

## THE INFLUENCE OF COUNTER-ION ADSORPTION ON THE $\psi_0/\text{pH}$ CHARACTERISTICS OF INSULATOR SURFACES

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The site-binding theory of Yates, Levine, and Healy is extended to include the possibility that counter-ion binding of anions and cations occurs at different distances from the insulator surface. A method for straightforward computation of the  $\psi_0/\sigma_0/\text{pH}$  characteristics is given. This theory is applied to the study of electrolyte/insulator/silicon structures, which makes it possible to measure the  $\psi_0/\text{pH}$  characteristics. Measurements are presented for structures where the insulator is  $\gamma\text{-Al}_2\text{O}_3$  deposited by chemical vapour deposition at  $900^\circ\text{C}$ . The influence of counter-ion binding on the  $\psi_0/\text{pH}$  curves is a second-order effect compared to the site-dissociation acid/base reactions, but it is clearly visible. Consideration of the influence of the ionic strength of the electrolyte leads to an estimated anion adsorption equilibrium constant in the range of 0.05 to  $0.4 \text{ mol}^{-1} \text{ dm}^3$  in chloride solutions, although no significant influence of the type of ions present could be observed. Application of the theory to existing measurements of the  $\psi_0/\text{pH}$  and  $\sigma_0/\text{pH}$  curves of  $\text{SiO}_2$  surfaces indicates that for this material the cation adsorption equilibrium constant is in the order of  $0.1 \text{ mol}^{-1} \text{ dm}^3$ .

### 1. Introduction

Verweij was the first to show that the potential-determining ions for oxide surfaces were  $\text{H}^+$  and  $\text{OH}^-$  ions [1]. In 1956, Payens [2] calculated the potential/pH relation for a monolayer of fatty acids, and showed that the potential only followed Nernst's law in the limit of high reactivity. This type of theory was applied to oxide and polymer surfaces from 1971 onwards, beginning with Levine and Smith [3]. Since then, ionizable surface group models of the insulator/electrolyte interface have become increasingly accepted [4–15]. The reactions of insulator surfaces with  $\text{H}^+$  and  $\text{OH}^-$  ions have been reviewed in detail by Healy and White [8]. With electrolyte/insulator/silicon structures

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variations in the surface potential  $\psi_0$  can be measured [16], and it can thus be verified directly that this potential is not Nernstian, especially for unreactive surfaces such as  $\text{SiO}_2$  [17–20]. This result cannot directly be obtained with the methods available to colloid chemists.

A further point of discussion concerns the surface charge  $\sigma_0$  of  $\text{SiO}_2$  which is much higher than the charge in the Gouy–Chapman layer as derived from zeta potential measurements. Two explanations for this have been proposed: porosity of the surface [21,22], and site-binding of cations [5]. In view of the experimental evidence that vitreous  $\text{SiO}_2$  or  $\text{Si}_3\text{N}_4$  surfaces are not porous [23–25], it is now generally accepted that counter-ion binding reactions are involved. This has also been verified directly with radiotracer measurements [23] which have shown that at pH 10 in  $10^{-4}$  M NaOH, 80% of the negative charge on an  $\text{SiO}_2$  surface is neutralized by adsorbed cations. Thus, in addition to the reactions with the potential-determining ions, binding of counter ions must be considered to explain the measured surface charge and it can be expected that the  $\psi_0/\text{pH}$  relation will be influenced as well.

This paper will examine the influence of such counter-ion binding on the  $\psi_0/\text{pH}$  relationship, thereby extending the simple site-dissociation theory of ref. [20]. The treatment is based on the equations proposed by Yates et al. [5] and Davis et al. [9], but adds the following aspects:

- The equations of the model are solved analytically to enable a parametric representation of the  $\psi_0/\sigma_0/\text{pH}$  relationship to be calculated in a straightforward way. Thus there is no need to resort to either the graphical technique reported by Healy et al. [7] or the computer-generated solutions used by Davis et al. [9] or Westall and Hohl [11].
- The potential which determines adsorption of cations and anions is not assumed to be the same. This implies that in principle four layers of charge are allowed in the description of the interfacial region. The usual models involve the assumption that all ions are adsorbed at the same distance from the surface, as pointed out by Hunter [26]. Smit and Holten [14] have shown experimentally that this assumption is incorrect.
- The electrical double layer is not assumed to be globally neutral, due to the presence of charges elsewhere in the structure.

It will be shown here that the experimental  $\psi_0/\text{pH}$  relation of  $\text{Al}_2\text{O}_3$  surfaces clearly reflects the influence of counter-ion binding reactions. For  $\text{SiO}_2$  surfaces, the experimental results available in the literature of surface charge obtained on colloidal dispersions will be related to the  $\psi_0/\text{pH}$  curves previously obtained around the point of zero charge [20].

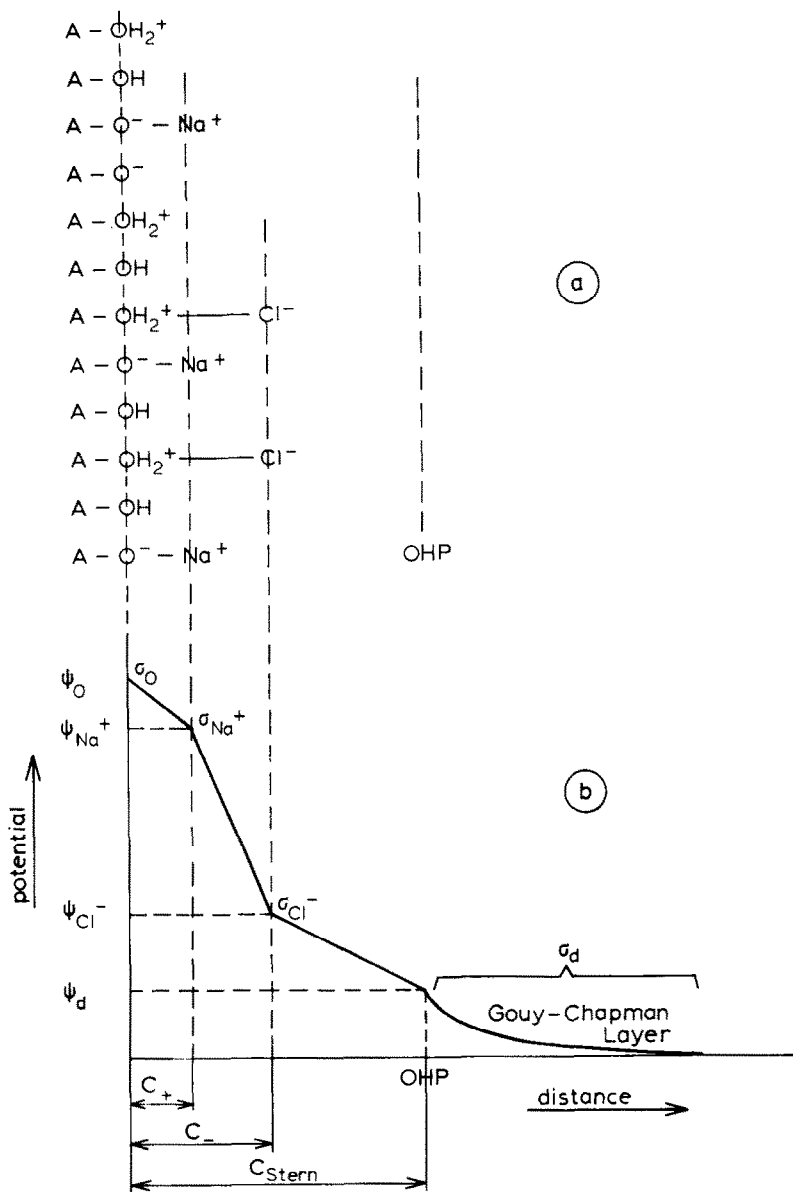


Fig. 1. (a) Assumed structure of the insulator/electrolyte interface. (b) Charges and potentials at the insulator/electrolyte interface.  $C_+$ ,  $C_-$  and  $C_{\text{Stern}}$  are the capacitances per unit area between the planes of charge indicated.

## 2. Theory

### 2.1. Analysis of surface equilibria

The equilibrium equations which describe the reactions occurring at the insulator/electrolyte interface have been discussed by many authors [5,6,8–10,14]. We will write the equations of the model of Yates et al. and Davis et al. in the form proposed by Drzymala et al. [10] and Smith and Holten [14], assuming for simplicity of notation that the electrolyte is a NaCl solution (see fig. 1):

$$K_a = ([A-O^-][H^+]/[A-OH]) \exp(-e\psi_0/kT), \quad (1)$$

$$K_b = ([A-OH_2^+]/[A-OH][H^+]) \exp(e\psi_0/kT), \quad (2)$$

$$K_{Na^+} = ([A-O^-Na^+]/[A-O^-][Na^+]) \exp(e\psi_{Na^+}/kT), \quad (3)$$

$$K_{Cl^-} = ([A-OH_2^+Cl^-]/[A-OH_2^+][Cl^-]) \exp(-e\psi_{Cl^-}/kT). \quad (4)$$

In these expressions,  $\psi_0$ ,  $\psi_{Na^+}$  and  $\psi_{Cl^-}$  represent the potential of the surface and of the locations where  $Na^+$  and  $Cl^-$  ions (called counter ions in what follows) are adsorbed, respectively. The first two equations have been derived statistically by Healy and White [8]. The second two equations contain the ion-pair formation concept introduced by Yates et al. [5]. Recently, Foissy et al. [27] have presented experimental evidence for the validity of this idea. A discussion of the assumptions involved in eqs. (1) to (4), including the questions of activity coefficients for the surface concentrations and micro-potentials, is given by Smith and Holten [14].

Note that the site-binding model views the adsorbed counter ions to be individually associated with an oppositely charged surface site, and assumes that only the types of site present in eqs. (1) to (4) can occur. This implies that direct acid–base reactions of sites such as  $A-O^-Na^+$  are impossible, because they would create sites of the type  $A-OHNa^+$ .

Although it is usual to write the positive or negative sites as shown above, there is some evidence that the positively charged sites may in fact assume the form  $A^+$  rather than  $A-OH_2^+$  [14]. In addition, there may be several types of neutral sites [13,28], or dipolar neutral sites [12]. None of these possibilities influences the treatment which follows, provided we consider  $[A-OH_2^+]$  as the formal way of writing the number of positively charged sites, and consider  $[A-OH]$  to be the total number of neutral sites, of whatever type. The total number of sites is a constant of the model, giving:

$$N_s = [A-OH] + [A-O^-] + [A-OH_2^+] + [A-O^-Na^+] + [A-OH_2^+Cl^-]. \quad (5)$$

The charge on the surface arises from the sites that are not in the neutral state  $A-OH$ . These charged sites will contribute charges located in three different planes: the charge due to  $A-O^-$  or  $A-OH_2^+$  groups of the surface itself (which

are assumed to be in one plane), and that due to the adsorbed  $\text{Na}^+$  or  $\text{Cl}^-$  ions. The plane of adsorbed charge of a particular ion will depend of course on the size of that ion, and the type of interaction with the surface that it undergoes. When considering the charge balance, it is important to note that, although an adsorbed site of the type  $\text{A-O}^-\text{Na}^+$  is globally neutral, it is in fact a dipole and will contribute charge to two different planes in the interface. In terms of the surface concentration, the charges on the surface can be written as (see fig. 1):

$$\sigma_0 = e([A-OH_2^+] + [A-OH_2^+ Cl^-] - [A-O^- Na^+]), \quad (6)$$

$$\sigma_{\text{Na}^+} = e[A-O^- Na^+], \quad (7)$$

$$\sigma_{\text{Cl}^-} = -e[A-OH_2^+ Cl^-]. \quad (8)$$

The charge balance equation can be written as:

$$\sigma_d + e([A-OH_2^+] + [A-O^-]) = \Delta\sigma, \quad (9)$$

where  $\sigma_d$  is the charge in the Gouy-Chapman diffuse charge layer, and  $\Delta\sigma$  is the charge unbalance in the double layer, equal to the opposite of the sum of the total charge in the insulator and the silicon substrate. It is convenient to introduce dimensionless notations, namely:

$$\alpha_n = [A-OH]/N_s, \quad \alpha_+ = [A-OH_2^+]/N_s, \quad \alpha_- = [A-O^-]N_s,$$

$$X = \alpha_+ - \alpha_-, \quad \alpha_{\text{Na}^+} = [A-O^- Na^+]/N_s, \quad \alpha_{\text{Cl}^-} = [A-OH_2^+ Cl^-]/N_s,$$

$$\alpha_d = \sigma_d/qN_s, \quad \text{and} \quad y_s = e\psi_s/kT, \text{ for all subscripts } s.$$

The extent of specific adsorption will be characterized by the following equations:

$$n = \alpha_{\text{Cl}^-}/\alpha_+ = n_0 \exp(y_{\text{Cl}^-}), \quad (10)$$

$$p = \alpha_{\text{Na}^+}/\alpha_- = p_0 \exp(-y_{\text{Na}^+}). \quad (11)$$

These can be derived from eqs. (3) and (4), where  $n_0 = cK_{\text{Cl}^-}$  and  $p_0 = cK_{\text{Na}^+}$ , and  $c$  is the concentration of NaCl. The equations above can be solved, following the procedure indicated by Dousma [29], in terms of a function  $F(X)$  defined as:

$$F(X) = (\alpha_+/\alpha_-)^{1/2}. \quad (12)$$

The expression of this function is found by solving eqs. (5), (10), (11) and the product of (1) and (2), and is given by:

$$F(X) = \frac{(X/\delta) + \left\{ (X/\delta)^2 + [1 + (1+p)X][1 - (1+n)X] \right\}^{1/2}}{1 - (1+n)X}. \quad (13)$$

The constant  $\delta$  used here is defined as  $\delta = 2(K_a K_b)^{1/2}$  and was first introduced by Healy et al. [7]. Since  $\delta$  is usually very small for insulator surfaces [7],

it will often be possible to use the following approximation of  $F(X)$ :

$$F(X) \approx z + (z^2 + 1)^{1/2}, \quad z = X/\delta. \quad (14)$$

This will be valid for  $\delta^{-1}$  much larger than  $n$  or  $p$ , and when  $(1+n)X$  is not near one. The same approximation has been used in the case where only eqs. (1) and (2) are considered [20], which means that the ratio  $\alpha_+/\alpha_-$  is insensitive to the extent of counter-ion binding. The expression of the pH of the electrolyte in terms of the function  $F(X)$  follows from eqs. (1), (2) and (12):

$$v = 2.303(\text{pH}_z - \text{pH}) = y_0 + \ln F(X), \quad (15)$$

where  $\text{pH}_z = -\log_{10}(K_a/K_b)^{1/2}$ . Note that this is different from  $\text{pH}_{\text{pzc}}$ , which is the pH at which  $\sigma_0 = 0$ .

Eq. (15) relates pH with both  $\psi_0$  and  $\sigma_0$ . To obtain  $\psi_0/\text{pH}$  characteristics, a second relationship between those three quantities is needed, and this will be obtained from double-layer theory.

## 2.2. Electrostatic relations in the double layer

Calculating the potentials generated by a given charge distribution in the electrolyte is a matter of simple electrostatics. The only possible complication is the fact that the charges due to counter-ion binding are themselves potential-dependent. Moreover, assuming two planes of adsorption implies that the potential at one plane depends on the amount adsorbed on the other plane. This difficulty can be overcome by using the charge in the diffuse part of the double layer as a parameter from which the other charges and potentials can be evaluated, going from right to left in the representation given in fig. 1. That figure also shows the capacitances  $C_-$  and  $C_+$ , which are assumed to be sufficient to describe the potential induced by the charge on the planes of adsorption. Note that due to the rapidly varying dielectric constant in this region of the double layer these capacitances are not simply inversely proportional to distance. The equations will be given here for the case that positive ions adsorb closer to the surface than negative ions. The opposite assumption results in similar equations.

At the OHP, the relation between charge and potential in the diffuse part of the double layer follows from the classical Gouy–Chapman theory, written in terms of dimensionless quantities:

$$y_d = -2 \sinh^{-1}(a\alpha_d), \quad a = \frac{eN_s}{(8\epsilon_w RTc)^{1/2}}. \quad (16)$$

The potential for negative adsorption in eq. (4) will now be assumed to be defined by:

$$y_{\text{Cl}^-} = y_d - b\alpha_d(1 - r_-), \quad (17)$$

with the symbols  $b = e^2 N_s / k T C_{\text{Sterrn}}$  and  $r_- = C_{\text{Sterrn}} / C_-$ . The charge adsorbed on this plane now follows from eq. (10), on condition that  $\alpha_+$  is known. It is possible, however, to express  $\alpha_+$  and  $\alpha_-$  as a function of  $X$  and  $F(X)$  with eq. (12), giving:

$$\alpha_{\text{Cl}^-} = nX F^2(X) / [F^2(X) - 1]. \quad (18)$$

The potential at the inner adsorption plane can be written in terms of the charge in the diffuse layer, and the charge of the outer adsorption plane as:

$$y_{\text{Na}^+} = y_d - b\alpha_d(1 - r_+) + b\alpha_{\text{Cl}^-}(r_- - r_+), \quad (19)$$

where  $r_+ = C_{\text{Sterrn}} / C_+$ . Again, the amount of charge adsorbed on this plane can be deduced from its potential:

$$\alpha_{\text{Na}^+} = pX / [F^2(X) - 1]. \quad (20)$$

The last step is the calculation of the quantities  $\sigma_0$  and  $y_0$  at the surface;  $\sigma_0$  has been defined in eq. (6), which can be rewritten as:

$$\alpha_0 = \sigma_0 / eN_s = X + \alpha_{\text{Cl}^-} - \alpha_{\text{Na}^+}. \quad (21)$$

The total normalized interface potential finally becomes:

$$y_0 = y_d + b(-\alpha_d + r_- \alpha_{\text{Cl}^-} - r_+ \alpha_{\text{Na}^+}). \quad (22)$$

Starting from  $\alpha_d$  and  $X$ , we have calculated  $\psi_0$ ,  $\sigma_0$  and pH, giving both  $\psi_0/\text{pH}$  and  $\sigma_0/\text{pH}$  curves as a result. One difficulty remains, however: when  $F(X)$  is required in eq. (18) the value of  $n$  is known, but  $p$  is not. Therefore the exact expression (13) for  $F$  cannot be applied, and the only recourse is to use the approximation (14) which does not involve  $n$  or  $p$ . This points the way to a convenient iterative process which yields an exact solution, free of approximations: first approximate  $F$  to calculate  $p$ , the extent of positive adsorption, and then use this value of  $p$  to improve the value of  $F$ .

In most cases, however, the first iteration is sufficient to yield precise values of  $\psi_0$ ,  $\sigma_0$ , and pH. Near the point  $X = 0$ ,  $n$  and  $p$  will be near  $n_0$  and  $p_0$ , which are as a rule smaller than  $\delta^{-1}$ . In that case, the approximation (14) is a very good one. Near saturation, the term  $(1 - (1 + n)X)$  becomes small, and the value of  $n$  becomes critical. Since  $F(X)$  is large near saturation, however, eqs. (18) and (20) reduce to  $\alpha_{\text{Na}^+} \approx 0$  and  $\alpha_{\text{Cl}^-} \approx nX$  (for positive  $X$ ), which means a precise value of  $F(X)$  is not needed anymore to evaluate  $n$  and  $p$ . Therefore the second value calculated for  $F(X)$  will be nearly exact. The only circumstances in which several iterations are required are: a very reactive surface (low  $\delta^{-1}$ ), or very strong counter-ion binding (very high  $n_0$  or  $p_0$ ).

Figs. 2a and 2b show calculated  $\psi_0/\text{pH}$  and  $\sigma_0/\text{pH}$  curves for a surface with  $\delta = 7 \times 10^{-4}$  and  $N_s = 5 \times 10^{14} \text{ cm}^{-2}$ , which are the parameters for  $\text{SiO}_2$  [20], when only cation adsorption occurs. The reaction constant  $p_0$  is very important in determining the surface charge; for  $p_0 = 10$  the whole surface can become charged at high pH values, whereas for low  $p_0$  the surface charge is consider-

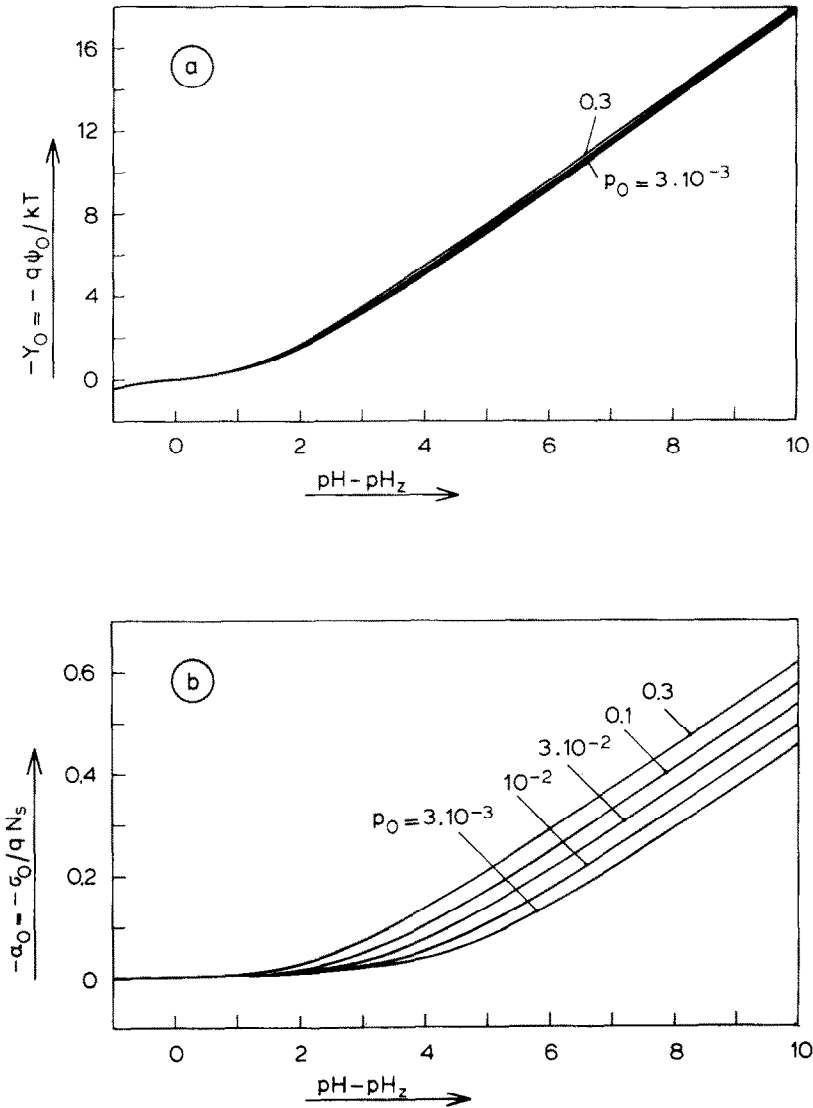


Fig. 2. Influence of a single type of ion on  $\psi_0/\text{pH}$  (a) and  $\sigma_0/\text{pH}$  (b) curves. Parameters used are for  $\text{SiO}_2$ :  $\delta = 7 \times 10^{-4}$ ,  $N_s = 5 \times 10^{14} \text{ cm}^{-2}$ ,  $r_- = 0.15$ , solution concentration is 0.1M, and  $C_{\text{Stern}} = 20 \mu\text{F}/\text{cm}^2$ .

ably smaller. The influence of  $p_0$  on the  $\psi_0/\text{pH}$  curves is considerably smaller however; when  $p_0$  is  $\geq 3$ , an increase in the slope around  $\text{pH}_{\text{pzc}}$  occurs. Saturation at high pH values is not visible for the value of  $r_- = 0.15$  chosen here. These features of the characteristics will now be examined in more detail.



### 2.3. Properties around the isoelectric point

In the case that there is no counter-ion binding, and that  $\Delta\sigma = 0$ , a solution pH exists where the insulator surface has the following properties:

- (1)  $\sigma_0 = 0$  (this condition is known as the point of zero charge, pzc);
- (2)  $\psi_d = 0$  (this condition is known as the iso-electric point, iep);
- (3)  $\psi_0 = 0$ ;
- (4)  $\text{pH} = \text{pH}_z = -\log_{10}(K_a/K_b)^{1/2}$ ;
- (5)  $d\psi_0/d(\text{pH})$  is minimum.

In the absence of specific adsorption, the point with these five properties is called the point of zero charge, and the corresponding  $\text{pH} = \text{pH}_{\text{pzc}}$ . The first two conditions can be determined with colloidal dispersions. The iep is in fact defined as the point of zero zeta potential, and we follow the usual practice of identifying  $\zeta$  with  $\psi_d$  [26]. In addition, with EIS structures the pH of minimum  $d\psi_0/d(\text{pH})$ ,  $\text{pH}_{\text{ms}}$ , can be found experimentally [20]. With specific adsorption, each of the properties enumerated above will occur at a different pH value.

In general, however, both  $\Delta\sigma$  and asymmetric counter-ion binding will shift  $\text{pH}_{\text{iep}}$ ,  $\text{pH}_{\text{pzc}}$ , and  $\text{pH}_{\text{ms}}$  by negligible amounts. The effect of a non-zero  $\Delta\sigma$  has been treated in ref. [20], where it is shown that the shift of  $\text{pH}_{\text{pzc}}$  is always smaller than 0.1 pH unit for the ISFET transistor structures which are used to measure variations of  $\psi_0$ . A quantitative discussion of the influence of asymmetric counter-ion adsorption is given in ref. [19]. The experimental result that no difference between  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{iep}}$  is observed for most materials [30] places an upper limit of about one on the adsorption parameters  $n_0$  and  $p_0$ .

We have shown previously [20] that the normalized slope of the  $\psi_0/\text{pH}$  curve at  $\text{pH}_{\text{pzc}}$ ,  $dy_0/dv$ , in the absence of counter-ion adsorption, is given by  $\beta/(\beta + 1)$ . The parameter  $\beta$  characterizes the sensitivity of a surface, which in the present notations is given by  $(2a + b)\delta$ . The value of  $\beta$  can be determined from the minimum observed slope of the  $\psi_0/\text{pH}$  curve. Typical values found for  $\beta$  are 0.14 in the case of  $\text{SiO}_2$  and 4.8 in the case of an  $\text{Al}_2\text{O}_3$  surface. It is logical to extend the previous definition of  $\beta$  to the theory with counter-ion adsorption, and introduce an apparent  $\beta$ :

$$\left. \frac{dy_0}{dv} \right|_{\text{min}} = - \frac{e}{2.303kT} \left. \frac{d\psi_0}{d(\text{pH})} \right|_{\text{min}} = \frac{\beta_{\text{app}}}{\beta_{\text{app}} + 1}. \quad (23)$$

In the case that  $\Delta\sigma = 0$ ,  $n_0 = p_0$  and  $r_+ = r_-$  it can be calculated that:

$$\beta_{\text{app}} = \beta + \delta br_- n_0 (1 + \beta - br_- \delta), \quad (24)$$

assuming that  $\delta \ll n_0$ . Therefore, adsorption should not affect the apparent value of  $\beta$  provided  $r_- n_0 \ll 1$ . For example, in the case of a  $\text{SiO}_2$  surface with  $n_0 = p_0$ , and the other parameters as in fig. 2, it can be calculated that  $a = 21.7$  and  $b = 157.5$  at  $22^\circ\text{C}$ . Eq. (24) may then be written as:  $\beta_{\text{app}} = 0.14(1 + 0.132p_0)$ . It is obvious that  $\beta_{\text{app}} = 0.14$  for all values of  $p_0$  used in fig. 2a,

which explains why the curves cluster together. It would require  $p_0 > 3$  to produce a significant increase in the slope around  $\text{pH}_{\text{pzc}}$ .

The result that strong counter-ion adsorption causes an increase in the apparent reactivity of the surface might at first sight seem paradoxical. It is due to the fact that for  $r \neq 0$  the adsorbed sites themselves contribute to the interface potential, and the adsorption draws more sites out of their neutral state  $\text{A-OH}$  to a charged state. Since  $\delta$  for insulators is much smaller than one, it is apparent from eq. (25) that  $F(X) = (\alpha_+/\alpha_-)^{1/2}$  is not affected by the adsorption reactions; the net effect is therefore an amplification of the potential generated by the reaction of neutral sites with  $\text{OH}^-$  and  $\text{H}^+$  ions.

For asymmetrical adsorption, the minimum slope must be found numerically. A good approximation, however, is given by eq. (23), with:

$$\beta_{\text{app}} \approx \beta + \delta b(1 + \beta)(r_- n_0 + r_+ p_0)/2, \quad (25)$$

if the third term in the parentheses of eq. (24) can be neglected. Therefore, adsorption reactions affect the  $\psi_0/\text{pH}$  relation around the iep as a function of  $r_- n_0 + r_+ p_0$ ; if this quantity is much smaller than one, no effect will be observed. Any effects that are found can only lead to a value of  $r_- n_0 + r_+ p_0$ , and cannot be resolved in the individual parameters  $r_-$ ,  $r_+$ ,  $n_0$ ,  $p_0$ .

#### 2.4. Properties near saturation

The maximum possible positive charge on a surface occurs when  $\alpha_- = \alpha_n = 0$ , and:

$$(1 + n)\alpha_+ = (1 + n)X_{\text{sat}} = 1. \quad (26)$$

It is seen from eq. (13) that the pH needed to obtain this value of  $X$  is indeed infinite. Since the surface charge at saturation  $X_{\text{sat}}$  is large, we will ignore the difference between  $X$  and  $-\alpha_d$  introduced by  $\Delta\sigma$ . The point of saturation of the pH response is therefore defined by:

$$n = n_0 \exp[2 \sinh^{-1}(aX_{\text{sat}}) + b(1 - r_-)X_{\text{sat}}] = X_{\text{sat}}^{-1} - 1, \quad (27)$$

and the maximum value of  $\psi_0$  is then given by:

$$y_0|_{\text{max}} = e\psi_0/kT|_{\text{max}} = \ln[(X_{\text{sat}}^{-1} - 1)/n_0] + br_-. \quad (28)$$

We can infer from eqn. (28) that the maximum  $y_0$  contains a term:

$$br_- = e^2 N_s / kTC_-. \quad (29)$$

This is the normalized potential developed across the capacitor  $C_-$  (see fig. 1) between the surface and the plane of adsorption when the surface charge has its maximum value. The value of  $X_{\text{sat}}$  and the maximum  $y_0$  do not depend on the surface reactivity; however, the pH needed to reach this point does.

It is possible to estimate  $y_{0,\text{max}}$  and  $\text{pH}_{\text{sat}}$  in the case of  $\text{SiO}_2$  where large

values of  $|\text{pH}_z - \text{pH}|$  can be applied since  $\text{pH}_z \approx 2$ . From the work of Yates et al. [5] and Davis et al. [9] we can obtain the value  $C_+ \approx 130 \mu\text{F}/\text{cm}^2$ , implying that with  $N_s = 5 \times 10^{14} \text{ cm}^{-2}$  for  $\text{SiO}_2$ ,  $\psi_{0,\text{max}}$  is larger than 600 mV, corresponding to a  $\text{pH} - \text{pH}_z$  of at least 13. As this is more than can be reached in an aqueous solution, the available experimental results derived from colloid measurements predict that no saturation should be visible for  $\text{SiO}_2$  surfaces with a site density of  $5 \times 10^{14} \text{ cm}^{-2}$ , which corresponds to a fully hydroxylated surface [31]. The same conclusion holds for  $\text{Al}_2\text{O}_3$  surfaces, because then  $\text{pH}$  cannot be larger than about 7, if we assume that the inner capacitance for adsorption on  $\text{Al}_2\text{O}_3$ ,  $C_-$  or  $C_+$ , is of the same order of magnitude as for  $\text{SiO}_2$ .

### 3. Adsorption measurements on $\text{Al}_2\text{O}_3$ surfaces

#### 3.1. Experimental conditions

The same type of ISFET structure with an  $\text{Al}_2\text{O}_3$  gate insulator layer as reported in ref. [20] was used for these measurements. The gate insulator was polycrystalline  $\gamma\text{-Al}_2\text{O}_3$  deposited by a process described by Balk and Stephany [32]. The grain size of the 500 to 600 Å thick  $\text{Al}_2\text{O}_3$  layer was verified by SEM observation to be about 400 Å.

The flat-band voltage of an electrolyte/insulator/silicon structure is given by [33]:

$$V_{\text{FB}} = E_{\text{ref}} - (1/e)\Phi^{\text{Si}} - \psi_0 - Q_i/C_i + \chi^{\text{sol}} + \delta\chi, \quad (30)$$

where  $E_{\text{ref}}$  is the reference electrode potential relative to vacuum,  $\Phi^{\text{Si}}$  is the work function of silicon,  $Q_i$  and  $C_i$  are the effective insulator charge and capacitance per unit area,  $\chi^{\text{sol}}$  is the surface dipole potential of the solvent, and  $\delta\chi$  is the sum of a number of variations of  $\chi$  potentials (for more details, see ref. [33]). Measurements with an ISFET rely on determining the threshold voltage  $V_T$  of the transistor, which differs from the flat-band voltage by a constant which only depends on the substrate doping density. The threshold voltage is measured with electronic circuitry described by Bergveld [34]. Eq. (30) contains terms, such as  $E_{\text{ref}}$  or  $Q_i$ , which are not known precisely. Therefore, only variations of  $\psi_0$  can be determined directly. The method of measuring these variations depends on the assumption that the variations of dipole potentials grouped in  $\delta\chi$  do not depend on  $\text{pH}$ . In that case, we have:

$$\Delta V_T = \Delta V_{\text{FB}} = -\Delta\psi_0. \quad (31)$$

To eliminate the influence of possible drift effects, it has been found necessary to measure the variations of  $\psi_0$  relative to a fixed reference  $\text{pH}$ . Since the  $\text{pH}_{\text{pzc}}$  of an  $\text{Al}_2\text{O}_3$  surface has been determined to be about  $\text{pH} = 8$  [20] this value was chosen as the reference. All experimental results are therefore the

measurement of the variation of  $\psi_0$  when the electrolyte pH is varied from pH = 8 to another value. To enable different pH values to be applied without interrupting the continuity of the electrical measurement, a continuous flow of electrolyte was used. A valve selected one of two possible electrolyte solutions. This measurement system, which can be considered as a type of flow analysis, has been described in more detail elsewhere [35].

### 3.2. Results

It is known that the  $\psi_0/\text{pH}$  characteristics of  $\text{Al}_2\text{O}_3$  are nearly linear due to the high value of the sensitivity parameter ( $\beta = 4.8$ ) for this material [20]. To represent the data in a more meaningful way, the following reduced interface potential is plotted in fig. 3:

$$\psi'_0 = \psi_0 + 0.048(\text{pH} - 8). \quad (32)$$

$\psi'_0$  is a potential from which most of the linear variation has been removed. The slope of 0.048 V/pH is chosen because it is slightly below the measured minimum slope of 48.5 mV/pH which has been determined before [20], and  $\text{pH}_{\text{pzc}}$  is taken to be 8.

In both the NaCl and the phosphate electrolyte, the minimum slope lies around pH = 8, and is 48 to 49 mV/pH. This confirms the previous result in  $\text{NaNO}_3$  solutions [20], and implies that both  $\text{pH}_{\text{pzc}}$  and  $\beta_{\text{app}}$  do not depend visibly on the electrolyte.

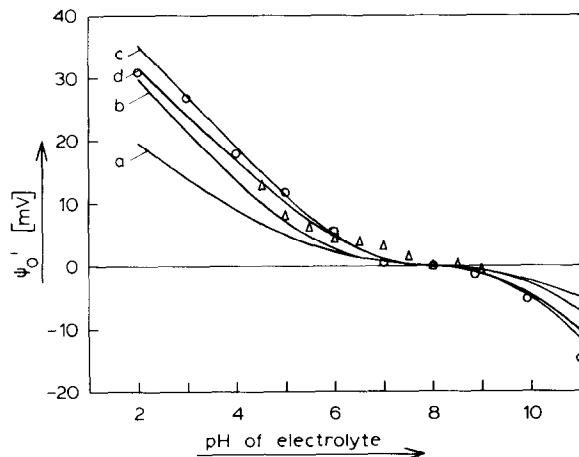


Fig. 3.  $\psi'_0/\text{pH}$  curves for  $\text{Al}_2\text{O}_3$  surfaces in 0.1M electrolytes. Experimental points: (○) 0.1M NaCl; (Δ) titration of  $\text{NaH}_2\text{PO}_4$  with  $\text{Na}_2\text{HPO}_4$  (0.1M); (□) pH = 6 citrate/NaOH buffer by Merck. Theoretical curves with  $N_s = 8 \times 10^{14} \text{ cm}^{-2}$ ,  $C_{\text{Stern}} = 20 \mu\text{F}/\text{cm}^2$ ,  $r_- = r_+ = 0.20$  [9]: (a)  $\delta^{-1} = 65.96$  and  $n_0 = p_0 = 0$ ; (b)  $\delta^{-1} = 66.5$  and  $n_0 = p_0 = 10^{-2}$ ; (c)  $\delta^{-1} = 75$  and  $n_0 = p_0 = 1.9 \times 10^{-1}$ ; (d)  $\delta^{-1} = 200$  and  $n_0 = p_0 = 5.8$ .

In fig. 3 are also shown a number of theoretical curves, using combinations of  $\delta$  and values of  $n_0 = p_0$  chosen to yield  $\beta_{app} = 4.8$ , to agree with the slope observed around  $\text{pH} = 8$ . Symmetrical adsorption ( $n_0 = p_0$  and  $r = r_1$ ) has been assumed in the absence of information concerning differences of adsorption constants for cations and anions. Curve (a) where no counter-ion binding is assumed deviates considerably from the other curves, and from the experimental results. In particular, the slope observed in the acid region, from  $\text{pH} = 2$  to  $\text{pH} = 4$  is around  $55 \text{ mV/pH}$ , and this cannot be explained by the simple theory where  $n_0 = p_0 = 0$ . Therefore our conclusion is that *counter-ion binding is definitely present*.

The theoretical  $\psi_0/\text{pH}$  curves when adsorption is present, however, all cluster together, and a wide range of values of  $n_0$  appear to fit the data equally well. Therefore the data in fig. 3 show that the theory developed here correctly predicts the influence of specific adsorption; but it is not possible to determine a value of the adsorption equilibrium constant with any confidence from measurements at a single ionic strength. However, it can be seen from eqs. (23) and (24) that assuming the parameters of curve (d) in fig. 3 implies that about a quarter of the observed slope of the  $\psi_0/\text{pH}$  curve around  $\text{pH}_{pzc}$  would be caused by counter-ion adsorption, instead of the acid–base site dissociation reactions. This would have the following consequences:

- The pH sensitivity would depend on the type of ions present. Such variations are not observed in experiments involving  $\text{NaNO}_3$ ,  $\text{NaCl}$ , phosphate and citrate buffers.
- The pH sensitivity would depend on the concentration, and would be much higher at higher ionic strengths. For example, with the constants used in calculating curve (d), a slope around  $\text{pH}_{pzc}$  in  $1 \text{ M NaCl}$  of  $56 \text{ mV/pH}$  would be predicted. If no adsorption were present, the increased capacitance of the Gouy–Chapman diffuse charge layer would tend to lower the sensitivity when the ionic strength increases; and this variation should become negligible when the ionic strength is high.

It appears therefore that the influence of solution concentration can distinguish between the cases of high or low adsorption. Fig. 4 shows a comparison of the response of an ISFET in  $1 \text{ M NaCl}$  and  $0.1 \text{ M NaCl}$  in the acid region. No significant difference is observed. To explain this, a value  $K_{\text{Cl}^-} = n_0/c$  must be assumed in the order of  $0.05$  to  $0.4 \text{ mol}^{-1} \text{ dm}^3$ . The expected theoretical curves for  $K_{\text{Cl}^-} = 0.1 \text{ mol}^{-1} \text{ dm}^3$  are also represented in fig. 4. Given the reproducibility of the measurements of a few millivolts, a reasonable agreement is found. A value of  $K_{\text{Cl}^-}$  of this order of magnitude also explains why the sensitivity of the device does not depend markedly on the electrolyte used.

The data points for  $\text{pH} > 8$ , where adsorption of  $\text{Na}^+$  ions is expected, show a larger increase in slope than for  $\text{pH} < 8$  (fig. 3). The region of cation adsorption is too small, however, to contain sufficient data points which would allow a quantitative conclusion concerning adsorption of cations.

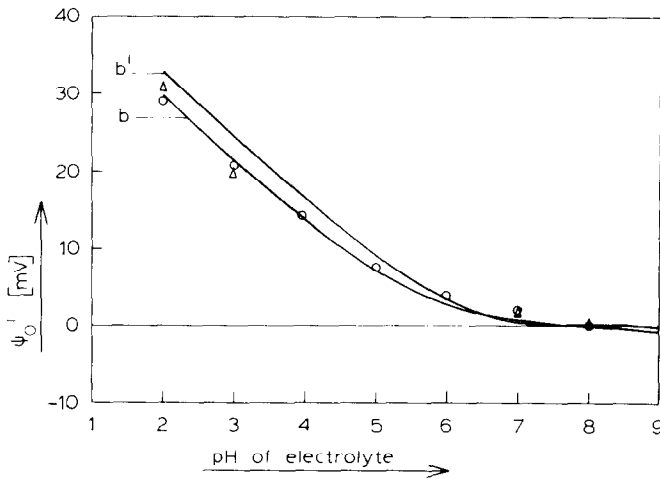


Fig. 4.  $\psi_0$ /pH curves for  $\text{Al}_2\text{O}_3$  surfaces in 0.1M and 1M NaCl electrolytes. Experimental points: (O) 1M NaCl; ( $\Delta$ ) 0.1M NaCl. Theoretical curves with  $N_s = 8 \times 10^{14} \text{ cm}^{-2}$ ,  $C_{\text{Stern}} = 20 \mu\text{F}/\text{cm}^2$ ,  $r_- = r_+ = 0.20$ ,  $K_{\text{Cl}^-} = K_{\text{Na}^+} = 10^{-1} \text{ mol}^{-1} \text{ dm}^3$ ; (b)  $c = 0.1\text{M}$ ; (b')  $c = 1\text{M}$ .

#### 4. Adsorption on $\text{SiO}_2$ surfaces

From fig. 2, it can be readily concluded that the  $\psi_0$ /pH curves of  $\text{SiO}_2$  surfaces are very insensitive to the specific adsorption of cations. A variation of  $p_0$  by a factor of 10 causes only a few millivolts shift in the  $\psi_0$ /pH relation. In addition, as opposed to  $\text{Al}_2\text{O}_3$  surfaces, it is known that  $\text{SiO}_2$  surfaces are particularly susceptible to drift effects which increase the error in measurements. Such drift effects have been reported by Leistiko [36], Schenck [37], and ourselves [20]. In particular, we have observed that for samples exposed to electrolytes at  $\text{pH}_{\text{pzc}}$  for a long time, drift effects made subsequent measurements at  $\text{pH} > 5$  on  $\text{Si}/\text{SiO}_2$ /electrolyte capacitances unreliable. The  $\psi_0$ /pH characteristics of  $\text{SiO}_2$  are therefore not suitable to characterize counter-ion adsorption. Experimental confirmation of this exists in the literature: in measurements by Fung et al. on a  $\text{SiO}_2$ -gate ISFET in LiCl, KCl and NaCl electrolytes no significant influence of the cation could be observed [38].

This does not mean such measurements are useless in the determination of the extent of counter-ion adsorption. In fact, information can be obtained from measurements known to be insensitive to adsorption effects. We have reported a value of  $\beta = 0.14$  for  $\text{SiO}_2$  in a 0.1M solution [20], which corresponds to  $\delta = 7 \times 10^{-4}$ , assuming  $N_s = 5 \times 10^{14} \text{ cm}^{-2}$  and  $C_{\text{Stern}} = 20 \mu\text{F}/\text{cm}^2$ . These parameters can then be used to interpret surface charge measurements on colloidal dispersions of non-porous  $\text{SiO}_2$  which are available in the

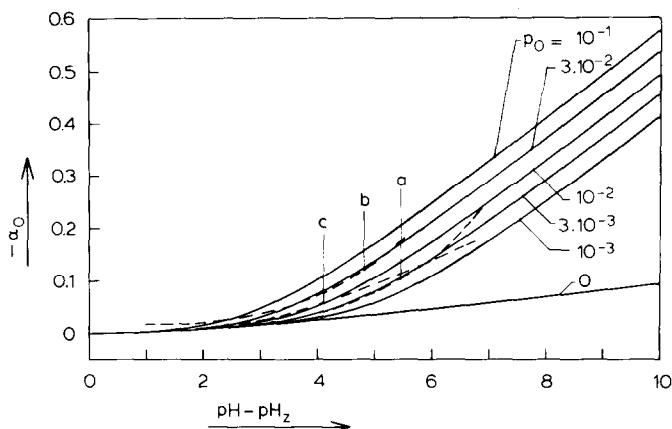


Fig. 5. Theoretical  $\alpha_0/\text{pH}$  curves for  $\text{SiO}_2$  with  $\delta = 7 \times 10^{-4}$ ,  $N_s = 5 \times 10^{14} \text{ cm}^{-2}$ ,  $C_{\text{Stern}} = 20 \mu\text{F}/\text{cm}^2$ ,  $r_+ = 0.15$ , and concentration = 0.1M. Experimental results from the literature for 0.1M solutions: (a) Bolt [39] (assuming  $\text{pH}_{\text{pzc}} = 3$ ), in NaCl; (b) Abendroth [40], in KCl; (c) Yates and Healy [41] (with  $N_s = 3.8 \times 10^{14} \text{ cm}^{-2}$ ), in  $\text{KNO}_3$ .

literature, as shown in fig. 5. The surface charge is very sensitive to the adsorption parameters chosen. A value of  $K_{\text{K}^+} \approx K_{\text{Na}^+} \approx 0.1 \text{ mol}^{-1} \text{ dm}^3$  seems reasonable to interpret these measurements, although the various results differ considerably. The important question is here of course the extent to which thermally grown  $\text{SiO}_2$  layers have the same properties as the dispersions. It can be expected that this would be especially true for the pyrogenic silica used by Abendroth [40].

## 5. Discussion and conclusion

To compare the results obtained by  $\psi_0/\text{pH}$  measurements with those obtained by titrations of colloidal dispersions, it is useful to examine the ion-exchange point of view of counter-ion binding. This follows from the product of eqs. (1) and (3), in the case of cation exchange:

$$K_{\text{ex}} = K_a K_{\text{Na}^+} \\ = \frac{[\text{A-O}^- \text{Na}^+][\text{H}^+]}{[\text{A-OH}][\text{Na}^+]} \exp\left[-e(\psi_0 - \psi_{\text{Na}^+})/kT\right], \quad (34)$$

which corresponds to the equilibrium:



All descriptions using any two of the equations (1), (3) and (34) are of course equivalent. The difference between  $\psi_0$  and  $\psi_{\text{Na}^+}$  is due to the difference in size

between  $H^+$  and  $Na^+$  ions. The experimental observation that  $C_+$  is very large [5,9] means that this difference is small. Therefore, the influence of  $\psi_0 - \psi_{Na}$  in eq. (34) will be small compared to the influence of  $\psi_0$  in eq. (1), and therefore ion exchange has only a second-order influence on the  $\psi_0/pH$  relation. On the other hand, it is reaction (35) which supplies by far the largest number of  $H^+$  ions released to the electrolyte solution, and this is detected by titration. The insensitivity of ion-exchange to potential justifies its neglect around  $pH_{pzc}$ , as we have done in ref. [20].

In some cases, values of  $K_{ex}$  have long been established. In 1964, Dugger et al. reported values of  $K_{ex}$  for silica gel [42]. Exchange of  $K^+$  ions occurred with a  $pK_{ex}$  of 6.9, while a more recent value reported by Davis et al. [9] for pyrogenic silica was 6.7. Concerning the values of the individual equilibrium constants  $K_a$  and  $K_{Na^+}$ , however, there is wide disagreement in the literature. For example, values of the parameter  $\Delta pK = (pK_a + pK_b)$  for  $\gamma-Al_2O_3$  have been reported from 1.2 [4] to 5.8 [9]. Concerning the value of the adsorption equilibrium constants for this material, Davis et al. [9] cited values of about  $160 \text{ mol}^{-1} \text{ dm}^3$  for both  $K_{Na^+}$  and  $K_{Cl^-}$ , which is considerably above the range we report here.

A possible reason for such wide variations of reported values is that every experimental method is mainly sensitive to a particular subset of the parameters of the model presented here. We will assume here that the site density  $N_s$  is independently known. Smit and Holten [14] have shown that the  $\psi_0/pH$  curves from a titration are mainly sensitive to  $C_{Sterm}$ ,  $r_+$ , and  $K_{ex}$  for  $pH > pH_{pzc}$ , and the corresponding parameters for anion exchange below  $pH_{pzc}$ . The  $\psi_0/pH$  curves presented here, on the other hand, are mainly determined by  $K_a$ ,  $K_b$ , and  $C_{Sterm}$ . The result in each case is that the experimental data can be fitted by a wide range of model parameters. The curves in fig. 3 are a good example of this phenomenon, since a variation by a factor of 580 in  $K_{Na^+}$  can be compensated by a change in  $\delta$ . Therefore, it is not really surprising that our results for adsorption on  $Al_2O_3$  are clearly different from those obtained from titration studies by Davis et al. [9]. Here is referred to a difference in experimental methods, namely titration experiments to determine  $\sigma_0$  as function of pH and our experiments which determine  $\psi_0$  as function of pH.

Two methods for solving this difficulty are available. The first is combining two different methods for the same material to obtain both  $\sigma_0/pH$  and  $\psi_0/pH$  curves. In principle, the  $\sigma_0/pH$  relations in the regions of strong anion and cation adsorption are sufficient to determine all adsorption parameters, including both  $r_-$  and  $r_+$  [14]. This meets the objection which could be raised against our model that its parameters cannot be individually determined. This is in fact the procedure followed here for  $SiO_2$ , with a result of  $pK_{Na^+} \approx pK_{K^+} \approx 1$ . The accuracy of this result is limited by the variation in the  $\sigma_0/pH$  data of various authors. Another possible source of inaccuracy is the value  $\Delta pK = 6.9$  for  $SiO_2$  we have used. Other authors have reported values around 8 for  $\Delta pK$



on the basis of the  $\psi_0/\text{pH}$  relationship [38], which would shift  $pK_{\text{Na}^+}$  and  $pK_{\text{K}^+}$  to about zero.

The second method is to vary the ionic strength when measuring the  $\psi_0/\text{pH}$  relation, which according to eqs. (3) and (4) should give the influence of the adsorption equilibrium constant (although  $r_+$  and  $r_-$  cannot be determined in this way). The results on  $\gamma\text{-Al}_2\text{O}_3$  reported here show no visible influence of ionic strength between 0.1M and 1M, which is rather difficult to explain even with low values of  $K_{\text{Na}^+}$ . One possible explanation would be that the adsorption process obeys eqs. (10) and (11), but that  $n_0$  and  $p_0$  are not strictly proportional to the ionic concentration as predicted by (3) and (4). However, the independence of the observed  $d\psi_0/d(\text{pH})$  around  $\text{pH}_{\text{pzc}}$  on the type of ions present makes it unlikely that the adsorption equilibrium constants are above  $1 \text{ mol}^{-1} \text{ dm}^3$  for  $\gamma\text{-Al}_2\text{O}_3$  (i.e.  $n_0$  and  $p_0$  are probably below 0.1).

In conclusion, the measurements on  $\gamma\text{-Al}_2\text{O}_3$  surfaces reported here show that by including counter-ion binding in the site-dissociation theory, it is possible to explain the results over a wide pH range. Counter-ion binding remains clearly a second-order effect for ISFETs, however, and the model explains why  $\gamma\text{-Al}_2\text{O}_3$  ISFETs are good selective sensors for  $\text{H}^+$  ions.

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