxide particles. If clearly distinct crystal faces are developed, each face may exhibit its own particular surface potential. The PZC of different crystal faces may also differ due to variation in the chemical composition of the faces.

For a complete adsorption model not only is knowledge of the proton binding needed, but also knowledge of the double layer structure.

## DOUBLE LAYER STRUCTURE

Before discussing the double layer on metal (hydr)oxides, we shall first discuss as a starting point some aspects of the double layer structure on the classical AgI colloid, which is rather well established. In the section on metal (hydr)oxides the similarities and dissimilarities between the two types of mineral surfaces will be pointed out.

### *AgI*

The silver iodide surface may be charged by a relative excess of one of the constituent ions,  $\text{Ag}^+$  or  $\text{I}^-$ , in the interface. For silver iodide it is common practice to assume a Stern layer in combination with a diffuse double layer. The value of the empty Stern layer is rather well established and amounts to about  $0.2 \text{ F m}^{-2}$  [27]. The Stern layer is introduced because the inert coun-

terions retain at least their primary hydration water, creating a minimum distance of approach to the plane where the surface charge is situated. The Stern layer can be treated as an electrostatic condenser. The capacitance is related to the relative dielectric constant  $\epsilon_r$  and the distance  $d$  of charge separation between both electrostatic planes of the Stern layer, according to

$$C = \frac{\epsilon_0 \epsilon_r}{d} \quad (5)$$

in which  $\epsilon_0$  is the absolute dielectric constant ( $8.85 \cdot 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$ ). In order to interpret the observed Stern layer capacitances it is necessary to assign a value to  $\epsilon_r$  and  $d$ . At 298 K the relative dielectric constant of water may vary between 78 for bulk water to around 6 for electrical saturation. Before a physical interpretation of the structure of the double layer is given, it is of interest to evaluate first the static dielectric properties of hydrated ions in electrolyte solutions.

A strong orientation of water molecules is found in the electrostatic field around cations and anions in solution. In a first simple approach it can be thought that primary hydration water molecules are completely oriented and electrical saturation can be reached, e.g. the dielectric constant equals for instance 6 [28]. The water molecules situated in the second hydration sheet are thought to be only loosely bound. In the calculation of the hydration energy of primary hydrated ions in solution using Born's treatment of ionic hydration, it is generally assumed that the relative dielectric constant of the secondary bound water molecules is already close to that of bulk water [29,30]. This indicates that the dielectric constant falls off over a relatively small distance. If the electrical field is considered as a continuum, an estimation of the relation between the field strength and the relative dielectric constant  $\epsilon_r$  can be approximated [30] by

$$\epsilon_r = \frac{\epsilon_{\text{bulk}} - n_{\infty}^2}{1 + b \left( \frac{\partial \psi}{\partial x} \right)_x} + n_{\infty}^2 \quad (6)$$

in which the value of  $n_{\infty}^2$  determines the dielectric constant at electrical saturation, which is set at 6. The constant  $b$  has a value of  $1.2 \cdot 10^{-17} \text{ m}^2 \text{ V}^{-2}$ . The field strength  $\partial \psi / \partial x$  is a function of the distance from the centre of an ion. As shown by Sacher and Laidler [31] Eqn (6) can be used to calculate  $\epsilon_r$  as a function of the distance from the centre of an ion (Fig. 1). The model indicates a very strong change in the dielectric constant over the distance of one water molecule.

The above analysis can be used for the construction of a model of the structure of the solid/solution interface of AgI. The surface consists of  $\text{Ag}^+$  and  $\text{I}^-$  ions. If they are present in equal amounts, the overall surface charge would be

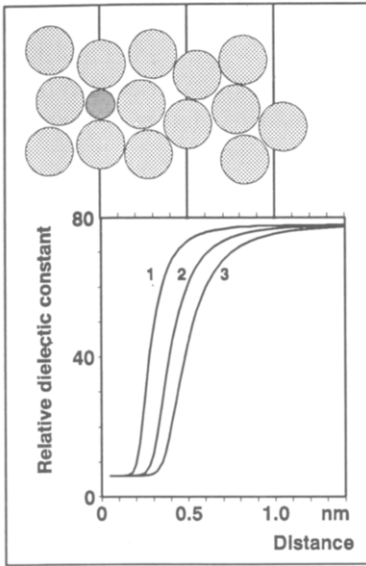


Fig. 1. Calculated dielectric constant around a cation as a function of the distance from the centre of the ion (nm). The various lines are for ions with a valence of 1, 2 and 3. The dielectric constant varies from 6 close to the ion as a result of electrical saturation, to 78 in the bulk.

zero. In other cases a surface charge is developed. The  $\text{Ag}^+$  and  $\text{I}^-$  ions at the surface are partly hydrated. In accordance with the picture sketched for the dielectric constant around an ion in solution (Fig. 1), it may be assumed that the first layer of water molecules adjacent to the solid surface is electrically saturated ( $\epsilon_r = 6$ ) and that the dielectric constant of the water further away from the surface layer is much higher, maybe close to that of bulk water ( $\epsilon_r = 78$ ). If one assumes that the inert counterions do not form inner-sphere complexes with the solid, e.g. there is no exchange of ligands from the first sheet of  $\text{H}_2\text{O}$  and  $\text{O}(\text{H})$  molecules in the solid and hydrated counterions, at least two water molecule sheets will be situated between the charged  $\text{AgI}$  surface and the counterions. The minimum distance of approach to the surface can be estimated, assuming a diameter of 0.28 nm for a water molecule, and, for the mean radius of the counterions, a value between 0.1 and 0.15 nm (Fig. 2).

Because of the presence of two types of water molecules in the interface the overall Stern layer capacitance follows from

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (7)$$

where  $C_1$  is the capacitance of the layer of water molecules that forms the primary hydration of the surface and  $C_2$  the capacitance of the second layer of water molecules.

For the model the capacitances can be calculated as  $C_1 = 0.19 \text{ F m}^{-2}$  and

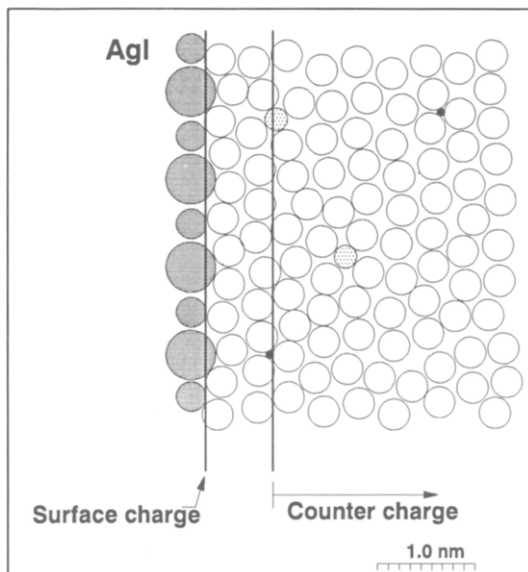


Fig. 2. Schematic representation of the interface of AgI. Surface charge is formed by the relatively higher adsorption of one of the constituent ions ( $\text{Ag}^+$ ,  $\text{I}^-$ ). The potential is located in an electrostatic plane that coincides with the location of the  $\text{Ag}^+$  and  $\text{I}^-$  ions. The surface  $\text{Ag}^+$  and  $\text{I}^-$  ions are hydrated by water molecules which are strongly oriented in the local electric field. The counterions are also hydrated. The distance between the surface charge plane and the plane of minimum approach is equal to the size of about two water molecules.

$C_2 = 1.7 \text{ F m}^{-2}$ . The overall value for the Stern layer capacitance  $C$  equals  $0.17 \text{ F m}^{-2}$ , comparable with the experimental value found for AgI. The low value of the overall capacitance is mainly due to the presence of the first hydration layer which is nearly electrically saturated.

### *Metal (hydr)oxides*

As stated before for metal (hydr)oxides, large differences can be found in the literature with respect to the assumed structure of the double layer. It is possible to describe the charging behaviour with a purely diffuse double layer in combination with a homogeneous classical 2-pK model [11,12,32]. The difference between the two proton affinity constants,  $\Delta\text{p}K$ , affects the shape of the charging curves and is used as a fitting parameter. The model is mainly advocated because of its simplicity. Physically it is not very realistic since, similar to the case of AgI, the counterions cannot reach the plane where the excess protons are situated. Moreover, in the MUSIC approach it is predicted that the  $\Delta\text{p}K$  should be around  $14 \log K$  units, which is not in accordance with the values found when the 2-pK/diffuse double layer model is applied.

Generally it has been assumed that the charge and potential at the surface

may be thought to be smeared out. The relatively high mobility of protons in solution and the high exchange rate of protons at the surface compared with counterions support this assumption. It has been suggested [23] that in addition to a smeared-out potential, local electrostatic effects should also be taken into account because according to the authors local interactions may lead to a variation in proton affinity constants of 2–3  $\log K$  units as a function of salt level. However, the mean distance of charge separation at the highest experimental charging observed is still high, approximately 0.6 nm, a distance that is equivalent to the mean distance of ions in a salt solution with a concentration of about 0.5  $M$ . This indicates that the suggested large additional local electrostatic interaction between protons is unlikely.

The double layer structure near the interface of metal (hydr)oxides can be developed along the same lines as used for the AgI system. For a hydrated ion in solution the primary water molecules that are bound as ligands to the metal ions, are considered as electrically saturated. For metal ions that form part of the solid and which are close to the surface of the metal (hydr)oxide particle, the primary ligands are the partly protonated surface oxygens which should be considered as part of the metal (hydr)oxide surface, in contrast to the primary hydration water molecules for AgI, that are part of the empty Stern layer. The inert counterions will retain their primary hydration water. The closest distance of approach of the counterions to the (partly protonated) surface oxygens is restricted by the presence of one water molecule. The total thickness of the Stern layer is thus approximately 0.4 nm. This picture for the compact part of the double layer of Me (hydr)oxides is depicted in Fig. 3. Since the water molecules in the Stern layer are separated from the metal ions in the solid of (hydr)oxides by (partly protonated) surface oxygens, it follows from Fig. 1 that the dielectric constant of the Stern layer for metal (hydr)oxides is high. If it is assumed that it approaches the value for bulk water, a Stern layer capacitance of about  $1.7 \text{ F m}^{-2}$  can be calculated. According to this approach this value should be interpreted as an upper limit. If the dielectric constant of the Stern layer is lower than that of bulk water, e.g. a value halfway between bulk water and  $\epsilon = 6$ , a lower value ( $0.5 \text{ F m}^{-2}$ ) for the Stern layer capacitance is expected (Eqn (5)).

The main difference between the AgI model picture and that for metal (hydr)oxides is that, in the case of AgI, primary ligands (water molecules) are not part of the surface where the surface charge is residing, but part of the Stern layer, whereas for metal (hydr)oxides the primary ligands of the Me ions of the solid are part of the surface since the surface charge of Me (hydr)oxides results from protonation reactions on the surface oxygen ligands. Using essentially the same reasoning with respect to the distance of approach of counterions and the dielectric constants, a large difference results for the expected overall Stern layer capacitance values,  $0.2 \text{ F m}^{-2}$  for AgI and around  $0.9\text{--}1.7 \text{ F m}^{-2}$  for metal (hydr)oxides.

In the section on the charging of Me (hydr)oxides we shall discuss to what



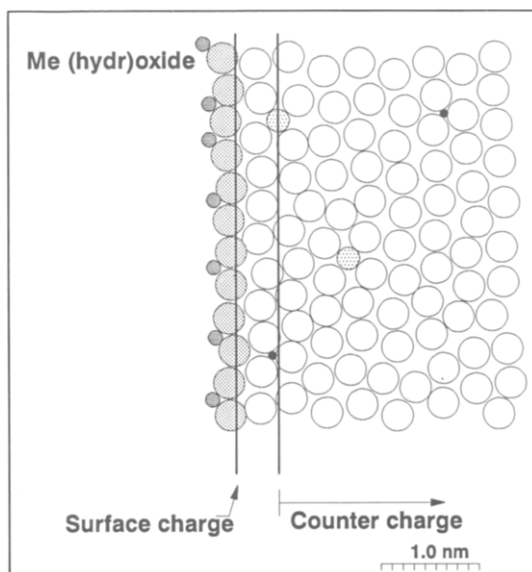


Fig. 3. Schematic representation of the interface of metal (hydr)oxides. Surface charge is formed by the adsorption or desorption of protons on the surface oxygens which are coordinated to the underlying metal ions of the solid. These oxygen ligands form the outer part of the solid. The surface charge is located in an electrostatic plane situated at these ligands. The hydrated counterions cannot reach the plane of proton adsorption. The distance between the surface plane and the plane of minimum approach equals the size of about one water molecule. Note the difference with the interface of AgI in Fig. 2.

extent the experimental charging behaviour of Me (hydr)oxides can be physically interpreted in terms of the MUSIC model and the physical picture of the double layer described above. However, first the triple layer model as presented in the literature [3,13,17] to describe the compact part of the double layer will be discussed. In this approach the Stern layer is split into two capacitances, as in the case of AgI. The value of  $C_1$  can be fitted, whereas for  $C_2$  a value of  $0.2 \text{ F m}^{-2}$  is assumed. The overall empty Stern layer capacitance will be nearly equal to that of AgI. These assumptions lead, for an empty Stern layer, to a strong underestimation of the charging behaviour of Me (hydr)oxides. This is why in the triple layer model approach one has to assume that simple counterions can enter the Stern layer and will reside in the plane separating the regions with different capacitances. The fitted value for  $C_1$  equals about  $1\text{--}1.4 \text{ F m}^{-2}$ . Note that the fitted  $C_1$  value for the triple layer model nearly equals the  $C_2$  value for AgI and vice versa. If the triple layer model is physically interpreted, it has to be assumed that the counterions lose part of their surrounding water molecules when entering the Stern layer, leading to the formation of inner-sphere complexes, which seems unlikely. Furthermore, the assumed value for  $C_2$  is difficult to understand based upon our view of the compact part of the double layer.

The triple layer model can, in the same way as the purely diffuse double layer model, perfectly describe the observed charging behaviour by adjusting the model parameters. The triple layer model has the advantage that when it is assumed that the measured zeta potential equals the potential of the plane where the diffuse double layer starts, this potential is reasonably well described by the model. However, many uncertainties exist with respect to the interpretation of zeta potentials in terms of these models, because of the uncertainty in the location of the shear plane amongst others [5,12].

If pair formation of electrolyte ions is assumed in the physical picture as sketched in Fig. 3, it must be assumed that they reside in the plane separating the Stern layer and the diffuse double layer. Only ions that may form inner-sphere complexes (specifically adsorbed) by the mechanism of ligand exchange may penetrate the Stern layer.

#### CHARGING OF METAL (HYDR)OXIDES

Metal (hydr)oxides may differ widely in their behaviour. Many aspects of the variation can be interpreted with the ideas formulated above. In the following we shall attempt to interpret the charging behaviour of several important Me (hydr)oxides, namely  $\text{Al}(\text{OH})_3$  (gibbsite),  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{FeOOH}$  (goethite).

##### *Gibbsite*

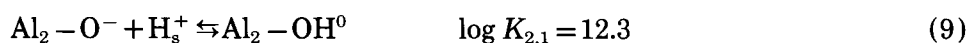
The experimental charging curves of crystalline gibbsite exhibit a very low experimental capacitance ( $\partial\sigma_0/\partial\text{pH}$ ) if the data are expressed per unit BET surface area [7,33]. This low charging can be understood on the combined basis of the crystal morphology and the MUSIC model approach. Two clearly different crystal planes are developed, a dominating planar 001 face and edge faces [7]. Both types of crystal planes have a different chemical composition. The 001 face has only doubly coordinated surface groups whereas the edge face has singly and doubly coordinated surface groups. The charging behaviour in the pH range 5–10 is due to the protonation of singly coordinated surface groups at the edges, according to Refs [7,10,18,19,21]:



The overall low charging in the given pH range is due to the dominant presence of the planar 001 face, which does not develop a surface charge in the normal pH range ( $<\text{pH } 10$ ). The charging curves can be described very well [7] without using the crystallographic information, but this leads to a fitted Stern layer capacitance ( $C=0.26 \text{ F m}^{-2}$ ) that is difficult to understand in terms of the above physical interpretation of the double layer structure for metal (hydr)oxides. A higher Stern layer capacitance ( $C=1.4 \text{ F m}^{-2}$ ) is found

if only the reactive edge surface area is taken into account and is close to the value that is expected from the physical picture of the double layer given here. In order to obtain a reasonable description of the data, rather strong pair formation with electrolyte ions had to be assumed [7]. In general the ion-pair formation decreases the fitted value of the Stern layer capacitance. The necessity of ion-pair formation for a proper description of the data in combination with a physically sound value for the capacitance  $C$  supports the concept of the presence of pair formation.

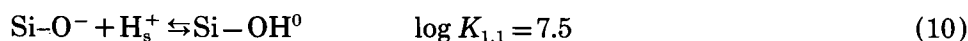
At pH values above 10 the 001 planar face develops a negative surface charge, resulting in a strongly asymmetric charging curve [10]. This behaviour is predicted by the MUSIC model [10,21] in combination with the assumption of ion-pair formation and of a Stern layer capacitance of  $1.4 \text{ F m}^{-2}$ . The charging reaction taking place at the 001 face is due to the dissociation of doubly coordinated surface hydroxyls. The relevant reaction may be formulated as:



The second protonation step ( $K_{2,2}$ ) for doubly coordinated surface groups at gibbsite does not affect the measured charging curves, which follows from the predicted large  $\Delta pK$  value.

### *Silica (SiO<sub>2</sub>)*

Another Me (hydr)oxide with low experimental capacitance is silica. The charging behaviour of this Me oxide has been classified in the literature as anomalous. However, the charging can be understood very well on the basis of the MUSIC model and the double layer structure presented here. Silica generally has no distinct crystal planes and only one type of reactive surface group is present in the interface of silica, namely singly coordinated SiOH. Doubly coordinated surface groups are predicted to be inert, as is generally accepted. For both reasons silica is treated as electrostatically homogeneous. The charging curve can be described by:



The charging curve of silica is quite different from that of most other Me (hydr)oxides. The difference in shape is mainly due to a difference in the charge attribution to the surface group in comparison to that of many other Me (hydr)oxides (compare Eqns (8) and (10)). This charge attribution is imposed by the crystal structure. According to the reaction (Eqn (10)) singly coordinated surface groups at silica are either negatively charged or non-charged, whereas in many other Me (hydr)oxides, for instance gibbsite, the reactive surface groups are either negatively or positively charged. For further discussion see Hiemstra et al. [10].

In the case of non-porous silica a high value for the Stern layer capacitance

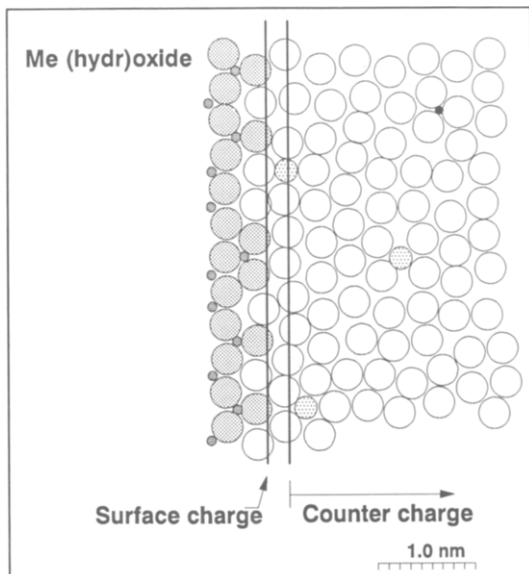


Fig. 4. Schematic representation of the interface of silica. The surface structure, imposed by crystallographic properties, is formed by a less condensed packing of surface oxygens and reactive surface groups protrude into the solution. The mean distance of approach will be smaller than in the case of a close-packed surface layer, causing a higher Stern layer capacitance.

is found ( $C = 3\text{--}4 \text{ F m}^{-2}$ ) [10]. At first sight this high capacitance seems in conflict with the double layer structure discussed above, because a value of about  $1.7 \text{ F m}^{-2}$  can be seen as the upper limit for the Stern layer capacitance of non-porous metal (hydr)oxides. However, this high value for silica can be understood as due to the less condensed surface structure of non-porous silica and the presence of reactive surface groups protruding from the surface [3]. As a result the mean distance of charge separation will be lower (Fig. 4), leading to a higher Stern layer capacitance. If the mean distance of charge separation in such a case is half the distance for a close-packed Me (hydr)oxide surface, the estimated capacitance would be within the experimental range obtained for non-porous silica. This picture seems reasonable (Fig. 4).

Extremely high charging of silica has been reported by Tadros and Lyklema [34], even much higher than can be understood assuming a purely diffuse double layer. The high charging is due to the presence of pores in which part of the charge is situated [34].

### $\text{TiO}_2$

Two types of surface groups are of interest in determining the charging of  $\text{TiO}_2$ ,

namely singly and doubly coordinated surface groups. According to the MUSIC Model the reaction of relevance for singly coordinated OH groups is



and for doubly coordinated OH groups



As predicted by the MUSIC model, triply coordinated  $\text{TiO}_3$  surface groups will not be protonated and can be considered as chemically inert with respect to protons. Although the protonation reactions for both types of reactive surface groups are completely different (hydroxo vs. oxo) the predicted difference in  $\log K$  is small. Both types of surface groups contribute to the charging. The small difference in  $\log K$  implies that variation in the chemical interfacial composition between different preparations will not lead to a large variation in the PZC. This is also experimentally observed.

The data for  $\text{TiO}_2$  of Yates [3], Bérubé and DeBruyn [35] and Fokkink et al. [5] will be analysed with the above surface reactions. The crystal faces present in colloidal  $\text{TiO}_2$  are unknown. However, the chemical composition of crystal faces identified on macroscopic crystals varies only in the total site density of the reactive surface groups ( $N_s = 7.8\text{--}9.6 \text{ nm}^{-2}$ ). It follows from the surface structure [3,10] that for these crystal faces the ratio of singly and doubly coordinated ions is equal. Because of the rather small differences between the various faces the surface will be treated as electrostatically homogeneous.

A reasonable description of the data of Yates [3], especially if the high salt level is included, is only possible if pair formation with electrolyte ions is assumed. Using equal fractions  $f$  ( $=0.5$ ) for the two different reactive surface groups (assuming  $N_s = 8 \text{ nm}^{-2}$ ) and symmetrical pair formation ( $\log K = -0.6$ ), the data of Yates [3] can be described with a Stern layer capacitance of  $0.8 \text{ F m}^{-2}$  (Fig. 5). The data of Fokkink et al. [5] can be described using the same pair-formation constant (Fig. 6). The PZC value of this  $\text{TiO}_2$  is slightly lower and can only be described if the fraction  $f$  of doubly coordinated surface groups is increased ( $f=0.6$ ) or if both predicted  $\log K$  values for reactions (11) and (12) are slightly adjusted ( $0.2 \log K$  units). The capacitance  $C$  equals in both cases  $1.7 \text{ F m}^{-2}$ ; similar results are found for the data of Bérubé and DeBruyn [35]. The charging of the  $\text{TiO}_2$  of Yates is unusually low in comparison with the data presented by most other authors [4,5,23,35,36]. The difference in capacitance between the data of Yates and those of the other sets can possibly be explained in terms of the presence of inert surface groups (triply coordinated  $\text{Ti}_3\text{O}$ ) in the case of a  $\text{TiO}_2$  with a low experimental capacitance, or some porosity for the other  $\text{TiO}_2$  oxides.

In the past, one of the reasons for using ion-pair formation in combination with a triple layer (TL) model was the aim to describe the zeta potentials with

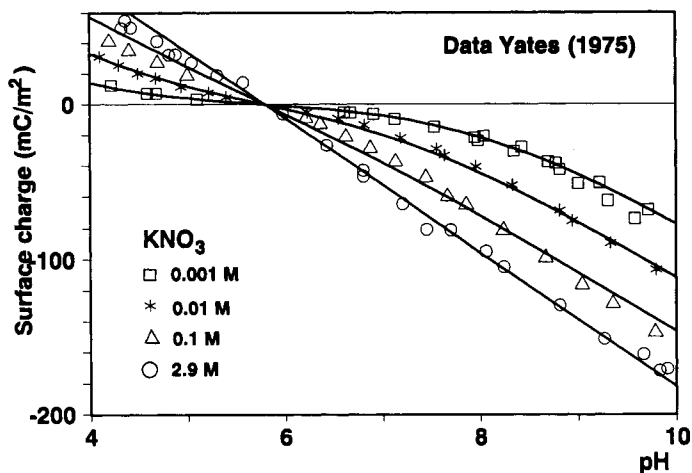


Fig. 5. The calculated charging behaviour of  $\text{TiO}_2$  at four different levels of  $\text{KNO}_3$ , using the MUSIC model. The experimental data [3] are indicated with symbols. The surface is treated as electrostatically homogeneous (see text). The site density of both reactive groups (singly and doubly coordinated) is set at  $4 \text{ nm}^{-2}$ . The capacitance of the Stern layer equals  $0.8 \text{ F m}^{-2}$ . The affinity constants for the protonation of singly and doubly coordinated surface groups (reactions (11) and (12)) equal 6.3 and 5.3 respectively. The pair-formation constants are  $\log Ka = \log Kc = -0.6$ .

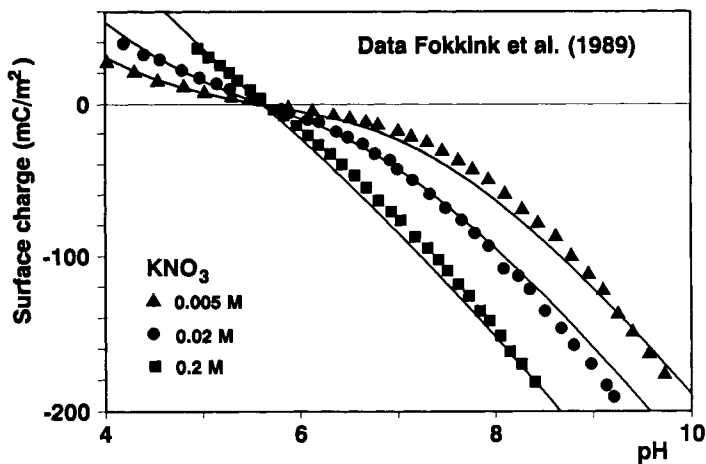


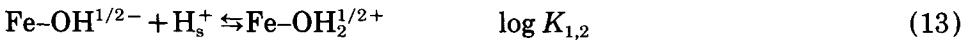
Fig. 6. The calculated charging behaviour of  $\text{TiO}_2$  at three different levels of  $\text{KNO}_3$ , using the MUSIC model. The experimental data [5] are indicated with symbols. The surface is treated as electrostatically homogeneous (see text). The site density of the reactive groups (singly and doubly coordinated) is set at  $3.2$  and  $4.8 \text{ nm}^{-2}$  respectively. The capacitance of the Stern layer equals  $1.7 \text{ F m}^{-2}$ . The affinity constants are equal to those in Fig. 5.

the model. However, here it has been shown that the physical interpretation of the TL model, assuming a  $C_2$  value of  $0.2 \text{ F m}^{-2}$ , is not clear. The MUSIC model approach in combination with pair formation and the proposed double layer structure, leads to a difference in  $\psi_d$  compared to zeta potentials. It should, however, be noticed that a large uncertainty exists about the location of the slipping plane in the double layer and even about the zeta potential itself, because of the difficulties involved in the calculation of zeta potential from electrophoretic mobility. Measured zeta potentials in  $0.001$  and  $0.01 \text{ M KNO}_3$  can be explained by assuming a position of the slipping plane  $2\text{--}4 \text{ nm}$  away from the surface [12]. With our approach similar values are found.

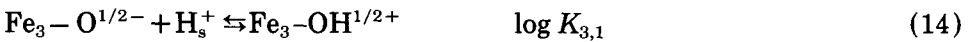
### Goethite

Many reported PZC values of iron (hydr)oxides are in the range of  $8 \pm 0.5$ . Recently higher values up to close to 10 have also been reported [6,10,37–39]. The higher values were only found in cases where  $\text{CO}_2$  was carefully excluded. It has been shown that failure to exclude  $\text{CO}_2$  may easily cause an apparent PZC shift of  $0.5\text{--}1.0 \text{ pH}$  units [37,39,40], complicating an unambiguous interpretation of the variations in PZC.

Three types of surface groups are present at the interfaces of Fe (hydr)oxides [3]. It has been shown that generally only two types of surface groups contribute to the formation of surface charge at the interface of Fe (hydr)oxides, namely singly coordinated surface groups and triply coordinated surface groups [10]. Doubly coordinated surface groups can often be considered as inert. The relevant proton adsorption reaction for singly coordinated surface groups is



and for triply coordinated surface groups



The predicted proton affinity constants of these two reactions are  $\log K_{1,2} = 10.7$  and  $\log K_{3,1} = 4.3$  respectively. A crystal plane that is dominated by singly coordinated surface groups will have a high PZC while a plane with a high number of triply coordinated surface groups is expected to have a low value for the PZC.

The crystal morphology of goethite has been evaluated by Cornell et al. [41]. Three important types of crystal planes have been reported; the 100, 010 and 001 faces. The 100 face has singly, doubly and triply coordinated surface groups present in equal numbers. Both the other planes have only singly and doubly coordinated surface groups [10]. Recently it has been shown that a multiple domainic goethite preparation may develop 110 faces [42]. On this crystal face triply coordinated surface groups are dominant. The uncertainty about the type of reactive surface groups and the relative presence of clearly developed

crystal planes complicates the interpretation of experimental PZC values and  $\sigma_0$ -pH curves of these Me (hydr)oxides.

The charging of goethite can be evaluated with the above affinity constants. The experimental data of Hiemstra et al. [10] have been shown to be representative of the charging characteristics of well-structured goethites, which generally have a BET surface area of more than about  $50 \text{ m}^2 \text{ g}^{-1}$  [10]. Our goethite preparation [10] was monodomainic and it is assumed that it develops the three crystal faces as identified by Cornell et al. [41], namely the 100, 010 and 001 faces. Because of the large similarity in charging of the last two faces [10], these planes may be treated as one face. The estimated ratios of the 100 and 010+001 faces and the site densities of the 100 and 010 faces have been given elsewhere [10]. The  $\sigma_0$ -pH data can be described without the assumption of pair formation. The fitted Stern capacitance then yields  $2.23 \text{ F m}^{-2}$  (Fig. 7). A lower value can be derived when weak pair formation is assumed. For instance the data can be also be described very satisfactorily with  $C=1.7 \text{ F m}^{-2}$ . Analysis of the calculations shows that the 100 face hardly contributes to the charging behaviour [10] because of the simultaneous presence of two types of surface groups with widely different p*K* values for the proton adsorption

Some goethites are characterized by a much higher experimental capacitance [10] as illustrated in Fig. 8. These particles are formed from rapidly precipitated iron hydroxide. The resulting BET surface area is generally lower than  $50 \text{ m}^2 \text{ g}^{-1}$ . When we analysed these particles by electron microscopy, it

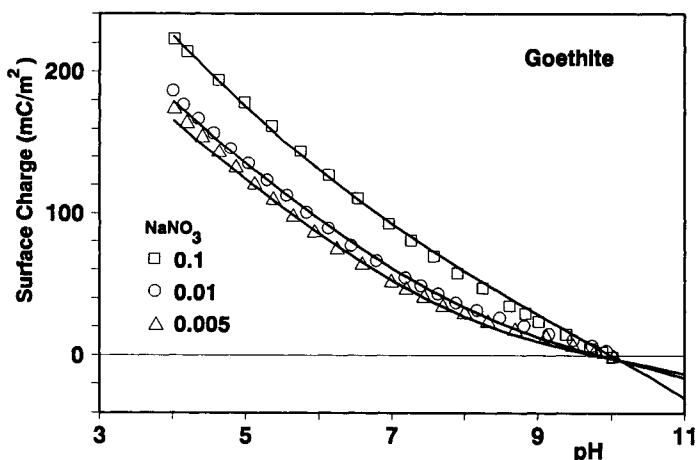


Fig. 7. The calculated charging behaviour of non-porous goethite at three different levels of  $\text{NaNO}_3$  (solid lines). The experimental data [10] are indicated with symbols. Two different types of crystal plane are assumed, 100 and 010+001. The fraction of the 100 face equals 0.5 of the total surface area. The protonation constants are given in the text. The pair-formation constants are  $\log Ka = \log Kc = -1.5$ . The Stern layer capacitance equals  $1.7 \text{ F m}^{-2}$ .



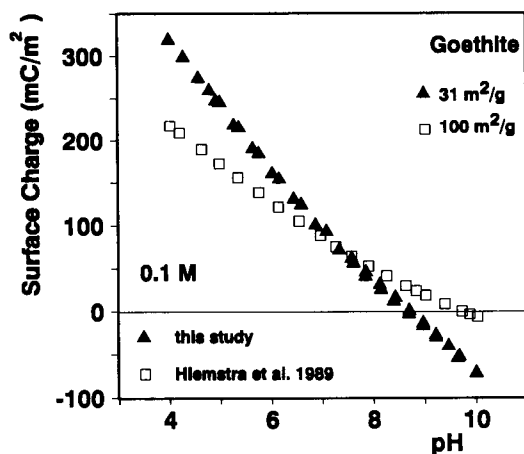


Fig. 8. The experimental  $\sigma_0$ -pH curves at the 0.1 M salt level ( $\text{NaNO}_3$ ) of two different preparations of goethite (data of Hiemstra et al. [10] and this study). The experimental capacitance is related to the specific surface area. Goethites with a relatively low BET surface area ( $< 50 \text{ m}^2 \text{ g}^{-1}$ ), formed from rapidly neutralized iron nitrate solutions, charge significantly better. These preparations consist of multidomainic porous crystals.

was observed that the surface is partially disordered and that the particles are multiple domainic. An explanation for the observed high charging for these types of goethites (Fig. 7) could be the presence of other or disordered crystal faces which charge much better than the poorly charging 001 face of goethite. Analysis of the BET curves of these particles showed porosity, which might also be a possible explanation.

## CONCLUSIONS

For a physical interpretation of the charging behaviour of metal (hydr)oxides it is essential to take into account the surface structure of the colloids with respect to chemical heterogeneity, different crystal planes, degree of porosity etc.

The charging behaviour as well as the double layer capacitance of gibbsite and titanium dioxide support the presence of pair formation.

The Stern layer capacitance of non-porous particles with well-ordered planar crystal face(s) is about  $0.8\text{--}1.7 \text{ F m}^{-2}$ . This range is in accord with the physical interpretation of the compact part of the double layer for metal (hydr)oxides.

Using essentially the same approach to derive the compact double layer structure of AgI and Me (hydr)oxides, leads to an explanation for the large difference in the Stern layer capacitance observed between AgI ( $0.2 \text{ F m}^{-2}$ ) and Me (hydr)oxides.

Fitted Stern layer capacitances much higher than  $1.7 \text{ F m}^{-2}$  are an indication of porosity and/or a disordered or a non-condensed surface structure.

The TL model with  $C_2 = 0.2 \text{ F m}^{-2}$  is in conflict with the physical double layer interpretation presented here.

The model constants obtained (affinity constants, Stern layer capacitance) when applying the classical models are difficult to interpret physically since these models ignore the presence of different types of reactive surface groups and other differences in surface structure (different crystal faces) that have an effect on the resulting charging behaviour.

The charging behaviour of silica, which is often indicated as anomalous, perfectly fits within the general physical-chemical model used here (MUSIC model). The high Stern layer capacitance can be physically interpreted because of the non-close packed surface structure (reactive groups protruding from the surface).

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